Reactive and/or enzymatic extrusion process for phycocolloids extraction: application to sea products

Procédé d'extrusion réactive et/ou enzymatique pour l'extraction de phycocolloïdes : application aux produits de la mer

Dounia Makoure[1,2], Abdellah Arhaliass[1], Adil Echchelh[2], Régis Baron[3], Jack Legrand[1]*

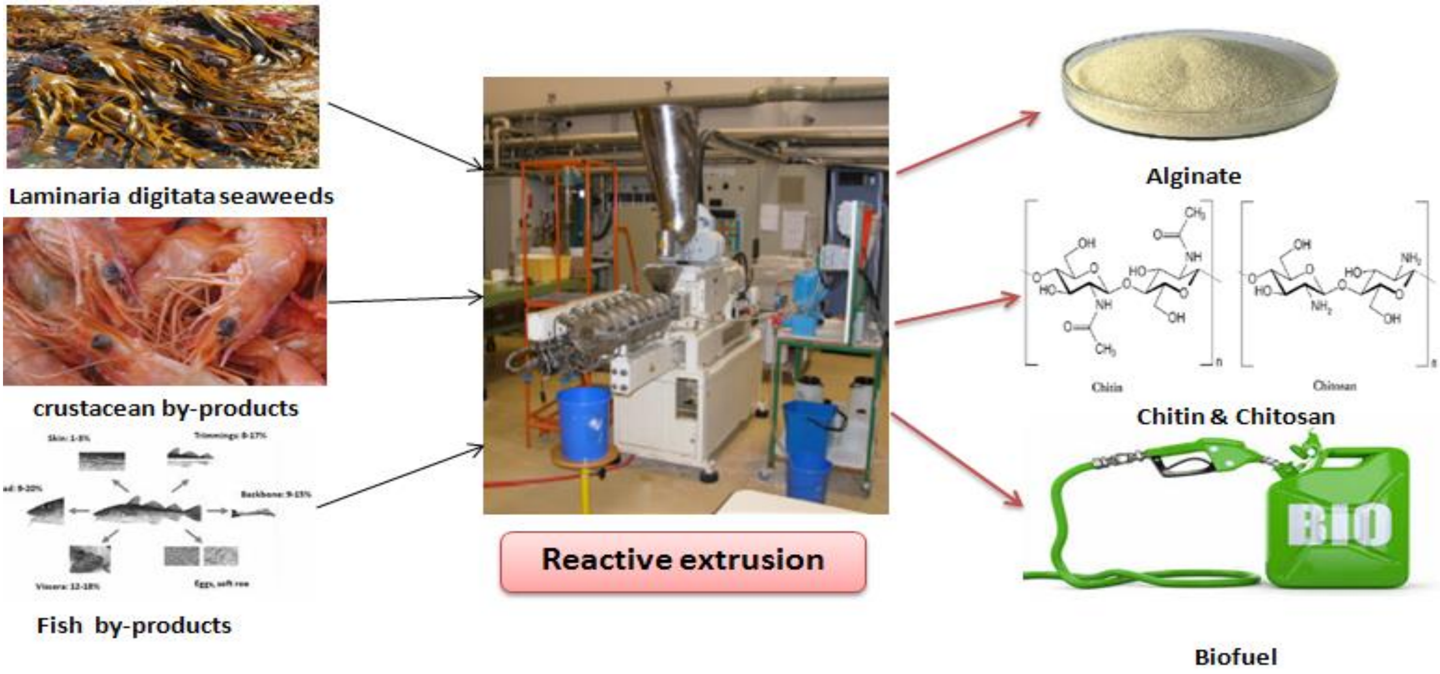
[1] GEPEA, Université de Nantes, CNRS, UMR 6144, CRTT, 37 Bd de l'Université, 44602, Saint-Nazaire Cedex, France, {dounia.makoure, abdellah.arhaliass, jack.legrand}@etu.univ-nantes.fr,
[2] Université Ibn Tofail, b.p 133 av. université, 14000, Kenitra, Maroc, adilechel@gmail.com
[3] IFREMER, Dpt. BRM, rue de l'Ile d'Yeu, Bp 21105,44311 Nantes Cedex 03, France, regis.baron@ifremer.fr
*Corresponding author

RÉSUMÉ. Dans cet article, nous présentons le procédé d'extrusion réactive pour extraire les phycocolloïdes des produits de la mer. En le comparant avec d'autres techniques, ce procédé présente plusieurs avantages comme le rendement économique, la flexibilité, la production de différents produits avec des caractéristiques différentes et des gains de temps. IL existe deux types d'extrudeuses : monovis et bivis, chacune ayant ses propriétés spécifiques. Les produits solides sont introduits par la trémie équipée d'une pompe doseuse pour la régulation du débit. Les produits liquides sont généralement injectés dans les zones non remplies, par une pompe externe. Les produits subissent des modifications thermo-mécaniques et ensuite la mise en forme des produits finis est réalisée par la filière. L'extrusion réactive est appliquée dans plusieurs domaines : l'agro-alimentaire où il existe trois utilisations principales (extrusion simple, cuisson-extrusion, extrusion réactive), dans l'industrie plastique pour le recyclage des déchets plastiques ménagers et aussi pour créer des mélanges entre de différents polymères, ainsi que dans le domaine de la chimie et la pharmacie. L'extrusion réactive est également utilisée pour la valorisation des produits de la mer comme l'extraction des phycocolloïdes, en particulier l'alginate à partir des algues marines, ainsi que la chitine des coproduits de crustacés. Une autre application intéressante du procédé d'extrusion réactive est la production d'énergie. Des recherches récentes visent à valoriser les coproduits de la pêche pour la production du biocarcurant.

ABSTRACT. In this paper we present the reactive extrusion process to extract the phycocolloids from the sea products. By comparing with other techniques, this process has a several advantages like the economic return, the flexibility, the production of various products with different characteristics and time gains. There are two types of extruder: single-screw and double-screw, each one has its specific properties. The solid products are introduced by means of the hopper that is equipped with a dosage pump for the regulation of the flow. Liquid products are, generally, injected in the not filled zones, through an external pump. The products undergo thermo mechanical modifications and then the shaping of the final products was done in the die. The reactive extrusion is applied in several fields: agri-food where there are three main types of operating conditions (simple extrusion, extrusion-cooking, reactive extrusion), in the plastic industry for the recycling of household plastic waste and also to create mixtures between different polymers, as well in the field of chemistry and pharmaceutics. The reactive extrusion is used also to add value to the sea products like to extract phycocolloids especially the alginate from the seaweeds, also the chitin from crustacean by-product. A further interesting application of the reactive extrusion process is the energy production. Recent research is aimed to the valorization of fish by-products for the extraction of lipids for biofuel purpose.

MOTS-CLÉS. Extrusion réactive, valorisation, coproduits, produits de la mer, Phycocolloïdes alginate.
KEYWORDS. Reactive extrusion, valorization, by-products, sea-products, phycocolloids, alginate.

GRAPHICAL ABSTRACT.



1. Introduction

The process of extrusion consists in conveying raw materials by one or two screws, through a barrel where they experience several thermo-mechanical treatments. These treatments can be generated by mixing, shearing, heating, cooling, shaping, partial drying and blowing. These conditions lead to physicochemical modifications of the extruded materials. The various process parameters determine the thermo-mechanical treatments provided to the raw materials and the final properties of the extruded [1]. When chemical reactions are voluntary induced, the process is called reactive extrusion.

There are different types of extruders. Each of them represents different characteristics such as mixing capability, process flexibility, control of process parameters, process productivity, economical opportunities and business potential [2]. Due to these advantages and characteristics, the process of reactive extrusion has become vital in different fields.

The first extrusion food application dates from the middle of the 19th century when the meat was minced by a piston extruder. The application of the extrusion now is developed. In plastic industry, different mixtures of alloys and polymers were carried out [3] and also systems of plastic packaging have been introduced [4].

The researches conducted in the field of chemistry, there are some new materials that were developed like fire-retardant [5] and bio-sourced materials [6]. The process showed a positive development compared to the other traditional extraction processes of chitin [7] (substance that presents an important role in agricultural, cosmetic and medical sector) and alginates [8] from sea products.

The current study is carried out to investigate the potential of reactive extrusion in the field of renewable energy to produce biofuel from the coproducts of fish (head, skin, bones).

2. Reactive extrusion and their benefits

The reactive extrusion is a complex process covering two different fields, the chemistry and the classic thermos-mechanic extrusion. In this case, the extruder is considered a continuous chemical reactor.

This discipline is in full extension and development over the last thirty years, in particular in the field of polymers [9], where chemical reactions occur wish can develop and elaborate a new products [10]. Several parameters have to be taken into consideration in reactive extrusion. They are classified in 4 categories [11]:

- The residence time controlled by the screw profiles and by the flow rates,
- The mixture and the rheology of the melted material,
- The thermal exchange, including the viscous dissipation, which is more or less important,
- The reaction rates controlled by the kinetics and the heats of reaction…

The reactive extrusion is a technology that allows intensifying processes with a lot of benefits:

-The reactive extrusion is a cost-effective and an economic process: the use of high concentration of raw materials leads a cost reduction of solvent, of storage, purification, separation and recovery. The reactive extrusion does not require solvents for the dilution of the molten polymers with high viscosity. The more the system is viscous, the better the flow in the extruder is continuous and stable.

-Possibility of using various parameters and a wide range of mixture conditions: the extruder is able to mix high viscosity and low viscosity reagents. The extruder accepts the high temperatures up to 500°C when the polymers which are reacted have a high fusion temperature. The extruder can work under high pressure for the reactions involving low boiling point catalysts or reagents. It works also in a high vacuum for the purification of the main product by eliminating the volatile products.

-Flexibility of the process: the simplicity of the operation and the dumping of products allow to produce a wide range of finished products and to use different raw materials while minimizing the losses of products.
The extruder geometry facilitates the operations such as polymer melting and conveying section, the reagent mixing, the reaction and the shaping. The screw and barrel geometries are also important; they facilitate the interchange of filled and not filled zones. The extruder can be used as a reactor to create special products in order to meet the specific customer needs. Therefore, the extruder is multifunctional equipment [3], [12], [13].

Despite the advantages, the reactive extrusion has some disadvantages and it faces some challenges:

-The conveying and mixture capacity is limited: for the single screw extruder, just the high viscosity fluids that are conveyed and mixed.

-The short residence time: the extruder is not a good solution for slow reactions due to the rather low residence time.

-The difficulty in obtaining a copolymer with two immiscible polymers: The degree of reaction between immiscible polymers is low. Because of the heterogeneous reaction medium, the reaction will be at the interfaces.

-The limitation of reactive extrusion process to the reactive systems with the controlled released heat: in an extruder, the heating of a polymer is easier than its cooling. The thermal balance for a polymer in an extruder is described in the form of the following equation:

$$\rho\, cp\, (T_2 - T_1) = Ef + E\eta + Er - Ec$$

with: ρ (kg/ m^3) density of polymer,
cp (J/ kg.˚C) specific heat capacity ,
T_1 (˚C) initial temperature,
T_2 (˚C) final temperature,
Ef (J/m^3) energy density transmitted by conduction through the barrel,
Eη (J • m−3) energy due to viscous dissipation,
Er (J • m−3) energy released by the reaction,
Ec (J • m−3) energy evacuated by the cooling system.

In heating, Ef, Eη, Er contribute to increase the temperature of the polymer and in cooling, just Ec contributes to decrease the temperature. So the energy dissipated by the cooling system is hard to control for the exothermic and fast reactions [3].

-The use of the extruder as a chemical reactor is recent: due to the insufficient training of the engineers, the extruder has always been a way for compounding and shaping operations [3].

3. The extruder types

There are 2 types of extruder, single screw and twin screw:

For the single screw extruder, the friction forces provide the material transport and its efficiency depends on the material adhesion: The more the material sticks on the screw, the more there is a difficulty of material progress. When the friction coefficient raw material-screw is high, the material progresses easily to the output of the extruder. The mechanical energy supplied by the screws is converted into thermal energy by raw materials viscous dissipation. The mixture is forced to go through the shaping die where there is a sudden drop in pressure to the atmosphere resulting an evaporation of solvents contained in the finished product [1], [14].

Due to the screw geometry and the low raw materials volume in the barrel, the raw material mixing is low. The use of premixed raw materials before going into the extruder is necessary to increase the mixing [15].

For the twin screw extruder, the adhesion constraint raw material-screw decreases because of the screw thread that sweeps the material from the other one then the material goes into the barrel. Due to the high flexibility and the thermo-mechanical treatment, the twin screw extruder produces different innovative products [16].

There are several types of twin screw extruder: co-rotating or counter-rotating screws, and interpenetrating or not-interpenetrating screws.

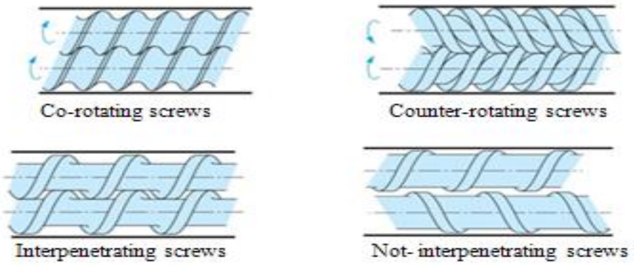


Figure 1. *Classification of the twin-screw systems [17]*

The not-interpenetrating twin-screw extruder is assimilated like two single screw extruders, so the extrusion capacity was doubled in comparison with the single screw extruder. For the interpenetrating twin-screw extruder is assimilated as a volumetric pump. The raw material flow is controlled by screws geometry.

The comparison between the single and double screw extruder is represented in the table 1:

	single screw extruder	double screw extruder
Mixing capability	-Limited capability -The use of specific screw elements reduces the extruder throughput.	-Remarkable mixing capability. -Possibility of using various screw elements: single lead screws, Barrier, Mixing screws…
Process flexibility	-The efficiency depends on the screws speed -The combination of the processes in one single extruder is limited	-Independence of process parameters: the raw materials flow, screws speed… -The possibility to combine different processes in one single extruder.
Control of process parameters	-weak control	-Best control of coefficients «shearing-time-temperature », resulting a good quality of end product.
Process productivity	-Limited productivity by screw wear.	- High productivity due to the possibility to adjust the speed screws to the screw wear.
Economical opportunities and business potential	-Limited productivity and raw materials use.	-High productivity and diversity of raw materials as well as end products. - Good quality of products with a good precision and uniformity.

Table 1. *Characteristics of single-screw or twin-screw extruder [2]*

4. The main components of an extruder

The main constituent elements of an extruder are:

-A barrel which is thermally regulated,
- One or two parallel screws,
-A motor with variable speed and a reducer which makes screws rotation,
- A shaping die,
-A hopper for the solid products and
-An external pump for the liquid products with a variable flow

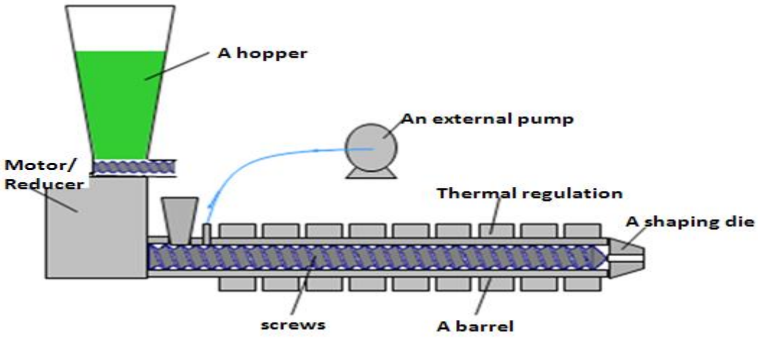


Figure 2. *Main components of an extruder*

The barrel

The barrel is the fixed outer sheath where the screws rotate. It forms with the screws a dynamic system where the material processing is carried out. The extrusion process starts by introducing the solid products in the hopper that is equipped with a dosage pump for the regulation of the flow. Liquid products are generally injected in the not filled zones, through an external pump. The material is conveyed to the shaping die by the screws rotation [10].

The shaping die

The shaping die is a mechanical tool used to shape and to give to the extruded products the required dimensions, generally, by compression.

The screws

For the twin screw extruder, the two screws are rectangular or cylindrical. The screw barrel assembly is consisted of sections mounted on splined shafts and there are three types [10]:

Figure 3. *Screws section and splined shafts [17]*

Single lead screws

This screws design is used on the feed section on the barrel to build up the pressure needed to conveying the material [18].

Figure 4. *Single lead screw*

Barrier screws

Barrier screws are used in the melting section and they help to make a distributive mixing [18].

Figure 5. *Barrier screw*

Mixing screws

Due to its homogeneous rate of mixing, the mixing screws provide a good mixing than the barrier screws. The mixers elements are specified by the disk number, the disk thickness and the angle between two disks [18].

Figure 6. *Mixing screw*

5. The application fields of reactive extrusion process

5.1. *Agri-food sector*

The extrusion process is a technique widely applied in the agri-food sector due to its competitive advantages:

-Sustainable technique thanks to the high productivity with the reduction of the energy, water consumption and the materials loss.

-It allows using several types of raw materials and to product a different finished products including some innovations in flavor, texture and nutritional value.

-Cost-effective technique in view of its reduction of investment and operating costs.

There are three main types of applications:

•Simple extrusion: it is a simple shaping of food products

•Extrusion-cooking is used for cereal products

•Reactive extrusion that exploits the intensive mixing capacity of the extruder to make contact the reagents.

The reactive extrusion is used also to product nutritionally balanced pet food and fish feed.

5.2. *Plastic industry*

In the field of plasturgy, the extrusion is used to transform the plastic materials. It performs a lot of actions and steps principally: the material transport, the kneading for the plasticization of the raw material, the pressure increases for transporting the material to the shaping die. Considering its characteristics, the extrusion process is used for various finished products such as plastic film, extruded sheet, tubes and extruded profiles and also it is used to recycle the plastic wastes.

We can also realize alloys and polymers mixtures, reactions of mass polymerization, polycondensation, chemical modification of polymers, polymers mixtures compatibilizing, dynamic vulcanization and polymer recycling [3]. In the field of plastic packaging systems, the development of sodium caseinate films for effective, antimicrobial and active packaging applications was carried out by the extrusion process [4].

5.3. *Chemistry field*

The extruder as chemical reactor presents a lot of benefits that are used in chemistry field to avoid the problem encountered for certain applications when we use the classic technologies: low yield, incomplete reactions, long reaction time.

In order to study the copolymers emulsification efficiency, the reactive extrusion was applied for the synthesis of graft copolymers with polyamide and polystyrene [19] and also for the synthesis of nano-structured alloys [20].

For the development of new fire-retardant materials while preserving the materials physical and mechanical properties, Sahyoun [17] applied the reactive extrusion process to generate inorganic fillers in polymer matrix which is melted by hydrolysis and condensation reactions. The process was applied also to incorporate volatile molecules and to encapsulate agro-material matrices so as to develop new bio-sourced materials [6].

5.4. *The valorization of plant material*

N' Diaye and al. [19, 20] showed that alkaline extraction of poplar wood hemicellulose can be realized by reactive extrusion. The high shear capacity provides the plant material fractionation with a yield similar to the batch yield. Two operations can be simultaneously realized in the extruder: the extraction and the solid/liquid separation [21], [22]. The process of reactive extrusion is used also to add value to agricultural co-products such as lignocellulosic biomass (sugar cane bagasse, wheat bran) [23].

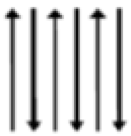
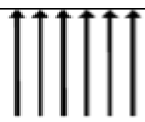
6. Application of reactive extrusion to sea products

In a context of sustainable development and increase of the market of sea products, the current researches intend to value the marine by-products by extraction of biopolymers. The researches were made to extract the chitin from crustacean shells and also to extract the interest compounds from the seaweeds by reactive extrusion: phycocolloids especially alginates.

6.1. *Extraction of chitin from crustacean by-product*

The shrimp shells contain 30-40 % of chitin and 20-30 % of carbonate of calcium ($CaCO3$), the shell elasticity is related to the bonding extent between chitin and proteins, and their distribution in the matrix. The chitin is the most abundant natural polymer in the globe. It protects the body against the radiations, heat, chemical and physical attacks. The chitin forms with proteins the crystalline microfibrils [7].

This substance has three different arrangements [24]:

Type of chitin	**arrangement representation**	**characteristics**
α -Chitin		- anti-parallel chains structure -the most common - Present in arthropods such as crustaceans. -Due to the hydrogen and covalent bonds between chains, it’s the most stable form.
β- Chitin		-parallel chains structure -Less stable and

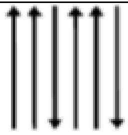
		crystalline and rarer.
γ -Chitin		-The combination of α – Chitin and β- Chitin -anti-parallel and parallel chains structure

Table 2. *Chitin types and their characteristics*

The chitin is used in the agricultural sector as an elicitor for the plants. The chitinous products decomposition releases the nitrogen, contributing to soil and plant enrichment [25].

Chitosan is one of the derivatives of chitin; it is produced commercially by deacetylation of chitin. For the waste water treatment, the chitosan is used as a flocculant [26].

In cosmetics field, the chitin and chitosan films are used in skin and hair care products. This application is based on electrostatic properties of chitosan [27].

In the food-processing, the chitin and its derivatives have an antioxidant and antimicrobial effects for food quality preservation, and also it is used as food additives for the addition of flavours and colours [28]. The chitosan is an antibacterial and antifungal used for dental and veterinary care as a bandage for lesions, in the medical sector [29] [30].

The chitin is extracted according to two different processes, by using the chemical process or biological treatments.

6.1.1. *Chemical process*

The chemical extraction consists of an acid treatment for the demineralization and an alkaline treatment for the deproteinization.

- The demineralization

The acid treatment eliminates minerals, which turns into a salt in the solution.

$$2\ HCl(aq) + CaCO_3(s) \rightarrow CaCl_2(aq) + H_20(l) + CO_2(g)$$

The demineralization lasts 15 min to 48 h and from the ambient temperature to 50°C [31] [32].

- The deproteinization

It is a basic treatment removes proteins by solubilization. The reagents used are strong bases such as sodium hydroxide (KOH) [31], [32].

6.1.2. *Biological treatments*

- The fermenting process

Several researches have been conducted on the bacterial fermentation to extract the chitin. The fermentation was carried out by different bacteria such as *Pseudomonas aeruginosa* K-187, *Pseudomonas maltophilia*, *Bacillus subtilis*, *Streptococcus faecium*, *Pediococcus pentosaseus* and *Aspergillus oryzae* with a different pH, fermentation time and temperature. Each fermentation process has a different chitin extraction yield [33], [34].

- The enzymatic process

The investigations have focused on the chitin extraction from crustacean by-products using enzymes like protease, papain, pepsin and alcalase. The enzymatic reaction conditions and the chitin fraction obtained differ for each enzyme used [33], [35], [36].

The previous treatments show a long treatment period and need two steps to extract the chitin: minerals elimination and proteins elimination.

In a part of her research, K. Le Roux [22] used the reactive extrusion process to carry out the enzymatic hydrolysis in order to extract the chitin from the by-products of shrimp, Penaeus vannamei, by using the pepsin enzyme in an acidic medium. Tests were carried out to study the chitin purification parameters such as the enzyme used, its concentration, temperature and raw materials fragment size. Two experience plans were performed: for the first one, the experiences were realized by using the pepsin enzyme and the phosphoric acid in the reaction medium. The best performances for this experience plan are obtained when the raw material fragment sizes are reduced and the pepsin concentration is higher. For the second experience plan, the enzyme used is Acid Stable Protease and the acid is formic acid. The experience performances are close to those of pepsin [7].

6.2. *Extraction of alginates from Laminaria digitata*

The seaweeds are the sea product that has the most rate of production. The production is more than 27 million tons. Every year, the seaweeds industry operates approximately 8 million tons of fresh seaweed and provides a wide range of products which represent a total annual market of 6 billions of dollars. The seaweeds come either from natural features or seaweed farming that was developed from the 1950s and now it is practised in about thirty countries [37].

The 8 million tons of fresh seaweed exploited every year are used and valorized on different fields: agricultural sector, phycocolloid production, cosmetic and pharmaceutical field and food distribution [38].

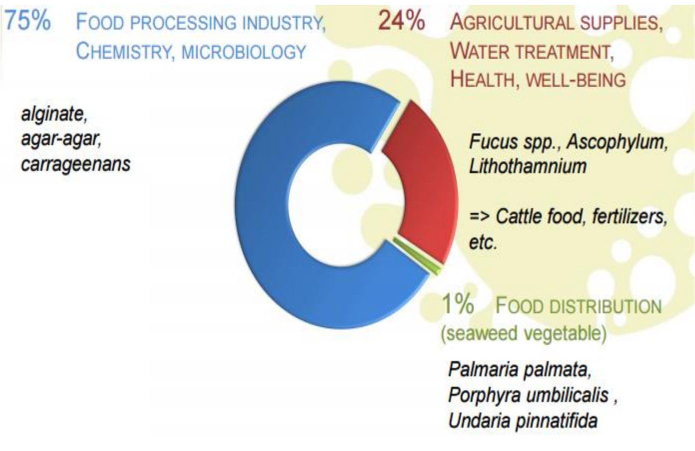


Figure 7. *Exploitation fields of seaweeds [38]*

The food processing industry, chemistry and microbiology are the largest exploitation of seaweeds especially the extraction of phycocolloids principally the alginates.

The alginates are the compounds that are naturally present in the cell wall of the brown seaweeds in the form of salts of sodium, magnesium, and calcium. They have been discovered in 1883 by Stanford who has obtained, due to frond alkaline extraction of the seaweed *Laminaria digitata*, a gelatinous substance called algin [39].

There are several assumptions about the alginate physiological function in seaweeds. The most common attribute to alginates a mechanic resistance and flexibility [40]. Various works showed a correlation between the seaweed parts rigidity and the alginate thickening nature. The alginates present in the blade are less gellant than that present in the stipe [41]. They have also a role of protection against dehydration, ionic regulation within the cells and reserve substance [42].

6.2.1. *Application fields of alginate*

For a long time, under the code names E401 and E405, the alginates are used in agri-food sector as thickening or preservative agents for sauce, mustard, mayonnaise, as stabilizing agents too for ice cream. The use of alginates in the paper industry improves the paper quality. The addition of alginates gives brilliance to the papers and cardboards surface. They are also used as stabilizing and thickening agent in adhesives.

In pharmaceutical industry, the alginates are at first the active ingredient of the bandages and also they are present on different medicines as a viscosity and stabilizing agents. In textile industry, the alginates are exploited as a colour preserving that protects the fabric from the sunlight, and as waterproofing, film-forming and plasticizing agent [43], [44].

6.2.2. *Extraction methods of alginate*

There are various methods to extract the alginates. The alginate industry extraction protocol is divided into five steps: acidification, alkaline extraction, solid/liquid separation, precipitation and dying [45]. The main step is the alkaline extraction. An optimum extraction in terms of yield requires several hours depending on the seaweed species [43], [45]. The extraction time has an influence on the obtained alginate rheological properties.

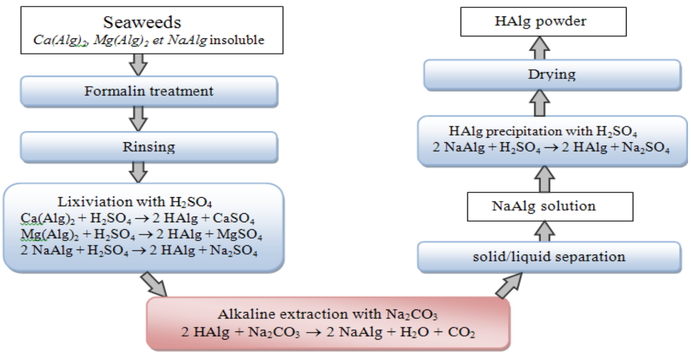
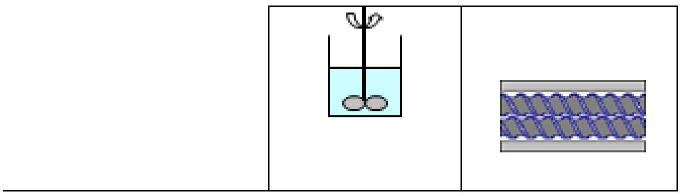


Figure 8. *Alginate extraction protocol [8]*

Vauchel [8] used the reactive extrusion as a new process for the alkaline extraction from the seaweed *Laminaria digitata*. Firstly, she conducted a comparative study between batch and reactive extrusion process to accomplish the carbonation step. The purpose of this study is to demonstrate the gains made by using the new process.

The compared factors are: the extraction yield, water and reagents demands, product quality and its rheological properties. The important advantage of the reactive extrusion is an important time savings: the extraction time is reduced from 1 hour in batch to only a few minutes in reactive extrusion. Due to this extraction time reduction, the alginate rheological properties are preserved. This process halves the water and reagents consumption [8].



	Batch	Reactive extrusion
Extraction yield (%)	33.3 (±1.8)	38.5 (±1.9)
Extraction time (min)	60	5
Reactant demand ($kg.kg^{-1}$ dry seaweed)	0.5	0.2
Water demand ($kg.kg^{-1}$ dry seaweed)	25	10

Table 3. *Comparison of batch and reactive extrusion parameters [8]*

The recovered alginate quantity is more important by using the reactive extrusion. So the extraction yield increases by more than 15%. For the sodium alginate solution viscosity, the reactive extrusion makes an improvement over the batch process: the dynamic viscosity is clearly higher. The alginate chain extracted from the reactive extrusion is three times longer. The precipitation is more efficient with long chain molecules therefore the extraction yield is more important.

Due to the shear capacity and the mixing of the twin-screw extruder, the reactive extrusion process is more effective than the batch. The seaweed pieces are closely mixed with the reagent as a result the extraction time, water and reagent consumptions are reduced. The time gains minimize the depolymerization phenomena and then ensure alginates at a high molecular weight, with a high yield and improved rheological properties against the batch process.

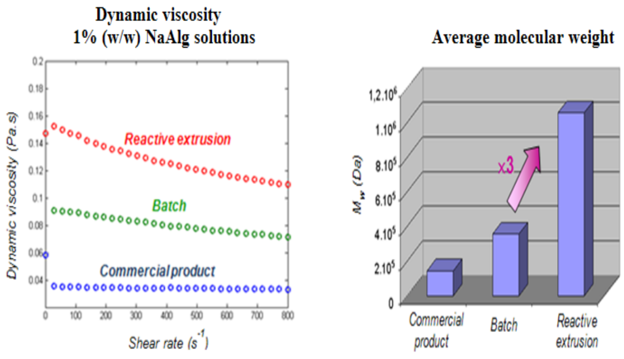


Figure 9. *Rheological characteristics [8]*

6.3. *Lipids extraction from coproducts of fish*

The depletion of oil resources of the planet and the enhancement of laws and regulations promoting “green” fuels oriented the scientific research toward the discovery of new sources of energy. The activities of smoking fish and canning industry generate every year several tons of by-products representing the residue of fish and crustaceans manufacturing. The valorization of these by-products (residue biomass) constitutes an important issue to allow a more profitable and more sustainable exploitation of the marine resource. Moreover, the residue marine biomass represents an alternative source for biofuel production.

Some works are in progress to extend the reactive extrusion application. This process is used to extract lipids from coproduced of fish such as the fish head, skin, and bones. The pre-crushed fish coproducts are enzymatically hydrolysed in the twin-screw extruder while adjusting the extrusion parameters: raw materials and enzymatic solution flow, screws speed and barrel temperature. The extrusion is carried out by using different types of fish. The extrudate is recovered and centrifuged. The centrifugation results four phases: the pellet, liquid, oil emulsion and the oil phase that is the most interesting phase. The oil part is recovered and then it is transesterified to produce the methyl esters. These esters are considered as biofuel and they are analyzed. The analysis results are used to compare between the physicochemical properties (chemical composition, viscosity, density, the acid number) of biofuel and that of diesel fuel. The study focuses on the characterization of the extracted lipids in order to establish the technical feasibility of their use as additive (between 5 and 40 % v/v) of diesel.

7. Conclusion

The extrusion reactive is a simple, productive, economic and ecological process. Due to its advantages, it becomes a solution to avoid the problems encountered for certain applications by using classic technologies. Currently, the technology requested is an economic, fast and energy technology. Because of that the scope of reactive extrusion application is broad; it is used on current fields such as green energy, environment and renewable energies, and also to add value to by-products like the sea products.

The valorization of sea products helps in marine waste management. When the waste is recovered, two demands can be addressed: the pollution reduction by using recycling marine by-products and the extraction of the compounds of interest.

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