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"An expert is a person who has made all the mistakes that can be made in a very narrow field"

Niels Bohr (1885-1962)

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a	Parameter of the calibration J. vs TMP in Eq.[4.16]
A	Membrane Surface (m^2)
b	Parameter of the calibration J. vs TMP in Eq.[4.16]
b_i	Single effect coefficient in Eq[2.2]
b_{ii}	Quadratic effect coefficient in Eq[2.2]
b_{ij}	Interaction effect coefficient in Eq[2.2]
COD	Chemical Oxygen Demand
c_P	Concentration of solute in the permeate (g/L)
c_R	Concentration of solute in the retentate (g/L)
E_c	Cleaning efficiency (%) in Eq.[4.24]
FR	Flux recovery in Eq[4.26]
FT	Retentate flowmeter
g	Gram
h	Hour
J	Flux of permeate ($L \cdot m^{-2} \cdot h^{-1}$)
J*	Rate of back particle transport ($L \cdot m^{-2} \cdot h^{-1}$) in Eq[4.4]
J_0	Initial flux of permeate ($L \cdot m^{-2} \cdot h^{-1}$)
J_∞	Flux of permeate at steady state ($L \cdot m^{-2} \cdot h^{-1}$)
J_{max}	Maximum permeate flux in Eq[4.18]
J_w	Flux of water ($L \cdot m^{-2} \cdot h^{-1}$)
k	Cake permeability in Eq.[2.1]
k	First-order kinetics constant (h^{-1})
k	Phenomenological coefficient for dead-end filtration in Eq[4.3]
k	Constant of proportionality in Eq[4.27]
kg	Kilogram
L	Litre
L_p	Membrane permeability ($bar \cdot m^2 \cdot h \cdot L^{-1}$)
LI	Level Indicator
m	Masse (g) in Eq.[4.13]
m	Meter
M	Mass of deposited cake in Eq[4.6]
M*	Critical mass of deposited cake in Eq[4.6]

mg	Miligram
min	Minute
mL	Mililitre
n	Fouling index in Eq[4.3]
N	Newton
nm	Nanometer
ppm	Parts per million
PR	Ratio of protein removal in Eq[4.28]
PI	Pressure Indicator
Q	Fluid volumetric flow ($L \cdot min^{-1}$)
R	Protein rejection rate in Eq.[4.23]
$\mathbf{R_1}$	Hydraulic resistance of the fouled membrane ($bar \cdot m^2 \cdot h \cdot L^{-1}$)
$\mathbf{R_3}$	Hydraulic resistance after the cleaning treatment ($bar \cdot m^2 \cdot h \cdot L^{-1}$) in Eq[R.2]
$\mathbf{R_B}$	Hydraulic resistance of the gel layer ($bar \cdot m^2 \cdot h \cdot L^{-1}$)
$\mathbf{R_F}$	Hydraulic resistance of fouling ($bar \cdot m^2 \cdot h \cdot L^{-1}$) in Eq[4.2]
$\mathbf{R_{F\infty}}$	Hydraulic resistance of fouling at steady state ($bar \cdot m^2 \cdot h \cdot L^{-1}$) in Eq[4.10]
RFD	Relative Flux Decline (%) in Eq[4.20]
$\mathbf{R_{GP}}$	Hydraulic resistance of the gel layer ($bar \cdot m^2 \cdot h \cdot L^{-1}$) in Eq[4.2]
$\mathbf{R_M}$	Membrane intrinsic resistance ($bar \cdot m^2 \cdot h \cdot L^{-1}$) in Eq[4.2]
$\mathbf{R_r}$	Residual hydraulic resistance ($bar \cdot m^2 \cdot h \cdot L^{-1}$) in Eq[4.25]
s	Second
SS	Content of suspended matter (g of solids/ g of raw material)
t	Time
T	Protein transmission (%) in Eq[4.22]
TMP	Transmembrane pressure (bar)
TT	Temperature Transmitter
u	Pore-fluid pressure (Pa) in Eq[2.1]
V	Volume (mL) in Eq[4.13]
V1 to V4	Valves
VRF	Volume Reduction Factor in Eq.[4.21]
w/w	Weight for weight
$\mathbf{Y_1}$	Yield of press liquor (g of liquid/ g of raw material)
$\mathbf{Y_2}$	Content of suspended matter (g of solids/ g of raw material)
$\mathbf{q_z}$	Volumetric flow in the direction of the z-axis ($m^3 \cdot s^{-1}$) in Eq[2.1]

$\boldsymbol{\alpha}$	Constant of proportionality in Eq[4.6]
$\boldsymbol{\Delta P_m}$	Transmembrane pressure (bar)
µm	Micrometer
$\boldsymbol{\rho}$	Density ($kg \cdot m^{-3}$) or ($g \cdot L^{-1}$)
$\boldsymbol{\rho_w}$	Density of water ($kg \cdot m^{-3}$) or ($g \cdot L^{-1}$)

RÉSUMÉ

1.1 CONTEXTE ET OBJECTIVES DE LA THÈSE

Cet étude s'inscrit dans le cadre de la Réforme de la Politique de Pêche Communautaire, qui vise à réduire progressivement le volume des rejets et des pertes accessoires dans les eaux communautaires. La politique de zéro-rejets, récemment intégrée à la politique européenne en matière de pêche, entraîne l'introduction d'une interdiction des rejets et des pêches accessoires, pour laquelle tous les poissons, mollusques et crustacés capturés devront être débarqués, y compris les espèces non-ciblées et les individus en dessous de la taille minimale réglementaire.

Ce volume supplémentaire de biomasse devra être à stocké à bord ce qui demande le développement de solutions techniques permettant une bonne préservation des matériaux biologiques en vue de leur valorisation ultérieure à terre, tout en minimisant le coût énergétique associé à leur surgélation et stockage. Dans ce contexte, un compactage préliminaire peut réduire ce volume à stocker, c'est d'ailleurs la solution proposée par le Code de Conduite pour une Pêche Responsable de la FAO (FAO, 1995). Cette technique de compactage peut par ailleurs diminuer les coûts associés au stockage, transport et manipulation des déchets et co-produits issus des activités de transformation des produits d'origine marine à terre (halles de mareyage et industries de transformation du poisson).

A l'issue d'une opération de compactage, deux fractions sont obtenues : un gâteau de presse qui peut être stocké à bord pour une valorisation ultérieure à terre, i.e. l'obtention de farine de poisson (Bimbo, 1990 ; Folador *et al*., 2006) et un jus de pressage comprenant une phase aqueuse (contenant des protéines solubles) et une phase huileuse, ainsi que une quantité variable des particules solides en suspension. Etant donnée la haute charge organique de cet effluent, il ne pourra pas être rejeté dans l'environnement sans suivre un traitement d'épuration préalable, afin d'obtenir un rejet final conforme à la norme.

Dans ce contexte, le projet européen BE-FAIR (co-financé par le LIFE ENVIRONMENT PROGRAMME), vise à développer une gestion efficiente des déchets et co-produits issus des activités de la pêche autant à bord des bateaux qu'à terre (halles à mareyage et industries de transformation du poisson), ainsi qu'à promouvoir leur valorisation. Le projet a comme objectif premier de proposer des solutions techniques aux acteurs de la filière pêche pour

pouvoir répondre à la future implantation de la politique de zéro-rejets. Huit partenaires de 3 pays (Portugal, Espagne et France) font partie du projet BEFAIR ; ils représentent les instituts de recherche sur la pêche, les autorités portuaires et les usines de transformation du poisson.

Ce travail de Doctorat s'insère directement dans ce projet BE-FAIR et porte sur :

1. L'estimation des rejets de la pêche française, ainsi que du tonnage des déchets provenant des activités de transformation à bord et à terre. Le premier chapitre est consacré à cette tâche,

2. Le deuxième chapitre étudie la faisabilité d'une opération de compactage de sardine, espèce est symptomatique de la situation des pêcheries Françaises en termes de rejets et de captures accessoires. Les critères particulièrement étudiés sont la réduction volumique et le rendement et teneur en matière en suspension du jus obtenu lors du pressage. Les paramètres opérationnels pour ce processus de pressage ont été identifiés et optimisés à l'aide d'un modèle statistique de surface de réponse.

3. Ce modèle a été validé par la construction d'un prototype à échelle semi-industrielle capable de traiter jusqu'au 10 kg de produit par batch. Le troisième chapitre analyse les aspects du design et construction de ce prototype, ainsi que l'influence des paramètres opérationnels sur trois variables de réponse : le rendement en jus de pressage, sa teneur en matière en suspension et sa demande chimique d'oxygène (DCO).

4. Le traitement des effluents issus du compactage des déchets de sardine a été abordé dans le quatrième chapitre. Deux étapes successives de microfiltration sur cartouche puis d'ultrafiltration sur membrane s'avèrent nécessaires pour réduire la charge organique de l'effluent et générer un perméat conforme à la norme et pouvant ainsi être rejeté dans l'environnement.

1.2 INTRODUCTION GÉNÉRALE SUR LES STRATÉGIES DE GÉSTION DES RESOURCES MARINES.

Ce chapitre a été structuré en trois parties différentes :

1. Situation mondiale des rejets de la pêche ainsi que des déchets et co-produits issus des procédés de transformation industrielle.
2. État de l'art sur les voies de valorisation pour les co-produits d'origine marine.
3. Évaluation, à l'aide des coefficients de conversion et des études bibliographiques précédents, des tonnages annuels de rejets, de déchets et de co-produits provenants des activités provenant de la pêche et la transformation du poisson en France.

1.2.1 Introduction aux rejets de la pêche, les déchets à bord et les co-produits provenant de la transformation à terre.

Une conséquence directe des activités de la pêche et de la transformation des produits d'origine marine c'est la génération des déchets et co-produits, qui posent un problème environnemental et économique important au regard de la situation actuelle de décroissance des ressources marines disponibles. Ces biomasses peuvent être classées en trois groupes : les rejets de la pêche, les déchets issus de la transformation du poisson à bord et les déchets et co-produits générés par la manipulation et transformation du poisson à terre.

1.2.1.1 Rejets de la pêche.

Les rejets se définissent comme la portion de la capture totale qui est jetée par-dessus bord tandis que le navire est en mer. On considère généralement les rejets comme un gaspillage des ressources en poisson, incompatible avec une gestion responsable des pêcheries (Kelleker, 2004). On peut différencier deux groupes des rejets, ceux composés des individus de taille au-dessous la taille minimale et ceux composés par des espèces non ciblées dont la valeur commerciale est trop faible pour être retenues à bord. On parle alors des captures accessoires.

Le rapport SOFIA de la FAO propose une mise à jour du volume des rejets des pêches maritimes mondiales, sur la base d'une approche pêcherie par pêcherie. Le taux pondéré de rejets est estimé à huit pour cent (proportion des captures faisant l'objet du rejet). Sur cette base, on peut estimer à 7,3 millions de tonnes par an les rejets moyens au cours de la période 1992-2001.

Plusieurs résolutions des Nations Unies ont attiré l'attention sur la nécessité de réduire les rejets et les prises accessoires non visées, ainsi que d'en faire l'objet d'un suivi permettant d'évaluer leur impact sur les ressources marines, et de promouvoir tous moyens technologiques et autres concourant à leur réduction.

De nos jours, deux pays européens appliquent dores et déjà une politique de zéro-rejets, c'est-à-dire, une politique obligeant les bateaux à débarquer la totalité des captures : la Norvège et l'Islande. Dans le cadre de la Reforme de la Politique Communautaire de Pêche, les communications de la Commission Européenne COM (2002) 656 et COM(2007)136 proposent une amélioration de la sélectivité des métiers de pêche, accompagnées de mesures « punitives », visant à obtenir une réduction progressive des rejets dans les pêcheries communautaires. Les premières mesures ont été appliquées dans deux pêcheries pilote : le chalutage du poisson plat dans les zones IV et VIId et le chalutage du langoustine dans la zone VII. La politique de zéro-rejets devrait avoir une implantation définitive à partir de 2010.

1.2.2 État de l'art des voies de valorisation des co-produits d'origine marine.

La transformation du poisson implique plusieurs opérations qui génèrent une quantité importante de co-produits. Le tonnage total des co-produits générés à terre est en augmentation constante à cause de la transformation de plus en plus importante des biomasses débarquées mais également une concentration de ces déchets grâce l'implantation progressive de grandes halles de mareyage et à l'augmentation de la taille des unités de transformation. Ces opérations impliquent le filetage, le pelage, l'étêtage et l' éviscération générant parfois un volume conséquent de déchets (de 50 à 70% du poids du poisson entier). De nombreuses voies de valorisation de ces déchets ont été étudiées et parfois mises en pratique, certaines sont présentées dans ce chapitre :

1. **Farine et huile de poisson**. La fabrication de farine et d'huile de poisson est la voie privilégiée pour la transformation des co-produits d'origine marine mais aussi des prises accessoires.Cependant, les plus gros volumes résultent de la transformation d'espèces commerciales telles que l'anchois, le menhaden ou le capelan. La farine de poisson est composée principalement de protéines (70%), minéraux (10%), graisse (9%), et d'eau (8%). Elle est destinée à l'alimentation animale, principalement à l'aquaculture, grâce à sa teneur en acides aminés essentiels tels que la lysine, méthionine ou cystéine (Keller, 1990).

2. **Collagène et gélatines de poisson**. La gélatine est obtenue à partir du collagène, qui est la principale protéine structural de la peau, des os et du tissu conjonctif animal. La conversion du collagène en gélatine soluble est obtenue par chauffage du collagène en milieu acide ou alcalin. Parmi les différentes sources d'obtention de la gélatine, la production de gélatine de poisson ne représente qu'un 1% de la production totale de gélatines, environ 25.000 tonnes (Blanco *et al*., 2007).

3. **Chitine et chitosan**. La chitine est un polymère constitutif de la carapace des crustacés et des insectes et intervient également dans la structure interne d'autres invertébrés. Plusieurs dérivés de la chitine sont utilisés pour leurs propriétés notamment biologiques. Parmi eux , la forme la plus commune est le chitosan , qui est obtenue par déacétylation de la chitine. Le chitosan est utilisé dans un très grand nombre de secteurs tels l'agriculture, la nutrition, le textile, la nutraceutique, la cosmétique et même dans le domaine de la santé pour ses propriétés antibactériennes et antifongiques.

4. **Valorisation aromatique**. Environ 2.100 tonnes par an de co-produits, principalement des têtes et des arêtes d'espèces commerciales telles que l'anchois, le thon ou le saumon, font l'objet d'une valorisation aromatique en France. Ils sont formulés dans différents produits destinés à l'alimentation animale et humaine, tels que des soupes, des sauces, produits à base de fromage, surimi, etc. (Prost *et al*., 2008).

5. **Biodiesel**. Le biodiesel est une source renouvelable qui peut être obtenu par transesterification des triglycérides. Plusieurs études ont montré que le biodiesel obtenu à partir d'huile de poisson présente des performances énergétiques similaire

sà celle des dérivés du pétrole (Kato *et al.*, 2004 ; El-Mashad *et al*., 2008 ; Preto *et al.,* 2008 ; Lin et Li, 2009).

6. **Extraction des composants bioactifs.** Le développement de nouvelles techniques d'extraction/purification a permis l'identification et l'isolement d'un nombre croissant de composés bioactifs, extraits à partir de la chair de poisson, du collagène et de la gélatine, de l'huile de poisson, des arêtes, des organes internes et des coquillages et des carapaces crustacées. Ces composés bioactifs trouvent des applications dans les champs de la biotechnologie, de la nutraceutique, de la cosmétique et de la pharmacie.

7. **Hydrolysats d'origine marine.** Les procédés biologiques utilisant des enzymes protéolytiques (protéases) sont désormais beaucoup plus souvent utilisés pour l'obtention des hydrolysats de protéine de poisson, car la protéolyse enzymatique est généralement un processus doux débouchant sur des produits de haute fonctionnalité, avec de bonnes propriétés organoleptiques et une excellente valeur nutritive et ce sans la formation de sous-produits toxiques (Mackie, 1982; Vilhelmsson, 1997; Christinsson et Rasco, 2000a).

1.2.3 Etude sur les rejets, et les co-produits en France.

1.2.3.1 Les rejets de la pêche française.

Diverses études portant sur les rejets de la pêche dans les différentes pêcheries françaises (Morizur *et al.*, 1996 ; Morizur *et al.*, 2000 ; Rochet *et al*., 2001 ; Pierce *et al.*, 2002 ; Allain *et al.*, 2003), ont permis d'estimer un taux de rejet moyen en France d'environ 14% par rapport aux captures totales, ce qui a représente environ 60.000 tonnes en 2006. Les volumes de rejets les plus élevés correspondent à des espèces telles que la sardine (avec un taux de rejet proche du 50% dans quelques pêcheries artisanales méditerranéennes), le merlan, le merlu (avec un taux de rejet du 56% dans le Golfe de Gascogne), le hareng, le maquereau et la baudroie.

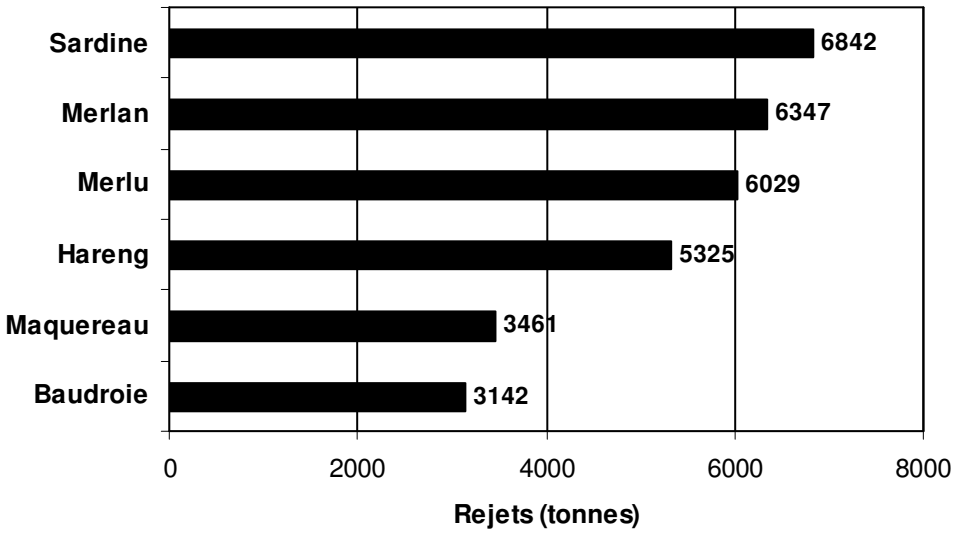

Figure R.1. Espèces générant les tonnages les plus importants de rejets.

Les espèces ayant les taux de rejet les plus élevés sont le lieu, avec 70% de rejets dans le Golfe de Gascogne, la plie dans l'Atlantique Nord, le merlu et la daurade dans le Golfe de Gascogne, et la sardine dans quelques pêcheries méditerranéennes.

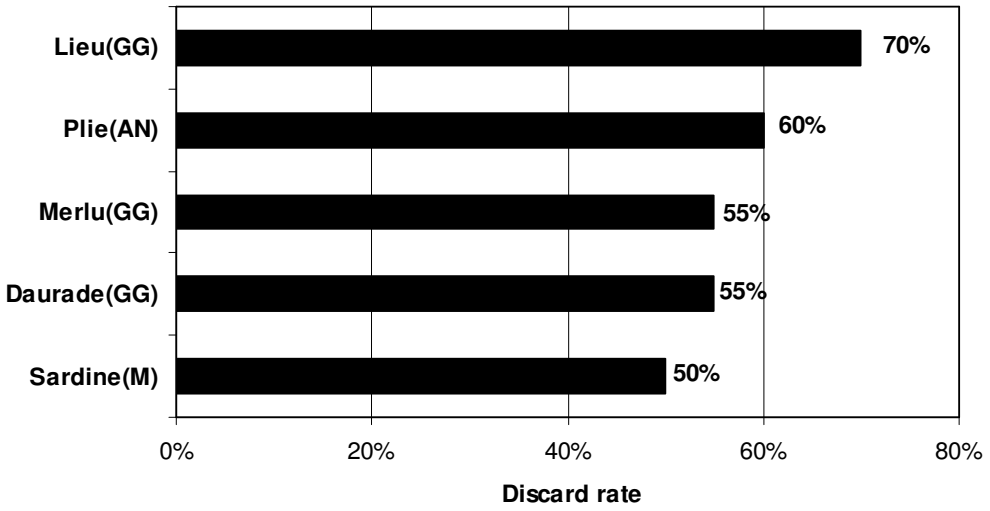

Figure R.2. Pêcheries françaises ayant les taux de rejet les plus élevées.

1.2.3.2 Les déchets générés par la transformation du poisson à bord.

Les sous-produits générés à bord des bateaux de pêche sont généralement des viscères. Celles-ci doivent être stabilisées par congélation en raison de leurs teneurs importantes en bactéries intestinales. De nos jours, seuls les foies et les œufs sont parfois conservés à bord pour les revendre à terre et particulièrement les foies de lotte et de sikiş.

À la différence des poissons dits « bleus » (sardine, maquereau, etc.), les poissons blancs sont traditionnellement éviscérés à bord (lotte, morue, congre, églefin, merlan, lieus, etc.) ainsi que les espèces cartilagineuses comme les requins. D'autres espèces comme le sabre noir (grenadier) sont étêtés ou équeutés. Ces activités génèrent une quantité importante de déchets qui sont généralement jetés à la mer. Une estimation du tonnage total de déchets issus des activités de transformation du poisson à bord a été réalisée à l'aide des coefficients de conversion, et ce pour chaque espèce. Ceci permet d'évaluer le poids vif d'un individu par rapport à la masse résiduelle du poisson transformé (Caillart *et al.*, 1996).

D'après notre estimation, 12800 tonnes de déchets ont été générés par des activités de transformation du poisson à bord. Parmi eux, 81% correspondent à des poissons blancs et quatre espèces, la lotte, le lieu jaune, les requins et le merlu représentent à elles seule 60% du tonnage total de ces déchets.

1.2.3.3 Les déchets et coproduits issus de la transformation du poisson à terre.

La quantité de sous-produits varie selon la transformation (conserverie, fumage), l'activité commerciale (halles à marée) et l'espèce du poisson traité (poissons blancs, poissons bleus, cartilagineux et salmonidés). La quantité totale de sous-produits peut aussi être étudiée par type de sous-produits : têtes, viscères, arêtes et peaux. En outre, un aspect important concerne les processus de valorisation subits par les sous-produits de poisson. Après estimations, nous pouvons conclure que :

- Environ 215.000 tonnes des co-produits ont été générés en France en 2005 issus des activités de mareyage et de transformation du poisson. Les activités liées au mareyage génèrent 52% du tonnage total des co-produits, suivies par les activités de conserverie (36%) et de saurisserie (12%).

- Par rapport à l'origine des co-produits, 45% de la masse totale des co-produits générés proviennent des espèces « bleues », 29% de salmonidés, 21% de poissons blancs et le reste d'espèces cartilagineuses.

- Les têtes constituent 40% de la masse de co-produits, suivies par les arêtes et les queues (27%), les viscères (25%), les peaux (7%) et les nageoires (1%).

- À l'heure actuelle, 96% des co-produits d'origine marine générés en France font l'objet d'une valorisation. Le diagramme ci-dessous montre la répartition des co-produits utilisés selon les différentes voies de valorisation :

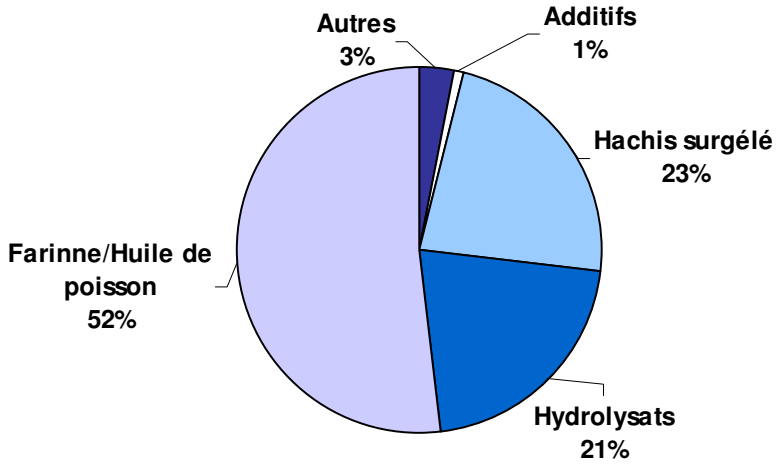

Figure R.3. Répartition des co-produits utilisés par mode de valorisation (Andrieux, 2004)

1.3 VALIDATION DU COMPACTAGE DES DÉCHETS À L'ÉCHELLE DU LABORATOIRE.

Dans le cadre de la future application de la politique de zéro-rejets, qui obligera les bateaux pêcheurs communautaires à débarquer tous les rejets, déchets et prises accessoires, une opération préliminaire de compactage peut contribuer à réduire ce volume supplémentaire à stocker à bord et minimiser ainsi les besoins d'espace et d'énergie pour la préservation à bord. Cette solution a déjà été proposée par le Code de Conduite pour une Pêche Responsable (FAO, 1995) Au niveau des déchets et sous-produits issus des activités de transformation à terre (mareyage, conserverie, saurisserie), une opération de compactage peut également réduire les coûts associés liés à leur manipulation et à leur transport, ainsi que faciliter leur préservation en réduisant leur activité de l'eau.

La sardine a été retenue comme modèle d'étude, car elle est symptomatique de la situation des pêcheries Françaises en termes de rejets et de captures accessoires. Des sardines entières ont ainsi été pressées à l'aide d'une presse hydraulique fonctionnant à différentes valeurs de pressions, de vitesse de compression, du nombre de phases de compression et du temps de relaxation entre chacune d'elles. L'influence de ces facteurs expérimentaux a été estimée sur deux réponses : le rendement en jus de presse (quantité de jus collecté lors du pressage par rapport à la masse initiale de matière première introduite dans la presse), et la teneur en solides (masse de solides mesurée après centrifugation du jus de pressage par rapport à la masse initiale de matière première introduite dans la presse). La méthodologie des plans d'expérience a été retenue en utilisant un plan d'expériences central composite avec trois répétitions du point central. Les résultats ont ensuite été analysés à l'aide de la méthode des surfaces de réponse. Le tableau ci-dessous illustre la matrice expérimentale avec les différents niveaux testés pour les facteurs expérimentaux : la pression (P), vitesse de compression (v), nombre de paliers (N) et temps de relaxation (t) ainsi que les valeurs mesurées pour les deux variables de réponse : le rendement en jus (Y_1) et la teneur en solides en suspension (Y_2). Afin d'obtenir une meilleur corrélation lors de la régression quadratique, le logarithme $-LN(Y_2)$ a été préféré à la variable brute Y_2.

Tableau R.1. Matrice expérimentale pour le pressage hydraulique des sardines entières.

Exp. #	Facteurs expérimentaux				Variables de réponse	
	P (bar)	**v** (cm/min)	**N**(-)	**t**(s)	$\mathbf{Y_1}$ (w/w)	$\mathbf{-ln(Y_2)}$ (-)
1	125	1,485	2	150	0,058	4,978
2	275	1,485	2	150	0,103	4,091
3	125	2,585	2	150	0,058	4,870
4	275	2,585	2	150	0,093	4,208
5	125	1,485	4	150	0,074	4,723
6	275	1,485	4	150	0,113	4,335
7	125	2,585	4	150	0,071	4,873
8	275	2,585	4	150	0,106	4,681
9	125	1,485	2	250	0,067	4,673
10	275	1,485	2	250	0,108	4,110
11	125	2,585	2	250	0,062	5,024
12	275	2,585	2	250	0,086	4,582
13	125	1,485	4	250	0,085	4,697
14	275	1,485	4	250	0,121	3,872
15	125	2,585	4	250	0,084	4,763
16	275	2,585	4	250	0,114	4,504
17	50	2,035	3	200	0,059	5,193
18	350	2,035	3	200	0,129	3,728
19	200	0,935	3	200	0,103	4,203
20	200	2,585[a]	3	200	0,094	4,032
21	200	2,035	1	200	0,073	4,718
22	200	2,035	5	200	0,116	4,201
23	200	2,035	3	100	0,093	4,258
24	200	2,035	3	300	0,106	4,182
25	200	2,035	3	200	0,101	4,259
26	200	2,035	3	200	0,102	4,284
27	200	2,035	3	200	0,108	4,168

Après le pressage hydraulique, un gâteau partiellement déshydraté a été obtenu traduisant une réduction volumique de l'ordre de 40 à 45% de la matière première initiale. Cette réduction de volume signifie que cette opération pourrait permettre de réduire en 33% les besoins frigorifiques et de stockage par rapport à ce qui serait nécessaire pour des poissons non pressés (Johnson *et al.*, 1994). Par rapport aux deux réponses étudiées, les modèles du second degré montrent une bonne adéquation avec les données expérimentales, les coefficients de corrélation étant respectivement de 0,982 et 0,924. Ces polynômes permettent ainsi

d'optimiser chacune des deux réponses étudiées. Les deux figures suivantes montrent les courbes de niveau obtenues dans les conditions optimales des facteurs expérimentaux.

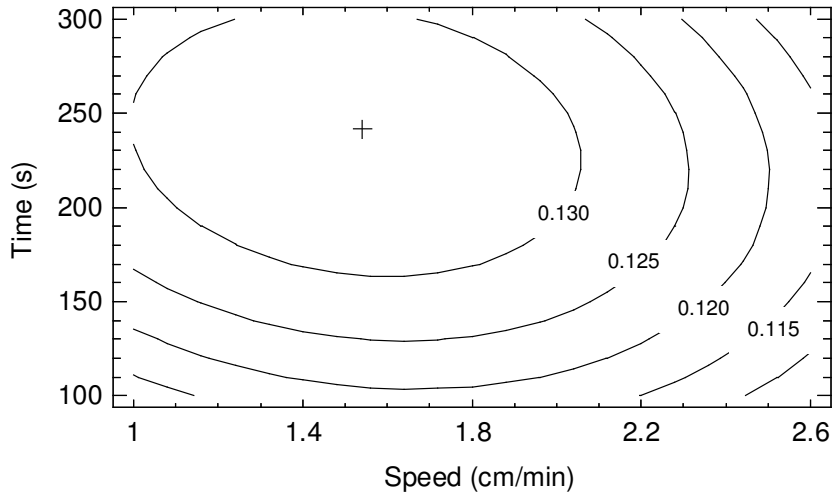

Figure R.4. Représentation en courbes de niveau du rendement pour 4 paliers de pressage et 350 bar de pression finale.

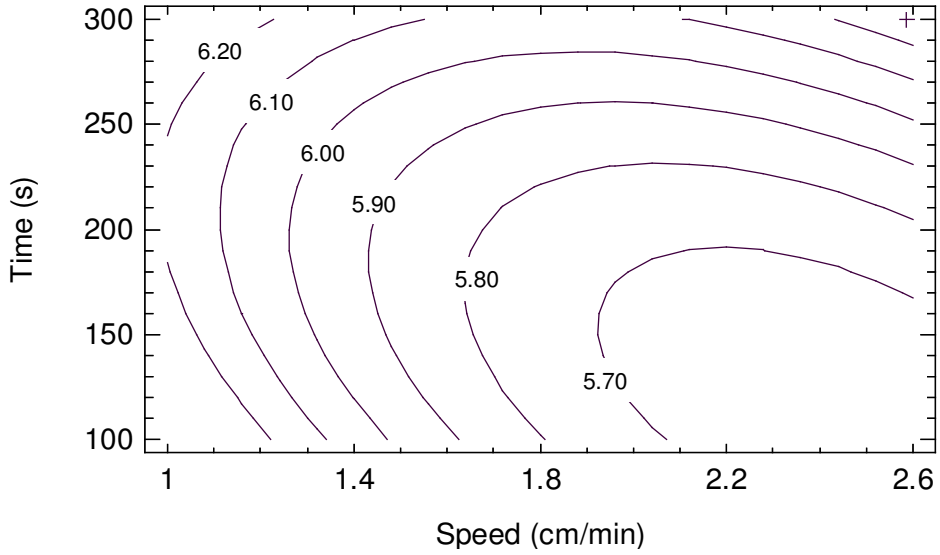

Figure R.5. Représentation en courbes de niveau de la teneur en solides pour 1 étape de pressage et 66 bar de pression finale.

Le rendement maximal de jus (13,45% en masse par rapport aux sardines introduites dans la presse) est atteint pour une pression de 350 bars, une vitesse de compression de 1,54 cm/min, 4 compressions successives et des temps de relaxation de 242 secondes entre les

compressions. D'autre part, la teneur minimale en particules en suspension (0,2% en masse par rapport au total de jus de pressage//m/m par rapport aux sardines utilisées) est obtenue pour une pression de 66 bars, une vitesse de compression de 2,585 cm/min, 1 seule étape de compression et un temps de relaxation de 300 secondes.

Les deux objectifs d'optimisation (maximisation du jus récupéré et minimisation de sa teneur en particules) sont atteints séparément avec des conditions de facteurs expérimentaux distinctes. Il a donc été nécessaire d'établir un compromis par une technique d'optimisation multi-objectifs. La méthode « ε-constraint » a été choisie pour générer un ensemble de solutions optimales (« Front de Pareto ») qui assurent une grande production de jus avec une teneur limitée en éléments en suspension.

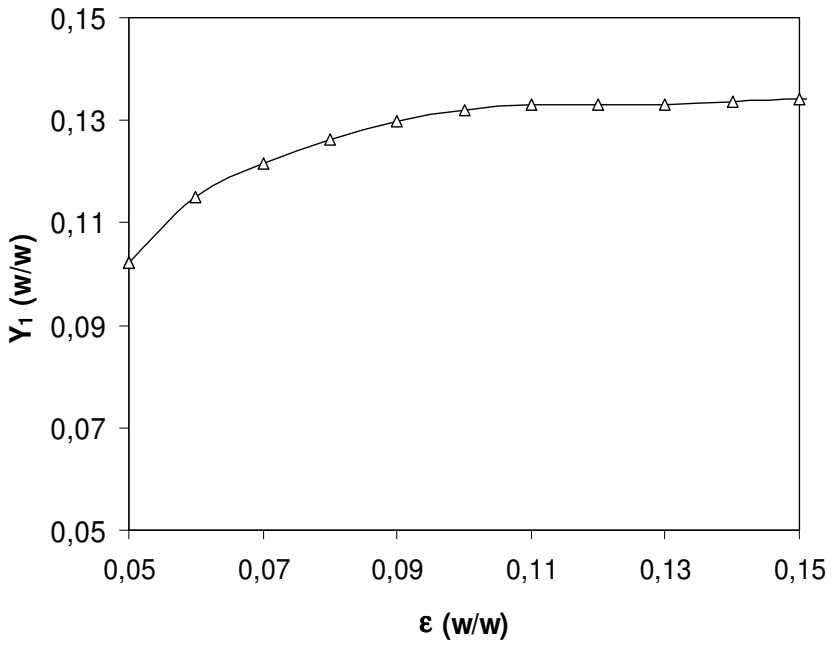

Figure R.6. Front de Pareto. Représentation du maximal rendement achevable (Y_1) pour une teneur en solides fixée (ε).

C'est le traitement ultérieur des effluents de l'opération de pressage qui déterminera la sélection d'une seule solution issue du front de Pareto selon des impératifs de flux ou de concentration maximales acceptables. Il peut cependant être conclu qu'il n'est pas souhaitable d'augmenter la production de jus de pressage au-delà de la valeur critique de 13% en masse afin de limiter la concentration de matière en suspension et les coûts résultants du traitement ultérieur de l'effluent.

L'intérêt d'un prétraitement avant pressage (comme des opérations de découpe ou de broyage par exemple) a été étudié. Un broyage préalable influence négativement les performances de l'opération de pressage par rapport aux prédictions du modèle statistique des surfaces de réponse. En effet, il augmente l'exposition de l'eau aux protéines myofibrillaires qui possèdent une forte capacité de rétention d'eau. Dans ces conditions, le gâteau issu du pressage acquière une texture pâteuse qui gène la circulation de liquide, donnant lieu à une récupération de jus en plus faible quantité et plus chargé en matières en suspension.

Ceci implique que la majorité du liquide collecté lors du pressage est issu des têtes puisque les protéines contenues dans les muscles offrent une résistance à la perte d'eau. Il peut donc être conclu qu'il est préférable de réaliser l'opération de pressage sur des matériaux à teneur en chaire réduite, à savoir des co-produits ou des têtes seules, si l'on souhaite augmenter le rendement en jus de pressage.

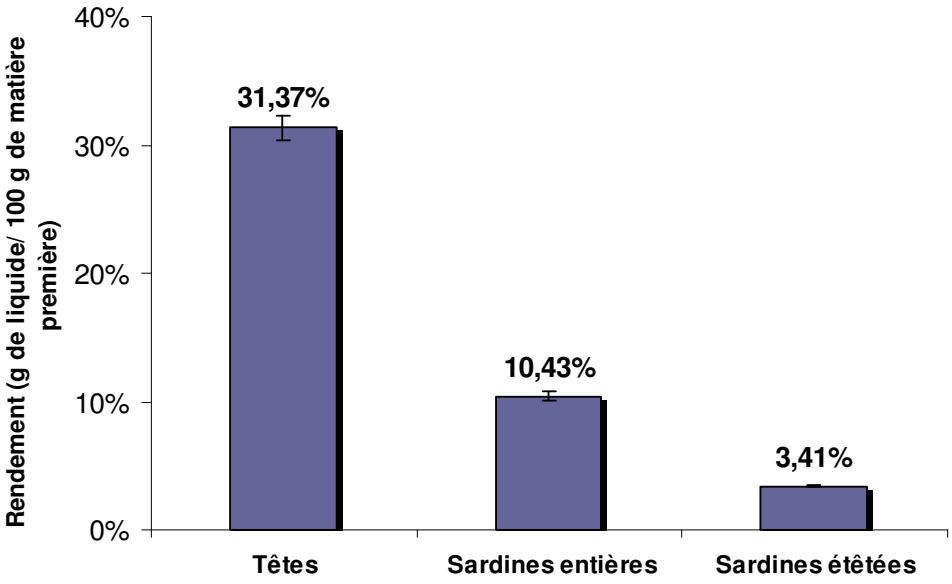

Figure R.7. Rendement du jus obtenu lors du pressage des sardines entières, des têtes et des sardines étêtées.

1.4 VALIDATION DE LA TECHNIQUE DE COMPACTAGE DANS UN PROTOTYPE.

Le principe du compactage des déchets à l'aide d'une presse hydraulique, dont la procédure a été analysée et optimisé à l'échelle de laboratoire, a été validé avec succès sur un pilote. Les paramètres opérationnels pour la presse hydraulique ont été identifiés et optimisé pour donner un rendement maximal tout en minimisant la teneur en particule en suspension. Ces paramètres ont été pris en considération lors de la construction du prototype. Cependant, quelques limitations techniques concernant les matériaux de construction et l'échelle réelle ont suggéré de réduire la pression maximale de 370 bars à 150 bars. Le schéma ci-dessous illustre les différentes étapes unitaires du prototype .

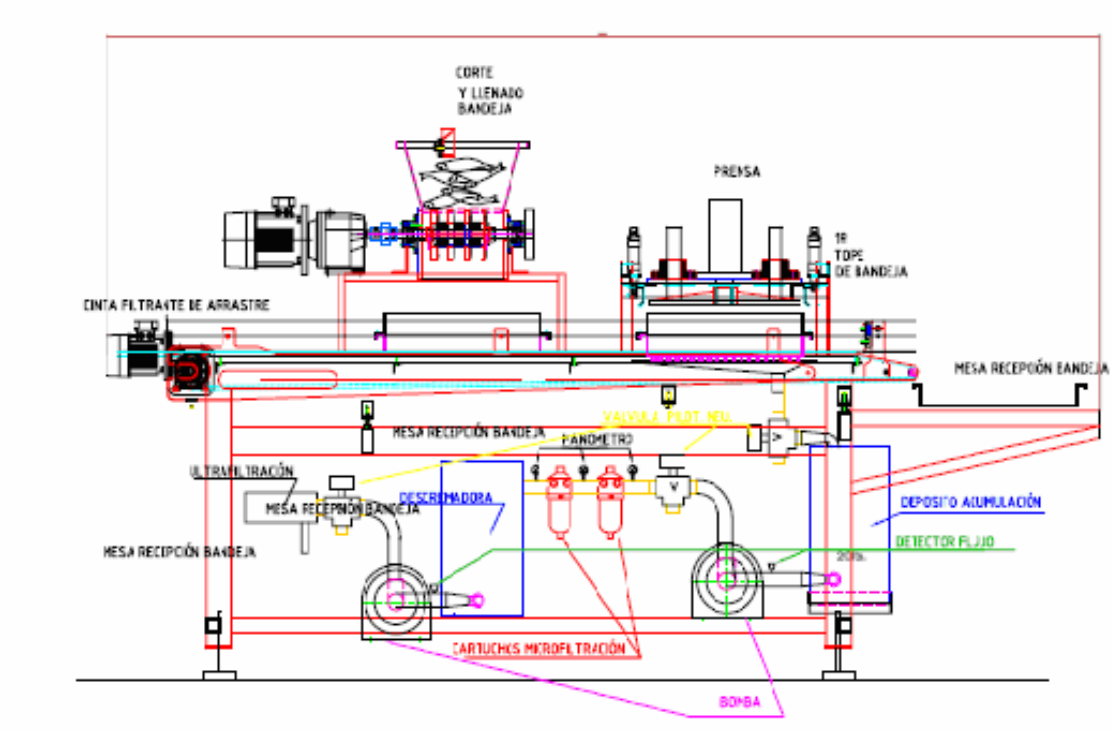

Figure R.8. Schéma du prototype de compactage de déchets.

Les co-produits sont introduits dans une machine à couper, ensuite transporté dans la presse hydraulique où ils suivront le traitement de pressage. La presse permet de récupérer d'un côté le gâteau de presse, et de l'autre les jus de pressage, qui sont collectés dans un première cuve.

Quand le niveau de liquide dans cette cuve atteint une valeur seuil, le système de pompage se déclenche et le jus est envoyé vers deux cartouches de filtration en série pour être finalement collecté dans une deuxième cuve. S'ensuit alors une opération de filtration membranaire qui permet de récupérer un retentât concentré en protéines et un perméat avec une DCO faible.

La performance du nouveau prototype a été validée grâce à un nouveau plan d'expériences. Pour chaque expérience, 8 kg de matière première ont été pressées, avec 3 à 5 paliers de compression, une pression de 150 bars et une vitesse de compression fixée à son optimum (50 % de la gamme de vitesse), ce qui a nécessité la réalisation de 11 expériences. Le rendement du jus de pressage, sa teneur en matière en suspension et sa demande chimique d'oxygène (DCO) ont été choisis comme variables de réponse.

Table R.2. Matrice expérimentale pour le pressage hydraulique des co-produits.

Expérience	Nombre de paliers N(-)	Temps de relaxation t(s)	Rendement Y (w/w)	Solides en suspension SS (w/w)	DCO (g O_2/L)
1	3	60	0,1659	0,0168	131
2	3	90	0,1751	0,0237	121
3	3	120	0,1911	0,0254	121
4	4	60	0,1869	0,0279	137
5	4	90	0,1970	0,0245	130
6	4	90	0,2003	0,0307	125
7	4	90	0,1972	0,0264	121
8	4	120	0,2301	0,031	121
9	5	60	0,1829	0,0247	140
10	5	90	0,1870	0,0167	118
11	5	120	0,1951	0,0183	115

Par application de la méthodologie des surfaces de réponse, les trois réponses ont été ajustées à un modèle prédictif de deuxième ordre avec des bons coefficients de corrélation (0,9064, 0,8742 et 0,9121, respectivement). Les graphiques de réponse montrent qu'un rendement maximal (0,2195 g de liquide / g de matière première) a été obtenu avec 4 étapes de compression et un temps de relaxation de 120 s. La teneur en matière en suspension et la demande chimique d'oxygène ont présenté des valeurs minimales (0,017 g liquide/g de

matière première et 114 g O_2/L, respectivement) à 5 étapes de compression et un temps maximal de relaxation (300s).

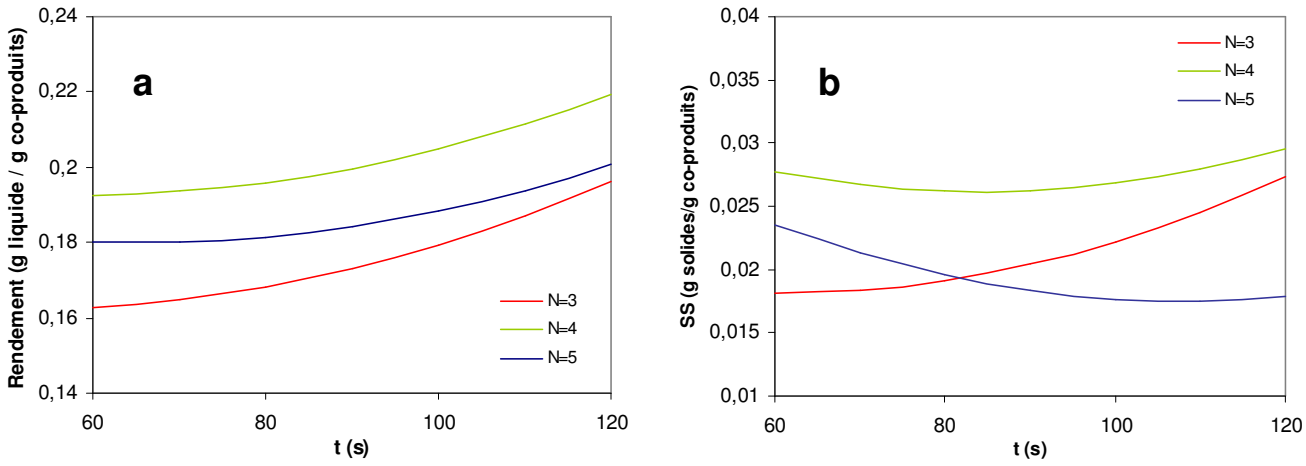

Figure R.9. (a) Modèle prédictif pour le rendement. (b) Modèle pour la matière en suspension.

L'analyse biochimique du jus de pressage met en évidence l'influence des facteurs expérimentaux (nombre de paliers et temps de relaxation) sur la teneur en protéines qui est similaire à celle observée pour la matière en suspension. Ceci suggère qu'une proportion importante des protéines sont essentiellement sous formes de particules suspendues solides et que seulement une petite quantité est présente sous la forme soluble. Les faibles teneurs en lipides détectés dans le jus de pressage ont exclu la nécessité d'une opération de récupération d'huile dans le traitement de dépuration de ces effluents.

Le traitement de compression comprenant cinq étapes à la pression maximale et à un temps de relaxation maximal permet d'obtenir le plus haut rendement en limitant la quantité des particules en suspension dans le jus de pressage et ainsi sa DCO.

1.5 TREATMENT DES EFFLUENTS PROVENANTS DU COMPACTAGE DE DÉCHETS

Parallèlement à la réduction volumique des déchets par compression, le traitement des effluents liquides générés lors de ce pressage a également été abordé par utilisation de technologies de filtration membranaire. Deux étapes successives de filtration sur cartouche puis d'ultrafiltration sur membrane s'avèrent nécessaires pour réduire la charge organique de l'effluent et générer ainsi un perméat conforme à la norme et pouvant ainsi être rejeté dans l'environnement.

1.5.1 Filtration sur cartouche

L'étape de filtration sur cartouche consiste à utiliser deux cartouches en série, de seuils de rétention 465 µm et 250 µm, respectivement, avec une surface de filtration de 0.1022 m^2. Différents tests ont été menés pour estimer la performance de chaque étape de filtration, en termes de rétention des particules en suspension et de réduction de la teneur en protéines et de la DCO dans l'effluent filtré. Les résultats permettent d'estimer un taux de rétention globale de 28,34% pour la matière en suspension et une réduction de 42,74% dans la teneur de protéines du jus filtré (par rapport au jus brut). Cependant, ces cartouches n'ont pas permis d'avoir une réduction significative de la Demande Chimique d'Oxygène (DCO), induisant la nécessité de procéder à une étape ultérieure de filtration membranaire avec des seuils de coupure inférieurs.

Table R.3. Taux de rétention des particules et des protéines par les cartouches de filtration.

Échantillon	Rétention des particules (%)	Rétention des protéines (%)	Réduction DCO (%)
Jus brut	-	-	-
465 µm	10,80	14,11	2,00
250 µm	19,66	33,33	3,67
Total	**28,34**	**42,74**	**5,60**

1.5.2 Essais de micro et d'ultrafiltration

L'objectif de cette étude est de trouver une membrane permettant de concentrer la charge organique de l'effluent mais avec un colmatage minimum. Afin de trouver le seuil de coupure adéquat, des test préliminaires ont été réalisés à l'aide du pilote d'ultrafiltration tangentielle MAXIM (PALL), avec trois membranes céramiques tubulaires de diamètre 7 mm, longueur 250 mm et seuils de coupure 50 nm, 200 nm et 1,4 μm.

Après caractérisation de chaque membrane (perméabilité hydraulique et calibration avec jus de pressage), 2 litres de jus ont été filtrés à une pression transmembranaire de 1,5 bar et une vitesse tangentielle de 3 m/s, avec re-circulation du rétentat et du perméat. Le débit du perméat a été suivi pendant 3 heures, et des échantillons ont été prélevées après 30 minutes, 1 h, 2h et 3h afin d'effectuer le dosage des protéines, des lipides, de la matière minérale et de la DCO. Le montage expérimental est illustré sur la figure ci-dessous :

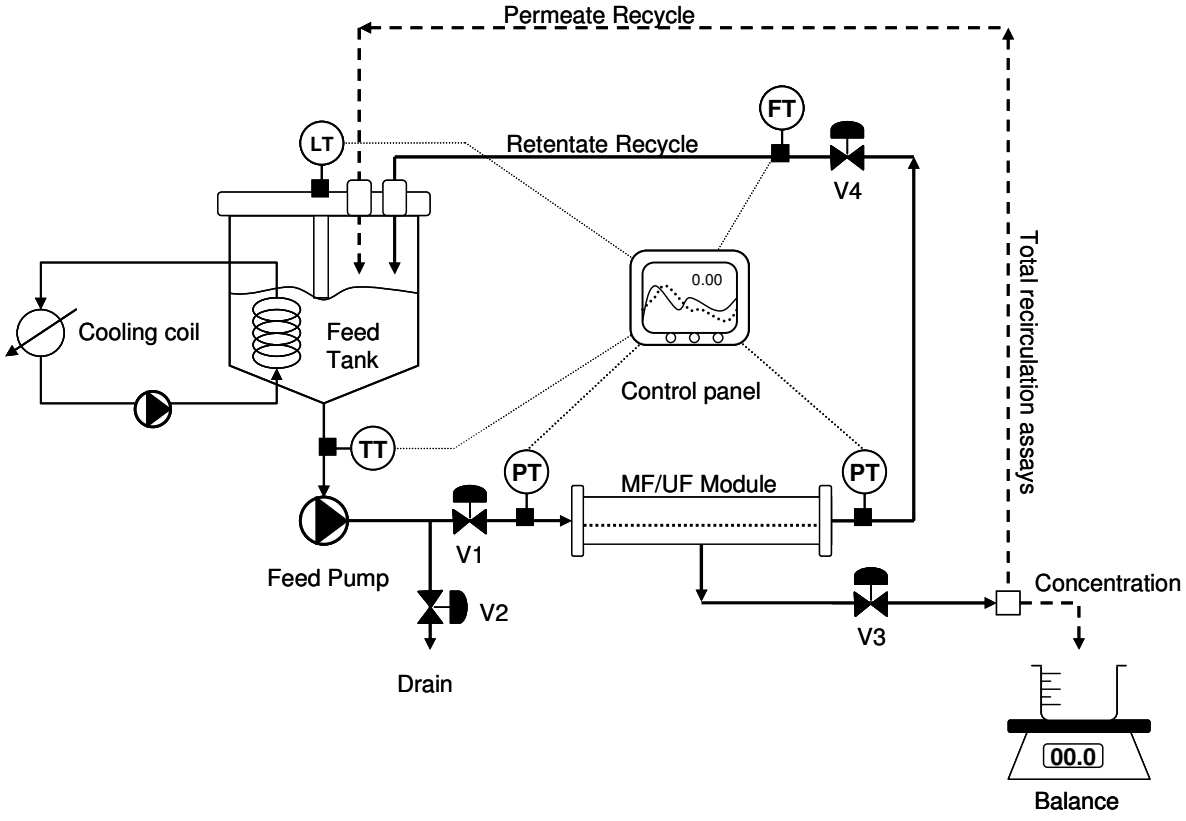

Figure R.10. Schéma du fonctionnement du pilot d'UF/MF Pall.

La pression transmembranaire, le débit de rétentat et le niveau du jus dans la cuve et sa température sont contrôlés pendant les essais. Le volume du perméat est mesuré à l'aide d'une balance avant d'être réintroduit dans la cuve contenant la solution à filtrer.

L'évolution du flux de perméat au cours de l'ultrafiltration a été ajusté au modèle de Suki (1984) qui assume que la chute initiale du flux de perméat est liée à la formation d'une couche de colmatage sur la surface de la membrane ce qui augmente sa résistance hydraulique. La résistance hydraulique de cette couche de colmatage augmente avec la durée de l'ultrafiltration, suivant une cinétique de premier ordre jusqu'à atteindre une valeur maximale $R_{F\infty}$. Le flux de perméat J peut être donné par l'équation suivante :

$$J = \frac{\Delta P}{R_M + R_B + R_{F\infty}\left(1 - e^{-k \cdot t}\right)} = \frac{J_0}{1 + \left(\frac{J_0 - J_\infty}{J_\infty}\right)\left(1 - e^{-k \cdot t}\right)} \qquad \text{(R.1)}$$

où le terme ΔP est la pression transmembranaire, R_M représente la résistance de la membrane, R_B la résistance de la couche de polarisation, k la constante cinétique et J_0 et J_∞ sont, respectivement, les flux du perméat initial et final.

Les paramètres du modèle ont été estimés pour chaque membrane par régression non linéaire des données expérimentales. D'après le tableau ci-dessous, la membrane de 200 nm présente le flux du perméat le plus élevé après 3 heures d'ultrafiltration. Malgré un seuil de coupure supérieur, la membrane de 1,4 μm présente un flux de perméat moyen inférieur à celui observé pour les autres deux membranes.

Table R.4. Estimation des paramètres du model de Suki pour les trois membranes

Seuil de coupure	J_0 L/(m²·h)	J_∞ L/(m²·h)	k (h^{-1})	$R_{F\infty}$ (bar·m²·h/L)	$R_M + R_B$ (bar·m²·h/L)
50 nm	33,69	23,50	2,15	$1{,}93 \cdot 10^{-2}$	$4{,}45 \cdot 10^{-2}$
200 nm	38,74	25,82	2,20	$1{,}94 \cdot 10^{-2}$	$3{,}87 \cdot 10^{-2}$
1.4 μm	26,69	20,35	1,50	$1{,}75 \cdot 10^{-2}$	$5{,}62 \cdot 10^{-2}$

Ceci peut s'expliquer par un meilleur degré d' interactions des composants présents dans le jus (notamment des protéines) avec la couche active de la membrane (α-alumine), qui

présente, au pH de la solution, une charge résiduelle négative, à la différence des autres membranes qui présentent une charge proche à la neutralité.

Après l'ultrafiltration, les trois membranes ont suivi un cycle de nettoyage composé d'un nettoyage alcalin (NaOH 20 g/L, à 50ºC pendant 30 minutes) suivi d'un nettoyage acide (HNO_3 2% vol., à 50ºC pendant 15 minutes) et finalement une étape de désinfection à l'hypochlorite sodique (250 ppm de Cl_2, à 20ºC pendant 15 minutes). Entre chaque étape, les membranes ont été rincées avec de l'eau MilliQ jusqu'à neutralité des eaux de lavage. La régénération de la perméabilité initiale de la membrane a été déterminé par la formule suivant :

$$TR = \frac{R_3 - R_W}{R_0 - R_W} \cdot 100 \qquad \text{(R.2)}$$

Où TR représente le taux de régénération de la perméabilité, R_W est la résistance intrinsèque de la membrane (résistance au passage de l'eau), R_0 est la résistance initiale de la membrane colmatée (après l'UF) et R_3 est la résistance de la membrane après avoir suivi le protocole de nettoyage. Selon les résultats obtenus après les tests de filtrabilité et de nettoyage, ainsi que les analyses de DCO des perméats, la membrane de 200 nm permet d'obtenir le plus grand flux de perméat, avec la DCO la plus réduite parmi les trois membranes. Les cycles de nettoyage permettent de récupérer la perméabilité initiale des trois membranes. Néanmoins, les étapes à l'acide nitrique montrent un effet inverse ou peu effectif sur l'efficacité du nettoyage. Ce constat a déjà été notifié par d'autres auteurs (Weis et Bird, 2001; Vaïsänen *et al.*, 2002 et Blanpain-Avet *et al.*, 2004).

Table R.5. Résumé des résultats obtenus après les tests d'UF pour les trois membranes.

Seuil de coupure	Descend relative du flux (%)	Flux stationnaire ($L \cdot m^{-2} \cdot h^{-1}$)	Taux de rétention (%)	DCO (mg O_2/L)	Taux de régénération (%)
50 nm	30,24	23,50	85,21	16750	100,21
200 nm	33,35	25,82	78,11	16300	99,79
1,4 µm	23,75	20,35	76,90	18775	99,52

La membrane de 200 nm a été donc choisie pour la mise en ouvre d'une opération de concentration du jus de pressage, avec re-circulation du rétentat tandis que le perméat est éliminé de façon continue pendant 8 heures, jusqu'à atteindre un facteur de réduction volumique VRF=1,7. La figure ci-dessous montre l'évolution du flux de perméat au cours du temps: à différence des essais de re-circulation totale (perméat et rétentât entièrement recyclés), le flux n'atteint pas un état stationnaire, mais il descend de façon continue pour atteindre une valeur finale d'environ 19 L/m^2·h après 8 heures de concentration.

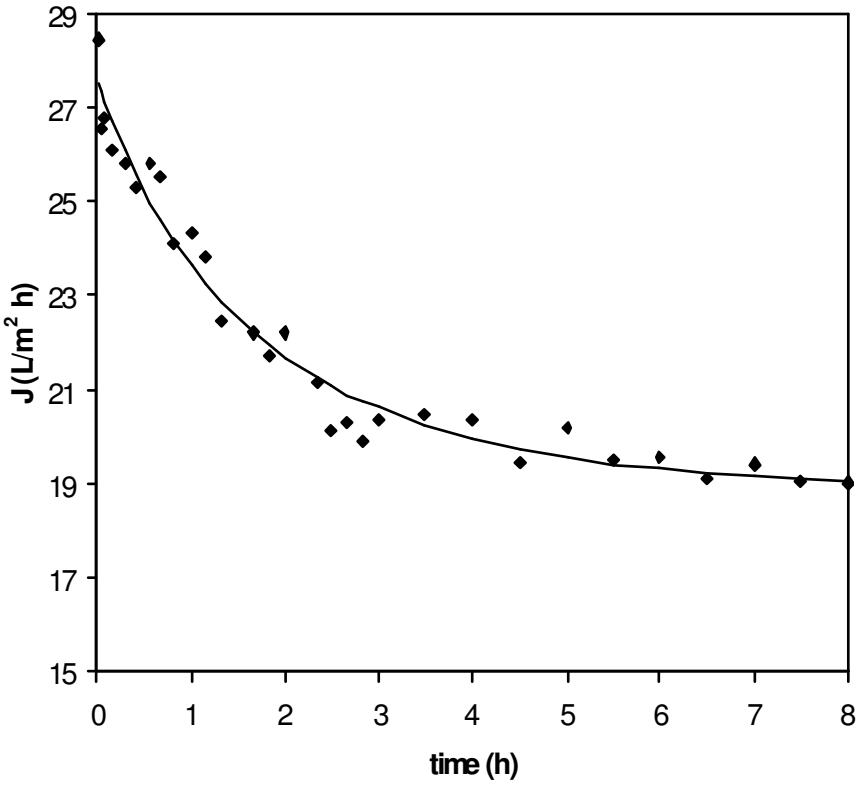

Figure R.11. Évolution du flux de perméat au cours de l'opération de concentration.

Les analyses réalisés sur le perméat collecté lors de la concentration montrent une DCO moyenne de 15.800 O_2/L, soit une réduction de 87% par rapport à la DCO moyenne du jus de pressage (125.000 mg O_2/L).

1.GENERAL INTRODUCTION ON MANAGING STRATEGIES OF MARINE RESOURCES

1.1 WORLDWIDE SITUATION OF FISHERIES, DISCARDS AND BY-PRODUCTS

A direct consequence of traditional fishing practices is the considerable quantities of wastes and by-products that are generated. They represent an economical and environmental problem since not all obtained from the sea is adequately used but thrown back into the sea as a waste.

With the aim of classifying and quantifying the by-products, three main groups are considered: discards, wastage on board and by-products and wastage on shore.

1.1.1 Discards

Discards are defined as being "that portion of the catch which is returned to the sea" for whatever reason (FAO 1996; Kelleher, 2005).

The quantification of discards and knowledge of trends in discarding practices are of value in the design of fisheries management regimes and initiatives to promote responsible fishing operations and catch utilization. Discards estimation is a very difficult task due to the lack of statistical data or scientific studies concerning this issue.

The definition of discards is taken from the FAO Fisheries Technical Paper T470 (Kelleher, 2005), adapted from the FAO Fisheries Report 547 (FAO, 1996):

Discards, or discarded catch is that portion of the total organic material of animal origin in the catch, which is thrown away, or dumped at sea for whatever reason. It does not include plant materials and post harvest waste such an offal. The discards may be dead, or alive.

The FAO definition includes both commercially exploited marine species and any other marine animal which is caught incidentally such as non-target finfish, crustaceans, mollusks, sea mammals and seabirds. The unintentional capture of non-target fish species, which are not retained for sale, but are thrown back into the sea because of their low value or legal requirements, has significant ecological impacts. Regarding trawl fisheries, nearly all fish, about half the non-commercial crustaceans and 98% of non-commercial cephalopods are dead when discarded (Bozzano and Sardà, 2002). By discarding juvenile fish, fish of little or no

economic interest or those which are over-quota, future yields (and hence income) are being lost. Discard of mature fish both waste resources in the short term and reduce the amount of adult fish which would otherwise have been available to support future productivity. No global estimates have been made of how much value is lost to the industry through discarding. However, a 2001 study by the Agricultural Economics Research Institute (ILE) in The Hague (Holland) on three specific European fisheries estimated that the discards of the Dutch beam trawl fishery in 1998 had a value in market around € 160 million, which represented 70% of the value of their landings for the same period. UK North Sea whitefish trawlers discarded cod, haddock and whiting worth € 75 million in 1999, equivalent to 42% of the value of their landings. The third fishery studied was the French nephrops' one, with a discard rate between 20% and 45% of the catch by weight according to species in 1997, representing fish worth nearly 100% of annual landings.

Discards of non-target species may be economically neutral, but it can have a serious environmental impact, in particular on marine biodiversity. represents a conservation problem because valuable living resources are wasted while global marine catches are declining. This problem starts to receive more attention from policy makers, industry and general public (FAO, 1996; FAO, 2005).

Discards may be attributed to many factors (FAO, 1996; Kelleher, 2005):

- **Fishing area**. Discard rates vary among different fishing grounds, due to the presence of reproductive areas where small-sized juvenile species are abundant, or the different composition of the fish populations on the ground, i.e., a different proportion between target and non-target species.

- **Fishing gear**. The gears employed to catch fish are an important factor in the selectivity of the fishing practice and therefore the quantities and composition of the discards. The selectivity of the fishing gear, as well as the is mainly determined by two parameters, mesh size and time of immersion. The folder influences the size and age of the specimens making up the catch and the last determines both the presence of non-target species and their degree of survival.

- **Fisheries policy**. Regulations concerning minimal landed size or minimal mesh size. A management system which relies on landing quotas as the main regulator of fishing

activity will lead to discards, particularly when various species are caught together in mixed fisheries. Regulations specifying a maximum percentage composition of a species kept on board will lead to a similar result. Minimum landing size regulations also lead to some discards when the selectivity is such that some fish below the minimum landing sizes are caught. The national regulations concerning the discard practices are varied; there are countries, such as Norway, where no-discard policies are applied, minimizing the quantities of non-target species caught and promoting the use of non commercial species for other applications, mainly fish meal or fish oil.

- **Fish markets**. They determine which species are targeted and which other are discarded. Market-driven discarding, know as high-grading, can take place in two ways: when the by-catch is a species with low market value and when the target species fish being caught are not as valuable as those which the operator hopes to find later. In this regard, discards may be composed of small-sized specimens of target species, whose commercial value is low, even if their size is higher than that allowed by minimal landing size regulations.

Some concepts related to discards, whose definitions are taken from the FAO Fisheries Technical Paper T470 (Kelleher, 2005) are used in this chapter:

- **Bycatch.** Bycatch is a subset from the overall catch made up of non-target animals. We cannot consider that the whole discards are due to bycatch species, since small sized target species are often discarded. Due to the changes in the value and use of bycatch over time, the term by-catch is interpreted in numerous ways based on arbitrary assessments of catch usage. Murawski (1992) summarised the arbitrarity of the traditional definition for by-catch with the slogan: “yesterday’s by-catch can be tomorrow’s target catch” .

- **Discard rate** is the proportion (percentage) of the total catch that is discarded.

- **Catch.** Catch includes all living biological material retained, or captured by the fishing gear, including corals, jefflyfish, tunicates, sponges and other non-commercial organisms, whether brought on board the vessel, or not.

- **Landings**. This term refers to the portion of the total catch brought ashore, or transhipped from the vessel.

1.1.2 Wastage on board

Nowadays, the number of vessels processing the captures on board is increasing (OFIMER 2005c, 2006). As a consequence of fish processing on board, an important quantity of subproducts is generated (heads, viscera, skins, etc).

Demersal species are traditionally gutted on board (monkfish, cod, conger, haddock, lings, pollack and whiting) as well as cartilaginous species such as sharks. Other species like black scarbbardfish are headed or tailed (grenadier). As a consequence of these activities an important amount of wastage is generated, and generally discarded into the sea (Andrieux, 2004).

These by-products, being easily perishable, need to be stabilized immediately by freezing. Only livers and eggs from some species, such as sikis and monkfish, have enough commercial value to be sold on land. Therefore, most of the wastage generated on board is discarded to the sea. Discarding these wastes to the sea can result in a high environmental impact as well as alter the ecosystem structure. Efforts towards the research of new techniques able to up-grade or stabilise these wastes should be done in order to avoid its dumping.

1.1.3 By-products and wastage on land.

Fish processing companies employ raw fish as raw material to be processed in order to obtain a final product with higher commercial value. Several operations are involved in fish processing: heading, gutting, filleting, removing tails and peeling . These operations generate by-products such as heads, viscera, tails, skins and fins which are not put on market due to their low acceptation by consumers or sanitary regulations which avoid their employ in human foods (Arvanitoyannis and Kassavetii, 2008). Other operations involved in fish processing, such as washing, thawing and cooking are the origin of aqueous effluents which are normally discarded. Wastewaters generated by fish meal industries contain a high organic load due to the presence of oils, proteins (0.5-20 g/l) and suspended solids (Afonso and Bórquez, 2002). They present high turbidity, strong greenish yellow colour, and stinky odour. Therefore, they should not be discharged without a suitable treatment in order to prevent negative environmental impacts and allow the recovery of high added value products.

1.1.4 Worldwide situation of discards

The quantification of discards and knowledge of trends in discarding practices are of value in the design of fisheries management regimes and initiatives to promote responsible fishing operations and catch utilization. FAO is mandated to report periodically to the United Nations on the implementation of the resolutions and to promote efforts to reduce or minimize discards, drawing the attention to wastage of fishery resources.

The last FAO assessment (SOFIA 2008) (FAO, 2009) includes the results of a previous study compiling information on catches and discards from the world's fisheries during the period from 1992 to 2001. This study assumes that discards are a function of a fishery, defined in terms of an area, fishing gear and target species, and has estimated global discards to be 7.3 million tonnes, with a global discard rate (quantity of discards as a percentage of the total catch) of 8 percent.

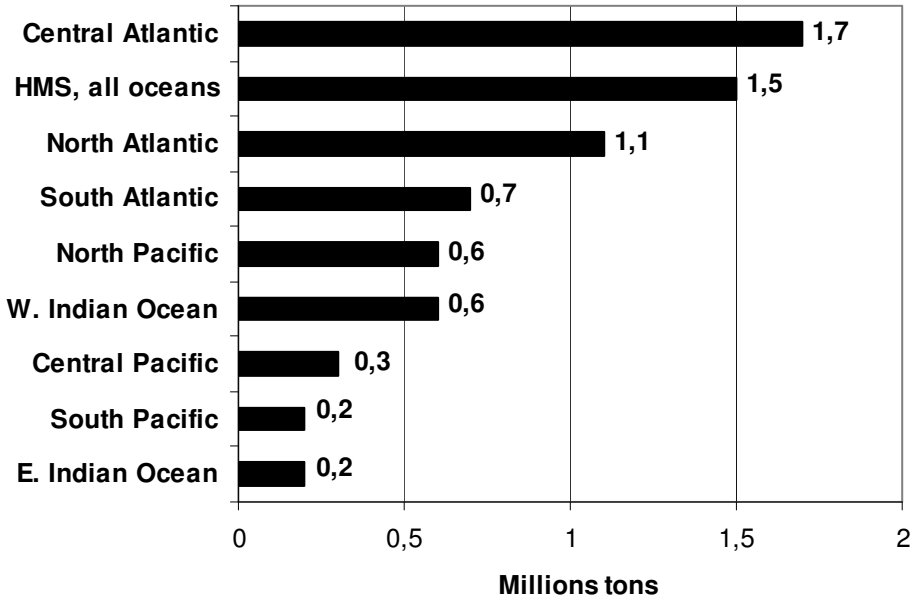

Figure 1.1. Yearly tonnage of discards by fishing area.

The highest quantities of discards are found in Northeast Atlantic and Northweast Pacific, as shown in Figure 1.1, which jointly account for 40 percent of the discards (FAO, 2009) . Regarding the fishing gear (Figure 1.2) trawl fisheries for shrimp and demersal finfish account for over 50 percent of the total estimated discards.

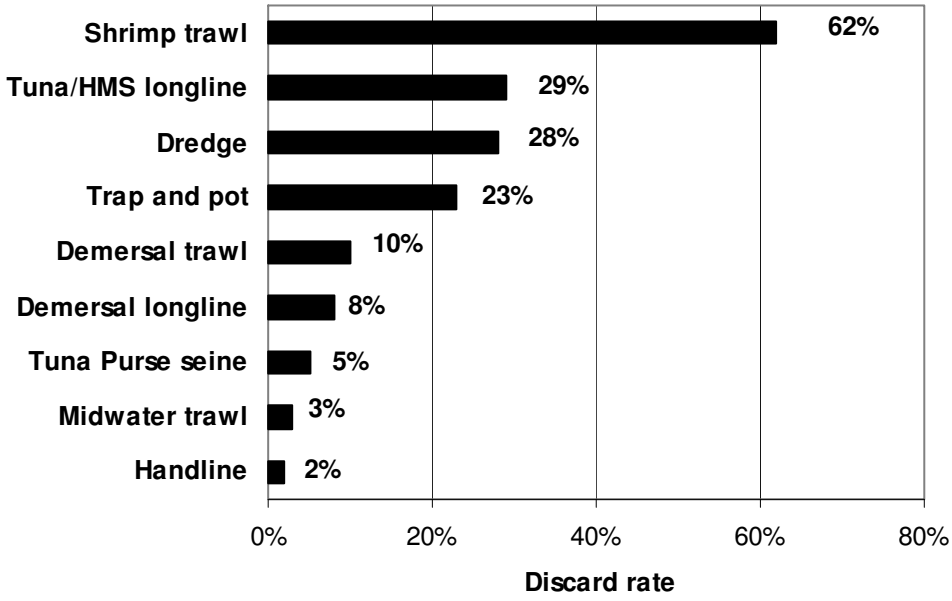

Figure 1.2. Discard rate by fishing year.

1.1.5 Legal framework

International instruments, including UN resolutions, the Kyoto Declaration and the Code of Conduct for Responsible Fisheries have highlighted the need to reduce, or minimise discards.

Worldwide there are 19 countries applying a no-discard policy. In European waters, discard bans are implemented in Iceland, Norway and Faeroe Islands. Iceland and Norway display particularly developed policies that served as examples for the on-coming EU no-discard policy.

Since 2004, Norway prohibited discards of any specimen caught (dead or alive) for all commercially important species, including cod, haddock, saithe, mackerel, herring, capelin and whiting. The discard ban is completed by other measures such as the compulsory use of sorting grids for shrimp and cod fisheries, temporary real-time closures and the obligation to leave fishing grounds when discards levels are too high or when a critical proportion of juveniles is observed in the haul.

In the case of Iceland, a discard ban was introduced in 1996, supplemented by other managing measures such as real-time closures when the proportion of undersized specimens is over a

critical value, and mesh sizes larger than those used in the European Union and minimum market sizes which are defined to permit all species to reproduce at least once.

The EU Commission Communication Com 2002/186, in the framework of the Reform of the EU Fishery Policy, aims to integrate environment needs into Fishery Policies. The European Code of Sustainable and Responsible Fisheries Practices, following the guidelines given by the FAO Code, claims to avoid the dumping of fish wastes or discards when possible, and to treat waste generated on board as if it were domestic waste, for example, by means of a compactor on vessels. This material must be retained on board for later treatment where suitable structures and equipments exist on land.

European Commission communications COM(2002) 656 and the earliest COM(2007)136 aim to initiate a policy which will reduce unwanted by-catches and progressively eliminate discards in European fisheries.

To accomplish with this objective, these communications propose to introduce a discard ban, where all finfish and crustaceans caught will have to be landed. A requirement to land all fish will mean that occasionally fish above the quota or below minimum market size will be landed. Other supplementary measures are to be introduced, such as encouragement to improve the selectivity of fishing gear, requirements to change fishing ground and real-time closures. The implementation principles of this policy have been discussed with Member States in 2007. In January 2008, a resolution emitted by the European Parliament showed its approval to this policy, paving the way for the development of regulations to be applied on specific fisheries from 2008 on. The first measures were applied in two pilot fisheries: the nephrops trawling fishery in the ICES statistic fishing area VII and flatfish trawling in the areas IV and VIId. The definitive regulations will come into force in 2010 and will imply a progressive reduction of the discards and a high grading ban which implies a prohibition to discard species subject to quota that can legally be caught and landed under Community fisheries legislation.

Technical solutions to handle these by-catches are to be considered, whether they will be sold through normal market systems, for human consumption, for reduction to fish meal and oil or otherwise (Kristinsson and Rasco, 2000; Bentis *et al.*, 2005; Dumay *et al*., 2006; Folador *et al.*, 2006). A compacting operation, able to reduce the volume of materials to store on board will result in less space and refrigeration requirements. In the case of by-products generated

by in land activities, a preliminary operation able to reduce their volume and water activity will facilitate their handling and transport. The use of a compactor has been already proposed by the Code of Conduct for Responsible Fisheries in order to reduce the volume of by-catches and wastes to be stored on board. As a consequence of pressing operations, two fractions are obtained: a solid cake which is stored on board and can be subsequently reduced to fish meal on shore (Bimbo, 1990; Folador *et al.*, 2006) and a press liquor consisting in an aqueous phase (containing valuable proteins) and an oily phase, as well as a variable amount of fine suspended solids. The press liquor should be subsequently submitted to a depuration treatment according to the regulations on effluent standards for the open sea and coastal zones and the maximum discharge limits established for the fish processing industry in land.

1.2 MANAGING AND UPGRADING STRATEGIES OF MARINE WASTES

1.2.1 Overview of fish processing.

Fish processing is not an exact term, as this industry is very widespread and quite varied in terms of types of operation, it may include processes such as sorting, grading, gutting, de-skinning (peeling if shellfish), filleting and trimming. For some fish or shellfish products, the processing may include breading and filling as well as boiling, pickling, freezing and smoking and different types of packaging, e.g. canning.

The end products from fish processing may be fresh, frozen or marinated fillets, canned fish, fish meal, fish oil or fish protein products, such as surimi. Surimi is an important fish product, with the majority of catches for some species used solely for its production.

Although the processing depends on the type of product, and it varies with the species and local fishing regulations or consumers demand, three main processing lines, clearly differentiated, can be defined, the processing of demersal fish (codfish or flatfish), the processing of pelagic fish (e.g. herring and mackerel), and the processing of shellfish (e.g. shrimp, prawn, lobster and mussels).

The processing of demersal or white fish is relatively simple, as it consists basically in gutting and filleting operations. White fish species have a low oil content and are generally gutted, cleaned and sometimes de-headed on board the fishing vessel. The fish are kept on ice boxes before being delivered to the fish processing plant. Once ashore, the fish may be re-iced and placed in chilled storage until required for further processing. Demersal fish processing in land usually consists in filleting, which involves cutting the fillets from the backbone and removing the collarbone. Some fish fillets may also be skinned at this stage. After inspection of fish fillets to ensure they meet product standard, they are packaged in different ways, depending on if the final product is intended for fresh consumption or will we marketed as frozen product. Fresh products are just packaged in boxes, and covered with a plastic layer which avoids direct contact with the ice. Frozen products are usually packed as 6-11 kg blocks in waxed cartons. The blocks are typically frozen and then kept in cold storage.

In contrast with white fish, pelagic fish species are very rarely gutted or cleaned on board the fishing vessels, due to the fact that they usually present high oil content, with the consequent risks associated with oily surfaces. Keeping the skin of the fish intact also reduces oxidation of the oil and thus maintains flesh quality. Therefore, pelagic fish is normally kept as whole fish in ice boxes until being off-loaded at the plant. The processing given in land differs also of that of white fish, since it usually involves greater elaboration before obtaining the final products, such as picked herring and canned mackerel. As a result of fish processing in the factory, the amount of by-products generated (heads, tails, viscera, fins) is higher, as well as the organic load of the wastewaters, due to its content in oil. Adding to this, some operations such as skinning of mackerel fillets, involve the immersion in a warm caustic batch which generates a very pollutant effluent which has to be neutralised before being discharged.

The term Shellfish includes various species of crustacean (e.g. crabs, prawns and shrimps), molluscs (e.g. mussels) and echinoderms, they are processed into many different types of products, which are usually boiled before being canned, contributing to higher levels of water and energy consumption. The by-products obtained after this processing consist normally in heads, tails and shells which can be up-graded thanks to their high content in chitin, which can be marketed as a fish food additive.

Canning is a final step common to all the three types of processing considered before. The canning process depends basically on the size of the fish. Small fish species such as sardines and pilchards are generally canned whole, with only the heads and tails removed. These products are cooked in the can after it has been filled with brine or oil. Regarding the effluent generation, canning operations involve the discharge of wastewaters, coming from the draining of cans after precooking (an operation undertaken for some species prior to can filling with oil or sauce), the spillage of sauces, brines and oil in the can filling process, and from the condensate generated during cooking operations. Can cooking may involve a high consumption in terms of energy and water.

1.2.2 Upgrading of fish by-products.

Modernization and increased capacity of fishing vessels has increased opportunities and ability to find and harvest fish in the ocean; now we are at a stage where most fish species are

being harvested to their limit. Sustainability of the stock and increased or total utilization of the harvested fish therefore is very important from an environmental point of view.

Fish industry involves a varied number of processing operations to transform the raw material in edible products, directly intended for human or animal consumption. Fishery waste on land is increasing nowadays driven by three factors. First, greater elaboration of fishery products, generating larger quantities of waste, second, a greater concentration of waste due to the implantation of new larger industries rather than smaller ones, and third less and bigger fish auctions (Blanco *et al.*, 2007).

Although much of this waste is already being handled, either for fish meal and oil production or treated as urban solid waste, it is considered that this kind of utilization is inefficient and that, with present technological development, a more intelligent and profitable use of them is possible.

Of the estimated 131 million tonnes of fish produced in 2000 in the world, nearly 74% (97 million tonnes) was used for direct human consumption. The remainder (about 26%) was utilised for various non-food products, mostly for reduction to meal and oil. As a highly perishable material, fish has a significant requirement for processing. In 2000, more than 60% of total world fisheries production underwent some form of processing. An important waste reduction strategy for the industry is the recovery of marketable by-products from fish wastes (Jespersen *et al.*, 1999).

Commercial processing of aquatic foods (or seafood) requires removal of bones, skin, head and viscera (by-products), which account for approximately 60-70 g /100 g of the fish weight. In general, fish meat and oil left on the by-products range widely, but typically account for 20 – 30g/100g and 5-15 g / 100 g, respectively (Torres, Chen, Rodrigo-Carcia, and Jaczynski, 2007). While it is not uncommon to “grind-and-discard” or landfill the 60-70 g / 100g of the by-products, these practices should be considered an irresponsible utilization of the natural resources.

The table 1.1, adapted from Arvanitoyannis and Kassaveti (2008) shows the average outputs of solid waste and liquid effluents generated by some of the most common fish processing operations. It is noticeable that the processing of oily fish (e.g. filleting, skinning, handling) results in higher organic loads in the wastewaters, due to its oil content. Some up-grading

operations, such as fish meal production from fish by-catches or small-sized species, permit a better utilisation of marine resources. The main drawback of fish meal processing is that this processing comprises cooking, evaporation and drying operations which are energy-intensive.

Table 1.1. Average outputs of wastewaters and solid wastes from the main fish processing operations (adapted from Arvanitoyannis and Kassaveti, 2008).

Operation	Wastewater (per ton of raw material)	Solid waste (per ton of raw material)
White fish filleting	5 – 11 m^3, BOD 35 kg, COD 50 kg	Skin 40-50 kg Heads 210 – 250 kg Bones 240- 340 kg
Oily fish filleting	5 – 8 m^3, BOD 50 kg, COD 85 kg	400 – 450 kg
Canning	15 m^3, BOD 52 kg, COD 116 kg	Heads/entrails 250 kg Bones 100 – 150 kg
Frozen fish thawing	5 m^3, COD 1-7 kg	-
De-heading of white fish	1 m^3, COD 2 – 4 kg	Heads and debris 270 – 320 kg
Trimming and cutting white fish	0.1 m^3	Bones and cut-off 240 – 340 kg
Filleting of de-headed white fish	1 – 3 m^3, COD 4 – 12 kg	Frames and cut-off 200 – 300 kg
Filleting of un-gutted oily fish	1 – 2 m^3, COD 7 – 15 kg	Entrails, tails, heads and frames 400 kg
Skinning white fish	0.2 – 0.6 m^3, COD 1.7 – 5 kg	Skin 40 kg
Skinning oily fish	0.2 – 0.9 m^3, COD 3 – 5 kg	Skin 40 kg
Handling and storage of fish	COD 130 – 140 kg	-
Pressing of the cooked fish	750 kg water, 150 kg oil	Press cake 100 kg
Stickwater evaporation	-	Concentrated stickwater 250 kg Dry matter 50 kg
Fish oil polishing	0.05 – 0.1 m^3, COD 5 kg	-

The FAO statistics also show that 75% of world fisheries are used for direct human consumption and the remaining 25% are reduced to fishmeal, oil, etc. However, while on weight basis the reduction fisheries account for a quarter of the total fish utilization, they only contribute 3.8% to the fisheries total economic value (FAO, 2009).

A characteristic of fish that has a bearing on the waste loads generated, is its highly perishable nature compared with other food products. If not properly refrigerated it spoils rapidly, the flesh becomes soft and loose, and pieces are easily lost. As the quality of the fish deteriorates over time, product yield decreases and product losses contribute to the waste loads. These losses often find their way into the effluent stream.

Fish processing plants often have little direct control over the handling of the fish catch before it arrives at the plant, except where the finfish vessels are owned by the processing company. In this case, the processor can set quality standards and expect certain handling practices.

1.2.2.1 Fish meal and fish oil production.

Fish meal is one of the main products obtained from fish waste, by-catch and other abundant species, such as anchovy, menhaden and capelin. Fish meal is a relative dry product composed mainly of protein (70%), minerals (10%), fat (9%) and water (8%); it can have different qualities, in terms of amino acid profile, digestibility and palatability, depending on the raw material used for its production and the type of process employed for obtaining the meal (FAO, 1986). Fish meal has been used as a livestock feed for many years. It is popular because of its high nutritional value. It has high levels of essential amino acids such as lysine which is often deficient in grain products that are the typical base for most animal feeds (Hall, 1992). It also has a high methionine and cysteine content and a high digestibility and biological value (Keller, 1990). It also contains vitamins such as B12, choline, niacin, pantothenic acid and riboflavin and is a good source of calcium (Ca), copper (Cu), iron (Fe), phosphorous (P) and other trace minerals. Fish meal is low in fibre and easy to produce (Hall, 1992).

Fish used for meal production may be divided into three categories:

- Fish caught for the sole purpose of fishmeal production (e.g. Peru, Norway, Denmark, South Africa, and U.S.A.).
- By- catches.
- Fish off cuts and offal from the consumption industry (FAO, 1986).

Fish meal is derived from the dry components of the fish, and the oil from the oily component. Water, which makes up the rest of the fish matter, is evaporated during the process, which increases notably the energy consumption associated to this type of processing. The evaporation must assure a minimal content in protein over 70 and a maximum content of fish oil up to 12. The table 1. shows the specifications for the so-called low temperature fish meal (LT fish meal), according to Ruiter (1995). One key parameter for the fish meal intended for aquaculture or animal feeding is its content of salt, which must be lower than 2.5.

Table 1.2. Specifications for LT fish meal (Ruiter, 1995).

Component	Fish meal composition	
	Minimum (w/w)	Maximum (w/w)
Crude protein	72	-
Crude fat	-	12
Water	6	10
Salt	-	2.5
Ash (salt free)	-	14
Ammonia (NH_3-N)		0.18

On the basis of a global survey conducted between December 2006 and October 2007 (Tacon and Metian, 2008) concerning the use of fish meal and fish oil within compound aquafeeds over 50 countries, it is estimated that in 2006 the aquaculture sector consumed 3724 thousand tonnes of fish meal (68.2% of total global fish meal production in 2006) and 835 thousand tonnes of fish oil (88.5% of total reported fish production in 2006). The top consumers of fish meal in 2006 were marine shrimp, followed by marine fish, salmon, Chinese carps, trout, eel, catfish, tilapia, freshwater crustaceans, miscellaneous freshwater fishes, and milkfish. Results from several studies (Tacon *et al.*, 2006) suggest that the use of fish meal and fish oil in compound aquafeeds will decrease in the long term, estimating a decrease of 44.5 % for fish meal and 15.5 % for fish oil in the period from 2005 to 2020. The main reason why fish meal and fish oil use is expected to decrease in the long run is due to a combination of a decreasing market availability of fish meal and fish oil from capture fisheries, increasing market cost for these finite commodities and increased global use of cheaper plant and animal alternative protein and lipid sources (Tacon *et al.*, 2006)

Most fish meal and fish oil production processes are automated and continuous, and comprise several process lines, each with a certain processing capacity. Production rates vary considerably, according to the season and types of fish being processed (FAO, 1986). On board the fishing vessels, the catch is normally stored in tanks of water. Upon arriving at the processing plant the fish are pumped to holding bins, where they are stored until required for processing. Extra sea water may need to be added to pump the fish.

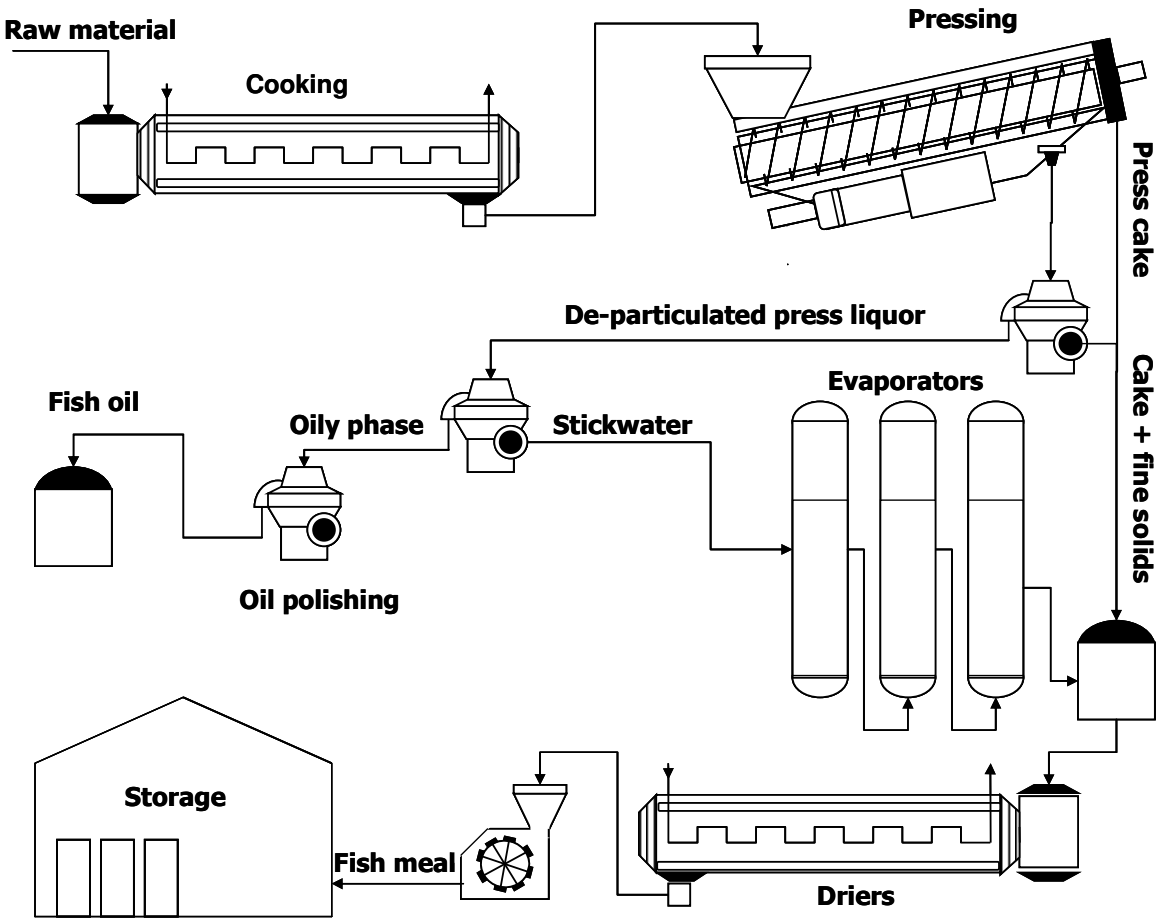

Figure 1.3. Flowsheet of the fish meal production process.

The purpose of the process of fish meal production is to separate the fractions present in the raw material composition (solids, oil and water) from each other as completely as possible, with the least possible expense and under conditions rendering the best possible products. Fish can be reduced to meal and oil in a number of ways. The bulk of the world's fish meal and oil is today manufactured by the wet method (Bimbo, 1990). From the storage bins, the fish are transported by screw conveyors to a cooking process which acts to coagulates the protein. The cooked mixture is then screened, using a strainer conveyor or a vibrating screen,

and then pressed to remove most of the water from the mixture. The pressed cake, containing 60-80 of the oil-free dry matter (protein, bones) and oil, is then dried by means of an indirect steam drier or a direct flame dryer. The meal passes through a vibrating screen and on to a hammer mill, which grinds it to the appropriate size. The ground meal is automatically weighted and bagged.

The pressed liquid generated from the previous processes passes through a decanter to remove most of the sludge, which is fed back to the meal dryer. Oil is separated from the liquid by centrifuges, polished and refined to remove any remaining water and impurities. The separated aqueous phase, referred to as stickwater, in multi-effect evaporators and the concentrate is thoroughly mixed with the press cake, which is then dehydrated usually by two-stage drying. The dried material is milled and stored in bags or in bulk. The oil is stored in tanks. The overall fish meal production process is depicted in the figure 1.3.

Fish meal production is a well optimised process which enables the recuperation and re-utilisation of all the valuable fractions originating from the screw press, i.e., the press cake, the fish oil and the stickwater. As mentioned before, the main drawback is found in his high energy consumption.

1.2.2.2 Fish minces and restructured products.

Muscle is the most frequently used part of the fish since it is the edible portion. In order to obtain this muscle, fish can be prepared before sale, by hand, or using mechanical filleters, leaving some parts like trimmings, etc., which can be used for different products such as fish mince and restructured products.

Restructured fishery products are made from minced or chopped muscle, which is subjected to a gellification process. In order to improve the gelling properties, certain techniques and binding agents, such as transglutaminase, could be employed (Uresti *et al.*, 2004).

Surimi products are based on techniques used traditionally in Japan, and the resulting products have a variety of forms and textures, imitating the characteristics of natural products (Borderias and Pérez-Mateos, 2005). Surimi is a paste formed by miofibrillar proteins obtained from mechanically debonned fish flesh washed with salt solutions to remove sarcoplasmic proteins and stabilized with the inclusion of cryoprotectans. It is an intermediate

product used in a variety of products such as the traditional Japanese kamaboko or different preparations of shellfish substitutes (crab legs, crab meat, young eel, etc.).

1.2.2.3 Collagen and gelatines

Gelatin is derived from the fibrous protein collagen, which is the major structural protein constituent of animal skin, bone and connective tissue. Gelatine is obtained from the partial hydrolysis of native collagen. Conversion of collagen into soluble gelatin can be achieved by heating the collagen in either acid or alkali. This provokes thermal solubilization of the gelatin due to the cleavage of a number of intra- and intermolecular covalent crosslinks that are present in collagen. The processing parameters (pH, temperature and time), as well as the pre-treatment and preservation method given to the raw material can strongly affect the final quality of the final gelatin obtained, as this is directly related to the final length of the polypeptide chains obtained after hydrolysis, and hence the functional properties of the final product.

The last report of GME (Gelatin Manufacturers of Europe) indicates that the annual world output of gelatin is nearly 326,000 tons, with pig skin-derived gelatin accounting for the highest output (46%), followed by bovine hides (29.4%), bones (23.1%) and other sources (1.5%). Mammalian gelatines (porcine and bovine), although being the most popular and used, are subject to major constraints and skepticism among consumers due to socio-cultural and health-related concerns. Both Judaism and Islam forbid the consumption of any pork-related products, while Hinduism does the same with products coming from cow. In addition, the outbreak of the Bovine Spongiform Encephalopathy (BSE) has increased the reluctance among consumers and researchers to consume gelatins obtained from bovine sources, although it is proved that the risk of BSE transmission associated with bovine bone gelatin is close to zero (Schrieber and Gareis, 2007). All these constraints have increased the research of alternatives to mammal-derived gelatin. In this framework, gelatin from marine sources stands for a good substitute as it meets the religious requirements from Jewish, Muslims and Hinduism markets and it is not associated with the risk of outbreaks of the BSE. Furthermore, fish skin, which is a major byproduct of the fish-processing industry, as it represents, together with fish bones and fins, around 30% of fish fillet processing waste (Blanco *et al.*, 2007). The yield of collagen obtained from these sources ranged from 36% to 54% (Nagai and Suzuki,

2000). However, fish gelatine production is still minor nowadays, yielding about 1 of the annual world gelatine production of 250,000 tonnes (Blanco *et al.*, 2007).

Production of fish gelatine is based, since 1960, on the thermal solubilisation of the collagen contained in the fish skins, basically from ray finned fishes (cod, tuna, pollock, etc.) as well as chondrichthyes (namely shark and ray) . A complete description on the manufacturing process of fish gelatine is given by Grossman and Bergman (1992) in a United States Patent. All gelatine manufacturing processes consist of three main stages :

- **Pre-treatment of the raw material**, it consists in several consecutive acid-alkali washes of the raw material with the purpose of removing unwanted material such as noncollagenous proteins and soluble solids, accompanied of a partial cleavage of the crosslinks between polypeptide chains present in the collagen structure.

- **Extraction**. The process can follow different treatment sequences, carried out at neutral, acid or alkali pH. In this stage, the solubilisation and partial hydrolysis of the initial collagen take place at a greater extend, resulting in the release of polypeptide chains from the initial cross-linked collagen structure.

- **Purification.** This stage is devoted to transform the solution resulting from the extraction into a product with the required specifications. In terms of micro constituents, the desired properties are achieved by means of treatments such as activated carbon filtering, oxidation and/or deionization whereas the specifications in terms of water content require the concentration and drying of the gelatin solution. This has been traditionally carried out by means of a triple effect evaporator followed by a drum drier, a process which energy intensive and very sensitive to scale in fuel costs. Pressure driven processes, such as membrane diafiltration, can overcome this drawback as they demand for lower energy consumption and can be carried out at room temperature, thus minimising protein denaturation.

Fish gelatine finds a wide range of applications thanks to its low melting point and emulsifying properties (Karim and Bhat, 2009) and can be summarised as below:

- Microencapsulation of pharmaceutical products, such as vitamins or azoxanthine.

- Foodstuffs. Its good emulsifying properties and low calorific content make them suitable to be used as ingredients in low-fat products. Gelatin melts in the mouth to give excellent sensory properties resembling fat.

- Cosmetics: moisturizing and texturing agents.

- Technical material: base of light-sensitive coatings that are important to the electronics trade. Gel for photographic emulsions.

1.2.2.4 Natural pigments

Carotenoids are a group of fat-soluble pigments that can be found in many plants, algae, microorganisms and animals, and are responsible for the colour of many important fish and shellfish products. Most expensive seafood, such as shrimp, lobster, crab, crayfish, trout, salmon, redfish, red snapper and tuna, have orange-red integument and / or flesh containing carotenoid pigments (Haard, 1992).

Shrimp waste is one of the most important sources of carotenoids. In a review on the uses of fish wastes from aquaculture, Arvanitoyannis and Kassavetii (2006) compared the extraction of carotenoids from shrimp waste with various organic solvents (methanol, ethyl methyl ketone, isopropyl alcohol, ethyl acetate, ethanol, petroleum ether and hexane). The results showed that the highest yields were achieved with a mixture of 40% isopropyl alcohol and 60% hexane (43.9 μg /g waste). The recovered carotenoids can be used instead of synthetic carotenoids in aquaculture feed formulations, or in the colouration of some surimi based products (Blanco *et al.*, 2007), and the residue available after extraction may be used for the preparation of chitin/chitosan.

Furthermore, some pigments like asthaxanthin are important in medical and biomedical applications as they have shown antioxidative activity and are precursors of vitamin A (Blanco *et al.*, 2007).

1.2.2.5 Chitin and chitosan

Another important category of by-products from marine bioprocessing plants includes crustacean shells and shellfish wastes. Efficient utilization of these marine by-products also

become an environmental priority due to increased quantity of accumulation from processing plants as well as slow natural degradation of these materials.

Chitin is a polysaccharide found in the outer skeleton of insects, crabs, shrimps, and lobsters and in the internal structures of other invertebrates. It is one of the major components of crustacean shell waste (it represents 1/3 of the shrimp carapace), and can be identified as a biologically active polysaccharide and thus valuable for many applications. Chitin is a high-molecular weight linear polymer of N-acetyl-D-glucosamine (N-acetyl-2-amino-2-deoxy-D-glucopyranose) units, which is used in a number of applications, such as a flocculating agent, a wound healing agent, a sizing and strengthening agent for paper, and a delivery vehicle for pharmaceuticals and genes. Chitin can be processed into many other bioactive derivatives. Among them, the most common form is chitosan, which results from the removal of considerable amount of acetyl groups from chitin.

Chitosan is produced commercially by deacetylation of chitin. The degree of deacetylation (DA) can be determined by NMR spectroscopy, and it ranges from 60-100 % in commercial chitosans. In industrial-scale procedures, chitin is produced by treating seafood waste, especially shells from crustaceans (shrimps, crabs, lobsters, krills, etc) by acid hydrolysis, obtaining a final product with a DA of 20-30%, which must be further processed to complete de-acetylation and thus meet the market requirements. This reaction can be also carried out by enzymatic way by means of chitin-deacetylases. These methods are preferable as they do not involve the production of harmful industrial chemicals and result in greater yields of oligomers with higher degree of polymerisation (Kim and Mendis, 2006). Chitin and Chitosan chemistry have been extensively reviewed by Roberts (1992).

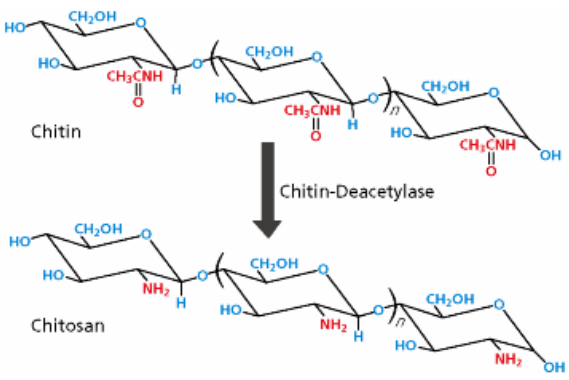

Figure 1.4. Transformation of chitin into chitosan by enzymatic deacetylation.

The amino group in chitosan has a pKa value around 6.5, thus, chitosan is positively charged and soluble in acidic to neutral solution. In other words, chitosan is bioadhesive and readily binds to negatively charged surfaces such as mucosal membranes.

Chitosan enhances the transport of polar drugs across epithelial surfaces, and is biocompatible and biodegradable. Purified qualities of chitosans are available for biomedical applications. Chitosan has also been identified as effective in reducing LDL-cholesterol levels in liver and blood (Kanauchi, *et al.*, 1995). The mechanism suggested is that these compounds act as fat scavengers, removing fat and cholesterol in the digestive tract and promoting their excretion. Beside these applications derived of its adhesive properties, chitosan has shown strong antimicrobial activity against a variety of microorganisms, and has also revealed certain antitumor properties both in vitro and in vivo (Jeom and Kim, 2002).

Chitin and chitosan production from by-products is not available nowadays in France, as the the production costs associated France (150 €/kg) are very high compared to those of other non-European countries (around 20 €/kg). These costs, added to the fact that the quantity available of by-products able to be transformed into chitin and chitosan is not enough, makes not feasible the development of a chitin market in France (Andrieux, 2004).

1.2.2.6 Aromatic upgrading

Nearly 2100 tons of by-products are transformed for an aromatic use each year in France. They are used as intermediate foodstuffs in the formulation of many cooked dishes, bisques, cheese-making preparations, snack bars, soups, aromas, sauces or surimi (Prost *et al.*, 2008). The high availability of the raw material (marine by-products) and techniques employed in the aroma compounds extraction allow high diversity of marine flavour production. These flavour compounds present several advantages (Prost *et al.*, 2008):

- They give a natural character to the flavour and increase the persistence in mouth.
- They are available all year long, have a standardized quality and an easy way of utilisation (by the removal of the nonedible parts), meeting all the requirements in hygienic quality.

Flavour compounds from seafood by-products, being mainly extracted via enzymatic hydrolysis of protein materials, provide a high protein rate to the foodstuffs where they are added.

Not all the by-products available from the fish processing operations are retained for aromatic upgrading, the raw material for this kind of valorisation consists in heads and fish-bones, essentially those of anchovies, mackerel, tuna, salmon and white fish, as well as shellfish heads and carapaces (shrimps, prawn, lobster, crawfish or common crab).

The processes used nowadays for the aromatic extraction comprise four unitary operations: mechanical crushing, extraction, separation and concentration. The extraction stage is main critical, since it must assure no loses in the organoleptical quality of the raw material. Enzymic hydrolysis procedures can provide a wide range of aromatic extracts, depending on the nature of the enzymes employed and the operating parameters of the enzymatic reaction, such as ratio enzyme/substrate, or pH and temperature at which the hydrolysis was carried out. To this respect, the amino acid composition of the hydrolysate will influence the organoleptic properties of the marine flavour. For example, an extract wealth of hydrophobic amino acids like Phenylalanine, Tyrosine, Arginine, Leucine, Isoleucine, Valine, Methionine and Histidine will be bitter and an extract wealth of Gycine will be soft (Prost. *et al*, 2008).

The marine flavour market is nowadays is expansion, favourised by the increasing trend in "ready-to-cook" and "ready-to-eat" products. According to the report of Andrieux (2004), on the management and upgrading of the by-products from fish processing in France, the marine flavour market is less competitive than that of their direct competitors (Japan, Norway, Russia and the USA), due to the higher production costs and the weak availability of by-products, specially those from shellfish processing (most of the shellfish in the French market is imported from other countries, such as Canada, India or Madagascar), estimating the total production of marine aromatic extracts to be 2400 tons in 2004.

1.2.2.7 Biodiesel

Fish oil is produced in large quantity by fish-processing industry which has similar calorific value to petroleum distillates. Active studies have been carried out for using fish oil as fuel for diesel engines. Biodiesel (fatty-acid alkyl esters) is a renewable and environmentally friendly energy source. The most commonly used technique to produce biodiesel from fats is the

transesterification in which triglycerides are reacted with alcohol, usually methanol, in the presence of a catalyst, usually potassium or sodium hydroxide (KOH or NaOH), to produce mono alkyl esters. A general review on the recent trends in biodiesel production from fatty sources (vegetal or animal) can be found in Demirbas (2007).

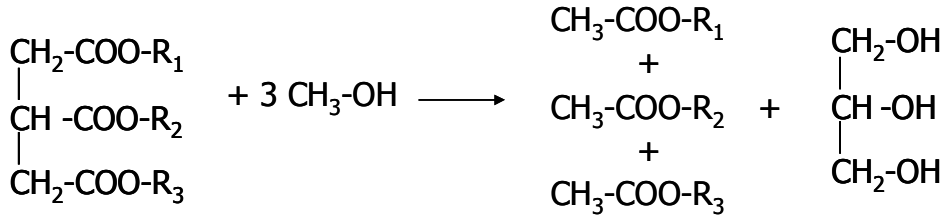

Figure 1.5. Transesterification of a triglyceride molecule into three alkyl ester units.

Besides the reaction parameters (alcohol/oil ratio, reaction temperature and time), the free fatty acid (FFA) content of the raw material is an important variable since it affects the development and the final products obtained after the reaction (El-Mashad *et al.*, 2008). High FFA would result in soap formation when alkali-derived catalyst are used in the transesterification due to neutralisation reactions between the alkali and the free fatty acids. The soap formation could decrease the biodiesel yield and complicate the separation and purification of the biodiesel product. Several pretreatments are reported in literature to overcome these drawbacks and improve the biodiesel yield and its performance.

Kato *et al.*, (2004) evaluated the ozone-treated fish waste oil as a transportation diesel fuel. The biodiesel was tested for its density, flash point (temperature at which ignition starts), pour point (lower temperature at which the oil is pumpable), heating value, distillation test and sulphur content, showing almost identical higher heating value (10700 kcal/kg) and density (0.87 g/cm^3 at 15°C), lower flash and pour points (37 and –16°C, respectively) compared with commercial diesel fuel.

El-Mashad *et al.*, (2008) subjected fish oil from salmon to an acid pre-treatment, followed by an alkali-catalysed transesterification in order to improve the biodiesel yield up to 97.6 % (biodiesel/salmon oil ratio). The main disadvantage of this biodiesel was it high cost, compared to those obtained from vegetal wastes, due to the high price of the salmon oil (950 US$/ton).

Lin and Li (2009) evaluated the fuel properties of biodiesel produced from the crude fish oil from the soapstock of marine fish. The fuel characteristics from crude oil were measured and compared with those of biodiesel from waste cooking oil, shower higher heating value and cetane index (this last is a measure of a fuel's ignition delay), with lower peroxide value (lower extent of rancidity reactions during its storage), and lower flash point and distillation temperature, which determines that the ignition of this diesel with air can be started at lower temperatures.

Preto *et al.* (2008) carried out several combustion tests for fish oil, to evaluate fish oil as an alternative fuel for conventional boilers and furnaces. The results showed that fish oil burned easily in the furnace and the boilers, and it could reduce effectively the viscosity of the residual fuel oil. The emission was generally lower than the pure commercial fuel oil except that of NO.

1.2.2.8 Bioactive compounds

The development of new extraction technologies and research has permitted the identification and isolation of an increasing number of bioactive compounds from remaining fish muscle proteins, collagen and gelatine, fish oil, fish bone, internal organs and shellfish and crustacean shells. These bioactive compounds can be extracted and purified with technologies varying from simple to complex and such compounds may include bioactive peptides, oligosaccharides, fatty acids, enzymes, water-soluble minerals and biopolymers for biotechnological, nutraceutical and pharmaceutical applications.

Kim and Mendis (2006) reviewed most of the current sources and applications for these bioactive compounds:

1.2.2.8.1 Bioactive compounds from fish muscle protein.

Fish frames and cutoffs result from mechanically deboned fish contain considerable amounts of muscle proteins. They can be hydrolysed enzymatically to recover protein biomass otherwise discarding as processing waste. Peptides present in protein hydrolysates from fish muscle protein have exhibited numerous bioactivities such as antihypertensive, antithrombotic, immunomodulatory and antioxidative activities (Gormley, 2006; Nagai *et al.*, 2008; Je *et al.*,2009, among others). The antihypertensive activity reported for some fish

peptides is due to the inhibition of angiotensin I converting enzyme (ACE), even stronger than that of many other natural peptides . This activity has been tested in vivo by lowering blood pressure in spontaneously hypertensive rats (Lee *et al.*, in press) . There is an increasing interest to explore natural antioxidative substances without side effects. In this framework, peptides from fish hydrolysates have shown a great potential to develop safe and non-hazardous natural antioxidants. Researchers have also identified that fish protein hydrolysates possess hormone-like peptides and growth factors to accelerate calcium absorption (Fouchereau-Peron *et al.*, 1999). Therefore, these peptides could be used in the treatment of osteoporosis and Paget's disease.

1.2.2.8.2 Bioactivities from skin collagen and gelatin.

Enzymatically hydrolysed fish skin gelatin have shown better antioxidant and antihypertensive activies than those exhibited by peptides derived from fish muscle protein (Kim and Mendis, 2006). It is presumed that the observed antioxidative and antihypertensive properties of gelatin peptides can be associated with the repetition of the amino sequence Gly-Pro-Ala in their structure, which is exclusive from these peptides.

1.2.2.8.3 Fatty acids from fish oil.

The fat content of fish varies from 2-30, depending on the type of species, diet, season, environment, and geographic variations. Composition of fish oil is different from that of other oils and mainly composed of two types of fatty acids, eicosanpentaenoic acid (EPA) and docosahexaenoic acid (DHA). These are polyunsaturated fatty acids classified as omega-3 fatty acids and predominantly found in many marine animals, which have been reported to promote several benefits on human health. Among the properties of omega-3 fatty acids the best known are prevention of atherosclerosis, reduction of blood pressure and protection against arrhythmias, which are extensively reported in the literature.

1.2.2.8.4 Minerals from fish bone.

Fish bone is separated after removal of muscle proteins on the frame. It can be upgraded in a double way. On the one hand, it can be considered as a source to isolate collagen and gelatin, in addition to fish skin, since it is the major component of the organic material in the fish

bone, which represents 30%. On the other hand, fish bone consists of 60-70% of inorganic substances, mainly calcium phosphate and hydroxyapatite. Fish bone is considered as a potential source to obtain calcium, whose absorption to the body has been tested in vivo (Larsen *et al.* 2000). Arvanitoyannis and Kassaveti (2008) reported that one of the most promising techniques for fish bone utilisation is its use as Chromium complexating agent.

1.2.2.9 Fish Protein Hydrolysates

Proteolytic modification of food proteins to improve palatability and storage stability of the available protein resources is an ancient technology. Different techniques exist for extracting and or hydrolysing protein from fish. These include using aqueous and organic solvents to extract proteins and concentrated acid or alkali to extract and hydrolyse proteins at elevated temperatures. These methods normally adversely affect the functional and organoleptic properties of the fish protein hydrolysates (FPH) and may product toxic by-products.

Biological processes using proteolytic enzymes (proteases) are now far more frequently employed in industrial practices to make FPH, because enzyme hydrolysis is usually a mild process that results in products of high functionality, good organoleptic properties and excellent nutritional value without the formation of toxic by-products (Mackie, 1982; Vilhelmsson, 1997; Kristinsson and Rasco, 2000a).

Enzymatic hydrolysis can be done via proteolytic enzymes already present in the fish viscera and muscle (endogenous proteases), or by adding enzymes from other sources. In the first case, the reaction is referred as to autolysis. An autolytic process depends on the action of the digestive enzymes of the fish itself (Mukundan *et al.*, 1986). There are no enzyme costs involved, and it is a simple operation. The end product of autolytic hydrolysis is generally a fairly viscous liquid rich in free amino acids and small peptides. The digestive enzymes are primarily the serine proteases trypsin and chymotrypsin, and the thiol protease pepsin, all major enzymes of fish viscera and digestive tract. Lyosomal proteases, or catheptic enzymes, present in fish muscle cells also contribute to proteolytic breakdown to some extent (Mukundan et al, 1986; Yamashita and Konagaya, 1992).

Endogenous proteolytic enzymes are used to produce hydrolysed products, specially fish sauces and fish silage (Al-Jedah and Ali, 1999). The production of fish sauce has thousands of years of tradition in Asia, and it is used mainly as a condiment on rice dishes like the popular

Nuoc-Nam produced in Vietnam (Gildberg, 1993). The substrate (fish from several pelagic species such as anchovies or sardines or species of low commercial value) is immersed in a solution containing high concentrations of salt (20% to 40%) at ambient tropical temperatures with no addition of acid or base to modify natural pH. This fermentation usually takes 6 to 12 months to obtain a liquefied fish sauce composed predominantly of free amino acids. Even if the high salt concentration is responsible for the slow hydrolysis rate, it is necessary to avoid microbe spoilage.

The addition of exogenous enzymes to hydrolyse food proteins is a process of considerable importance used to improve the physicochemical, organoleptic and functional properties of the initial protein substrates. Enzymatic hydrolysis has been investigated on several marine protein sources, such as cod (Aspmo *et al.*, 2005; Šližyte *et al.*, 2009), shark (Diniz and Martin, 1997), sardine (Dumay *et al.*, 2006; Kechaou *et al.*, 2009), pollack (Se-Kwon *et al.*, 2001; Jae-Young *et al.*, 2005), whiting (Pacheco-Aguilar, 2008) and Atlantic salmon (Kristinsson and Rasco, 2000b; Liaset *et al.*, 2002), among others.

In contrast with the autolysis, the hydrolysis of fish protein with selected proteolytic enzymes provides the possibility of controlling the degree of cleavage inside the protein structure by using an appropriate enzyme/substrate ratio and reaction time. Among the different proteolytic enzymes assayed on fish materials, Alcalase, an alkaline enzyme produced from *Bacillus licheniformis* and developed by Novo Nordisk (Bagsvaerd, Denmark) has been proven repeteadly by many researchers to be one of the best enzyme used to prepare fish protein hydrolysates (FPH) (Kristinsson and Rasco, 2000a).

The functional properties exhibited by the fish protein hydrolysates have been extensively reviewed by Kristinsson and Rasco (2000a):

- Increase of the solubility of the hydrolysates, compared to the raw protein material, due to the hydrolysis of myofibrilliar proteins, which have found to be responsible for protein insolubility, as well as the mayor exposure of ionic residues in the course of the hydrolysis, which increase the repulsion between the peptide units and favours the solubilisation of the final hydrolysate.

- Water-holding capacity. This term refers to the capacity of the protein matrix to retain water molecules inside its structure. Fish protein hydrolysates have excellent water-holding capacity, and thus useful properties for certain food formulation.

- The emulsifying properties of hydrolyzed protein are improved by carefully controlling the extent of hydrolysis. Extensive hydrolysis results in a drastic loss of emulsifying properties.

- Food foams consist of air droplets dispersed in and enveloped by a liquid containing a soluble surfactant lowering the surface and interfacial tension of the liquid. Onodenalore and Shahidi (1996) studied the foam formation and foam stability of shark and capelin protein hydrolysates.. Both exhibited good foam formation. Capellin hydrolysates presented higher foam stability after 30 s that dropped significantly compared to shark protein hydrolysates.

- The main drawback to the introduction of FPH in the food formulations is the apparition of bitterness, which is related to the hydrophobic amino acids of peptides. Strict control of the hydrolysis and termination at a low degree of hydrolysis is desirable to prevent the development of bitterness in the final hydrolysate.

1.3 GENERATION OF DISCARDS, WASTES AND BY-PRODUCTS BY THE FRENCH FISHERIES AND FISH PROCESSING INDUSTRY.

1.3.1 Discards in French fisheries.

In this study, an estimate of discards, wastage on board and by-products from onshore processing was made, focused on French fisheries.

French fisheries provide a great number of target species, with more than sixty species of bony and cartilaginous fish (Andrieux, 2004).Most of these species are caught by inshore fishing (92%), with only a few industrial fishing vessels sailing during long periods, and provided with storage and processing systems on board (OFIMER, 2006; EU Fisheries Yearbook, 2003; Annuaire Eurostat 2005), as shown in figure 1.6.

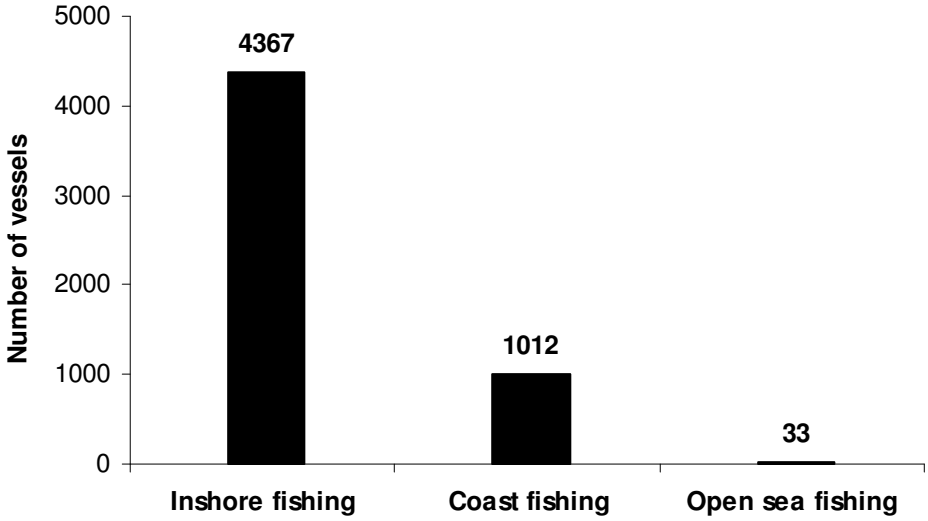

Figure 1.6. Number of vessels in French fleet. Distribution by fishing practice. OFIMER 2004

Most of the fleet is concentrated in the Atlantic-North-East; while Mediterranean Sea fisheries

target blue fish species (tuna, anchovy, sardine). The main ports, considering the landings, are Boulogne-sur-Mer in the West Channel, and Concarneau, Guilvinec and Lorient in the Bay of Biscay. Information about discards from finfish and crustacean species has been mainly taken from five previous reports on this subject:

Discards in the world's marine fisheries: an update. Report from the FAO (2005) which evaluates the discard rate for every fishery. The main difference between this report and other previous studies is the fact that this report evaluate the discards for every fishery, while previous reports try to establish a direct relationship between each target specie and its discard rate, which is not correct if we consider that the discards are influenced by traditions, fishing policies, and fishing techniques employed in each country. This study gives an estimate of 500,000 to 880,000 tonnes in the North Sea in the 1990's.

Report of the scientific, technical and economic committee for fisheries (STECF). Discards from Community Vessels. This report from the STECF group, compiles an overview of discards from community vessels in the Mediterranean and the North East Atlantic by fleet, stock and quarter, in order to provide estimates of the total amount of discards due to EU fleet practices. STECF has therefore not been in a position to estimate the overall absolute amount of discards in European fisheries.

Les rejets dans le pêche artisanale de Manche occidentale (Yvon Morizur, Stephane Poaureau and Annie Guenole, 2000). Report from the Department of Fishing Resources of the IFREMER (French Institute for Marine Research). This study was done over a full year and is the first one in the Western Channel. It concerns several French fishing techniques: fixed netting, inshore trawling and offshore trawling. According to this study, the main variables affecting discard rate has been found to be the immersion time of the nets, with a different significance depending on the specie.

Les rejets de la pêche (Morizur *et al.*, 1996) Report from the Department of Fishing Resources of the IFREMER which studies the main fishing techniques used in the Bay of Biscay, focusing on the main target species. It analyses the rate and composition of the discards, taking into account both by-catch species as well as length-frequency distribution of discards from target fish.

Estimation des rejets de pêche des chalutiers français en Mer Celtique (Rochet M.J., Trenkel V., Peronnet, 2001). Discards of the French trawler fleet operating in the Celtic Sea in 1997 were studied. The fleet discarded an estimated 30,000 tons of animals in 1997, while landing 63,000 tons. The total quantity discarded did not differ among metiers, but the species composition of discards did. Benthic trawlers discarded mainly by-catch species, whereas demersal and Nephrops trawlers discarded primarily their target species.

Scientific articles. Information about discards is often very disperse and related to a specific area or fishery. Two interesting articles dealing with discards in the West and North Coast of British Isles (which provide species with high commercial interest such us mackerel and herring) are:

Allain *et al.* (2003) made an estimation about the French deepwater fishery discards in the Northeast Atlantic Ocean. The target species studied are the roundnose grenadier *C. rupestris* with other commercialised species such us the black scabbard fish *A. carbo* ,the "siki" sharks and the orange roughy *H. atlanticus*, focusing on the by-catch species composition of the discards.

Pierce *et al.* (2002) performed a study on the by-catches and discards in the pelagic fisheries in Scothland. Observers were placed on pelagic vessels in the Scottish fisheries for mackerel (*Scomber scombrus*), herring (*Clupea harengus*), "maatje" herring (herring caught just before their first spawning) and argentines (*Argentina silus*) to monitor by-catch composition and discarding practices. Discarding rates in the fisheries varied, with herring and argentine fisheries showing no discards, the mackerel fishery a discard rate of around 4% and the "maatje" herring fishery a discard rate of around 11%. The level of by-catch generally ranged from <1% to around 2.5% of the total catch

1.3.1.1 Discards by main French fishing areas.

1.3.1.1.1 Discards in West Channel and Celtic Sea

Most of the information concerning discards in West Channel are reported by Morizur *et al.* (2000) . This study, made by the Department of Fishing Resources of IFREMER, was a first approach for assessing French discards in the Western Channel. It identifies the main species

discarded and produces a rough estimate of discard rates and size composition of discards. No data about by-catch composition is reported, only total discard quantities are compiled.

Three fishing gears are studied in order to compare the discard rates and size composition: fixed netting, inshore trawling and offshore trawling.

Fixed netting. The discards occurring in this metier differ according to equipment and gears. Small mesh nets must be separated from large mesh ones.

Small mesh nets (<200 mm stretched mesh size) are fixed in the inshore areas. They target principally pollock, ling and cod. Their short immersion time does not produce damaged fish which have to be discarded, so most of the discards are due to by-catch species with low commercial value like red gurnard, spotted dogfish and pout whiting. Crustaceans are the species with the highest discard rate (80-90% of captures discarded), due to small size or low value.

Large mesh nets (270 to 360 mm) are fixed in more offshore areas inside 12 miles during winter and sometimes outside 12 miles in summer. Their immersion time varies from two to six days, and is the principal factor explaining discards. Gadoids are the species more sensible to immersion, they start to be discarded from the 3th day, while a immersion time of five days induces discards in all species.

Inshore trawling. The discard rate is greater than 50 for some species, due to minimum landing size regulations or economical reasons (small sizes with low commercial value). This metier was found to have a great spatial heterogeneity in the catches and discard practices. There are species, like rays, pouts and spider crab with similar discard rates between fishing grounds. On the other hand, species like sole, red mullet or black bream have different discard rates in West and East sides of the channel, due principally to the distribution of reproduction areas.

Offshore trawling. Fishing activities using this metier are developed from West Channel (7E area) towards Bristol Channel (7F) and Smalls (7G), with differences between species composition . Species like gurnards, whiting, pouts and horse mackerel are almost completely discarded, and are caught in great numbers.

After characterization of the principal fishing gears employed in this area, the report concludes that netting is more selective than trawling in species diversity and in size composition. Regarding large mesh nets, an optimal immersion time of 3-4 days may limit fish discards and increase fish landings for the studied area. Another important study about discards from trawl fishing in the Bay of Biscay was made by IFREMER in collaboration with other European institutes (CTNC, RIVO/DLO, and UCC) During 379 days scientific observers have studied different fisheries, most of them French, widespread along the Bay of Biscay and also West Channel and Celtic Sea.

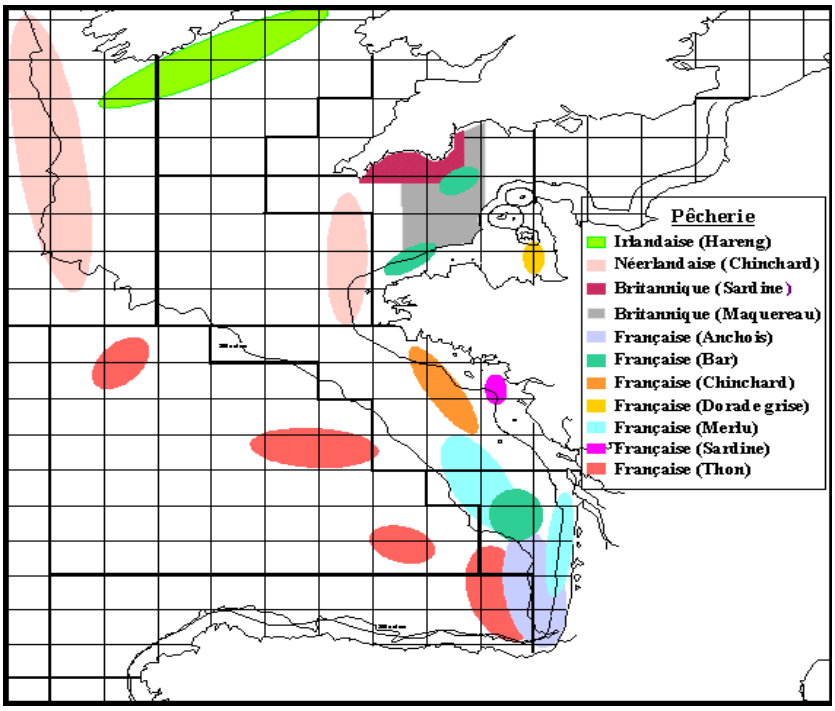

Figure 1.7. Fisheries covered by the IFREMER 's study about discards from trawl fishing. Department of Fishing Resources, IFREMER Brest.

This study give us complete information about the discard rate, size composition and by-catch composition of the material discarded. There are seven French fisheries studied, anchovy, seabass, horse mackerel, black seabream, hake, sardine and albacore, all of them employing trawling in the Bay of Biscay. The percentage of discards (related to the total catch) varies from 5% to 69% , depending on the fisheries and species.The table below summarizes the main characteristics observed for each French fishery studied, taking into account the discards due to their small size.

Table 1.3. Discard rates and by-catch composition of the fisheries studied by IFREMER.

Species	Discard rate (%)	Discard composition			
		Small-sized discards	Main by-catch species		
		Size (percentage)	Species (percentage of total discards)		
Hake	56	< 25 cm (10%)	H. Mackerel (67%)	Sardine (7%)	Mackerel (3%)
Anchovy	29	< 10 cm (5%)	Sardine (54%)	H. mack (33%)	Mackerel (3%)
Black seabeam	19	< 23 cm (30%)	Sardine (33%)	Mackerel (28%)	H. mack (8%)
Horse mackerel	17	< 38 cm (67%)	Atl.H. Mack (33%)		
Sardine	6	< 18 cm (15%)	Sprat (78%)	Garpike (4%)	H. mack (3%)
Albacore	4	< 50 cm (28%)	Bluefin tuna (4%)	Sunfish (65%)	
Seabass	2	< 35 cm (2%)	H. Mack (26%)	Sardine (25%)	Lumpsucker (22%)

Some conclusions may be extracted from this study :

1. Anchovy is by far the first species caught by the French trawl fleet. Anchovy landings represent 68% from total catches. Discards are mainly due to mixed by-catches of sardine and horse mackerel. Discards of small-sized anchovy (less than 10 cm) are unusual.

2. Discards from seabass fisheries are weak and the selectivity of the fishing gear is good. Discards from target species consist of adult specimens with size smaller than 35 cm.

3. The landings of horse mackerel represent 83% of total catches. Discards are weak and due generally to technical problems or the presence of horse mackerel species without commercial value, such as the Atlantic Horse Mackerel.

4. Trawl fishing is used all over the year to catch black seabream, principally in West Channel. One third of discards are due to small specimens with low commercial value. The rest of discards are composed of by-catch species :sardine and mackerel.

5. Hake stands for the second species in value caught by French trawl fleet. Whiting is also a target species from this fishery. Discards represent more than the half of the total catches. They are composed principally by horse mackerel by-catches.

6. Sardine fisheries present a very low discard rate, mainly due to sprat by-catch. 15 of discards are composed by sardine specimens with less than 18 cm, with less commercial value although minimal catch size in EU is 11 cm for the Atlantic Ocean.

7. Albacore represents the third species in value for the French trawl fleet. Other target species caught in the Bay of Biscay are bluefin tuna and swordish. The discard rate is wake and is composed of both target and by-catch species. By-catch are composed mainly by sunfish, which represents 65 of total discards. Discards of target species are due to specimens with less than 50 cm .

1.3.1.1.2 Discards of pelagic species in West Coast of British Islands

French deepwater fish exploitation began off the West coast of the British Islands in 1973, and since 1995 has landed 19,500 t of deepwater species, of which the grenadier *Coryphaenoides rupestris* has been the most abundant. The report Preliminary estimates of French deepwater fishery discards in the Northeast Atlantic Ocean (Allain *et al.*, 2003) studies the French trawl fisheries of roundnose grenadier focusing on discard rate and by-catch composition.

Table 1.4. Discard rates and by-catch composition of the French trawl fisheries of roundnose grenadier.

Target Species	**Discard rate(%)**	**Bycatch composition** Species (percentage of total discards)
R. Grenadier	20	Baird's Smooth-head (58%)
B. Scabbardfish	8	Dogfish (12%)
Siki	7	Atlantic Codling (4%)
Lings	5	Grenadier (12%)
Others	4	Others (14%)

Catch composition presents other landed species with commercial value such us Scabbardfish and sikis. On the other hand, Grenadier fisheries present high discard rate (57%) which is due principally to by-catch species from which baird's smooth-head is the most abundant followed by dogfish.

Other data concerning pelagic species with high commercial interest such as herring and mackerel are taken from Pierce *et al.* (2002) who performed different studies on Scottish fisheries. These fisheries present very low discard rates, 13 for herring and 8 for mackerel. In both cases the proportion of by-catch species in discards is low, since they are mainly due to small-size specimens of the target species (77% of herring discards and 87% of mackerel discards) with low commercial value.

1.3.1.1.3 Discards in the Mediterranean Sea

French Mediterranean Fisheries target pelagic species with high commercial value such as sardine, anchovy and hake. No data about French discards in Mediterranean Sea are available at the moment, although some studies quantifying discards in French Mediterranean Fisheries are being undertaken. Estimates on discard rates are taken from EU Commission Communication COM (2002) 656 about EU policies to reduce discards. These estimates are applicable to the whole Mediterranean Sea, and thus, they are not very precise in order to quantify the discards generated by French fishing activities .

Trawl Fisheries. Estimates on total catches and discards by trawl fleet vary from 15% to 70%. This percentage depends on the depth of trawling. Those fishing up from 150m depth have a discard rate varying from 20% to 70%. This percentage descends to 20% -60% at 150 m-350 m. The lowest discard rates are obtained below 350 m, varying between 20% and 40%.(EU Commission, 2006).

Small-scale Fisheries. One of the most important small-scale fisheries is practiced with fixed netting having as main target species common sole (*Solea Vulgaris*) , as well as ray (*Raja asterias*), gurnard (*Trigla lucerna*) and crustacean (*Squilla mantis*). Between 8%-9% of total catch is discarded. Fixed netting is also used to catch big specimens of hake (*Merluccius merluccius*), which represent the 6%-8% of the total catch.

Small pelagic fisheries. The fishing gears commonly employed in these fisheries are trawling and purse seine, using light to attract fish. Catches are composed by anchovy and sardine generally mixed. Discard rates from these fisheries may raise up to 80%, mainly in anchovy fisheries where great amounts of sardine are discarded.

1.3.1.2 Methodology employed to estimate French discard rates

Taking into account all the discard rates collected from different reports on French fisheries, a mean discard rate for each species can be estimated, considering its geographical distribution along French coast. This methodology can give us a rough estimation of the quantities discarded by French vessels, so these results must be taken with care.

In order to make an accurate estimation, discard rates should be evaluated for smaller fishing areas, considering the different species and principally the different fishing gears employed. To accomplish with this methodology more studies about discard rates should be undertaken, but at this moment, even if a great effort is been done in order to evaluate discard rates in more areas (Mediterranean fisheries), the lack of data avoid us to do a more accurate study.

Estimations are based on some previous studies on some specific areas and fishing gears, two factors which affect enormously the discard rate. Considering the main areas studied (West Channel, Celtic Sea, Bay of Biscay), an extrapolation to the whole country should be made, even if we know that the factors determining discards in an specific area (fish ground, fishing gear, season,…) are not completely reproducible in other areas, and thus, their extrapolation to larger territories imply a lack of accuracy. The main steps followed to make this estimation are described below:

Sample of main target species. 29 different species, belonging to white, cartilaginous, pelagic and crustacean species have been selected in order to evaluate their discards. 16 species from white fish have been considered, which represent 76% of white fish catches in France. All pelagic fish species have been considered, without considering species such as tuna (expect the albacore in the Golf of Biscay) whose main part is caught in Tropical areas. A mean discard rate of 10% was considered for Mediterranean pelagic fisheries (FAO 2004).Cartilaginous and Crustacean species are well represented by the sample (98% and 95% respectively). No data from Mediterranean fisheries concerning these species are reported on OFIMER statistics, since French Mediterranean fisheries target mainly pelagic species.

Mean discard rate for each species. Discard rates have been estimated considering data from Mediterranean, West Channel, Celtic See and Gulf of Biscay. Geographical distribution of catches has been considered, in order to estimate discards in Atlantic and Mediterranean fisheries. Two approximations have been used:

1. When no data about Mediterranean fisheries are available, a main discard rate of 10 (FAO, 2004) has been employed in order to quantify discards.

2. With regard to the Atlantic fisheries, discards from some species have been estimated taking into account discard rates for only one fishing area (West Channel, Celtic See or Gulf of Biscay), due to the lack of data. In this case, we have considered only one mean discard rate for the whole catches in Atlantic Ocean.

Once a discard rate for each species has been obtained, we have calculated **two mean discard rates**, corresponding to the Atlantic and Mediterranean fisheries. These have been applied to total French catches in order to estimate the amount of discards generated by French fisheries.

1.3.1.3 Results and conclusions about French fisheries discards.

The 29 fish species were divided into four subsets: pelagic fish, white fish, cartilaginous fish and crustacean. Table 1.6 shows the average estimations for the sample of pelagic fish.

Table 1.5. Mean discard rates of pelagic fish species from French fisheries in Atlantic Ocean and Mediterranean Sea.

Species	Area of reference	Discard rate (%)	Total catches (tons)	Estimated discards (tons)
Anchovy	Bay of Biscay	29	1001	290
	Mediterranean	50	2429	1215
Horse mackerel	Bay of Biscay	17	17610	2994
Herring	Celtic Sea	13	40960	5325
Mackerel	Celtic Sea	18	19230	3461
Sardine	Bay of Biscay	6	27318	1639
	Mediterranean	50	10406	5203
Albacore	Bay of Biscay	4	8170	327
OVERALL PELAGIC FISH SAMPLE			**127124**	**20454**

With respect to the white fish species, a sample of 16 species was chosen, which represents 76 of the global catches from French fisheries, as shown in table 1.6.

Table 1.6. Mean discard rates of white fish species from French fisheries in Atlantic Ocean and Mediterranean Sea

Species	Area of reference	Discard rate (%)	Total catches (tons)	Estimated discards (tons)
Pollack	Bay of Biscay	70	481	337
	Channel	5	3053	153
Plaice	North Atlantic	60	3191	1915
Hake	Bay of Biscay	56	9935	5564
	Channel	12	3078	369
	Mediterranean	8	1195	96
Ling	Bay of Biscay	55	215	118
	Channel	41	1840	754
Black bream	Bay of Biscay	55	532	293
	Channel	31	2445	758
Whiting	North Atlantic	47	13505	6347
Sole	Channel	18	8320	1498
Monkfish	Bay of Biscay	10	5238	524
	Channel	17	15110	2569
	Mediterranean	10	485	49
Grenadier	Channel	21	4613	969
Haddock	North Atlantic	15	5111	767
Megrim	Channel	10	3060	306
Pout	Bay of Biscay	7	718	50
	Channel	9	5167	465
Cod	Bay of Biscay	7	472	33
	Channel	9	5088	458
Conger	Channel	7	5131	359
Saithe	Bay of Biscay	5	61	3
	Channel	5	16731	837
Seabass	Bay of Biscay	2	2776	56
	Channel	1	2674	27
OVERALL WHITE FISH SAMPLE			**120225**	**25670**

Tables 1.7 and 1.8 show the average results obtained for the cartilaginous and crustacean samples, which represent a high percentage of the global catches from French fisheries (98% and 95%, respectively).

Table 1.7. Mean discard rates of cartilaginous fish species from French fisheries in Atlantic Ocean and Mediterranean Sea.

Species	Area of reference	Discard rate (%)	Total catches (tons)	Estimated discards (tons)
Spotted dogfish	North Atlantic	25	5819	1455
Other sharks	North Atlantic	24	5553	1333
Rays	Channel	15	8792	1319
	Mediterranean	9	333	30
OVERALL CARTILAGINOUS FISH SAMPLE			**20497**	**4136**

Table 1.8. Mean discard rates of crustacean species from French fisheries in Atlantic Ocean and Mediterranean Sea.

Species	Area of reference	Discard rate (%)	Total catches (tons)	Estimated discards (tons)
Spider crab	Channel	34	3778	1285
Edible crab	Channel	24	5076	1218
Cray fish	Channel	2	6764	135
OVERALL CRUSTACEAN SAMPLE			**15618**	**2638**

From the sample considered in the study, a mean discard rate of 13% has been obtained for Atlantic fisheries, and 31 for Mediterranean Sea. Mediterranean discard rate is higher due to the high by-catches registered in anchovy and sardine fisheries (50%).

Extrapolating these mean rates to the whole catches in French fisheries, we conclude that almost 60000 tonnes of catches have been discarded during 2005, which represents a 14% of French catches (table 1.7). This mean rate is lower than that estimated by the FAO report for the period 1992-2001 (21% of discard rate), and this may be attributed to a decrease in catches, as well as more effective regulations and fishing gears, following the general trends in world's global discards.

Table 1.9. Mean discard rate for French fisheries

Group	Atlantic Ocean (tons)	Mediterranean Sea (tons)
White fish	157700	5559
Cartilaginous	20825	149
Pelagic fish	204746	22587
Crustacean	16476	497
TOTAL	**399747**	**28146**
Discards (tons)	**52002**	**7742**
MEAN RATE (Atlantic + Mediterranean)	**14%**	

Discard rates vary among the different species. Mean discard rates for each group can be estimated: 18% for white fish, 17% for cartilaginous species, 6% for pelagic species and 6% for crustacean species. These means are not representative, since discarding depends on other factors such as fishing gears, fisheries regulations and commercial preferences. Lowest discard rates are found for pelagic species and crustaceans. In the case of pelagic species, most of them are targeted in North See fisheries, such as salmon or herring, which have negligible discard rates. The fishing gears employed to catch crustacean are very selective, with small discard rates.

Species generating the highest discards are sardine (with high discard rate in Mediterranean fisheries due to anchovy and sardine by-catches),whiting, hake (with a discard rate of 56% in the Gulf of Biscay), herring (with low discard rates but high catches), mackerel and monkfish (figure 1.8).

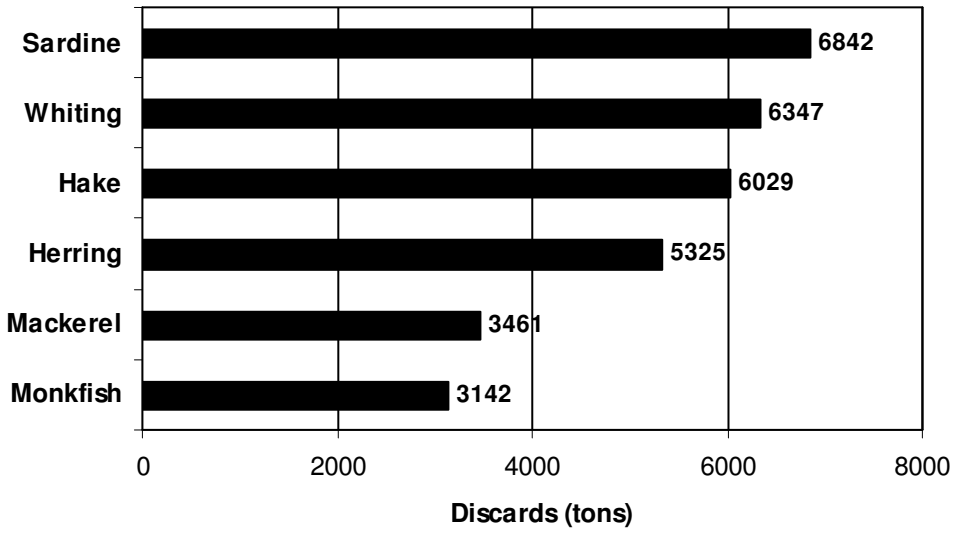

Figure 1.8. Species generating the highest tonnages of discards.

Highest discards rates are observed in pollack in the Bay of Biscay (70%), plaice in North Atlantic (60%) due to by-catch species, hake in the Bay of Biscay (55%) and sardine in Mediterranean See (50%) due to the presence of mixed banks of sardine and anchovy.

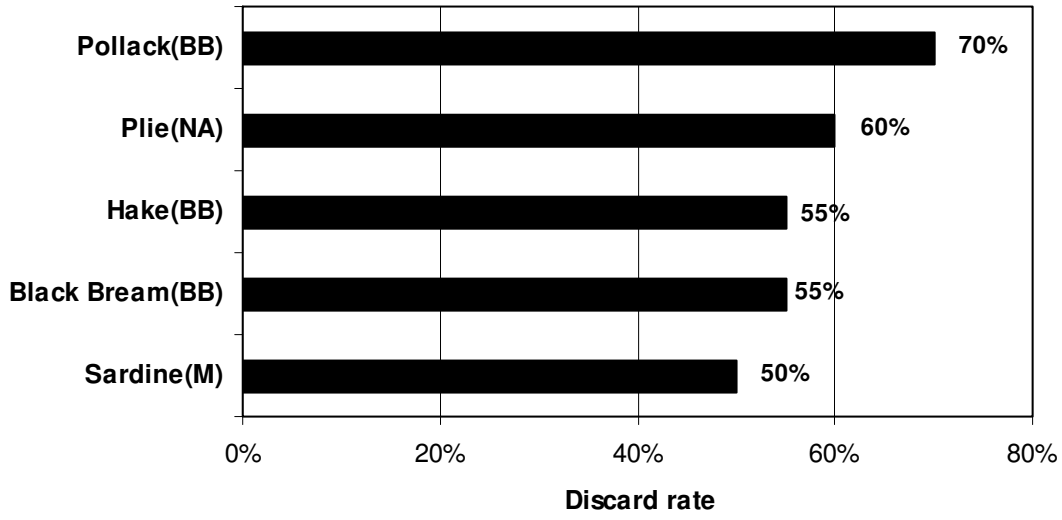

Figure 1.9. French fisheries with highest discard rates. Note: BB=Bay of Biscay, M=Mediterranean and NA=North Atlantic.

Species with the lowest discard rates are Sardine and Albacore in the Bay of Biscay, with discards around 5%, and Cray Fish fisheries using fixed nets (2%).

1.3.2 Wastes from fish processing on board.

By-products generated on board of fishing vessels are normally viscera, which must be stabilised by freezing due to their important content in intestinal bacteria. Nowadays, only livers and eggs are sometimes collected to be sold on land. Livers from monkfish and sikis are the most commercialised by-products.

The presence of industrial fishing vessels, equipped with fish on board processing lines and freeze stocking systems is not very usual in French fleet, since most of French fishing vessels practice inshore fishing and do not process catches on board. Nevertheless, demersal species are traditionally gutted on board (monkfish, cod, conger, haddock, lings, pollacks and whiting) as well as cartilaginous species such as sharks. Other species like black scarbbardfish are headed or tailed (grenadier). As a consequence of these activities an important amount of wastes are generated, and generally discarded into the sea.

Pelagic species are generally landed as whole fish to be processed on land by fish trade enterprises and canning or smocking industry, so the amount of wastes generated on board by these species can be reduced to those derived from black scabbardfish gutting.

Crustacean are not processed on board. Only 1% of langoustines are tailed before landing. This activity has generated one ton of wastes in 2005

1.3.2.1 Methodology used to evaluate on board wastes.

The estimation on wastes originating from fish processing was performed by means of the conversion coefficients. Conversion coefficients are factors employed to estimate the live-weight equivalent of catches. The weight of fish landed is multiplied by a coefficient to offset the lost of weight due to processing at sea (gutting, removal of heads, filleting) to arrive at the weight if the fish were whole and alive.

There is an important study about the origin and different values of conversion coefficients in EU (Caillart *et al.*, 1996). The study attempted to ascertain the origins of the conversion coefficients in the three Member States, France, Denmark and UK. After studying the origin and different values of these coefficients, a method is proposed for revising these coefficients, in order to make an harmonised European list. These coefficients have been modified in order

to quantify the amount of wastes generated by fish processing, so coefficients used in these study represent the mass of raw fish to be processed to generate one kilogram of waste. Dividing the whole fish catches to be processed (part of the catches are discarded) between the correspondent coefficient, the mass of wastes is obtained, most of it corresponding to viscera. Data from landings are disperse or not available, so total catches from two consecutive years, 2004 and 2005, have been used. The term total catches includes discards, which are subtracted from the total catches to obtain the amount of landings (proportion of catches brought ashore). This data are available on the **Annex II** (Fish wastes generated by on-board processing).

1.3.2.2 Results from waste estimation.

Some conclusions can be obtained after the estimation:

- **12,800 tons** of wastes have been generated by on board processing in 2005, which represents a decrease of 5% respect 2004, which corresponds to a decrease in catches during this period.

- **81% of wastes** belong to white fish species, most of them demersal which are normally gutted on board before landing, followed by cartilaginous species(sharks) .

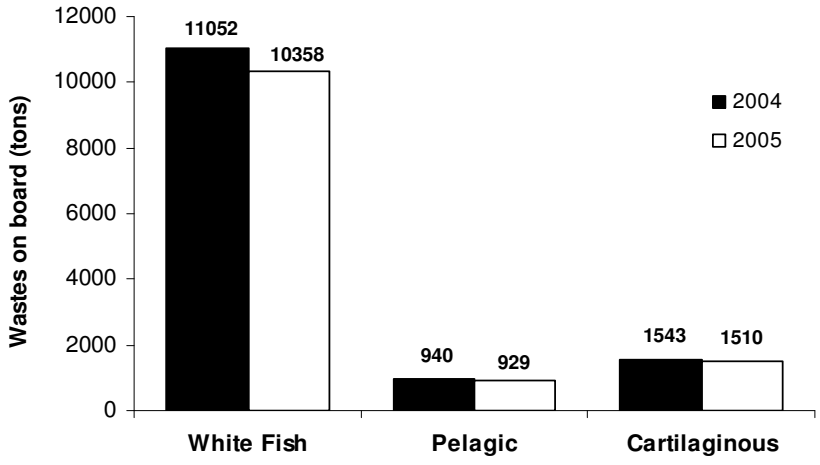

Figure 1.10. Wastage on board for white, pelagic and cartilaginous species during 2004/2005.

Four species, **monkfish**, **saithe**, **sharks** and **hake**, represent **60%** of the total amount of wastes. Catches from these species are important in quantity and value. These species are generally gutted on board, so wastes correspond entirely to viscera.

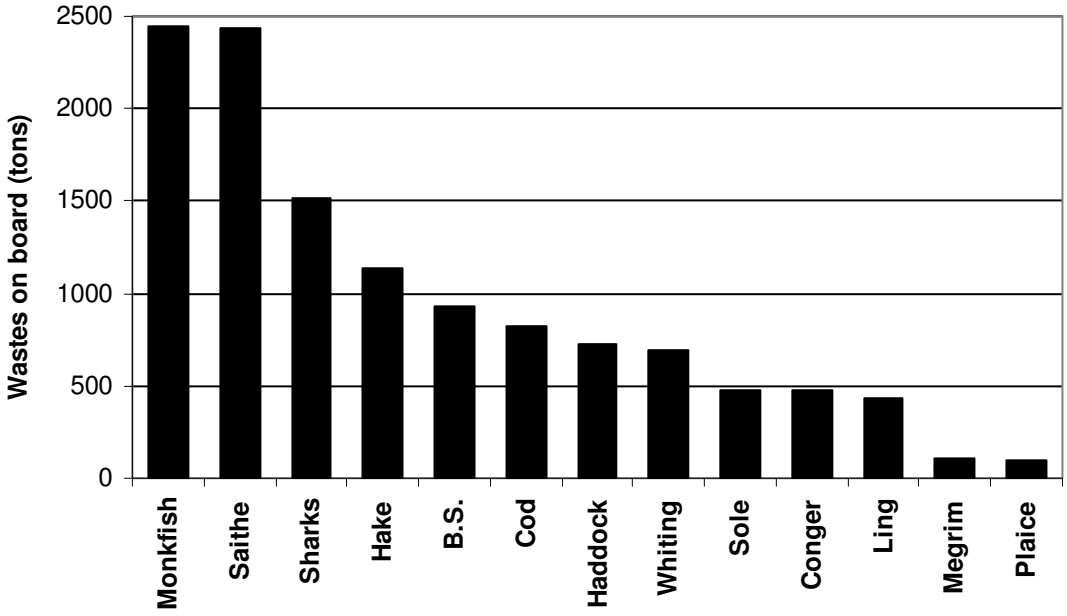

Figure 1.11. Main species generating wastes on board

Most of these wastes are generated by industrial fishing vessels, most of them registered in South Britanny and the ports of Boulogne-sur-Mer and Fecamp. On the other hand, wastes on Mediterranean Sea are negligible since Mediterranean fisheries target pelagic species such as anchovy and sardine which are commonly landed as whole fish.

1.3.3 By-products from fish processing in land.

Fish processing companies employ raw fish as first material to be processed in order to obtain a final product with higher commercial value. Several operations are involved in fish processing: heading, gutting, filleting, removing tails and peeling . These operations generate by-products such as heads, viscera, tails, skins and fins which are not put on market due to their low acceptation by consumers or sanitary regulations which avoid their employ in human foods.

Other operations involved in fish processing, such as washing, thawing and cooking are the origin of aqueous effluents which are normally discarded. Wastewaters generated by fish meal industries contain a high organic load due to the presence of oils, proteins (0.5-20 g/l) and suspended solids. They present high turbidity, strong greenish yellow colour, and stinky odour. Therefore, they should not be discharged without a suitable treatment in order to prevent negative environmental impacts and allow the recovery of high added value products.

Only the solid by-products from mechanical processing are considered in this study. Solid by-products are classified in heads, viscera, skins and fins, and can be accounted considering conversion factors for each species and processing operation.

1.3.3.1 Activities involving by-product generation.

Due to the diversity of operations involved in fish processing , producers can be placed in different levels inside the fish and aquaculture industry.

1.3.3.1.1 By-products generated on board.

Fishermen are the first agents who generate by-products, because many species are directly gutted on board (monkfish, cod, conger, haddock, ling, pollack, whiting and sharks) and sometimes headed (black scabbardfish) or tailed (grenadier). These by-products, being easily spoilable, have to be quickly stabilised by freezing or any other preservation method. Only livers (principally from Monkfish and Sikis) and eggs are sometimes collected, the rest is dumped at sea and has been quantified as wastes from fish processing on board.

1.3.3.1.2 By-products generated by Fish Trade.

According to OFIMER there are 380 companies dealing with fish trade in France (figure 1.12). Most of them consist of small-sized enterprises, dealing with conditioning of sea food. 37% of the total number of Fish Trade companies are placed in Brittany, whose activity generates the 33% of the total business affairs of French fish trade and processing industry (figure 1.13).

In the biggest enterprises (44), other processing operations are done, such as freezing, cooking and smocking, so they can be considered as by-products producers from fish processing

industry. Few of the non-gutted species put on the market by fish trade companies are filleted, so by-products from these activities consist mainly of heads, fishbones and skins.

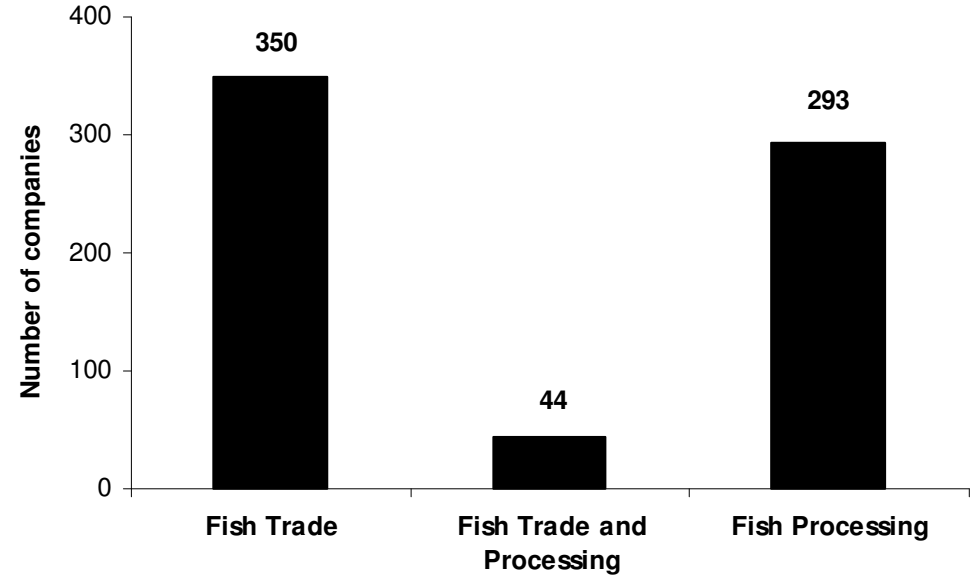

Figure 1.12. Number of fish trade and processing companies in France.SOURCE : Les chiffres clés de la filière de pêche et aquaculture en France 2006. OFIMER

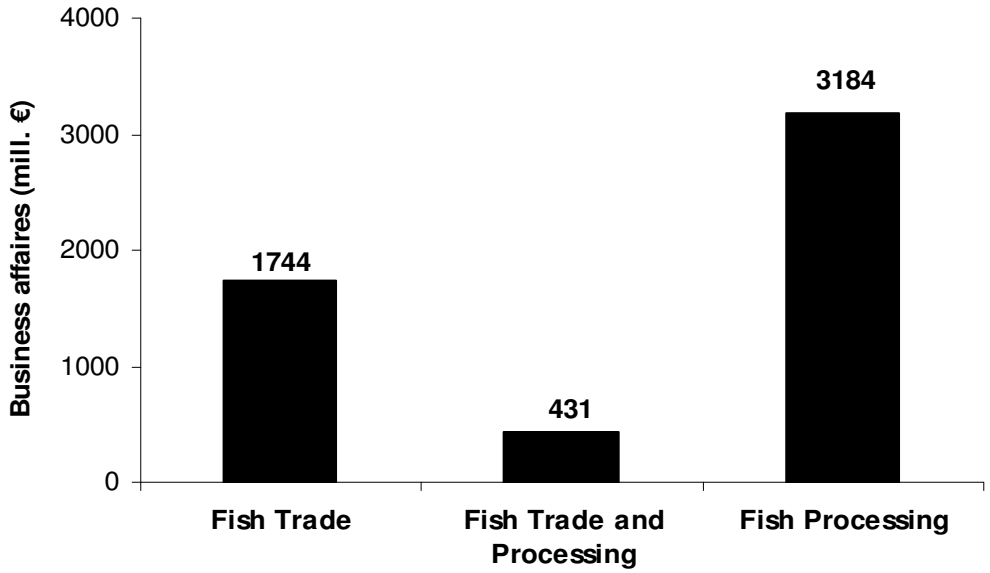

Figure 1.13. Business affaires of fish trade and processing companies. SOURCE : Les chiffres clés de la filière de pêche et aquaculture en France 2006. OFIMER

1.3.3.1.3 By-products generated by Fish Processing Industry.

Canning and salting-smocking industries are the main activities dealing with fish processing to be considered as solid by-product producers, while other activities such as surimi elaboration or shrimp cooking use frozen material, previously processed by other companies. Therefore, these activities do not generate solid by-products but wastewaters containing high organic loads (mainly proteins).

There are 293 companies dealing with fish processing activities, and 44 companies involved in both fish trade and fish processing. Both type of companies have generated 3615 millions € of business affairs during 2004 (OFIMER, 2004) (figure 1.13). 57% of the fish processing companies in France are placed in the Atlantic coast, which corresponds to 67% of the overall business affairs generated by the fish processing industry.

With regard to the canning industry, there are 12 French canning industries processing sardine, tuna, mackerel and herring. Eleven of them are belonging to the French Federation of Canned Food Industries.(Andrieux, 2004)

Salt-smocking activities are focused on four species as raw material, haddock, herring, mackerel, salmon, and recently, the big trout with more than 2 kg. There are 24 enterprises processing smoked salmon, two of which are also processing smoked trout . Seventeen of them are belonging to the National Syndicate of Smoked Salmon Industry. (Andrieux 2004) Salmon and Trout Industry use whole fish as raw material for the transformation. Once the fish is headed and gutted, the fillets with skin are smoked, and skin is retired after slicing the smoked product. All the types of by-products are generated by these operations : heads, viscera, skin and fishbones. Smoked haddock and red herring are mainly processed in Boulogne-sur-Mer. Herring generates all kind of by-products, while haddock is sold with skin to avoid fraudulence (Andrieux,2004).

The figure 1.14, extracted from the report OFIMER (2006), summarises the overall business affairs generated by the French fish trade and fish processing companies.

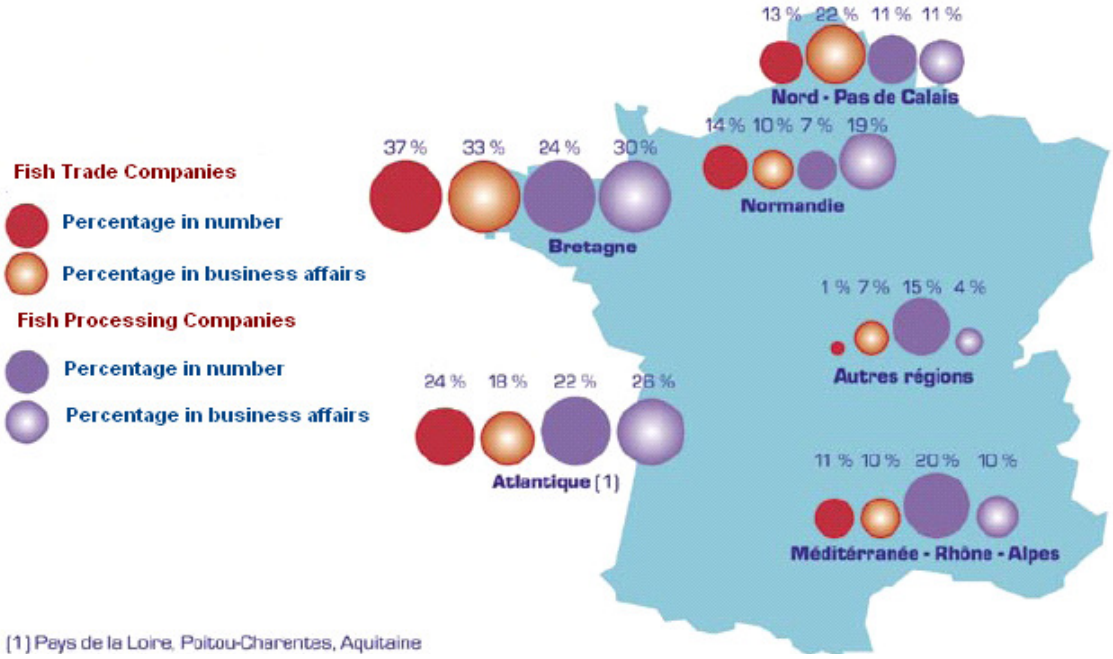

Figure 1.14. Number and business affairs of French fish trade and fish processing companies. OFIMER 2006

1.3.3.2 Methodology employed to estimate the amount of by-products *generated by ashore fish trade and processing activities.*

An estimation of the amount of by-products generated by fish processing operations can be obtained taking into account the conversion coefficients, which consider the loss of weight derived from fish processing operations such as heading, gutting, tailing and skinning.

Once the conversion factors for each fish species and processing operation is been applied , we can estimate the quantities of by-products generated on board and on land (fish food trade and industry).

These coefficients have been modified in order to quantify the amount of wastes generated by fish processing, so coefficients used in these study represent the mass of raw fish to be processed to generate one kilogram of waste. Dividing the fish tonnage to be processed, the mass of heads, viscera, skin and fins generated can be obtained.

The methodology and coefficients applied to estimate the amount of by-products were taken from the report from Gaële Andrieux (OFIMER, 2004) about the by-products generated by

trade and industry processing of fish in France. In this study, fourteen species were studied in order to evaluate the amount of by-products generated by their processing. Extrapolating these results to the whole tonnage of fish processed in France, it has been concluded that 150,000 tons of by-products (heads, tails, viscera) were generated in 2002 by industry and trade processing in land. The different ways to re-use these by-products were also considered, since 96 of by-products are employed afterwards as raw material for different applications, mainly animal feed (fish meal).

Following the methodology employed by this study to quantify the tonnage of by-products, the first step consists in classifying the species into three main groups:

1.3.3.2.1 Species processed by fish trade companies: white fish and cartilaginous fish

The table 1.10 summarises the main species processed by fish trade companies as well as their market presentation, which enables to calculate the portion of the whole fish which is transformed.

Table 1.10. Market presentation of species processed by fish trade companies. Andrieux (2004).

Species	Processed portion (%)	Market presentation
Monkfish	100	Skinned tails
Brosme	100	Skinned fillets
Cod	90	Skinned fillets
Pollock	89	Skinned fillets
Ling	100	Skinned fillets
Whiting	64	Skinned fillets
Rays	100	Peeled fins
Sikis	100	Skinned slices
Perch	100	Skinned fillets
European Conger	100	Slices
Grenadier	100	Skinned fillets
Hoplospete	100	Skinned fillets
Black Scabbardfish (1)	100	Skinned fillets

(1) It is normally consumed fresh although it belongs to the blue fish species

1.3.3.2.2 Species processed by fish trade companies and smocking industry

Table 1.11. Market presentation of species processed by fish trade and smocking industry. Andrieux (2004).

Species	Proportion (%)	Processed portion (%)	Market Presentation
Haddock	54 smocking industry	100	Smoked fillets with skin
	46 restaurants and home	100	Fillets without skin
Herring	76 canning industry	100	Fillets with skin, canned
	19 smocking industry	100	Fillets without skin
	5 restaurants and home	0	Whole fish
Salmon	43 Smocking Industry	100	Smoked slices
	21 restaurants	42	Skinned fillets
	36 home	75	Skinned fillets
Trout	15 Smocking Industry	100	Smoked slices
	85 restaurants and home	98	Gutted trouts / skinned fillets

1.3.3.2.3 Species processed by fish trade and fish canning industry : blue fish

Table 1.12. Market presentation of species processed by fish trade and canning industry.

Species	Proportion (%)	Processed portion (%)	Market Presentation
Mackerel	84 Canning Industry	100	Fillets with skin, canned
	16 Home and restaurants	0	Whole fish
Herring	76 Canning Industry	100	Fillets with skin, canned
	19 Smocking Industry	100	Fillets without skin
	5 Home and restaurants	0	Whole fish
Sardine	40 Canning Industry	100	Fillets with skin and gutted fish
	60 Home consumption	0	Whole fish
Tuna	46 Canning Industry	100	Sliced fish, canned
	39 Home	90	Sliced fish
	15 Restaurant	57	Sliced fish

The amount of products to be processed before being put on market can be estimated by the following balance (**Annex :III**).

Apparent Consumption = fish landings in France + imports (whole fish) – exports (whole fish)

Data from fish landings in France are not available, but can be approximated by the consulting the statistics from OFIMER about auction sells in fish markets (OFIMER, 2005b). These quantities are representative for most of demersal species, which are almost entirely sent to auction sells in fish markets. The best percentages of auction sells , more than 85, are those corresponding to saithe, haddock, hake, whiting, megrim, monkfish, pollack and langoustine (Caillart,1996).

On the other hand, data from auction sells are not representative from small pelagic species such as horse mackerel, mackerel and herring, which are sold on hire, imported or exported to foreign countries. The amounts of these species put on market can be obtained by an indirect way, taking into account the consumption of derived products (canned, smocked fish, fillets, whole fish) and applying conversion coefficients to obtain the whole fish weight before being processed.

Data from imports-exports of each species are available on OFIMER Statistical Reports from 2005 (OFIMER, 2005a), as well as aquaculture production.

Taking into account the proportion of each species which is transformed by each activity, by means of the tables 1.10, 1.11 and 1.12 and applying conversion factors to each raw material, the amount of each by-product generated after processing can be obtained. These conversion coefficients are modified in order to give us direct information about the quantity of raw material processed to obtain one kilogram of each specific by-product. Dividing the tonnage of raw fish to be processed between each conversion coefficient, the mass of heads, tales, skin and viscera generated by processing activities can be estimated.

1.3.3.3 Results and conclusions about fish by-products *in land.*

The amount of by-products varies depending on the fish processing or trade activity, and the fish species processed (white fish, blue fish, cartilaginous and salmonids). The global quantity of by-products can also be studied from the viewpoint of the type of by-products: heads, viscera, fishbones, fins and skins. Finally, an important aspect is the up-grading processes followed by fish by-products.

1.3.3.3.1 By-products *generated by each activity*

- **215,000 tons** of by-products have been generated in France in 2005 as a result of fish trade and fish processing activities.

- Fish trade is the activity which has generated the highest amount of by-products, 106,762 tons which represents a 52% of the total amount of by-products (figure 1.15) . With regard to the Canning and smocking industries have generated 85,000 tons (36%) and 27000 tons (12%) of by-products respectively (figure 1.15).

- 48 % of the total inputs processed by fish trade and fish smocking industry are by-products. This percentage is lightly lower in canning industry (46 %). In the case of the fish processing industry, it generates similar quantities of final processed fish and by-products.

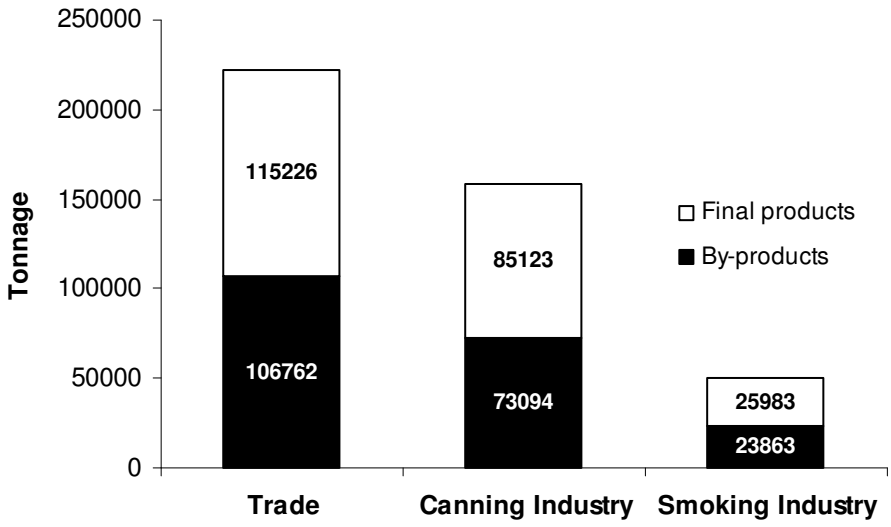

Figure 1.15. Tonnages of by- products and final products by fish processing activity.

1.3.3.3.2 Origin of the by-products

Pelagic species, to which belong species caught by industrial vessels such as herring, tuna or mackerel, count for 45% of the overall amount of by-products. Theses species are intended to fish trade and fish processing industry. The figure 1.16 summarises the percentages of by-products by fish group From this table it can be concluded that 29% of the total amount of by-products belongs to salmonids, which are mainly imported as whole frozen fish or produced

in France by aquaculture. White fish, whose species are commonly processed by fish trade companies, are responsible for 21% of by-products. The remaining 5% corresponds to the processing of cartilaginous fish.

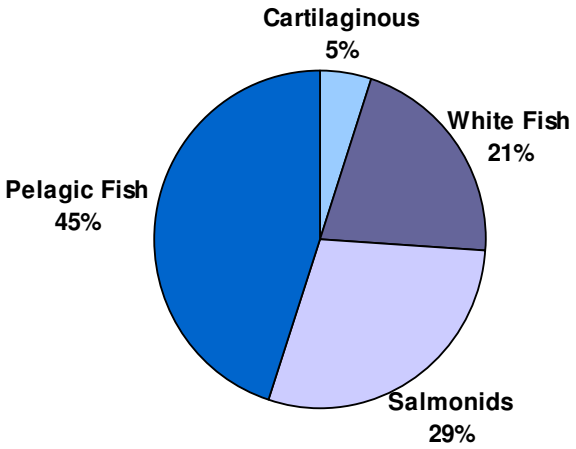

Figure 1.16. Percentage of by-products generated by fish group.

1.3.3.3.3 Type of by-products

The figure 1.17 shows that 40% of total mass of fish by-products correspond to heads, followed by fishbones 27% and viscera 25%.

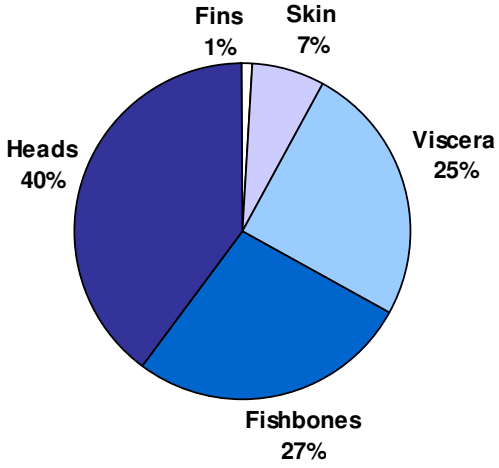

Figure 1.17. Type of by-products generated during fish processing.

1.3.3.3.4 By-products up-grade

Fishery waste in land is increasing nowadays driven by greater elaboration of fishery products, implantation of new larger industries and less and bigger fish auctions (Blanco *et*

al., 2007). Although most of this waste is being handled, a more profitable use of waste is possible, since most of it is treated to produce fish meal and oil.

French fishing and aquaculture handles 96% of the fish by-products (Andrieux, 2004). 75% of the fish by-products are valorised to take part in the formulation of animal feedstuffs, such as fish meal or oil (52 %) or frozen minced by-products (23 %). Fish meal is one of the main products obtained from fish by-products, with a high content of protein (minimum content above 70%) and low content of fats (below 12%). Fish meal is mostly used as an ingredient in feedstuffs intended for aquaculture.

Other applications, able to provide a higher added-value to the by-products, only account for a reduced percentage of the applications for the re-utilised by-products. The up-grading of marine by-products intended for cosmetic, nutraceutical or pharmacological applications only represents 4%. The main constraints to a higher use of up-graded by-products in dietary and nutraceutical products are due to French Food Regulations, which is more restrictive than that of other European countries. In contrast, a significant amount of the by-products (21%) are used as raw material for the production of fish hydrolysates, mostly intended to animal feedstuffs.

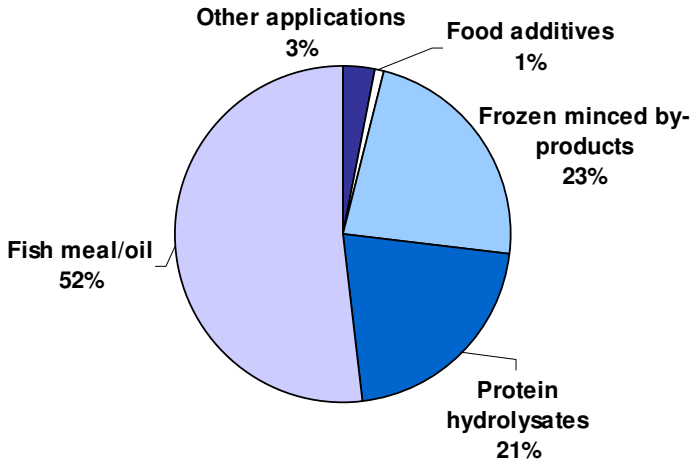

Figure 1.18. Different applications for the up-graded by-products. Andrieux (2004).

2.VOLUME REDUCTION STRATEGY: VALIDATION AT LAB SCALE USING SARDINE

2.1 INTRODUCTION: TECHNICAL SOLUTIONS FOR WASTE COMPACTION.

2.1.1 Advantages of waste compaction pre-treatments.

As said in the previous chapter, considering that all the fish discards must be landed, a preliminary pressing operation may reduce the volume to be stored on board, and thus the refrigeration and space requirements. This is a solution which was already proposed by the Code of Conduct for Responsible Fisheries in order to reduce the volume of by-catches and wastes to be stored on board:

Do their utmost to treat waste generated on board as if it were domestic waste, for example, by using a compactor on vessels where that is economically possible to treat refuse and other on-board waste during fishing trips; not dump the waste but retain it for later treatment where suitable structures and equipment exist on land.

On the other hand, focusing on fish trade and processing industry in land, the management, elimination or disposal of the wastes and effluents generated by these activities poses environmental, economical and logistical problems. A parameter of great concern in wastes management is their content of water. Minimising the volume, and thus the content of water in the biomass, implies two direct benefits:

1. Better manipulation of wastes. In general, a lower moisture content in cake facilitates the ulterior waste handling and processing (García *et al.*, 2005). Transfer-transport of the waste is a key factor in solid waste management from technical and financial viewpoint. A previous compacting operation results in lower transport costs and facilitates its processing (Ghiasinejad and Abduli, 2007).

2. A reduction in the water activity assures a better microbiological stability during the handling and processing of the wastes.

For those wastes to be stored (on board the vessels until they will be landed or in cold stores prior to their processing in land), this reduction in volume after a compacting operation results

in less energetic costs and a better capacity in the cold store .This results in less construction costs and refrigeration loads for insulation and air changes, which depend directly on the cold store dimensions (Johnston *et al.*, 1994)

The daily compaction of waste is a well established process in municipal solid waste (MSW) management because it increases the capacity of landfills The degree of compaction influences the permeability and mechanical properties of the landfill, which is an important factor prior to a composting procedure (Srebro *et al.*, 2007) or to control the aeration and thus the emission of methane and other gases from waste biodegradation, for biogas production or in order to minimise the risk of explosions.

With regard to the compaction of solid wastes from slaughterhouses, a report from the French Stockbreeding Office (Office d'Elevage, 2007) tested different dehydration techniques in terms of volume reduction and economic savings. Among the different techniques analysed in this document (filtration devices, centrifuges, decanters, presses), pressing operations were the only ones able to develop enough pressure to compact and dehydrate solid, non-pumpable wastes. Screw press was preferred since it involves less personal and maintenance costs and it permits to operate in a continuous mode After comparing the performance of a screw press on several raw materials (bovine and ovine manures, pork and sheep guts, bovine coagulated raw material) ranged from pork guts (17%) to bovine and ovine manures (75%), as shown in Figure 2.1.

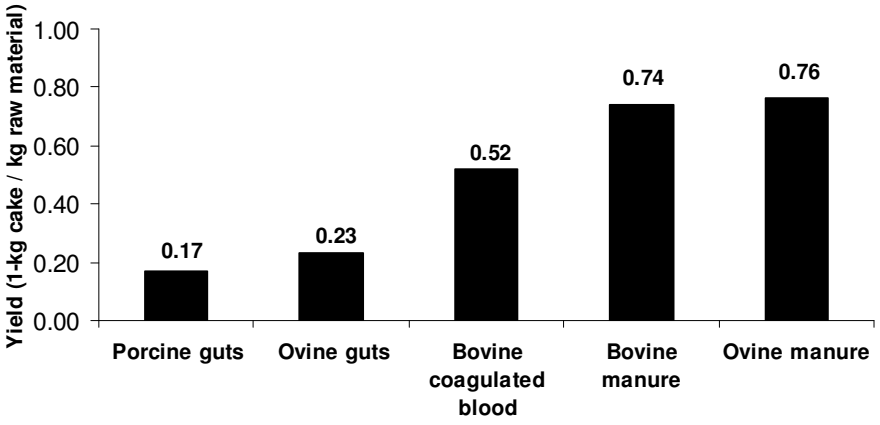

Figure 2.1. Yield of the dewatering of several raw materials from slaughterhouses.

2.1.2 Compaction of by-products from marine sources

In the case of marine materials, compacting-dewatering operations can be carried out in continuous mode by screw presses or batchwise, by means of a hydraulic press. Screw presses need a constant supply of by-products to be treated, they are widely used as dewatering pretreatment for fish meal production (Bimbo *et al.* 1990, Tiller 1999), surimi fabrication, preparation of fish laminates (Jeevanandam 2001) and also in fish oil extraction from fatty species such as herring (Aidos *et al.*, 2003).

A screw press works on the principle of one of two parallel helical screw conveyors rotating in a tightly fitting cylinder, which is provided with perforations for the drainage of press liquid. Raw material, previously crushed, is fed continuously at the inlet end of the press and conveyed by the screw towards a fix bottom in order to be compressed material. As it is conveyed by the screws along the perforated barrel, the volume between the screw flights is gradually reduced, thus increasing the pressure at which the material is subjected and thus the amount of liquid expressed. The partially dewatered cake resulting from the process is continuously discharged by the outlet end The performance of a screw press depends on two design factors (FAO, 1986):

The speed of the screw, which can be varied by means of a handwheel. This variable determines the residence time of the material inside the press, and thus, the frontal pressure applied against the fixed bottom and the yield of liquid to be obtained during the process. The control of this variable determines the degree of dewatering of the pressing cake.

The spacing between the screw and the draining surface. Thickening the space between the screw and the draining surface will result in more axial pressure applied to the liquid leaving the barrel. A good adjustment of this construction parameter is to be done in order to improve the dewatering yield without blocking the filtering surface.

In a hydraulic press, the raw material is placed in the press chamber where it is compressed by means of a piston actuated by a hydraulic force. This operation involves both compaction of the material and dead-end filtration of the draining liquid through the porous of the raw material until the collecting outlet. The pressing of the raw material should not be accomplished in one single step, since liquid has not enough time to drain, and blocking of the filtrate drum may appear. In order to obtain a better yield, and avoid obstruction of the filtrate

drum, the applied pressure is normally risen step-wise, with a relaxation time between the consecutive stages in order to help the liquid to drain.

The above-mentioned variables (pressure, number of stages and time of relaxation), as well as the speed of the piston, will determine the time of residence of the raw material inside the press chamber and the total compressive force exerted on it, so its correct adjustment is crucial to assure a good performance of the procedure.

The batch operation mode offered by hydraulic presses is preferred when small amounts of raw material are to be processed as would be the case of inshore fishing. Moreover, on board of a fishing vessel, the supply of raw material (discards and wastes/by-products from fish processing on board) is not continuous during the day (for example, trawling nets are normally hauled after three hours, three of four times a day).

When handling fish by-products in land (i.e. those generated by trade or fish processing industries),a continuous mode, offered by the screw press, should be preferred, as concluded by the French Stockbreeding Office rapport (Office d'Elevage, 2007). Nevertheless, this has not been the alternative chosen for our prototype, for several reasons:

1. For testing purposes, as in our case, the control of operational parameters at any time is essential. The hydraulic circuits are easy to be controlled for precise pressure, speed and position of the piston. New generation valves, with shorter response time, deliver the oil to the actuator faster, to offer the better efficiency With regard to the pressure, one important advantage is that the target pressure remains constant and is fully applied on the product surface through the processing time, unlike screw presses, where the pressure increases along the barrel and only reaches a maximal value at the outlet end. Added to this, the spacing between the screw and the barrel only can be modified manually (Beckwood Press Co's website).

2. The cake obtained from the hydraulic press is more compact and presents a lower moisture content, which involves a greater volume reduction. In our case, the volume reduction was easy to determine by directly measuring the reduction in the cake thickness.

3. For similar operational conditions, the yield of expressed liquid obtained by a screw press is higher than that obtained by an hydraulic press. This is due to the development of

shearing forces along the press barrel, in combination to the axial compressive pressure (FAO 1986). However, this results in a higher tissue disruption of the raw material, and hence a higher organic load in the press effluents.

4. Finally, the hydraulic pressing involves lower energetic costs than mechanical-driven presses, as the screw press. The energy consumption in hydraulic presses comes down to that involved in the pumping of the hydraulic oil. This is a critical point when thinking about the implementation of a compaction procedure on board a fishing vessel. Hydraulic force is commonly used to haul the nets, so fishing vessels are usually provided with hydraulic central units. Added to this, hydraulic presses do not need a water supply to facilitate the pressing performance.

It is noticeable the lack of references in literature concerning the hydraulic pressing of seafood species. Among the few works, Chantachum *et al.* (2000) studied the yield and quality of the fish oil extracted from precooked and non-precooked tuna heads by using a hydraulic press. Optimum conditions for separation of crude oil involved heating precooked and non-precooked samples at 85ºC for 30 min, followed by pressing at 140 tons/m^2 .This procedure gave a yield of crude oil of 4.8%, higher than that obtained from precooked heads (2.8%), with a higher quality, in terms of peroxide value and colour.

Wu and Chang (1980) employed hydraulic pressing for the recovery of proteins from Antarctic krill, obtaining an optimum yield of 50 % of crude protein by pressing at 2000 – 2500 psi. Although the yield was lower than those obtained by extraction with salt or alkali (85%), the protein recovered was of good nutritional value and functional properties.

As a consequence of pressing operations, two fractions are obtained: a partially dehydrated cake, and a press liquor which should be treated in order to obtain a final filtrate with low COD (Afonso *et al.*, 2004) whose discard represents a minimal environmental impact

The partially dewatered cake resulting from the pressing operation is an easily perishable product since its moisture content is still important. These by-products should be stabilised in order to prevent microbial proliferation. In the case of a fish vessel, it must be kept in a cold store at -16ºC until being brought ashore to be re-utilised in aquaculture or other applications. Among all the alternatives able to turn these by-products into valuable products (see *Section*

1.2. about fish up-grading technologies), and considering the trends in the French market, two technological solutions could be proposed:

1. Reduction to fish meal: This method is widely employed to up-grade fish wastes (Bimbo, 1990). It consists on employing a heat pre-treatment in order to coagulate proteins and separate them from fish oil, followed by a pressing or decanting operation in order to recover the different phases (FAO, 1986). Its use as animal feedstuff obliges to reduce the cake moisture content to less than 10% w/w, normally by means of several evaporation units, which is energy intensive. In this context, a previous dehydration operation (such mechanical pressing) can reduce the amount of water to be removed and thus the energetic costs and protein denaturation associated with this process.

2. Enzymatic processing: The utilization of endogenous enzymes in autolytic processes has been traditionally used to produce fish sauce and fish silage (Gildberg, 1993). Methods for fish protein hydrolysates production by enzyme addition (fish heterolysates) have been worldwide developed, although its commercial production is still limited in a world basis. Fish protein hydrolysates are used in pet foods (Folador *et al.*, 2006), milk replacers (Pigott, 1982) or seafood flavourants (Pigott, 1982; Le Guen *et al.*, 2000). A more detailed review of the main applications involving the addition of exogenous enzymes is given on section 1.2.2.9.

Concerning the press liquor, it constitutes an effluent with a protein load varying from 0.5 to 20 g/L (Afonso and Bórquez, 2002; Bechtel, 2005). Therefore, they should not be discharged without a suitable treatment which minimises environmental impact and allows the recovery of high added value products.

2.2 MATERIALS AND METHODS

2.2.1 Raw material

Fresh whole sardine was provided by a local market and directly stored in a refrigerated room at 4°C. All the pressing tests were carried out in the same day in order to keep the freshness of the raw material.

2.2.2 Pressing operation

Whole sardine at an initial temperature of 4 ºC was pressed at a room temperature of 10 ºC using a hydraulic press (Tinkturenpressen HP-5M, Fischer-Maschinenfabrik, Neuss, Germany) able to apply pressures up to 370 bar. For each test, 3 Kg of sample were fed into a press basket of 200 mm diameter and 150 mm high. The size of the openings located in the base was 1 mm. No heat was applied to the samples, in order to minimize the energetic costs of the process.

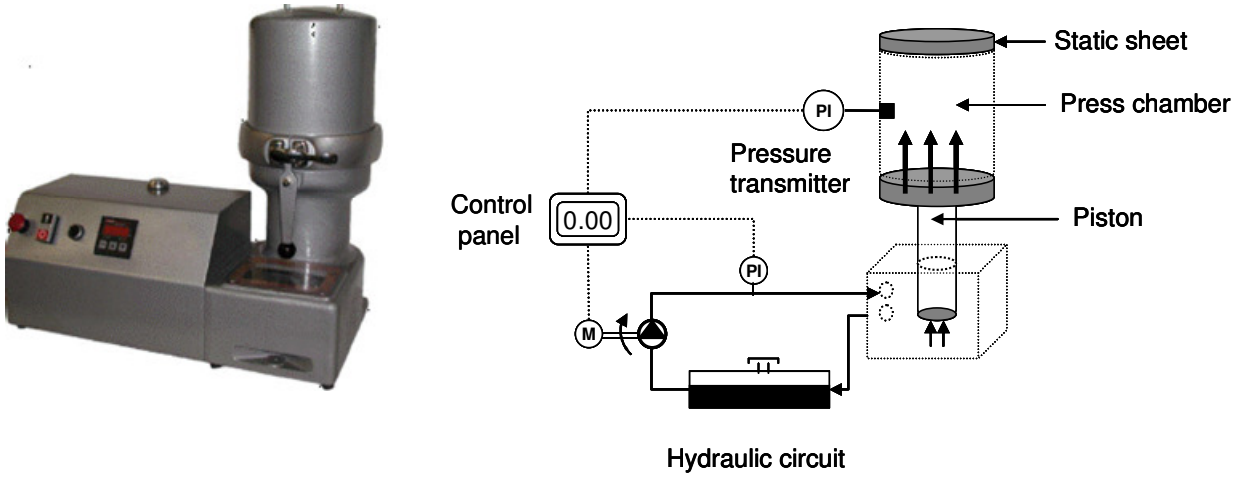

Figure 2.2. Photograph and schematical representation of the hydraulic press employed for the waste compaction assays.

The pressure reached inside the press chamber was monitored by means of a press transmitter (dTRANS p30, Jumo, Fulda, Germany), attached to a software tool designed to control the

process, in terms of compression speed, number of compression steps and time of relaxation between two consecutive compression steps.

2.2.3 Input variables

The raw material was pressed until the target pressure was achieved. As described before, this is performed in several stages, which are composed of a compression stage, where the piston descends exerting direct pressure on the material, followed by a relaxation period where the piston stops, helping the liquid to drain. The pressure declines slightly during the relaxation period due to the flux of liquid leaving the basket. An example of this type of operation can be seen in Figure 2.3. A target pressure of 300 bar is achieved in 4 stages in a total time of 18.6 min. The increment of pressure performed in each stage is equal for all the stages (75 bar in the example).

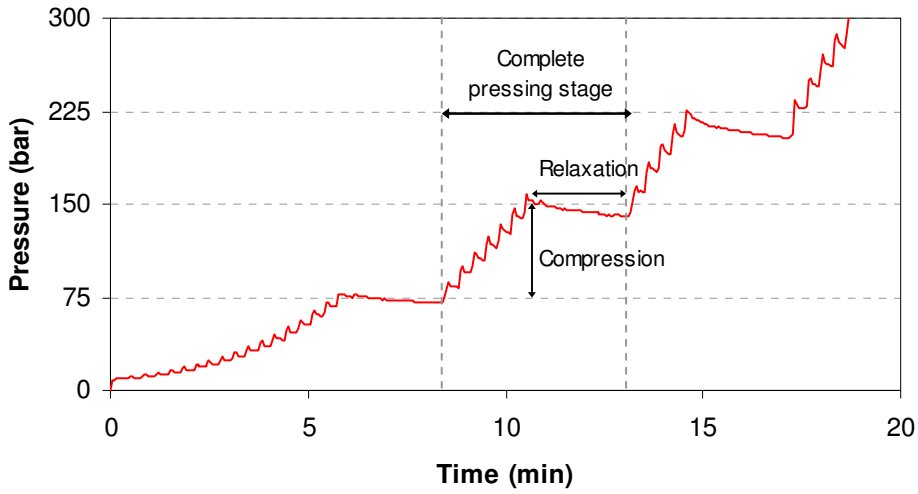

Figure 2.3. Evolution of pressure inside the chamber of the hydraulic press.

With the aim of optimising this operation, four input variables were studied: the final pressure after all the pressing stages (X_1), the compression speed at which the piston descends (X_2), the number of stages involved in the operation (X_3) and the time of relaxation between two consecutive compression stages (X_4).

2.2.4 Output variables

Two responses or output variables were measured for each experience: the yield of press liquor (Y_1) and its content in suspended solids (Y_2).

The yield of press liquor (Y_1) was defined as the mass of press liquor collected after pressing, divided by the mass of raw sardine fed into the press. It was measured by weighting all the press liquor collected after all the compression-relaxation stages were accomplished.

The content in suspended solids in the liquor (Y_2) was defined as the mass of solids in the press liquor divided by the mass of raw sardine fed into the press. Once the press liquor was collected, it was centrifuged at 4000 g at 4 °C for 15 minutes (Avanti J-E Centrifuge, Beckman Coulter USA) in order to separate it into three phases, an oily phase, an aqueous phase containing most of the soluble compounds and a solid residue. The wet weight of this solid phase was measured, because this value will be more useful with regard to an ulterior filtration operation.

2.2.5 Experimental design

2.2.5.1 Flux prediction based on a cake consolidation model.

The compression of the raw material in the hydraulic press can be assumed to be analogous to the consolidation of a saturated soil, and thus obey the Terzaghi's (1943) theory. The term consolidation in soils mechanics refers to volume change due entirely to the expulsion of pore fluids under pressure (Bargale *et al.*, 2000). Models adapted from Terzaghi's theory have already been used in the yield of Food Engineering to predict the cake consolidation and the flux of oil expressed from oilseeds under uniaxial compression (Venter *et al.*, 2007; Willems *et al.*, 2008). This theory predicts that a direct compressive force applied on the free surface of the cake will develop a pressure gradient along the cake thickness . The flux of liquid expelled from the pores (q_z, m^3/s) will be proportional to this gradient, as stated by the Darcy's law:

$$q_z = \frac{k}{\rho} \cdot \frac{\delta u}{\delta z} \qquad (2.1)$$

where the term u refers to the pore-fluid pressure (Pa), z is the direction where the compression is applied, k is the cake permeability (m/s) and ρ the unit weight of the fluid in N/m^3.

In our case, the cake cannot be considered as homogeneous as the raw material is introduced inside the press basket without being grinded previously, the press liquor is a mixture of different liquid phases (water, oil, blood) with different rheological properties, and no data are available concerning the cake consolidation, in terms of porosity, permeability or mechanical behaviour of the cake. Added to this, Tergazhi's law assumes that the fluid drains in the direction of the compressive force (similarly to a dead-end filtration), while in our hydraulic press the liquid drains in both in axial and normal direction. For this reason, the effects of the 4 independent variables on the liquor yield and the fraction of suspended solids were investigated statically by Response Surface Methodology, instead of applying a phenomenological model.

2.2.5.2 Response Surface Methodology (RSM).

The term Response Surface Methodology (RSM) refers to different mathematical procedures employed to search for a optimum of a studied variable Y inside a range of the experimental variables assayed (Montgomery and Myers, 1995; Erikson *et al.*, 2000).

Considering a system where the studied process of phenomenum is taking place, it should be described and quantified by one or several output variables Y which are function of the experimental factors or input variables, which must be measurable, according to Equation 2.2.:

$$Y = \phi(X_1, X_2, X_3, ..., X_n, \varepsilon) \qquad (2.2)$$

where X_i are the experimental measurable factors and ε the error associated to the measure.

Response Surface Methodology consists in fitting the output or response variable Y to a polynome containing the experimental factors. 1st or 2nd grade polynome are normally assayed for this purpose, which corresponds to the equation of a plane (n=1) or a curved surface (n=2).

$$Y = \beta_0 + \sum_{i=1}^{N} \beta_i X_i + \sum_{i \neq j}^{N} \beta_{ij} X_i X_j \qquad \text{for n=1} \tag{2.3}$$

$$Y = \beta_0 + \sum_{i=1}^{N} \beta_i X_i + \sum_{i \neq j}^{N} \beta_{ij} X_i X_j + \sum_{i=1}^{N} \beta_{ii} X_i^2 \qquad \text{for n=2} \tag{2.4}$$

Once the values of the parameters $\beta_1 \ldots \beta_{NN}$ are obtained by multiple regression, the solution vector $\mathbf{X}(x_1,\ldots.x_N)$ which optimise (minimise or maximise) the response variable can be obtained, by means of different optimisation techniques.

There are several available software handling with multiple regression and response surface optimisation problems: STATGRAPHICS™, MODE™, MATLAB™.

The choice of the range for the experimental variables is very important, since the optimal value for the response variable may not be placed inside this area, or this optimum is local in the case or a multimodal function. In this case, the initial range should be moved to an adjacent region, in order to assay a new range for the experimental variables. The path of deepest ascent (or descent), is the vector from the centre of the current experimental region along which the estimated response Y changes most quickly for the smallest change in the experimental factors. It indicates a new location of the centre-point to run additional experiments when the initial range of the experimental factors did not give a satisfactory optimum for the output variable. This vector corresponds mathematically to the gradient of the response variable

$$\mathbf{V}\left(\frac{\partial Y}{\partial X_1}, \frac{\partial Y}{\partial X_2}, \ldots\ldots\ldots, \frac{\partial Y}{\partial X_N}\right).$$

2.2.5.3 Experimental Designs.

As remarked before, a good selection of the experimental design is of great importance in order to minimise the number of experiments and assure a good distribution of the measured.

A basic experimental design is the $\mathbf{2^k}$ factorial design, where each experiment is performed at a the combination of the k experimental factors, set at their maximal and minimal values.

These extreme values for the experimental values are normally coded as **-1** and **+1**. The total number of runs N will depend on the number of experimental factors considered (k) , $N = 2^k$.

A $\mathbf{3^k}$ factorial design offers a higher density of the points inside the experimental space, since each experimental factor is set at its minimal, middle and maximal values of range, noted as (-1, 0, +1) . The greater number of experiments required to generate this type of designs suggested employing fractional designs $\mathbf{3^{k-p}}$, where **p** is the fraction of points selected to generate the fractional design.

The drawbacks of the factorial designs, specially 3^k designs, are overcome by the Central Composite Designs (CCD). They involve less runs of the experimental variables than a 3^k design, but their density inside the experiment space is higher, which permits a better fit of the output variable to the response surface. A Central Composite Design (CCD) contains an imbedded factorial or fractional factorial design with central points that is augmented with a group of axial points that allow estimation of curvature. Depending on the distance from the centre of the design space to the factorial point, a CCD of *k* experimental factors will contain:

- **2^k factorial points**. The kernel of a CCD is a 2^k factorial design where k is the number of levels for the experimental factors.

- **2k star points** . The star points represent new extreme values (low and high) for each factor in the design. The distance from the centre of the design space to a star point is $\pm \alpha$ where normally $|\alpha| > 1$. The precise value of α depends on certain properties desired for the design (whether it will be inscribed or circumscribed) and on the number of factors involved.

- **n_0 central point runs**. The centre contains the middle values (X_{1m}, X_{2m}, …, X_{Nm}) of the range assayed for each experimental factor.

The Figure 2.4. (left-side) illustrates a CCD for k = 3 experimental factors, which are spatially arranged in a cube whose vertex are the factorial points.

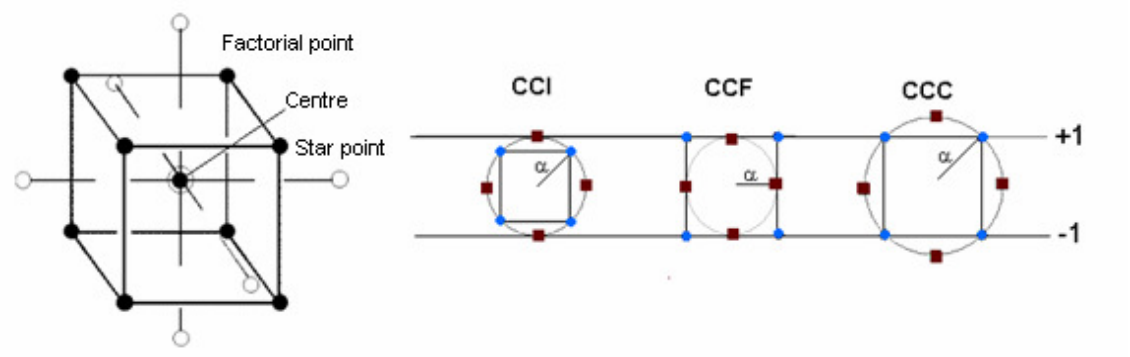

Figure 2.4. Space representation of a CCD for k=3 (left) and comparyson of the three types of CCD for k=2.

The value of the axial distance α is chosen to give rotatability to the experimental design. A CCD is rotatable when all the experimental points (either factorial or star points) are placed at the same distance to the centre point. This means that both factorial and star points will describe a circle circumscribed around the factorial square (k=2) or an sphere around the factorial cube (k=3). To maintain rotatability, the α will be calculated by:

$$\alpha = \sqrt[4]{2^k} \qquad (2.5)$$

The Central Composite Designs can be classified, depending on the value of α, in three types (Figure 2.4. right-side):

- **Central Composite Circumscribed (CCC)**. The star or axial points are placed at some distance $\alpha > 1$ from the centre. These designs have circular, spherical, or hyperspherical symmetry and require 5 levels for each factor ($-\alpha$, -1, 0, +1, $+\alpha$).

- **Central Composite Inscribed (CCI).** This design is a scaled down CCC design with each factor level of the CCC design divided by α to generate the CCI design. This design also requires 5 levels for the experimental factors placed at (-1, $-1/\alpha$, 0, $+1/\alpha$, +1) units from the centre.

- **Face Centered (CCF).** The axial points are placed at $\alpha = \pm 1$ units from the centre of the experimental space. This variety requires 3 levels for the experimental factors.

In our case, the influence of the input variables upon the liquor yield and its content in solids was studied by a means of a rotatable CCC design, where the four input variables are set at 5

levels as shown in Table 2.1.The ranges assayed for the pressure and the speed of the piston were chosen according to the technical limitations of the hydraulic press.

Table 2.1. Levels of the input variables essayed for the pressing of whole sardine at lab scale..

Level	Pressure (bar)	Speed (cm/min)	Steps (-)	Time (s)
	X_1	X_2	X_3	X_4
-2	50	0.935	1	100
-1	125	1.485	2	150
0	200	2.035	3	200
+1	275	2.585	4	250
+2	350	3.135	5	300

The Statgraphics™ software (version 5.1) was used to generate the experimental design, the statistical analysis and the regression model. The response functions were related to the input variables by a second degree polynomial as follows:

$$Y_1 = b_0 + \sum_{i=1}^{4} b_i X_i + \sum_{i=1}^{4} b_{ii} X_i^2 + \sum_{i<j}^{4} b_{ij} X_i X_j \qquad (2.6)$$

$$-\ln(Y_2) = b_0 + \sum_{i=1}^{4} b_i X_i + \sum_{i=1}^{4} b_{ii} X_i^2 + \sum_{i<j}^{4} b_{ij} X_i X_j \qquad (2.7)$$

where the coefficients b_i and b_{ii} are related to the linear and quadratic effects, respectively, of each input factor on the response and the cross-product coefficients b_{ij} represent the interactions between two input variables. The modified variable $-\ln(Y_2)$ was chosen (instead of the original Y_2) in order to obtain a better correlation when fitting the data to the regression model.

2.2.6 Multi-objective optimisation

A problem of multi-objective optimisation arises when several objectives (possibly conflicting) must be satisfied. For example, one may want to optimise the performance of a process while minimising its costs. Such problems can normally be formulated as a Multiple Objective Nonlinear Program (MONP). A MONP can be defined (Osyczka, 1985) as the problem of finding a vector of decision variables which satisfies constraints and optimises a

vector function F(x) whose elements represent the single objectives f(x). The solution vector should give values of all the objective functions acceptable to the decision maker. This consists in finding the solution vector x:

$$x = [x_1, x_2, ..., x_n] \; x \in \Re^n \tag{2.8}$$

which minimises the objective function F(x)

$$F(x) = [f_1(x_1,.,x_n), f_2(x_1,...,x_n),..., f_n(x_1,...,x_n)] \tag{2.9}$$

Subject to the constraints:

$$\begin{array}{lll} x_{LB} \le x_i \le x_{UB} & \text{for i=1,..,n} & \text{(n boundary constraints)} \\ g_j(x) = 0 & \text{for j=1,...,m} & \text{(m equality constraints)} \\ h_j(x) \le 0 & \text{for j=m+1,...,p} & \text{(p-m inequality constraints)} \end{array} \tag{2.10}$$

The sub-index LB and UB refer to the lower and upper bounds of the independent variables.

If any of the components of the objective function are competing, there is no unique combination of independent variables x, which solves the optimisation problem. Then the concept of Pareto Front must be used in order to find and adequate solution.

The Pareto Front is defined as the set of noninferior solutions which satisfies all the constraints of the multi-objective optimisation problem. A noninferior solution is one vector x = [x_1, x_2, …,x_n], minimising the objective function F(x) in which an improvement in one individual objective f_i requires a degradation of another (Kim and Weck, 2005; Halsall-Whitney and Thibault, 2006).

The most popular methods to solve a MONLP are the weighted-sum strategy and the ε-constraint method. The folder consists in expressing the global objective function F(x) as a linear combination (or weighted sum) of the individual objectives f_i, so the optimisation problem will be defined as:

$$\begin{array}{l} \min \; F(x) = \sum_{i=1}^{n} \lambda_i \cdot f_i \\ g_i(x) = 0; \quad h_i(x) \le 0 \end{array} \tag{2.11}$$

where λ_i is the weight factor of the i-th objective. Weight factors are normally chosen such that:

$$\sum_{i=1}^{n} \lambda_i = 1 \qquad (2.12)$$

The problem here is in attaching weighting coefficients to each one of the individual objectives, as the weighting coefficients do not necessarily correspond directly to the relative importance of the individual objectives, and some combinations of weight factors could not lead to a feasible solution.

Some of the problems associated to the weighted-sum method can be overcome by applying the ε-constraint method, developed by S. Marglins in 1967. This strategy involves minimising an individual objective $f_j(x)$ and expressing the other objectives in the form of inequality constraints:

$$\begin{aligned}
&\text{Minimise } f_j(x_1,...,x_n) \text{ subject to:} \\
&x_{LB} \le x_i \le x_{UB} \quad \text{for i=1,..,n} \quad \text{(n boundary constraints)} \\
&g_j(x) = 0 \quad \text{for j=1,...,m} \quad \text{(m equality constraints)} \\
&h_j(x) \le 0 \quad \text{for j=m+1,...,p} \quad \text{(p-m inequality constraints)} \\
&F_i(x) \le \varepsilon_i \quad \text{for i=1,...,p; for } i \neq j
\end{aligned} \qquad (2.13)$$

With regard to the optimisation algorithms employed to minimise the global objective function, it is out of the scope of this work to provide an extensive review of methods, which have been extensively described in the literature (Horst and Pardalos, 1995; Nash and Sofer, 1996).

The optimisation methods are divided into two groups, local and global, depending on the strategy employed to search for the optimum. Local methods start from an initial guess and compute iteratively different search directions in order to find a local optimum. These methods present as inconvenient their highly dependence on the initial guess provided by the user, and often converge to local solutions close to the starting point, which does not correspond to the global optimum. Global methods can overcome these limitations by applying different search techniques able to find the global optimum.

In this work, among the different available methods of global optimisation, a Branch and Bound (B&B) method (Pibouleau *et al.*, 2000) was chosen as it can solve problems with integer variables (in our case, the number of compression steps X_3). This method is based on the following two basic principles:

- A partitioning method for the independent variables to divide up all the possible feasible solutions into subsets.

- A search for the optimum solution in the most promising subsets. The Solver Tool, included in the MS Excel software was chosen for this purpose as it incorporates B&B algorithms for mixed integer nonlinear optimisation.

2.3 RESULTS AND DISCUSSION

2.3.1 Volume and water content reduction in the final cake.

As a consequence of pressing a partially dewatered cake was obtained. For each experiment the reduction in volume of cake was measured. An average reduction of 40-45% was measured for all the samples, showing no significant variability or correlation with experimental factors. This may be attributed to the fact that the volume reduction was calculated by opening the press chamber and directly measuring the cake thickness, which partially expanded and recovered its initial form. Considering that an average yield of liquor of 10% (mass of water per mass of whole sardine) is obtained after pressing with a volume reduction in the cake of 40%, the storage density (mass stored per pallet) is increased in a 50%. For a fixed storage capacity and pallets layout, this results in a decrease of the store area of about 33% . This results in less construction costs and refrigeration loads for insulation and air changes, which depend directly on the cold store dimensions (Johnson *et al.*, 1994)

Figure 2.5. Dewatered cake resulting from a pressing operation on Black Bream.

2.3.2 Regression model and analysis of variance

Table 2.2. shows the experimentally measured and the regression model predicted values of the response variables. Employing a complete CCD, with four independent variables and three central points, a total of 27 experiments were conducted, as shown in Table 2.2.

Table 2.2. Rotatable central composite design.

Exp. #	Input Variables				Output variables	
	X_1 (bar)	X_2 (cm/min)	X_3 (-)	X_4 (s)	Y_1 (w/w)	$-\ln(Y_2)$ (-)
1	125	1.485	2	150	0.058	4.978
2	275	1.485	2	150	0.103	4.091
3	125	2.585	2	150	0.058	4.870
4	275	2.585	2	150	0.093	4.208
5	125	1.485	4	150	0.074	4.723
6	275	1.485	4	150	0.113	4.335
7	125	2.585	4	150	0.071	4.873
8	275	2.585	4	150	0.106	4.681
9	125	1.485	2	250	0.067	4.673
10	275	1.485	2	250	0.108	4.110
11	125	2.585	2	250	0.062	5.024
12	275	2.585	2	250	0.086	4.582
13	125	1.485	4	250	0.085	4.697
14	275	1.485	4	250	0.121	3.872
15	125	2.585	4	250	0.084	4.763
16	275	2.585	4	250	0.114	4.504
17	50	2.035	3	200	0.059	5.193
18	350	2.035	3	200	0.129	3.728
19	200	0.935	3	200	0.103	4.203
20	200	2.585[a]	3	200	0.094	4.032
21	200	2.035	1	200	0.073	4.718
22	200	2.035	5	200	0.116	4.201
23	200	2.035	3	100	0.093	4.258
24	200	2.035	3	300	0.106	4.182
25	200	2.035	3	200	0.101	4.259
26	200	2.035	3	200	0.102	4.284
27	200	2.035	3	200	0.108	4.168

[a] 2.585 cm/min (level +1) were applied in this experiment instead of 3.135 (level +2) due to technical limitations

The experimental data were fitted to a complete quadratic model and the regression coefficients were calculated, as well as their statistical significance by means of an analysis of

variance, as shown in Table 2.2. Figure 2.6. shows the correlation between experimental and predicted values for the output variables Y_1 and $-\ln(Y_2)$. The higher the correlation is, the lowest is the deviation between the trend line followed by the experimental data and the diagonal y = x.

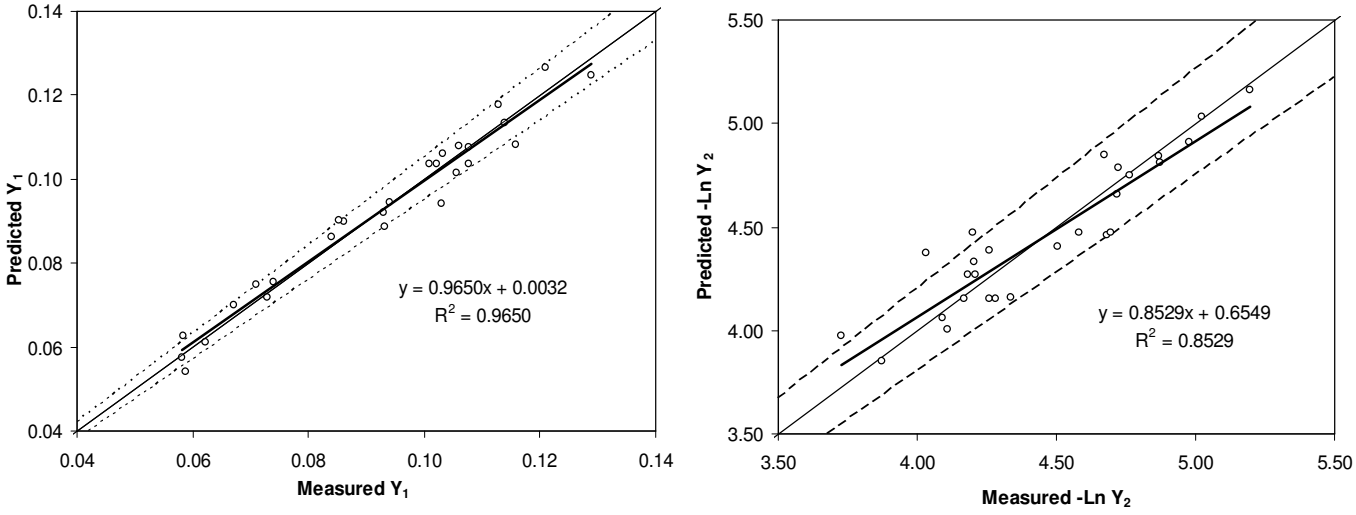

Figure 2.6. Correlation between predicted and measured values for the output variables.

Most of the experimental points present a deviation of ±5% between predicted and measured variable, that is, they are placed in the region delimited by the dotted lines. A better correlation was obtained for the liquor yield Y_1, with R^2 = 0.9650. In the case of the suspended matter, $-\ln Y_2$, the correlation was less satisfactory, with R^2=0.8529, although only three experimental points have a residual higher than 5%. In conclusion, the quadratic models assayed can adequately predict the influence of the experimental factors upon both responses Y_1 and $-\ln Y_2$.

Table 2.3. Regression coefficients and *p-values* for the response variables.

Term	Y_1		$-\ln(Y_2)$	
	Coefficient	p-value	Coefficient	p-value
b_0	-0.1365	-	10.1591	-
b_1	0.0007	0.0000	-0.0172	0.0000
b_2	0.0645	0.0047	-2.1208	0.0298
b_3	0.0184	0.0000	-0.6477	0.3020
b_4	0.0004	0.0192	-0.0086	0.5219
b_{11}	$-6.29\cdot10^{-7}$	0.0122	$1.85\cdot10^{-5}$	0.0361
b_{12}	$-5.45\cdot10^{-5}$	0.1407	0.0017	0.2154
b_{13}	$-4.33\cdot10^{-5}$	0.8236	0.0007	0.3148
b_{14}	$-3.90\cdot10^{-7}$	0.3255	$6.44\cdot10^{-7}$	0.9644
b_{22}	-0.0152	0.0113	0.3486	0.0901
b_{23}	0.0021	0.4262	0.0411	0.6770
b_{24}	$-3.23\cdot10^{-5}$	0.5455	0.0023	0.2533
b_{33}	-0.0034	0.0148	0.1039	0.0366
b_{34}	$3.78\cdot10^{-5}$	0.2105	-0.0013	0.2530
b_{44}	$-8.44\cdot10^{-7}$	0.1016	$1.76\cdot10^{-5}$	0.3390

Similar statistical procedures have already been employed to optimise fish oil quality from herring by-products using a three-phase decanter (Aidos *et al.*, 2003) or to study the performance of several enzymes on the hydrolysis of fish wastes from several sources such as sardine (Dumay, 2006) or Atlantic salmon (Liaset *et al.*, 2002).

2.3.2.1 Statistical Analysis for the liquor yield

The main effect of each factor is estimated as the difference between average of the measurements made at high and low levels of the factor. In a factorial design, the estimate of the two-factor interactions is the average of the runs in which both the factors are at high or low setting (i.e., high–high and low–low), minus, the average of the runs in which the factor levels are at mixed settings (i.e., low–high and high–low). The effect for each of the factors is plotted on the Pareto chart.

The Pareto graph shows in an intuitive way the significance of each input variable, quadratic effect or interaction (cross-product of two input variables) upon the yield (Figure 2.7).

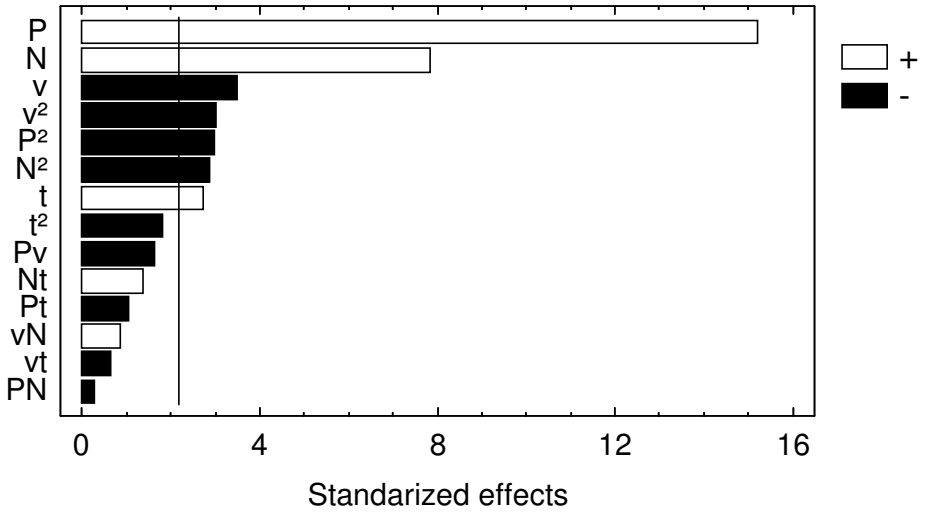

Figure 2.7. Pareto Graph for the liquor yield at a level of confidence of 95%. P=pressure, v=compression speed, N=number of pressing stages, t=relaxation time.

For a level of confidence 1-α = 0.95, p-values higher than 0.05 show that the effect is statistically not significant on the response variable, that is, it can be removed from the quadratic model as it influence on the response Y is negligible. A p-value is a measure of how much evidence one has against the null hypothesis and evidence against null hypothesis is more for smaller p-value. In other words, a p-value of 5% means that the supposed statistical model will fail to predict the response 5% of the time. This value is represented in the Pareto graph as a vertical line, where those effects not exceeding it are considered as not significant.

The statistical analysis states that the four independent variables are significant on the liquor yield, as well as the quadratic effects of pressure, compression speed and number of compression stages. The effect of interactions on the liquor yield was not significant as their associated probabilities were higher than 0.05.

Figure 2.8. shows the response surfaces obtained for the effect of the pressure, speed and time of relaxation on the yield of press liquor. Pressure exerts a positive effect on the liquor yield (Figures 2.8a and 2.8b), so working at higher pressures should report an increase in the quantity of press liquor collected. The yield increases rapidly with pressure at the lowest levels of compression speed (Figure 2.8a), but this rate decreases at higher compression speeds owing to the negative contribution of this second factor (Figures 2.8a).

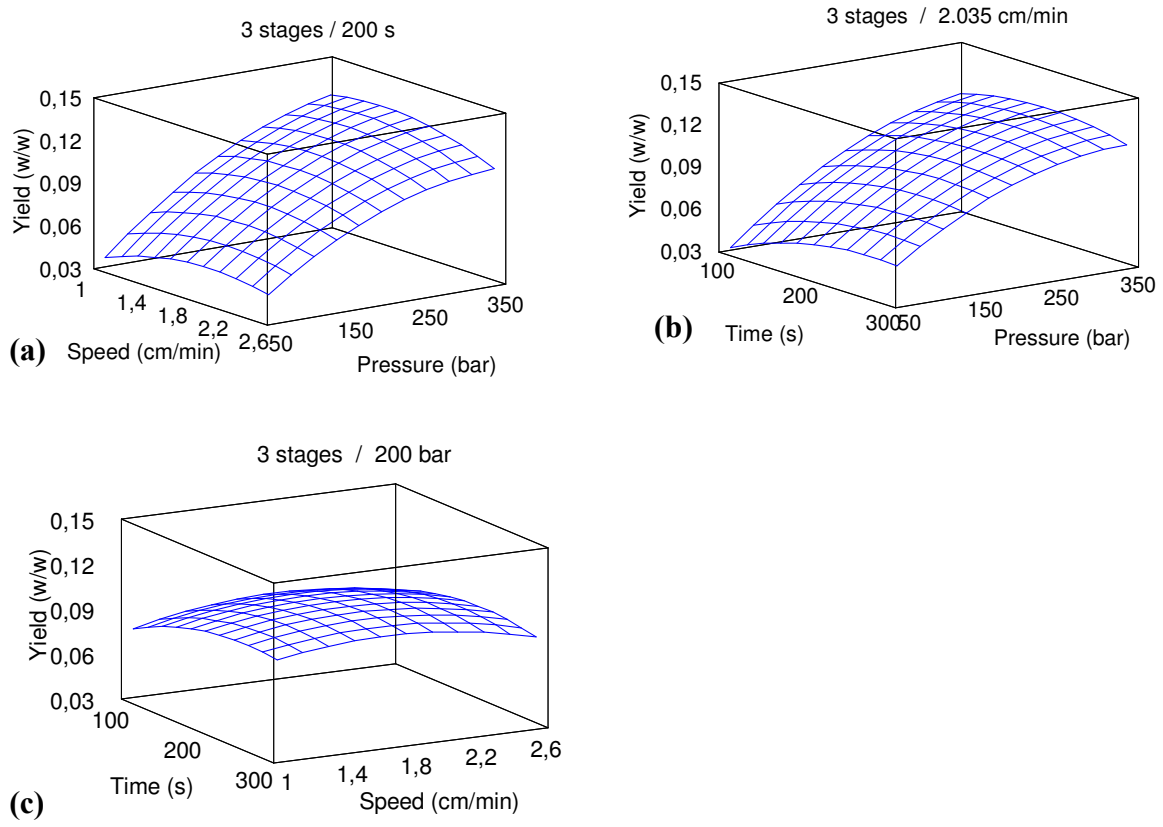

Figure 2.8. Response surface for the yield of press liquor as a function of (a) pressure and compressing speed, (b) pressure and time of relaxation and (c) compressing speed and time of relaxation. For each plot, the rest of input variables were set at their central values.

With respect to the time of relaxation (Figure 2.8b), the yield of press liquor increases rapidly with the time of relaxation to a certain level and then remains stable as the contribution of its quadratic effect and its interaction with pressure (both negative) become more relevant. In general, the amount of liquid collected can be increased by allowing longer times of drainage after each pressing stage.

The influence of the number of compression stages upon the responses variables cannot be visualised by means of a surface, due to its integer nature.

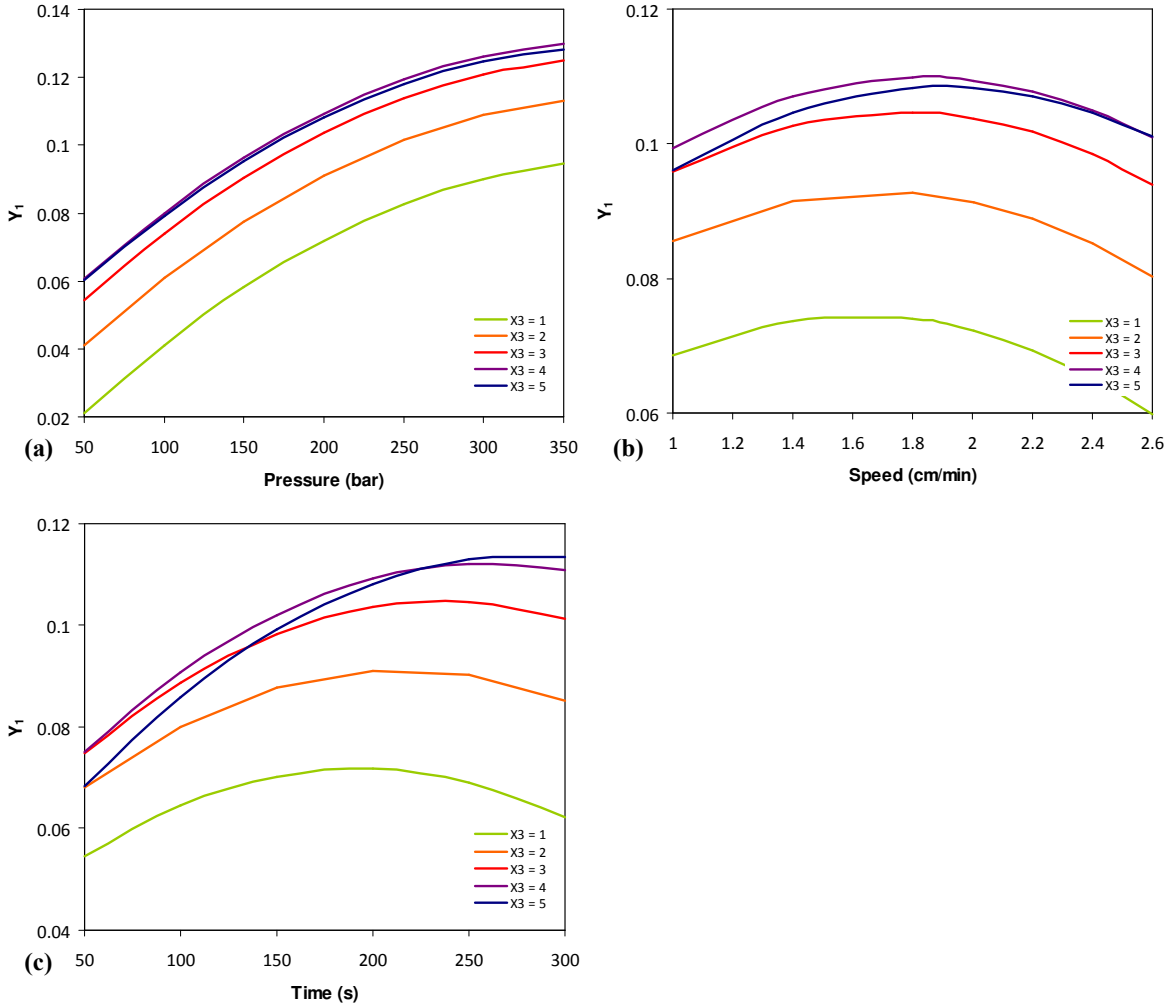

Figure 2.9. Response Profiles of the liquor yield Y_1 versus the experimental factors at a different number of compression stages.

Figure 2.9.a, b and c show that each experimental factor (P, v and t) follows different patterns depending on the relative weight of its linear or quadratic effects. From the analysis of these curves, it should be stressed that the addition of a new compression step to the pressing operation results in an improvement in the yield of the press liquor. However, this improvement decreases from stage to stage, that is, the amount of liquid collected after each new compression stage is lower. It can be concluded that the fact of applying 5 compression stages do not improve significantly the liquor yield resulting from the 4-th stage.

2.3.2.2 Statistical Analysis for the suspended matter

The Pareto Graph for the second response, -Ln Y_2 is depicted on Figure 2.10.

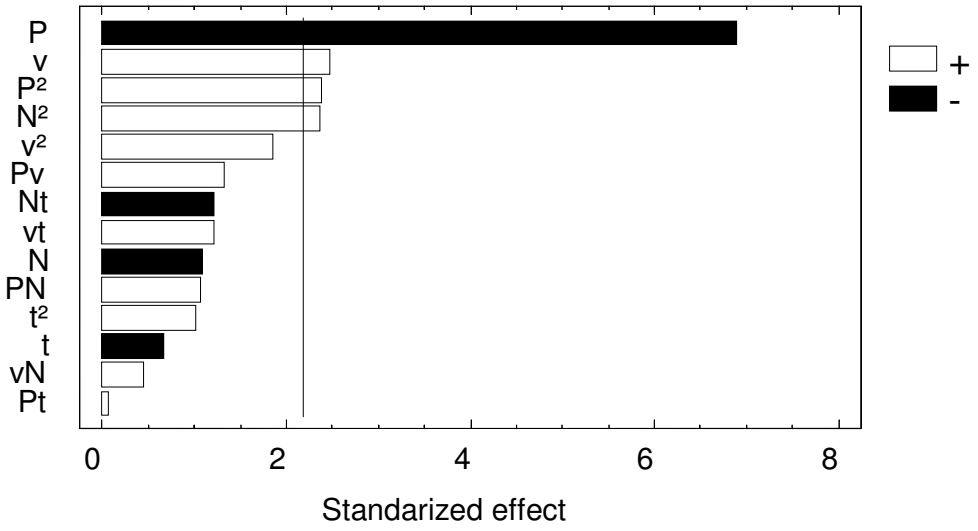

Figure 2.10. Pareto Graph for the content of suspended matter (-Ln Y2) at a level of confidence of 95%. P=pressure, v=compression speed, N=number of pressing stages, t=relaxation time.

The modified response –Ln Y_2 is negatively related to the linear and quadratic effects of pressure. This means that an increase in the pressure applied on the raw material will result in a more charged press liquor (and then a lower value of the variable –Ln Y_2).

The linear effect of the speed of compression is positive and significant on the response variable, although the similar weight of its quadratic effect (both linear and quadratic contributions are positive) determines a parabolic profile. The number of stages is significant only in its quadratic effect, with a minimal value of – LnY_2, and hence a maximal content of suspended matter, which is placed inside its experimental range. No individual, quadratic or interaction effect containing the time of relaxation was found to be significant on the output variable.

With respect to the response surfaces (Figure 2.11), the pressure exerts a negative effect on the response – Ln Y_2. This implies that a higher pressure will imply a press liquor more charged in solid particles, which is owed to the tissue disruption in the raw material. Its interaction with the time of relaxation is almost negligible, that is, the influence of pressure on the response variable is not affected by a change in the time of relaxation (Fig. 2.11a).

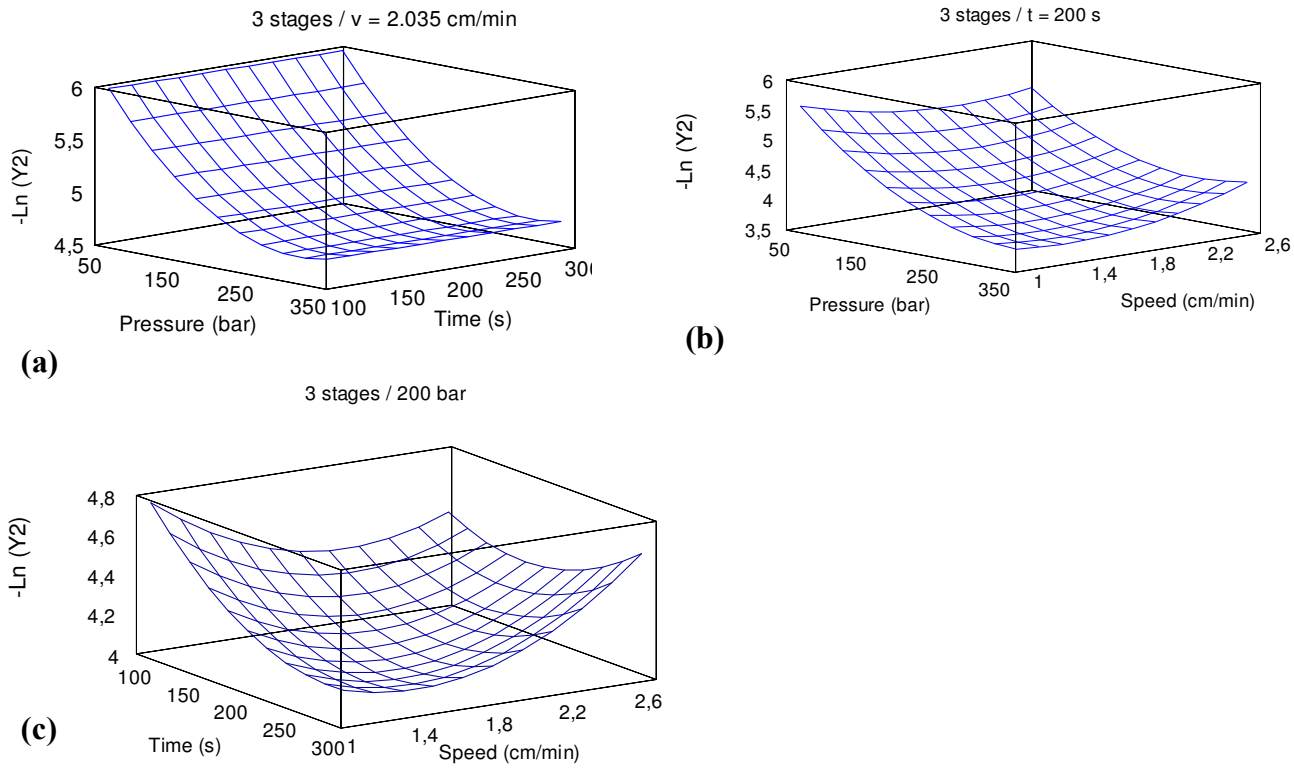

Figure 2.11. Influence of the individual effects upon the liquor yield. P=pressure, v=compression speed, N=number of pressing stages, t=relaxation time.

As shown in figures 2.11b and 2.11c, a higher compression speed leads to a lower concentration of suspended solids in the press liquor. The Pareto graph gives a strong linear dependence and no quadratic or interaction effects of significance (Fig. 2.10), so the optimal values for the response variable (maximal or minimal content of suspended solids) will be placed in its lower and upper bounds. The combination of low compression speed and high time of relaxation determined the minimal value for –Ln (Y_2) (Fig. 2.11c). This means that under these co (slow speeds of compression accompanied by long times of drainage), the press liquor will present a high content of suspended matter.

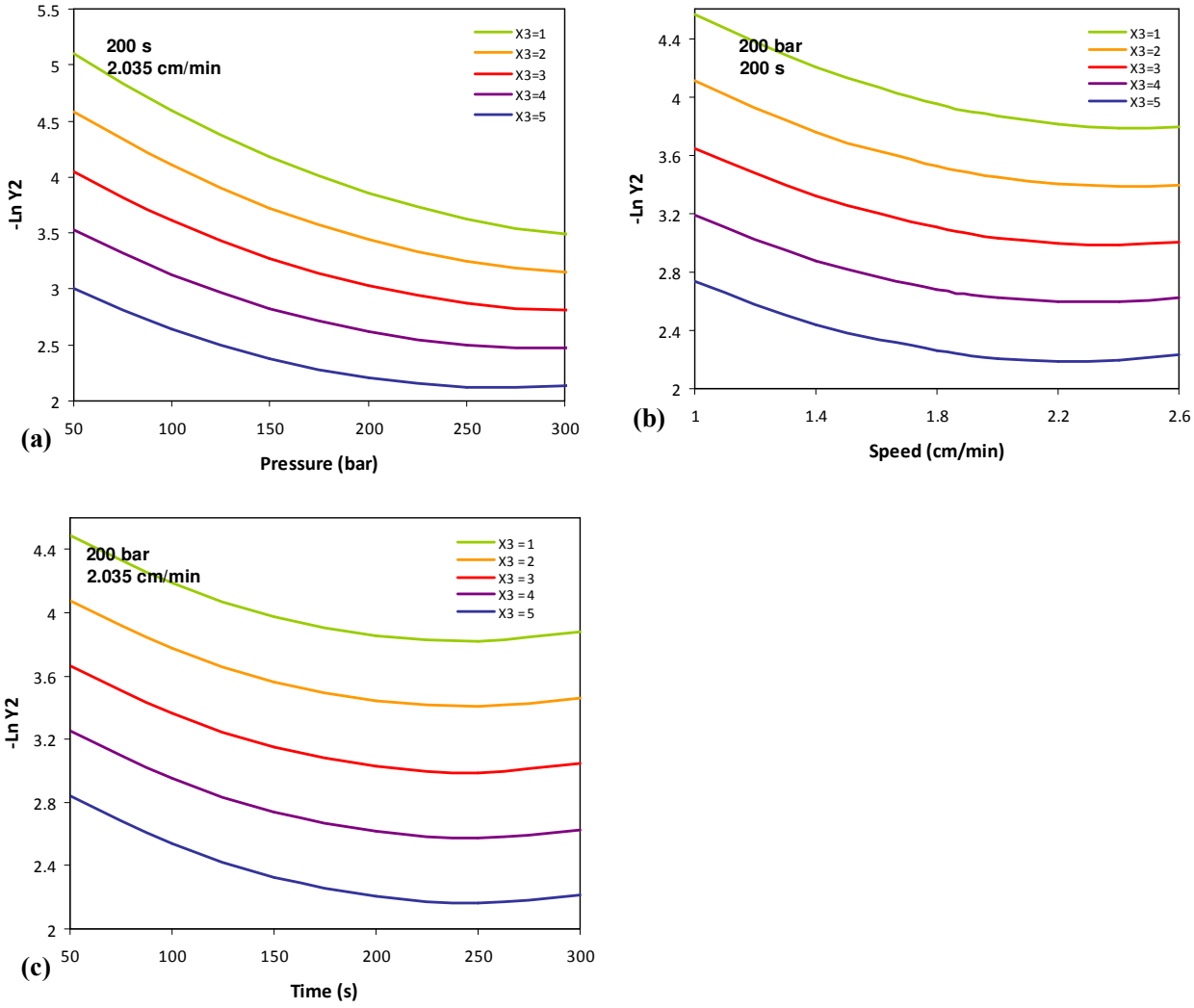

Figure 2.12. Response Profiles of –ln Y2 versus the experimental factors at a different number of compression stages.

The different profiles for the response variable –ln Y_2 depicted on Fig, 2.12a, 2.12b and 2.12c show that the larger the number of pressing steps, the lower is the content of suspended matter in the press liquor. Logically, the overall amount of suspended matter in the will increase in the course of time as more liquid is collected from the press. From the results above mentioned, it can be concluded that a pressing operation comprising several compression steps performed at low intensity (in terms of applied pressure and duration of the compression steps) can assure that the level of suspended solids in the press liquor would be limited. The regular patterns followed by the curves is attributed to the negligible contribution of the interactions between the number of compression steps and the other experimental factors.

2.3.3 Optimisation of the response variables

With the help of the regression model, the combination of factors which determine a maximal liquor yield (13.45 %) can be obtained by means of branch and bound at 350 bar of final pressure, 1.540 cm/min of compression speed, 4 compression stages and a time of relaxation of 242 s as illustrated by the contour map (Figure 2.13).

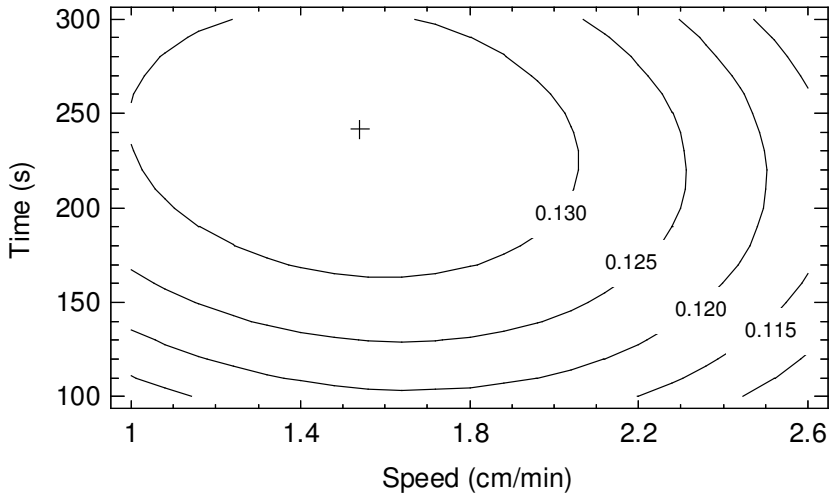

Figure 2.13. Contour map for the liquour yield at 350 bar and 4 compression stages.

This yield is inferior to those obtained for other animal wastes, like those exposed in Figure 2.14, although it must be taken into account that the initial moisture and porosity of those materials are higher, and the compaction was performed by means of a screw press, which offers better yields of liquid due to the combination of compressive and axial forces experienced by the raw material during its processing.

The fact of employing 5 or more compression stages does not improve the liquor yield (Figure 2.9a) , as well as relaxation times longer than 240 seconds. The compression speed has a significant quadratic effect ($p = 0.0113$) which determines an optimal value placed inside its range of experimental data (0.95 - 2.59 cm/min).

Concerning the fraction of suspended solids, the maximum value of the variable $-\ln(Y_2)$, and therefore the minimal value of Y_2 (0.002) is reached at 66 bar, a maximal compression speed of 2.585 cm/min, 1 compression stage, and the maximal time of relaxation allowed (300 s) (Figure 2.15). As concluded from the Pareto Graph (Figure 2.10), the variable which mostly

influenced the fraction of suspended solids was the pressure, with both linear and quadratic effects of significance. This fact implied that the optimum was found inside the range of experimental data (50 - 350 bar). Its effect was positive on the content of suspended solids, as an increase in the final pressure determines a more charged press liquor.

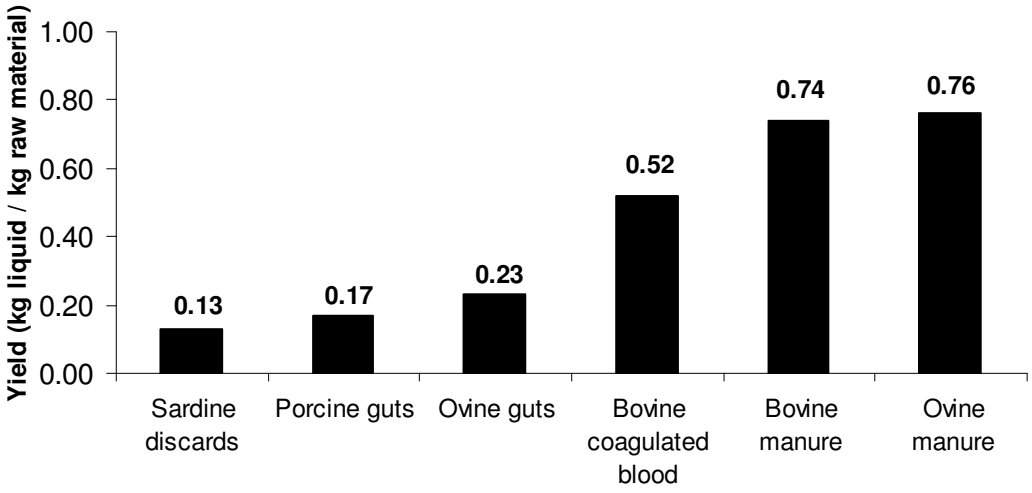

Figure 2.14. Comparative yield obtained for sardine discards and other animal wastes subjected to compaction procedures.

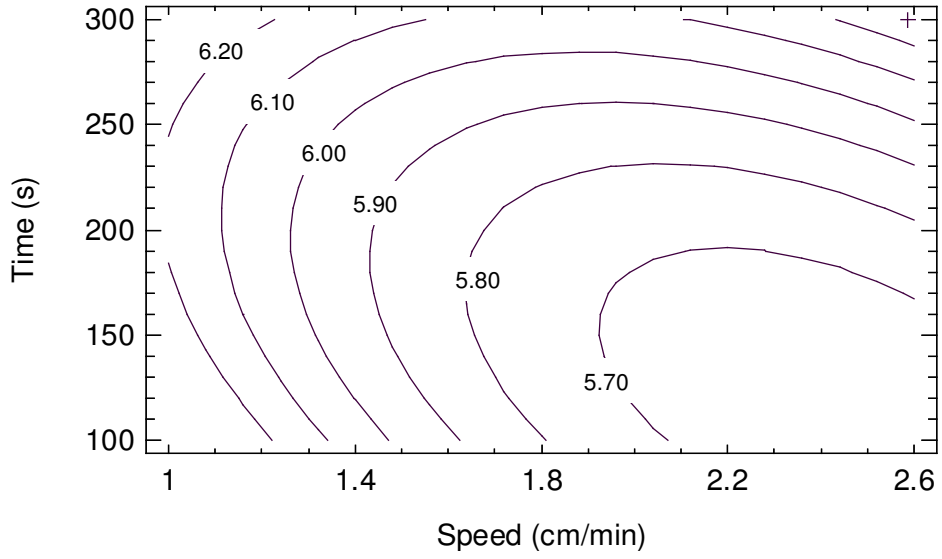

Figure 2.15. Contour plot for –lnY2 at 66 bar and 1 compression stage.

These results indicate that the effect of pressure on the optimisation of both responses is opposite. While a higher pressure leads to a better efficiency of the pressing operation, the degree of damage on the raw material is higher, and as a consequence the press liquor is more charged in suspended solids. A higher compression speed implies shorter compression stages, and thus a lower compression work. This results in a lower liquor yield but also less issue disruption in the raw material, obtaining a press liquor with lower organic load.

The relaxation time exerts a positive effect on the accomplishment of both objectives. An increase of this variable gives rise not only to a higher quantity of press liquor, but also to a lower content of suspended solids in it. This might be due to the blocking of the press outlet by the particles of suspended solids, so only liquid can leave the press chamber.

This suggests that better results concerning the content of suspended solids in the press liquor could be achieved by working at higher times of relaxation and speeds of compression, but this would result in lower yields.

2.3.4 Multiobjective optimisation.

The conflict between the two responses suggested employing a multiobjective optimisation technique. A Pareto Front was generated in order to find a set of solutions which satisfied in an adequate degree both objectives. The ε-constraint method was chosen for this purpose. The optimisation problem consisted in estimating the maximum yield that could be achieved without exceeding a fixed fraction of suspended solids in the press liquor. This fraction of suspended solids was calculated as the ratio between Y_2 and Y_1. The solution should be obtained by a combination of factors inside the ranges of the independent variables or decision space. This is a multiobjective optimisation problem with constraints which could be formulated as follows:

$$\begin{aligned} &\max Y_1 \text{ subjected to:} \\ &\frac{Y_2}{Y_1} \le \varepsilon \\ &50 \le X_1 \le 350; 0.94 \le X_2 \le 2.59; 1 \le X_3 \le 5; 100 \le X_4 \le 300 \\ &X_3 = \text{integer number} \end{aligned} \qquad (2.14)$$

The results generated after the optimisation (Table 2.4) show the maximum liquor yields that could be obtained by allowing a set of fractions of suspended solids from 0.05 to 0.15. As expected, the higher the limitation in suspended solids, the higher the yield obtained. Liquor yield ranges from 0.1021 to 0.1342 when the fraction of suspended solids allowed increases from 0.05 to 0.15. This latter value is close to the unrestricted maximum yield shown above (0.1345). All this set of non-inferior solutions corresponds to the maximum pressure allowed (350 bar), which optimises the yield of press liquor, and different combinations of the rest of decision variables. Up to a fraction of suspended solids of 0.14, the optimum number of compression stages is 5. This value changes to 4 afterwards. This may be explained by the blocking of the filter basket and press outlet by the particles of suspended solids, which avoids collecting more liquid when a next compression step is applied. While the optimum number of steps is 5, the optimum relaxation time increases from 100 to 256 s. Similarly, when 4 steps are optimum, optimum time increases from 213 to 230 s.

Table 2.4. Set of optimal solutions (Pareto front) for the multiobjective optimisation problem.

Upper bound ε (-)	Optimum X_1 (bar)	Optimum X_2 (cm/min)	Optimum X_3 (-)	Optimum X_4 (s)	Maximum Y_1 (-)
0.05	350	2.585	5	100	0.1021
0.06	350	2.585	5	177	0.1149
0.07	350	2.422	5	209	0.1217
0.08	350	2.200	5	209	0.1263
0.09	350	2.003	5	218	0.1297
0.10	350	1.830	5	230	0.1318
0.11	350	1.674	5	245	0.1330
0.12	350	1.575	5	256	0.1332
0.13	350	1.575	5	256	0.1332
0.14	350	1.704	4	213	0.1335
0.15	350	1.559	4	230	0.1342

The Pareto front is generated by plotting the optimum liquor yield (Y_1) against the limited mass concentration of solids in the press liquor (ε), as shown in the Figure 2.16. This figure shows the maximal yield which can be attained by the pressing operation, if a limited amount of suspended matter in the press liquor is desired. The selection of a single optimal solution inside the Pareto Front will depend on the technical requirements of the subsequent operations to treat the effluents, specially the maximal content in suspended solids able to be removed by the micro and ultrafiltration devices.

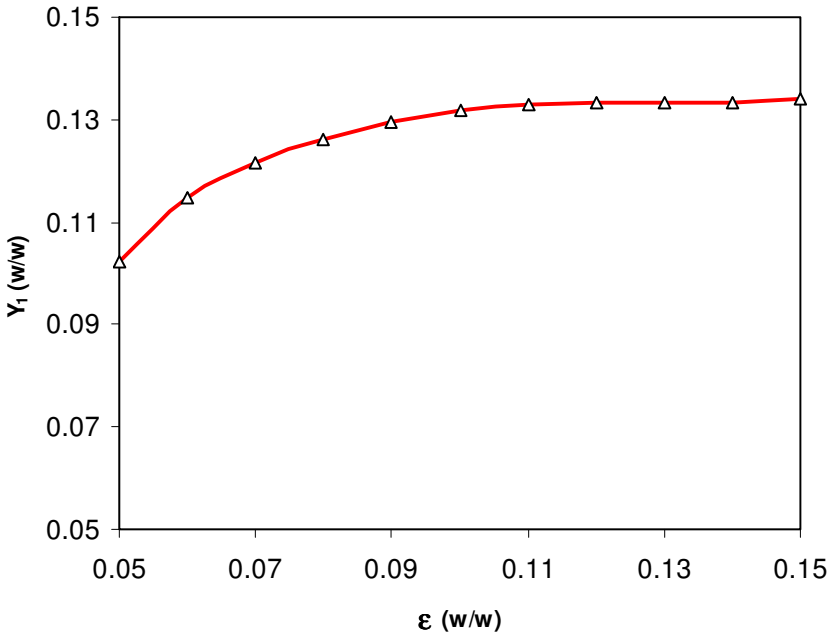

Figure 2.16. Pareto Front representation.

If the maximum allowable limit of suspended matter in press liquor increases, a higher yield of press liquor could be achieved by the pressing operation. However, it can be concluded that it is not desirable to improve the yield of press liquor above 13% (w/w), since a slight improvement above this critical value (from 13% to 13.42%) will result in a steep increase in the content of suspended particles in the liquor yield. From an economic point of view, this is not viable since the benefits of a higher yield (higher volume reduction, less moisture content in the final cake, higher yield of protein or lipid recovery from the press liquor, etc) will be offset by the increasing costs of the depuration treatment, since the initial raw effluent has a higher organic load.

2.3.5 Water holding capacity (WHC) assays on the raw material.

2.3.5.1 Pressing tests on sardine heads and de-headed sardines.

The results obtained from the pressing tests with whole sardine showed lower yields than expected, with large differences with respect to those reported from similar compacting operations carried out on other waste materials. This may be attributed to the water holding capacity of the muscular proteins, which accounts for 20 % of the sardine flesh (Dumay, 2006).

Most of the functional properties of animal meat (and specifically fish flesh) can be explained by three kinds of flesh protein interactions: protein-water, protein-protein and protein-fat (Sikorski, 1997). This first interaction determines the water-holding capacity (WHC) of meat or flesh materials, which is defined as the ability of muscle to resist water loss. An understanding of the water-binding mechanism of meat proteins was given by Hamm (1986) or Offer and Trinick (1983). They related the WHC with the swelling of the myofibrillar proteins, which make up the muscle fibres. Myosin, actin and tropomyosin are the main water-binding components in muscle tissue. The high content of acidic and basic amino acids impairs a high electrical charge to these proteins and determines their capacity to bind water molecules by polar interaction (Sikorski, 1997). With regard to fish flesh, 90% of the water found in fish tissues is held by capillary action, mainly in intracellular locations. Many authors have reported changes in the WHC of fish flesh related to its processing: salting (Honikel, 1989; Erikson *et al.*, 2004), freezing (Lambelet *et al.*, 1995) and pressing (Lakshmanan *et al.*, 2007). The last mentioned author reported an increase of the WHC of fresh salmon when it was subjected to a high-pressure treatment of 150 MPa. Taking into account the above-mentioned studies, the release of liquid in the hydraulic pressing of whole sardine would be offset by a higher water retention by the fish muscular proteins.

To validate this assumption, three samples of 3 kg of whole sardine were de-headed, separating heads from the rest of the sardine. Each sample (3 samples of heads and other 3 of de-headed sardines) was fed into the press and subjected to a pressing treatment with all the input variables set at their central value (i.e. 200 bar, 2.02 cm/min, 3 compression steps and

200 s of time of relaxation). The heads accounted for 24 ± 2 % of the wet weight of the whole sardines. Figure 2.17 shows the average yields of press liquor obtained for the heads and the de-headed sardines, compared to those obtained for the whole sardine. Each yield was expressed as mass of press liquor related to the mass of raw material (heads, whole sardine and de-headed sardine) fed into the press, in order to compare the results.

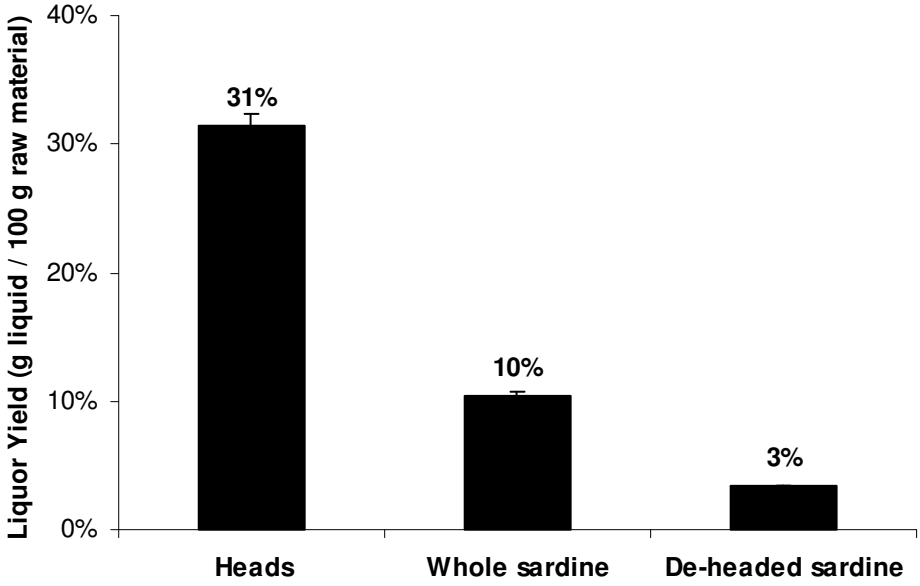

Figure 2.17. Comparison between the average yields of press liquor (w/w) obtained for heads,whole sardine and de-headed sardine.

It is noticeable that the pressing sardine heads, which are mostly composed of water, with small amounts of protein, gave the best results, with an average yield of 31.37 ± 0.95 % while that obtained from the de-headed portions, containing all the muscle tissue, was only 3.41 ± 0.05 %. Both results contribute to the average value of liquor yield obtained for whole sardine (10.43 ± 0.38 %). It can be concluded that most of the liquid collected from the pressing of whole sardines is released by the heads, since the muscle proteins resist the water loss.

2.3.5.2 Pressing tests on grinded sardines

The better results, in terms of liquor yield, obtained for sardine heads, could also be attributed to the lower particle size of this raw material, which determines a higher draining surface. According to this assumption, a previous grinding pre-treatment of the whole sardine prior to

its pressing should increase the expected yields. The effect of a grinding pre-treatment upon the yield of press liquor and its content in suspended matter was tested. For each experiment, 3 kg of raw material was grinded (Blender, Waring Comercial, USA) and then fed into the press. The pressing tests were performed at 15, 50, 80 and 125 bar pressure, while the other experimental factors were set at their centre values (2.02 cm/min, 3 steps and 200 s).

The yields of press liquor obtained after the treatment were plotted against the different pressures assayed, and compared with the predicted model for whole sardine. Since the statistical model for whole sardine is valid in the interval between 50 and 350 bar (the axial points in the experiment design), the portion of curve between 15 and 50 bar was obtained by extrapolation (dotted line).

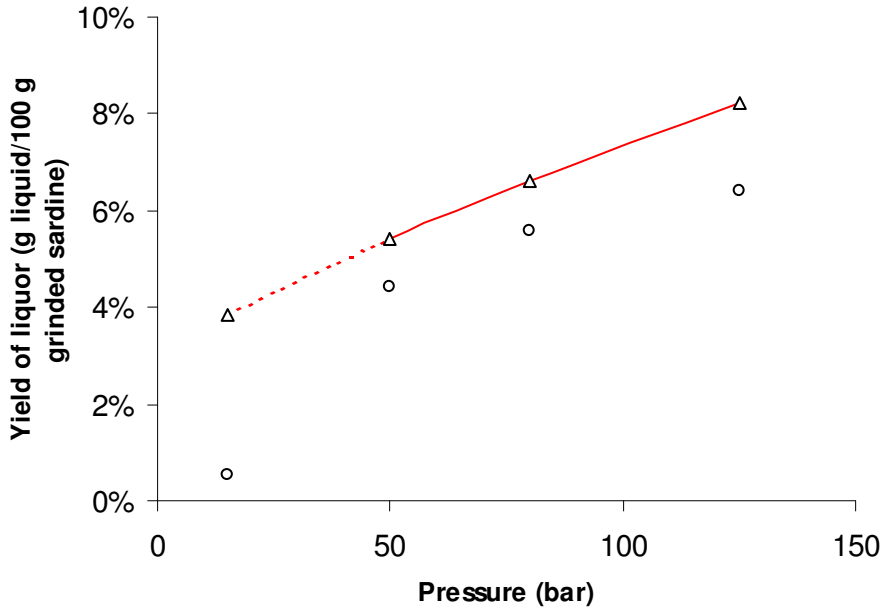

Figure 2.18. Yields of press liquor measured for grinded sardine (●) and predicted for the whole sardine (Δ). The dotted line represents an extrapolation of the statistical model.

As shown in Figure 2.18, a grinding pre-treatment do not improve the amount of press liquor collected after the pressing. The results obtained for grinded material are always lower than that obtained in the same conditions for the whole sardine. The grinded material acquired a doughy consistence, which enhanced the water holding capacity of the material. With regard to the suspended matter, the results show that the fraction of suspended solids in the press liquor, expressed in mass of solids per mass of raw liquid, increased with the target pressure

for whole and grinded sardine. However, the increase predicted for whole sardines in this range of pressures is limited (from 10 % to 14 %), while that observed for the grinded material was pronounced, reaching a weight fraction above 20% at 125 Pa, as shown in Fig. 2.19. Only solid particles are released to some extent from the press cake, which determines a high organic load in the press liquor.

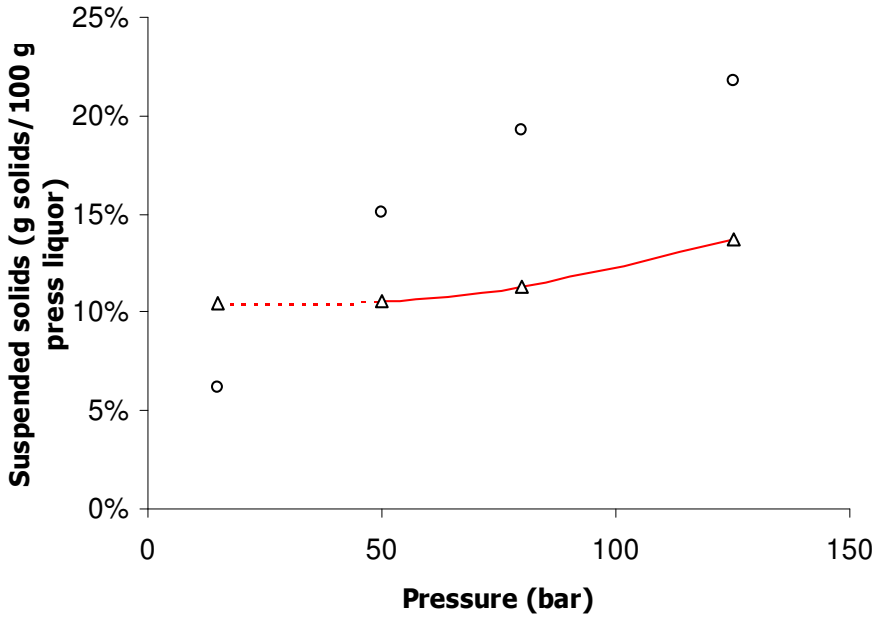

Figure 2.19. Weight fraction of suspended solids in the press liquor measured for grinded sardine (●) and predicted for whole sardine (Δ).The dotted line represents an extrapolation of the statistical model.

In conclusion, a grinding pre-treatment affects negatively the performance of the dewatering operation, since the press cake acquires a doughy consistency which prevent the fluid flow, giving rise to a press juice containing a high load of suspended particles.

2.4 CONCLUSIONS

- Whole sardine was pressed out using a hydraulic press, working at different combinations of pressure, speed of compression, number of compression steps and time of relaxation between them. As a result of this, a partially dewatered cake is obtained, with a reduction of volume of 40 - 45 % related to the initial raw material. This implies less refrigeration and space requirements, related to the storage of the whole fish.

- The yield of press liquor and its content in suspended solids were measured and fitted to a second-order model with high correlation coefficients (0.982 and 0.924, respectively). Once the polynomial models were obtained, the optimisation of both responses was carried out. The surface response graphs show that a maximum yield of 13.45 % w/w (related to the mass of sardine fed into the press) was obtained at the pressing conditions of pressure of 350 bar, compression speed of 1.54 cm/min, 5 compression steps and maximal time of relaxation. The minimal content in suspended solids was found to be 0.2 % w/w at a pressure of 66 bar, compression speed of 2.585 cm/min, 1 compression step and maximum time of relaxation.

- The opposite behaviour of the experimental factors towards the accomplishment of the optimisation objectives obliges to find a compromise solution by using multiobjective optimisation techniques. The ε-constrain method was chosen for this purpose, generating a set of optimal solutions (Pareto Front) which assures a maximal yield with a limited content in suspended solids in the press liquor. The ulterior treatment of the effluents of the pressing operation will determine the selection of a single solution inside the Pareto Front, in terms of minimum flux of liquid required or maximum concentration of suspended solids allowed. However, it can be concluded that it is not desirable to improve the yield of press liquor above a critical value 13% (w/w), in order to limit the concentration of suspended matter in the liquor yield and thus, the costs associated with the ulterior effluent treatment.

- With regard to the convenience or not of a size reduction pre-treatment (e.g. grinding, cutting operation), the water holding capacity of the myofibrillar proteins present in

the muscular flesh reduces the expected liquor yield. It can be concluded that most of the liquid collected from the pressing of whole sardines come from the heads, since the muscle proteins resist the water loss. A grinding pre-treatment affects negatively the performance of the dewatering operation, since it improves the exposure of the water to the myofibrillar proteins, the press cake acquires a doughy consistency which prevents the fluid flow, giving rise to a lesser yield of press juice and a higher content of suspended particles. It can be concluded that a pressing operation will give better results, in terms of liquor yield and suspended matter in the press juice, if it is performed on fish by-products (where the proportion of fish flesh is expected to be minimal) or whole fish where the heads have been previously separated from the fish flesh (e.g. by a cutting machine).

3. VOLUME REDUCTION STRATEGY: SCALING UP TO A PILOT PROTOTYPE USING SARDINE BY-PRODUCTS

3.1 INTRODUCTION

Most of the activities involved in the BEFAIR project concentrated on the assessment, development and implementation of efficient and integral waste management and processing practices both on-board (fishing fleets) and in-land (fish auctions and fish industry) to recycle and to reuse wastes produced by the fishing industry, including discards, by-catch and by-products from the fish processing. In particular, three main lines of action were pursued during the project life:

- The definition of viable management and processing practices. In this regard, IFREMER bet on compaction technologies as a solution for handling and storing all these materials resulting from the fishing and fish processing practices.

- The validation of this approach at the pre-industrial scale by designing, constructing and starting up demonstration prototypes.

- A complete demonstration, diffusion and dissemination plan through the elaboration and distribution of didactic materials, good practice guides and manuals, participation in congresses and workshops dealing with this issue, as well as the organization of demonstration sessions. These sessions were performed once the prototype were constructed and validated. They were intended for fishermen, fish traders and processors, marine researchers and harbour authorities, who received some information concerning the fish waste problems, legal aspects and the different solutions proposed by the BE-FAIR partners, followed by a practical session where the prototype was put into operation.

In our case, the volume reduction approach, so far employed in the management of other by-products from animal origin, was analysed and the mechanical compaction by means of a hydraulic press was tested in the laboratory on whole sardine as model discards. The variables governing the pressing procedure were identified and optimised to assure an optimal performance in terms of yield and organic charge of the press juice. These results were taken into account for the construction of a prototype at plant scale, able to compact fish by-

products and recover and give a suitable treatment to the different fractions (dewatered cake, press juice) obtained from this process.

This chapter will be devoted to two main issues:

- The construction, calibration and starting up of a prototype at a pre-industrial scale, and its subsequent validation with sardine by-products. The construction of the prototype was commissioned to an external factory (Hermanos Rodríguez S.L., Spain), while the starting up and the validation of the waste compaction procedure was carried out at the IFREMER with the help of the technical and research staff.

- In the same way that was proceeded with the laboratory tests, the influence of the operational factors on the prototype performance (yield of liquid and degree of compaction of the press cake) and the characteristics of the press liquor (suspended solids, COD, biochemical composition) were analysed by means of an experimental design. The outcomes from this step will permit to optimise the operating procedure of the prototype as well as to plan a suitable treatment for the wastewaters resulting from this procedure.

The first part will be treated among the *introduction* and *material and methods* section, due to its descriptive nature, while the second part will be revised in the *results and discussion* section.

3.1.1 Fish waste compaction flowsheet

The compaction procedure should be able to treat the fish wastage on board/in land, in order to achieve two main objectives:

- Minimise the volume of solid by-products to be handled or stored. In the case of its implementation on board, these by-products will be kept at -16ºC until being brought ashore, so a previous compaction will reduce the energy and space needs of the cold store. Once in land, a dewatering operation facilitates the transport and handling of these by-products and retards their microbial spoilage.

- Treat the effluents from the pressing operation so their discarding causes a minimal environmental impact. The final effluents discharged should meet the maximum discharge limits of suspended solids, fats and COD disposed by the environment regulations. Depending on the composition of the press liquor and the procedure proposed, this treatment could also recover some fractions of interest (fish oil, fish proteins) whose sell or up-grading could report additional revenues to the waste handler.

The overall process of waste compaction should involve the following steps :

Pre-treatment of raw material. As concluded from the laboratory test, the raw material must be pre-treated in order to obtain a better yield in the press. Two basic options could be proposed: heating or crushing.

a) Heating. Common methods to produce fish meal (Bimbo, 1990) involve heating the raw material at 85-95°C as a first step to coagulate fish proteins and separate them from oil. Although this pre-treatment improves the oil recovery and the yield of the pressing operation, it has some drawbacks. Stream heating involves a high energy consumption and its implementation in small fish processing factories or on board of small fishing vessels is unviable. Added to this, the heat treatment could alter the quality of the proteins and lipids in the press cake and liquor yield, reducing their up-grading alternatives.

b) Grinding. This pre-treatment was chosen instead of heating as it can be easily done in a continuous mode both on board and in land. Raw material is grinded before being fed into the press, thus increasing its porosity and draining surface in order to improve yield of liquid and the degree of compaction in the press cake.

Pressing. The grinded material should feed the press batchwise, by means of a belt conveyor. An hydraulic press was chosen for this purpose, instead of a screw press, as it assures a better compaction of the press cake, minimises the water and energy consumption -which is a critical point, specially on board a fish vessel- and hydraulic circuits are easy to control. The stepwise pressing procedure optimised during the preliminary lab tests should be respected as far as possible during the prototype construction. Another important requirement is that all the operating variables should be easily modified, controlled and monitored during the pressing process, since the prototype was intended for research purposes.

Separation of the press cake and press liquor. Both phases should be easily separated after the pressing operation. The press liquor should be pre-filtered before being collected in an storage tank, prior to its depuration treatment. With regard to the press cake, it should be easily taken off the press and placed in trays inside the cold store.

Depuration of the effluent. This treatment will be studied in detail in chapter 4. The bulk of the press liquor consists in a an aqueous solution, containing blood and other soluble proteins, with variable amounts of suspended solids and oil. Considering this composition, IFREMER proposed a mild procedure comprising several filtration cartridges to recover the fine solids, a 2-phase centrifuge to recover the fish oil and a membrane ultrafiltration unit able to concentrate most of the soluble proteins and obtain a "clean" filtrate with an organic load under the discharge limits.

Cleaning in place system. The prototype should be provided with a clean in place (CIP) system able to provide water to the cutting machine, belt conveyor, press and the different units involved in the effluent treatment (cartridges, membranes). The cleaning of the ultrafiltration unit must assure the adequate removal of the foulant agents (salts, protein aggregates, lipids, etc) deposited on the membrane surface or inside the pores. To this end, the prototype should be provided of one or several storage tanks containing the cleaning agents.

Control devices. Each operation involves the control and monitoring of different variables. The prototype needs an operation interface, which enables the user to adjust the set points for each control variable, and monitor their evolution in the course of the pressing operation. Each unit operation involved in the whole process needs some key variables to be controlled. The different units comprising the compacting process are listed in the table 3.1, as well as the operation parameters to be controlled for each specific operation.

Table 3.1. Variables to be controlled for each unit operation involved in the compaction process and the treatment of effluents.

Unit	Variables to be controlled.
Cutting machine	Power of the cutters
Hydraulic press	Pressure of the oil
	Speed at which the piston descends
	Time of relaxation
	Number of compression steps
Storage tanks	Level of liquid
Filtration cartridges	Manometric pressure
Ultrafiltration unit	Inlet and outlet pressure
	Flow of the retentate
	Cross velocity
	Temperature of the feed solution

Considering all these requirements, the overall process of fish wastes compaction can be represented by the process flowsheet depicted in the figure 3.1.

The raw material is fed into the cutting machine. The grinded material is conveyed into the press, which is driven by means of an hydraulic power station. Once all the compression steps are accomplished, the press cake is received in a tray and kept in the cold store. The press liquor is collected in the storage tank 1, from which it is pumped to the effluent depuration line, comprising two series dead-end filtration cartridges, where the fine solids are retained, and a centrifuge . This last apparatus can be by-passed depending on the amount of oil present in the press liquor. After these preliminary operations the wastewater consists in an aqueous solution containing a variable amount of soluble proteins (blood proteins for most of them). It will be stored in the tank 2, before being pumped through the ultrafiltration unit. The ultrafiltration will consist in a batch concentration where the retentate is recycled several times in order to concentrate the proteins from the bulk solution and eliminate the water and other solutes of small molecular weight (filtrate stream).

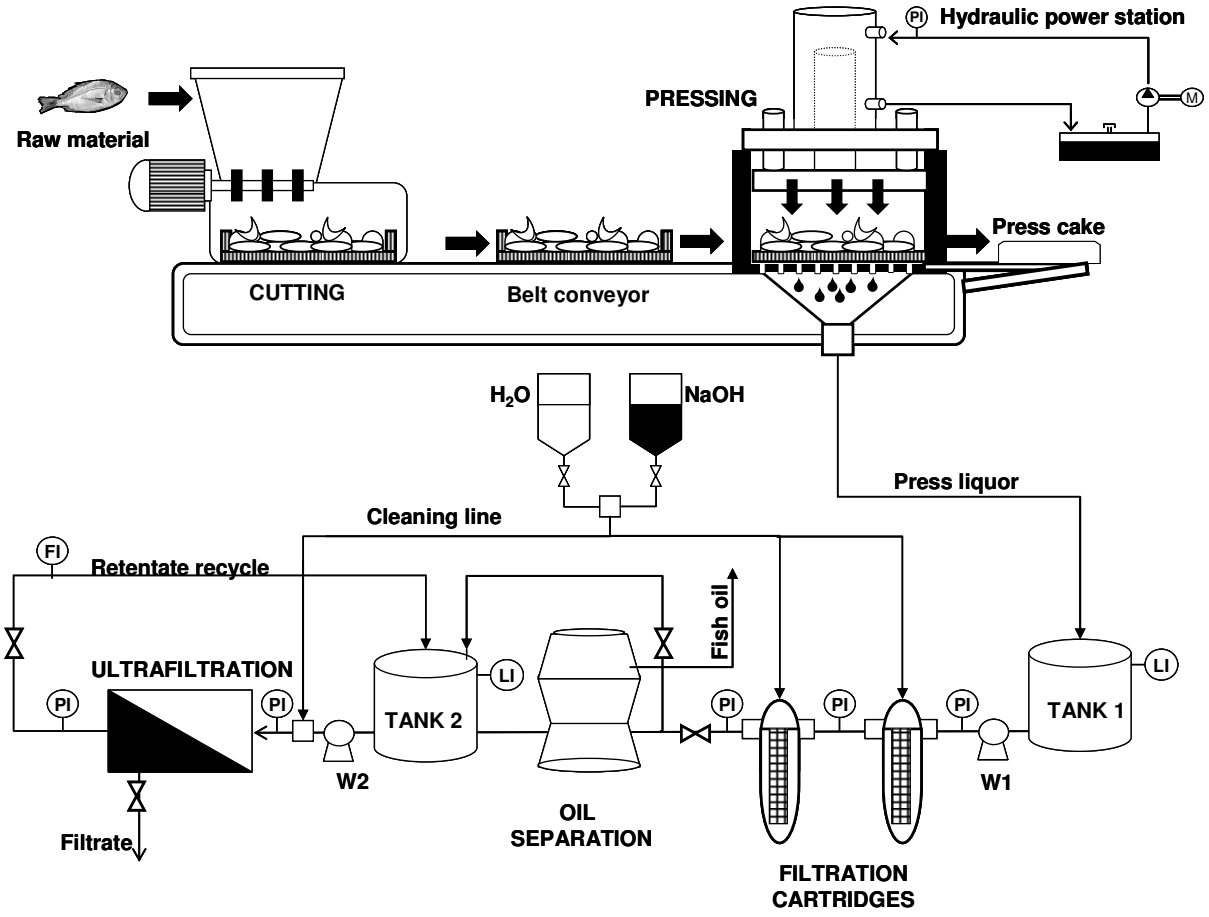

Figure 3.1. Flowsheet of the fish waste compaction process, including the effluents treatment line.

3.1.2 Technical limitations during the construction

The hydraulic press employed for the laboratory tests was a single piece made of casting iron. Its cylindrical shape and the lack of welding joints favoured an uniform distribution of the pressure all over the lateral surface. In our case, we wanted a final press cake to fit inside the normal dimensions of a cold store tray (45 cm L x 22 cm W), so the press sheet had a rectangular shape, instead of cylindrical.

The prototype press consisted basically in a cylindrical piston directly attached to a steel sheet, and supported on a steel structure. When steel structures are constructed by welding, deformations and welding residual stresses can occur as a result of the high heat input and

subsequent cooling. The welding process can create significant locked-in stresses and deformations in the fabricated structure, which can reduce the strength of the structure under a variable loading (Farkas and Jármai, 1997). In our case, when the steel sheet descends and exerts a direct pressure on the raw material, an opposite vertical load is developed which concentrates on welding joints and other "weak points", such as screws, drill holes, etc. If this load is very high and continuous on time, the fatigue will increase the probability of failure in the structure (Maddox, 1991).

These arguments were discussed with the company in charge of the prototype construction, which suggested that the maximal pressure exerted on the raw material should not over-ride 150 bars. To this end, an hydraulic circuit of medium pressure was chosen. These circuits work at a maximum medium pressure from 80 to 210 bars, which are commonly used in small fishing vessel (e.g. for hauling the nets) as they utilise pipes and components of small size, their construction and maintenance is relatively simple, and their cost is lower than other hydraulic systems working at lower or higher pressures (Czekaj, 1989). The press was attached to a hydraulic system able to develop a maximum pressure of 150 bars. This is the maximum pressure at which the oil will be pumped from its deposit to the press cylinder. The hydraulic circuit is governed by the Pascal principle, which states that this pressure will be equal to that acting on the piston. When the piston descends, it transmits a vertical force on the sheet which in turn transmits it to the raw material . Solids transmit forces, but not pressures. The pressure exerted on the raw material (P_{sheet})will be given by the equation 3.1.:

$$P_{sheet} = \frac{F_{piston}}{A_{sheet}} = \frac{P_{oil} \cdot A_{piston}}{A_{sheet}} \qquad (3.1)$$

where A_{piston} and A_{sheet} refer to the area of the piston and sheet, respectively, and P_{oil} is the working pressure of the hydraulic circuit. Considering the ratio between the piston and sheet surfaces, and a maximum working pressure for the oil circuit of 150 bar, the maximum pressure exerted on the raw material will be around 100 bar.

3.2 MATERIALS AND METHODS

3.2.1 Raw material

Sardine by-products were provided by the fish canning company Saupiquet, located in Quimper (France). They were transported to the IFREMER centre in Nantes and pressed the same day to minimise the fermentation and spoilage of the raw material.

3.2.2 Prototype description

All the units involved in the fish compaction process (cutting, pressing and depuration treatment) were assembled in a compact unit fabricated in steel AISI314. The prototype has a dimensions of 2.85 m (L) x 0.85 m (W) x 1.45 (H) m. Together with the hydraulic power station, it takes up a surface of 3.33 m^2 . The following figures show, respectively, an AutoCAD plan showing the frontral view of the prototype (figure 3.2.), and a photograph (figure 3.3), provided by the manufacturing company HERMANOS RODRIGUEZ S.L.

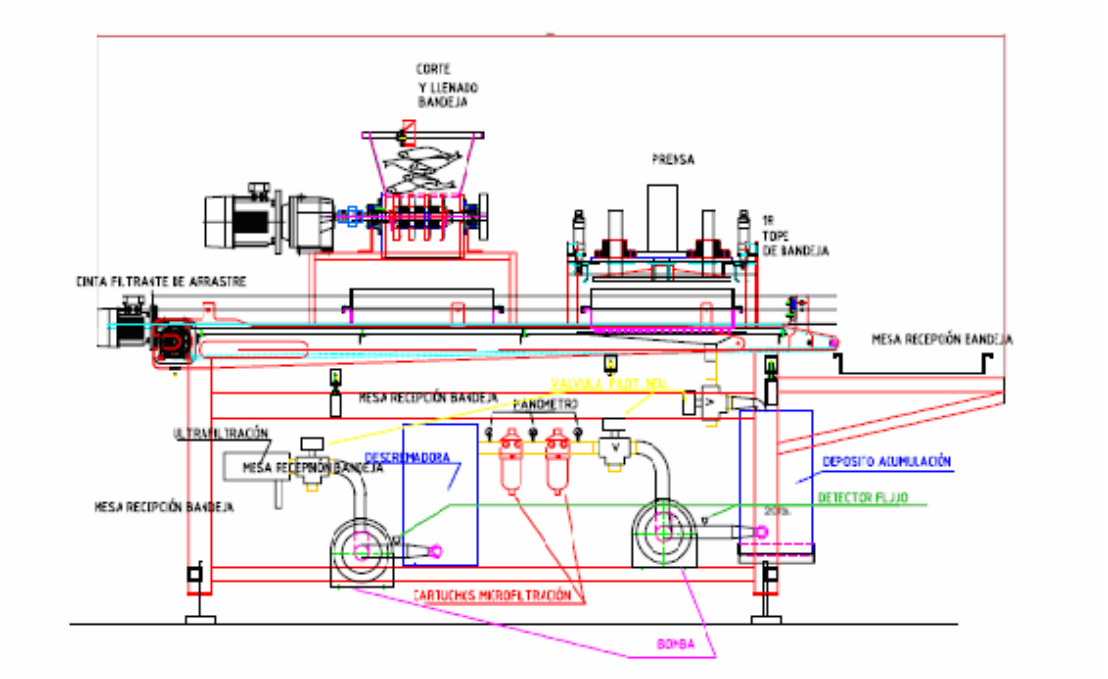

Figure 3.2. AutoCAD plan of the prototype.

Figure 3.3. Frontal view of the prototype and the hydraulic power station.

The main characteristics of each element comprised in the prototype will be outlined next:

3.2.2.1 Cutting machine

As a pre-treatment prior to the pressing, the raw material is introduced into a cutting machine. It is entirely fabricated in AISI314 steel. It consist in a reception hopper, where the raw material is fed, which provided with two metallic sheets disposed obliquely as a safety measure to prevent the direct contact with the cutters, as depicted in figure 3.4. The raw material is grinded by means of a rotary cutter, consisting in four circular blades aligned along their rotary axis, and attached to an engine driven by the hydraulic circuit. The following pictures show a plan of the cutting machine, with details of the hopper and the blade disposition (figure. 3.4) provided by HERMANOS RODRIGUEZ S.L., as well as a photograph (figure 3.5).

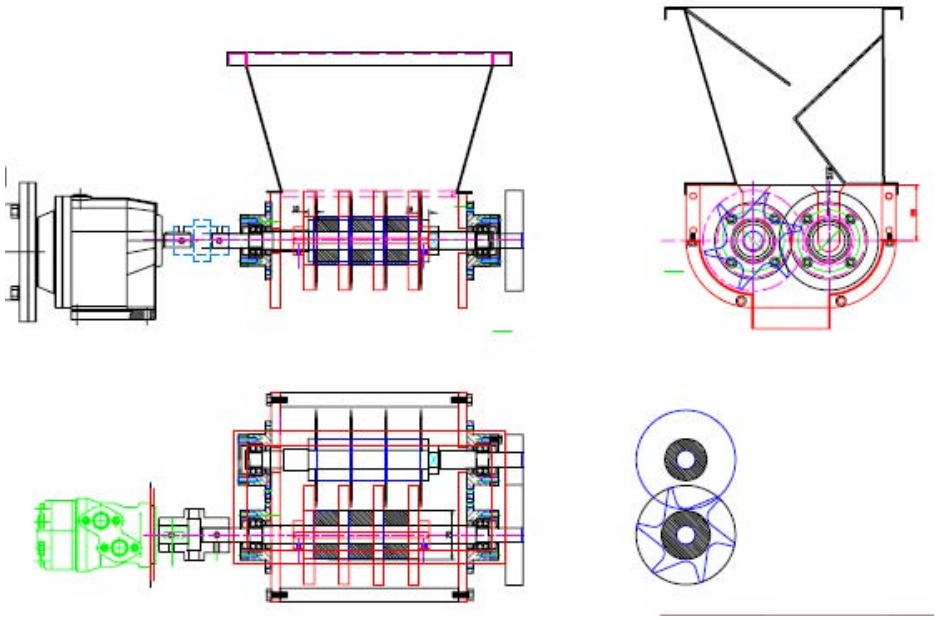

Figure 3.4. Plan of cutting machine, with detail of the hopper and cutters.

Figure 3.5. Frontal view of the prototype and the hydraulic power station.

The main inconvenient found in the cutting machine was its cleaning. Although it can be connected to the water mains to be flushed, it was not enough to remove the flesh fibbers that remained locked in the spacing between the bladders or tangled around the

rotary axis. To this end, the bottom half can be pulled out like a slicing drawer, exposing the bladders which can be easily cleaned or replaced.

3.2.2.2 Belt conveyor

The grinded sardine is received inside a parallelepiped-shaped steel mould with a removable perforated bottom. The mould can be filled with up to 11 kg of the grinded material, and then it is conveyed towards the press by means of a belt conveyor. It consists in a modular turn belt conveyor fabricated in PVC with dimensions 0.75 m (W) x 4 m (L) and 40 mm of turn radius. The belt is driven thanks to the hydraulic circuit, it can be set in motion from the control panel and its speed can be controlled by automated electric valves. The belt is set in motion from the control panel, conveying the mould into the press. Some motion detectors were placed under the press so that the mould could stop just below it. The distance between both detectors and the dimensions of the mould (length by width) are such so the press sheet, can fit exactly inside the mould and exerts direct pressure on the grinded by-products. The following picture (figure 3.6) shows the plastic belt conveyor from one of its ends, as well as the steel mould just below the press.

Figure 3.6. View of the belt conveyor (1), steel mould (2) and motion detectors (3).

3.2.2.3 Hydraulic press

As mentioned before, the motion detectors placed under the press stop the belt when the mould is under the press sheet. An hydraulic press depends on Pascal's principle: the pressure throughout a closed system is constant. At one end of the system is a piston with a small cross-sectional area. Small-diameter tubing leads to the other end of the system. In our case, an hydraulic oil will be pumped from the hydraulic power station to the press reservoir. This reservoir consists in a cylinder of 19 cm diameter filled with the hydraulic oil, in contact with a piston of . The pressure exerted by the hydraulic oil pushes the piston outwards. This piston is directly attached to a steel sheet of dimensions 22 cm (W) x 45 cm (L), which descends inside the mould pressing the raw material. Added to the motion detectors, which stop the belt conveyor once the mould is under the press, just in front of the press sheet, the press is provided of an anchorage system which prevents the mould from moving during the pressing. All these parts are depicted in the figure 3.7.

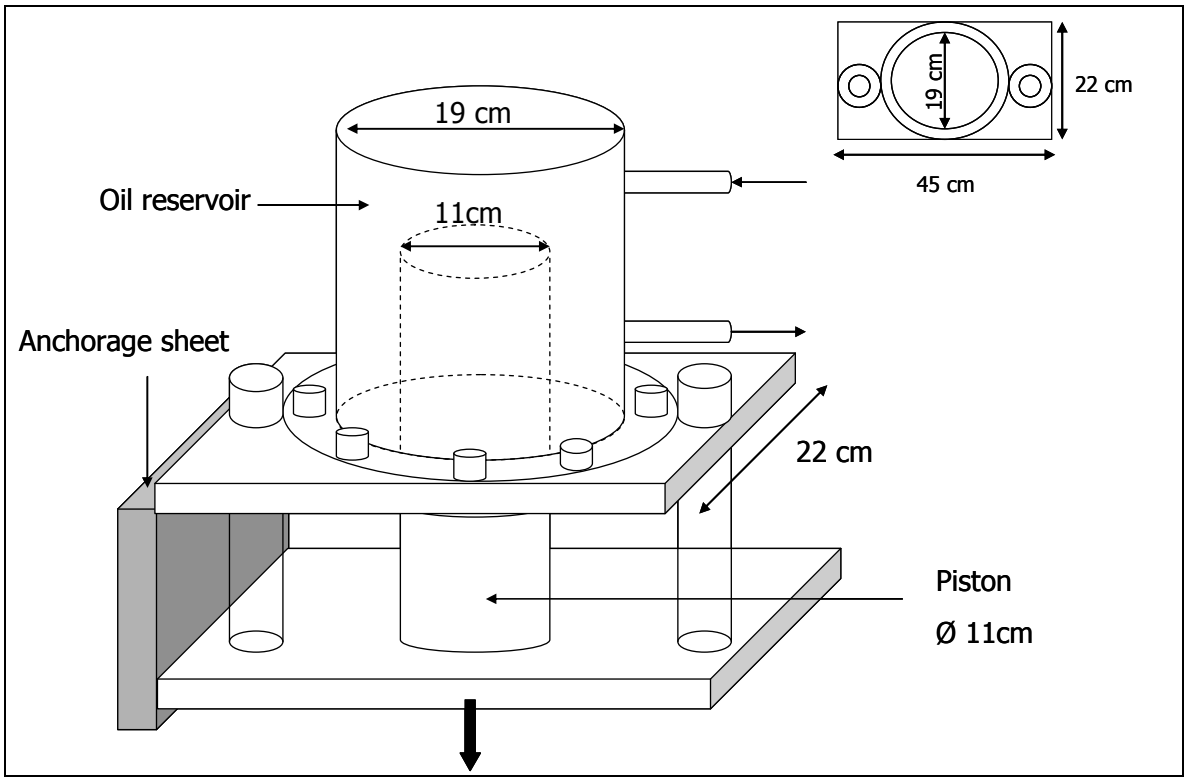

Figure 3.7. Diagram showing the main elements and measures of the hydraulic press.

The ascendant – descendant movement of the piston will be controlled by means of the hydraulic oil, which flows into and out of the cylindrical oil reservoir. All the operational

parameters of the press are controlled by means of electric valves and monitored on the control panel. The pressure of the hydraulic oil flowing into this cylinder is measured by an analogical manometer, and it can also be monitored on the control panel. The picture below shows a lateral view of the press, the cylinder containing the piston, with the inlet and outlet connexions with the oil circuit. It can be seen that both anchorage sheets are connected to the hydraulic circuit.

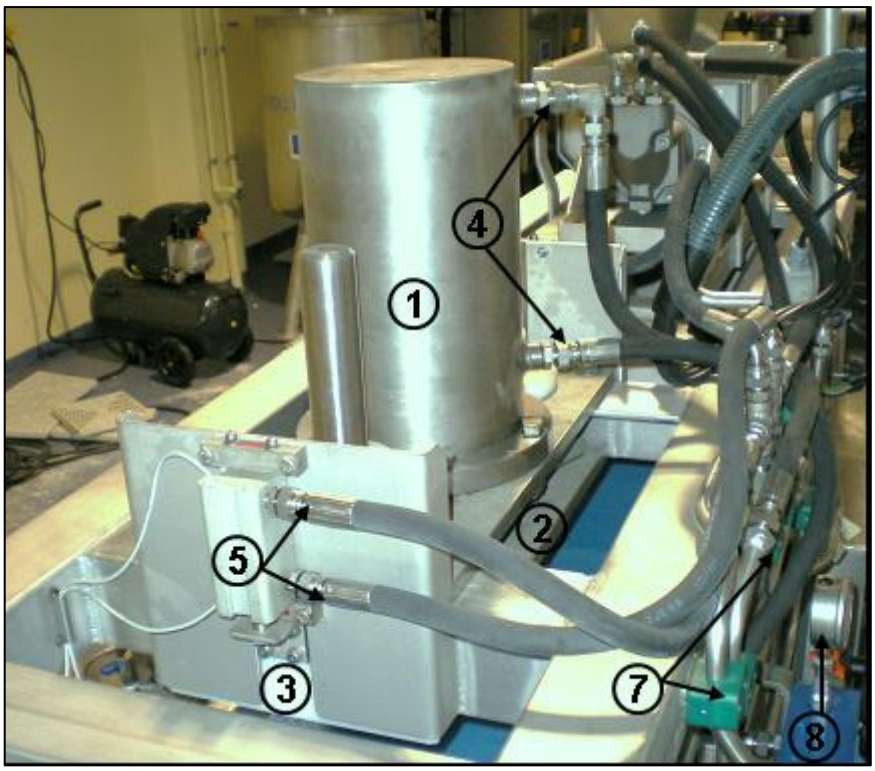

Figure 3.8. Lateral view of the hydraulic press. Oil reservoir and piston (1), sheet (2), anchorage sheet (3), hydraulic connections for the piston (4) and the anchorage system (5), electro valves (7) and oil press manometer (8).

3.2.2.4 Effluent treatment line: storage tanks, filtration cartridges and pumps.

The raw press liquor released from the press is directly collected in a storage tank fabricated in steel AISI316. This tank is parallelepiped-shaped with dimensions 20 cm (W) x 25 cm (L) x 40 cm (H) and a storage capacity of 20 L. It is covered with a 3 mm diameter perforated tap, which acts as a first pre-filtering element retaining solid particles of large size. The tank is provided with a level indicator (model LK3123, IFM Electronic, Germany) and a 1 ½ inch

liquid flow detector (model SI5000, IFM Electronic, Germany) placed at its underflow outlet. When the level of liquid contained in the tank attains a maximum set level, a seawater magnetic drive pump (model HCM-75LX, UNO, Taiwan) starts pushing the liquid through two consecutive filtration cartridges (Dynamesh Series, PALL, France) of decreasing particle removal ratings (465 µm and 250 µm, respectively). The pressure at the inlet and outlet of each cartridge is measured by in-line presostates (model PN2026, IFM Electronic, Germany) with a range of measurement from 0 to 25 bar. The filtration cartridges remove fine solids from the bulk press liquid, which is finally received in a second storage tank. This tank is a cylinder of 20 cm diameter and 40 cm height, fabricated in steel AISI314. It has two overflow inlets, one of them receiving the pre-filtered liquid from the filtration cartridges and the other attached to the retentate recycle from the ultrafiltration unit. Like the first storage tank, it is provided of a level indicator and once the level reaches a maximum set value the controller activates a second centrifugal pump (model AM-GAM10, SOLDALUX, Spain) which was chosen to provide enough driving force to the liquid so that it overcome the pressure drop along the membrane module and return as a retentate stream to the tank.

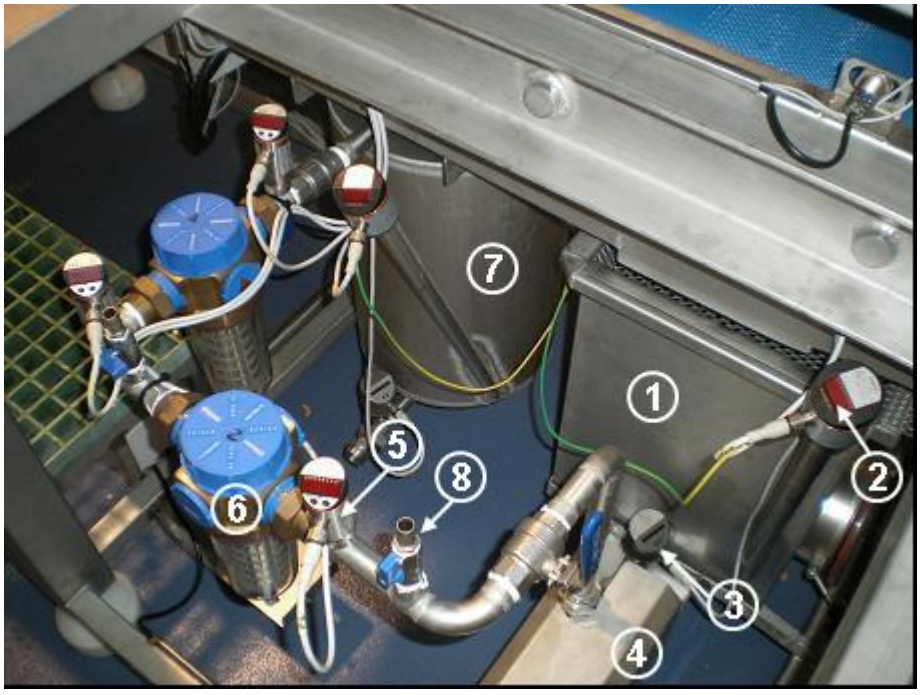

Figure 3.9. View of the effluent treatment line. Raw liquid storage tank (1), level indicator (2), liquid flow detector (3), centrifugal pump (4), pressure captor (5), filtration cartridge (6), pre-filtered liquid storage tank (7) and cleaning water supply (8).

3.2.2.5 Control panel

All the operations involved in the overall process were controlled and monitored by means of a control panel. It consists in an electronic operator interface (Panel View Plus 600, Allen-Bradley, USA) which enables the user to control, monitor and display information about the different operations by means of a touch screen. Panel View Plus^{TM} is programmed with RSView Studio Machine Edition (Rockwell Automation, USA), which features several graphic tools to design graphic objects for each operation involved in the process The main sub-menus are listed in the Table 3.2.:

Table 3.2. Sub-menus layout and tools displayed in the control panel.

Submenu	Options	Actions
Parameters	No flow detection time	Time to stop the pump once no signal from the flow detector is received.
	Belt - blades pressure	Pressure of the oil circuit terminals acting the belt and blades.
	Tank 1-2 level	Minimum/maximum level to stop/start the emptying pump of the tank 1 and tank 2.
Press parameters	Number of steps	Number of pressing steps, ranging from 1 to 5 steps.
	Compression speed	Compression speed ranging from 1 to 3 cm/min
	Oil pressure	Pumping pressure of the hydraulic oil ranging from 0 to 150 bar.
	Overall time	Overall time involving compressing and relaxation time.
	Time for descending	Time for the piston to descent during a compressing stage.
	Time for moving up	Time required for the piston to move up to its initial position.
Manual	Hydraulic power	It starts pumping the oil from the hydraulic power system.
	Belt conveyor	It sets the belt conveyor in motion.
	Cutting machine	It starts the blade rotation in the cutting machine.
	Anchorage system	It descends the anchorage sheets or moves them up back to their initial position.
	Piston	It descends the piston or moves it up back to its initial position.
	Pump 1 - 2	It starts or stops the emptying pump of the storage tank 1-2.
Automatic	The same options included in the manual submenu	All the actions covered by the manual submenu can be undertake automatically, by accepting/refusing the command messages displayed on the screen.
Alarms	Active alarms	The active alarms are displayed on the screen. The user can reset them from the screen.

It must be stressed that the program offers to the user two different modes, manual or automatic. In the first one, all the parameters and different actions involved in each operation are activated/deactivated by the user from the touching screen. This mode is useful for testing purposes, as a single action can be tested independently from the whole process (e.g. different times of descent for the piston). In the automatic mode, a diagram of the process is displayed on the screen, showing the different units involved in the process as well as the current operation being undertaken. The user must confirm each action by accepting or refusing the command messages displayed on the screen (e.g. descend piston, move up piston, descend anchorage sheet, etc.

3.2.3 Experimental procedure

8 kilograms of raw material were weighted and compacted following a face centred central composite design, as described in the following section. For each experiment, the degree of compaction of the press cake was evaluated, expressed as the ratio between the initial and final cake thickness. Concerning the press liquor, it was characterised in terms of mass and biochemical composition, including its chemical oxygen demand. These data permit to design an adequate effluent treatment

3.2.4 Experiment design

A face-centered central composite design was generated to study the influence of the number of pressing (X_1 or N) stages and the time of relaxation (X_2 or t) upon three output variables:

1. The yield of press liquor, reported as the ratio between the mass of liquid collected after the pressing operation and the initial mass of raw material (sardine by-products) fed into the press.

2. The proportion, related to the initial mass of raw material, of suspended matter removed from the press liquor after centrifugation at 10000g and 4ºC during 15 minutes.

3. The COD of the press liquor, determined by the Standard Open Reflux Method (5220 B). This value is a direct index of the pollutant effect that the discharge of an effluent causes on the environment.

The experimental design comprised 11 experiments, containing $2^2 = 4$ factorial points, 4 axial or star points and three replicates of the centre (figure 3.10).

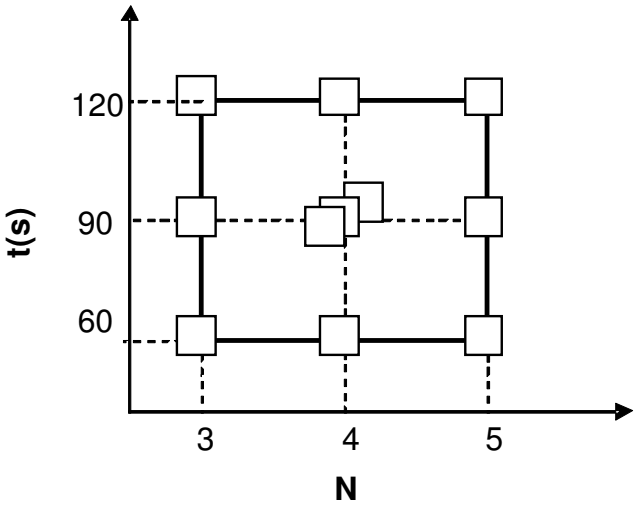

Figure 3.10. Graphical representation of the 2^2 Face Centered Design

Each experimental factor was set at three levels, corresponding to the coded values -1 (lowest range value), 0 (centre) and +1 (highest value), as shown in table 3.3.

Table 3.3. Levels of the experimental factors for the 2^2 Face Centered Design

Level	Number of stages	Time of relaxation (s)
-1	3	60
0	4	90
+1	5	120

3.2.5 Analytic Methods

The analytical procedures employed in this chapter meet with the official methods recognised by the international organizations, such as the Association of the Official Analytical Chemists

(AOAC) and American Oil Chemists Society (AOCS). This section overviews the analytical protocols employed to characterise the raw material (fresh sardine and press liquor). With regard to the statistical treatment of the results, some guidelines have been followed:

Every test have been applied in triplicate, in order to check the repeatability of the procedure and obtain a representative mean value.

The analytical measurements will be reported in the form:

$$\bar{X} \pm \sigma \tag{3.2}$$

where $\bar{X}$ is the arithmetic mean and σ is the standard deviation of the three measurements.

The standard deviation σ is the most commonly used measure of the spread of experimental measurements, which stands for the error committed during its determination or measuring. Every analytical procedure involves several steps with associated errors which accumulate to determine an overall error in the final result. When a variable Z is obtained by addition or subtraction of two measurements, X and Y, Z=X+Y or Z=X-Y, with known errors ΔX and ΔY, its overall error ΔZ is given by the equation:

$$\Delta Z = \sqrt{(\Delta X)^2 + (\Delta Y)^2} \tag{3.3}$$

In the case that Z is obtained by multiplication or division of X and Y, the overall error will be calculated by:

$$\frac{\Delta Z}{Z} = \sqrt{\left(\frac{\Delta X}{X}\right)^2 + \left(\frac{\Delta Y}{Y}\right)^2} \tag{3.4}$$

Every measurement will be reported as a numerical value with such significant figures as the number of digits which are known to be correct plus a final one which is known to be uncertain. The result (Z) of a multiplication or division should report as many significant figures as the number from which it was obtained (X or Y) containing the lowest number of significant figures. In the case of subtraction or addition, Z will have as many significant figures as the number X or Y containing the last significant figure in its highest decimal column.

3.2.5.1 Determination of the moisture content

(a) Principle. The moisture content of a material is defined through the following equation:

$$\%Moisture = \frac{m_w}{m_0} \cdot 100 \quad (3.5)$$

Where m_w is the mass of the water contained by known mass of sample m_0. Evaporation methods rely on measuring the mass of water in a known mass of sample. The moisture content is determined by measuring the mass of a food before and after the water is removed by evaporation:

$$\%Moisture = \frac{m_0 - m_{dried}}{m_0} \times 100 \quad (3.6)$$

Where m_{dried} refers to the mass of the sample after drying. The basic principle of this technique is that water has a lower boiling point than the other major components within foods, e.g., lipids, proteins, carbohydrates and minerals. The main disadvantage of these methods is that the removal of water at high temperatures may be accompanied by changes in the solid matrix, e.g. due to volatilization or chemical changes of some components. In order to minimise these practical constraints, and assure the reproducibility of the assays, these methods are standardized in terms of temperature and time of evaporation.

(b) Procedure. The samples were conveniently homogenised by means of a Blender (Waring Commercial, USA). Three portions of 4 ± 1 g were taken and weighted (let be m_0 the initial mass). Then they were placed inside a furnace at 103 ± 2 ºC. After 6 hours, the dried samples can be removed from the furnace and cooled down at room temperature in contact with a desiccative agent (e.g. silica gel). The residues remaining after drying are weighted and the moisture content is calculated by Eq. (3.6).

3.2.5.2 Determination of the ash content

(a) Principle. Ash is the inorganic residue remaining after the water and organic matter have been removed by heating in the presence of oxidizing agents, which provides a measure of the total amount of minerals within a food. Analytical methods for providing a measure of the

mineral content in seafood materials are commonly based on the fact that minerals are not destroyed by heating at high temperatures, and that they have a low volatility compared to other food components, which avoids its evaporation. According to this definition, ash content should be defined by this equation:

$$\%Ash = \frac{m_{dried}}{m_0} \times 100 \quad (3.7)$$

Where m_0 is the wet weight of the raw material and m_{dried} refers to the weight of the mineral matter remaining after the heating treatment.

(b) Procedure. The material was blended (Waring Commercial, USA) until obtaining the desired homogeneity. Three replicates of each sample, with mass 4 ± 1 g, were weighted and heated during at least 5 hours in a furnace at 550ºC. The dried residues were removed from the furnace and cooled down to room temperature inside a desiccator containing silica gel, and then weighted (m_{dried}) to obtain the ash content by Eq. (3.7).

3.2.5.3 Determination of overall protein concentration

(a) Principle. The Kjeldahl method was developed in 1883 by Johann Kjeldahl, a Danish chemist. A food is digested with a strong acid so that it releases nitrogen which can be determined by a suitable titration technique. The amount of protein present is then calculated from the nitrogen concentration of the food by employing a conversion factor. A conversion factor of 6.25 (equivalent to 0.16 g nitrogen per gram of protein) is commonly used in food applications, however, this is only an average value since each protein has a different conversion factor depending on its amino-acid composition. This method is divided into three steps

(b) Procedure. The analytical procedure can be divided into three steps:

Acid digestion. The samples to be analysed, previously homogenised and weighted (around 4 ± 1 g for each sample), are transferred to a digestion flask, and then digested by heating progressively up to 450ºC in the presence of 20 mL of Sulphuric Acid (H_2SO_4 96%) and a mixture K_2SO_4/$CuSO_4$ (5/2, w/w) to speed up the reaction by raising the boiling point. Digestion converts any nitrogen in the food (other than that which is in the form of nitrates or

nitrites) into ammonia, and other organic matter to CO_2 and H_2O. Ammonia gas is not liberated in an acid solution because the ammonia is in the form of the ammonium ion (NH_4^+) which binds to the sulphate ion (SO_4^{2-}) and thus remains in solution:

$$organic\ N\ +\ H_2SO_4 \rightarrow (NH_4)_2SO_4 + H_2O + CO_2 \tag{3.8}$$

Neutralisation. Digestion is stopped when the solution acquires a pale green or blue colour, normally after at least 2 h. This residue is suspended on 20 mL of distillate water. This new solution is made alkaline by addition of NaOH 10 M until a final volume of 80 mL . Soda turns the ammonium ion into ammonia gas (NH_3).

$$(NH_4)_2SO_4 + 2NaOH \rightarrow 2NH_3 + Na_2SO_4 + 2H_2O \tag{3.9}$$

Ammonia is recovered in a distillation unit (Model K-314, Büchi Labortechnick AG, Switzerland) by bubbling it into a solution of Boric Acid (H_3BO_3, 2% w/w) which captures ammonia by forming an ammonium-borate complex:

$$NH_3 + H_3BO_3 \rightarrow NH_4^+ + H_2BO_3^- + H_3BO_3(excess) \tag{3.10}$$

Titration. The nitrogen content is then estimated by titration of the ammonium borate formed with hydrochloric acid of known normality, using a suitable indicator to determine the end-point of the reaction.

$$NH_4^+ + 2H_2BO_3^- + HCl \rightarrow (NH_4)Cl + 2H_3BO_3 \tag{3.11}$$

The Nitrogen content is directly related to the volume of acid consumed by the equation:

$$\%N = \frac{1.4 \cdot n \cdot V}{M} \tag{3.12}$$

where N is the Nitrogen content (%), n the normality of the hydrochloric acid (eq/L), V the volume of base consumed (mL) and M the mass of the sample to be analysed (g).

The overall percentage of proteins in the sample (P) will be related to the Nitrogen content by employing the conversion factor above mentioned:

$$\%P = N \cdot 6.25 \tag{3.13}$$

3.2.5.4 Determination of lipids

(a) Principle. NMR spectroscopy is routinely used to determine the total lipid concentration of foods. The lipid content is determined by measuring the area under a peak in an NMR chemical shift spectra that corresponds to the lipid fraction. Lipid contents can often be determined in a few seconds without the need of any previous sample preparation, using commercially available instruments.

(b) Procedure. Weight around 0.5 g of raw material for each sample and transfer it to a cube. This cube is introduced in another longer one and then heated at 40ºC during 1 h in a water bath. This one can directly introduced in the spectrophotometer in order to determine its lipid content. Previously, a standard curve should be made, where the NRM response is plotted against known quantities of fish oil. The lipid content of our portion test is determined by direct interpolation of the NRM response on the standard curve.

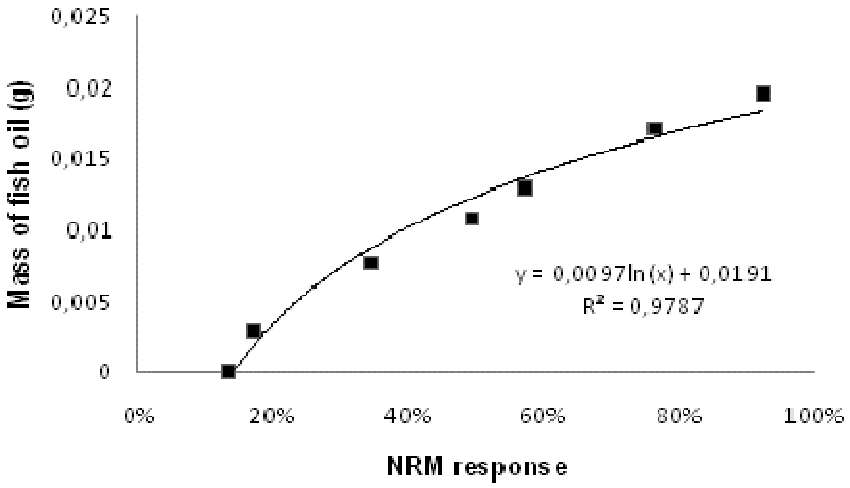

Figure 3.11. Calibration curve for the NMR method.

3.2.5.5 Chemical Oxygen Demand

Principle. COD is defined as the amount of a specified oxidant which reacts with the sample under controlled conditions. The quantity of oxidant consumed is expressed in terms of its oxygen equivalence (mg O_2 / L sample). The standard method, known as the Open Reflux

Method (5220 B, American Public Health Association, 1998), employs dichromate as oxidant, since Cr (VI) oxidises almost all the organic compounds in 50% sulphuric acid medium. The organic matter present is oxidized and, as a result, the dichromate ion (orange colour) is consumed and replaced by the chromic ion (green colour):

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \qquad (3.14)$$

The COD is calculated by titrating the excess of dichromate with a solution of ferrous ammonium sulphate ($(NH_3)_2Fe(SO_4)2{\cdot}6H_2O$), until the colour changes from brilliant green to reddish brown, in the presence of ferroin as indicator solution. The titration reaction corresponds to the oxidation of the ferrous ammonium sulphate by the dichromate:

$$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O \qquad (3.15)$$

In wastewaters from fish processes, the presence of chlorides (Cl^-) resulting from the contact with the seawater or any salting operation, interferes the COD determination since these salts are also oxidised by the dichromate. The addition of mercuric sulphate ($HgSO_4$) prevents this interference as it reacts to form mercuric chloride ($HgCl_2$), which precipitates.

Procedure. Transfer 10 mL of the sample to the reaction flask. Add 5.00±0.01 mL of the standard reference solution of potassium dichromate ($K_2Cr_2O_7$) for a fixed period (usually two hours), as well as 15 mL of a solution of silver sulphate (Ag_2SO_4) in diluted sulphuric Acid (H_2SO_4). The presence of silver sulphate as catalyst is needed to assure the complete the oxidation of the aliphatic carbon compounds. The reaction mixture is brought to boiling and the oxidation takes places during 2 hours. After the two-hour digestion period, the sample is cooled down to 60ºC and the excess of dichromate is titrated with the solution of ferrous ammonium sulphate using 1 or 2 drops of ferroin as indicator solution. The chemical oxygen demand, reported as milligrams of oxygen per litre, is given by the expression:

$$COD = \frac{8000 \cdot C \cdot (V_1 - V_2)}{V_0} \qquad (3.16)$$

Where C is the concentration (moles/L) of the solution of ferrous ammonium sulphate, V_1 and V_2 are the volumes (mL) of this reagent used for the titration against the blank and the test sample, and V_0 is the volume (mL) of wastewater to be analysed.

3.3 RESULTS AND DISCUSSION

3.3.1 Degree of compaction

For each experiment, 8 kg of sardine by-products were fed into a parallelepiped-shaped mould of dimensions 22 cm x 45 cm x 12cm. The height reached by the raw material inside the mould was measured before being conveyed to the hydraulic press. Its average value was found to be 10 ± 0.5 cm. Once all the pressing stages were accomplished, the thickness of the press cake remaining inside the mould was measured and compared to the initial height, thus obtaining the volume reduction as the ratio between both measures.

$$VR = \frac{h_c}{h_0} \cdot 100 \qquad (3.17)$$

where VR (%) is the volume reduction , h_0 (cm) is the initial height of the raw material inside the mould and h_c (cm) is the final cake thickness.

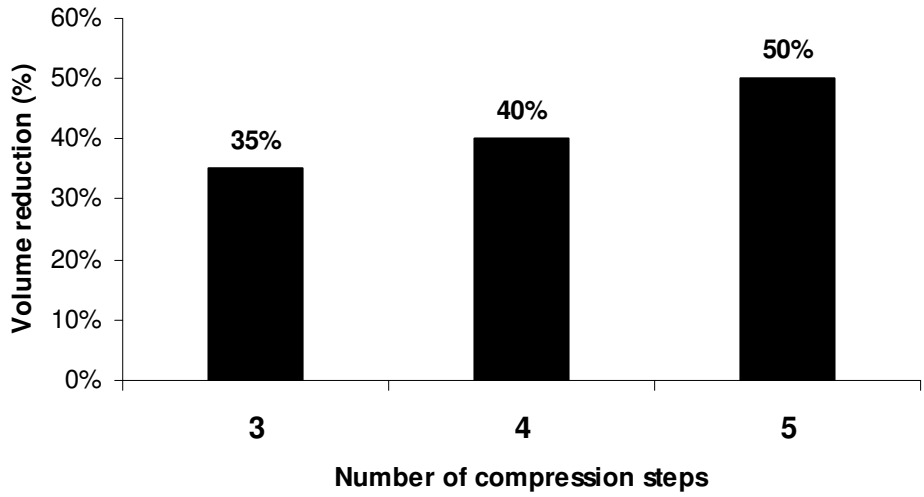

Figure 3.12. Volume reduction of the press cake in function of the number of pressing steps.

Figure 3. shows that the degree of compaction was higher as more steps were involved in the pressing operation, reaching a volume reduction of 50 % for 5 stages.

3.3.2 Regression model and analysis of variance

A 2^k Face Centred Design was employed to study the influence of two experimental factors (k=2) upon three output variables, the yield of press liquor (Y, w/w), the content of suspended matter in the press liquor (SS, w/w) and the chemical oxygen demand of this liquid (COD, mg O_2/L). Starting from the input factors considered previously in the laboratory test, Three replicates were taken from the centre point, which added to the 4 factorial points plus four centre points sums an overall number of 11 experiments.

Table 3.4. Face Centred Design employed for the pressing tests at pilot scale.

Exp. #	Number of stages N(-)	Time of relaxation t(s)	Liquor yield Y (w/w)	Suspended solids SS (w/w)	COD (g O_2/L)
1	3	60	0.1659	0.0168	131
2	3	90	0.1751	0.0237	121
3	3	120	0.1911	0.0254	121
4	4	60	0.1869	0.0279	137
5	4	90	0.1970	0.0245	130
6	4	90	0.2003	0.0307	125
7	4	90	0.1972	0.0264	121
8	4	120	0.2301	0.031	121
9	5	60	0.1829	0.0247	140
10	5	90	0.1870	0.0167	118
11	5	120	0.1951	0.0183	115

COD analysis were carried out by an external laboratory (IDAC, Nantes, France), employing the standard determination method (5220 B) described above. No data concerning the experimental errors were provided (in terms of standard deviation for the three replicates from which the mean value was obtained). The influence of the experimental factors on the three output variables was analysed by employing response surface methodology techniques, likely to the initial compaction test in lab scale. The responses were fitted to a complete quadratic model. The correlation between the measured values and the regression models assayed was found to be acceptable, with correlation coefficients R^2 ranging from 0.8742 (suspended matter) to 0.9108 (COD), as showed in the figure 3.13.

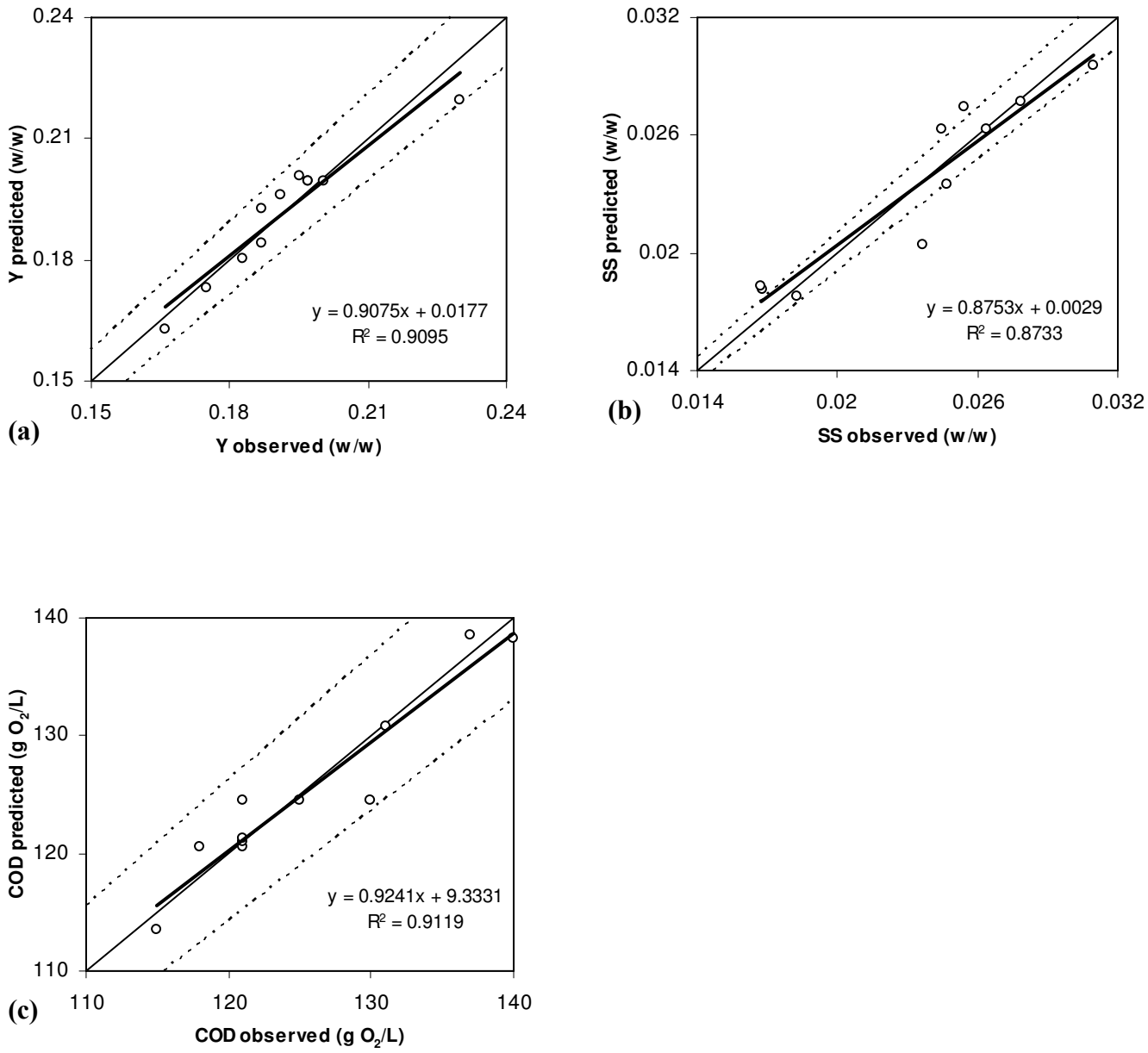

Figure 3.13. Predicted vs. observed values for press liquor (a), suspended matter (b) and chemical oxygen demand (c).

The yield of press liquor and the chemical oxygen demand reported high correlation coefficients, with no points having a deviation higher than ±5% (delimited by the dotted lines) between observed and predicted values. The fit of the measured suspended solids to the regression model (R^2=0.8742) is similar to that obtained for the laboratory tests (R^2 = 0.8529), but in this case there was no need to standardise the values of SS to assure an acceptable

correlation. This may be owed to the tighter spread of the measured solids, which in this case varies from near 0.02 to 0.03 w/w, instead of the wide range of variation observed for the laboratory tests (from 0.005 to 0.023 w/w).

The three response functions were related to the input variables by a second degree polynomial as follows:

$$Y = b_0 + b_1 \cdot N + b_2 \cdot t + b_{11} \cdot N^2 + b_{12} \cdot N \cdot t + b_{22} \cdot t^2 \quad (3.18)$$

$$SS = b_0 + b_1 \cdot N + b_2 \cdot t + b_{11} \cdot N^2 + b_{12} \cdot N \cdot t + b_{22} \cdot t^2 \quad (3.19)$$

$$COD = b_0 + b_1 \cdot N + b_2 \cdot t + b_{11} \cdot N^2 + b_{12} \cdot N \cdot t + b_{22} \cdot t^2 \quad (3.20)$$

The table 3.5 shows the value of the coefficients for the quadratic models assayed, as well as their statistical significance, which is evaluated by the associated probability or p-value. An interval of confidence of 5% was set for the ANOVA analysis, which means that those effects with a p-value higher than 0.05 can be considered as non significant on the output variables.

Table 3.5.Regression coefficients and p-values for the response variables

Term	Y (w/w)		SS (w/w)		COD (g O_2/L)	
	Coefficient	**p-value**	**Coefficient**	**p-value**	**Coefficient**	**p-value**
b_0	-0.1806	-	-0.1067	-	89.0050	-
b_1	0.1836	0.1603	0.0655	0.3786	43.8214	1.0000
b_2	-0.0004	0.0135	$6.09 \cdot 10^{-5}$	0.4455	-0.8690	0.0051
b_{11}	-0.0210	0.0146	-0.0069	0.0146	-4.0714	0.1906
b_{12}	$-1.08 \cdot 10^{-4}$	0.4517	$-1.25 \cdot 10^{-4}$	0.0428	-0.1250	0.1156
b_{22}	$7.12 \cdot 10^{-6}$	0.2780	$2.60 \cdot 10^{-6}$	0.2345	0.0060	0.0827

3.3.3 Yield of press liquor

The yield of press liquor varies from 16.59% (w/w) to 23.01% (w/w) (Table 3.4 while the laboratory tests only achieved a maximal yield of 13.4% (w/w). This improvement is related to the different nature of the raw material fed into the press. Sardine by-products were used in these new assays, instead of whole sardines. These by-products are mainly composed by

heads and tails, with a high content of water (in heads), and a low proportion of flesh attached to the fish frame. Hence. this raw material will have a lower water-retention capacity and will be able to release more water during the compaction. This improvement in the liquor yield will be partially offset by a smaller filtering surface area, since the liquor flux only follows the normal direction, only draining through the opposite side to the compressive effort and not through the lateral surface, as in the lab test with the basket press.

It is remarkable that the maximal pressure applied to the by-products was 150 bar, while it was raised up to 350 bar in the laboratory tests. This new pressure gives an acceptable yield and it is more achievable by an hydraulic central, involving lower investment and operative costs.

With the help of the p-values obtained by the ANOVA analysis, the Pareto chart shows that the more significant effects influencing the yield of press liquor are the linear effect of the time of relaxation (t, with p=0.0135) and the quadratic effect of the number of pressing stage (N^2 , p=0.0146). The interaction between the two factors is negligible, i.e. both experimental factors may be considered as independent, since the p-value attached to the cross-product is higher than 0.05 (p=0.4517).

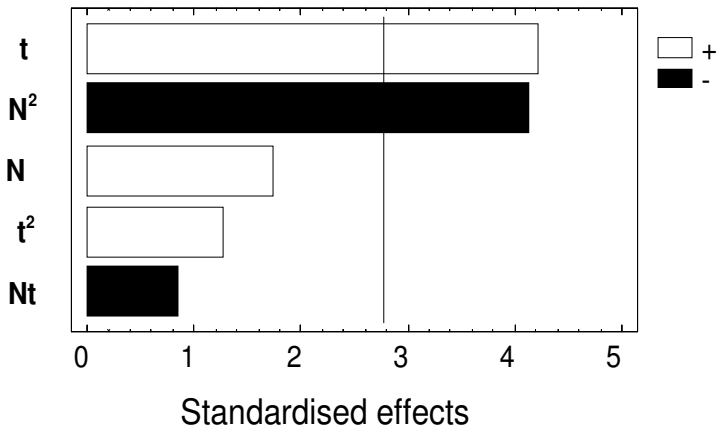

Figure 3.14. Pareto Chart for the yield of press liquor (Y, w/w)

The predicted curves for the liquor yield (figure 3.15.) show that the yield of press liquor increases with the time of relaxation between the pressing stages for each level of N. This is logical as longer times of drainage will increase the amount of liquid collected, i.e. more water molecules will have enough time to cross the cake and reach the draining surface.

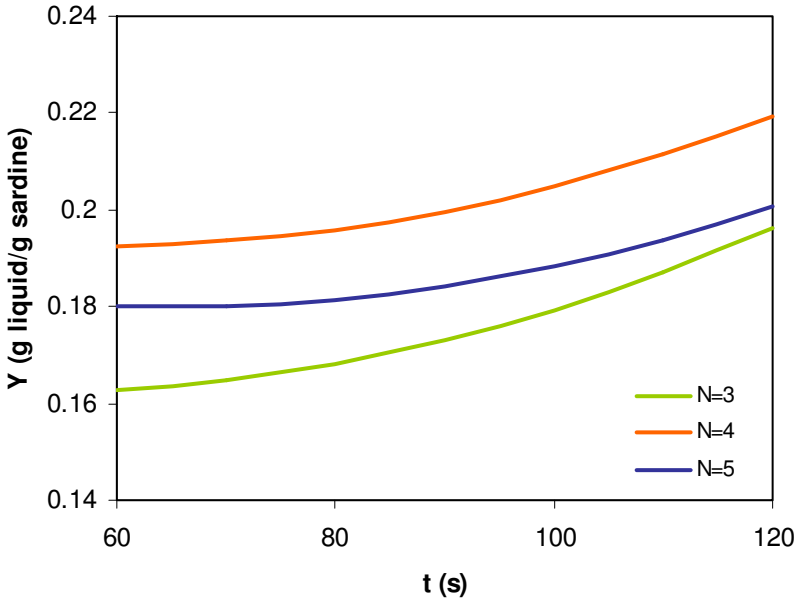

Figure 3.15. Predicted curves for the yield of press liquor (Y, w/w)

Concerning the number of compression stages N, two comments can be made:

1. The higher yields are obtained at N=4. From the laboratory tests it was concluded that the application of a fifth compression stage did not improve the yield and in this case it clearly decreases the amount of liquid collected.

2. The interaction effect between N and t, although negligible, becomes more remarkable for N=5 and high times of relaxation. This interaction is negative, so the yield increases with the time of relaxation at a lower rate than that observed for N=3 and N=4.

Unlike the laboratory tests, the release of liquid from the press chamber only takes place in one direction, following the direction of the compressive force. The flux of liquid must overcome the cake resistance before leaving the press chamber, and this resistance increases with the degree of compaction of the cake. Even if the compressive work developed by a five-stage pressing is higher, with a higher release of the fluids contained in the raw material, this also increases the cake resistance preventing the liquid from reaching the bottom end and leaving the press. This can be explained mathematically by considering the Darcy's law :

$$q_z = \frac{k}{\rho} \cdot \frac{\partial u}{\partial z} \qquad (3.21)$$

where two terms are competing: on the one hand, a reduction in the cake thickness (z) causes that the pore-fluid pressure gradient ($\partial u / \partial z$)developed between the upper surface in contact with the piston and the draining surface would be more pronounced , thus increasing the flux in the z-axis. On the other hand, this increase is offset by a decrease in the cake permeability (k), due to the cake compaction.

The maximisation of the objective function Y=f(N, t) leads to the solution N=4, t=120 s and Y=0.2195 (w/w). This yield is higher than that obtained for the sardine discards in the laboratory tests. Comparing to other dewatering operations reported in the literature (report of the French Stockbreeding Office, 2007), this yield is close to that obtained by mechanical compaction of ovine guts by means of a screw press (figure 3.16).

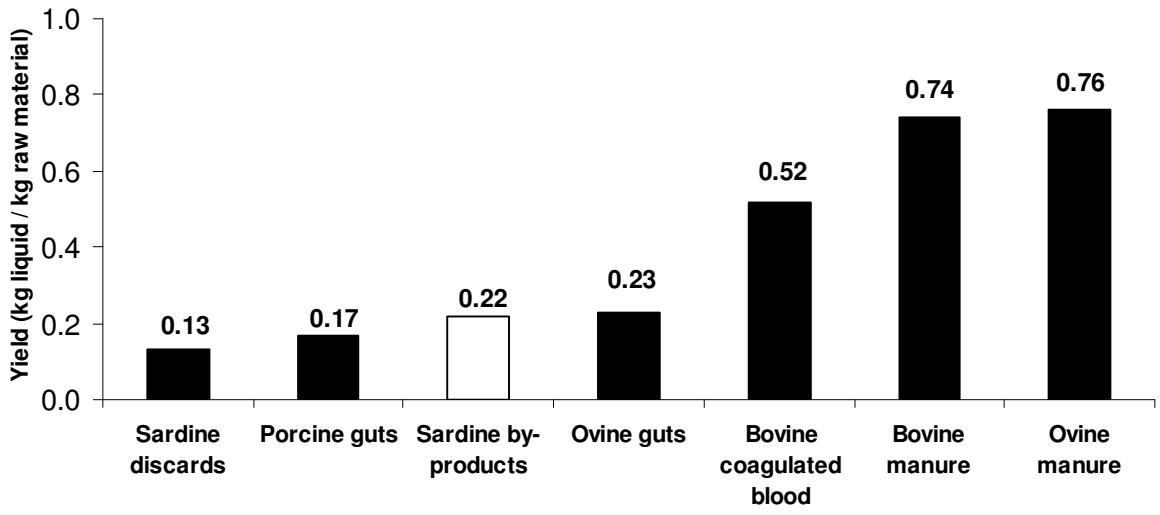

Figure 3.16. Yield of press liquor from sardine by-products compared to that obtained from other wastes.

3.3.4 Suspended matter

As mentioned before, the content of suspended solids ranges from 0.02 to 0.03 g solids/g raw material. The spread of these measures is tighter than that observed for the laboratory tests. This may be due to these reasons:

In the prototype tests the pressure applied from the hydraulic central and the piston at which the piston descends were kept constant. These experimental factors are very significant on the content of suspended matter in the press liquor, as concluded from the laboratory tests.

Shorter times of relaxation were assayed for the pilot plant tests. A longer time results in a higher volume of fluid released by the raw material, and thus a higher amount of suspended solids carried out by this liquid.

The Pareto graph for the content of suspended matter (figure 3.17) shows two significant effects: the quadratic effect of the number of pressing stages (p=0.0146) and its interaction with the time of relaxation (p=0.0428).

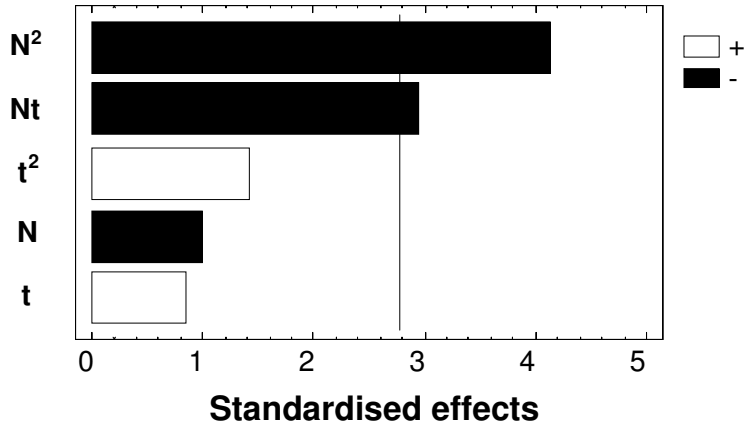

Figure 3.17. Pareto Chart for the suspended matter (SS, w/w)

Both terms are negative, and this is evidenced by the curves obtained from the quadratic models, depicted on the figure 3.18. On the one hand, for N=3 and N=4, the content of suspended matter follows an increasing trend with the time of relaxation. In the case of N=4, the curve hardly decreases until reaching a minimum at t =90 s and then undergoes a slightly ascent. On the other hand, this trend is clearly decreasing for N=5, with a minimal content of suspended solids at t=120s.

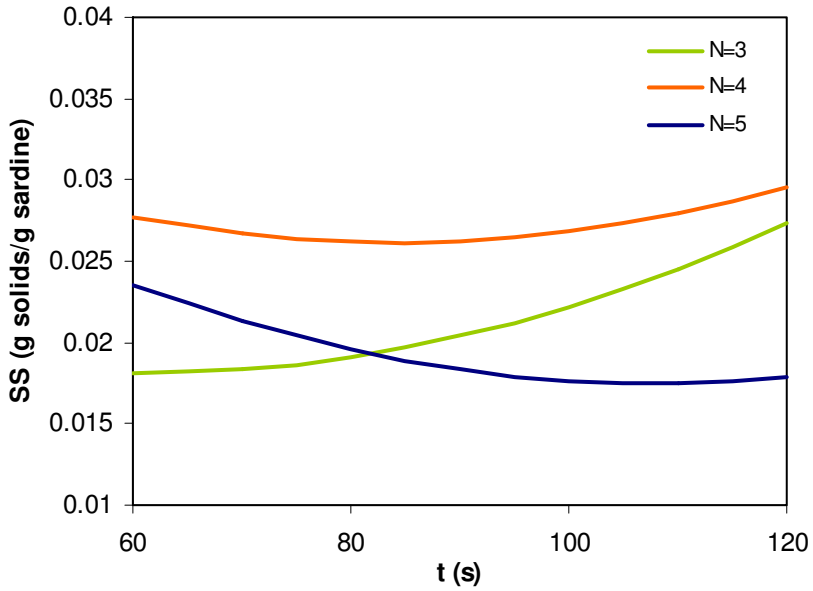

Figure 3.18. Predicted curves for content of suspended matter (SS, w/w)

This behaviour of the curves can be explained by the different degree of disruption of the raw material during the pressing process. In a three-step pressing, where the volume reduction per step is higher, the degree of damage in the raw material is important, resulting in a charged press liquor. As the number of steps is increased, the compressive work performed on each step will be lower, and the drained liquid will carry less solid particles, resulting in a lower content of suspended matter in the press liquor. At this respect, the high values of SS for N=4 can be seen as inconsistent with this explanation. It should be noticed that SS is related to the mass of sardines fed into the press by the equation 3.22:

$$SS = \frac{m_{solids}}{m_{sardine}} = \left(\frac{m_{solids}}{m_{liquid}}\right) \cdot \left(\frac{m_{liquid}}{m_{sardine}}\right) \qquad (3.22)$$

where the first term of the product (m_{solids}/m_{liquid}) stands for the content of solids in the press liquor, and the second term is the yield of press liquor. As mentioned above, the yield of press liquor is maximal at four compression stages, and it causes the product SS to be higher than expected.

The three-step treatment provokes a high damage in the raw material, releasing solid particles which are continuously carried by the liquid out of the press cake. In the course of time, as

more liquid is collected from the press, the overall amount of suspended matter will be higher. This trend is less marked for N=4, as the volume reduction per stage is lower, resulting in less release of particles, while for N=5 the response SS decreases with the time of relaxation. In the case of five compression stages, the high degree of compaction achieved by the press cake reduced its permeability retaining both water and solid particles inside its structure, which resulted in a less charged press liquor.

Considering the equation 3.22, the fraction of solids in the press liquor (m_{solids}/m_{liquid}) should decrease as more time of drainage is left after a compression step. Added to this, it was observed that enlarging the time of relaxation did not significantly improve the mass of press liquor collected from the press (which is directly related to the term $m_{liquid}/m_{sardine}$ in the equation 3.22). The release of liquid out of the cake took place to a great extent during the first seconds, and then rapidly decreased carrying less suspended matter. Both evidences explain the decline of SS with time when N=5 (figure 3.20).

The statistical model was optimised to minimise SS. This minimum was obtained at N = 5 and a maximum time of relaxation, giving a value for SS= 0.017 g of solids / g of sardine received in the press. This result is clearly higher than that obtained in the laboratory tests (0.002 w/w). In that case, the pressure exerted on the raw material was lower (66 bar), as well the average yields of press liquor, due to the different nature of the raw material (whole sardine instead of sardine by-products). The figure 3.19 compares this value to that obtained for other animal press waters:

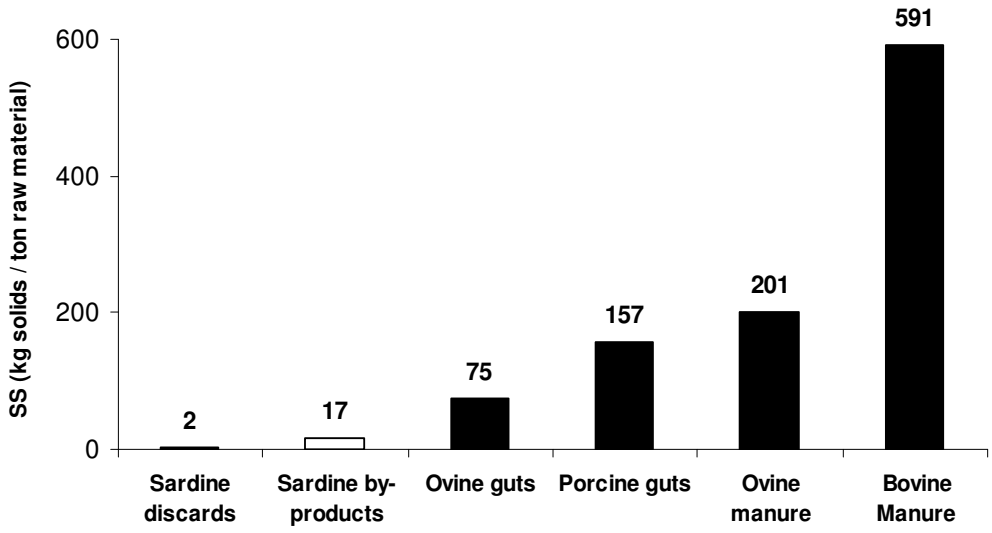

Figure 3.19. Comparison between the content of suspended matter for several press waters.

These results support our initial choice of the hydraulic press for the dewatering operation, since the press liquors resulting from screw presses have a higher organic load, which can difficult the performance of the effluent treatments prior to their discharge.

With regard to other effluents from fishing industry, L. Guerrero (1998) points out a content of suspended solids of 5 – 40 g/L for wastewaters generated by the fish meal industries. Considering that the production of wastewaters is around 5.4 m^3 per tonne of fish processed, this yields an average amount of 160-650 kg/ton of suspended solids. This value, although 10 to 40 times higher, should be interpreted cautiously, since the fish meal production involves other unit operations apart from the mechanical dewatering in a screw press, such as steam cooking, centrifugation and drying of the press cake until obtaining a fish meal with a moisture content below 10% (Ruiter, 1995). All these intermediary steps will generate wastewaters with more or less content of suspended solids.

3.3.5 COD

The Chemical Oxygen Demand (COD) is a direct indicator of the pollutant effect of an effluent. In order to plan an adequate depuration strategy, able to reduce the organic load of the effluent below its maximal discharge limits, it is important to characterise the press liquor in terms of its COD. This parameter, together with the biological oxygen demand (BOD_5) and the total suspended solids, are widely considered by the environment regulations.

The operating conditions, at which the pressing procedure was carried out, influenced both the yield of press liquor and its content of suspended solids, as mentioned above. It can be assumed that the COD will exhibit a similar behaviour, and can be consequently related to the experimental factors by a statistical model. The statistical design of experiments is widely reported effective in the characterisation, optimisation and modelling of depuration processes where the COD was the response variable. At this respect, many examples can be found in literature employing RSM techniques to optimise the performance of a variety of effluent treatment processes , such as the anaerobic digestion of palm oil mill effluents (Zinatizadeh *et al.*, 2006) , the electrochemical coagulation applied to pulp and paper wastewaters to remove organic contaminants (Soloman *et al.*,2008) or the bioconversion of activated sludge (Mannan *et al.*, 2007) among others.

The COD was analysed statistically with the help of a face centred design where 11 experiments were conducted. As shown in table 3.4., the values of COD range from 115 to 140 g O_2/L. The measured values of COD exhibited a good correlation with the predicted values obtained from the regression polynomial, with a coefficient of correlation R^2 =0.9108 .

The pareto graph (figure 3.20) shows that only the effect of time of relaxation was significant on the response COD, with a p-value lower than 0.05 (p=0.0051). The response COD is negatively affected by the time of response. No effect involving the number of compression steps (N) , neither single nor quadratic, were significant, and the interaction between N and t had a high p-value (p=0.1156).

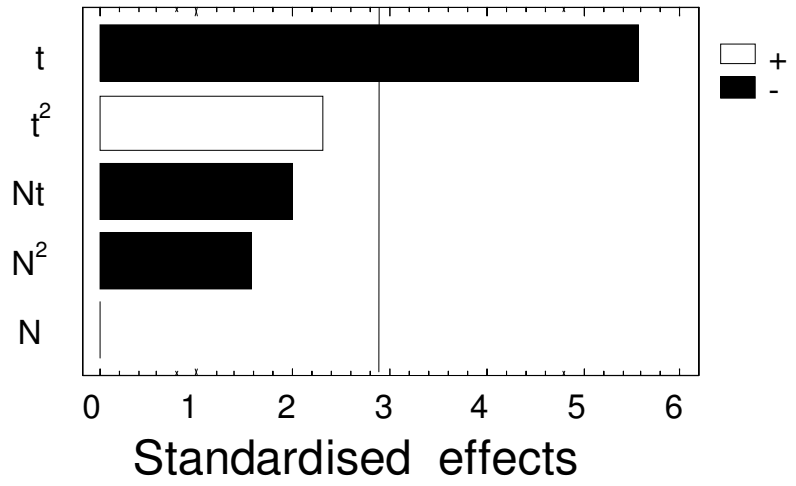

Figure 3.20. Pareto Graph for the Chemical Oxygen Demand (COD).

With the help of the statistical model, the curves of COD against the time of relaxation were plotted (figure 3.21) at different levels of N. For the three levels of N, the COD decreases with the time of relaxation. This descent is steeper for N=5, where the COD attains its minimal value at t=120 s.

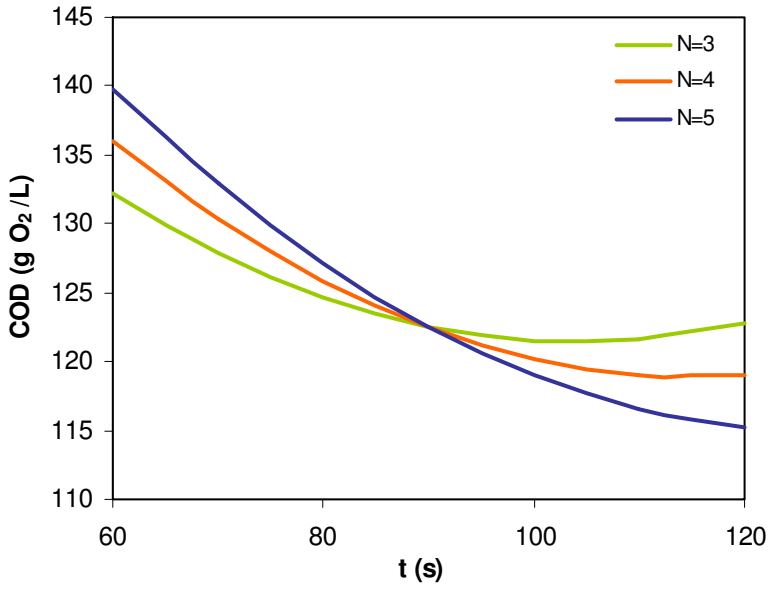

Figure 3.21. Predicted curves for the COD related to the volume of press liquor.

These results agree with the assumption made for the suspended solids, the deposition of solid particles, carried by the press liquor, reduced the filtration surface. This phenomenon was enhanced by the progressive compaction of the press cake as more compression stages were accomplished. Both phenomena resulted in a less charged press liquor, and thus a lower COD.

This parallelism between the behaviour observed for the suspended solids and the COD is clear when COD is also related to the mass of sardine pressed, that is, it is expressed as grams of O_2 per kilogram of raw material, as shown in the figure 3.22. These curves are the product of the liquor yield (Y) and the chemical oxygen demand expressed as a concentration (g O_2/L). Similarly to the behaviour observed for the suspended solids, a three-step treatment clearly provokes tissue disruption on the raw material as the amount of suspended matter in the press liquor increases with the time. In the case of four compression steps, the average values of COD are higher, since the yield of press liquor are maximal. As observed for the suspended solids, the curve initially decreases until reaching a minimal value and then undergoes a slight increase. Finally, COD clearly decreases with time for N=5, where the degree of compaction in the press cake was maximal and more particles should be trapped inside the solid matrix.

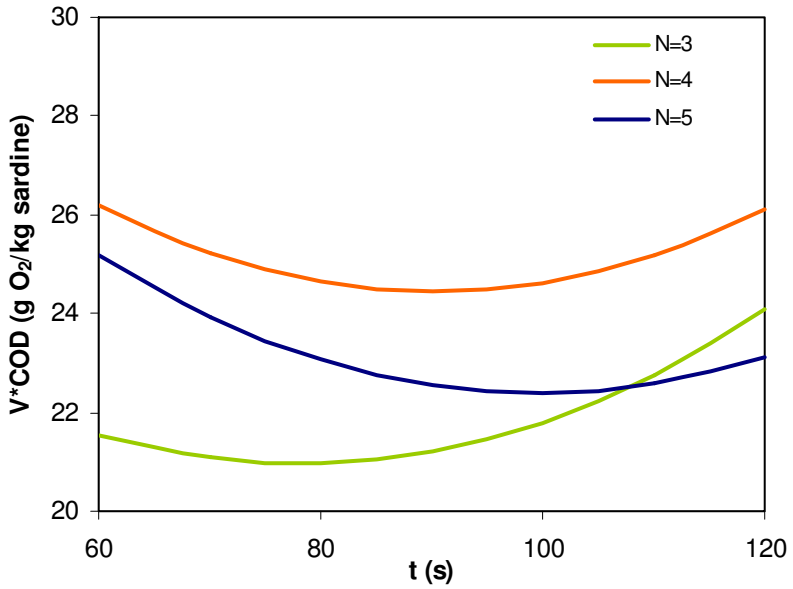

Figure 3.22. Predicted curves for the COD related to the mass of raw material.

The statistical model for COD was optimised in order to determine under which conditions (t and N) the COD was minimal. In terms of concentration, a minimal value of COD = 114 g O_2/L was reached at 5 compression steps and 120 seconds. In terms of total COD (related to the mass of raw material fed into the press), it attains a minimal value of 21 g O_2/kg of raw material at N=5 and t=80 s.

Considering an average value of COD = 120 g O_2/L, the COD for sardine press waters is similar to that obtained for fresh or coagulated blood, and lower to that measured for press waters from porcine guts (French Stockbreeding Office), as shown on figure 3.23.

Regarding the wastewaters from fishery industries, most of the references concern wastewaters generated after complex processing (surimi elaboration, cooking,canning, fish meal production, etc) which cannot be directly compared to the crude effluents from a pressing operation. The average result of COD is similar to that reported by Billiet and Fenyo (1981) for wastewaters from fish waste pressing (130 g O_2/L). According to Haart and Squires (1985), a 50% of the overall COD of wastewaters from fish meal production is attributed to the bloody water generated during the unloading. Although this fraction only represents a 8% of the total flow of wastewaters, bloody water can bear high organic loads with COD up to 170 g O_2/L. Other authors (Civit *et al.*, 1982) reported a mean value of 98 g O_2/L for the

bloodwaters generated in a fishmeal plant. Concerning the overall production of effluents by the fish meal processes, Guerrero *et al.* (1997) estimated a COD ranging from 30-120 g O_2/L, depending on the fish species and type of processing. It can be concluded that the high values of COD observed for the hydraulic pressing of sardine by-products are in accordance to an important presence of blood in the press liquor.

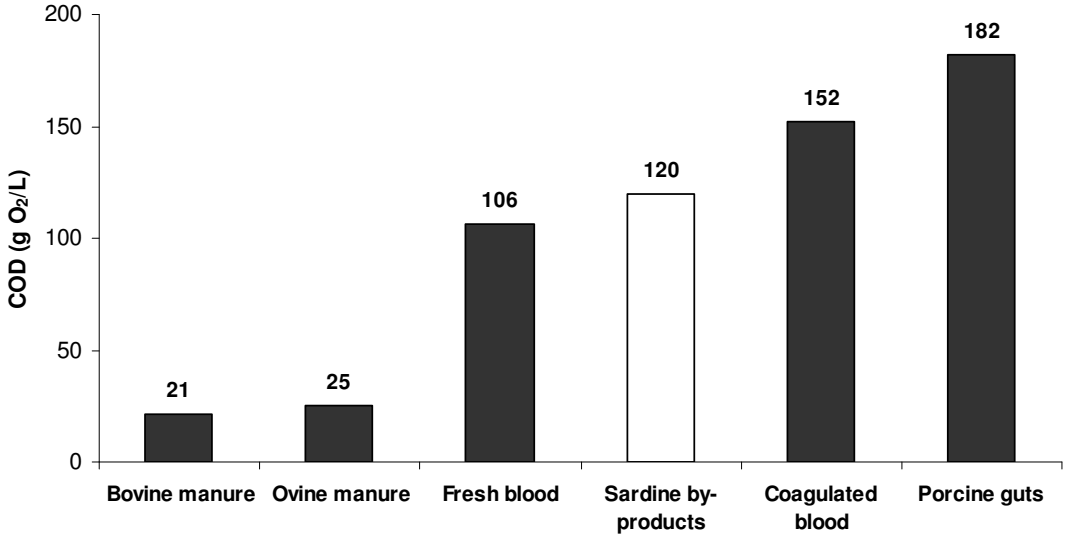

Figure 3.23. Comparison of the average COD for the sardine press juice and those reported for other effluents from animal origin.

3.3.6 Biochemical Analysis

The degree of pollution of a wastewater will depend on several parameters of which the most important are the operation being carried out and the fish species being processed. Considering only one type of operation, the operating routine in each factory also exerts strong influence on the wastewater characteristics. All these factors explain the variability found in the wastewater compositions reported in the literature, where the biochemical parameters often present a wide range (González, FAO Fisheries, 1996). Added to this, some species like sardines present seasonal variations in the raw material composition, which result in different compositions for their processing effluents, specially concerning their lipid content (Dumay, 2004).

In our case, a complete biochemical analysis was conducted for the press liquor collected after each experiment. The aim of these analysis was double:

- To find significant differences in the proximate composition of the press liquor, motivated by a change in the pressing parameters. This assumption lies on the considerations made before (dependence between processing and wastewater pollution) and it is evidenced by the good correlation between the number and duration of the pressing steps and the COD of the press liquor (R^2 =0.9018).

- To compare the average results to those reported in literature for wastewaters from fish processing. The studies concerning the composition of wastewaters from pressing operations are few and disperse. At this respect, Bechtel *et al.* (2005) studied in detail the biochemical composition of the stickwater from fish meal processing, which is generated by mechanical dewatering of the fish by means of a screw press.

The biochemical compositions of the press juices are summarized in the table 3.6. The composition was expressed in terms of concentration, that is, in grams of water, ash, protein or lipid per 100 grams of press liquor. For each experiment, the water, ash, protein and lipid content was determined, employing the analytic procedures described before. Each result was reported as the mean of three measurements plus/minus the standard deviation of the three replicates.

Table 3.6. Proximate composition of the press liquor from sardine by-products (%, w/w).

Exp. #	Water (%)	Ash (%)	Proteins (%)	Lipids (%)	Total (%)
1	90.17 ± 0.08	0.59 ± 0.07	3.94 ± 0.01	1.62 ± 0.05	96.32 ± 0.12
2	90.06 ± 0.02	0.76 ± 0.07	6.13 ± 0.12	1.15 ± 0.25	98.10 ± 0.29
3	90.12 ± 0.06	0.90 ± 0.09	6.34 ± 0.06	1.26 ± 0.04	98.62 ± 0.13
4	89.85 ± 0.07	0.76 ± 0.17	6.78 ± 0.06	1.49 ± 0.03	98.88 ± 0.20
5	90.54 ± 0.12	0.89 ± 0.02	6.18 ± 0.13	1.06 ± 0.11	98.67 ± 0.21
6	90.03 ± 0.07	0.96 ± 0.01	6.68 ± 0.05	1.39 ± 0.02	99.05 ± 0.09
7	91.71 ± 0.07	0.78 ± 0.04	6.08 ± 0.19	1.51 ± 0.02	100.08 ± 0.21
8	90.13 ± 0.01	0.87 ± 0.04	5.29 ± 0.19	0.82 ± 0.06	97.11 ± 0.20
9	90.98 ± 0.09	0.60 ± 0.07	6.17 ± 0.19	0.89 ± 0.15	98.64 ± 0.27
10	89.37 ± 0.08	0.87 ± 0.01	6.08 ± 0.19	1.16 ± 0.01	97.48 ± 0.21
11	91.62 ± 0.03	0.82 ± 0.01	5.91 ± 0.19	0. 88 ± 0.01	99.23 ± 0.19

A final mass balance was calculated on the last column, with will give a value normally lower than 100%, due to the experimental inaccuracies and other organic compounds which were not determined (mainly carbon hydrates). In the case of a mass balance adding up more than 100%, a possible reason, given by Bechtel *et al.* (2005) is the presence of small amounts of non protein nitrogen in the samples, which would be multiplied by 6.25 as a part of the protein calculation by the Kjeldahl method.

From the table 3.6, it can be concluded that the experimental conditions at which the juice was pressed did not influence significantly its ash and lipid content, which presented the averages values of 0.80 ± 0.02 % for ash and 1.20 ± 0.03 % for the lipids.

With regard to the protein content, it ranges from 3.94% to 6.78% (w/w). The protein composition of the press liquor was plotted against the time of relaxation, obtaining three curves corresponding to N=3, 4 and 5. The behaviour exhibited by the protein content in the press water was similar to that found for the suspended solids or the COD. For three compression steps, the proportion of proteins in the press liquor increases with the time of relaxation, that is, this treatment should provoke issue disruption on the raw material, enhancing the release of both solid particles and dissolved compounds carried by the press liquor. Similarly to the content of suspended solids, the content of proteins for N=4 and N=5 undergoes a slight decrease as longer times of relaxation were assayed. The damage induced on the raw material after the compression should be more limited in the case of four or five compression steps, since the compaction of the press cake is carried out employing more steps. This means that the volume reduction per step will be lower, and thus the compression work exerted on the raw material. Added to this, as suggested before, the high degree of compaction attained after four or five compression steps should prevent solid particles to drain, remaining trapped in the solid matrix.

This parallelism between the protein content and the suspended matter is logical, if it is assumed that most of total amount of nitrogen determined by the Kjeldahl method corresponds to the insoluble proteins which make up the solid particles.

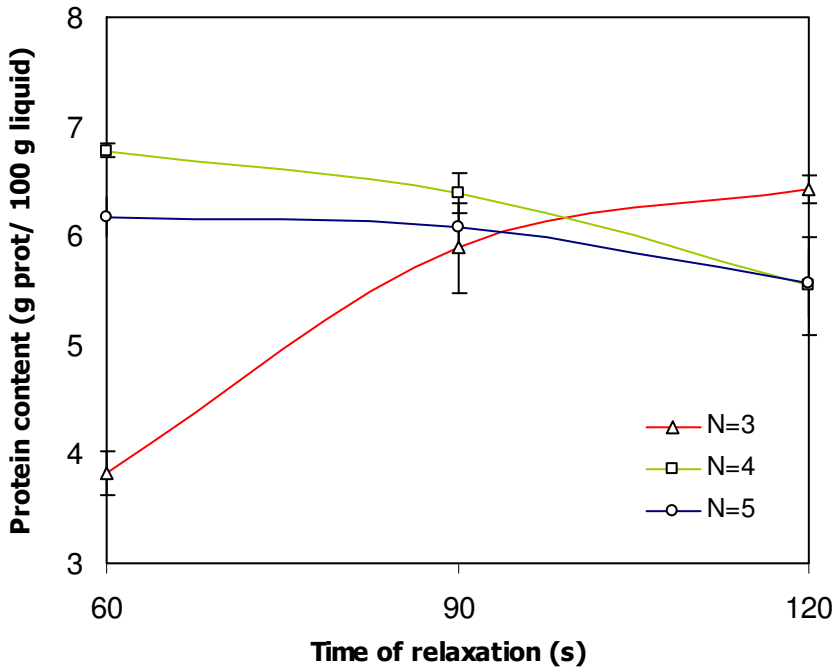

Figure 3.24. Influence of the experimental factors on the content of proteins in the press liquor.

These results were compared to the proximate compositions of 4 different wastewaters from fish processing:

1. The press liquor obtained from the sardine discards. To this end, three samples of press liquor, collected from the experiments performed at the laboratory scale with whole sardines (see Chapter 2) where analysed to obtain an average composition.

2. Bloodwater. Three samples of bloodwater were collected from the bottom of the storage container where the Sardine by-products were transported.

3. Literature references. As mentioned before, there is a lack of studies on the biochemical composition of fishery wastewaters, since they are commonly characterised in terms of DBO_5, total suspended solids (TSS) and DCO. Bechtel *et al.* (2005) studied the analytic composition of stickwater from two fish meal factories, one processing a mixture of Pollock and Cod by-products, and other working with Salmon by-products.

Since the samples of stickwater were freeze-dried prior to their analysis, with no data about the water content are available, the composition of all the wastewaters will be expressed in a dry weight basis:

Table 3.7. Proximate composition of some wastewaters expressed on a dry and wet weight basis.

Type of effluent and origin	% Ash wet basis (dry basis)	%Proteins wet basis (dry basis)	% Lipids wet basis (dry basis)
Press juice Sardine by-products	0.80 ± 0.05 (10.06 ± 0.63)	5.95 ± 0.14 (74.84 ± 1.82)	1.20 ± 0.07 (15.09 ± 0.88)
Bloodwater Sardine by-products	0.84 ± 0.13 (11.82 ± 1.83)	3.74 ± 0.20 (84.39 ± 4.60)	0.27 ± 0.10 (3.80 ± 1.41)
Press juice whole Sardine	1.55 ± 0.06 (11.27 ± 0.85)	7.89 ± 0.62 (57.38 ± 5.86)	4.19 ± 1.80 (31.35 ± 3.62)
Stickwater Pollock/Cod by-products	< 1 (13.56 ± 0.16)	□ 6 (83.92 ± 0.09)	< 0.5 (2.52 ± 0.14)
Stickwater Salmon by-products	< 1 (11.23 ± 1.02)	□ 6 (86.86 ± 0.92)	< 0.5 (1.91 ± 0.05)

From the results above presented, it can be concluded that:

- The ash content is similar for the five wastewaters. This value normally depends on the salinity of the raw material. In this case, no significant differences were observed.

- The lipids content is maximal for the press juice from whole sardine. The amount of lipids found in the press juice from sardine by-products is residual, since the raw material consisted in heads, viscera and tails whose content in oil is low (Dumay, 2004). From this results it can be concluded that an oil recovering operation of these effluents would be neither necessary nor viable. Concerning the stickwaters, the amount of oil present in the freeze-dried samples is residual, since stickwaters are obtained from the raw press liquor after centrifugation to remove the fish oil (Bimbo, 2003). The samples of bloodwater also contained a small amount of lipids. These wastewaters are defined as the liquid phase, consisting mainly of fish blood, associated with the storage of whole fish and offal (EPS Canada, 1975). They are

mostly composed of water (92.69 ± 0.04 % on a wet basis), polluted by the fish blood. The residual content of lipids found in the press juice from sardine by-products suggested that an oil recovery operation would not be in order to depurate these effluents.

- Stickwaters are reported to contain approximately 6% of protein on a wet basis (Bechtel *et al*.,2005). This value is similar to that observed in the press juice from Sardine by-products (5.95 % on a wet basis). Press juice was the wastewater having the highest protein content (7.89 % on a wet basis) although the composition of its dry matter is varied, with a ratio lipid/protein higher than ½. With regard to the bloodwaters, the proteins are the major component of their dry matter, although their total amount is low (3.74 % on a wet basis).

3.4 CONCLUSIONS

The principle of the waste compaction by means of an hydraulic press, whose procedure was analysed and optimised at lab scale, was successfully validated with a pilot plant. The operation parameters governing the performance of the hydraulic press where identified and optimised to give a maximal yield while keeping the content of suspended matter under a maximum limit. These results were considered and respected during the construction of the prototype. To this respect, some technical limitations concerning the construction materials and the real scale suggested reducing the maximum pressure achievable from 370 bar to 150 bar.

The performance of the new prototype was validated by a new experimental design. Each experiment required 8 kg of raw material, so the number of experimental runs was limited by setting the pressure at its maximum value (150 bar) and the compression speed at its optimum value (50% of the speed range). A face centred design was chosen for this purpose, involving 11 experimental runs. The yield of press liquor and its content in suspended solids and its COD were chosen as output variables and they were fitted to second order polynomials with high correlation coefficients (0.9064, 0.8742 and 0.9121, respectively). The response graphs show that a maximum liquor yield (0.2195 g liquid / g sardine) of press liquor was achieved at 4 compression steps and a time of relaxation of 120 s. Both the content of suspended solids and the COD presented their minimum values (0.017 g liquid/g sardine and 114 g O_2/L, respectively) at 5 compression steps and a maximum time of relaxation.

Beside this, from the biochemical analysis of the press juices it was concluded that the protein content in the press juice was influenced by the experimental factors in a similar fashion that the suspended particles, which suggested that most of these proteins made part of the solid suspended particles and only a small amount corresponded to soluble proteins. The small amounts of lipids detected in the press juice ruled out the necessity for an oil recovering unit in the depuration treatment of these effluents.

It can be concluded that a compression treatment comprising five stages at maximum pressure and maximum relaxation time enables to obtain a high liquor yield, while limiting the amount of suspended solids in the press liquor and thus the COD of the effluent.

From an economical point of view, it is interesting to obtain a good volume reduction (ranging from 35% to 40%), involving less compression stages (3 or 4). This involves lower energy consumption, as well as a lower amount of waste waters. On board a fishing vessel, it is desired to limit the amount of waste waters to treat. Nevertheless, one cannot assure that the costs associated to the membrane filtration will be lower, since the effluents generated after a 3-stage or 4-stage compaction bear higher concentrations of suspended matter. An economic balance is necessary to find a compromise between energy savings during the compaction (by applying less compression steps) and lower costs associated to the effluent depuration.

4 .TREATMENT OF THE EFFLUENTS RESULTING FROM THE COMPACTING OPERATION

4.1 INTRODUCTION

4.1.1 Quality standards for fishery wastewaters.

As in most wastewaters, the contaminants present in fisheries wastewaters are an undefined mixture of substances, mostly organic in nature. The composition of these effluents is varied as it is produced by different sources. These include water from vehicles, equipment and installation, cleaning and washing of raw materials, besides the liquid effluents generated after the unit operations involved in the fish or fish by-products processing, e.g. press waters, blood water, water from drying or evaporation (EU Commission, 2005, 2006).

The term effluent standard refers to the maximum concentration of a pollutant (e.g., in milligrammes/litre) or the maximum load (e.g., kilograms/day) which can be discharged into a receiving waterbody. The discharge limits for fish processing effluents are covered by several international guidelines which are progressively incorporated to the national regulations. In the case of the United States, the Environment Protection Agency (EPA) establishes the quality standards for fisheries wastewaters depending on the type of processing and the fish species being processed, as shown in Table 4.1.

Table 4.1. Summary of discharge limits for fisheries effluents proposed by the US Environmental Protection Service (2007).

Effluent	BOD_5 (kg/ton raw fish)	TSS (kg/ton raw fish)	Grease/Oil (kg/ton raw fish)	pH
Crabs	0.30 - 10	0.90	0.6 – 1.8	6 - 9
Fish meal	7.0	3.7	1.4	6 - 9
Salmon	2.7	2.6	0.31	6 - 9
Sardine	-	36	1.4	6 - 9
Shrimps	63 - 155	110 - 320	36 - 126	6 - 9
Tuna	20	8.3	2.1	6 - 9
Other finfish	1.2	3.1 – 3.6	1.0 - 43	6 - 9
Clams and oysters	-	24 - 59	0.6 – 2.4	6 - 9

In the case of the European Union, there are a wide range of regulations and standards controlling the fisheries wastewaters, both inside and outside the EU. Some works can be found in literature comparing the regulatory structures of different EU Member States concerning fisheries wastewater standards. As an example, Rosenthal *et al.* (1993) compared the legislation on aquaculture effluents of 19 European Countries.

The EU Urban Waste Water Treatment Directive 91/272/EEC (EU, 1991) came into operation in response to concerns about the collection, level of treatment and discharge of urban waste water and waste water from certain industrial sectors, included the Fish processing industry. In practice, this Directive requires all urban sewage and industrial waters to be treated prior to their discharge. The urban wastewater treatment will be more or less stringent depending on the population equivalent (p.e.) of the agglomeration, as well as the nature of the receiving waterbody. 1 p.e. (population equivalent) means the organic biodegradable load having a five-day biochemical oxygen demand (BOD_5) of 60 g of oxygen per day. Discharge from urban waste water treatment plants must satisfy the relevant requirements listed in Table 4.2.

Table 4.2. General requirements for discharge from urban waste water treatment plants

Parameter	Discharge limit
BOD_5 at 20ºC	25 mg O_2/L
COD	125 mg O_2/L
Total Suspended Solids (TSS)	< 35 mg/L (>10000 p.e.) < 60 mg/L (2000-10000 p.e.)

The EU Directive establishes special discharge requirements if the receiving water defined sensitive area. This definition refers to freshwater lakes, estuaries and coastal waters which are found to be eutrophic or which in the near future may become eutrophic if no protective action is taken. In the case of discharge into sensitive areas, the wastewater treatment should ensure a concentration of the phosphorus and nitrogen compounds under the maximum limits shown in Table 4.3.

In the case of biodegradable industrial waste waters from plants belonging to the industrial sectors concerned by this Directive (in our case, fish processing industries) which does not enter

urban waste water treatment plants before discharge to receiving waters, representing 4000 p.e. or more, they should meet the national regulations of each State Member, since no general guidelines have been given by this Directive in this respect

Table 4.3. Requirements concerning the N and P content for treated urban waste waters discharged on sensitive areas.

Parameter	Concentration
Total phosphorus	< 2 mg/L (10 000 -100 000 p.e.) < 1 mg/L (> 100 000 p.e.)
Total nitrogen	< 15 mg/L (10 000 - 100 000 p.e.) < 10 mg/L (> 100 000 p.e.)

A marine water body or area can be identified as a less sensitive area if the discharge of waste water does not adversely affect the environment as a result of morphology, hydrology or specific hydraulic conditions which exist in that area.

The quality standards for discharge are essential requirements to be fulfilled in the design of an effluent treatment process. Beside this, there are many other factors which influence the choice of waste water treatment among the different processes able to remove the pollutants and produce an innocuous effluent:

- Volume and composition of the waste water to be treated. The effluent treatment will be influenced by the raw material (fish by-products, fatty fish, white fish, shell fish, etc) and its processing (canning, fish meal production, filleting, etc).

- The local situation in terms of the receiver of the discharge, e.g. municipal waste water treatment plant (MWWTP), river, estuary, lake, sea, etc, since the discharge limits applied to the effluent may differ considerably depending on the nature of the receiving water body, and thus the treatment will be more or less stringent.

- Economics. Among the different techniques developed to remove the pollutant content of waste water, the different unit operations involved in the overall treatment should be chosen under an economics criterion. This means that they should involve acceptable

installation and operation costs, provided that it assures a final effluent meeting all the legal requirements for its discharge.

In our case, the effluent is the press liquor originating from sardine by-products, which bears a high organic load, with high COD and solids content, but oil content lower than 1% (w/w). As described in chapter 3, the effluent treatment will consist in a conventional filtration by means of two series filtration cartridges, followed by a membrane ultrafiltration, able to remove most of the protein content from the bulk liquid, leading to a final filtrate whose discharge supposes a minimal environmental impact.

4.1.2 Conventional filtration

Conventional filtration refers to the process of passing the waste water through a standard medium to remove particles. The filter medium is periodically backwashed to remove trapped particulates. The retention rate can be increased by the addition of coagulant chemicals. There are several available filtration technologies, e.g. slow filtration, fast filtration, deep-bed filtration, surface filtration (microscreening), biofiltration and coagulation filtration, which can be used as a waste water polishing step to remove solids from end-pipe wastewaters (EU Commission, 2006). Unlike sedimentation or dissolved air flotation (DAF), filtration does not require any difference in density between the particles and liquid. The flow of liquid through the filter medium is driven by gravity or a pressure difference between the two sides of the filter, allowing the passage of water through the filter but retaining the particles. Depending on the driving force, filters may be either gravity or pressure filters. The principle of a pressure filter is the same that other pressure-driven membrane separation such as microfiltration, but, by convention, the term filtration is usually limited to structures that separate particulate suspensions larger than 10 μm (Baker, 2004).

4.1.2.1 Cartridge filters

A cartridge filter can be defined as a cylindrical filter element, held in a correspondingly housing, that carries the liquid inlet and outlet pipes, and can open in some convenient way to allow the cartridge to be changed when it is full or exhausted (Sutherland, 2009). Most of the cartridge elements consist of some filter medium surrounding a central cylindrical perforate core, where the liquid flows from the outside, through the medium and out from the axis. Suspended solids in

the feed stream are thus deposited outside the element or in the interstices of the filter medium. The element acts as a particle holder which can then be cleaned in place by backflushing (reverse liquid flow) or brushing the collected solids. It can be also easily removed and cleaned mechanically or chemically.

Cartridge filters are mainly used to clarify liquids of low solids concentration. Thanks to the recent advances in manufacturing techniques, particularly in the control of pore size and the development of new media, cartridge filters are nowadays available for removing particulates with diameters down to 0.006 μm and for handling fluids with viscosities up to 100,000 cP, temperatures from near zero to 400ºC and pressures up to 200 bar (Williams and Edyvean, 1995a). This wide range of tolerance for the operational parameters has favoured their extensively employment throughout the chemical and environmental process industries in applications from laboratory-scale to commercial operations. According to the McIlvaine Co's report (Filtration Unit Analyst, 2007), the worldwide market for filter cartridges intended for water purification accounted for US$15 billion in 2007 and will increase up to US$21 billion in 2012.

With regard to the waste water treatment processes, filtration cartridges are normally used as a pre-treatment to remove most of the suspended particles and also non emulsified grease from the effluent, but they can also act as a polishing filter, with reported phosphorous removal efficiencies of 20%-50% (EU Commission, 2006). Some applications of filter cartridges in wastewater treatment processes are listed in the table 4.4 (Cheremisinoff, 2002).

Table 4.4. Typical applications and operating ranges of cartridge filters.

Feed stream	Filtration range
Residual Oil	25-50 μm
Sea water	5-10 μm
Fresh water	30-200 mesh
River water	20-400 mesh

As shown in the table above, an important parameter for classifying cartridge filters is the filtration range or filter rating, which is an indicator of the size of particulates that the filter is expected to retain.

As all sieving operation, the performance of a filter cartridge is also negatively affected by the accumulation of particulates both on the surface and within the pores of the filter medium. This phenomenon is known as fouling, and it results in loss of flux and a reduction in the filter life (Williams and Edyvean, 1995b). Two key parameters should be controlled during the filtering operation in order to detect fouling and determine the frequency of filter cleaning or replacement.

- Pressure drop through the filter medium. If the maximum pressure tolerance of the filter is exceeded, the particulate retention of that element rapidly declines, suggesting filter replacement.

- Fluid flow. Particle deposition determines a decay of the fluid flow. The filter element should be cleaned in order to restore its initial permeability.

4.1.3 Membrane technologies

Membrane separation processes are increasingly used in the fields of chemical engineering, effluent treatment processes and separation/purification of biotechnology products. In separation processes, the key property that is exploited is the ability of the membrane to allow one or more components of a mixture to permeate the membrane freely, while rejecting the others (Cheryan, 1998). Separations with membranes do not require additives, and they can be performed isothermally at low temperatures with less energy consumption compared to other thermal separation processes (Jaouen and Quéméneur, 1992). Membrane-based technologies have been easily scaled to industrial processes and they can be easily attached to other unit operations, e.g. reactors with enzyme recovery (Tu *et al*., 2009; Prieto *et al.*, 2009) or fractioning of the peptides resulting from a hydrolysis reaction (Chabeaud *et al.*, 2009; Wang *et al.*, 2009).

Industrial membrane processes may be classified into five major groups according to the size range of materials that they are to separate and the driving force used in separation, as shown in the table 4.5 (Najafpour, 2007). All these technologies have been implemented in large-scale industrial processes, while the dialysis is commonly employed in medical applications. The three

pressure driven membrane water separation processes, reverse osmosis, ultrafiltration and microfiltration, differ on the size range of the materials separated.

- Microfiltration membranes are employed to filter colloidal particles and bacteria from 0.1 to 10μm in diameter. The separation is based on the difference of size between the pore and the particle. Those particles with sizes larger than the pore diameter will be rejected by the membrane (Zydney, 1994).

- Ultrafiltration membranes can be used to filter dissolved macromolecules, such as proteins, from solutions. As in microfiltration, separation of solutes is controlled by the gradient pressure and the pore size distribution, although other phenomena such as the electrical charge of the membrane may influence the membrane selectivity (Saxena *et al.*,2009).

- Nanofiltration membranes can retain low molecular weight molecules (100 – 200 Da). It is considered an intermediary process between ultrafiltration and reverse osmosis. The transport of solutes across the membrane is governed by the pressure gradient, as ultrafiltration, but the diffusion transport plays an important role on the separation and permeation of the feed solutes.

- In reverse osmosis membranes, the membrane pores are very small, from 3 to 5 Å in diameter, and the solutes consist of dissolved salts or small organic compounds which permeate the membrane by dissolving in the membrane material. This transport is governed by a solution-diffusion mechanism, so separations in RO are based on the difference in solubilities and mobilities of the different solutes (Najafpour, 2007). The principal application of reverse osmosis is the desalination of brackish groundwater (Belkacem *et al.*, 2007) or seawater (Murrer and Rosberg, 1998).

The fifth fully developed membrane process is electrodialysis, in which charged membranes are used to separate ions from aqueous solutions under the driving force of an electrical potential difference. The process utilises an electrodialysis stack, built on the filter press principle and containing several hundred individual cells, each formed by a pair of anion and cation exchange membranes. The principal application of electrodialysis is the de-salting of brackish groundwater (Lee, 2002). However, industrial use of the process in the food industry, e.g., to d(Greiter *et al.*, 2002) is growing, as is its use in pollution control applications (Mohammadi *et al.*, 2005).

Table 4.5. Range of application of the different membrane separation processes for liquid streams.

Process	Driving force	Separation size range	Examples of materials separated
Microfiltration	Pressure gradient (0.5 – 3 bar)	0.1-10 μm	Small particles, large colloids, microbial cells
Ultrafiltration	Pressure gradient (1 – 10 bar)	5 nm – 0.1 μm	Emulsions, colloids, proteins and other macromolecules
Nanofiltration	Pressure gradient (3 – 20 bar)	0.5 – 5 nm	Small organic compounds, multivalent ions
Reverse Osmosis	Pressure gradient (10 – 50 bar) Diffusivity	< 0.5 nm	Dissolved salts, monovalent ions
Electrodialysis	Electric field gradient	< 0.5 nm	Dissolved salts

4.1.3.1 Types of membranes

In essence, a membrane is a discrete, thin interface that moderates the permeation of chemical species in contact with it. Membranes can be classified under two different criterions, its morphology and the materials employed for its construction.

According to the material being employed for the membrane construction, membranes can be organic, inorganic and liquid (Zeman and Zydney, 1996).

4.1.3.1.1 Organic membranes

Organic membranes are fabricated with polymeric materials, either polar, hydrophilic polymers (cellulose esters, polyamides, etc) or non polar, hydrophobic materials (polyethylene, polypropylene, etc). The first organic membranes were fabricated with cellulose acetate. These membranes implied low construction and material costs, and presented good resistance to protein fouling. The main drawback was their low mechanical and cleaning resistance (Daufinn *et al.*, 1991). This inconvenient was overcome by polyamide-based membranes, employed in NF and RO applications, which present more chemical stability, but are easily fouled by protein adsorption. A second generation of organic membranes, recently developed, is the polysulphonic membranes, which exhibit good thermal stability, high tolerance extreme pH (1 – 13), and chlorine concentrations (up to 200 mg/L), facilitating their chemical cleaning. Their main

disadvantage is their moderate mechanical resistance, so they are limited to applications with pressure under 25 bar (Martínez, 2003).

4.1.3.1.2 Inorganic membranes

Ceramic membranes have recently emerged as a separation technology for applications requiring high thermal or chemical stability (long cleaning cycles or abrasive cleaning agents), and a adequate fouling control. A ceramic membrane is an asymmetric structure composed of a porous support and a filtering layer (Zeman and Zydney, 1996). The support is the most porous part of the membrane. In most of the cases, it is produced by sintering alumina particles, which creates a highly permeable and strong macroporous structure. The active layer is composed of ceramic particles (alumina, zirconia or titania depending on the desired pore size), and it has a thickness on the order of 20µm. It is in direct contact with the fluid, acting as a filtering layer. The selectivity and separation efficiency of the membrane depend on the pore size (usually 2 – 6 µm) distribution among this layer. It is usually bedded on an intermediary layer by high temperature sintering to increase the robustness of the structure.

Ceramic membranes can bear extreme temperatures (up to 350ºC) and pH (1 – 13), and resist most of the chemical solvents and oxidant agents, except fluorhidric, sulphuric and phosphoric acid (for alumina membranes), enabling severe cleaning protocols (vapour stream sterilisation, oxidant agents, high chemical agents concentration). They can also resist mechanical backflushing (water cleaning pulses in reverse sense). As main drawback of these membranes, they involve high manufacturing costs and brittleness (Siskens, 1996) added to their high dead volumes (1.5 L/m^2).

4.1.3.1.3 Metal and liquid membranes

Dense metal membranes, in special palladium membranes, is a yet-to-be-developed membrane separation technology which has been successfully applied in the separation of hydrogen from gas mixtures. Liquid membranes, formed by a liquid film with or without a porous support, have been applied, among others, in the recovery of CO_2, ammonia or H_2 from gas mixtures (Krull *et al.*, 2008), or desalination of seawater (Naim and Monir, 2002).

4.1.3.2 Membrane configurations

The module is the physical unit that actually houses the membranes in an appropriately designed configuration. The membrane module must provide a necessary physical support for the membrane, minimise the pressure drop through the device and maximise the membrane packing densities, i.e. the ratio of membrane are to device volume, thus minimising the manufacturing costs. The module should permit easy access to each of their membrane component, in order to facilitate the membrane cleaning or replacement. Among the different module configurations, there are four main types of module developed for large-scale commercial applications.

4.1.3.2.1 Plate-and-frame modules

The basic unit consists of a rigid flat plate where a membrane sheet is placed, separated from the plate by a net-like spacer to provide the channel for the permeate flow. Another membrane sheet and permeate spacer are placed on the opposite side of the plate. Several of these units are arranged in a vertical or horizontal stack, sealed to a supporting structure, forming the module (Cheryan, 1998). The feed flow is distributed among the different channels at one end of the device, and the retentate is is collected at the opposite end. The permeate from each single membrane sheet drains towards the collection channels on the edge of each holding plate.

Their industrial application is limited since these modules are difficult to clean, and susceptible to particulate plugging, since the fluid flow inside these units is normally laminar. To overcome this inconvenient, many of the newer flat plate designs use net-like feed-side spacers to improve the mass transfer and enhance the turbulence (Zeman and Zydney, 1996).

4.1.3.2.2 Tubular modules

The tubular membranes are usually cast in place within a porous support tube made of fibreglass, ceramic, plastic or stainless steel. The tubes, which are normally 1 – 6 m length and 10 – 25 mm in diameter, are placed together inside a plastic or stainless steel carcase, forming a single cartridge. The feed flows through the bore of the tubes, while the permeate flows radially outward across the membrane and the support tube to be collected and exit the module by one or more permeate placed on the surface of the outer tube. The retentate flows along the tube axis and it is collected on the opposite end of the module (Zeeman and Zydney, 1996). Tubular modules

are widely used for applications where a turbulent flow is desirable, e.g. solutions with high solids content.

4.1.3.2.3 Spiral-wound modules

The spiral modules are constructed placing two flat sheet membranes together with their active sides facing away from each other. They are separated by a turbulence-promoting mesh spacer material and glued to each other and to a central perforated tube. This configuration produces a cylindrical module with is placed inside an outer pressure tube. The feed solution enters at one end of the pressure tube, following the narrow channels along the surface of the membrane sheets. The permeate traverse the membrane layers and spirals radially towards the perforate tube where it is collected (Najafpour, 2007).

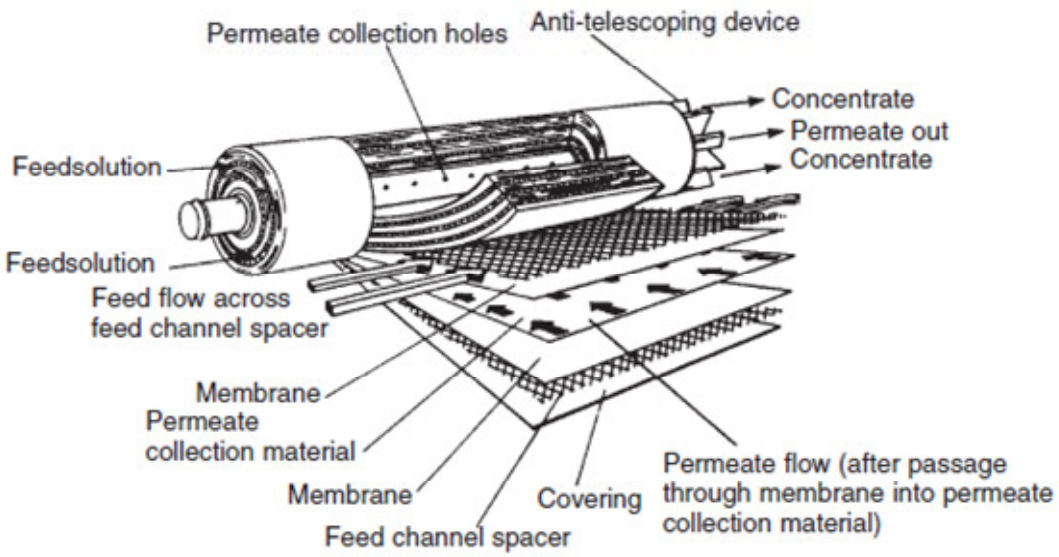

Figure 4.1. Schematic diagram of a spiral-wound module (Najafpour, 2007).

4.1.3.2.4 Hollow fibre modules

Hollow-fibre modules are similar to the tubular configurations previously mentioned, but in this case the membranes consist of bundles of fine fibres, 0.1 – 2.0 mm diameter, sealed in a tube. They are commonly used in osmosis desalination applications, where the feed is pumped from the shell side and the permeate is removed through the inside of the fibre. For UF and MF

applications the feed is pumped through the inner core of the tube and the permeate flows radially outwards from the fibres to two permeate ports, as shown in fig. 4.2.

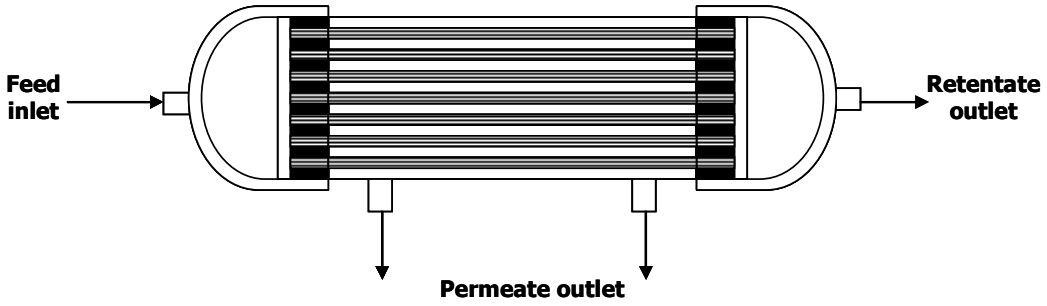

Figure 4.2. Schematic diagram of a hollow-fibre membrane module.

The choice of a membrane module will depend on a balance between the economic costs and many other factors, such as the fouling control, the cleaning, the resistance to high pressures or whether the membrane material can be fabricated into a particular module design, e.g. many membrane materials cannot be fabricated into a hollow fine fibres. The main characteristics for each type of module are listed in the table 4.6.

Table 4.6. Comparison between the main membranes modules used in industrial applications (adapted from Cheremisinoff, 2002 and Najafpour, 2007).

Parameter	Plate-and-frame	Spiral-wound	Tubular	Hollow fiber
Surface area (m^2/m^3)	300-500	1000	300	15000
Inner diameter/spacing (mm)	3 - 10	4 - 20	20 - 50	0.5 - 2
Feed flow rate (L/m^2 day)	-	300 - 1000	300 - 1000	30 - 100
Permeate-side pressure drop	Low	Moderate	Low	High
Fouling control	Good	Moderate	Very good	Poor
Pre-treatment requirements	Average	Average	Simple	High
Suitability for high-pressures	Marginal	Yes	Marginal	Yes
Limitation to specific types of membrane material	No	No	No	Yes
Mechanical cleaning	Not possible	Not possible	Possible	Not possible
Chemical cleaning	Poor results	Possible	Possible	Possible
Manufacturing costs ($\$/m^2$)	50 - 200	5 - 50	50 - 200	2 - 10

Taking into account the different advantages and disadvantages of each membrane module, each membrane separation application will require a given module configuration, depending on whether a high degree of turbulence is desirable or not, the possibility of particulate deposition on the membrane material, the cleaning protocol, the range of pressure, the initial load of the feed stream or the required filtration surface, as well as the value of the final product (either permeate or concentrate/purified retentate) and lifetime of the membrane, compared to the manufacturing and operating (pumping) costs. Table 4.7 shows some of the major industrial applications and technologies, as well as the module configurations usually employed for them.

Table 4.7. Module designs commonly used in the main membrane separation processes.

Application	Module type
RO applied to seawater	Both hollow-fibers and spiral-wound modules
RO applied to industrial water	Spiral-wound modules used almost exclusively
Ultrafiltration	Tubular modules for highly fouling streams and spiral-wound for clean feeds (ultrapure water)
Gas separation	Hollow fibres for high-volume applications involving low-selectivity membranes. Spiral-wound modules for feed gases more contaminated and a problem of polarisation concentration

4.1.3.3 Membrane fouling.

In an ideal situation, considering the flux of pure water through a membrane (with no suspended particles or dissolved solutes able to interact with the membrane surface) will be related to both the fluidodynamic conditions (permeate viscosity and pressure drop through the pore) and the dimensions of the pore channel (pore radius and thickness). The flow rate through the membrane should obey the Hagen-Poiseuille law for stream-line flow through channels (Cheryan, 1986):

$$J = \frac{\varepsilon \cdot r^2 \cdot \Delta P}{8 \cdot \eta \cdot \Delta x} \qquad (4.1)$$

Where J stands for the permeate flux, i.e., the volume per unit area and unit time passing through the membrane, η is the permeate viscosity, ΔP is the pressure drop along the channel of thickness Δx and radius r, and ε represents the surface porosity of the membrane.

However, flux during membrane processing of a solution or suspension is usually much lower than that observed for pure water, due to several reasons (Cheryan, 1986):

- Deterioration of the membrane, mostly attributed to harsh cleaning regimens, employing pH, temperature and cleaning agents incompatible with the membrane material.

- Changes in the feed stream properties, in terms of viscosity, solute concentration, etc, which influences the mass transport to the membrane surface and within the membrane pores.

- Concentration polarisation. The solute molecules are carried from the bulk solution to the membrane surface. Proteins and other larger particles are largely rejected by the membrane, tending to form fairly viscous and gelatinous-type layers on the membrane, resulting in a further resistance to the flow of permeate.

- Fouling of the membrane. The term fouling refers to the flux decline due to the deposition or accumulation of particles on the membrane surface, and/or the precipitation of smaller solutes on the surface or within the pores. Unlike the concentration polarisation effects, fouling is irreversible, and the permeate flux of the membrane cannot be restored without a suitable cleaning process.

4.1.3.3.1 Flux decline due to concentration polarisation.

Proteins and other hydrocolloid particles are carried by the convective transport from the bulk solution to the membrane surface. These solutes are largely rejected by the membrane, and tend to accumulate on the membrane surface developing a concentration gradient which increases from the bulk solution to the membrane surface. This concentration gradient is the driving force starting a molecule diffusion transport from the membrane surface back into the bulk solution, opposite to the convective transport which conveys the solution materials to the membrane. At steady state, the two transport mechanisms will balance each other, stabilising a gel viscous layer of a given thickness and concentration between the bulk solution and the membrane surface (Song, 1998a, 1998b). The permeate flux through the gel layer will no longer be governed by the Hagen-Poiseuille (eq. 4.1) law, i.e., the permeate flux will not be pressure-dependent, but controlled by the mass transfer within the gel layer. The effect of concentration polarisation explains the asymptotic trend shown in figure 4.3:

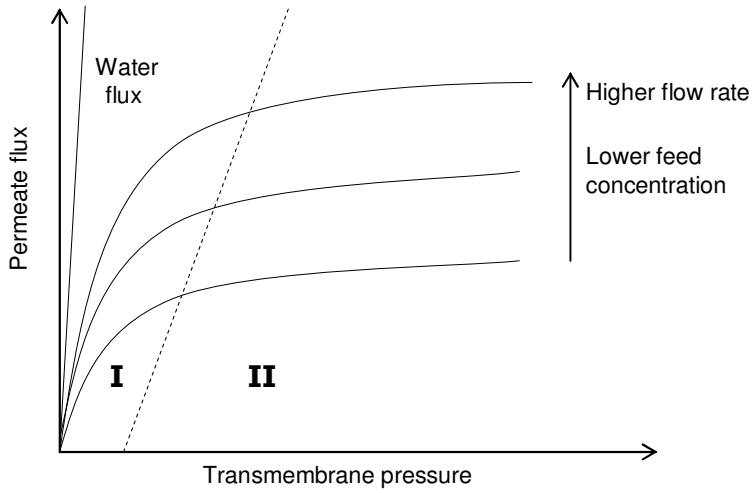

Figure 4.3. Correlation between the flux and the transmembrane pressure, showing the pressure controlled region (I) and the mass transfer controlled region (II).

4.1.3.4 Flux decline due to membrane fouling.

The figure 4.4 shows the typical evolution of the permeate flux in the course of a crossflow filtration operation. The flux-time curve can be divided into three zones: a rapid flux decline with takes place at the beginning of the operation (zone I), a permeate flux decline at a lower rate (zone II) and a steady state where flux remains constant in time (zone III).

In the beginning of the filtration operation the flux of permeate is maximum since all the pores of the membrane are opened, offering a maximum filtration area. The sharp descent of the permeate flux is due to the rapid plugging of the membrane pores by the feed solutes, which reduces the effective filtration area. The membrane pores will be fully or partially blocked depending on the relative sizes of the solutes and the membrane pores. The more the solute size and pore diameter are similar, the more complete is the pore blockage (Belfort *et al.*, 1994; Hlavacek and Bouchet, 1993). In all cases, pore-plugging is a very rapid phenomenon, much faster than the formation of the gel polarisation layer, since it attains its maximum extent after the deposition of only a monolayer of solute molecules (Hlavacek and Bouchet, 1993). As more solutes molecules or particulates from the feed solution are rejected by the membrane, other phenomena acquire importance, such as the formation of a gel layer due to concentration polarisation, specially in ultrafiltration of hydrocolloids such as proteins (Baccin *et al.*, 2002) and the deposition of foulant materials on the membrane surface, more relevant in microfiltration operations with larger

particules (Ho and Zydney, 2000). All these phenomena, which increase the hydraulic resistance to flow, are known as fouling

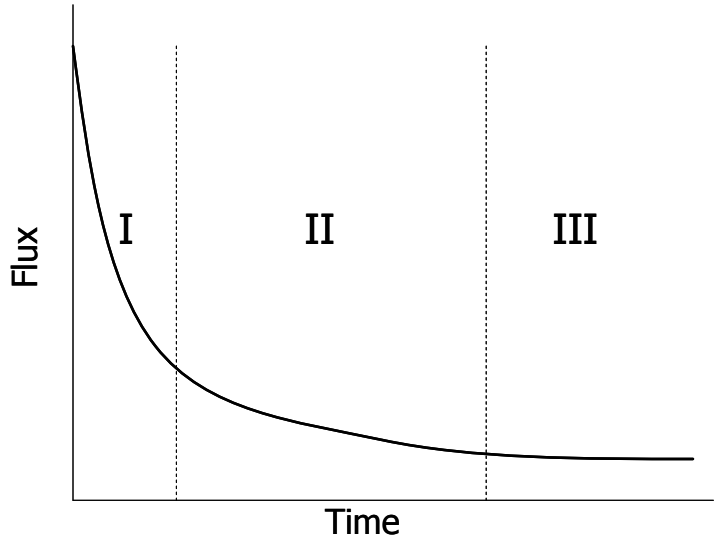

Figure 4.4. Schematical representation showing the decline of the permeate flux during a crossflow filtration operation.

The final plateau observed for the permeate flux (zone III) may indicate that the gel layer has reached its maximum thickness of equilibrium (Song, 1989b). In processes with high transmembrane pressure and low feed concentrations, where the solutes are rapidly conveyed from the bulk solution towards the membrane surface, the permeate flux decreases continuously without attaining a steady state (Song, 1998a).

The flux decline due to the fouling and gel polarisation phenomena can be described mathematically by the resistance model (Eq. 4.2), which expresses the permeate flux (J) as the quotient between a driving force (the transmembrane pressure ΔP) and a series of hydraulic resistances (Cheryan, 1998)

$$J = \frac{\Delta P}{\mu \cdot \left(R_M + R_F + R_{CP} \right)} \qquad (4.2)$$

where μ is the fluid viscosity and R_M, R_F and R_{CP} stand for the hydraulic resistance provided by the membrane, the fouling or cake layer and the concentration polarisation layer,

respectively. A schematic representation showing the physical meaning of these resistances is provided by Figure 4.5.

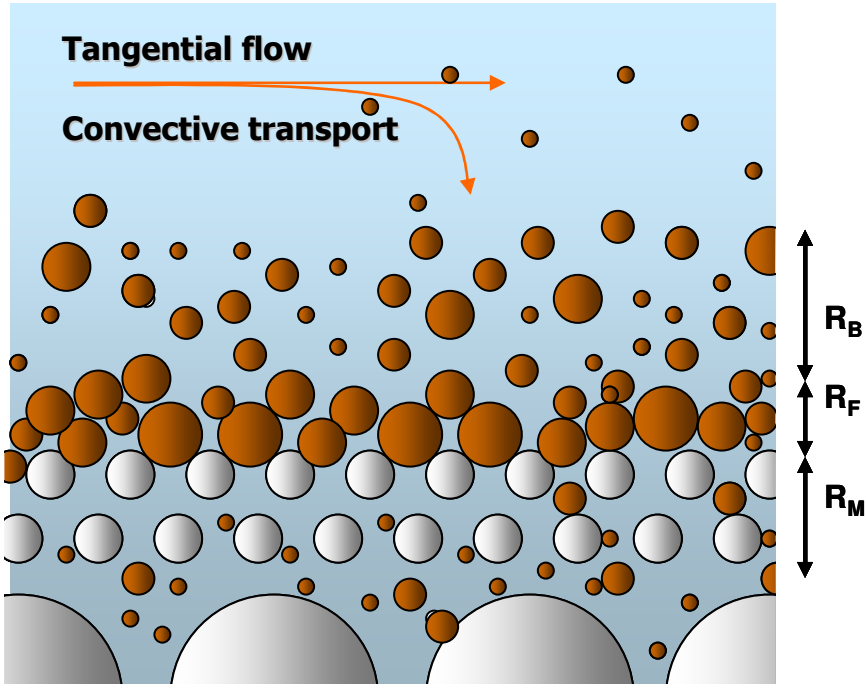

Figure 4.5. Schematical representation of the hydraulic resistances involved in a crossflow filtration.

4.1.3.4.1 Flux prediction models based on fouling.

The so-called Hermia models are a series of empirical models developed by Hermia (1982) which relate the permeate flux decay with the fouling mechanism. Depending on the relative size of the foulant aggregate or molecule and the pore size distribution, there are four main fouling mechanisms, as shown in Figure 4.6

- Complete pore blocking. Due to deposition of large molecules or aggregates larger than the pore diameter, able to seal the pore entrance.

- Intermediate pore blocking. The particles may bridge a pore by obstructing the entrance but not completely blocking it, or they seal completely the pore but are subjected to a dynamic equilibrium of blocking/unblocking (de Barros *et al.*, 2003).

- Cake formation. The cake consists of a packed layer of particles or macrosolutes, larger than the pore diameter, which form an additional resistance in series with the membrane one.

- Internal pore blocking or pore constriction. For membranes with relatively large pores that are easily accessible to the microsolutes (Zeman and Zydney, 1996). Foulant particles are adsorbed onto the membrane wall, decreasing the effective pore radius.

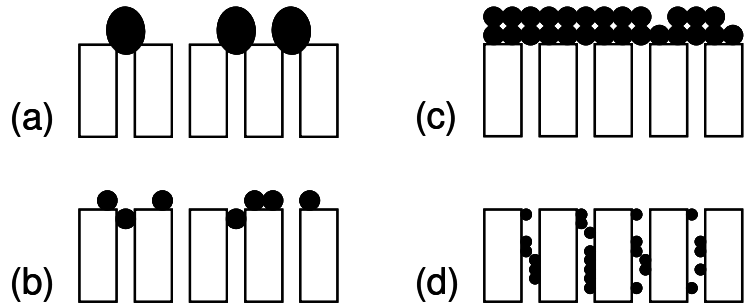

Figure 4.6. Schematical representation of the fouling mechanisms: (a) complete pore blocking, (b) intermediate pore blocking, (c) cake formation and (d) pore constriction.

Hermia (1982) has developed a series of equations predicting the permeate flux decline when one of these basic fouling mechanisms is present. These models are based on the characteristic equation for the constant-pressure dead-end filtration, and were reformulated in a common frame of power-law relationship, according to Eq. 4.3:

$$\frac{d^2t}{dV^2} = k \cdot \left(\frac{dt}{dV} \right)^n \qquad (4.3)$$

where k is a phenomenological constant and n is the fouling index with takes different values depending on the fouling mechanism: n=0 for cake formation, n=1 for intermediate blocking, n=3/2 for pore constriction and n=2 for complete pore blocking.

In order to extend these simple filtration equations to cross-flow systems, it is necessary to account for the foulant removal mechanism, due to the intermolecular forces acting on the particle and affecting its deposition. Field (1995) has adapted Hermia models to cross-flow

filtration by adding a new term, J* which accounts for the rate of back particle transport, as shown in the following differential equation:

$$-\frac{dJ}{dt}\left(J^{n-2}\right)=k\left(J-J^{*}\right) \tag{4.4}$$

where k and n are the phenomenological coefficient and fouling index mentioned above. J* can be considered as a critical flux under which fouling phenomena are not observed, it corresponds to the steady-state flux reached in the course of a membrane filtration operation.

The physical interpretations given to the critical flux vary among the authors. For example, Cohen and Probstein (1986) attributed the back transport to the electrical repulsion between the charged particles in the bulk suspension and those in the growing cake and Suki *et al.* (1984) assumed that J* was determined by the lateral migration of deposited particles which are dragged from the cake surface by the tangential flow. This model relies on the basic series-resistance model (Eq. 4.3), where the viscosity μ is included in the resistance terms R. This model considers three series resistances: the membrane intrinsic resistance (R_M), the resistance of the boundary layer (R_B) and that of the fouling material R_F, which is time dependant:

$$J=\frac{\Delta P_m}{R_M+R_B+R_F(t)} \tag{4.5}$$

The fouling resistance depends on the amount M of matter deposited on the membrane surface.

$$R_F(t)=\alpha\cdot M(t) \tag{4.6}$$

The mass of deposited cake follows a first-order kinetics of rate constant k, until reaching a critical value M* where the rate of deposition of foulant solutes on the cake surface balances the lateral migration towards the retentate flow.

$$\frac{dM}{dt}=k\cdot\left(M^{*}-M\right) \tag{4.7}$$

Integrating this equation and substituting on the equations 4.6 and 4.5:

$$J=\frac{\Delta P}{R_M+R_B+\alpha\cdot M^{*}\cdot\left(1-e^{-k\cdot t}\right)} \tag{4.8}$$

where the product α·M* stands for the maximum cake resistance, $R_{F\infty}$.

The initial flux, at time = 0, where no cake resistance is still provided, will only depend on the membrane and gel layer resistance, according to the equation:

$$J_0 = \frac{\Delta P}{R_M + R_B} \tag{4.9}$$

For large filtration times (t→∞), the flux will attain a steady value given by the equation:

$$J_\infty = \frac{\Delta P}{R_M + R_B + \alpha \cdot M^*} = \frac{\Delta P}{R_M + R_B + R_{F\infty}} \tag{4.10}$$

Re-ordering all these expressions, the equation 4.8 can be re-formulated as:

$$J = \frac{J_0}{1 + \left(\frac{J_0 - J_\infty}{J_\infty} \right) \cdot \left(1 - e^{-k \cdot t} \right)} \tag{4.11}$$

4.1.4 Cleaning strategies

The aim of cleaning and disinfection procedures is to obtain a structure that is physically clean (providing adequate flux and separation performance in subsequent operations), chemically clean (free from residues which might contaminate subsequent batches of product), and biologically clean (where adequate reduction of the microbial load has been achieved) (D'Souza and Mawson, 2005). Cleaning can be accomplished by physically removing the foulants from the membrane, e.g., by backflushing or mechanical scrubbing, or it can involve the use of detergents and/or chemicals. Key components of an effective cleaning strategy include the type and composition of the detergent and sanitizer solutions employed the order and duration of the cleaning steps, and the physical operating parameters.

4.1.4.1 Cleaning agents

The chemical agents should meet some requirements to be used for membrane cleaning. Not only they must provide an adequate fouling removal and membrane disinfection, but also they should be compatible with the membrane itself and other components of the filtration system such as

seals, spacers or glued joints. The major agents used to clean membrane plants can be divided into six groups, according to their chemical nature: alkalis, acids, enzymes, surfactants, sequesterants and disinfectants (Trägård, 1989). Their main properties are summarised in the Table 4.8.

Table 4.8. Cleaning agents commonly used for membranes (D'Souzas *et al.*,2005)

Group	Cleaning agents	General properties
Alkalis	Hydroxides, carbonates and phosphates	Hydrolysis and solubilisation of the proteins and carbohydrates, fat saponification.
Acids	Nitric and phosphoric acids	Dissolution of inorganic salts.
Enzymes	Proteases and lipases	Hydrolysis of proteins and lipids. Compatible with sensitive membranes
Surfactants	Anionics, non-ionics	Solubilisation of the fouling material and prevention of its re-deposition.
Sequesterants	Ethylenediaminetetra acetic acid (EDTA)	Prevention of re-deposition and solubilisation of inorganic salts.
Disinfectants (and oxidants)	Hypochlorite, hydrogen peroxide and metabisulphite	Destruction of pathogenic micro-organisms.

4.1.4.1.1 Cleaning sequence

A typical cleaning cycle, as shown by Trägårdh (1989), generally includes the following stages: product removal from the system, rinsing with water to remove product, cleaning in one or more steps, rinsing with water to remove detergents and any remaining soil, and final disinfection.

The flush and rinse times are always dependent on the membrane area, but they are usually between 5 and 20 minutes. During the rinsing step, both retentate and permeate should be discharged until both these streams are clear and neutral. Cabero *et al.* (1999) reported an increase in the permeate flux up to 90% after rinsing.

Most cleaning regimes consist of an alkali detergent step followed by an acid step, with appropriate rinses in between. The duration of a chemical cleaning step will depend on the membrane area, but a maximum time should not be exceeded since it may reduce the membrane permeability (Makardij *et al.*, 1999; D'Souza *et al.*, 2005). This may be attributed to an extended solubilisation of the fouling materials (e.g. hydrolysis of the protein aggregates) giving rise to smaller solutes which can deposit inside the pores during the subsequent rinsing (Cheryan, 1989).

With respect to the sequence in which cleaning agents are applied, it is commonly recommended an initial alkali step, to solubilise and remove the protein deposits, followed by an acid step acting on the inorganic precipitates and finishing with a disinfection step (e.g. with sodium hypochlorite) (D'Souza, 2005).

4.1.4.1.2 Physical operating parameters

The product should be rinsed from the membrane at the same temperature used in the filtration process, particularly for products that tend to form gels at low temperatures. Concerning the alkali/acid steps, a higher temperature favours the flux recovery since it increases the solubilisation of cleaning agents and foulant materials, increases reaction rates and promotes fat melting. Some authors (Bartlett *et al.*, 1995; Makardij *et al.*, 1999; Bird and Bartlett, 2002) reported an optimum temperature of 50-55ºC beyond which the flux recovery declines. These authors attributed the lower flux recovery values to the greater disintegration and solubilisation of the foulant deposits, which provided smaller molecules or particles able to enter the pores and adsorb onto their inner surface. The flow rate of the cleaning solution should be enough to provide an adequate turbulence, facilitating the mechanical removal of the foulant deposits. However, this factor will be limited by the pump capacity and the membrane mechanical resistance.

4.1.4.2 Membrane applications in the seafood industry.

The term "process wastewaters" includes all the liquid effluents from the processing of fish, shellfish and crustaceans. This processing involves the generation of a large quantity of washing, cooking and pressing wastewaters, polluted with fats, proteins, bones and blood. The treatment of these wastewaters is one of the most likely potential uses for membrane techniques, aiming to produce dischargeable water, complying with the increasingly strict legislation on industrial pollution. Membrane technologies take advantage over biological treatments, since the folder permit to recover part of the valuable material instead of transforming it into a sludge which has to be disposed of in landfills.

Membrane technologies are available for two main applications:

1. Reduction of the organic load of polluted effluents or process waters from fish industry. These effluents contain a varied amount of organic matter. Membrane separation

technologies are able to reduce their organic load, rendering a final filtrate whose discharge has a minimal impact on the environment. The use of membranes for the treatment of process and waste waters from marine sources is extensively reviewed by Afonso and Bórquez (2000) and Massé *et al.* (2008).

2. Recovery of valuable molecules. These effluents are rich in valuable compounds, such as lipids or proteins, able to be recovered and make up the formulation of animal or human feedstuffs. In this regard, it is of special interest the combination of enzymatic hydrolysis to membrane separations. This technique permits to separate the peptides, lipids or other compounds released after the hydrolysis of fish materials. Ultrafiltration is widely used to fractionate the peptidic fractions resulting from a enzyme hydrolysis. Once isolated, each fraction is tested for its biological activity. A complete review on the use of membrane separation techniques in the fields of peptide or lipid fractionation, aroma up-grading and recovery of carbohydrates from marine sources is provided by Bourseau *et al.* (2008).

4.2 MATERIALS AND METHODS

4.2.1 Materials

4.2.1.1 Filtration cartridges

The filtration pre-treatment comprised two Dynamesh^{TM} filter cartridges of 465 and 250 µm rating size, manufactured by PALL (USA). The filter media is composed of micronised metallic fibres with 60% porosity. The filter cartridge consists of a 316 stainless steel central cylindrical core of 6.4 cm diameter and 25.4 cm length covered by a woren 316 stainless steel cloth of the desired pore size, wich provides a filtration area up to 0.1022 m^2 . It tolerates a maximum temperature up to 400 ºC and a maximum pressure up to 172 bar. Each filter cartridge is placed inside a 316 stainless steel housing (2022 Series Filter Assembly, PALL, USA).

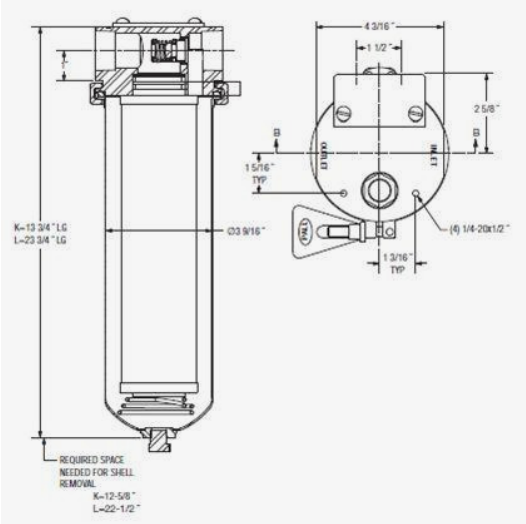

Figure 4.7. Dimensional drawing of the 2022 filter housing.

The feed solution enters the housing element and fills a hold-up volume of 2.75 L between cartridge and housing. Once the steady state is reached, the feed solution flows from the outside, through the medium and out from the axis. Suspended solids in the feed stream are thus deposited outside the element or in the interstices of the filter medium. The overall element (cartridge + housing) acts as a particle holder which can then be also easily removed and cleaned mechanically or chemically. It can be also be cleaned in place by means of pressurised water.

4.2.1.2 Ceramic membranes

Three ceramic tubular membranes Membralox™ ET1-070, manufactured by PALL (USA) were used for the ultrafiltration and microfiltration tests. The Table 4.9 summarises the average pore size and materials of the ceramic membranes assayed:

Table 4.9. Average pore sizes and materials of the Membralox™ membranes tested.

Operation	Average pore sizes	Dimensions	Composition of the active layer
Ultrafiltration	50 nm	7 mm diameter x 250 mm length	Zirconia
Ultrafiltration	200 nm	7 mm diameter x 250 mm length	Zirconia
Microfiltration	1.4 μm	7 mm diameter x 250 mm length	α - alumina

Each ET1-07 tubular membrane provides an overall filtration surface of 0.005 m^2. The Membralox™ ceramic membranes are asymmetric membranes composed of a porous support and a filtering layer (so-called active layer) of the desired pore size and material (zirconia for ultrafiltration and α-alumina for microfiltration), followed by an intermediary layer. Both layers lye on a macroporous support structure of 35% porosity and 12 μm of average pore size, as shown in Figure 4.8b.

The ceramic membrane must be mounted in a housing that allows the feed stream to enter, to separate into permeate and concentrate streams, and to exit after passing through the membrane. The tubular membranes assayed are contained in standard holding modules of 316 stainless steel where the feed and retentate ports are connected to the system piping by j-clamp connections and the permeate outlets by weldable ferrule connections

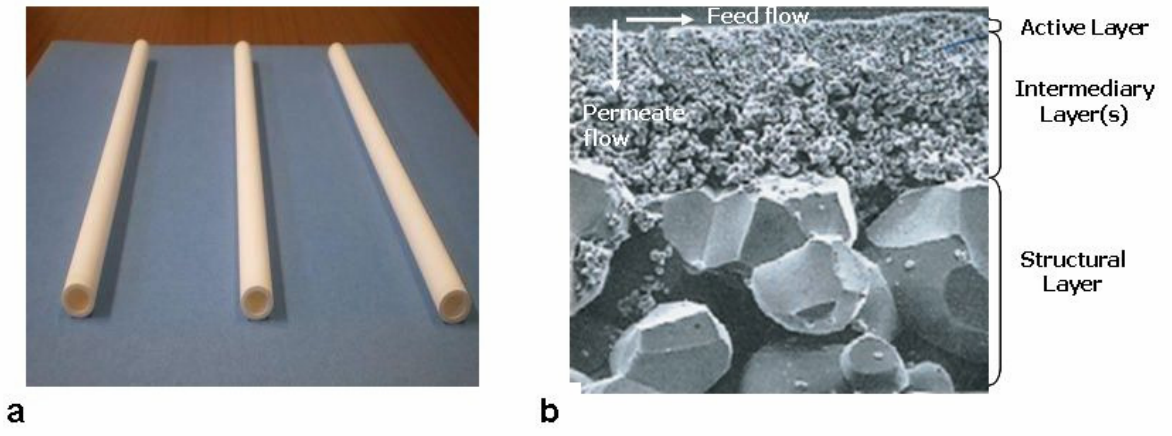

Figure 4.8. (a) Membralox^{TM} tubular membranes ET1-070. (b) Structure of a ceramic membrane.

4.2.1.3 Experimental set-up

The microfiltration and ultrafiltration assays were undertaken at lab scale by means of a MAXIM UF/MF System^{TM} from PALL (USA). As shown in Figure 4.9., the product to be filtered is transferred to the feed tank (a 10-litre glass vessel) via the inlet connection port. The temperature of the feed solution must be kept constant, to avoid changes in the viscosity able to disturb the membrane separation. The shear forces induced by the pump and the membrane separation itself on the retentate stream increase its temperature to a large extent. The excess of temperature is absorbed by means of a cooling coil introduced into the feed tank, which employs glycol as refrigerant fluid. Under action of a diaphragm-type positive displacement pump (feed pump), the product is pumped via valve V1 through the UF/MF filter module. The drain recovery valve V2, enables the user to empty the feed vessel or take some samples of the feed solution. The level of cross-flow velocity and transmembrane pressure are controlled by manually adjusting the speed of the pump and partially closing the backpressure control valve V4 in the retentate recirculation loop. The cross-flow velocity was chosen to be 3.3 m/s. This velocity provides a turbulent regime, required to minimise the concentration polarisation adverse effects (Cheryan, 1998). However, a very high tangential velocity is not desired; since most of the feed solutes will be carried by the tangential flow out of the membrane, with less residence time in the membrane, resulting in lower permeate flows.

The total recirculation assays are preferred to determine the optimal conditions (transmembrane pressure, cross-flow velocity, membrane molecular weight-off) for a given membrane separation.

They are performed with both retentate and permeate being recirculated to the feed tank, so the feed concentration remained constant. The volumetric flow of the retentate stream returned to the feed tank is measured by means of a flowmeter (model 511-3892, RS Electronic, UK) placed after the backpressure valve V4.

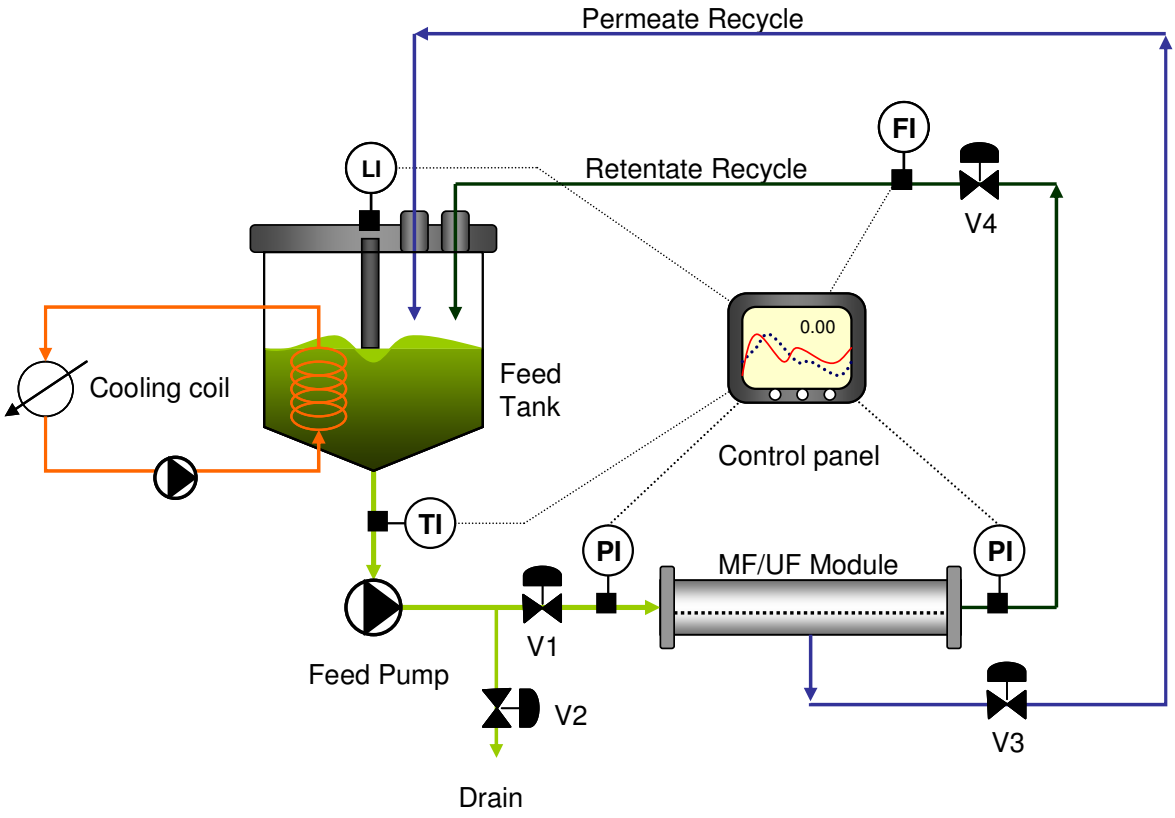

Figure 4.9. Experimental set-up for the total recirculation assays and the batch concentration.

In the batch concentration mode, which simulates an industrial production process, the retentate is returned back to the feed tank, while the permeate is recovered in a collection recipient by means of a flexible pipe. The volume in the feed tank decreases in the course of time, accompanied by an increasing concentration of the rejected solutes. The system enables the user to select a desired volume reduction. The maximal volume reduction is limited by the increase in the viscosity of the retentate solution, which difficulties the performance of the pump and can provoke its over-heating. The mass of permeate collected can be continuously measured by means of a balance. The figure 4.10 shows the picture of the pilot system in a batch concentration configuration.

Figure 4.10. Photograph of the Maxim MF/UF Pilot System™.

All the process variables associated with the Maxim System™ device can be adjusted by the operator via the Operator Interface Terminal (OIT). This control panel allows the user to adjusts variables such as the pump speed or tank level, and monitor the variables involved in the filtration operation, such as transmembrane pressure, retentate flow rate, feed temperature, etc.Other components are operated manually, such as the valves.

These monitoring and control functions are possible thanks to several transmission devices placed all over the installation, listed on the table 4.10, which permit to follow the evolution of the operating variables (pressure, volumetric flow, temperature and level of the liquid in the tank) in the course of the ultrafiltration. Each variable can be limited by a lower and/or upper alarm point, which are set by the user.

Table 4.10. Pump, valves and transmission devices of the Maxim MF/UF System™

Element	Symbol	Operation range
Inlet pressure transmitter	PI	0 – 6 bar
Outlet pressure transmitter	PI	0 – 6 bar
Temperature transmitter	TI	0 – 100ºC
Level transmitter	LI	0 – 10 L
Retentate flowmeter	FI	2 – 10 L/min
Pump	-	1 – 16 L/min
Feed inlet valve	V1	0 – 100 %
Drain recovery valve	V2	0 – 100 %
Permeate valve	V3	0 – 100%
Backpressure valve	V4	0 – 100%

4.2.2 Experimental procedure

4.2.2.1 Objectives and experimental sequence

The effluent treatment given to the press liquor originating from the hydraulic pressing of sardine by-products comprised a filtration pre-treatment, by means of filter cartridges, in order to recover fine particles suspended in the press liquor, followed by a batch ultrafiltration concentration. Two goals were set for the membrane filtration operation:

1. To render a final filtrate able to be discharged to the receiving waterbody, according to the general EU wastewater standards reported in Table 4.2 or, lacking that, to provide a considerable COD removal to be transferred to a municipal waste water treatment plant (MWWTP).

2. To recover a concentrate rich in proteins able to undergo an up-grading process (e.g. enzymatic hydrolysis, extraction of aroma compounds, etc).

The Table 4.11 summarises the experimental procedure followed to design the effluent treatment line, including the different objectives set for each task.

Table 4.11. Outline of the steps involved in the design of the effluent treatment.

Stage	Description	Objectives
Filtration pre-treatment	The press liquor was pumped through two filter cartridge in series of decreasing size ratings.	Assess the particle removal efficiency of both filter cartridges. Determine their adequate operating parameters.
Membrane MF/UF	3-hour membrane UF or MF of the press liquor originating from the filter cartridges. Total recycling mode. Tests on three membranes of different pore size.	Selection of the best tubular membrane according to average permeate flux, COD removal and water flux recuperation after a cleaning cycle.
Batch membrane concentration	Batch membrane concentration of 8 h with the selected membrane	Monitoring of the operation in terms of permeate flux, COD of the final filtrate, volume reduction factor, concentration and molecular distribution of the species in both permeate and concentrate.
Cleaning protocol	Cleaning cycle following an alkali-acid-oxidant sequence.	Asses the efficiency of the cleaning protocol to restore the initial water flux.
Simulation and scaling-up	The fouling mechanism causing the flux decline was investigated in order to obtain a predictive flux model able to simulate the membrane performance.	Fitting of the experimental data to a prediction model for the flux decline. Simulation and scaling up to a semi-industrial scenario.

4.2.2.2 Filtration pre-treatment

The circulating pump was calibrated with water and product (press liquor). For each calibration test, carried out at room temperature, the flow rate of the feed stream (either water or product) was raised progressively, monitoring the overall pressure drop (filter cartridge + housing) thanks to the digital manometers placed at feed inlet and permeate outlet of the filter module. These data enabled to obtain the corresponding pressure-flow curves for each filter cartridge. With regard to the filtration operation itself, the single pass configuration was chosen. Five litres of the press juice obtained from the pressing operation were transferred to the feed tank and then pumped at 5 L/min through the 450 μm filter cartridge. The permeate was collected at the opposite end and stored for a subsequent filtration through the 250 μm cartridge under the same operating conditions described above.

4.2.2.3 Membrane MF/UF

4.2.2.3.1 Membrane conditioning

Before each microfiltration or ultrafiltration test, the membranes were hydrated during 1 hour and then underwent a complete cleaning procedure, comprising the alkali, acid and oxidant step, with the respective rinsing in between. After the last rinse, the clean membrane permeability was determined.

4.2.2.3.2 Determination of the membrane permeability and resistances

The membrane permeability is defined as the inverse of the resistance for the permeate to flow. The membrane permeability will be determined before and after the ultrafiltration, as well as after each cleaning step.

The initial membrane permeability (L_p) is evaluated on the clean membrane and water, the only resistance to permeate flow will be that of the membrane material. According to the series resistance model (Eq. 4.2), the water flux will be given by the equation :

$$J_w = \frac{\Delta P_m}{R_M} = L_p \cdot \Delta P_m \qquad (4.12)$$

where ΔP_m is the transmembrane pressure (bar), J is the permeate flux (L/m^2 h) and R_M is the membrane resistance (bar m^2 h /L). For each transmembrane pressure, the water flux can be estimated as the volume or mass of water collected (m and V, respectively) after a given interval of time (Δt) and a membrane surface A, by means of the equation 4.8 :

$$J_w = \frac{V}{A \cdot \Delta t} = \frac{m}{\rho_w \cdot A \cdot \Delta t} \qquad (4.13)$$

Where ρ_w is the density of water at the work temperature. The transmembrane pressure was risen slightly in intervals of 0.5 bar by means of the retentate valve and for each new pressure value the permeate flux was determined by equation 4.13. According to equation 4.12, the membrane permeability and resistance will be calculated from the linear regression of the water flux against the transmembrane pressure.

After the ultrafiltration operation or after each cleaning step, the membrane will be partially fouled by the feed materials, so the water flux will be expressed by the equation:

$$J_w = \frac{\Delta P_m}{R_M + R'_F} \qquad (4.14)$$

Where R'_F accounts for the overall resistance due to the concentration polarisation and the fouling phenomena (cake formation and pore blocking). This permits to evaluate the overall fouling resistance by the equation 4.15.

$$R'_F = \frac{\Delta P_m}{J_w} - R_M \qquad (4.15)$$

4.2.2.3.3 Determination of the optimal transmembrane pressure

The optimal transmembrane pressure was estimated once the temperature in the feed solution was stabilised at 20 ± 2 ºC. Both retentate and permeate were recycled to the feed tank, so the feed concentration remained constant. Under these conditions, the transmembrane pressure was risen slightly (0.5 bar) by means of the retentate valve and for each new pressure value the permeate flux was determined by Eq. 4.13 until it reached a plateau or even decreased. The Figure 4.11 shows an initial linear, pressure-dependant flux which undergoes concentration polarisation effects until attaining a final steady state .

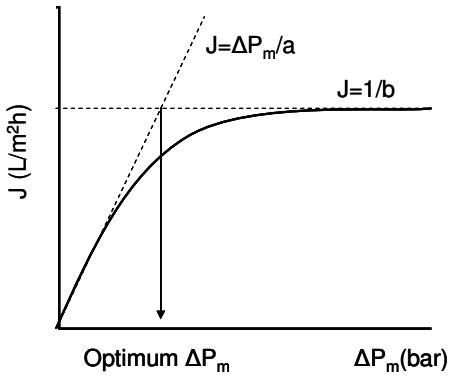

Figure 4.11. Determination of the optimum transmembrane pressure

This curve can be fitted to a the following rational equation:

$$J = \frac{\Delta P_m}{a + b \cdot \Delta P_m} \qquad (4.16)$$

where *a* is the hydraulic resistance provided by the membrane against the feed solution and the fouling resistance will be function of the applied transmembrane pressure, by means of the parameter *b*. For low transmembrane pressures the fouling resistance will be negligible, corresponding to the equation of the dotted line:

$$J = \frac{\Delta P_m}{a} \qquad (4.17)$$

As the transmembrane pressure increases, the fouling resistance becomes many times higher than the membrane resistance. This later can be neglected, obtaining the equation of the steady flux corresponding to the mass transfer control:

$$J = \frac{1}{b} \qquad (4.18)$$

The optimum transmembrane pressure is approximately determined by the intersection of both lines, so equating equations 4.17 and 4.18 :

$$\Delta P_{opt} = \frac{a}{b} \qquad (4.19)$$

Working at transmembrane pressures below this value is desirable, since the permeate flux will be controlled by the pressure (the fouling effects will be limited) and not by the mass transfer mechanism.

4.2.2.3.4 Ultrafiltration/Microfiltration operation

The performance of each one of the tubular ceramic membranes, once conditioned, was tested following the same procedure :

1. The membranes were hydrated during one hour and the membrane permeability was determined.

2. The feed tank was filled with 2 litres of press liquor. The temperature in the feed tank was kept constant at 20 ± 2ºC by means of a cooling coil. Once the temperature was stabilised,

the optimum transmembrane pressure was determined by the procedure described in section 4.2.2.3.3.

3. The press liquor underwent a 3 h ultrafiltration/microfiltration operation at constant transmembrane pressure. Both retentate and permeate will be recycled to the feed tank. The volume of permeate was weighted during the process.

4. After 3 hours, the feed tank and filtration system was emptied. The permeability of the fouled membrane was measured and the membrane was cleaned following the cleaning protocol described in the next section.

5. Taking into account the membrane performance, the protein and COD removal and flux restore after a complete cleaning treatment, one of the membranes was chosen to undertake a 8 hours batch concentration operation, where the retentate is continuously recycled to the feed tank while the permeate stream is collected in an independent storage recipient. The permeate flux was monitored during the process and the membrane was cleaning following the cleaning protocol described in the next section.

4.2.2.3.5 Cleaning protocol

A complete cleaning treatment, involving an alkali, acid and disinfection stage, was applied to restore the initial water flux after the ultrafiltration or microfiltration operation. Three different cleaning solutions were employed during the cleaning cycle:

- An alkali solution containing 20 g/L of Sodium Hydroxide (NaOH) with 2 g/L of Sodium Dodecyl Sulphate (SDS or NaDS) as surfactant agent.

- An acid solution of Nitric Acid (HNO_3) 0.5% w/w.

- A solution containing Sodium Hypochlorite (NaClO) (250 ppm of active Chlorine) and 0.5 g/L of Sodium Hydroxide (NaOH) to rise the pH over 11. This prevents the corrosion of the steel elements and piping (Daufin *et al.*, 1991).

The complete cleaning sequence comprised the following steps:

1. Initial rinse of the fouled membrane with water at room temperature and 350 L/min (3.3 m/s) to keep the turbulence. It comprises a first stage where the retentate port is drained at minimal transmembrane pressure, i.e., with the retentate valve completely open, while the valve at the permeate outlet remains closed. This stage removes the foulant material deposited along the membrane while the transmembreane pressure is minimal to prevent foulant materials to block the membrane pores. This step is followed by a second rinsing at 1.5 bar with the permeate valve opened and both ports being recycled to the feed tank. The high transmembrane pressure favours pore de-blocking.

2. Alkaline treatment at 50ºC and 350 L/h. It comprises an initial stage of 15 minutes where the permeate valve is closed and the retentate is recycled to the feed tank at minimal transmembrane pressure (retentate valve in the full-open position) followed by another stage of the same duration where both ports are recycled to the feed tank at a transmembrane pressure of 1.5 bar.

3. Rinsing of both ports with the same operating conditions (350 L/h, minimal pressure for the retentate port and 1.5 bar for the permeate port) until neutrality of both streams.

4. Acid treatment at 50ºC and 350 L/h. Both retentate and permeate are recycled to the feed tank during 15 minutes at a transmembrane pressure of 1.5 bar.

5. Rinse of both ports until neutrality of the water stream.

6. Disinfection stage with Sodium Hypochlorite at 350 L/h and room temperature. Following the same procedure described above, both ports were connected to the feed tank and the cleaning solution was recycled at 1.5 bar during 15 minutes.

7. Final rinse stage until neutrality of both water streams.

After each rinse stage, the membrane permeability and resistance were evaluated as described in the section 4.2.2.3.2.

4.2.2.4 Indices of membrane performance and cleaning efficiency.

4.2.2.4.1 Performance indices

The Relative Flux Decline (RFD) is given by the equation :

$$RFD = \frac{J_0 - J_\infty}{J_0} \cdot 100 \qquad (4.20)$$

This value is indicative of the initial flux decline observed in a typical J vs. time curve. In the case of a concentration operation, it is often used the Volume Reduction Factor (VRF), which stands for the decrease of volume of the feed solution during the batch concentration, according to the equation 4.21:

$$VRF = \frac{V_0}{V_0 - V_F} \qquad (4.21)$$

The passage of the solute molecules through the membrane pores to the permeate stream is evaluated by means of two symmetric concepts, the protein transmission and the protein rejection. The folder (T) is defined as the portion of the mass flow of solute in the feed solution which passes to the permeate side, according to the equation:

$$T = \frac{c_P}{c_0} \qquad (4.22)$$

Where c_P and c_0 are the concentrations (g/L) of the solute in the permeate and feed streams, respectively. The solute rejection is defined as the portion of the total mass of solute carried by the feed solution which is rejected by the membrane material:

$$R = 1 - T = 1 - \frac{c_P}{c_0} \qquad (4.23)$$

4.2.2.4.2 Cleaning efficiency indices

Cleanliness is usually assessed based on indirect indices, such as composition, appearance and smell of final rinse water, water flux, or flux and quality of the final product in a subsequent run. Overall, membrane cleaning efficiency is most commonly assessed by a comparison of the

hydraulic resistance of the membrane (R_{wc}), evaluated after a cleaning step or cycle, and the intrinsic membrane resistance (R_M), i.e., the initial hydraulic resistance of the unfouled membrane, according to Eq. 4.26. This index is known as cleaning efficiency (E_C). The membrane is assumed to be completely clean if its E_C value is less than 0.067 (Argüello *et al.*, 2003):

$$E_C = \frac{R_{wc} - R_M}{R_M} \tag{4.24}$$

The difference between the hydraulic resistance of the membrane after cleaning and the intrinsic membrane resistance is known as residual resistance, according to Eq. 4.25:

$$R_{rs} = R_{wc} - R_M \tag{4.25}$$

The ratio between both resistances is known as Flux Recovery (FR) (Blanpain-Avet *et al.*, 2004), which is usually expressed as a percentage, according to Eq. 4.26:

$$FR = \frac{R_M}{R_{wc}} \cdot 100 \tag{4.26}$$

4.2.3 Analytic methods

4.2.3.1 Characterisation of the wastewater

Wastewaters were characterised by performing the analytical methods already described in chapter 3: moisture content (105ºC), ash (550ºC), protein (Kjeldahl), lipids (NRM) and chemical oxygen demand (Open Reflux Method).

4.2.3.2 Soluble protein determination by the BCA method.

The concentration of protein in the permeate samples is supposed to be very low to be precisely determined by the standard Kjeldahl method. The overall amount of protein in the filtrate was determined employing the BCA method (Smith *et al.*, 1985).

a) **Principle**. Under alkaline conditions, the proteins can reduce the cupric ions Cu^{2+} to form cuprous ions Cu^{+}. The latter undergoes a complexation reaction with the Bicinchonicic Acid

(BCA), which results in the development of an intense purple colour with an absorbance maximum at 562 nm. The absorbance at 562 nm of the Cu(I)-(bicinchoninate) complex is directly proportional to protein concentration.

b) **Procedure**. A standard curve was prepared comprising a series of dilutions (0, 1, 2.5, 5, 10, and 20 µg/100 µL) of Bovine Serum Albumine (BSA). The permeate samples were diluted such that they would fall within the BSA standard range (0-25 µg / 100 µl). The standards and samples were prepared in triplicate and transferred to the microplate, 100 µl of the BCA™ working reagent was added to each well and mixed thoroughly with repeated pipeting. The working reagent is prepared by mixing 25 parts of the BCA™ reagent A (tartrate in alkaline carbonate buffer) with 24 parts of the reagent B (4% BCA in water) and 1 part of reagent C (4% $CuSO_4.5H_2O$ in water). The mixture was then incubated at 37ºC for 30 minutes to develop the colour. The microplate was then placed in a spectrophotometer microplate reader (Anthos Labtec HT3, Salzburg, Austria) set at 562 nm. The absorbance was read and related to the protein concentration by means of the standard curve regression.

4.2.3.3 Molecular profiles

a) **Principle**. Molecular size distribution of the species (mainly proteins) contained in the raw press liquor, filtered liquor and permeate and retentate samples, was obtained by means of a Gel Filtration Chromatography (GFC). Gel filtration is the mildest and simplest of all the chromatography techniques. It separates molecules on the basis of differences in their molecular size, as they pass through a gel filtration medium packed in a column. The medium is a porous matrix in the form of spherical particles than have been chosen for their physical stability and chemical inertness, packed into a column to form a packed bed. The void volume between the particles is filled with a buffer, referred to as mobile phase. The mobile phase passes continuously through the column, carrying the sample. Those sample molecules that are larger than the pores of the matrix are unable to diffuse into the pores and leave the column rapidly, while small molecules diffuse into the pores and are delayed into their passage down the column (Skoog *et al.*, 2006). Larger molecules will be firstly detected after leaving the column, followed by smaller molecules in decreasing order of their size.

b) **Procedure**. The molecular weight distribution of peptides in the hydrolysates was analyzed by gel filtration chromatography. The molecular weight fractions were separated using a high

performance liquid chromatography (HPLC) system equipped with a size exclusion column (Superdex peptide 10/300GL). The mobile phase consisted of water with trifluoroacetic 0.1% and acetonitrile 0.5% (70:30), the flow rate was 0.5ml/min. The chromatography was monitored by measuring the absorbance at 214 nm. The column was calibrated with standards: Ribonuclease A (13700 Da), Aprotinin (6500 Da), Renin (1760 Da), Vasopressine (1084 Da) and Leucine (294 Da). The molecular weight ranges of the different fractions were based on the retention times of the collected fractions and determined from a standards curve.

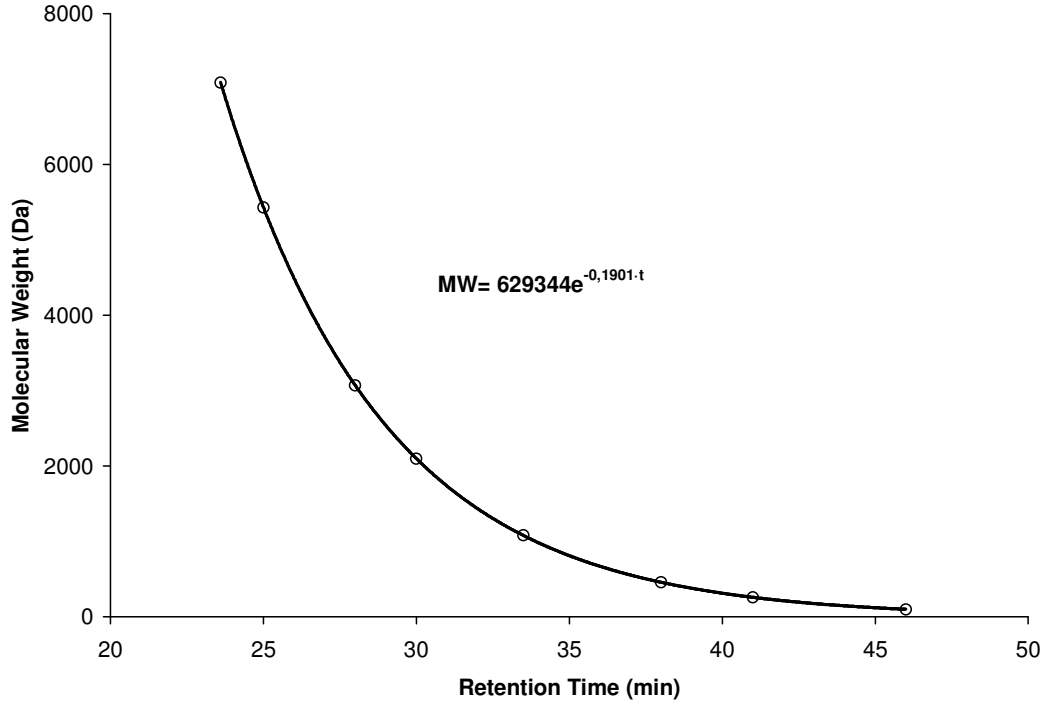

Figure 4.12. Calibration curve for a size fractionation between 100 and 7000 Da.

4.3 RESULTS AND DISCUSSION

4.3.1 Filtration pre-treatment

4.3.1.1 Pressure drop through the filter cartridges

The water pressure drop through both filter cartridges was determined by pumping a variable flow of MilliQ^{TM} at a variable volumetric flow, and measuring the pressure drop, as shown in Table 4.12. In order to evaluate the pressure drop through the filter element, two analogical manometers were placed at the inlet and outlet pipes. The pressure drop through a horizontal filter element will be proportional to the volumetric flow passing through the element and a friction factor, according to the Fanning's equation:

$$\frac{P_{inlet} - P_{outlet}}{\rho_{H_2O}} = k \cdot Q^2 \qquad (4.27)$$

where Pinlet and Poutlet refer, respectively, to the pressure measured at the inlet and outlet, respectively, ρ_{H2O} is the density of water at the work temperature, k is a constant depending on the friction factor and the geometry of the filter element, and Q is the fluid volumetric flow through the filter element.

Table 4.12. Pressure drop of water through the filter cartridges of 465μm and 250 μm rating size.

Q (L/min)	$\Delta P_{465\mu m}$ (bar)	$\Delta P_{250\mu m}$ (bar)
4.99	0.09	0.10
6.35	0.15	0.15
7.71	0.24	0.28
9.07	0.31	0.34
10.42	0.37	0.43

The Figure 4.13 shows a good correlation between the pressure drop and the water volumetric flow, with correlation coefficients $R^2 = 0.9748$ for the 465 μm filter cartridge and $R^2 = 0.9756$ for

that of 250 µm rating size. The slope of the line corresponds to the value of k, which depends on the friction factor and it is inversely proportional to the hydraulic diameter of the filter pores (i.e. the smaller the pore size, the highest is the hydraulic resistance). It is logical that the slope k for the 250 µm filter cartridge will be higher than that for the 465 µm (4.1 10^{-3} bar $(L/min)^{-2}$ against 3.6 10^{-3} bar $(L/min)^{-2}$, respectively).

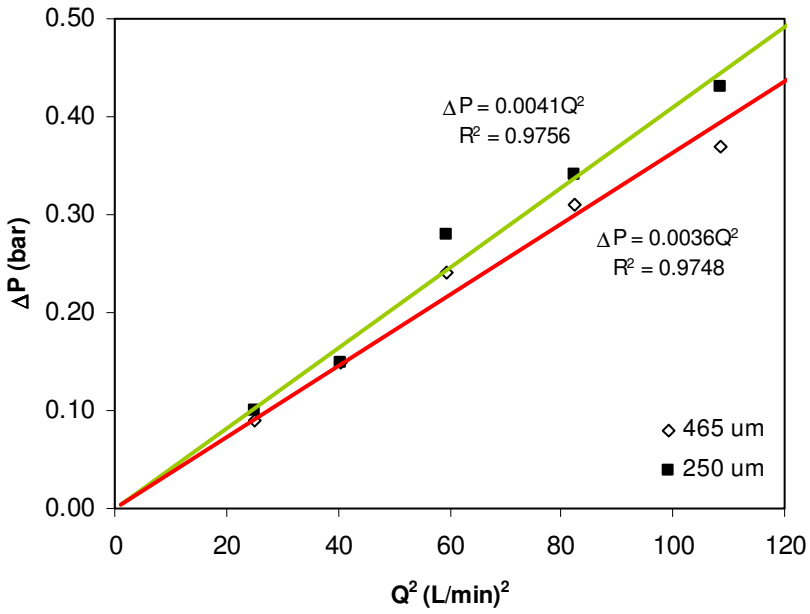

Figure 4.13. Relationship between the pressure drop and the water volumetric flow for the filter cartridges of 465 µm and 250 µm rating size.

When the press juice from the compacting operation passes through the filter elements, the solid particles are retained on the filter surface and within the filter media, partially blocking the filter pores, increasing the hydraulic resistance to the fluid passage. A similar test than that described above was performed on the press liquor, as shown in table 4.13. The correlation between the pressure drop and the volumetric flown was found to be good, with correlation coefficients R^2 =0.9646 and R^2=0.9929, for the 465 µm and 250 µm filter cartridges, respectively. With regard to the k value, the figure 4.14 shows that hydraulic resistance offered by the 250 µm filter cartridge is higher than that of the 465 µm rating size, as observed for the water flow. However, the difference between both slopes are more marked for the press liquor, since k for the 465 µm filter cartridge was similar to that obtained for water , while the slope for the 250 µm filter cartridge increased from $4.1 \cdot 10^{-3}$ bar $(L/min)^{-2}$ to $4.6 \cdot 10^{-3}$ bar $(L/min)^{-2}$. The 465 µm filter element does not provide a marked resistance to the passage of press liquor particles, only the suspended

particles of higher size could be retained for that filter, while the bulk fluid and most of the fine particles will pass through the filter media without any resistance.

Table 4.13. Pressure drop of the press liquor through the filter cartridges of 465µm and 250 µm rating size.

Q (L/min)	$\Delta P_{465\mu m}$ (bar)	$\Delta P_{250\mu m}$ (bar)
4.99	0.09	0.09
6.35	0.13	0.19
7.71	0.26	0.28
9.07	0.32	0.37
10.42	0.39	0.50

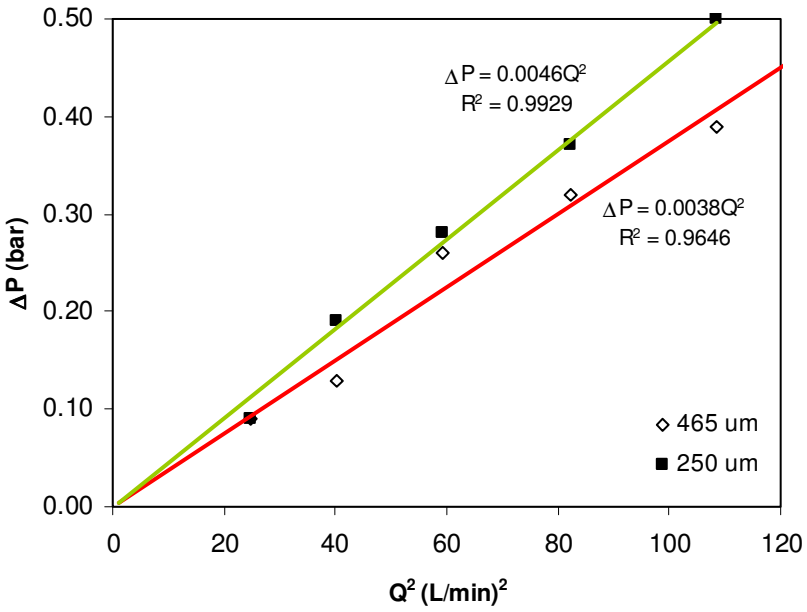

Figure 4.14. Relationship between the pressure drop and the volumetric flow of press juice for the filter cartridges of 465 µm and 250 µm rating size.

The 11% increase in the friction factor for the second filter cartridge may indicate higher particle retention, resulting in higher resistance to the passage of press juice through the filter medium. It is assumed that the pressure drop through the filter medium will increase in the course of time, as more particles will be retained on the filtering surface. This increase in the pressure drop must be controlled. If the maximum pressure tolerance of the filter is exceeded, the particulate retention of

that element rapidly declines, suggesting filter replacement. These results are summarised in the table 4.14.

Table 4.14. Comparison between the values of the friction factor k for both filter cartridges.

Filter cartridge Rating size (μm)	$k \cdot 10^3$ (bar· min^2/L^2) Water	$k \cdot 10^3$ (bar· min^2/L^2) Press liquor
465	3.6	3.8
250	4.1	4.6

4.3.1.2 Biochemical Analysis of the press liquor

The proximate composition of the press liquor, in terms of water, ash, protein and lipid content, was determined after passing the press liquor through each filter element at a low volumetric flow (5 L/min) to avoid the exhausting of the filter media. It was compared to the average composition of the raw press liquor before filtration, as shown in table 4.15.

Table 4.15. Biochemical composition (w/w) of the raw and filtered liquor.

Sample	Water (%)	Ash (%)	Proteins (%)	Lipids (%)	Overall (%)
Raw liquor	90.75 ± 0.02	0.70 ± 0.16	7.23 ± 0.14	1.20 ± 0.12	99.88 ± 0.06
465 μm	90.84 ± 0.03	0.76 ± 0.10	6.31 ± 0.07	1.25 ± 0.10	99.06 ± 0.04
250 μm	90.95 ± 0.01	0.77 ± 0.10	4.41 ± 0.03	1.43 ± 0.17	97.29 ± 0.04

The amounts of ash and lipids in the filtered liquids did not differ significantly from that determined for the raw press liquor, which may indicate that these compounds are not retained by the filter media, although their presence in the press liquor is very low to obtain a conclusion. With respect to the amount of total protein (determined by the Kjieldahl method) on the raw and filtered press waters, it decreases from 7.23 % w/w to 4.41% w/w.

It can be concluded that the particles retained by the filter media are mostly made up of proteins, originating from the flesh tissue disruption under the pressing treatment. These results can be expressed as percentage protein removal (%), according to the equation:

$$\%PR=\frac{m_{P(i-1)}-m_{P(i)}}{m_{P(i-1)}}\cdot 100 \qquad (4.28)$$

Where $m_{P(i-1)}$ and $m_{P(i)}$ refer to the amount of protein in the wastewater before and after the i-th filtration stage. As shown in figure 4.15., the filtration pre-treatment involves an overall 42.74 % protein removal, mostly attributed to the 250 µm filtration stage (33.33%).

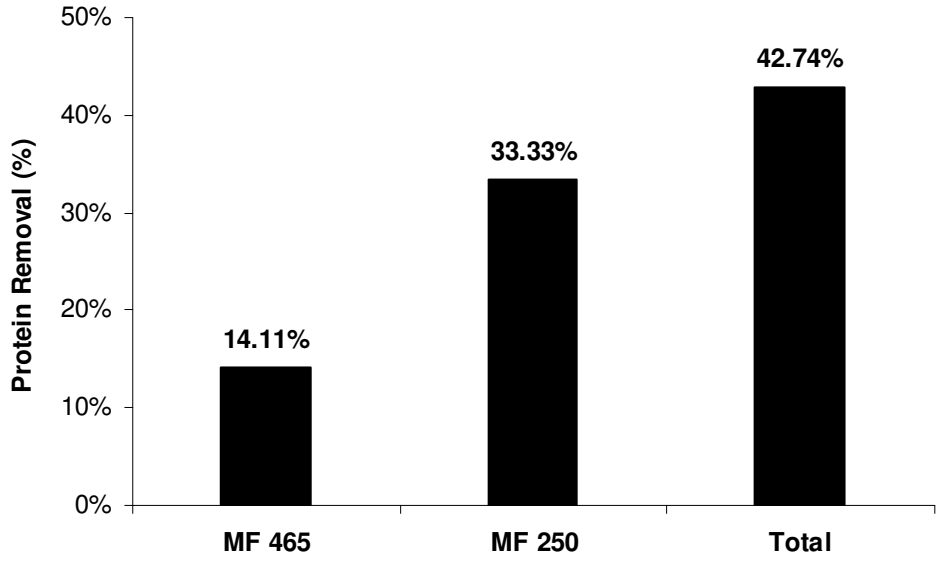

Figure 4.15. Protein removal after each filtration stage and for the overall pre-treatment.

An important index on the filter cartridge performance is the particle removal. This parameter was determined by determining the amount of suspended solids (residue after centrifugation at 10 000 x *g* and 15 min) for the raw and pre-filtered liquid.

Table 4.16. Particulate and COD removal for the raw and filtered liquor.

Sample	Suspended solids (%)	Particulate removal (%)	COD (mg O_2/L)	COD removal (%)
Raw liquor	13.46 ± 0.58	-	125 000	-
465 µm	12.01 ± 0.43	10.80	122 500	2.00
250 µm	9.65 ± 0.85	19.66	118 000	3.67
Overall 465 µm + 250 µm		**28.34**		**5.60**

Besides this, the average COD was determined for the raw press liquor, and the 465 μm and 250 μm filtered liquid. These results are shown in table 4.16. From these values it can be evaluated the particle and COD removal, in the same way that the protein removal was calculated with the equation 4.28.

From the table 4.16, it can be concluded that the overall 465 μm + 250 μm filtration treatments removed more than 28% of the suspended particles of the feed solution. The second cartridge, with filter rating 250 μm was more effective than the first, due to its lower rating size, although the first is also necessary in order to prevent large particles to exhaust the filter medium. Considering the intermediate particulate removals, it can be concluded that the 250 μm filter posses a contaminant holding capacity which is almost twice than that observed for the filter of 465 μm. In terms of COD, only a 5.6% decrease was achieved by the whole treatment, which indicates that most of the oxidising species are present in the form of soluble compounds, dissolved in the press liquor.

4.3.1.3 Molecular profiles for the raw and pre-filtered liquor.

Molecular size distribution of the species (mainly proteins) contained in the raw press liquor, filtered liquor and permeate and retentate samples, was obtained by means of a Gel Filtration Chromatography (GFC).

The molecular profile shows an average low molecular weight for all the species present in the press juice. This is in contrast with the results reported by Bechtel (2005), which performed gel electrophoresis to stickwaters from fish meal production process. The samples presented marked bands which corresponded to calculated molecular weights of 198, 120 and 39 kDa, while in our case only 18% of the peptides had molecular sizes larger than 7 kDa. These results may indicate that the press liquor had undergone rapid protein degradation, due to the exposure of the soluble or suspended proteins to the digestive enzymes contained in the fish viscera. Taking into account the composition of the raw material, which consisted of a mixture of sardine heads, viscera and fishbones, the pressing operation may favoured the release of autolytic enzymes present in the fish viscera particularly cathepsins and proteases, which are active between -10ºC and 60ºC (Mukundan *et al.*, 1986).

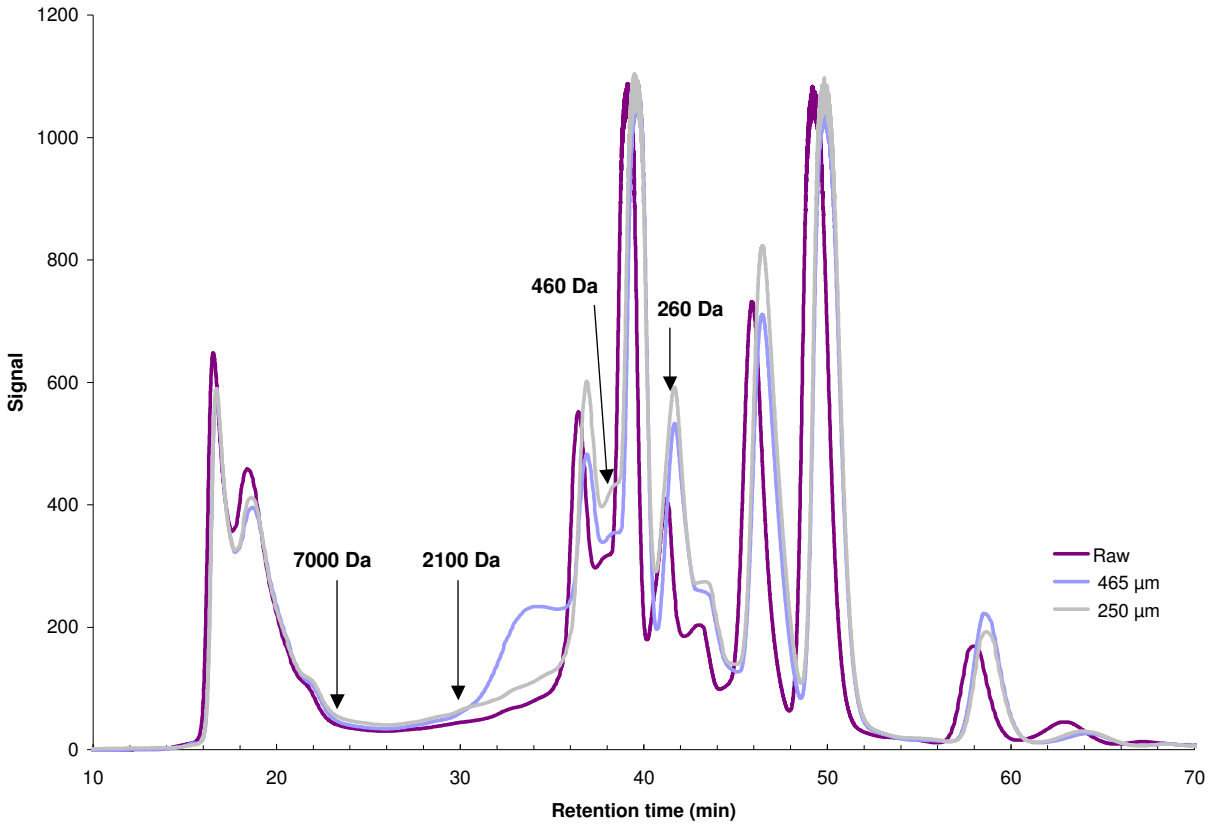

Figure 4.16. Molecular weight profiles for the raw and pre-filtered press liquor.

The evisceration of fish, followed by the tissue disruption after the pressing processes can be assumed to be responsible for the rapid degradation of the protein content of the press juice. According to the table 4.18, the filter element of 465 µm retains 13% of the high molecular species over 7.2 kDa, while the resulting filtered liquid is enriched in the peptides of molecular size under this value. This causes the profile peaks corresponding to the 465 µm and 250 µm to shift to the right, related to the molecular profile of the raw liquor. The molecular profiles for both 465 µm and 250 µm present the main peaks at coincident times.

According to the table 4.18, both prefiltered liquids presented similar concentration on the different peptide classes, although the molecular profile for the 250 µm treatment presented higher abundance of peptides between 2100 and 5400 Da, as well as those lower than 260 Da. In conclusion, the filtration treatment reduces slightly (13%) the proportion of high molecular weight species (mostly proteins making up the suspended particles), while it does not alter the content of low molecular species resulting from the autolysis reactions.

Table 4.17. Size-distribution of the different fractions present in the raw and filtered liquor (proportion of each fraction in w/w%).

Filtration Stage	Molecular Weight (Da)				
	> 7200	7200 - 5400	5400 - 2100	2100 - 260	< 260
Raw liquid	17.75	0.46	1.54	25.71	54.39
465 µm	15.41	0.49	1.73	29.87	52.27
250 µm	15.27	0.56	1.94	27.66	54.54

4.3.2 Membrane assays in total recirculation mode

The performance of three Membralox^{TM} ceramic membranes of average pore size 50 nm , 200 nm and 1.4 µm pore size was tested, in terms of permeate flux, protein rejection, COD removal and restoration of the water flux after a complete cleaning protocol.

4.3.2.1 Membrane permeability and optimum transmembrane pressure

The intrinsic resistance R_M was calculated as the slope of the regression line for the data of flux (J) against the transmembrane pressure (TMP), as shown in the figures 4.17- 4.19.

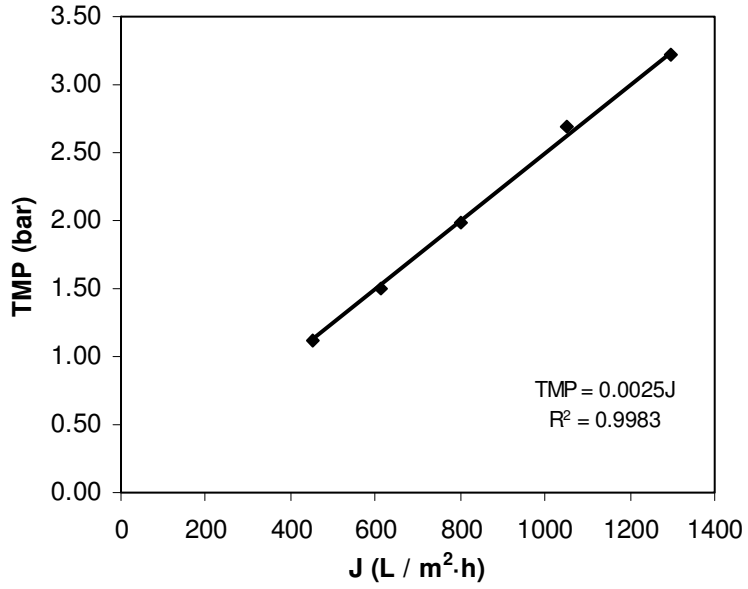

Figure 4.17. Determination of R_M for the 50 nm Membralox^{TM} membrane.

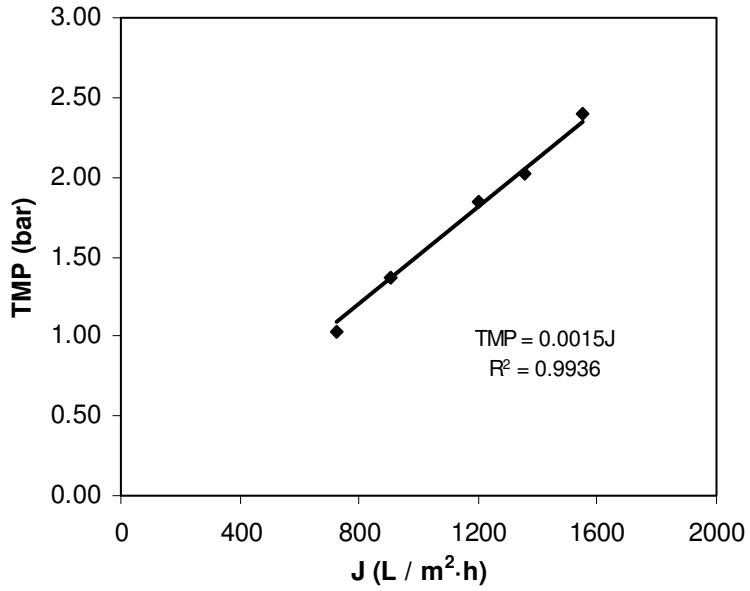

Figure 4.18. Determination of R_M for the 200 nm Membralox™ membrane.

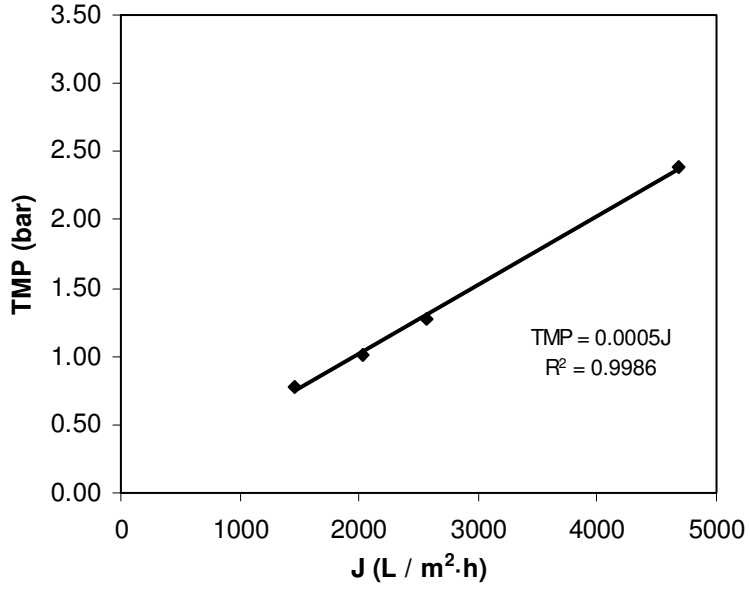

Figure 4.19. Determination of R_M for the 1.4 µm Membralox™ membrane.

Once the water permeability of the membrane was determined, a similar test was performed on the press juice. It was passed through the membrane with recycle of both permeate and retentate to the feed tank. The permeate flux was determined for a number of different transmembrane pressures, as shown in the figures 4.20-4.22. The transmembrane pressure is set by acting on the

backpressure retentate valve. The minimum pressure achievable with the valve fully opened was 1.19 bar.

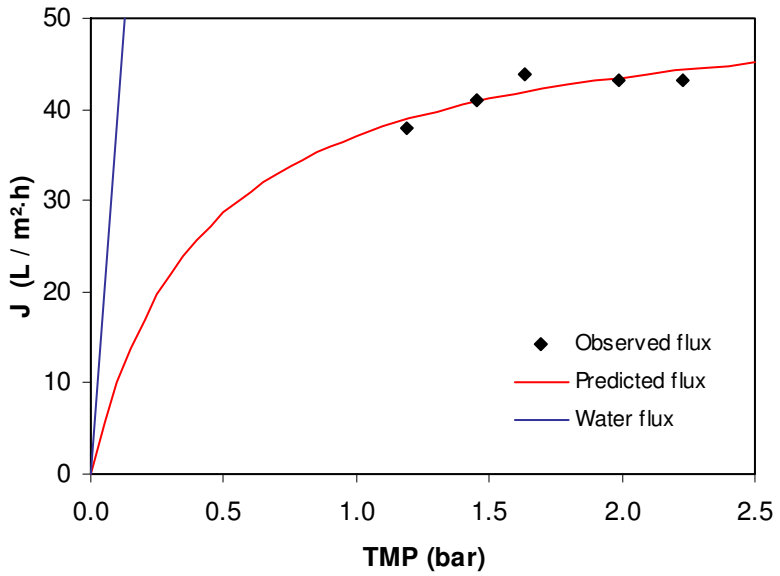

Figure 4.20. Relationship between the initial flux of press liquor and the applied transmembrane pressure for the 50 nm Membralox™ membrane.

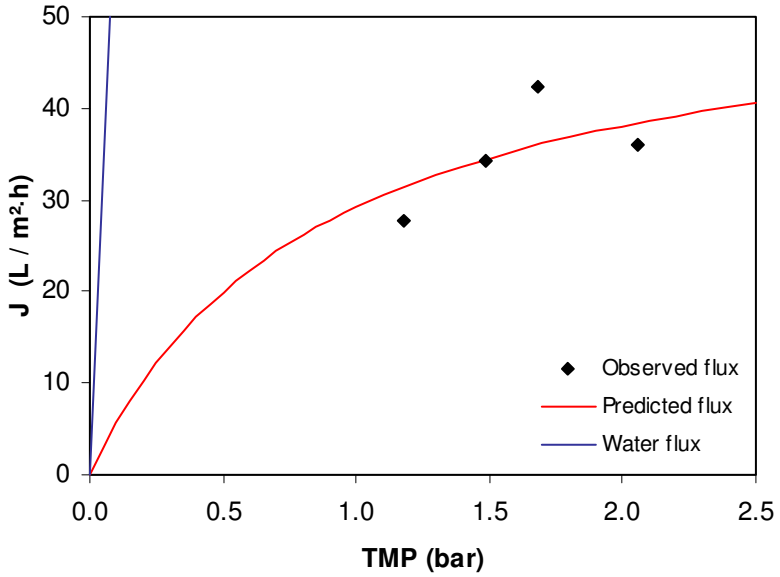

Figure 4.21. Relationship between the initial flux of press liquor and the applied transmembrane pressure for the 200 nm Membralox™ membrane.

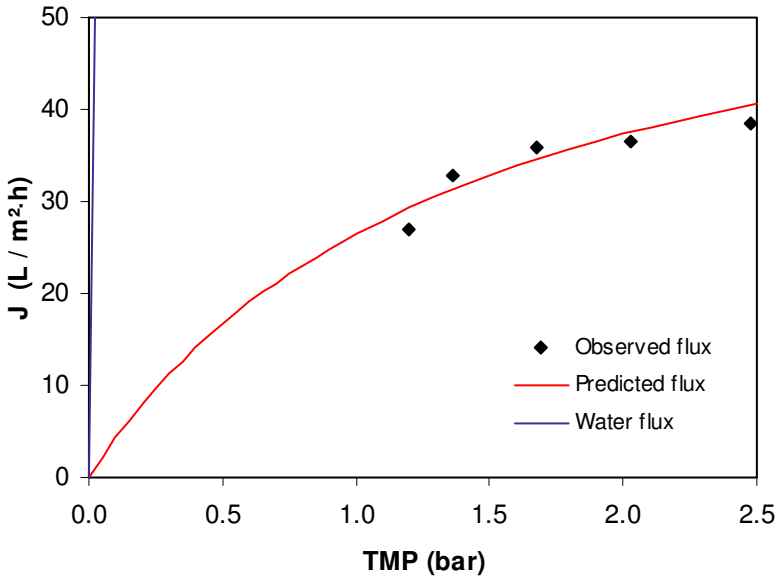

Figure 4.22. Relationship between the initial flux of press liquor and the applied transmembrane pressure for the 1.4 µm Membralox™ membrane.

The relationship between the permeate flux and the transmembrane pressure can be fitted to a series resistance model, according to the equation 4.16:

$$J = \frac{\Delta P_m}{a + b \cdot \Delta P_m} \qquad (4.27)$$

This relationship is represented by the dotted curves in the figure 4.20-4.22, which are compared to the water flux J_w (solid straight line).

According to the values of *a* and *b* (Eq. 4.29), the calibration curves undergo an initial steep ascent, with slope 1/a (Eq. 4.17) to rapidly attain a plateau corresponding to the maximum value achieved by the initial flux Jmax =1/b (Eq. 4.18). The optimum transmembrane pressure,will be the quotient between *a* and *b*, according to the equation 4.19. All these values are summarised in the table 4.18.

Table 4.18. Parameters obtained after calibration with water and feed solution for the three assayed membranes.

Membrane	R_M (bar·m2·h/L)	a (bar·m2·h/L)	b (m2·h/L)	Initial Slope L/(m^2·h·bar)	J_{max} L/(m^2·h)	ΔP_{opt} (bar)
50 nm	$2.50 \cdot 10^{-3}$	$7.97 \cdot 10^{-3}$	$1.90 \cdot 10^{-2}$	125.47	52.63	0.42
200 nm	$1.52 \cdot 10^{-3}$	$1.59 \cdot 10^{-2}$	$1.83 \cdot 10^{-2}$	62.89	54.70	0.87
1.4µm	$5.04 \cdot 10^{-4}$	$2.22 \cdot 10^{-2}$	$1.58 \cdot 10^{-2}$	44.82	63.29	1.41

From the previous results, it can be concluded that:

- Compared to the series resistance model (Eq. 4.2), the value of *a* corresponds to the hydraulic resistance provided by the feed solution. This value is many times higher than that provided by the clean water (R_M). Even if the pore size is higher, the value of a for the 1.4 um membrane is nearly 400 times higher than its intrinsic membrane, much larger than the difference observed for the 50 nm and 200 nm. This anomaly can be explained assuming that the filtration area decreases rapidly due to internal pore blocking of small solutes which are adsorbed on the pore wall.

- With respect to the parameter b, which stands for the gel layer resistance (Eq. 4.2), there is no significant difference between the three membranes.

- For the chosen crossflow velocity, the minimum pressure achievable when the valve is fully opened will be 1.19 bar. Due to practical reasons, the work transmembrane pressure was set at 1.5 bar for the three membranes. This pressure is close to the recommended value for the 1.4 um membrane, but higher than that recommended for the other membranes, i.e., placed in the mass-controlled transfer zone. It was assumed that the gel layer was not fully developed at this pressure, although the concentration polarisation effects cannot be neglected during the operation.

4.3.2.2 Membrane UF/MF in total recirculation mode

Once the membrane intrinsic resistance was determined and the working pressure was chosen, the feed solution was ultrafiltered during three hours, during which both permeate and retentate

streams were recycled to the feed tank. The flux permeate was measured every 10 min, according to the equation 4.13. The figure 4.23 shows the evolution of the permeate flux in the course of time for the three membranes: the permeate flux undergoes a steep descent during the first 30-50 minutes, attributed to the rapid blocking of the membrane pores by the feed solutes and the developing of a concentration-polarisation layer. Then the permeate flux decrease at a lower rate, reaching a steady state where the permeate flux remains constant in time.

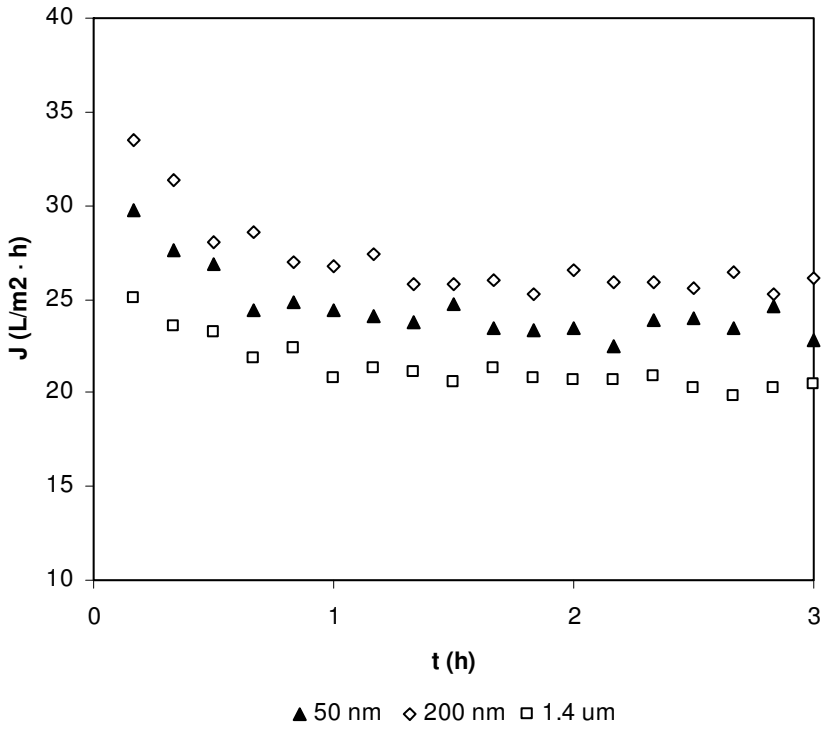

Figure 4.23. Evolution of the permeate flux during a 3 h total recirculation assay for the membrane of 50 nm Membralox^{TM} membrane.

The decline in the permeate flux is occasioned by the deposition of foulant macrosolutes on the membrane surface or inside the internal pore structure. Depending on the relative size between the pore and the foulant particle, the predominant fouling mechanism will different. When the complete pore blocking or the inner pore constrictions are predominant, the total hydraulic resistance increases with time with an increasing slope (Tracey and Davis, 1994). If the foulant particles are larger than the pore size, they are rejected and tend to accumulate on the membrane surface building up a cake layer. In this case, unlike the internal fouling models, the total membrane resistance increases with time with a decreasing slope (Tracy and Davis, 1994). An initial plot of the total resistance R_T as a function of time (figure 4.24) can give an initial

approximation of which fouling mechanism is predominant for each membrane. The total resistance can be calculated directly from the experimental data as the quotient $J/\Delta P_m$.

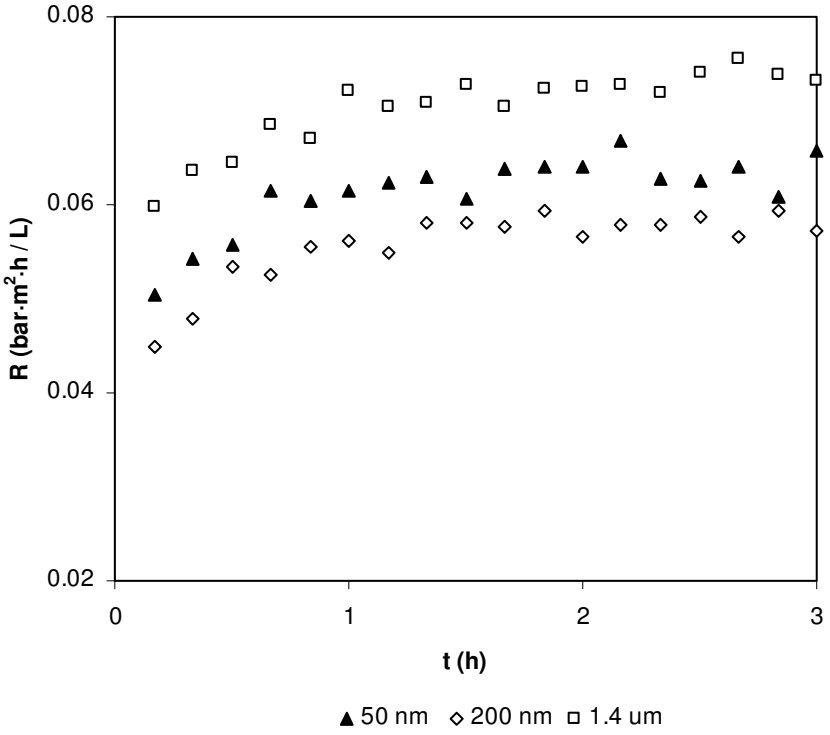

Figure 4.24. Total Resistance as a function of time for the three membranes assayed.

The figure 4.24 shows the evolution of the total resistance in the course of time. It can be observed that the total resistance increases in time with a decreasing slope, reaching a steady value after 30 – 50 minutes, depending on the pore size. This may indicate that the predominant fouling mechanism is the cake formation. While in dead-end ultrafiltration/microfiltration the total resistance increases continuously in time, the cross-flow filtration presents a characteristic final steady state, as mentioned before.

A cake forming-based model was chosen to predict the flux decline during the ultrafiltration.The Suki model assumes that the mass of deposited particles (cake) increases in time following a first order kinetics. However, this increase is limited to a maximum deposited mass, M*, where the build-up of the cake layer and the removal of deposited particles by the tangential flow are balanced (Suki *et al.*, 1984). This model predicts a flux decline during the filtration operation governed by the equation 4.28:

$$J = \frac{\Delta P}{R_M + R_B + R_{F\infty}\left(1 - e^{-k \cdot t}\right)} = \frac{J_0}{1 + \left(\frac{J_0 - J_\infty}{J_\infty}\right)\left(1 - e^{-k \cdot t}\right)} \qquad (4.28)$$

The figure 4.25 shows the fitting of the experimental data to the Suki's model. The correlation between the observed data and the predicted model was very good. The Suki's model predicts a steep initial flux decline, followed by a stabilisation zone where the permeate flux decreases at decreasing rate until attaining a steady value J_∞.

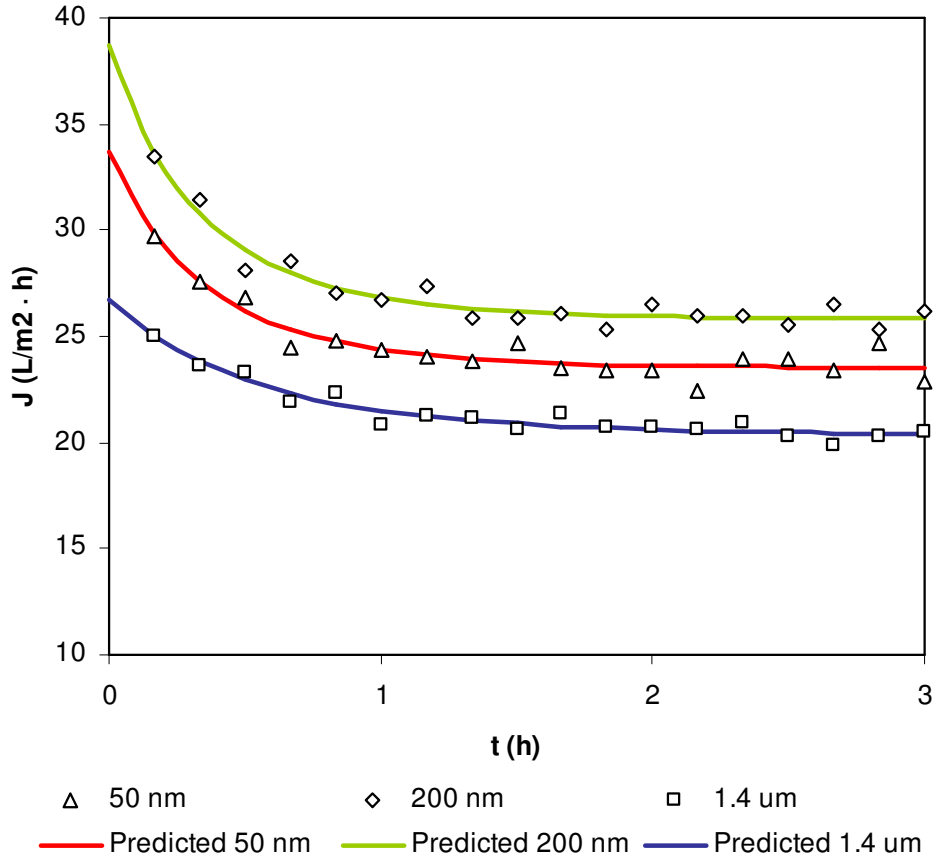

Figure 4.25. Comparison of the experimental data and the permeate flux predicted by the Suki's fouling model.

The table 4.19 compares the different values of the Suki's model parameters obtained by non-linear regression of the experimental data.

Table 4.19. Comparison of the estimated parameters of the Suki's fouling model.

Membrane	J_0 L/(m^2·h)	J_∞ L/(m^2·h)	k (h^{-1})	$R_{F\infty}$ (bar·m^2·h/L)	$R_M + R_B$ (bar·m^2·h/L)
50 nm	33.69	23.50	2.15	$1.93 \cdot 10^{-2}$	$4.45 \cdot 10^{-2}$
200 nm	38.74	25.82	2.20	$1.94 \cdot 10^{-2}$	$3.87 \cdot 10^{-2}$
1.4 μm	26.69	20.35	1.50	$1.75 \cdot 10^{-2}$	$5.62 \cdot 10^{-2}$

After comparing these parameters, some conclusions can be made:

(1). The initial permeate flux predicted for the 50 nm membrane is more reasonable than that observed from the calibration curve with the press liquor (fig. 4.20), which was 41.14 L/(m^2·h) at 1.5 bar. This discrepancy between the observed and expected flux might be attributed to a deficient temperature control during the calibration of the 50 nm membrane.

(2). The values of the parameters controlling the cake build-up (k and $R_{F\infty}$) are similar for both zirconite membranes, independently of the pore size. In contrast, the values for the initial membrane resistance ($R_M + R_B$) were different. This resistance is the result of two contributions, the hydraulic resistance provided by the membrane material (parameter *a*) and that provided by the gel layer, which is pressure-dependent (parameter *b*). The first resistance is a function of the average pore size (it decreases as the pore diameter is larger), while the second resistance is similar for both membranes at the same transmembrane pressure. The difference between the permeate flux observed for both membranes only depends on their average pore size.

(3). It must be stressed that the average permeate flux obtained for the membrane of 1.4 μm is lower than that obtained for the other membranes of lower molecular cut-off, which was unexpected. The reason for the lower permeate flux can only be found in the lower value of the initial flux J_0, since the fouling resistance increased in the course of the operation at a lower rate than that observed for the zirconia membranes, with lower values for the kinetic parameters k and $R_{F\infty}$. This can be attributed to the different material of the active layer and its larger pore size.

The active filtration layer for the membrane of 1.4 μm is made of α-alumina, instead of zirconia. In ceramic materials, the surface is covered by hydroxyl species (M-OH), where M is a metal such as Si or Al. These species are partially ionised depending on the pH of the feed solution. The point of zero charge (pzc) is the pH at which the surface carries no net electrical charge. At pHs above point of zero charge, the negative charged species are predominant; otherwise the

ionisation equilibrium is displaced towards the formation of $M\text{-}OH_2^+$ species. The isoelectric point for the alpha alumina oxides is 8 – 9 (Brunelle, 1978), while zirconium oxide membranes present a point of zero charge close to neutrality (Kosmulski, 2001). This determines that the membrane surface for the 1.4 μm will carry a net charge when the raw pre-filtered liquor (pH 6.8 – 7.2) is filtered. This charge distribution is responsible for the adsorption or repulsion of fouling solutes (mostly proteins) on the membrane surface or on the pore walls, which could explain the differences between the permeate flux and protein transmission. Added to this, its large pore size favours the deposition of foulant particles within the pores, reducing the filtration area.

This assumption was confirmed by other study found in the literature. Carić *et al.* (2000) studied the static adsorption of whey proteins on ceramic membranes, comparing a 50 nm pore size zirconia membrane with a 200 nm alumina membrane. He found that the rate of adsorption of proteins on the membrane surface was higher for the alumina membrane, while in 50 nm zirconia membranes the hydraulic resistance was controlled by the cake formation.

4.3.2.3 Cleaning treatment

Once the 3-hour ultrafiltration was finished, the membrane was cleaned following the cleaning protocol described in the section 4.2.2.3.5 of this chapter. After each chemical cleaning stage, the membrane was rinsed with MilliQ^{TM} water until neutrality in the permeate stream, and the hydraulic resistance was determined. These results can be plotted in a flux (J) against transmembrane pressure (TMP) representation, (figures 4.26-4.28) , where the experimental data are fitted to a straight line passing through the origin of coordinates.

The inverse of the slope of each line corresponds to the hydraulic resistance, evaluated after each treatment. From this representation, it can noticed that the permeability of the fouled membrane corresponds to the lowest slope, and increases after each cleaning stage until attaining a final slope close to the membrane initial permeability. This means that the three-stage cleaning treatment assayed is able to recover the initial water permeability of the membranes.

The efficiency of each cleaning stage can be evaluated by means of the efficiency index (%E) and Flux Recovery index (%FR). These indices are summarised in the table 4.19, as well the total (R_T) and fouling (R_F) resistances after each cleaning stage. The overall residual resistance (R_{rs}), was calculated as the remaining resistance after the complete cleaning treatment, i.e., the

difference between the membrane intrinsic resistance and the hydraulic resistance after the disinfection treatment with Sodium Hypochlorite.

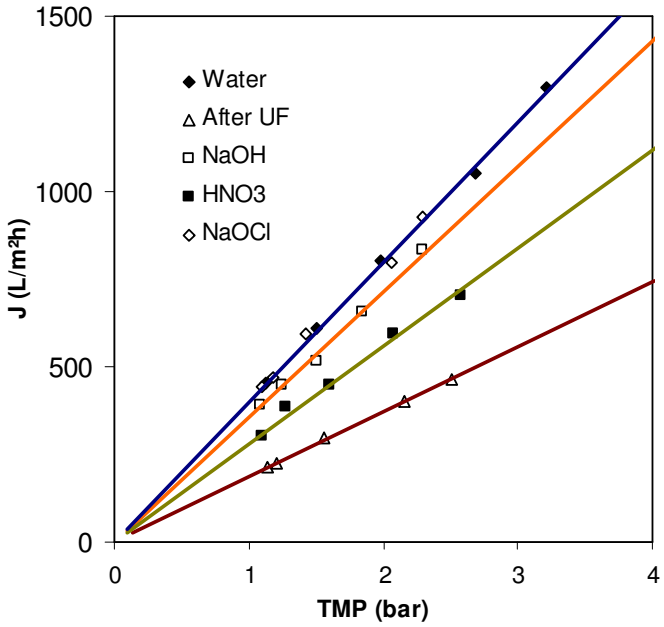

Figure 4.26. Evolution of the hydraulic resistance during the cleaning cycle for the 50 nm Membralox™ membrane.

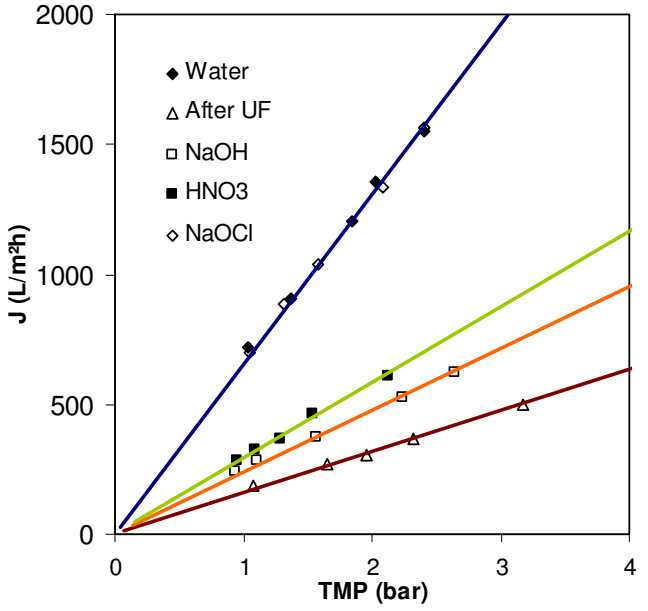

Figure 4.27. Evolution of the hydraulic resistance during the cleaning cycle for the 200 nm Membralox™ membrane.

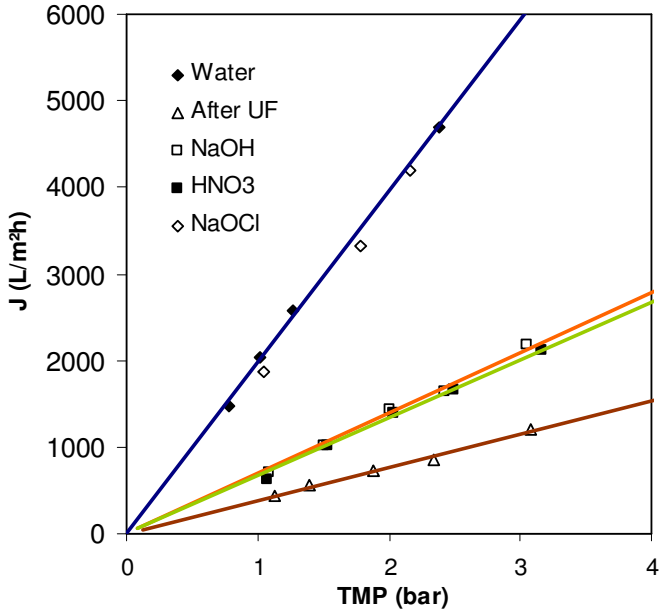

Figure 4.28. Evolution of the hydraulic resistance during the cleaning cycle for the 1.4 µm Membralox™ membrane.

Table 4.20. Hydraulic resistances and cleaning efficiency indices for the three membranes.

Membrane	Cleaning Stage	R_T (bar·m²·h/L)	R_F (bar·m²·h/L)	%E	%FR	R_{rs} (bar·m²·h/L)
50 nm	Clean	$2.50 \cdot 10^{-3}$	-	-	-	-
	After UF	$5.37 \cdot 10^{-3}$	$2.87 \cdot 10^{-3}$	-	-	-
	NaOH	$2.80 \cdot 10^{-3}$	$2.95 \cdot 10^{-3}$	89.72%	89.45%	-
	HNO_3	$3.56 \cdot 10^{-3}$	$1.06 \cdot 10^{-3}$	-26.66%	70.22%	-
	NaOCl	$2.49 \cdot 10^{-3}$	$6 \cdot 10^{-6}$	37.14%	100.24%	-
	Overall	-	-	100.21%	100.24%	$-6.00 \cdot 10^{-6}$
200 nm	Clean	$1.52 \cdot 10^{-3}$	-	-	-	-
	After UF	$6.31 \cdot 10^{-3}$	$4.79 \cdot 10^{-3}$	-	-	-
	NaOH	$4.20 \cdot 10^{-3}$	$2.68 \cdot 10^{-3}$	44.05%	36.19%	-
	HNO_3	$3.43 \cdot 10^{-3}$	$1.91 \cdot 10^{-3}$	16.08%	44.31%	-
	NaOCl	$1.53 \cdot 10^{-3}$	$1.00 \cdot 10^{-5}$	39.67%	99.35%	-
	Overall	-	-	99.79%	99.35%	$1.00 \cdot 10^{-5}$
1.4 µm	Clean	$5.10 \cdot 10^{-4}$	-	-	-	-
	After UF	$2.61 \cdot 10^{-3}$	$2.10 \cdot 10^{-3}$	-	-	-
	NaOH	$1.50 \cdot 10^{-3}$	$9.90 \cdot 10^{-4}$	52.86%	34.00%	-
	HNO_3	$1.43 \cdot 10^{-3}$	$9.20 \cdot 10^{-4}$	-3.33%	35.66%	-
	NaOCl	$5.20 \cdot 10^{-4}$	$1.00 \cdot 10^{-5}$	43.33%	98.08%	-
	Overall	-	-	99.52%	98.08%	$1.00 \cdot 10^{-5}$

From the figures 4.26-4.28 and the table 4.20 it can be concluded that:

- The three-stage cleaning treatment achieves a complete recovery of the initial water membrane resistance: the hydraulic resistance of the membrane after the cleaning treatment was slightly lower than that evaluated for the membrane before the ultrafiltration, with a cleaning efficiency and flux recovery close to or higher than 100 %.

- The alkali stage restores to a large extent the membrane permeability. An initial cleaning stage with alkali has proved to be very effective since it is able to hydrolyse, solubilise and remove the protein deposits (Bartlett *et al.*, 1995).

- The acid stage exhibited a detrimental effect on the permeability of the 50 nm membrane, since the hydraulic resistance measured after this treatment was 27% higher than that obtained after the alkali stage. For the other membranes, its effect on the water flux recovery was weak, with cleaning efficiencies of 16% and 3%, respectively. These results agree with those reported previously by some authours (Weis and Bird, 2001; Vaïsänen *et al.*, 2002 and Blanpain-Avet *et al.*, 2004). According to Blanpain-Avent *et al.* (2004), this poor cleaning efficiency was likely to be due to physico-chemical interactions between nitric acid and the fouling deposits remaining on the membrane surface after the alkaline cleaning. Vaïsänen *et al.* (2002) assumed that these deposits could form a gel-like structure which is resistant to cleaning. In contrast, Barlett *et al.* (1995) reported that a cleaning stage with 0.3 % w/w HNO_3 improved the results obtained by a previous 0.2% w/w NaOH treatment in ceramic membranes fouled after milk ultrafiltration, since it was able to solubilise and remove the deposits of inorganic salts, such as calcium phosphate.

- The disinfection stage with Sodium Hypochlorite is effective to restore the initial water flux of the membrane. Besides its disinfecting action, due to the release of free Chlorine (Cl_2), the NaOCl can remove the organic material deposited on the membrane surface and within the pores (Cheryan, 1998). This is owed to the oxidation of the organic compounds to other groups, such as aldehydes, ketones or carboxylic acids, which exhibit higher a hydrophilicity and thus, a lower adhesion to the membrane material.

4.3.3 Protein rejection and COD of the permeate

Four samples of permeate were collected after 30 minutes, 1, 2 and 3 hours of total recycle operation. The protein content of the retentate was supposed to remain constant in the course of the operation (44.1 ± 0.3 mg/mL), but not the concentration of proteins in the permeate, due to the fouling phenomena which limits the passage of feed solutes to the permeate stream. The table 4.21 shows the evolution of the protein transmission and protein rejection in the course of the 3-hour filtration. The membrane of 50 nm presented the highest values of protein rejection, with an average protein rejection of 85%. This is in accordance with its lower size, which results in higher solute retention by steric impediments. It is followed by the membrane of 200 nm, whose average protein rejection is 78%. The α-alumina membrane, despite its larger pore size, presented an average protein rejection (77%) similar to that obtained for the membrane of 200 nm. These results agree with the assumption of a higher protein adsorption on the alpha alumina membrane.

Table 4.21. Evolution of the protein content in the permeate during the 3-hour total recirculation assays for the three tested membranes.

Membrane	Time (min)	Feed protein (mg/mL)	Permeate protein (mg/mL)	Protein rejection (%)	Protein transmission (%)
50 nm	30	44.10 ± 0.30	5.90 ± 0.14	86.62%	13.38%
	60		6.57 ± 0.05	85.09%	14.91%
	120		6.60 ± 0.08	85.03%	14.97%
	180		7.01 ± 0.09	84.10%	15.90%
200 nm	30	44.10 ± 0.30	9.86 ± 0.34	77.65%	22.35%
	60		10.41 ± 0.12	76.40%	23.60%
	120		9.63 ± 0.33	78.16%	21.84%
	180		8.71 ± 0.11	80.25%	19.75%
1.4 µm	30	44.10 ± 0.30	10.21 ± 0.1	76.85%	23.15%
	60		10.40 ± 0.22	76.42%	23.58%
	120		10.61 ± 0.11	75.94%	24.06%
	180		9.52 ± 0.20	78.40%	21.60%

Concerning the evolution of the protein rejection in time (figure 4.29), it slightly decreases in time for the membrane of 50 nm. Both 200 nm and 1.4 µm membranes exhibited an initial decrease of the protein rejection and then an increase. These results agree to those of Marshall *et*

al., (1997), who reported an increase in time of the protein transmission during the ultrafiltration of β-globuline with a ceramic membrane of 50 nm and a crossflow velocity of 3 m/s. According to Hilal *et al.* (2005), fouling agents (especially proteins) tend to absorb onto the charged residues situated all across the membrane surface or within the pore walls. As these active points are neutralised by the foulant particles, the free charge of the membrane decreases, decreasing the electrostatic repulsion and then the protein rejection. Once all the free charges have been neutralised by the deposition of foulant particles, the protein rejection is governed exclusively by the steric effects.

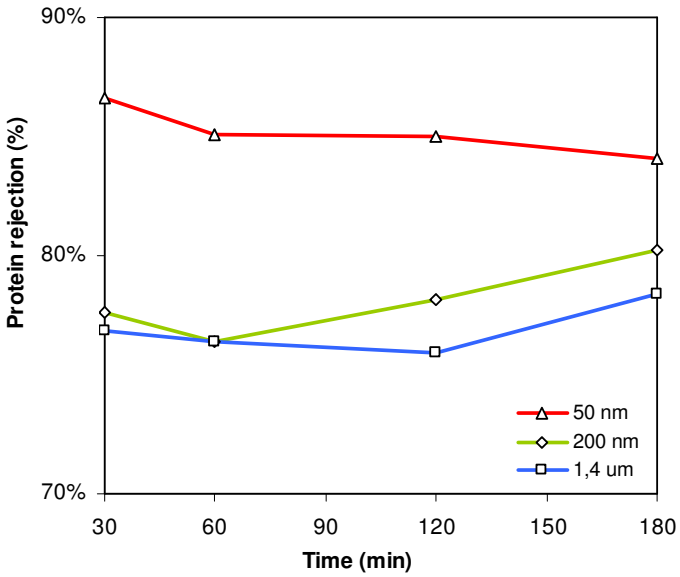

Figure 4.29. Evolution of the protein rejection during the 3-hour total recirculation assays for the three tested membranes.

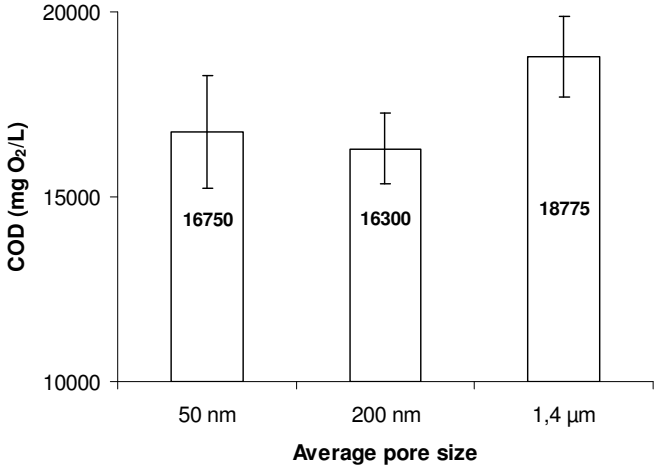

Figure 4.30. Average permeate COD for the three assayed membranes.

The figure 4.30 shows the average COD of the permeate for the three membranes studied in this chapter. It can be concluded that both the membranes of 200 nm and 50 nm achieved a COD removal of 86%, related to the 118000 mg O_2/L COD of the pre-filtered press liquor, followed by the membrane of 1.4 µm (84%). The higher COD value for this last membrane is explained by its higher average pore size and lower protein rejection, which results in a larger amount of organic solutes (mainly proteins) passing to the permeate stream. These values of COD are below the maximum discharge limits established by the EPA regulations (USA),while according to the EU water policy they should be transferred to the a municipal waste water treatment plant for a subsequent treatment. With respect to their discharge at sea, an example given by the FAO for the Province of Buenos Aires sets a maximum COD of 40 g O_2/L for the effluents discharged at open sea. Waiting for the development of future specific regulations on this issue in the framework of the EU Common Fishery Policy, these values are taken as reference.

4.3.3.1 Weight molecular profile of the permeate.

The figures 4.31 to 4.33 show the molecular weight profiles obtained for the permeates after 30 minutes of filtration, compared to those obtained for for the prefiltered press-liquor.

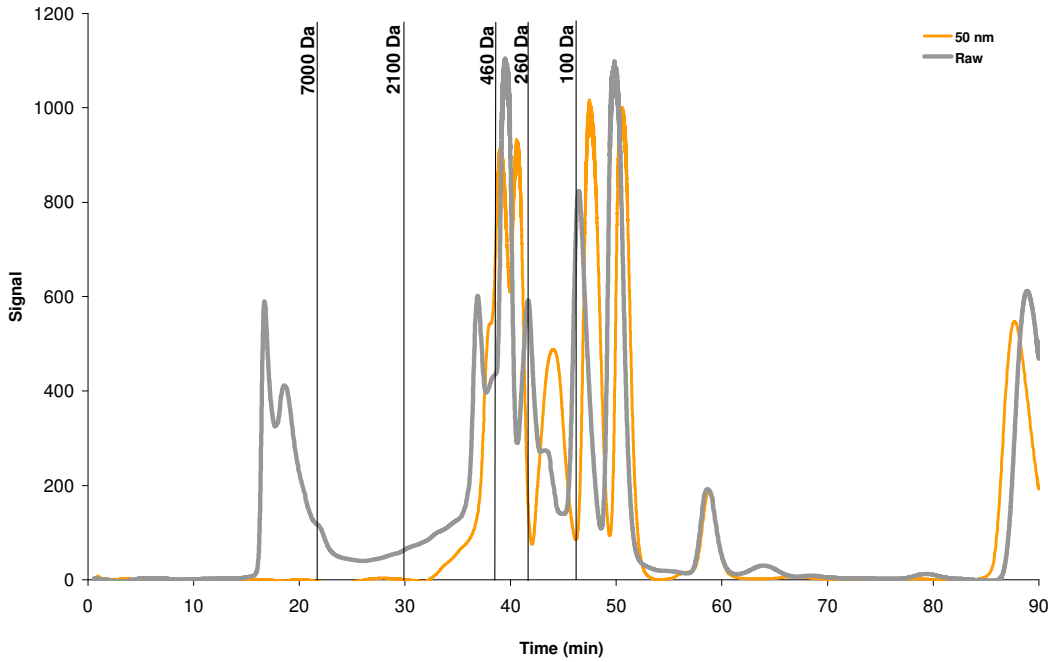

Figure 4.31. Comparison between the weight molecular profiles for the pre-filtered press liquor and the permeate from the 50 nm membrane.

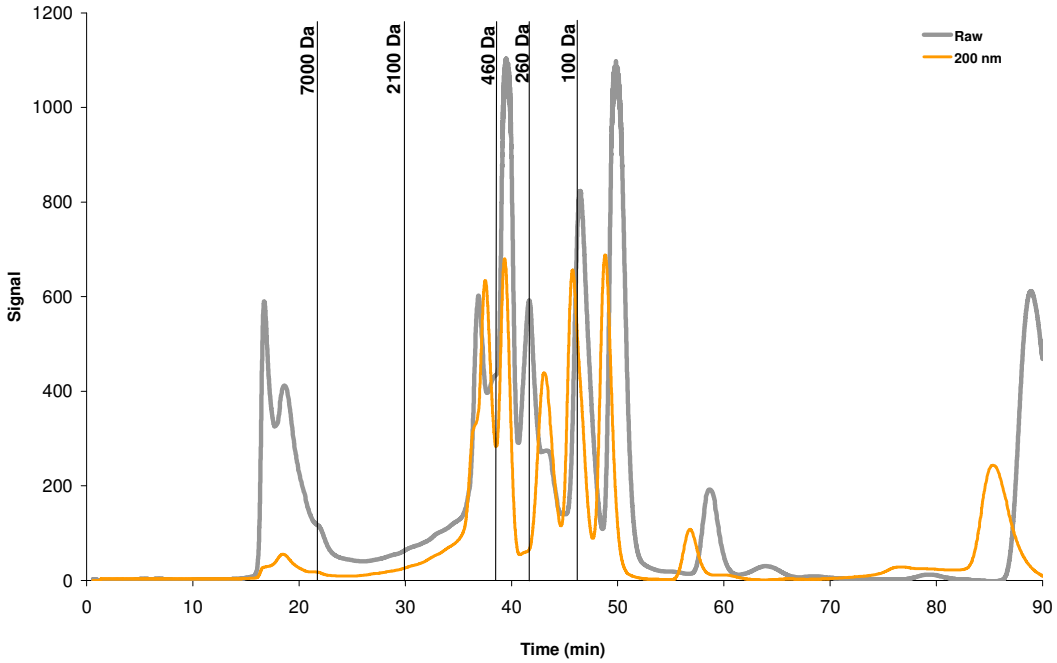

Figure 4.32. Comparison between the weight molecular profiles for the pre-filtered press liquor and the permeate from the 200 nm membrane.

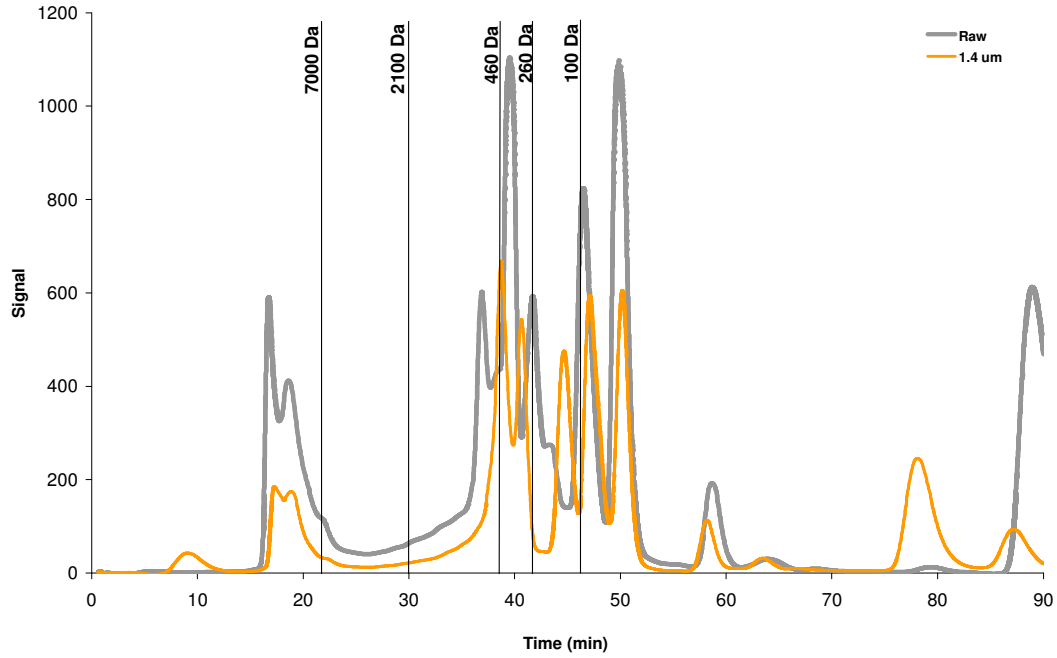

Figure 4.33. Comparison between the weight molecular profiles for the pre-filtered press liquor and the permeate from the 1.4 µm membrane.

Table 4.22 shows the size-distribution for the three permeate streams compared to that obtained for the pre-filtered liquor.

Table 4.22. Comparison between the molecular weight distributions of the pre-filtered press liquor (feed solution) and the permeates resulting from the three assayed membranes. Proportions (%w/w)

Sample	Molecular Weight (Da)				
	> 7200	7200 - 5400	5400 - 2100	2100 - 260	< 260
Feed solution	15.27	0.56	1.94	27.66	54.54
Permeate 50 nm	0	0	0.07	29.88	70.27
Permeate 200 nm	3.76	0.21	1.18	33.63	61.12
Permeate 1.4 μm	11.20	0.30	1.04	26.65	60.62

With respect to the larger size species, those with MW >7200 Da, they are fully rejected by the 50 nm membrane and, to a great extent, by the 200 nm membrane (75% of this fraction was rejected). The membrane of 1.4 um presented the higher transmission for larger species, since only 27% fraction over 7200 Da were retained. The fraction ranging from 7200 to 5400 Da was completely retained by the 50 nm membrane, while it was present in the permeates for the 200 nm and 1.4 μm, with 37% and 54% transmissions respectively. The retention of molecular species between 5400 and 2100 was almost complete for the 50 nm membrane (96%), while the 200 nm and 1.4 μm exhibited molecular transmissions higher than 50%.

On the whole it can be concluded that the smaller size fractions below 2100 Da passed entirely through the three membranes. The proportion of molecular species between 2100 and 260 Da in the permeate from the 1.4 um membrane was lower than that found for the feed solution. This may be interpreted as a sign of adsorption of peptide species on the membrane surface or inside the pores.

From the molecular profiles depicted on the figures 4.31 to 4.33, it is noticeable the displacement of the profiles towards lower retention times, i.e., higher molecular species, as the average pore size of the membrane is higher.

4.3.3.2 Choice of the membrane for the batch concentration.

Three ceramic membranes of average pore sizer 50 nm, 200 nm and 1.4 μm were tested in terms of hydrodynamic behaviour, organic load of the permeate and efficiency of an alkali-acid-oxidant cleaning sequence. The main results are summarised in the table 4.25:

Table 4.23. Comparison of the three studied membranes.

Average pore size	Relative Flux Decline (%)	Steady-state flux ($L \cdot m^{-2} \cdot h^{-1}$)	Average protein rejection (%)	Average COD (mg O_2/L)	Cleaning efficiency (%)
50 nm	30.24	23.50	85.21	16750	100.21
200 nm	33.35	25.82	78.11	16300	99.79
1.4 μm	23.75	20.35	76.90	18775	99.52

The 200 nm membrane was chosen for the batch concentration operation, since it presents the higher average flux at steady state (higher than 25 $L \cdot m^{-2} \cdot h^{-1}$), with a moderate relative flux decline. The permeate obtained from this membrane presented the lowest COD. In terms of cleaning efficiency, the cleaning sequence restored completely the initial permeability for the three membranes. Nevertheless, the acid stage with nitric acid will be removed from the whole cleaning treatment, since its effects on the cleaning efficiency or flux recovery are either adverse or negligible.

4.3.4 Batch concentration with the 200 nm Membralox™ membrane.

Two litres of feed solution were concentrated during eight hours, with recycle of the retentate stream to the feed tank while the permeate was collected in a separate recipient. The flux of permeate was measured every 5 minutes during the first 30 minutes, then every 10 minutes until 3 hours of concentration and every 30 minutes until the end of the experiment. According to the figure 4.34, the permeate flux undergoes an initial steep decline during the first hour, and then tends to stabilise falling at a decreasing rate. In this case, the final steady value was not reached at the end of the batch concentration, but it continued to decrease at a very low rate.

The overall volume of permeate collected after the concentration experiment was 831 mL; this represents a Volume Reduction Factor (VRF) given by the equation 4.29:

$$VRF = \frac{2000}{2000 - 831} = 1.71 \qquad (4.29)$$

The figure 4.34 shows the fitting of the experimental data to the Suki's model. The correlation between the observed data and the predicted model was very good, except for the initial flux decline, which is less sharpen than that observed experimentally. Indeed, the initial predicted flux J_0 was 27.64 L/(m^2·h), as shown in table 4.25, while the observed value is close to 29 L/(m^2·h).

From the model parameters, shown in table 4.24, it can be noticed that the values for the maximum fouling resistance $R_{F\infty}$ and the overall initial membrane resistance (R_M + R_B) are higher than those observed for the same membrane in the total recirculation assay.

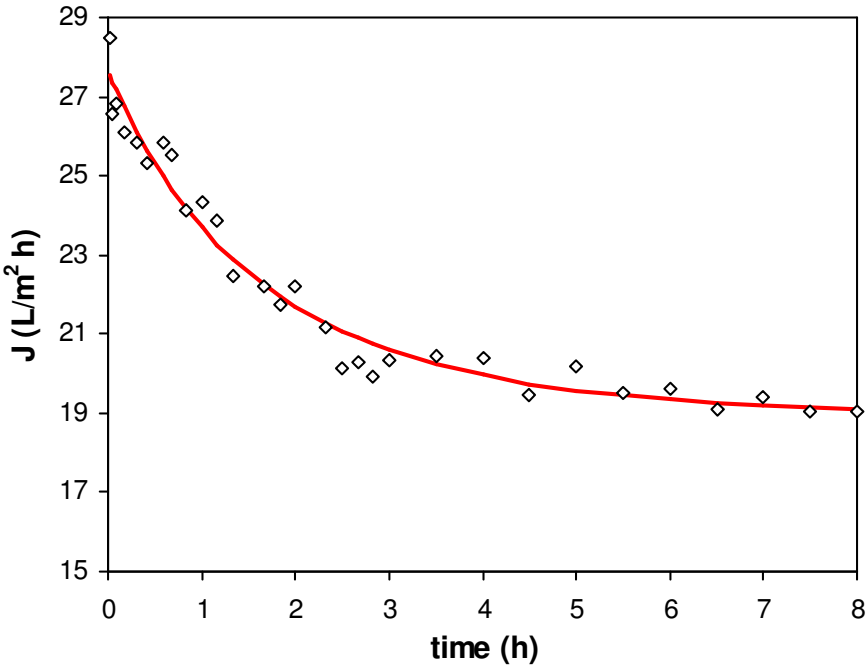

Figure 4.34. Fitting of the experimental data to the Suki's fouling model for the batch concentration with the Membralox™ 200 nm membrane.

In the batch concentration experiment, the concentration of proteins in the feed solution increases in the course of time. Although the transmembrane pressure remains constant during the concentration, the hydraulic resistance provided by the membrane material, as well as that provided by the gel layer will increase in time, due to the increasing viscosity and protein concentration of the feed solution. As the convective mass transport increases in time, the cake layer can grow to a larger extent, with a higher value for the maximum fouling resistance $R_{F\infty}$.

Nevertheless, the rate of formation of the cake layer is slower (k = 0.45 h^{-1} instead of 2.20 h^{-1}), although this value should be regarded with caution because the convective transport, and then

the rate of cake formation, is not constant during the batch concentration experiment (the convective transport is not constant in time).

Table 4.24. Estimated parameters of the Suki's fouling model for the batch concentration with the Membralox^{TM} 200 nm membrane.

Membrane	J_0 L/(m^2·h)	J_∞ L/(m^2·h)	k (h^{-1})	$R_{F\infty}$ (bar·m^2·h/L)	$R_M + R_B$ (bar·m^2·h/L)
200 nm	27.64	18.92	0.45	$2.50 \cdot 10^{-2}$	$5.43 \cdot 10^{-2}$

4.3.4.1 Cleaning treatment for the batch concentration membrane

The membrane was cleaned following the cleaning protocol described in the section 4.2.2.3.5 of this chapter, where the acid stage was ruled out, since its effect on the fouling removal was very limited or even adverse, as concluded before. The representation of the transmembrane pressure against the permeate flux (figure 4.35), shows that the cleaning treatment reduced the hydraulic resistance of the fouled membrane down to its initial intrinsic value.

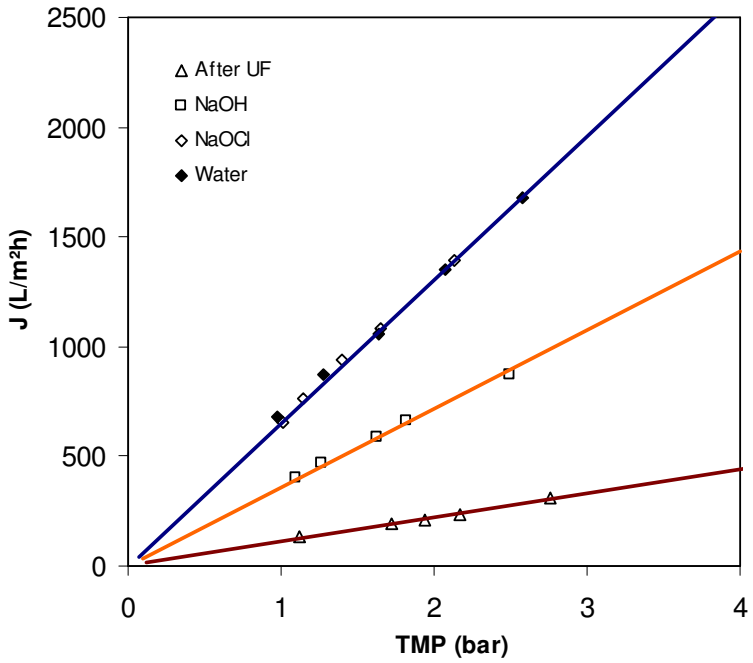

Figure 4.35. Evolution of the hydraulic resistance during the cleaning cycle for the batch concentration experiment.

The total and fouling resistances, as well as the efficiency indices and residual resistance after the complete cleaning treatment were evaluated and summarised in the table 4.25. It can be concluded that the chosen 2-stage protocol restored completely the initial water permeability of the membrane, with an overall cleaning efficiency of 99.87% and a residual resistance which represented less than 0.7% of the intrinsic membrane resistance.

Table 4.25. Hydraulic resistances and efficiency indices for the cleaning treatment after the batch concentration test.

Cleaning Stage	R_T (bar·m^2·h/L)	R_F (bar·m^2·h/L)	%E	%FR	R_{rs} (bar·m^2·h/L)
Clean Membrane	$1.52 \cdot 10^{-3}$	-	-	-	-
After UF	$9.01 \cdot 10^{-3}$	$7.49 \cdot 10^{-3}$	-	-	-
NaOH	$2.79 \cdot 10^{-3}$	$1.27 \cdot 10^{-3}$	83.04%	54.48%	-
NaOCl	$1.53 \cdot 10^{-3}$	$1.00 \cdot 10^{-5}$	16.82%	99.35%	-
Overall	-	-	99.87%	99.35%	$1.00 \cdot 10^{-5}$

4.3.4.2 Protein rejection and COD of the permeate

Seven samples of permeate were collected after 30 minutes, 1, 2, 3, 4, 6 and 8 hours of batch concentration. The Chemical Oxygen Demand (COD) of the permeate stream did not change significantly in the course of the concentration. The average value for the 7 samples was 15800 ± 68 mg O_2/L. As mentioned before, this value is below the maximum discharge limit established by the EPA regulations (USA),while according to the EU water policy these effluents should be transferred to the a municipal waste water treatment plant for a subsequent treatment. With respect to their discharge at sea, the maximum discharge limit for the Province of Buenos Aires (Argentine) can be taken as reference (40 g O_2/L), since the specific regulations on this issue in the framework of the EU Common Fishery Policy are not fully developed yet.

The protein concentration was analysed for the seven samples. In this case, the protein content of the retentate increased during the concentration experiment, from an initial 44.1 ± 0.3 mg/mL to 73.58 ± 0.09 mg/mL after 8 hours. The table 4.26 shows the evolution of the protein transmission and protein rejection in the course of the 8-hour concentration.

Table 4.26. Evolution of the protein content in the permeate during the 8-hour batch concentration assay with the 200 nm Membralox™ membrane.

Time (h)	Feed protein (mg/mL)	Permeate protein (mg/mL)	Protein rejection (%)	Protein transmission (%)
0.5	48.04 ± 0.46	8.24 ± 0.06	82.85	17.15
1	66.06 ± 0.09	8.42 ± 0.07	87.25	12.75
2	69.83 ± 0.31	8.30 ± 0.07	88.11	11.89
3	68.95 ± 0.13	8.23 ± 0.22	88.06	11.94
4	66.57 ± 0.20	8.32 ± 0.16	87.50	12.50
6	68.05 ± 0.55	8.21 ± 0.27	87.94	12.06
8	73.58 ± 0.09	7.80 ± 0.09	89.40	10.60

The figure 4.36 shows the evolution of the protein rejection in time. It undergoes a slight increase during the first hour, due to the rapid formation of a gel layer, followed by particle deposition on the membrane surface, which provides an additional hydraulic resistance which controls the passage of feed solutes through the pores. After 1 hour it attains a plateau, with a steady value of protein rejection around 88%, which remains constant the whole concentration operation.

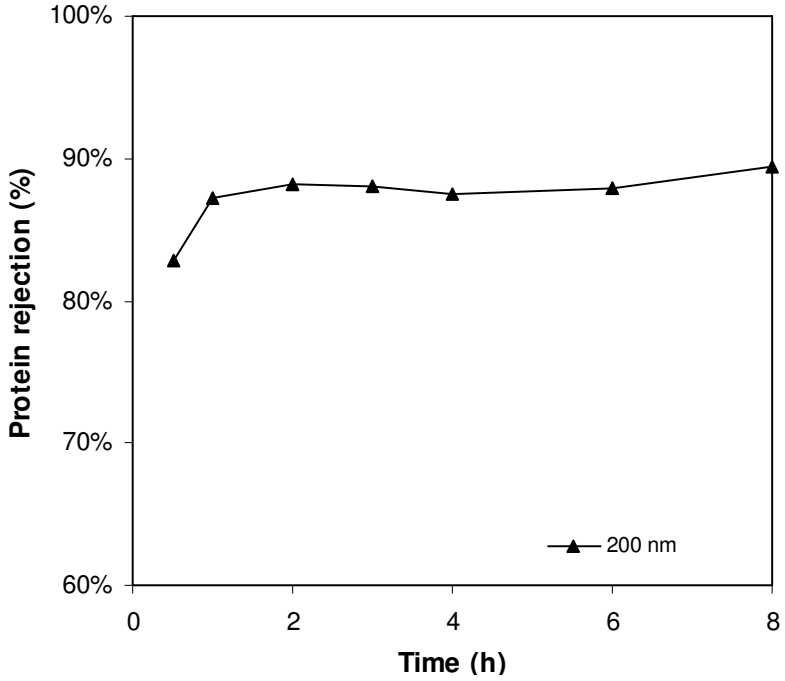

Figure 4.36. Evolution of the protein rejection during the 8-hour batch concentration assay.

4.3.4.3 Molecular weight profile of the permeate

Compared to the molecular size distribution obtained for the 200 nm membrane in the total recycle experiment (first row), the permeate has a lower content in large molecular-size species. The molecular size distribution was followed in the course of the 8-hour batch concentration. To this purpose, some samples were taken at 30 minutes, 1, 2, 3, 4, 6 and 8 hours. The size distribution of the different species is shown on the table 4.27, compared to that obtained for the total recirculation assay.

Table 4.27. Evolution of the molecular weight distribution of the permeate in the course of the batch concentration (proportion of each fraction in w/w%).

Time (h)	Molecular Weight (Da)				
	> 7200	7200 - 5400	5400 - 2100	2100 - 260	< 260
Total recycle	3.76	0.21	1.18	33.63	61.12
0.5	0.58	0.07	0.82	36.25	62.21
1	1.18	0.11	0.93	34.91	62.82
2	0.66	0.07	0.81	34.33	64.06
3	1.2	0.14	1.05	35.2	62.33
4	1.67	0.16	1.13	35.06	61.9
6	1.44	0.15	1.04	35.3	61.99
8	1.23	0.13	1.03	35.2	62.37

The proportion of smaller peptide species was expected to increase in the course of the batch concentration, as the average pore size decreased due to the fouling phenomena. This increase in the fraction of small size species will be enhanced by the autolysis of the remaining proteins and large peptides in the course of the batch concentration, since the temperature was set at 20ºC. Nevertheless, no significant difference was observed between the proportions of each type of peptides. More than 90% of the species had a molecular weight under 2100 Da. These results may be attributable to two different reasons:

1. An initial rapid pore constriction due to the particle deposition or adsorption onto the pore walls, giving rise to a reduction in the transmission of larger size species. The initial 200

nm average pore size membrane reduces rapidly its pore size limiting the passage of large molecules. This could explain the abundance of small peptides in the permeate stream.

2. The autolysis of the proteinaceous species may continue to a certain extent during the storage of the feed solution, as well as in the course of the batch ultrafiltration. Even at short ultrafiltration times, the proportion of large molecules over 7200 Da is around 4 times lower than that presented in the permeate from the total recycle experiment. The feed solution was obtained at the same day for both experiments (total recycle and batch concentration) and then stabilised at -16ºC during several days. As mentioned before, the cathectic and other proteolitic enzymes can survive at temperatures down to -10ºC. The samples were thawed during 8 hours before being fed into the ultrafiltration pilot. This period is supposed to be critical in the autolysis since the enzymes remaining after the congelation recover their proteolitic activity.

4.4 CONCLUSIONS

- The proposed effluent treatment (filtration cartridges + membrane ultrafiltration) has proved to be an available technology able to render a final permeate meeting with the quality standards for its discharge.

- Three ceramic membranes of average pore sizer 50 nm, 200 nm and 1.4 μm were tested in terms of hydrodynamic behaviour, organic load of the permeate and efficiency of an alkali-acid-oxidant cleaning sequence. The 200 nm membrane was chosen for the batch concentration operation, since it presents the higher average flux at steady state (higher than 25 $L \cdot m^{-2} \cdot h^{-1}$), with a moderate relative flux decline. The permeate obtained from this membrane presented the lowest COD (16300 ± 850). In terms of cleaning efficiency, the cleaning sequence restored completely the initial permeability for the three membranes. Nevertheless, the acid stage with nitric acid will be removed from the whole cleaning treatment, since its effects on the cleaning efficiency or flux recovery are either adverse or negligible.

- The observed flux in the course of the membrane filtration was fitted to a cake forming-based model developed by Suki *et al.* (1984). This model assumes that the mass of deposited particles (cake) increases in time following a first order kinetics, until attaining a maximum value M*, where the build-up of the cake layer and the removal of deposited particles by the tangential flow are balanced. The degree of correlation between the experimental data and the predicted model was found to be good, although the initial fluxes extrapolated from the Suki's equation are lower than those obtained after calibration of the feed solution.

- A 8-hour concentration with a 200 nm ceramic membrane permits to obtaina a final permeate flux of 27.64 L/ ($m^2 \cdot h$), with a VRF=1.71 whose average COD (15800 ± 68 mg O_2/L) is below the maximum discharge limit established by the EPA (USA). According to the EU water policy they should be transferred to a municipal waste water treatment plant before its discharge. With respect to their discharge at open sea, an example given by the FAO for the Province of Buenos Aires sets a maximum of 40 g O_2/L.

5.CONCLUSIONS AND PERSPECTIVES

- The application of a compacting operation has proved to facilitate the further managing and up-grade processing of the fish wastes and by-products, as it enables to obtain a volume reduction up to 50%. This reduction represents lower space and energy requirements for the storage and preservation of these materials. Bearing in mind the future application of the zero-discards policy, as well as the more stringent regulations concerning the discharge of liquid effluents both in land and in open sea.

- The first chapter of this thesis was devoted to the study of the different applications able to give a better utilisation of fish wastes and by-products, as well as to estimate the amount of discards/by-catches, wastes on board and by-products in land generated yearly by the French fisheries and French processing industry. This estimation is necessary in order to determine the amount and characteristics of the wastes and by-products from marine sources which are generated in France. Further work should be done in order to scale the compacting prototype (which is by far able to process up to 10 kg of raw material per batch) to the inputs of the French fishing and fish processing industry.

- The tests performed on the prototype were useful to validate the results obtained from the laboratory tests (variables influencing the liquor yield and content of suspended matter), but the showed up some limitations and technical constraints. Some aspects should be improved on the prototype in order to adequate to a larger scale:

    1. **Variability of the feed composition**. The content of oil of the sardine by-products was residual. This fact ruled out the incorporation of an oil recovery operation inside the effluent treatment. The industrial processing of fatty fish species (tuna, salmon, herring, etc) generates variable amounts of effluents whose content in fish oil may be significant. The removal of the oily phase from this effluent is necessary in order to minimise its adverse effects on the membrane filtration operations, as well as to recover valuable fractions (fish oil, fatty acids). Two unit operations are available for this purpose: a centrifugation or a coalescer filtration. Apart from the economics, the convenience of each unit will depend on the degree of dispersion of oil droplets in the emulsion as well as the stability of the oil-water interfaces.

    2. **Scaling-up of the UF operation to an industrial scenario**. The mass-transfer coefficient, which governs the protein transmission from the bulk solution to the

permeate stream, depends on the system geometry (channel height and length, presence of turbulence promoters) and the operating parameters. Further tests are required to study the influence of the module configurations on the performance of the batch concentration operation. The membranes should be easily replaced, and the fouling phenomena must be minimised during the operation (e.g., by means of a back-flushing system).

3. The prototype should be adapted for a **better cleaning and maintenance**. An important aspect in its construction was to provide it with a clean in place (CIP) system able to remove the residues from the hydraulic press, the cutting machine and the belt conveyor. An additional problem is the generation of waste waters containing toxic compounds (detergents, soda and hydrochloride acid from the membrane cleaning) and a variable amount of solid particles able to be recovered and re-integrated into the press cake. The incorporation of a centrifuge in the cleaning line could recover the available solids and re-use the cleaning solution, avoiding its direct discharge.

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7. ANNEXES

7.1 FISH WASTES GENERATED BY ON-BOARD PROCESSING

Species	Catches 2005	Catches 2005	Landings 2004	Landings 2005	Processed percentage	Presentation	Coefficient	Wastes 2004	Wastes 2005
Monkfish	21378	20833	18171	17708	100%	Gutted	7,25	2506	2442
Cod	7373	5560	6046	4559	99%	Gutted	5,55	1078	813
					1%	Headed	3,63	17	13
Conger	5605	5131	5213	4772	100%	Gutted	10	521	477
Haddock	7449	5111	6332	4344	100%	Gutted	6	1055	724
Saithe	17847	16792	16955	15952	100%	Gutted	6,56	2585	2432
Pollack	3067	3534	2914	3357	100%	Gutted	6,56	444	512
Blue ling	3975	3133	2186	1723	100%	Gutted	6,56	333	263
Ling	2308	2309	1269	1270	100%	Gutted	7,67	166	166
Whiting	13588	13505	6386	6347	30%	Whole			
					70%	Gutted	6,41	697	693
Megrim	2805	3060	2525	2754	100%	Gutted	26	97	106
Plaice	3625	3191	1450	1276	20%	Whole			
					80%	Gutted	10	116	102
Sole	8196	8320	6721	6822	30%	Whole			
					70%	Gutted	10	470	478
Hake	12059	14208	6994	8241	95%	Gutted	6,88	966	1138
					5%	Whole			
WHITE	**109275**	**104687**						**11052**	**10358**
Black Scabardfish	3090	3053	2596	2565	100%	Gutted-Whole	2,76	940	929
PELAGIC	**3090**	**3053**						**940**	**929**
Sharks	11626	11372	8720	8529	100%	Gutted	5,65	1543	1510
CARTILAG.	**11626**	**11372**						**1543**	**1510**
Langoustin	6318	133	4423	93	99%	Whole		0	0
					1%	Tailed	1,5	29	1
CRUSTAC.	**6318**	**133**						**29**	**1**
TOTAL France	**136627**	**119378**						**13565**	**12797**

7.2 CONVERSION COEFFICIENTS

Category	Species	Size	Raw material	By-products							Final presentation
				Viscera	Liver	Head	Fish-bones	Skin	Fins	Total By-products	
White fish	Monkfish	2	Whole	7.25		2.47				1.84	Tail with skin
		2	Gutted			2.09				2.09	Tail with skin
		3	Whole	7.25		2.19				1.68	Tail with skin
		3	Gutted			1.85				1.85	Tail with skin
		5	Whole	7.25		1.96				1.54	Tail with skin
		5	Gutted			1.67				1.67	Tail with skin
	Brosme		Whole	7.45		6.83	3.51	20.00		1.63	Skinned fillet
	Cod	3-4-5	Whole	5.55	10.0	5.35	4.50	23.61		1.58	Skinned fillet
		3-4-6	Gutted		8.20	4.39	3.48	20.00		1.77	Skinned fillet
	Conger		Whole	10.00		5.78	7.98	7.77		1.90	Skinned fillet
			Gutted			5.00	7.34	6.94		2.08	Skinned fillet
	Haddock		Whole	6.00		10.6	2.73	37.95		1.53	Skinned fillet
			Gutted			7.25	2.35	31.62		1.68	Skinned fillet
	Grenadiers		Whole	10.00		3.85	2.86	33.33		1.35	Skinned fillet
			Gutted without tail			3.71	2.48	30.03		1.42	Skinned fillet
	Hoplospete		Whole	10.00		2.86	4.76	33.33		1.45	Skinned fillet
	Pollocks	4	Whole	6.56	20.00	6.90	4.56	39.74		1.84	Skinned fillet
		4	Gutted		16.95	5.26	3.95	34.48		2.12	Skinned fillet
	Blue ling	4	Whole	6.56	20.00	6.71	6.40	25.26		1.84	Skinned fillet
		4	Gutted		16.95	5.13	4.37	20.00		2.11	Skinned fillet
	Ling	4	Whole	7.67	20.00	6.69	4.75	15.07		1.80	Skinned fillet
		4	Gutted		17.39	5.38	4.21	13.33		2.01	Skinned fillet
	Wolf-fish		Whole	6.00		6.74	3.26	20.00		1.49	Skinned fillet
		1-2	Whole	6.41		7.72	3.11	24.93		1.55	Skinned fillet
	Whiting	1-2	Gutted			6.51	2.55	21.56		1.69	Skinned fillet
	Perch		Whole	8.41		2.78	6.13	20.00		1.44	Skinned fillet
	Pout		Whole	5.88		8.33	3.08	25.00		1.53	Skinned fillet
			Gutted			6.92	2.55	20.75		1.71	Skinned fillet
Blue fish	Herring		Whole	9.33		5.17	5.60			2.09	Double fillet + skin
	Mackerel		Whole	9.33		5.17	5.78			2.11	Filet with skin
	Black Scabbardfish		Gutted, headed				2.76	20.00		2.76	Filet without skin
	Sardine		Whole	10.00		4.00	5.75			1.91	Filet with skin
	Tunny		Whole	7.67		5.00	4.77	16.67		1.67	Skinned fillet
	Bluefin tuna		Whole	7.25		4.44	8.89	14.29		1.83	Skinned fillet
Salmons	Salmon		Whole	7.25		10.36	5.53	16.15		2.11	Skinned fillet
	Truot		Whole	7.45		10.77	5.53	16.15		2.11	Skinned fillet
Cartilaginous	Siki: portuguese dogfish		Whole	2.54	3.70	9.12		19.29	36.49	1.36	Gutted-headed-peeled
			Gutted		2.24	6.76		14.29	27.03	1.92	Gutted-headed-peeled
	Rays		Whole	7.25		5.06	3.39			1.59	Peeled fins
	Small Catshark		Whole	5.65		20.90		16.67	3.33	1.61	Gutted-headed-peeled

7.3 IMPORT-EXPORT BALANCE

Species	Gross tonnage	Imports (tons)		Exports (tons)		Net tonnage
		Total	Whole	Total	Whole	
Monkfish	13799	10416	3896	2587	2208	15487
Bass	5104	3578	3530	3542	1690	6944
Cod	2355	53722	16063	3051	487	17931
Saithe	7095	24042	9211	1789	127	16179
Pollack	2665	46038	1814	2221	72	4407
Lings	4317	4252	3948	74	46	8219
Whiting	11117	3666	1918	1177	1128	11907
Hake	6523	21141	3063	1633	1127	8459
Sebastes	467	7893	4332	608	233	4566
Sole	6369	3577	2937	2649	2518	6788
WHITE FISH	***59811***	**178325**	**50712**	**19331**	**9636**	**100887**
Rays	7756		Net balance negligible			7756
Sharks	8919	3352	858	1023	730	9047
CARTILAGINOUS	**16675**	**3352**	**858**	**1023**	**730**	**16803**
Herring	40960	13540	426	654	261	41125
Salmon(aquaculture)	548	135840	96562	20868	11503	85607
Truot(aquaculture)	22670	2864	821	5563	524	22967
SALMONIDS	**80853**	**155596**	**98667**	**28108**	**13018**	**166502**
Anchovy	3289	8381	476	5291	2774	25850
Haddock	3673	4208	3145	349	276	6542
Mackerel	9195	28147	8760	8636	2468	15487
Sardine	21989	24598	3307	5117	2681	22615
Tunas	181168	136083	6498	157070	3360	184306
PELAGIC	**219314**	**201417**	**22186**	**176463**	**11559**	**254800**

7.4 TONNAGE OF RAW FISH TO BE PROCESSED

Species	Tonnage	Destination	Percentage	Quantity (tons)	Processed percentage	Processed tonnage
Monkfish	15487	Trade	100%	15487	100%	15487
Bass	6944	Trade	100%	6944	40%	2778
Cod	17931	Trade	100%	17931	90%	16138
Saithe	16179	Trade	100%	16179	89%	14399
Pollack	4407	Trade	100%	4407	89%	3922
Lings	8219	Trade	100%	8219	100%	8219
Whiting	11907	Trade	100%	11907	64%	7620
Hake	8459	Trade	100%	8459	30%	2538
Sebastes	4566	Trade	100%	4566	28%	1268
Sole	6788	Trade	100%	6788	12%	815
WHITE FISH	**100887**			**100887**		**73183**
Rays	7756	Trade	100%	7756	100%	7756
Sharks	9047	Trade	100%	9047	100%	9047
CARTILAGEN.	**16803**			**16803**		**16803**
Salmon	85607	Smocking	43%	36811	100%	36811
		Trade	57%	48796	63%	30741
Truot	22967	Smocking	15%	3445	100%	3445
		Trade	85%	19522	98%	19132
SALMONIDS	**108574**			**108574**		**90129**
Herring	41125	Canning	76%	31255	100%	31255
		Smocking	19%	7814	100%	7814
Anchovy	*25850*	Canning	*75%*	*19388*	*100%*	*19388*
		Trade	*25%*	*6463*	*0%*	*0*
Haddock	3289	Smocking	54%	1776	100%	1776
		Trade	46%	1513	100%	1513
Mackerel	15487	Smocking	84%	13009	100%	13009
		Trade	16%	2478	0%	0
Sardin	22615	Smocking	40%	9046	100%	9046
		Trade	60%	13569	0%	0
Tunas	184306	Smocking	46%	84781	100%	84781
		Trade	54%	99525	81%	80615
PELAGIC FISH	**225697**			**290616**		**190740**

7.5 ESTIMATION OF BY-PRODUCTS GENERATED BY FISH PROCESSING

Species	Intended to	Tonnage	Heads (tons)	Viscera (tons)	Fishbones (tons)	Skin (tons)	Fins (tons)	Total by-products
Monkfish	Trading	15487	8282	1889	0	0	0	10170
Bass	Trading	2778	1111	383	0	0	0	1494
Cod	Trading	16138	3676	1968	4637	807	0	11088
Saithe	Trading	14399	2738	850	3645	418	0	7650
Pollack	Trading	3922	746	231	993	114	0	2084
Lings	Trading	8219	1563	479	1916	493	0	4450
Whiting	Trading	7620	1171	0	2988	353	0	4512
Hake	Trading	2538	390	0	995	118	0	1503
Sebastes	Trading	1268	152	216	412	51	0	830
Sole	Trading	815	272	81	0	41	0	394
WHITE FISH		**73183**	**20099**	**6096**	**15587**	**2394**	**0**	**44176**
Rays	Trading	7756	1533	1070	2288	0	0	4891
Sharks	Trading	9047	433	1601	0	543	2717	5294
CARTILAGINOUS		**16803**	**1966**	**2671**	**2288**	**543**	**2717**	**10184**
Herring	Canning	31255	6045	3350	5581	0	0	14977
	Smoking	7814	1511	837	1395	0	0	3744
Salmon	Smoking	36811	3553	4941	6657	2279	0	17430
	Trading	30741	2967	4126	5559	1903	0	14556
Truot	Smoking	3445	320	475	623	213	0	1631
	Trading	19132	1776	2639	3460	1185	0	9059
SALMONIDS		**129198**	**16174**	**16369**	**23275**	**5581**	**0**	**61398**
Anchovy	Canning	20126	6155	4994	0	0	0	11149
Haddock	Smoking	1776	245	0	756	56	0	1057
	Trading	1513	209	0	644	48	0	900
Mackerel	Canning	13009	2516	1394	2251	0	0	6161
Sardine	Canned whole	6785	1696	678	1180	0	0	3554
	Canned filets	2262	565	226	393	0	0	1185
Tunas	Canned	84781	17962	11365	12413	5477	0	47217
	Trading	80615	17080	10806	0	0	0	27886
PELAGIC FISH		**210866**	**46428**	**29464**	**17636**	**5581**	**0**	**99109**

7.6 FLUX OF PERMEATE FOR THE TOTAL RECIRCULATION ASSAIS AND THE BATCH CONCENTRATION

Membrane 50 nm		Membrane 200 nm		Membrane 1.4 um		Concentration 200 nm	
Time (h)	**J (LMH)**	**Time (h)**	**J (LMH)**	**Time (h)**	**J (LMH)**	**Time (h)**	**J (LMH)**
0,17	29,71	0,17	33,44	0,167	26,04	0,02	28,50
0,33	27,61	0,33	31,38	0,333	23,55	0,08	26,81
0,50	26,87	0,50	28,06	0,500	23,29	0,17	26,12
0,67	24,43	0,67	28,58	0,667	21,87	0,30	25,85
0,83	24,82	0,83	27,01	0,833	22,37	0,42	25,32
1,00	24,40	1,00	26,74	1,000	20,77	0,58	25,86
1,17	24,08	1,17	27,38	1,167	21,28	0,68	25,55
1,33	23,79	1,33	25,81	1,330	21,15	0,83	24,14
1,50	24,70	1,67	26,04	1,500	20,61	1,00	24,32
1,67	23,47	1,83	25,31	1,667	21,31	1,33	22,45
1,83	23,40	2,00	26,50	1,833	20,74	1,67	22,22
2,00	23,42	2,17	25,91	2,000	20,70	2,00	22,21
2,17	22,46	2,33	25,95	2,167	20,63	2,33	21,19
2,33	23,88	2,50	25,54	2,333	20,88	2,83	19,92
2,50	23,96	2,67	26,49	2,500	20,27	3,00	20,33
2,67	23,42	2,83	25,27	2,667	19,85	3,50	20,46
2,83	24,64	3,00	26,16	2,833	20,30	4,00	20,40
3,00	22,82	0,17	33,44	3,000	20,50	4,50	19,45
0,17	29,71	0,33	31,38	0,167	26,04	5,00	20,17
						5,50	19,53
						6,00	19.61
						6,50	19,10
						7,00	19,42
						7,50	19,06
						8,00	19,05

7.7. NOUVEAU CHAPITRE DE THÈSE

Association Bernard Gregory
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Valorisation des compétences des docteurs

«un nouveau chapitre de la thèse ®»

Procédés de valorisation des des co-produits de pêche à bord des bateaux

Institut de Sciences et Technologies Marines (STAM)–IFREMER, Nantes

Directeur de thèse : **Jean Pascal Bergé** (IFREMER)

Codirecteur de thèse : **Antonio María Guadix Escobar** (Univ. de Granada)

Soutenance de thèse prévue Décembre 2009

Cadre général et enjeux

Présentation

Les activités traditionnelles de la pêche génèrent un volume important de rejets. Cette fraction des prises, qui est normalement rejetée à la mer, se compose des espèces de faible valeur commerciale (on parle de pêche accessoire) et aussi des espèces commerciales dont la taille est inférieure à la taille légale pour la vente. Le dernier rapport FAO (Organisation des Nations Unies pour l'Alimentation et l'Agriculture) (2004) donne une estimation de **7,3 millions de tonnes annuelles** rejetées dans le monde, qui représente 8% des pêches globales. Les rejets de la pêche posent un double problème :

- ✓ **Gaspillage des ressources**. Dans le cadre actuel de la pêche, où la moitié des stocks de pêche sont en décroissance ou *ont disparu*, il est nécessaire de favoriser des pratiques et procédés qui assurent une utilisation intégrale de la matière première.
- ✓ **Problèmes environnementaux**. Le rejet des poissons entiers ou des déchets (notamment viscères) altère l'équilibre écologique des systèmes marins et favorise la propagation des virus, des parasites et des bactéries intestinales.

Le Code de Conduite pour une pêche Responsable (FAO) propose de traiter les déchets à bord, sans rejet en mer. Ses directives ont été reprises par l'Union Européenne, *qui a établi les bases de la politique zéro-rejet*. Une politique qui obligera les bateaux communautaires à débarquer la totalité des captures, y compris les captures accessoires, déchets et espèces de faible valeur commerciale ou de petite taille. Des solutions techniques doivent être trouvées pour minimiser l'impact du stockage dans la cale des bateaux.

Le titre de ma thèse : « Procédés de valorisation des coproduits à bord », montre les deux objectifs principaux à atteindre pendant le déroulement de ma recherche :

- ✓ Développer un processus permettant de « **valoriser les co-produits de la pêche** », c'est-à-dire, de donner une valeur ajoutée à la fraction des prises impropres à la consommation humaine qui est habituellement rejetée à la mer comme déchet.
- ✓ Adapter ce processus pour une future mise en place **à bord des bateaux.** Le prototype construit doit fonctionner à bord d'un bateau en *tenant en compte de toutes* les limitations (corrosion, personnel non *spécialisé*, disponibilité d'énergie, etc).

Mon projet propose la construction d'un prototype de compactage des rejets à bord des bateaux, à l'aide d'un système de pressage hydraulique. Les

effluents issus du pressage des rejets, étant toxiques pour l'environnement, ne peuvent pas être jetés en mer sans un traitement d'épuration approprié. Le prototype de compactage devra éliminer la plupart des fractions organiques de l'effluent à fin de le rendre propre pour être rejeté en mer.

Enjeux

I. Economiques et commerciaux.

- ✓ **Réduction des coûts énergétiques**. Le compactage des déchets facilite leur manipulation à bord d'un bateau et représente une diminution des besoins d'espace et de réfrigération dans la cale. Par exemple, une réduction de 50% du volume des déchets à stocker signifie une diminution de 30% des coûts associés à la réfrigération et isolation de la chambre froide.
- ✓ **Revenus**. Le stockage à bord des fractions issues du compactage et du traitement des effluents, tels que le gâteau de presse, l'huile de poisson et les fractions riches en protéines *peut représenter* un revenu potentiel pour les bateaux pêcheurs, car ces co-produits peuvent trouver diverses applications grâce à leur teneur en protéines (alimentation animale et aquacole, hydrolysats protéiques), *et* leurs effets bénéfiques pour la santé (huiles de poisson riches en acides oméga-3). En France, 96% des co-produits d'origine marine générés à terre font déjà objet d'une valorisation, notamment pour la fabrication de farine et d'huile de poisson, suivi des hydrolysats protéiques. Malheureusement, parmi ces 96%, seulement 1% est destiné à des applications à réelle valeur ajoutée telles que l'obtention de produits d'intérêt pour l'industrie pharmaceutique, cosmétique ou nutraceutique.

II. Environnementaux

- ✓ Ces travaux rentrent dans l'objectif écologique de ***consommer mieux en gaspillant moins***. Une meilleure utilisation des ressources marines permettra de conserver et récupérer les stocks actuels de poisson et aussi d'assurer la durabilité de la pêche.
- ✓ Les effluents issus des activités de manipulation et/ou de transformation du poisson ne peuvent pas être rejetés sans un traitement d'épuration approprié qui assure un ***impact minimal sur l'environnement***.

III. Législatifs

L'application des nouvelles normes européennes en matière de pêche oblige à trouver des solutions techniques qui permettent aux pêcheurs de s'adapter aux exigences de l'Union Européenne, tout en minimisant l'impact économique *de* ces mesures pour eux.

IV. Scientifiques et techniques.

Les travaux menés dans le cadre de ma thèse correspondent à la recherche appliquée. D'un point de vue scientifique, je me suis appuyé sur des travaux de recherche publiés dans les revues scientifiques et aussi sur les rapports statistiques sur les rejets publiés par l'IFREMER. Le manque d'études complètes sur les rejets de la pêche française a été comblé par des estimations à l'aide des chiffres données par des rapports de la Communauté Européenne et de la FAO, ainsi que des coefficients de conversion (rapport entre le poids de coproduits et le poids initial du poisson entier).

Le dessin et expérimentation de départ ont été menés grâce à une bonne planification expérimentale et un traitement ultérieur des résultats à l'aide d' outils mathématiques (modèles de microfiltration et ultrafiltration, bilans de matière et énergie) ou statistiques (analyse de variance et optimisation par surface de réponse).

Contexte général de ma thèse

Ma thèse s'inscrit dans le projet européen **BE-FAIR** (Benign and Environmentally Friendly Fish Processing Practiques to provide Added value and Innovative solutions for a Responsible and sustainable management of fisheries). Ce projet, financé par les fonds LIFE (programme de financement de l'Union Européenne qui soutient les projets de conservation et de développement durable), poursuit deux objectifs principaux :

- ✓ Étudier et développer des **stratégies viables** de gestion et de traitement des rejets, des prises accessoires, des déchets et des coproduits issus des activités de pêche et de transformation du poisson, tant à bord (flottes de pêche) comme *à* terre (halles à mareyage), capable de recycler et de donner une valeur ajoutée à ces résidus *prenant* en compte les **exigences légales** et les **conditions du marché**.

- ✓ **Valider** les alternatives proposées par la construction de **prototypes à échelle semi-industrielle** permettant de reproduire les procédés retenus.

Le projet BEFAIR comprend *différents* partenaires répartis dans trois pays, la France, le Portugal et l'Espagne, parmi lesquels on trouve l'Institut Français de Recherche pour l'Exploitation de la Mer (IFREMER) à Nantes, l'Institut Portugais de la Mer (IPIMAR) à Lisbonne et l'Institut Espagnol de Recherche sur la Mer (IIM-CSIC) à Vigo (Espagne). Le projet compte avec la collaboration de différentes entreprises du secteur de la transformation du poisson et aussi avec les autorités du Port de Vigo.

Au sein du projet BE-FAIR, la collaboration de l'IFREMER se déroule dans trois axes principaux, où je suis directement impliqué :

1. **Estimation sur les tonnages de rejets**, déchets et coproduits générés par les activités de la pêche française et de la transformation de poisson en terre.

2. **Dessin et construction d'un prototype** capable de réduire le volume de résidus à stocker à bord et de récupérer des fractions d'intérêt (protéines, lipides, etc).

3. Trouver un **traitement approprié pour les effluents** du procédé de réduction volumique des résidus.

Situation au regard de la concurrence

La politique de zéro-rejet, qui s'applique déjà dans des différents pays comme l'Islande ou la Norvège, va être mise en place progressivement dans toutes les pêcheries communautaires pendant une période d'adaptation de 5 à 10 ans, dans lequel la flotte communautaire devra faire toutes les modifications techniques nécessaires pour adapter les bateaux au stockage et à la conservation jusqu'au débarquement d'un volume de biomasse supplémentaire. Plusieurs équipes dans différents pays travaillent donc actuellement sur ce sujet.

Compétences mises à disposition pour le projet

I. Scientifiques

L'essentiel de ma thèse s'est déroulé dans le centre IFREMER de Nantes, notamment dans le **Département STAM** (Sciences et Technologies Marines). Parmi les différents groupes du Département STAM, je fais *partie* du groupe de Valorisation de Coproduits, dirigé par mon premier encadrant **M. Jean Pascal Bergé**. J'ai reçu de sa part un premier schéma avec les différentes étapes à étudier dans le dessin du procédé de traitement des rejets à bord, idée qui a été développée et complétée dans le parcours de ma thèse. J'ai pu bénéficier de son expérience dans les procédés de valorisation des coproduits de la pêche, et par son intermédiaire j'ai pu échanger avec les différents acteurs du secteur (pêcheurs, manipulateurs de poisson, industriels, etc).

Les aspects techniques et mathématiques du dessin et optimisation du procédé ont été supervisés par mon deuxième encadrant, **M. Antonio Guadix Escobar**, appartenant au **Département de Génie Chimique** de l'Université de Grenade (Espagne).

Une partie de ma thèse a eu lieu dans le centre **IIM-CSIC** à Vigo, où j'ai suivi la construction du prototype de compactage et j'ai reçu une formation sur

l'utilisation d'un logiciel de simulation, l'EcosimPro. Ce séjour a été supervisé par le Directeur du **Département de Génie de Procédés**, **M. Antonio Alonso**.

II. Competences humaines.

Au sein du groupe de Valorisation des Co-produits, au centre IFREMER-Nantes, j'ai bénéficié de l'aide d'un équipe technique composé par **Mme. Claire Donnay-Moreno** (Technicienne Analyste Biochimiste) et **M. Jean-Paul Gouygou** (Cadre Biochimie), qui m'ont aidé avec les protocoles et analyses de laboratoire. En outre, au sein de l'équipe de Génie de Procédés, j'ai collaboré directement avec **Mme. Christine Chopin** (Cadre Génie de Procédés) et **M. Jean-Yves Ragon** (Technicien Génie de Procédés et électricité industriel.

La construction du prototype a été à la charge de l'entreprise **Hermanos Rodríguez (HDR)**, située à Vigo. J'ai été en relation avec un Ingénieur en Mécanique de HDR, qui était responsable de la construction et mise en marche du prototype, avec collaboration directe de l'IFREMER, d'où il a reçu le cahier de charges et les donnés techniques nécessaires. Pendant un séjour en Espagne de six mois, j'ai pu suivre directement la construction du prototype.

Mon parcours professionnel

D'accord au système d'enseignement espagnol, après la formation obligatoire au lycée, on peut choisir parmi des différents modules de formation professionnelle ou des études proposés à l'université. J'ai fait Génie Chimique pendant 5 ans. Après la faculté, je voulais donner une côté multidisciplinaire à mes études, ce qui m'a mené à faire un Master en Politique Communautaire suivi par un Master en 1 et 2 dans l'université de Grenade. Ce dernier a été consacré à l'étude des technologies d'hydrolyse enzymatique et d'ultrafiltration membranaire.

L'intérêt pour appliquer ces techniques à la valorisation des co-produits de la pêche, a mené à M. Jean Pascal Bergé, responsable de l'équipe de valorisation des co-produits à l'IFREMER, à proposer une collaboration entre les deux centres de recherche, ce qui m'a permis de réaliser ma thèse au sein de l'IFREMER.

Raisons du choix de faire une thèse sur ce sujet

- ✓ Cette thèse recherche une solution pour un **problème actuel**, elle propose la construction d'un prototype d'application directe à bord des bateaux.
- ✓ Il s'agit d'une **thèse multidisciplinaire** : les estimations de rejets dans la pêche, le dessin mécanique des unités et l'analyse biochimique.
- ✓ La thèse fait partie d'un **projet international**, avec de la collaboration directe avec des instituts de recherche et des industriels de trois pays.

- ✓ L'**expérience personnelle** de faire une thèse à l'étranger et de s'adapter à une nouvelle langue et culture.

Déroulement, gestion et coût du projet

Ma thèse a comme objectif final la construction d'un prototype pouvant compacter les déchets et rejets de poisson à bord des bateaux, tout en respectant les limitations techniques dans les bateaux (manque de personnel qualifié, corrosion et difficultés d'approvisionnement d'énergie). Il faut pas oublier les aspects environnementaux : les activités de compactage génèrent des volumes importantes d'effluents liquides qui doivent être épurés avant leur rejet en mer.

Au niveau technique, le prototype devra donc être muni avec une machine à couper pour homogénéiser la taille des déchets, puis une presse hydraulique qui permet de compacter les déchets et finalement un système de filtration pour traiter les effluents liquides. Le diagramme ci-dessous montre les principales opérations impliquées dans ce procédé :

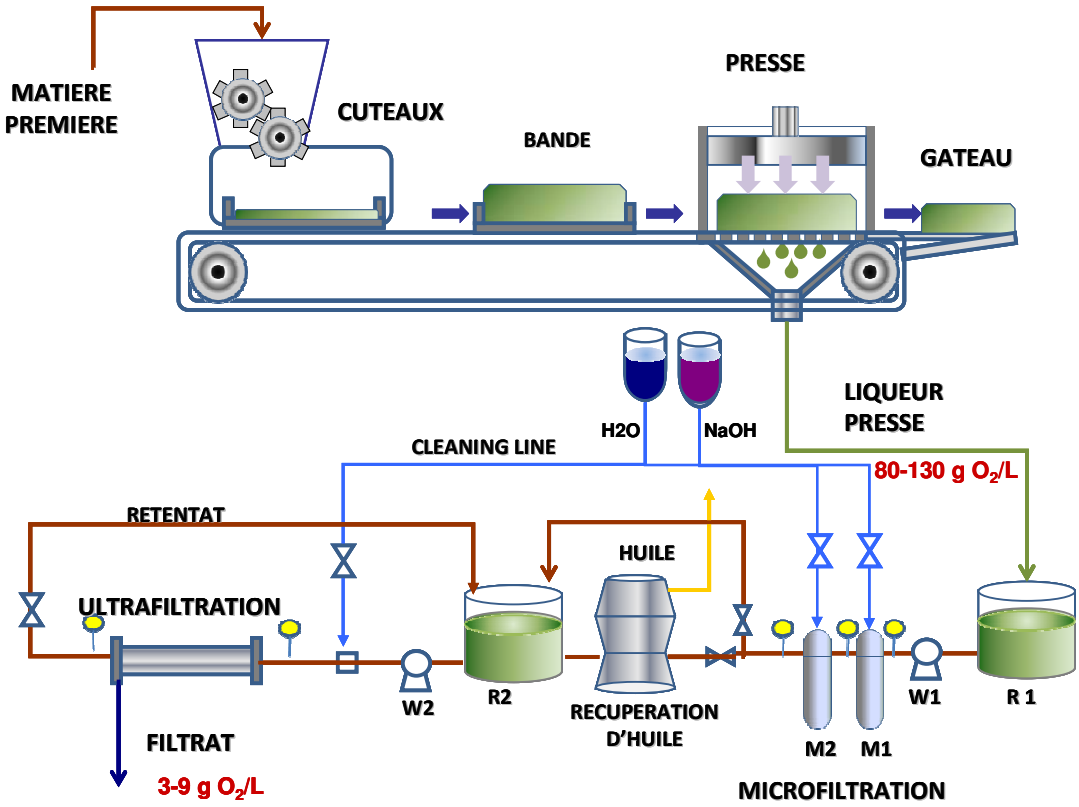

Figure 1 : Schéma du processus de compactage et de la ligne de traitement des effluents.

Etapes scientifiques

Ce projet a été conduit en plusieurs étapes, depuis les études préliminaires jusqu'à la construction et mise en marche du prototype. On peut diviser le travail de la thèse en 13 tâches principales, décrites dans le tableau ci-dessous :

Tâche	Description
1	Recherche Bibliographique sur la problématique actuelle des rejets de la pêche, quantification approximative du tonnage annuel de rejets en France.
2	Essais de pressage hydraulique de poisson (sardine) à échelle de laboratoire. Approche statistique conduisant à l'optimisation du pressage.
3	Analyse biochimique des jus de pressage obtenus dans les différentes expériences.
4	Définition du cahier de charges pour l'entreprise HDR. Première réunion pour définir les paramètres de construction du prototype.
5	Séjour à l'IIM-CSIC à Vigo. Maîtrise des techniques de simulation à l'aide du logiciel EcosimPro. Surveillance des étapes de construction du prototype.
6	Séjour dans le Département de Génie Chimique à Grenade. Maîtrise des techniques d'Ultrafiltration Tangentielle.
7	Rédaction d'un article sur les résultats obtenus après l'optimisation du pressage. Préparation d'une conférence à Florence.
8	Réception à l'IFREMER du prototype de compactage. Calibrage et mise en marche du prototype.
9	Essai de pressage hydraulique de poisson à échelle semi-industrielle. Analyse biochimique des effluents et interprétation statistique des résultats.
10	Essai des cartouches de microfiltration et optimisation de leur performance. Analyse biochimique des effluents après filtration.
11	Tests d'Ultrafiltration Tangentielle à l'aide de membranes céramiques : optimisation des paramètres opérationnels.
12	Rédaction de la thèse. Réunions avec les encadrants et corrections.
13	Stage prévu de 2-3 semaines pour étudier la filtration des effluents gras.

Tableau 1 : Principales tâches à accomplir pendant la thèse.

Le diagramme ci-dessous montre la distribution temporelle approximative des différentes tâches, pour la période 2006 -2009.

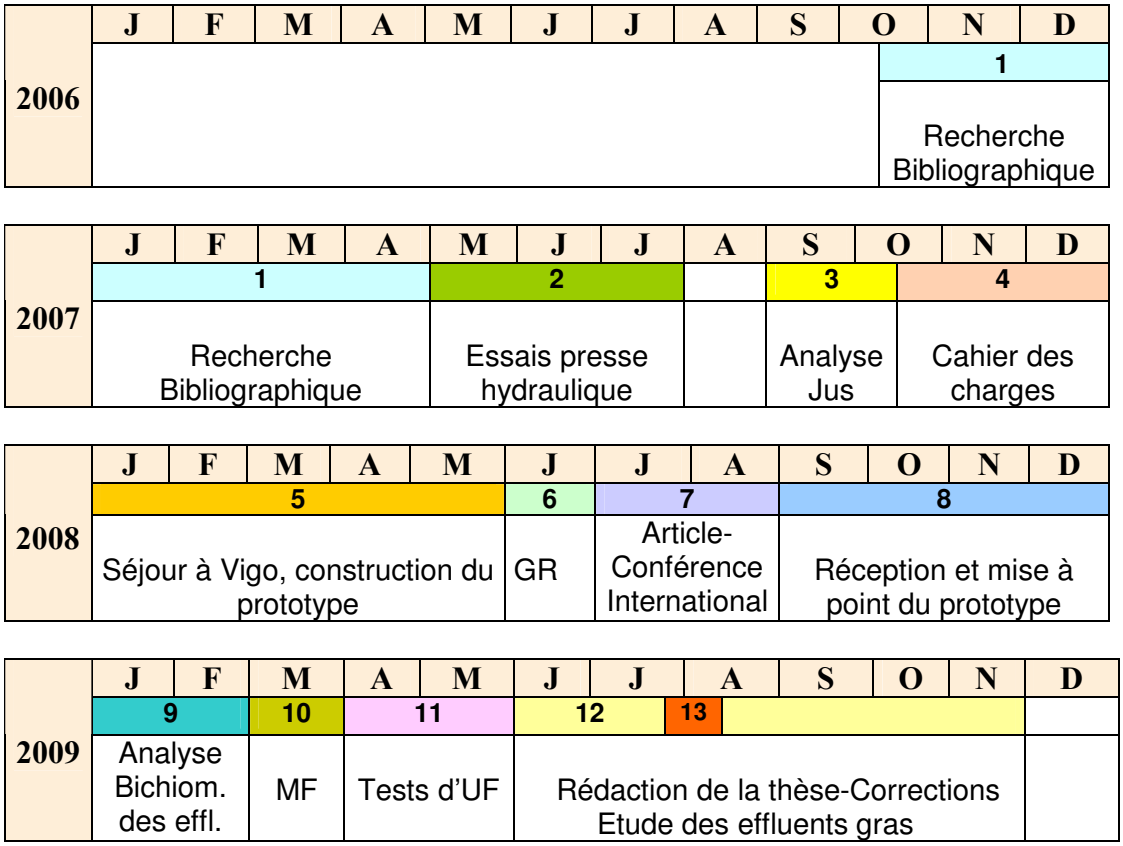

Figure 2 : Planning de déroulement de la thèse (2006-2009)

Réunions et périodicités.

Réunion	Lieu	Périodicité	Sujet à traiter
Jean-Pascal Bergé	IFREMER (Nantes)	Toutes les 1à 2 semaines	Résultat des analyses. Planification expérimentale. Rédaction des articles.
Antonio Guadix	Dép.Génie Chimique (Grenade)	3 fois par an.	Traitement statistique des résultats. Dessin de procédés et rédaction des articles.
Groupe BE-FAIR	Lisb. (2007) Nantes (2008) Vigo (2009)	1 fois par an.	Déroulement des tâches principales du projet. Planification des actions communes

Tableau 2 : Réunions et périodicités.

Préparation et cadrage du projet

I. Evaluation des facteurs de succès et de risques, stratégies de maîtrise des risques envisagées.

Suivant la chronologie des tâches illustrée dans le tableau 1, le tableau suivant montre les principaux problèmes et solutions/stratégies trouvées dans le parcours de ma thèse.

Tâche	Problème	Solution/Stratégie
Recherche Bibliographique	Manque d'études au niveau français, notamment sur les rejets dans la Méditerranée.	Estimation approximative des chiffres des rejets par rapport aux estimations pour autres pêcheries.
Essai de pressage	Absence de presse Hydraulique à l'IFREMER.	Emprunt d'une presse hydraulique à l'INRA-Rennes.
Réunions avec HDR	Différences entre le cahier de charges de l'IFREMER et les possibilités réelles de HDR.	Réduction de la pression du travail de la presse. Simplification de l'idée initiale.
Construction du prototype	Indisponibilité de l'Ingénieur Mécanicien chez HDR. Problèmes de budget liés à la construction du prototype.	Contact avec d'autres ingénieurs de l'entreprise. Substitution de l'étape de centrifugation par un filtre coalesceur.
Réception et mise en marche	Pression insuffisante du piston et problèmes d'automatisme.	Substitution du piston et visite d'un expert en automatismes pour corriger le fonctionnement du pilote.
Tests d'ultrafiltration	Problèmes de colmatage des membranes.	Assistance du Département de Génie Chimique de Grenade.
Impact sur les pêcheurs	Manque de sensibilité sur les problèmes environnementaux occasionnés par le rejet de déchets	Séances de démonstration des prototypes et tables rondes avec les différents agents impliqués dans les activités de la pêche

Tableau 3 : Problèmes principaux et solutions.

II. Choix des partenaires nationaux et internationaux.

Le port de Vigo a une longue tradition dans la gestion intégrale des déchets et coproduits d'origine marine. Il présente la halle à mareyage la plus grande d'Europe, où le poisson débarqué est distribué dans le reste de l'Espagne. Il présente un système de gestion intégrale des déchets et coproduits dans le

même port. La plupart des déchets générés par les industries de transformation du Nord de l'Espagne finissent dans le port de Vigo, où ils sont valorisés pour la fabrication de farine et huile de poisson. La collaboration avec l'Institut de Recherche Marine de Vigo et avec les autoritaires portuaires, nous a permis d'avoir un contact direct de terrain avec la problématique actuelle de la pêche, à travers les différents agents du secteur (pêcheurs, mareyeurs, industriels, scientifiques). Au sujet de la collaboration avec le Département de Génie Chimique de l'Université de Grenade (Espagne), son expérience avec l'ultrafiltration membranaire des protéines a été très utile pour nous car la plupart du traitement des effluents de notre processus repose sur ces techniques.

Evaluation et prise en charge du coût du projet

Quelques sont les considérations à prendre en compte :

1.-La quote-part d'utilisation du personnel a été calculé par rapport au temps consacré dans le projet BE-FAIR (fiches horaires). Les charges patronales oscillent entre 30%, pour mon salaire, et 40%.

2.-Dans la partie de consommables, seulement les dépenses faites avec les fonds BE-FAIR ont été considérées.

3.-D'après l'avis des responsables financiers de l'IFREMER, le coût total des infrastructures et des communications **par personne** peut être estimé *à* 63% du salaire brut. Une fois estimé le total, le coût d'infrastructures peut être découpé de la façon suivante :

- 36% destiné à payer le loyer + charges
- 7% pour le gardiennage, secrétariat, etc
- 16% pour l'eau, électricité et chauffage
- 4% pour l'internet, l'impression des posters et la maintenance des bases de données bibliographiques

4.- Quelques sigles et acronymes utilisés pour nommer les organismes de provenance des crédits :

- EGIDE : Bourse du Gouvernement Français qui finances les études d'étudiants étrangers en France.
- UGR : Université de Grenade (Espagne).
- BM : Laboratoire de Biologie Moléculaire, au sein de l'IFREMER.
- INTERREG III : Fond Européen de Collaboration Multinational.

	Nature de la dépense	Détails		Nombre d'unités	Coût Moyen (€ TTC)	Quote-part utilisation	Total (€ TTC)	Crédit
1	**Ressources Humaines**	**Salaire Brut**	**Charges**					
1.1	Doctorant	1400	420	36	1820	100,00%	65520	EGIDE
1.2	Encadrant 1	3689	1986	36	5675	34,54%	70564	IFREMER
1.3	Encadrant 2	3025	1296	36	4321	25,00%	38893	UGR
1.4	Autre personnel (hors sous-traitance)							
	Cadre Biochimie	4289	2310	36	6599	25,66%	60954	IFREMER
	Technicienne Biochimie	2517	1355	36	3872	28,22%	39342	IFREMER
	Cadre Biochimie, Ingénieur Procédés	4070	2192	36	6262	25,39%	57248	IFREMER
	Technicien Electricité	2856	1538	36	4394	14,93%	23624	IFREMER
1.5	**Sous-total** Ressources Humaines						**356144**	
2	**Consommables**							
2.1	Fournitures expérimentales							
	Produits de laboratoire			3	941	4%	119	BEFAIR
	Matière première (achat de poisson)			3	102	100%	306	BEFAIR
	Matèriels pour atelier			3	533	33,33%	533	BEFAIR
2.2	Fournitures de bureau			3	103	4%	12	BEFAIR
2.3	**Sous-total** Consommables						**970**	

	Nature de la dépense	Détails		Nombre d'unités	Coût Moyen (€ TTC)	Quote-part utilisation	Total (€ TTC)	Crédit
3	**Infrastructures**							
3.1	Entretien, gardiennage, secrétariat			36	98		3528	IFREMER
3.2	Loyers des locaux			36	504		18144	IFREMER
3.3	Electricité, eau, chauffage			36	224		8064	IFREMER
3.4	**Sous-total** Infrastructures						**29736**	
4	**Matériel (amortissements)**	**Amortissement**						
4.1	Matériel d'expérimentation							
	Ordinateur de bureau	200		3	200		600	BEFAIR
	Logiciels de bureau (Statgraphics)	735		3	735	4,2%	31	IFREMER
4.2	Autre							
	Spectrofotomètre	1119		3	3356	4,2%	140	INTERREG III
	Centrifugeuse	709		3	709	4,2%	88,625	BM
	Prototype Compactage	2451		3	2451	50,0%	3677	BEFAIR
	Autres	200		3	600	4,2%	75	IFREMER
4.3	**Sous-total** Matériel						**4611**	

Tableau 4 : Coût consolidé de la thèse.

	Nature de la dépense	Détails		Nombre d'unités	Coût Moyen (€ TTC)	Quote-part utilisation	Total (€ TTC)	Crédit
5	**Déplacements**	**Transport**	**Hébergement**					
5.1	Missions en France							
	Réunion BEFAIR Nantes	837	0	1	837		837	BEFAIR
	Autres missions			15	15		229	BEFAIR
5.2	Missions en l'étranger							
	Réunion BEFAIR Lisbonne Mars/07	723	389	2	1112		2223	BEFAIR
	Mise en marche pilote compactage			1	1558		1558	BEFAIR
	Programmation pilote compactage			1	783		783	BEFAIR
	Réunion BEFAIR Vigo	574	477	2	1051		2103	BEFAIR
5.3	Congrès en France				0		0	
5.4	Congrès à l'étranger							
	WEFTA 2007 Lisbonne Octobre/07			1	1216		1216	BEFAIR
	WEFTA 2008 Florence 17-19/09/08			1	1624		1624	BEFAIR
5.4	**Sous-total** Déplacements						**10572**	

Tableau 4(Cont.) : Coût consolidé de la thèse.

	Nature de la dépense	Détails		Nombre d'unités	Coût Moyen (€ TTC)	Quote-part utilisation	Total (€ TTC)	Crédit
6	**Formation**							
6.1	Frais Inscription Doctorat			3	351		1053	RAUL PEREZ
	Cours de français IRPFLE			1	300		300	RAUL PEREZ
	Cours anglais doctorat			1	150		150	Ecole Doctorale
	Formation Nouveau Chapitre de Thèse			1	500		750	Ecole Doctorale
6.2	**Sous-total** Formation						**2253**	
7	**Documentation et communication**							
7.1	**Sous-total** Doc/communication			36	56		**2016**	IFREMER
10	**TOTAL**						**406301**	

Tableau 4(Cont.) : Coût consolidé de la thèse.

Compétences, savoir-faire, qualités professionnelles et personnelles.

La thèse, comme tout travail scientifique, aborde plusieurs problèmes qui demandent l'acquisition ou la mise en œuvre des différents techniques ou expertises par le doctorant. Le tableau ci-dessous montre les compétences acquises ou mises en oeuvre pendant le déroulement de ma thèse en les mettant en relation aux différentes tâches à accomplir dans le projet.

Compétences liées au déroulement des différents tâches

Tâche	Compétences scientifiques	Compétences organisationnelles et administratives	Compétences en communication	Compétences en management
Recherche Bibliograph.	Chercher dans les bases bibliographiques disponibles. Maîtrise des logiciels de bibliographie Zotero, Scopus et EndNote.		Rédiger une synthèse bibliographique et faire une présentation orale dessus.	
Essai de pressage	Etablir un plan de travail et un protocole. Effectuer le choix entre les différents variables à étudier.	Planification du procédure de travail. Gestion de la logistique des manips.		Répartir les différents tâches entre moi et mes collègues techniciens.
Analyses de laboratoire	Plan de travail complet avec choix des protocoles, inventaire des réactifs et moyens techniques et humaines. Maîtrise des essais biochimiques.	Distribution du temps en fonction de la durée des manips et de la disponibilité des équipes de mesure et des techniciens.		Déléguer quelques manips aux collègues techniciens.

Tableau 5 : Compétences acquises au fur et à mesure du déroulement des missions réalisées pendant la thèse.

Tâche	Compétences scientifiques	Compétences administratives	Compétences en communication	Compétences en Management
Tests de filtration membranaire	Se former sur la théorie et le procéder expérimental de la filtration membranaire. Sélection des fournisseurs de membranes.	Organisation du temps parmi les essais de filtration et les cours de doctorat.	Médiation entre l'entreprise HDR et le fournisseur de membranes PALL.	
Construction du prototype	Maîtrise du logiciel de simulation EcosimPro. Sélection des fournisseurs. Définition et / ou modification des objectifs du dessin. Adaptation aux conditions d'un bateau.	Gestion de la périodicité des rendez-vous et des délais dans la construction. Gestion du transport et de la réception du prototype en France.	Savoir communiquer une idée théorique au milieu industriel. Capacité de négociation. Médiation entre l'entreprise et les fournisseurs.	Déléguer de tâches (dessin mécanique) à l'entreprise. Superviser l'accomplissement du cahier de charges par l'entreprise.
Analyse et interprétation des résultats	Définition des objectifs et émission/validation des hypothèses.	Répartition du temps entre la rédaction de l'article, les manips dans le laboratoire et la présentation orale.	Rédaction d'un article scientifique. Capacité de parler en public en anglais lors d'une conférence internationale.	
Rédaction et soutenance de la thèse	Décider quels sont les résultats à montrer dans la thèse. Synthèse du travail dans un document.	Distribuer le temps entre les tâches de transmission (rédaction de thèse et des articles, présentation orale) et administratives.	Rédaction d'un document scientifique en français et anglais. Savoir communiquer les résultats devant le public.	

Tableau 5 (Cont.) : Compétences acquises au fur et à mesure du déroulement des missions réalisées pendant la thèse.

Qualités personnelles

La première difficulté trouvée au début de ma thèse était la langue, que je maîtrisais pas quand je suis arrivé à l'IFREMER. Dans mon premier année de thèse j'ai partagé mon temps entre la recherche bibliographique et l'étude de la langue française. Cela m'a permis de me familiariser avec les enjeux et procédés de la pêche et valorisation des co-produits, et d'autre côté avec la langue et culture françaises.

Le sujet de ma thèse implique la diffusion, parmi les différents acteurs de la pêche, des résultats obtenus à partir de nos essais (dans le laboratoire et avec le prototype). La solution du compactage des rejets et déchets de la pêche est une solution qui a trouvé une bonne acceptation, mais il reste encore des secteurs, notamment les pêcheurs, qui ne sont pas sensibilisés avec la problématique environnementale occasionné par les rejets. Ce fait a été constaté pendant les différentes journées d'information et de démonstration prévues au sein du projet BE-FAIR. Les conférences et tables rondes m'ont donné une vraie perspective des plusieurs problèmes et enjeux du secteur, des difficultés des pêcheurs pour s'adapter aux normatives communautaires, et des difficultés des scientifiques pour faire comprendre l'importance d'appliquer des mesures de conservation et de développement durable dans le secteur de la pêche. Cela a été une expérience très enrichissant pour moi, car j'ai pu travailler sur une application réelle, avec des contraints ajoutés (légaux, économiques, etc) qui ne se trouvent pas dans une thèse purement théorique.

Impact de ma thèse

On peut analyser l'impact de ma thèse d'après trois optiques différentes : la contribution que ma thèse a pu apporter à la science, l'impact pour mon laboratoire et finalement pour moi.

Pour la science

Le compactage de déchets est une technique déjà bien implantée dans la gestion des résidus, tant au niveau urbaine (déchets déménageurs) que industriel (résidus inorganiques et résidus organiques des abattoirs et des industries agroalimentaires). L'application de cette technique aux déchets de poisson est très limitée, elle est appliquée à la fabrication d'hachis surgelées qui sont destinées à l'alimentation animal grâce à sa haute teneur en protéines. La vraie originalité de ma thèse se base sur deux axes :

1. L'opération de compactage ne cherche qu'une réduction de volume mais aussi la récupération des fractions d'intérêt nutritionnel ou pharmacologique telles que les protéines ou l'huile de poisson.

2. Il s'agit d'un procédé qui a été complètement adapté aux conditions à bord d'un bateau et à la future normative de zéro-rejets, au niveau de performance énergétique, automatisation, utilisation de l'espace, gestion des effluents, etc.

Pour le laboratoire

L'inscription de mon projet dans un réseau international, et la nature de ma thèse, en collaboration avec l'Université de Grenade et l'IFREMER, a ouvert des nouvelles voies de collaboration future parmi les différents centres de recherche. L'IFREMER fait partie actuellement du réseau BIOTECMAR, avec le centre de recherche sur la pêche de Vigo (CSIC) et des autres partenaires.

Au niveau d'ultrafiltration membranaire, l'IFREMER Nantes a initié de contactes avec l'Université de Grenade. Après le succès du projet BE-FAIR, il y a un compromis de reprendre la collaboration entre les partenaires au sein des autres projets européens, toujours dans la thématique de la valorisation des résidus d'origine marine.

Pour moi

A la lumière de l'analyse de la gestion de ma thèse, des contacts avec les différents partenaires et de l'ensemble de mes compétences, il a quelques pistes professionnelles qui peuvent être identifiées :

1. Un postdoc à l'IFREMER, dans le cadre de la simulation des procédés appliquées à la valorisation de co-produits (hydrolyse enzymatique, compactage, ultrafiltration, extrusion réactive, etc).
2. Proposition d'intégrer l'équipe d'ultrafiltration de l'Université de Grenade, dans le cadre d'un projet de recherche de deux ans sur l'ultrafiltration des effluents d'origine marine.
3. Des bonnes relations, au niveau professionnel et aussi personnel, avec les autres partenaires du projet BE-FAIR, notamment dans le centre CSIC à Vigo où j'ai fait un stage de six mois.
4. A long terme, la future implantation du Centre Européen de Recherche sur la Pêche à Vigo, un centre directement attaché à la Commission Européenne, ouvre des nouvelles pistes professionnelles très intéressantes pour moi, car cela me permet de valoriser mon travail dans le secteur des co-produits de la mer, et aussi la formation que j'avait reçu dans mon Master sur les Politiques Européennes. Je considère que le fait d'avoir fait la thèse à l'étranger, dans le centre IFREMER et au sein d'un projet européen, ma maîtrise de différentes langues et le Master sur les Politiques Européennes peuvent être des points très positives dans mon CV à l'heure de postuler pour un poste.