

**NEW PERSPECTIVES OF EUROPEAN OLEOCHEMISTRY**  
**LES NOUVELLES PERSPECTIVES DE L'OLÉOCHIMIE EUROPÉENNE**

# The thermo-mechano-chemical twin-screw reactor, a new perspective for the biorefinery of sunflower whole plant: aqueous extraction of oil and other biopolymers, and production of biodegradable fiberboards from cake

Philippe Evon<sup>1,2,\*</sup>, Virginie Vandebossche<sup>1,2</sup>, Laurent Labonne<sup>1,2</sup>, Justine Vinet<sup>1,2</sup>, Pierre-Yves Pontalier<sup>1,2</sup> and Luc Rigal<sup>1,2</sup>

<sup>1</sup> Université de Toulouse; INP; LCA (Laboratoire de Chimie Agro-industrielle); ENSIACET, 4 allée Emile MONSO, BP 44362, 31030 Toulouse Cedex 4, France

<sup>2</sup> INRA; LCA (Laboratoire de Chimie Agro-industrielle), 31030 Toulouse Cedex 4, France

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**Abstract** – Biorefinery of sunflower whole plant was performed successfully using a thermo-mechano-chemical twin-screw reactor. This led to the aqueous extraction of oil and other biopolymers like proteins, pectins and non pectic sugars. It resulted in the overall fractionation of biomass, thus allowing a complete valorization of the input. This biorefinery process was not only efficient but it was also environment-friendly. In addition, it contributed to the production of different end products for various industrial applications. Firstly, the hydrophilic phase will be recycled to the process. Secondly, the densest oil-in-water emulsion is a promising candidate for the formulation of cosmetic creams. Thirdly, the upper hydrophobic phase will be usable for the waterproofing treatment of the surface of agromaterials by coating. Its demixing will also lead to the production of proteins with tensioactive properties. These will serve for the food industry. Lastly, the cake was a mixture of plasticized proteins and lignocellulosic fibers. It was thus considered as a natural composite. Its molding into cohesive fiberboards was conducted successfully using both thermopressing and compression molding processes. The self-bonded boards with high density will be suitable for use as load bearing boards in dry conditions (floor underlayers, interior partitions, furniture, etc.). Positioned in walls and ceilings, boards with medium and low density will contribute to the heat insulation of buildings. In addition, the bulk cake will be also usable as a loose fill insulation material. As proposed, this flow chart thus allows a valorization for all fractions originating from the twin-screw reactor.

**Keywords:** Biorefinery / twin-screw extruder / sunflower whole plant / thermo-mechano-chemical fractionation / aqueous extraction

**Résumé** – Le réacteur thermo-mécano-chimique bi-vis, une nouvelle perspective pour le bioraffinage de la plante entière de tournesol : extraction aqueuse de l'huile et d'autres biopolymères, et production de panneaux de fibres biodégradables à partir du tourteau. Le bioraffinage du tournesol plante entière a été réalisé avec succès en utilisant un réacteur thermo-mécano-chimique bi-vis. Cela a permis l'extraction aqueuse de l'huile et d'autres biopolymères tels que des protéines, des pectines et des sucres non pectiques. Un fractionnement total de la biomasse a été obtenu, permettant ainsi une valorisation complète de la matière entrante. À la fois efficace et respectueuse de l'environnement, cette bioraffinerie a généré plusieurs produits finaux pour diverses applications industrielles. Tout d'abord, la phase hydrophile pourra être recyclée en tête de procédé. Puis, l'émulsion huile/eau la plus dense pourra être utilisée pour la formulation de crèmes cosmétiques. Pour sa part, la phase hydrophobe supérieure sera utilisable pour le traitement de surface des agromatériaux par enduction afin de les rendre moins sensibles à l'eau. Sa démixtion facilitera également l'obtention de protéines tensioactives, utilisables dans l'industrie alimentaire. Enfin, le tourteau étant un mélange de protéines plastifiées et de fibres, il a été considéré comme un composite naturel, moulable en panneaux de fibres cohésifs par thermopressage ou par moulage par compression. Les panneaux auto-liés de haute densité pourront

\* Correspondence: [philippe.evon@ensiacet.fr](mailto:philippe.evon@ensiacet.fr)

être utilisés comme des panneaux travaillants, utilisés en milieu sec (sous-couches pour le sol, cloisons intérieures, meubles, etc.). Positionnés dans les murs et les plafonds, les panneaux de densité moyenne ou faible pourront servir à l'isolation thermique des bâtiments. Par ailleurs, le tourteau pourra aussi être utilisé comme isolant en vrac. Tel que proposé, ce schéma de procédé permet ainsi une valorisation de toutes les fractions provenant du réacteur bi-vis.

**Mots clés :** Bioraffinage / extrudeur bi-vis / tournesol plante entière / fractionnement thermo-mécano-chimique / extraction aqueuse

## 1 Introduction

Faced with the awareness of the risks associated with the depletion of fossil resources on the one hand and with the emissions of greenhouse gases (especially CO<sub>2</sub>) that causes their intensive exploitation on the other hand, research has been conducted since several years for the development of new processes for the fractionation of agricultural resources, oilseeds in particular, according to the biorefinery concept (Nieddu and Vivien, 2013). Born in the nineties and based on the model of the oil refinery that uses crude oil from various sources to produce fuels and derivatives, the biorefinery concept was formalized from several criteria:

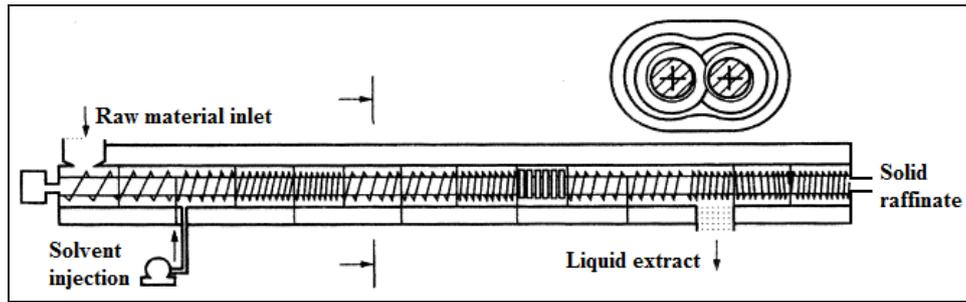
- (i) Considering the overall fractionation of biomass, including fractionation of whole plant, to allow a complete valorization of the input, including the cultivation by-products, in order to provide a valuation for all components of the plant.
- (ii) Optimizing the co-valuations.
- (iii) Designing an environmentally friendly process:
  - Reducing CO<sub>2</sub> emissions: because the biomass is considered as a sequestering agent of carbon dioxide, the balance between CO<sub>2</sub> absorbed by the plant during its growth and CO<sub>2</sub> emissions for crop production, plant processing and recycling of finished products is generally more favorable.
  - Reducing the release of effluents until, ideally, no longer producing wastes.
  - Reducing or eliminating the use or the generation of hazardous and/or toxic substances.
- (iv) Designing an efficient process:
  - Of reasonable size, versatile and flexible, the processing unit of raw material is located as close as possible to its place of production to minimize the transportation costs necessary for the supply of the raw material unit.
  - For the distribution of finished products to customers, it is also planned a geographical area as limited as possible to minimize the associated shipping costs.

Thus, the biorefinery concept is an opportunity for the development of an industrial biotechnology as today for petrochemistry. As a renewable resource, biomass would become an alternative to crude oil and a significant source of new products for multiple uses in the fields of energy (biofuels), non-energy (polymers, surfactants, solvents, lubricants, platform molecules, agromaterials, etc.) and food. Many studies have been made in this direction in the Agro-industrial Chemistry Laboratory (LCA) for the extraction, the separation and the purification of the constituents of several plant materials, for

their chemical transformation and their processing into renewable composite materials. The fractionation of different plant materials has been studied since a few years. In particular, a new biorefinery process of sunflower whole plant has been recently developed (Evon, 2008; Evon *et al.*, 2010a), and a patent has been filed on this occasion (Evon *et al.*, 2012a). For almost all these researches, the twin-screw extrusion technology was chosen as the industrial tool for the thermo-mechano-chemical (TMC) fractionation of the plant material.

## 2 The potential of twin-screw processes for the fractionation of plant materials

To maximize its effectiveness, the fractionation of plant materials usually requires the application of a triple constraint (*i.e.* thermal, mechanical and chemical) to the raw material. In addition, the use of an equipment operating continuously and capable of several elementary operations into a single step allows the intensification of fractionation processes as well as a better co-valuation of the obtained fractions. The twin-screw extrusion technology perfectly meets these two requirements. It is widely used in the food industry. And, even if it is a more expensive technology than the single-screw one, it allows a more elaborate work on the matter. More recently, the twin-screw extrusion has seen its scope expand to the field of thermo-mechano-chemical fractionation of plant material (Rigal, 1997, 2000). This new concept has allowed the development of real reactors capable of transforming or fractionating physically and chemically the plant material in a single step, thus leading to the separate production of a liquid extract and a solid raffinate through liquid/solid separation at the end of the screw profile (Bouvier and Campanella, 2014). The temperature rise is then due to both an external supply and the viscous dissipation of mechanical energy in the product. Conducted for nearly twenty-five years at LCA laboratory, several studies have highlighted the multiple possibilities of the twin-screw technology for both fractionation and valorization of agricultural resources. Some examples are following: (i) the mechanical pressing and/or the solvent extraction of vegetable oil from sunflower (Dufaure *et al.*, 1999a, 1999b; Amalia Kartika *et al.*, 2005, 2006, 2010; Evon *et al.*, 2007, 2009, 2010a, 2012a), neem (Faye, 2010), jatropha (Evon *et al.*, 2013) and coriander (Sriti *et al.*, 2012; Uitterhaegen *et al.*, 2015) oleaginous seeds, (ii) the extraction of hemicelluloses from lignocellulosic plant materials (Manolas, 1993; N'Diaye, 1996; Prat, 1998; N'Diaye and Rigal, 2000; Maréchal, 2001), (iii) the extraction of pectic substances from the pith of sunflower stalk (Maréchal and Rigal, 1999) or sugar beet pulp (Jorda, 2003), (iv) the extraction of vegetable proteins (Silvestre *et al.*, 1999;



**Fig. 1.** Schematic representation of a twin-screw extruder consisting of a bilobed barrel and two screws (case of the twin-screw extruder used as a liquid/solid extractor and separator).

Colas *et al.*, 2013a, 2013b), (v) the extraction of polyphenolic extracts with antioxidant activity (Celhay *et al.*, 2014), (vi) the enzymatic degradation of plant cell walls for the production of second generation bioethanol (Vandenbossche *et al.*, 2014, 2015, 2016), (vii) the defibring of lignocellulosic materials for the production of paper pulp (Manolas *et al.*, 1995; Maréchal and Rigal, 1999) and fiberboards (Markessini *et al.*, 1997), (viii) the production of composite agromaterials with proteins (Leyris *et al.*, 1998) or polysaccharides (Rigal *et al.*, 1999; Peyrat *et al.*, 2000; Rouilly, 2002; Jorda, 2003) used as the matrix, (ix) the production of thermoplastic agromaterials by compounding cereals and biobased and biodegradable polyesters (Chabrat *et al.*, 2012; Abdillahi *et al.*, 2013), and (x) the production of injectable biocomposites by compounding a biobased and biodegradable polyester, here used as a matrix, and vegetable fillers (Gamon *et al.*, 2013).

Due to the combination of chemical (injection points of liquid reagents), thermal (thermal regulation of the barrel) and mechanical (adjustment of screw profiles) actions in a single step, the twin-screw extruder is often considered as a thermo-mechano-chemical (TMC) reactor. It operates continuously and it can also be provided with one or more filtration modules in order to allow the separate obtaining of a liquid extract and a solid raffinate (Rigal, 1997, 2000).

### 3 The elements of a twin-screw extruder

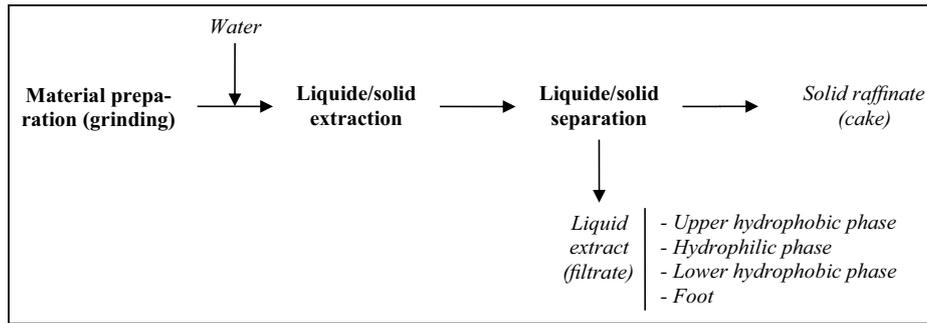
The twin-screw extruder comprises two parallel and identical screws of constant depth, turning at the same time and at the same speed in a bilobed barrel, and thermally regulated (Fig. 1). The co-rotating and co-penetrating twin-screw extruders are the most common ones. Identical and self-cleaning, the two screws are located inside the barrel. The latter and the screw sections are made of nitrided steel or special industrial alloys, and they are adapted to the most abrasive and/or corrosive operating conditions. In particular, the use of inorganic acids in combination with high temperatures is possible. The material moves axially from one screw to the other. Furthermore, it undergoes relatively uniform stresses. The screw sections are stacked on shafts, thus allowing multiple configurations for optimal treatments. A wide choice of screw elements is available to ensure very precisely and flexibly the various functions required.

The conveying screws (T2F, C2F and C1F) are direct screws that provide primarily a conveying action. The

monolobe paddle screws (DM) have a strong radial compression effect on the matter, the latter thus being crushed against the inside wall of the barrel. Therefore, they promote a strong shear but they have in contrast a reduced mixing effect. The bilobe paddle screws (BB) provide strong effects of shearing and mixing on the matter. Depending on their assembly angle (*i.e.* in a forward or a reverse pitch), a more or less strong action for conveying or axial compression can also be obtained in combination with the conveying screws. BB paddle screws thus promote an intimate mixing action, particularly desirable during the solvent extraction of components in the cell structure of the plant material processed. Finally, the reverse screw elements (CF2C and CF1C) are the most important restrictive elements of the screw profile. Indeed, they allow intense mixing and shearing to the material, thus leading to an increase in its residence time. Frequently used to put pressure on the matter, the reverse screw elements are essential for the subsequent separation of liquid and solid phases by filtration (Rigal, 1997, 2000). The pressed liquid extract can then be recovered by positioning a filtration module upstream from the reverse pitch screws.

### 4 The advantages of the twin-screw extrusion technology

Defined by the arrangement of the different screw elements (type, angle, length, pitch) along the shafts, the screw profile is most of the time the main factor influencing the effectiveness of the twin-screw extrusion process (Evon *et al.*, 2007, 2009, 2010a, 2012a; Evon, 2008). However, it should be noted here that the operating conditions used for the extrusion of biomass (*e.g.* temperature profile, screw rotation speed, device's filling coefficient, or reagent/biomass ratio) are also important parameters to achieve effectiveness. Thanks to its remarkable versatility, the screw profile especially acts on the transformation of the material, on the distribution of its residence time and on the mechanical energy transmitted during the extrusion process (Gogoi *et al.*, 1996; Choudhury *et al.*, 1998; Gautam and Choudhury, 1999a, 1999b). In addition, even if the same distinct zones can be found in a twin-screw extruder as in a single-screw one, these zones may appear several times if the restrictions are repeated and separated from each other by conveying zones. As opposed to the conventional presses, several elementary operations can thus be performed in the same twin-screw



**Fig. 2.** Simplified scheme of the thermo-mechano-chemical fractionation of sunflower whole plant by aqueous extraction in a twin-screw extruder.

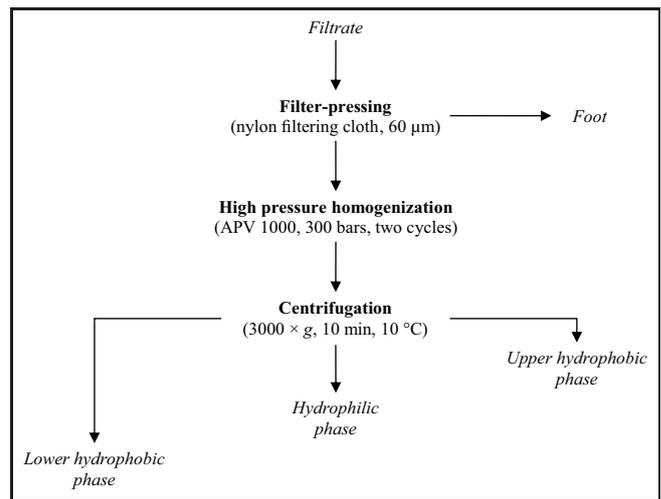
extruder (Rigal, 1997, 2000; Bouvier and Campanella, 2014): conveying, shearing and crushing, compression and expansion, heating and cooling, liquid introduction, solid introduction, mixing, reaction, liquid/solid extraction, steam distillation, liquid/solid separation, drying, extrusion, etc.

The arrangement of the modules along the barrel thus defines the configuration of the machine. The residence time of the material is generally quite short (of the order of a few tens of seconds to few minutes). It depends on the operating parameters of the machine. In particular, the residence time distribution can be extended by the presence of restrictive elements such as reverse pitch screws and kneading elements.

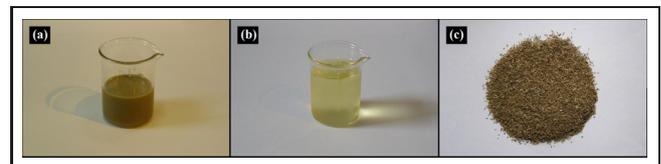
### 5 The twin-screw extrusion, an opportunity for the biorefinery of the sunflower whole plant

The biorefinery process of sunflower whole plant recently developed used the twin-screw extruder as a thermo-mechano-chemical reactor, and the whole plant fractionation was conducted using water as extracting solvent to make the fractionation process more sustainable (Evon *et al.*, 2010a, 2012b). As a first step, the aqueous process to extract sunflower oil was conducted from the seeds (Evon *et al.*, 2007) and then from two different press cakes (Evon *et al.*, 2009). For such configuration, the liquid/solid separation required the addition of a lignocellulosic residue upstream from the filtration zone, and two residues were tested successfully (*i.e.* wheat straw and sunflower depithed stalk). In the case of whole seeds, the best oil extraction yield obtained was approximately 55%, and the residual oil content of the cake was 32.8% instead of 49.7% for the seeds. The oil was extracted in the form of an oil-in-water emulsion, stabilized by phospholipids and proteins at the interface, which were natural surface-active agents co-extracted during the process.

Based on these initial results, the raw material used in a second stage was the sunflower whole plant. Indeed, its high content in lignocellulosic fibers (Tab. 1) enabled an effective liquid/solid separation at the end of the screw profile without adding any fibrous residue as from seeds or press cakes (Evon *et al.*, 2010a, 2012a). Such a configuration resulted in a simplification of the process while considering a valorization of the entire plant, thus satisfying the concept of biorefinery.



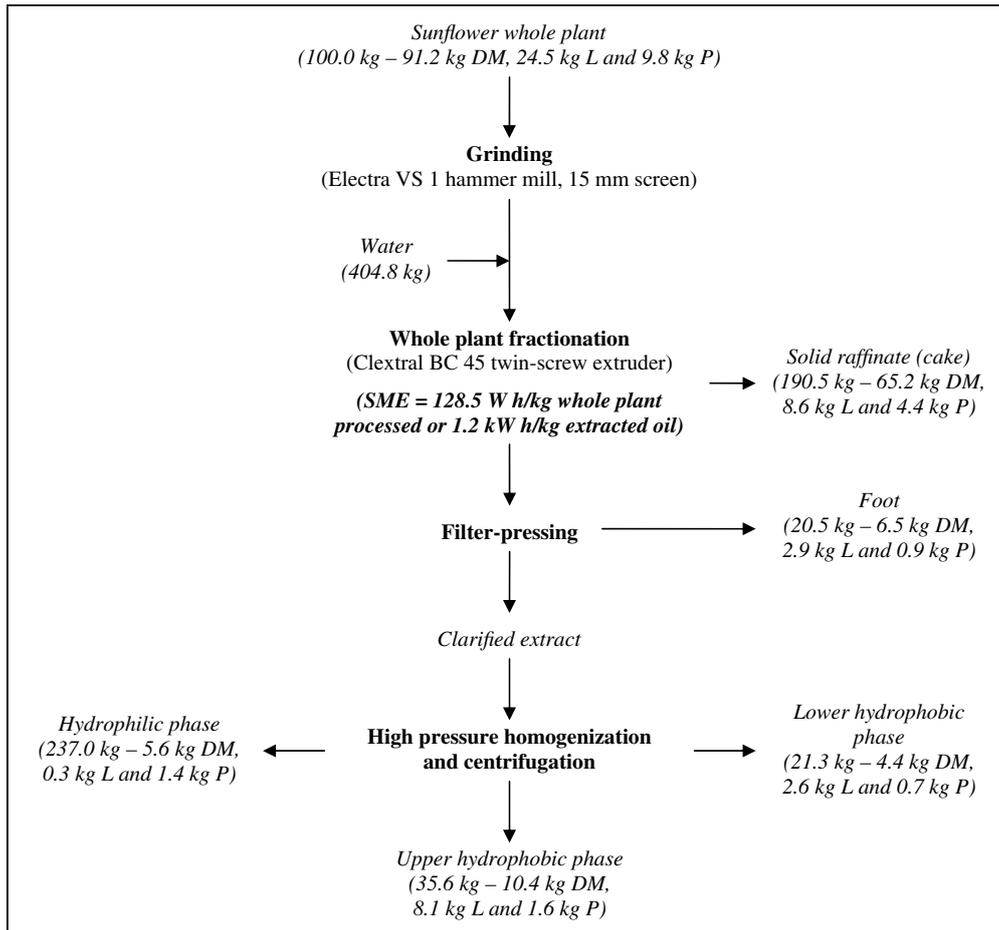
**Fig. 3.** Schematic representation of the filtrate's treatment.



**Fig. 4.** Photographs of the upper hydrophobic phase (a), the hydrophilic phase (b) and the cake (c).

The thermo-mechano-chemical fractionation using the twin-screw extruder allowed the three basic operations required for all fractionation schemes of plant materials, *i.e.* grinding, liquid/solid extraction, and liquid/solid separation, to follow one another in the same device (Fig. 2). The whole plant treatment then resulted in the continuous production of both an extract and a raffinate. The treatment of the extract consisted in three successive steps, *i.e.* filter-pressing, high pressure homogenization and centrifugation (Fig. 3). It allowed its reorganization into four distinct phases (from the least dense to the densest): (i) the upper hydrophobic phase (Fig. 4a), (ii) the hydrophilic phase (Fig. 4b), (iii) the lower hydrophobic phase, and (iv) the foot (*i.e.* the solid particles forced through the filter), which may be added to the cake.

A first assessment of the whole plant fractionation in the twin-screw extruder under the optimal operating conditions



**Fig. 5.** Assessment of the whole plant fractionation in the twin-screw extruder under the optimal operating conditions (DM, dry matter; L, lipids; P, proteins; SME, specific mechanical energy consumed by the motor).

(optimized screw profile, 80 °C temperature, 60 rpm screw speed, 5.0 kg/h inlet flow rate of whole plant, and 20.3 kg/h inlet flow rate of water) is given in Figure 5. From these conditions, residual oil and protein contents in the cake were 13.1% and 6.7% of dry matter, respectively (Tab. 1). These corresponded to oil and protein extraction yields of 64.9% and 54.9%, respectively. The liquid/solid separation in the twin-screw extruder resulted in a filtrate's foot content representing 7.1% of the inlet dry matter, including 11.8% lipids and 8.5% proteins from whole plant. The chemical composition of the three liquid phases are mentioned in Table 2.

- (i) The hydrophilic phase had a large majority in weight (75.4%). In addition to minerals that represented 20.6% of its dry matter, protein content was high (*i.e.* 23.3%). Conversely, lipid content was low (*i.e.* 5.3%), indicating a good separation between the hydrophilic phase and both hydrophobic phases.
- (ii) The upper hydrophobic phase represented 11.3% of the filtrate's weight. Its dry matter contained 77.3% lipids and 15.0% proteins.
- (iii) The lower hydrophobic phase represented 6.6% of the filtrate's weight. Its dry matter contained 60.2% lipids,

15.0% proteins, 9.7% pectic substances and 8.7% non pectic sugars.

Among the 44.5% extracted lipids, 43.2% were inside the two hydrophobic phases (*i.e.* 32.8% for the upper one and 10.5% for the lower one). Thus, the loss of lipids in the hydrophilic phase was limited to 1.2%. Moreover, the upper oil-in-water emulsion also contained the largest fraction of the extracted proteins (16.0% out of 36.1%). At the same time, 13.4% of the proteins from whole plant were in the hydrophilic phase, and 6.6% in the lower hydrophobic phase. In parallel, the cake (Fig. 4c), which represented 71.5% of the dry matter of whole plant, contained not only lipids and proteins but also 58.7% fibers (Tab. 1). Mixed with the filtrate's foot, it was then dried to facilitate its conservation.

During the whole plant fractionation in the twin-screw extruder under the optimal operating conditions, the specific mechanical energy (SME) consumed by the motor was estimated to 128.5 W h/kg whole plant processed or 1.2 kW h/kg extracted oil (Evon, 2008; Evon *et al.*, 2010a, 2012a). This corresponded to much higher energy consumption than for the mechanical pressing of sunflower oil from seeds using the same machine: 245.0 W h/kg seed processed or 0.6 kW h/kg pressed oil (Amalia Kartika *et al.*, 2006). Such a difference could be

**Table 1.** Chemical composition of sunflower whole plant, optimal cake and cakes used for thermopressing, *i.e.* without or with a deoiling extrastep using a Soxhlet extraction apparatus and cyclohexane as extracting solvent (% of dry matter).

|                          | Standard                                    | Sunflower whole plant | Optimal cake | Cake used for thermopressing | Deoiled cake used for thermopressing |
|--------------------------|---|-----------------------|--------------|------------------------------|--------------------------------------|
| Minerals                 | NF V 03-922                                 | 6.5 ± 0.2             | 4.4 ± 0.1    | 7.0 ± 0.0                    | 8.0 ± 0.1                            |
| Lipids                   | NF V 03-908                                 | 26.8 ± 0.4            | 13.1 ± 0.0   | 17.6 ± 0.1                   | 0.9 ± 0.3                            |
| Proteins                 | NF V 18-100                                 | 10.7 ± 0.2            | 6.7 ± 0.1    | 9.2 ± 0.2                    | 11.3 ± 0.4                           |
| Cellulose                | Van Soest and Wine method (1967, 1968)      | 23.9 ± 0.6            | 33.1 ± 0.5   | 31.0 ± 0.2                   | 38.8 ± 0.9                           |
| Hemicelluloses           | Van Soest and Wine method (1967, 1968)      | 7.8 ± 0.1             | 13.1 ± 0.2   | 12.6 ± 0.2                   | 5.9 ± 0.7                            |
| Lignins                  | Van Soest and Wine method (1967, 1968)      | 9.1 ± 0.0             | 12.5 ± 0.2   | 15.5 ± 0.0                   | 19.4 ± 0.6                           |
| Pectic substances        | Blumenkrantz and Asboe-Hansen method (1973) | 7.0 ± 0.2             | n.d.         | n.d.                         | n.d.                                 |
| Water-soluble components | 1 h in boiling water                        | n.d.                  | n.d.         | 12.4 ± 0.1                   | 14.4 ± 0.3                           |

Results in the table correspond to the mean values ± standard deviations. n.d., non determined.

**Table 2.** Mass distribution, density and chemical composition of the three liquid phases in the filtrate.

|                                     | Standard  | Upper hydrophobic phase | Hydrophilic phase | Lower hydrophobic phase |
|-------------------------------------|---|-------------------------|-------------------|-------------------------|
| Mass distribution (%)               | –   | 11.3                    | 75.4              | 6.6                     |
| Density                             | –   | 0.972 ± 0.00            | 1.008 ± 0.00      | 1.030 ± 0.00            |
| Chemical composition                | NF V 03-903   | 70.8 ± 0.1              | 97.6 ± 0.0        | 79.6 ± 0.1              |
| Moisture (%)                        |   |                         |                   |                         |
| Minerals (% of dry matter)          | NF V 03-922   | 1.9 ± 0.1               | 20.6 ± 0.1        | 6.5 ± 0.1               |
| Lipids (% of dry matter)            | Demixing using ethanol/ether (3/1) (Mechling, 2002) <sup>1</sup><br>Bligh and Dyer method (1959) <sup>2</sup> | 77.3 ± 0.1              | 5.3 ± 0.5         | 60.2 ± 0.4              |
| Proteins (% of dry matter)          | NF V 18-100   | 15.0 ± 0.1              | 23.3 ± 0.0        | 15.0 ± 0.0              |
| Pectic substances (% of dry matter) | Blumenkrantz and Asboe-Hansen method (1973)   | 0.6 ± 0.1               | 12.3 ± 0.3        | 9.7 ± 0.4               |
| Non pectic sugars (% of dry matter) | Colorimetric method of Dubois <i>et al.</i> (1956)  | 0.7 ± 0.0               | 8.7 ± 0.3         | 8.7 ± 0.2               |

<sup>1</sup> The demixing method using ethanol/ether (3/1) was used for the upper and lower hydrophobic phases. <sup>2</sup> The Bligh and Dyer method was used for the hydrophilic phase.

explained both by a lower lipid content in the raw material (26.8% in the dried whole plant instead of 48.5% for seeds) and a lower oil extraction efficiency (44.5% instead of 85.3%).

difficult and expensive. However, it could be recycled to the extraction in the twin-screw extruder, thus allowing a significant reduction in the water intake (Fig. 6).

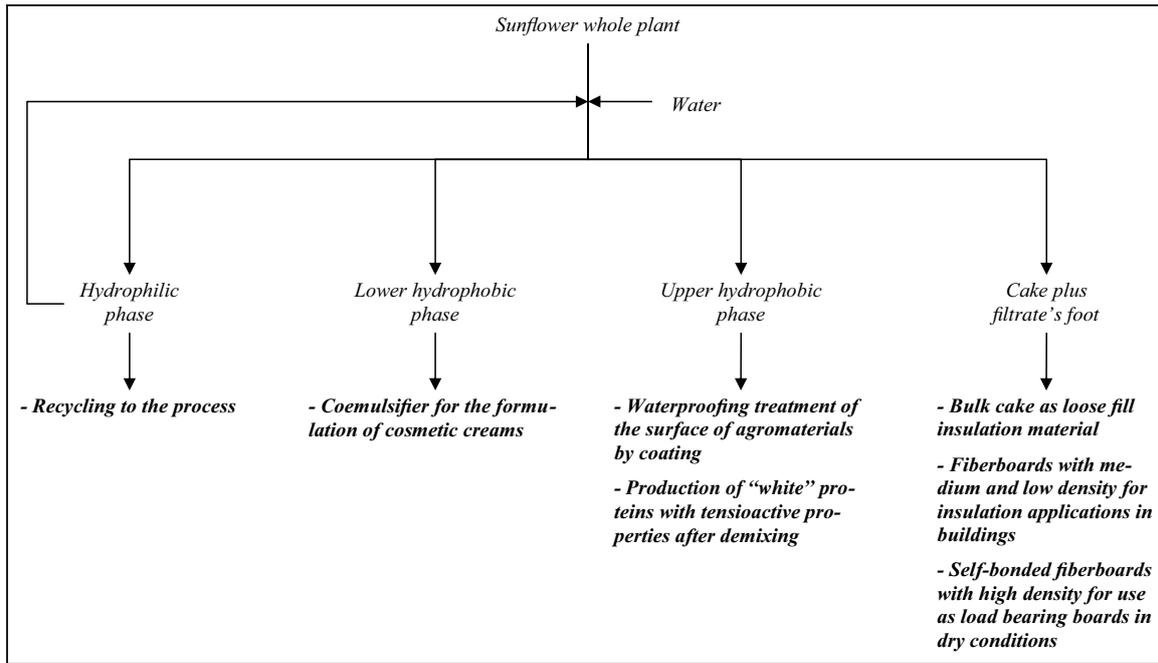
## 6 Characteristics and valorization of liquid extracts

### 6.1 Hydrophilic phase

Representing the main filtrate's fraction, the hydrophilic phase revealed no apparent turbidity (Fig. 4b). It represented 57.2% of the injected water. It contained 6.1% of the dry matter of whole plant, including 13.4% of initial proteins and about 11% of pectic substances. Although pectins are known for their gelling capacity, a market study revealed the low interest of sunflower pectins contained in the hydrophilic phase for use as gelling agents. Moreover, the hydrophilic phase constitutes a very dilute phase. Thus, its valorization would be quite

### 6.2 Hydrophobic phases

The upper and lower hydrophobic phases contained 32.8% and 10.5% of lipids from whole plant, respectively. Similarly, their protein contents corresponded to 16.0% and 6.6% of proteins from whole plant, respectively. Their observation using an optical microscope revealed that both had the form of oil-in-water emulsions, *i.e.* emulsions consisting of oil droplets dispersed in water. The stability of these two hydrophobic phases was ensured by the presence at the interface of natural surface-active agents co-extracted by water during the aqueous extraction process (Evon *et al.*, 2007, 2009, 2010a, 2012a; Evon, 2008), *i.e.* phospholipids and proteins or even pectic substances and non pectic sugars in the case of the lower



**Fig. 6.** Valorization scheme proposed for each fraction from the biorefinery process of sunflower whole plant using the thermo-mechano-chemical twin-screw reactor.

**Table 3.** Average size of oil droplets dispersed in water for the two hydrophobic phases.

|                              | Optical microscope<br>(Nikon Eclipse E 600) <sup>1</sup> | Laser particle sizer<br>(Malvern Mastersizer 2000) |
|------------------------------|--|--|
| Upper hydrophobic phase (µm) | 1.12 ± 0.26  | 1.10 ± 0.58  |
| Lower hydrophobic phase (µm) | 1.40 ± 0.31  | 1.20 ± 0.81  |

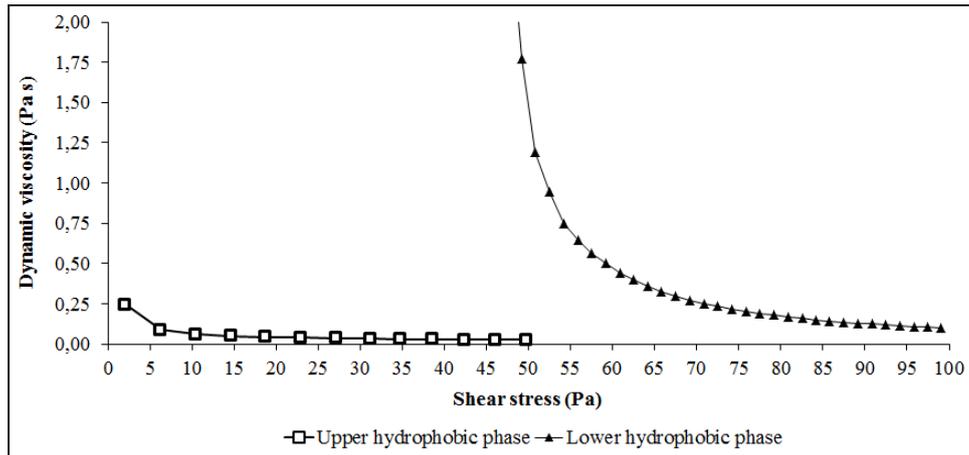
<sup>1</sup> Average values determined by manual measurement of the diameters of 200 droplets present on each microscope picture.

hydrophobic phase (Tab. 2). When observed using the optical microscope, the oil droplets inside the upper hydrophobic phase appeared a little smaller than in the lower one, and this was confirmed by a laser particle size analysis (Tab. 3). In addition, the particle size distribution curves in volume obtained from the laser particle sizer highlighted the presence of a second population in both hydrophobic phases. This new population consisted in particles with an average diameter of 10–15 µm for the upper hydrophobic phase and 30–35 µm for the lower one. However, it represented less than 0.30% and 0.15%, respectively, of the number of particles inside the emulsions. It could then correspond to some small cell debris from the raw material breakdown process, poorly separated from the filtrate’s foot during the centrifugation step.

Then, the rheological behavior of hydrophobic phases was studied using a cone-plate system rheometer operating at controlled stress, and the Herschel and Bulkley model applied to both oil-in-water emulsions. The existence of a yield point was demonstrated, and the latter could be estimated more precisely under low stress: only 0.5 Pa for the upper hydrophobic phase, and between 31 and 32 Pa for the lower one. At the same time, the viscosity of the upper oil-in-water emulsion appeared much lower than that of the lower one (Fig. 7). Secondly, the strength of the film located at the oil-in-water interface was evaluated thanks to the protein concentration at interface. It was estimated at 34 mg/m<sup>2</sup> for the upper hydrophobic phase,

and it reached a 54 mg/m<sup>2</sup> value in the case of the lower one. Lastly, the emulsion stability was studied over a three months period, by monitoring the average size of oil droplets dispersed in water, the zeta potential and the resistance to flow under controlled stress. This tracking showed good stability over time of both oil-in-water emulsions when stored in a refrigerator. Indeed, no coalescence of oil droplets was observed even after three months, their average size remaining nearly constant. In addition, no significant evolution of the zeta potential and the resistance to flow of both emulsions has also been noted over time.

In parallel, a market study revealed the possible interest of both oil-in-water emulsions for their use in the cosmetics industry. Therefore, these have been evaluated for such industrial application, which would favor their economic valuation (from 10 to 50 €/kg). And, even if the tests carried out from the upper hydrophobic phase (*i.e.* the more fluid emulsion) have not given satisfactory results, it has been demonstrated that the lower one (*i.e.* the more viscous emulsion) could be used as a coemulsifier (up to 10% by weight approximately) for the formulation of highly penetrating night creams with high emollient capacity (Fig. 6). Based on these initial results, other cosmetic applications were also considered for the lower hydrophobic phase, *e.g.* gels with strong film forming, shower gels, shower oils, etc. However, its greyish hue was persistent, and this could become a problem for its use in cosmetics.



**Fig. 7.** Dynamic viscosity of the two hydrophobic phases as a function of applied shear stress (TA Instruments AR 2000ex rheometer, 25 °C).

Indeed, on the one hand, this color resisted bleaching using clay. On the other hand, it required a very large amount of titanium dioxide to be eliminated. For future work, it will be necessary to identify the compounds that could be responsible for this natural color (*e.g.* chlorophyll, xanthophyll, etc.). Adjusting the emulsion's pH may also help to reduce or even to completely eliminate this color. In addition, the pH adjustment to values between 4.0 and 4.5 should facilitate the emulsion's conservation. It could be done by adding citric acid, a natural substance without toxicity for both humans and environment. Citric acid will then act also as a bactericide and fungicide. Lastly, the absence of allergens will also have to be confirmed in the future.

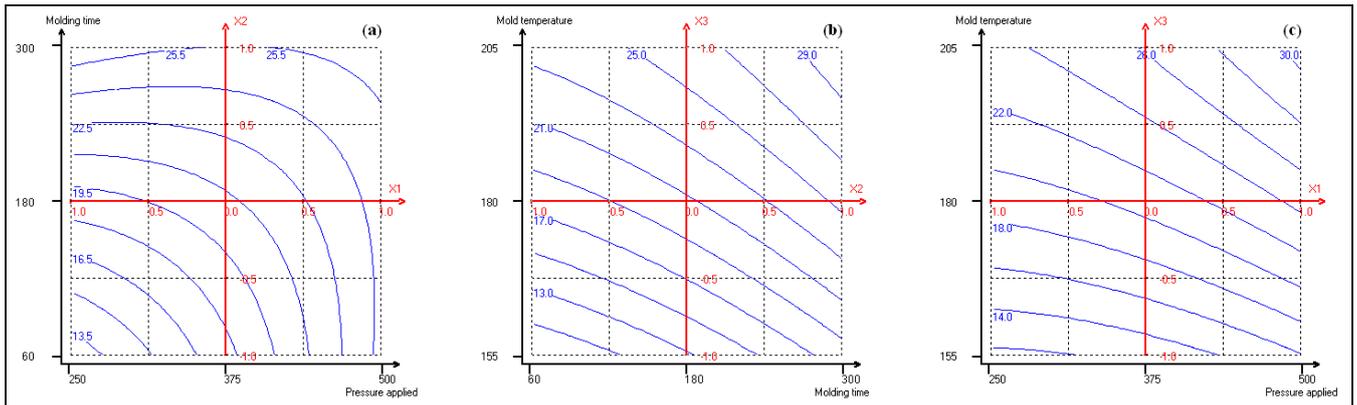
Regarding the upper hydrophobic phase for which the formulation tests to produce cosmetic creams were not satisfactory, two possible industrial applications were identified (Fig. 6). Firstly, it could be used for the coating of agromaterials to make them less water-sensitive and therefore more durable. This was successfully confirmed in the case of self-bonded fiberboards with high density made by thermopressing from cake generated at the end of the twin-screw process (Evon, 2008). Secondly, the rupture of the interfacial film between oil and water inside the upper hydrophobic phase could be obtained by treating this emulsion using ethanol/ether mixture (3/1) or absolute ethanol (Mechling, 2002; Evon, 2008; Evon *et al.*, 2010a). After demixing (*i.e.* phase separation), a centrifugation step then led to the separate obtaining of a supernatant and a solid pellet. On the one hand, the evaporation of ethanol/ether mixture or ethanol into the supernatant resulted in the production of a vegetable oil of high purity. On the other hand, the centrifugation pellet was in the form of a light-coloured powder, proteins (mainly albumins) representing two thirds of its dry weight. Their differential thermal analysis using a DSC analyzer revealed the presence of an endothermic peak at a 155 °C transition temperature (Evon, 2008; Evon *et al.*, 2010a). This indicated that proteins contained in the upper oil-in-water emulsion were not so much denatured during the TMC fractionation in the twin-screw extruder. Thus, till now penalized by their dark color, obtaining "white" sunflower proteins with a surfactant character could offer new opportunities, in particular for food applications (Canella *et al.*, 1985).

## 7 Characteristics and valorization of cake

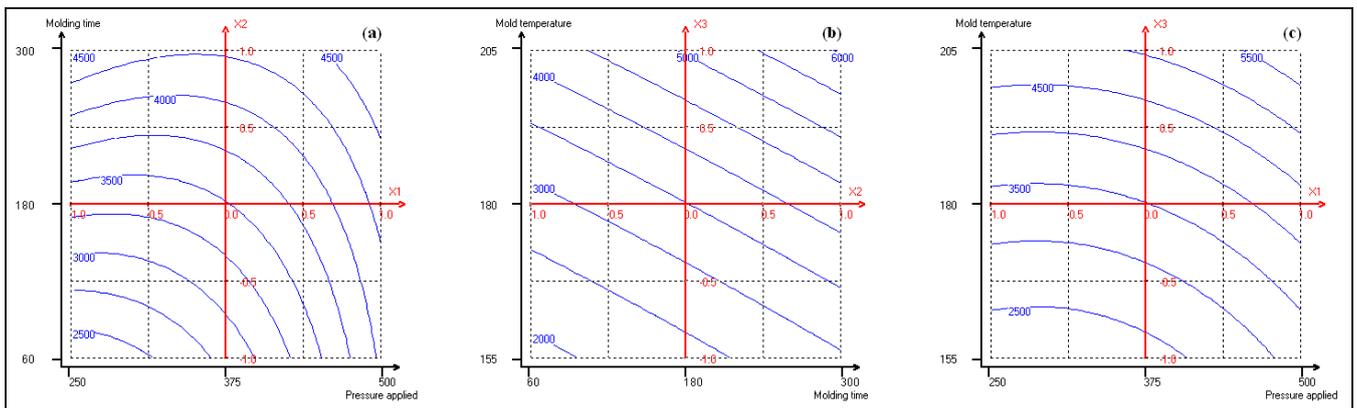
The cake (Fig. 4c) could be granulated for animal feed or for energy production in pellet boiler. However, because part of the proteins in cake, that is globulins, revealed a thermoplastic behavior (Evon *et al.*, 2010b), it could be also considered as a natural composite moldable into self-bonded materials (*e.g.* fiberboards) using thermopressing (Evon, 2008; Evon *et al.*, 2010a, 2010b, 2012a, 2012b, 2012c, 2014, 2015a, 2015b). The interest for such a valorization for cake was confirmed in a recent market study. Indeed, the latter revealed that the global market for agromaterials is particularly dynamic with growth of the order of 50 to 100% per year. In particular, the interest of self-bonded fiberboards for furniture or building applications is multiple. These are (i) renewable, (ii) environment-friendly (no formaldehyde emission), and (iii) biodegradable at end of life. They are also easy to implement, especially in terms of handling, machining and cutting. Thus, using the cake to produce agromaterials by thermopressing appeared as an original and a promising solution for its valorization.

A first work consisted in studying the thermo-mechanical behavior of the cake (Evon *et al.*, 2010b). DSC measurements indicated that denaturation of proteins in cake was almost complete, and DMTA spectrum of the cake revealed a significant peak at high temperature (175–200 °C). It was associated with the glass transition of proteins, and the latter was also observed through Pressure, Volume, and Temperature (PVT) analysis at around 180 °C. As a mixture of plasticized proteins and lignocellulosic fibers (Tab. 1), the cake could thus be considered as a natural composite, and it was successfully processed into self-bonded fiberboards, with proteins ensuring cohesion and fibers entanglement also acting as reinforcement.

Complementary studies revealed that the molding conditions (*i.e.* pressure applied, molding time, mold temperature and cake quantity per board's unit area) largely influenced the characteristics (*i.e.* bending properties, surface hardness, impact strength, plus thickness swelling and water absorption after immersion in water) of the obtained boards (Evon *et al.*, 2010b, 2012b, 2012c). Moreover, a pre-drying step of the cake in a ventilated oven before thermopressing contributed to minimize vapor generation during molding, thus reducing the risk



**Fig. 8.** Isoresponse curves for flexural strength at break of high density self-bonded fiberboards at 180 °C mold temperature (a), at 36.8 MPa pressure applied (b), and for 180 s molding time (c) (Evon *et al.*, 2015a).



**Fig. 9.** Isoresponse curves for elastic modulus of high density self-bonded fiberboards at 180 °C mold temperature (a), at 36.8 MPa pressure applied (b), and for 180 s molding time (c) (Evon *et al.*, 2015a).

of defects like blisters inside fiberboards. Finally, because of the high pressure applied on molding, part of the residual oil in cake was expressed through the sidewall vents of the mold during molding (Evon *et al.*, 2010b, 2012b, 2012c). Logically, this molding oil expression decreased the fiberboard residual oil content. However, it resulted in a reduction of the mechanical resistance of fiberboards, due to defects appearing within the material as the oil escaped.

Therefore, an additional study was conducted from a cake that was previously deoiled using a Soxhlet extraction apparatus and cyclohexane as extracting solvent (Evon *et al.*, 2015a). Its chemical composition is mentioned in Table 1, with proteins and fibers representing 11% and 64% of its dry matter, respectively. This work consisted in studying the effects of molding conditions (24.5–49.0 MPa pressure applied, 60–300 s molding time, and 156–204 °C mold temperature) on fiberboard characteristics using a Doehlert's experimental design. Before thermopressing, deoiled cake was dried in a ventilated oven (60 °C, 12h) to reduce its moisture content (2.8% on molding). Moreover, the deoiled cake quantity was 667 mg/cm<sup>2</sup> for all experiments, and this led to the manufacture of fiberboards with thicknesses after climatic chamber conditioning (at least 5.0 mm, and up to 5.8 mm) perfectly comparable to those of high density commercial fiberboards. The isoreponse curves in Figures 8 and 9 represent the effects

of thermopressing conditions on the bending properties (*i.e.* flexural strength at break and elastic modulus, respectively) of fiberboards. The increase in the three conditions tested resulted in improved flexural properties but the mold temperature was the most influential condition. With a 2.8% moisture content, the glass transition temperature of proteins in deoiled cake was estimated at 145 °C. This is the reason why the lowest mold temperature tested in this study (*i.e.* 156 °C) was chosen slightly higher. Thus, the glass transition occurred systematically for proteins during molding and they were always in a rubbery state. However, because the protein-based resin became less and less viscous with increasing mold temperature, this meant that the fiber wetting improved progressively. This could explain why the flexural properties of fiberboards increased significantly as the mold temperature increased.

Polynomial models were used to determine the optimal response for each analyzed characteristic, *i.e.* bending properties, Charpy impact strength, Shore D surface hardness, plus thickness swelling and water absorption after 24 h immersion in water. The corresponding molding conditions were identified at the same time. And, for each characteristic, the optimal response was always associated with a 204 °C mold temperature. This confirmed once again that the mold temperature was the condition affecting more the characteristics of fiberboard. The optimal values for flexural strength at break

(31.9 MPa) and elastic modulus (6.5 GPa) were both obtained from the same operating conditions, *i.e.* 49.0 MPa pressure applied, 300 s molding time and 204 °C mold temperature. Associated with an energy consumption of 122.6 kW h/m<sup>2</sup> fiberboard, these conditions were logically considered as the optimal ones, and one supplementary fiberboard was thus manufactured using these conditions. This high density (1267 kg/m<sup>3</sup>) self-bonded fiberboard revealed next characteristics: 30.3 MPa flexural strength at break, 5.9 GPa elastic modulus, 81.5° Shore D surface hardness, 30% thickness swelling and 23% water absorption. It largely complied with the French standard NF EN 312 (standard dedicated to the specifications for particleboards), type P4 (*i.e.* load bearing boards for use in dry conditions, including floor underlayers, interior partitions, furniture, etc.) regarding mechanical properties for bending (recommendations of 16 MPa and 2.2 GPa for flexural strength at break and elastic modulus, respectively) (Fig. 6), while this was slightly less valid for thickness swelling. An additional process such as the coating of its surface using the upper hydrophobic phase could achieve the 21% recommended value (Evon, 2008).

Unlike the previous study, using reduced values for both pressure applied and molding time (14.7–24.5 MPa and 40–76 s, respectively) led to fiberboards with medium densities (500–858 kg/m<sup>3</sup>) (Evon *et al.*, 2014). In parallel, the mold temperature was chosen at least equal to the glass transition temperature of proteins (about 140 °C) so that this phase change occurred systematically during thermopressing. Thus, as in the previous study, the proteic resin still ensured the board's cohesion. Such operating conditions, especially the low pressure applied, were not sufficient to cause the expression of part of the residual oil in cake during molding, thus avoiding its prior deoiling. The decrease in the board densities resulted in a significant decrease in their mechanical properties. Conversely, these medium density self-bonded fiberboards revealed promising heat insulation properties, their thermal conductivity at 25 °C decreasing simultaneously with the decrease in density (from 110.5 to 88.5 mW/m K). A good compromise between mechanical (272 kPa flexural strength at break, 26.3 MPa elastic modulus, and 37.3° Shore D surface hardness) and heat insulation properties (99.5 mW/m K thermal conductivity) was obtained under medium mold temperature (*i.e.* 160 °C), 24.5 MPa pressure applied and 76 s molding time. Such conditions corresponded to an energy consumption of 22.7 kW h/m<sup>2</sup> fiberboard. In addition, the lowest thermal conductivity (88.5 mW/m K, corresponding to a 0.23 m<sup>2</sup> K/W thermal resistance for the 20.2 mm board thickness) was obtained with the least dense fiberboard, the latter being produced from the lowest molding conditions (*i.e.* 140 °C mold temperature, 14.7 MPa pressure applied and 40 s molding time), these being associated with an energy consumption of only 10.0 kW h/m<sup>2</sup> fiberboard. Positioned on walls and ceilings, these medium density self-bonded fiberboards could be used for the thermal insulation of buildings (Fig. 6).

An additional reduction in both density (254–439 kg/m<sup>3</sup>) and thermal conductivity (64.0–84.8 mW/m K at 25 °C) of insulation fiberboards was obtained through the development of a new compression molding process using very low pressure (87 kPa), applied during only 30 s molding

time (Evon *et al.*, 2015b), and this logically contributed to a large decrease in the energy consumed during molding (1.0 kW h/m<sup>2</sup> fiberboard). This process was conducted at ambient temperature and an aqueous solution made of an external binder with physical curing was added to the cake before molding. All renewable, three different binder types were tested, *i.e.* a starch-based binder, a wood glue made of 96.6% casein, and a bone glue made of gelatin (purity of about 90%). This time, the board's cohesion was ensured by the external binder, once the water used for its dissolution was evaporated using a ventilated oven. It then resulted in the appearance of bonds, usually of hydrogen type, between the biopolymer in the glue and the molecules (proteins, cellulose, hemicelluloses, etc.) in the cake. The optimal low density fiberboard obtained in this study was a board containing 20% starch-based binder. With a 358 kg/m<sup>3</sup> density, it revealed improved heat insulation properties (77.6 mW/m K, corresponding to a 0.50 m<sup>2</sup> K/W thermal resistance for the 38.7 mm board thickness). Simultaneously, its mechanical properties would allow it to be handled without risk to break it. As previously, this insulation board will be also a viable option for the insulation of buildings when positioned on walls and ceilings (Fig. 6).

In addition to fiberboards, the cake used to manufacture them could itself be used as a loose fill insulation material. Indeed, when used in bulk, it revealed a thermal conductivity particularly low at 25 °C: from 62.0 to 65.6 mW/m K, depending on its residual oil content (Evon *et al.*, 2014, 2015b). For a 52 mm bed height, this corresponded to a thermal resistance between 0.79 and 0.84 m<sup>2</sup> K/W, and such insulation ability of the cake was due to its very low bulk density (204–215 kg/m<sup>3</sup>) as well as to its porous structure. Thus, the bulk cake would also be suitable for the thermal insulation of houses when used as loose fill in attic spaces (Fig. 6). And, such valorization seems judicious because the cake would be easy to apply. Indeed, it could be applied manually or using a blower, like for cellulose wadding for example. Complementary optimizing work will be required to make these insulation materials, *i.e.* the cohesive fiberboards and the bulk cake, suitable for commercial applications. Indeed, to comply with the requirements of the building industry, various characteristics are important for heat insulation materials: (i) no odor, (ii) moisture resistance, (iii) resistance to insects, rodents and other pests, (iv) resistance to fungal and bacterial growth, and (v) fire resistance. Regarding the latter, it may be improved by the addition of an additive such as borax.

## 8 Conclusion

The twin-screw extrusion constitutes a promising technology to conduct continuously the biorefinery of sunflower whole plant. The twin-screw reactor allows the thermo-mechano-chemical fractionation of the raw material, thus leading to the aqueous extraction of oil and other biopolymers (*i.e.* proteins from the albumin family, pectic substances and non pectic sugars) from whole plant. When positioned at the end of the barrel upstream from some reverse screw elements, a filter allows the collection of a liquid extract (*i.e.* the filtrate) and a solid raffinate (*i.e.* the cake). And, the liquid/solid separation is then promoted by the high fiber content of the stalk

in whole plant. Vegetable oil is extracted in the form of two oil-in-water emulsions stabilized at interface by natural surface-active agents co-extracted during the aqueous extraction process, *i.e.* phospholipids and proteins. Pectic substances and non pectic sugars complete the dry matter content of the densest emulsion, *i.e.* the lower hydrophobic phase.

The higher hydrophobic phase (*i.e.* the least dense emulsion) is a good candidate for coating the surface of agromaterials to make them less water-sensitive. In addition, its demixing using ethanol/ether mixture results in the production of tensioactive proteins usable for food applications. The lower hydrophobic phase can in turn be used as a coemulsifier for the formulation of cosmetic creams, in particular highly penetrating night creams with high emollient capacity. The biorefinery process also leads to the production of a hydrophilic phase containing some of the water-soluble constituents of whole plant, mainly proteins and pectic substances. It constitutes a very dilute phase. It could be recycled to the process, thus reducing the water intake at the twin-screw reactor inlet.

Mixed with the filtrate's foot (*i.e.* the solid particles forced through the filter at the liquid/solid separation), the cake is a mixture of lignocellulosic fibers and proteins. Because these have been denatured at the level of the reverse screw elements during the TMC fractionation in the extruder, they can be used as a protein-based resin to produce self-bonded fiberboards by thermopressing. Depending on the molding conditions used, boards produced reveal very different characteristics. The self-bonded fiberboards with high density are much more mechanically resistant and less water-sensitive. They will be usable as load bearing boards in dry conditions, including floor underlayers, interior partitions, furniture, etc. On the contrary, fiberboards with medium and low density are much fragile. But, their promising heat insulation properties would allow them to be used for the thermal insulation of buildings, in particular when positioned in walls and ceilings. Lastly, the bulk cake would be also usable as a loose fill insulation material in the attic spaces of houses.

In conclusion, the thermo-mechano-chemical twin-screw reactor is a new perspective for the biorefinery of sunflower whole plant. The overall fractionation of biomass can be considered using this commercial equipment, thus allowing a complete valorization of the input, including the by-products of sunflower cultivation like stalks and heads. As described, this efficient and environment-friendly biorefinery process thus provides a valorization for all components of the plant. Which in turn could generate an additional source of income for farmers.

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