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Manufacturing of renewable and biodegradable fiberboards from cake generated during biorefinery of sunflower whole plant in twin-screw extruder: Influence of thermo-pressing conditions

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Fiberboards

A B S T R A C T

The starting material used in this study was a cake generated during thermo-mechanical fractionation of sunflower (*Helianthus annuus L.*) whole plant in a twin-screw extruder. It was slightly deoiled (16.7% of oil in dry matter). Composed mainly of fibers and proteins, it could be considered as a natural composite and was processed successfully into fiberboards by thermo-pressing. This study aimed to evaluate the influence of thermo-pressing conditions on mechanical and heat insulation properties of fiberboards manufactured from this cake. All fiberboards were cohesive, proteins and fibers acting respectively as binder and reinforcing fillers.

Highest cake quantity (1000 mg/cm^2) led to the highest breaking load (60.7 N) with a flexural strength at break quite low (2.9 MPa), lowest elastic modulus (216.6 MPa), and highest Charpy impact strength (6.5 kJ/m^2 for resilience). The increase of pressure applied during molding (from 320 to 360 kgf/cm^2) led to an important increase of elastic modulus (from 352.6 to 728.6 MPa). Besides, fiberboard molded at 360 kgf/cm^2 was the most rigid of this study, and logically revealed the most important Shore D surface hardness (52.6°). Moreover, lowest molding time (60 s) led to the highest flexural strength at break (3.9 MPa). The low density of the fiberboards (less than 0.97) involved promising heat insulation properties. Indeed, thermal conductivity of fiberboards at 25 °C was low (from 103.5 to 135.7 mW/m K), and decreased with the increase of thickness.

According to their mechanical and heat insulation properties, fiberboards would be potentially usable as inter-layer sheets for pallets, for the manufacture of biodegradable containers (composters, crates for vegetable gardening) by assembly of fiberboards, or for their heat insulation properties in building industry. Moreover, thermo-pressing was not only a molding operation. It also improved the oil extraction efficiency as a part of residual oil was expressed from cake during molding, and total oil yield reached 79.3% with a pressure applied of 360 kgf/cm^2.

1. Introduction

Sunflower (*Helianthus annuus L.*) is cultivated for the high oil content of its seeds. Oil represents up to 80% of its economic value. The industrial process for oil production consists of four successive stages: trituration, pressing, extraction of the residual oil using hexane and refining [1,2]. The extraction yields are close to 100% with very good oil quality. However, the use of hexane for oil production is an increasingly controversial issue and could be prohibited due to its carcinogenicity [3]. Consequently, numerous solvents have been considered, including water [2].

Several researchers have studied the aqueous extraction of sunflower oil [4–7] that is an environment-friendly alternative to the solvent extraction. It can be conducted from whole seeds [6] or from a press cake [7], in a Clextral BC 45 (France) co-penetrating and co-rotating twin-screw extruder that enables an efficient mechanical lysis of the cells. Twin-screw extruder is used to carry out three essential unit operations in a single step and in a continuous mode: conditioning and grinding of the starting material, liquid/solid extraction, and liquid/solid separation. A filter section is outfitted along the barrel to collect separately an extract (filtrate) and a raffinate (cake). However, the introduction of a lignocellulosic

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residue upstream from the filtration module is essential to enable the liquid/solid separation.

When it is applied to whole plant, aqueous fractionation in twin-screw extruder does not require the addition of a lignocellulosic residue [8], due to the natural abundance of fibers in sunflower stalk [9], and twin-screw extrusion technology appears to be an original and powerful solution for the biorefinery of sunflower whole plant. In the best operating conditions, oil extraction yield reaches 57%, and residual oil content in the cake accounts for about 14.3% of the dry matter. These conditions lead to the co-extraction of proteins but also pectins and hemicelluloses. The corresponding protein extraction yield is 44%, and residual protein content in the cake is 7.3% of the dry matter.

The oil is extracted in the form of two different oil-in-water emulsions. These hydrophobic phases are stabilized by phospholipids and proteins at the interface, which are natural surface-active agents co-extracted during the process. These emulsions may have direct industrial applications for non food uses in various fields as the cosmetics market, the biolubricants market, the transport of active principles (odors, colors, bactericides, antifungals), and the treatment of surfaces with hydrophilic matter [8]. An aqueous extract containing part of the water-soluble constituents from whole plant, mainly proteins and pectins, is also generated. It is much more diluted, and would be potentially recyclable for aqueous extraction in the twin-screw extruder.

The cake moisture content is relatively high (at least 62%). The cake is dried to make its conservation easier. It has a porous structure, and it is mainly composed of lignocellulosic fibers (around 58% of the dry matter) coming principally from the depithed stalk [9]. It contains also cell debris from the kernel breakdown process. Actually, the cake is a lixiviated matter where soluble molecules (proteins, pectins…) and lipids are partly removed. At the same time, molecules from plant skeleton are not extracted. The cake is then suitable for use in animal feeds and for energy production in pellets burning furnaces for example. Nevertheless, new valorisations of the cake as a mixture of lignocellulosic fibers and proteins can be also considered [10–17].

Thermo-mechanical behaviour of the cake was previously studied [18] with a cake chosen for that study revealing a residual oil content of 13.1% of the dry matter. DSC measurements indicate that denaturation of proteins is almost complete in the cake. DMTA spectrum of its milled powder reveals a significant peak at high temperature (between 175 and 200 °C). As already observed with industrial sunflower cake [19], it can be associated with the glass transition of proteins. Because the cake is a mixture of lignocellulosic fibers and proteins, it can be considered as a natural composite. It is successfully processed into biodegradable and value-added agromaterials by thermo-pressing [18].

As for DMTA analysis, glass transition of proteins in the cake is also observed with PVT analysis around 180 °C. It makes easier the choice of the thermo-pressing conditions needed to produce panels with highest density as possible. The mechanical properties in bending of the panels increase simultaneously with temperature, pressure and time chosen for molding operation [18]. When thermo-pressing is conducted from a cake with a residual oil content of 14.5% of the dry matter, the highest flexural strength at break (11.5 MPa) and the highest elastic modulus (2.2 GPa) are obtained from the following molding conditions: 500 mg/cm^2 for the cake quantity, 200 °C for the temperature of the two aluminium plates of the heated hydraulic press, 320 kgf/cm^2 for the pressure applied, and 60 s for the time (3.9 mm for the panel thickness, and 1.04 for the corresponding mean apparent density). Drop angle measurements show that the panel with the highest flexural properties is also the most resistant to water. DMTA analysis of that panel reveals a significant vibratory oscillation peak at low temperature (between −20 and −14 °C). It is attributed to the β-transition of proteins (glass transition of their side chains) [16,20]. No significant transition is observed between 0 °C and 200 °C, meaning that proteins ensure the agromaterial cohesion without any phase change in this temperature range. Lignocellulosic fibers entanglement also acts like reinforcement.

This study aimed to evaluate the influence of thermo-pressing conditions (cake quantity, pressure, time) on mechanical (flexural properties, Charpy impact strength, Shore D surface hardness) and heat insulation properties of fiberboards manufactured from a cake slightly deoiled, and inside a mold equipped with vents to allow the expression of residual oil during molding.

2. Experimental

2.1. Material

Thermo-mechanical fractionation in the twin-screw extruder was carried out using a batch of sunflower (*Helianthus annuus L.*) whole plant from oleic type (La Toulousaine de Céréales, France) (Table 1). It was harvested in September, that is to say when the plant maturity was reached. Whole plant was previously dried in a ventilation oven (50 °C, 48 h) and crushed using a hammer mill (Electra VS 1, France) fitted with a 15 mm screen. The batch of the powdered plant weighed around 250 kg. Its moisture content was 7.64 ± 0.13%.

2.2. Twin-screw extruder

Thermo-mechanical fractionation was conducted with a Clextral BC 45 (France) co-rotating twin-screw extruder. The extruder had seven modular barrels, each 200 mm in length, and different twin-screws which had segmental screw elements each 50 and 100 mm in length (Fig. 1). Four modules (modules 3, 4, 5 and 7) were heated to 80 °C by thermal induction and cooled by water circulation. A filter section consisting of six hemispherical dishes with perforations 1 mm in diameter was outfitted on module 6 to enable the filtrate to be collected. The screw rotation speed (S_S), the sunflower whole plant feed rate (Q_S), and the barrel temperature (θ_c) were monitored from a control panel.

2.3. Thermo-mechanical fractionation of sunflower whole plant in the twin-screw extruder

Sunflower whole plant was fed into the extruder inlet port by a volumetric screw feeder (Clextral 40, France) in the first module. Water was injected using a piston pump (Clextral DKM K20-2-P32, France) at the beginning of module 4 (Fig. 1). The screw profile chosen in this study (Fig. 2) was already used successfully for the aqueous extraction of oil from sunflower whole plant [8]. The trituration zone was located in modules 2 and 3. It consisted of the

Table 1
Chemical composition of sunflower whole plant used for experiments and of cake obtained after its thermo-mechanical fractionation in the Clextral BC 45 twin-screw extruder (% of the dry matter).

Material	Sunflower whole plant	Cake
Minerals	6.46 (±0.19)	5.40 (±0.00)
Lipids	26.83 (±0.43)	16.69 (±0.08)
Proteins	10.65 (±0.17)	6.85 (±0.05)
Cellulose	23.93 (±0.55)	31.18 (±0.19)
Hemicelluloses	7.83 (±0.09)	12.46 (±0.16)
Lignins	9.13 (±0.03)	14.60 (±0.00)
Water-soluble components	n.d.[a]	18.72 (±0.44)

[a] Non determined.

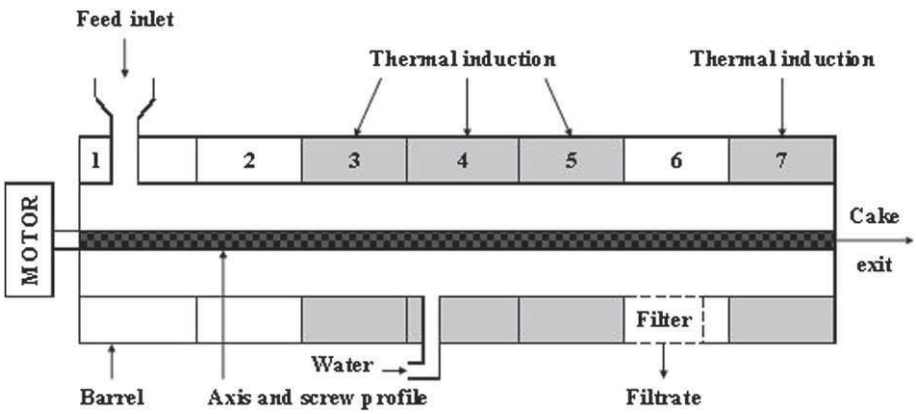

Fig. 1. Schematic modular barrel of the Clextral BC 45 twin-screw extruder used for thermo-mechanical fractionation of sunflower whole plant ($\theta_c = 80\ ^\circ C$).

succession of 10 monolobe paddles and 5 bilobe paddles, 5 cm apart. The extraction zone was situated in the modules 4 and 5. It was composed of a second series of 5 bilobe paddles. The reversed pitch screws were positioned in module 7, immediately downstream from the filtration module, to press the liquid/solid mixture.

Twin-screw extrusion was performed for 30 min before any sampling to ensure the stabilization of the operating conditions. Recorded operating conditions include feed rates of sunflower whole plant and water, temperature and current feeding the motor. Upon achieving steady operation, the filtrate and the cake were immediately collected over a period of 30 min to avoid any variability of the outlet flow rates. Sample collection time was determined with a stopwatch. Sample collection was carried out once. The filtrate and the cake were then weighed.

The oil extraction yield was calculated according to the following formula:

$$R_{L1} = \frac{(Q_S \times L_S) - (Q_C \times L_C)}{Q_S \times L_S} \times 100 \quad (1)$$

R_{L1} is the oil extraction yield based on the residual oil content in the cake (%), Q_S the inlet flow rate of the sunflower whole plant (kg/h), Q_C the flow rate of the cake (kg/h), L_S the oil content in the sunflower whole plant (%), and L_C is the oil content in the cake (%).

The protein extraction yield was calculated according to the following formula:

$$R_{P1} = \frac{(Q_S \times P_S) - (Q_C \times P_C)}{Q_S \times P_S} \times 100 \quad (2)$$

R_{P1} is the protein extraction yield based on the residual protein content in the cake (%), P_S the protein content in the sunflower whole plant (%), and P_C is the protein content in the cake (%).

The energy consumed by the motor was determined according to the following formulas:

$$P = U \times I \times \cos\varphi \times \frac{S_s}{S_{max}} \quad (3)$$

P is the electric power supplied by the motor (W), U the motor's operating voltage (U = 460V), I the current feeding the motor (A), $\cos\varphi$ the theoretical yield of the extruder motor ($\cos\varphi = 0.95$), and S_S and S_{max} are the test speed and maximum speed (600 rpm) of the rotating screws (rpm), respectively.

$$SME = \frac{P}{Q_s} \quad (4)$$

SME is the specific mechanical energy consumed by the motor per unit weight of sunflower whole plant (W h/kg).

2.4. Thermo-pressing

The cake was molded by thermo-pressing using a heated hydraulic press (Pinette Emidecau Industries, France) with 400 tons capacity. The aluminium mold used was equipped with vents to allow the expression during molding of residual oil from cake. The fiberboards produced were 150 mm × 150 mm squares.

The oil expression yield during molding was calculated according to the following formulas:

$$R_{L2} = \frac{(m_C \times L_C) - (m_{FB} \times L_{FB})}{m_C \times L_C} \times 100 \quad (5)$$

R_{L2} is the oil expression yield during molding relative to the remaining oil contained in the cake (%), m_C the mass of cake used for thermo-pressing (g), m_{FB} the mass of fiberboard (g), and L_{FB} is the oil content in the fiberboard (%).

$$R'_{L2} = R_{L2} \times \frac{100 - R_{L1}}{100} \quad (6)$$

R'_{L2} is the oil expression yield during molding relative to the total oil amount in the sunflower whole plant (%).

The total oil yield was calculated according to the following formula:

$$R_{LT} = R_{L1} + R'_{L2} = R_{L1} + \left(R_{L2} \times \frac{100 - R_{L1}}{100}\right) = \left(R_{L1} \times \frac{100 - R_{L2}}{100}\right) + R_{L2} \quad (7)$$

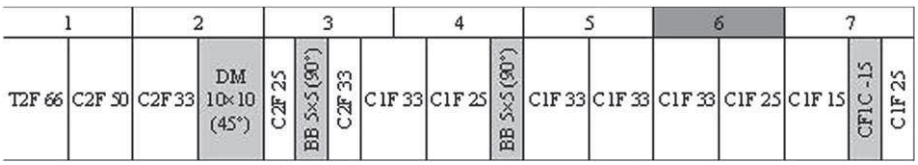

Fig. 2. Screw configuration of the Clextral BC 45 twin-screw extruder used for thermo-mechanical fractionation of sunflower whole plant.

R_{LT} is the total oil yield (oil extracted with water in the twin-screw extruder, and oil expressed during molding) relative to the total oil amount that the sunflower whole plant contains (%).

2.5. Analytical methods

The moisture contents were determined according to the French standard NF V 03-903. The mineral contents were determined according to the French standard NF V 03-322. The oil contents were determined according to the French standard NF V 03-908. The protein contents were determined according to the French standard NF V 18-100. An estimation of the three parietal constituents (cellulose, hemicelluloses, and lignins) contained in the solids was made by the ADF-NDF method of Van Soest and Wine [21,22]. An estimation of the water-soluble components contained in the cake was made by measuring the mass loss of the test sample after 1 h in boiling water. All determinations were carried out in duplicate.

2.6. Mechanical properties in bending

A Instron 33R4204 (USA) universal testing machine fitted with a 500 N load cell was used to assess the flexural properties of the test specimens according to the French standard NF EN 310, including breaking load (F), flexural strength at break (σ_f), and elastic modulus (E_f). The test specimens were 150 mm long and 30 mm wide. Their thickness was measured at three points with an electronic digital sliding caliper having a 0.01 mm resolution, and the mean value (t) was recorded to calculate their volume and section. All specimens were weighed to calculate their mean apparent density (d). The test speed was 3 mm/min and the grip separation was 100 mm. Test specimens were cut, and equilibrated in climatic chamber (60% RH, 25 °C) during three weeks before being tested. All determinations were carried out four times.

2.7. Impact strength

A 0-40 daN cm Testwell Wolpert (France) Charpy machine was used to assess the impact strength of the unnotched test specimens according to the French standard NF EN ISO 179, including absorbed energy (W), and resilience (K). The test specimens were 70 mm long and 10 mm wide. Their thickness was measured at three points with an electronic digital sliding caliper having a 0.01 mm resolution, and the mean value (t) was recorded to calculate their section. Impact strength measurements were realized at 23 °C according to the three points bending technique and the grip separation was 29.5 mm. Test specimens were cut, and equilibrated in climatic chamber (60% RH, 25 °C) during three weeks before being tested. All determinations were carried out ten times.

2.8. Surface hardness

A Bareiss (Germany) durometer was used to assess the Shore D surface hardness of the fiberboards according to the French standard NF EN ISO 868. Fiberboards were equilibrated in climatic chamber (60% RH, 25 °C) during three weeks before being tested. All determinations were carried out ten times.

2.9. Heat insulation properties

Thermal conductivity (λ) and thermal resistance (R) of fiberboards were determined at 25 °C according to the standard ISO 8302 08-91. The hot plate apparatus used for the measurements was a Lambda-Meßtechnik GmbH Dresden EP 500 (Germany) λ-Meter. The measurement area was 150 mm × 150 mm. The difference of temperature between the two plates was 5 K. Measurements were also conducted with the bulk cake using a Plexiglas box with a 50 mm height.

2.10. TGA measurements

Thermogravimetric analysis (TGA) of fiberboards was performed with a Shimadzu TGA-50 (Japan) analyzer. Dynamic analysis was conducted under air at a heating rate of 10 °C/min, from 20 to 650 °C. Fiberboards were previously crushed using a Foss Cyclotec 1093 (Denmark) mill fitted with a 1 mm screen. Before analysis, the crushed materials were equilibrated in a climatic chamber (60% RH, 25 °C) during three weeks. For all measurements, the mass of the test sample was around 10 mg. The weights of samples were measured as a function of temperature and stored. These data were later used to plot the percentage of undegraded sample (1 − D) (%) as a function of temperature, where

$$D = \frac{W_0 - W}{W_0}, \tag{8}$$

and W_0 and W were the weights at the starting point and during scanning (mg). All measurements were carried out in duplicate.

3. Results and discussion

3.1. Cake production by twin-screw extrusion

Thermo-mechanical fractionation of whole plant and aqueous extraction of sunflower oil were conducted simultaneously in the Clextral BC 45 twin-screw extruder with a screw configuration previously optimized [8]. A filtrate and a cake were collected continuously, due to the filter section outfitted along the barrel on module 6 (Fig. 1). Lipids and water-soluble components, mainly proteins but also pectins and hemicelluloses, were partly extracted during the process. Operating conditions used for cake production and results of the thermo-mechanical fractionation are mentioned in Table 2. The cake moisture was 64.9 ± 0.1%. The cake was dried in a ventilation oven (60 °C, 24 h) immediately after its production in the twin-screw extruder to make its conservation easier. Its chemical composition is presented in Table 1. It was slightly deoiled (16.7% of the dry matter) compared with other cakes described in previous studies [8,18]. This led to an oil extraction yield (yield based on the residual oil content in the cake) of only 50.0 ± 0.2%. At the same time, protein extraction yield (yield based on the residual protein content in the cake) was 48.3 ± 0.4%.

The low efficiency of aqueous extraction of sunflower oil from whole plant could be explained by a ratio of water to solid in the twin-screw extruder (Q_L/Q_S) quite low (3.5) compared with the ratio used for more efficient experiments (up to 4.1) [8,18]. It was also due to a low extruder filling ratio (0.08 kg/h rpm), defined as the ratio of the input flow rate of sunflower whole plant to the screw rotation speed (Q_S/S_S), resulting in an unsatisfactory liquid/solid separation of filtrate and cake in the reversed pitch screws. Best efficiency of sunflower oil extraction with water was obtained

Table 2
Operating conditions used for cake production and results of the thermo-mechanical fractionation of sunflower whole plant in the Clextral BC 45 twin-screw extruder ($\theta_c = 80$ °C).

S_S (rpm)	Q_S (kg/h)	Q_L[a] (kg/h)	Q_C (kg/h)	Q_F[b] (kg/h)	I (A)	P (W)	SME (W h/kg)
91	6.9	24.4	14.6	16.7	10.9	716.8	104.1

[a] Q_L is the inlet flow rate of the water.
[b] Q_F is the flow rate of the filtrate.

in a previous study with an extruder filling ratio of 0.17 kg/h rpm [8]. High filling ratio increases the compression of the matter inside the reversed screws, which is essential for an efficient separation of liquid and solid phases by filtration.

Because lipids and proteins were partly extracted by water during the process, their residual contents in the cake decreased logically when compared to initial values in the whole plant: from 26.8 to 16.7% of the dry matter, and from 10.7 to 6.8% of the dry matter, respectively. On the contrary, cellulose and lignins were not extracted because these two biopolymers are insoluble in water. Thus, a significant increase of their contents was observed at the same time: from 23.9 to 31.2% of the dry matter, and from 9.1 to 14.6% of the dry matter, respectively. In conclusion, chemical composition of the cake (Table 1) confirmed that it was a mixture of lignocellulosic fibers and proteins, meaning that it could be considered as a natural composite to be transformed into fiberboards by thermo-pressing.

3.2. *Influence of thermo-pressing conditions on fiberboards properties*

Nine fiberboards were manufactured using different thermo-pressing conditions (Table 3). Such conditions include cake quantity, pressure applied, and time. Temperature of the aluminium mold was 200 °C for all experiments. It was the same as the one that led to the highest mechanical properties in bending in a previous study [18], allowing the glass transition of proteins in the cake during molding. On the contrary, cake quantity, pressure applied, and time were higher: at least 555 mg/cm^2, at least 320 kgf/cm^2, and at least 60 s, respectively. The mold used was equipped with vents to favour the expression of residual lipids during molding. The cake moisture at molding was 7.2 ± 0.1%.

All fiberboards were cohesive. As previously observed [18], proteins acted as an internal binder inside fiberboards, and they contributed to ensure the agromaterial cohesion. At the same time, lignocellulosic fibers entanglement also acted like reinforcement. In all cases, flexural strength at break was low (less than 3.9 MPa) (Table 4), and it was clearly lower than the values obtained previously (until 11.5 MPa) with thermo-pressing conditions quite similar [18]. Such a difference could be explained by the use for the present study of a special mold equipped with vents on its side walls to allow the expression of residual oil in cake during molding. Oil expression resulted in the appearance of channels inside the fiberboards. Consequently, their internal structure was probably porous, leading to less resistant agromaterials. Such a hypothesis could be confirmed by the mean apparent density of fiberboards that never exceeded 0.97 (Table 4) instead of 1.13 for the previous study [18].

The increase of cake quantity from 555 to 1000 mg/cm^2 led to fiberboard thickness increase (from 5.4 to 10.2 mm). It contributed to a significant increase of breaking load from 18.6 to 60.7 N. Nevertheless, the same tendency was not observed with flexural strength at break. Indeed, it was quite stable (between 2.8 and 3.2 MPa) for all the cake quantities tested even if the thinnest fiberboard seemed to be a bit more resistant than the others (3.2 MPa for flexural strength at break). At the same time, elastic modulus of fiberboards decreased progressively with the increase of their thickness. It was only 216.6 MPa for the thickest fiberboard instead of 352.6 MPa for fiberboard from trial 1, meaning that the rigidity of fiberboards decreased progressively with the increase of cake quantity used for their manufacturing. As observed with breaking load, Charpy impact strength increased also a lot with an increasing cake quantity: from 0.13 to 0.66 J for absorbed energy, and from 2.3 to 6.5 kJ/m^2 for resilience. On the other hand, no significant effect of cake quantity was observed on Shore D surface hardness that remained quite stable (between 43.9 and 49.7°) for fiberboards from trials 1 to 5. In conclusion, the thickest fiberboard (10.2 mm for thickness) that was manufactured from the highest cake quantity (1000 mg/cm^2) revealed the most important values of this study for breaking load (60.7 N) and for resilience (6.5 kJ/m^2), and it was also the most flexible fiberboard (only 216.6 MPa for elastic modulus).

The increase of pressure applied during molding (from 320 to 360 kgf/cm^2) led to a slight decrease of the thickness (from 5.4 to 5.0 mm), to a very slight increase of flexural strength at break (from 3.2 to 3.5 MPa), to an important increase of elastic modulus (from 352.6 to 728.6 MPa), and to an increase of resilience (from 2.3 to 2.7 kJ/m^2). Fiberboard from trial 6 was the most rigid board of this study, and it logically revealed the most important surface hardness (52.6°). Thus, the increase of the applied pressure had a positive effect on all the mechanical properties in the pressure range investigated in this study, and it also contributed to a more efficient expression of residual oil in cake during molding.

Increasing the molding time from 60 to 150 s decreased the fiberboard thickness (from 5.9 to 5.0 mm). It also led to a decrease of breaking load (from 27.2 to 16.5 N), and therefore to a slight decrease of flexural strength at break (from 3.9 to 3.3 MPa). The same tendency was also observed on Charpy impact strength (from 0.18 to 0.13 J for absorbed energy, and from 3.1 to 2.5 kJ/m^2 for resilience), and on surface hardness (from 49.3 to 39.6°). Even if the increase of molding time tended then to fragilize the fiberboards, the decrease of mechanical properties was not so important (as an example, only −18% for flexural strength at break from trial 1 by comparison to the one from trial 7). Moreover, the elastic modulus that first decreased from 60 to 120 s (from 475.6 to 352.6 MPa) became clearly higher (636.1 MPa) when molding time was 150 s, leading to a more rigid board. It was just a little lower than the highest elastic modulus of this study (728.6 MPa) that was reached from the highest pressure applied. The increase of molding time also contributed to a better expression efficiency of residual oil in cake during molding.

Low mean apparent density of fiberboards (never more than 0.97) contributed to promising heat insulation properties. Thermal conductivity and thermal resistance were determined for fiberboards from trials 1, 3 and 5 to estimate the possible influence of their thicknesses on the results. Thermal conductivity at 25 °C was rather low for the three fiberboards tested (Table 5). It also decreased with the increase of thickness, and it was only 103.5 mW/m K for the thickest fiberboard (the one from trial 5) whose mean apparent density was only 0.92 (Table 4). At the same time, thermal resistance logically increased with the thickness, and it reached 0.099 m^2 K/W for the highest thickness (Table 5). Consequently, fiberboards would be potentially usable as heat insulation panels in buildings, and particularly the thickest one that revealed the best ability for thermal insulation. Measurements made on the bulk cake also indicated that it was an even better insulating material (only 63.1 mW/m K for thermal conductivity, and 0.792 m^2 K/W for thermal resistance), certainly due to its very low bulk density (0.20) (Table 5). It would be also suitable for the thermal insulation of houses, and more particularly when positioned in their attic spaces.

Table 3
Thermo-pressing conditions for the manufacture of the nine fiberboards (temperature of the aluminium mold was set at 200 °C).

Trial	1	2	3	4	5	6	7	8	9
Mass (g)	125	150	175	200	225	125	125	125	125
Pressure (kgf/cm^2)	320	320	320	320	320	360	320	320	320
Time (s)	120	120	120	120	120	120	60	90	150

Table 4
Mechanical properties of the nine fiberboards manufactured by thermo-pressing.

Trial	1	2	3	4	5	6	7	8	9
Flexural properties									
t (mm)	5.39(±0.25)	6.11(±0.28)	8.05(±0.76)	9.36(±0.28)	10.21(±0.32)	5.03(±0.26)	5.93(±0.43)	6.09(±0.17)	5.01(±0.56)
d	0.97(±0.02)	0.95(±0.03)	0.90(±0.02)	0.88(±0.01)	0.92(±0.01)	0.95(±0.04)	0.90(±0.01)	0.85(±0.02)	0.97(±0.02)
F (N)	18.6(±0.6)	21.0(±1.0)	37.4(±6.2)	48.7(±7.3)	60.7(±12.7)	17.5(±1.8)	27.2(±3.7)	23.6(±3.7)	16.5(±1.4)
σ_f (MPa)	3.2(±0.2)	2.8(±0.3)	3.0(±0.8)	2.8(±0.4)	2.9(±0.8)	3.5(±0.3)	3.9(±0.3)	3.2(±0.5)	3.3(±0.6)
E_f (MPa)	352.6(±40.9)	300.1(±29.9)	327.5(±55.4)	264.5(±68.9)	216.6(±32.3)	728.6(±42.6)	475.6(±43.1)	441.0(±47.5)	636.1(±52.8)
Charpy impact strength									
W (J)	0.13(±0.01)	0.17(±0.03)	0.25(±0.03)	0.38(±0.05)	0.66(±0.14)	0.12(±0.02)	0.18(±0.02)	0.16(±0.02)	0.13(±0.01)
K (kJ/m^2)	2.3(±0.3)	2.7(±0.6)	3.0(±0.4)	4.2(±0.6)	6.5(±1.5)	2.7(±0.5)	3.1(±0.3)	2.8(±0.3)	2.5(±0.3)
Surface hardness									
Shore D (°)	43.9(±4.3)	49.7(±3.2)	46.0(±4.0)	46.0(±2.7)	47.3(±5.2)	52.6(±5.9)	49.3(±4.6)	41.1(±2.7)	39.6(±0.9)

Thermogravimetric analysis of fiberboards showed that all TGA degradation curves under air had quite the same appearance, meaning that thermo-pressing conditions had no significant influence in thermal degradation phenomena inside fiberboards. Decomposition temperatures observed were always the same, and the TGA curve mentioned in Fig. 3 corresponded to the fiberboard from trial 5 chosen because it was the fiberboard that revealed the best breaking load in bending (Table 4), the best Charpy impact strength (Table 4), and also the best heat insulation properties (Table 5). A first mass loss was observed at 100 °C corresponding to water evaporation. Moisture content of the fiberboard from trial 5 was 7.4% after three weeks in a climatic chamber (60% RH, 25 °C) (Table 6), and the mass loss observed in TGA curve corresponded approximately to the same mass percentage. Then, the thermal degradation of organic compounds occurred mainly in one stage (between 200 and 375 °C) that led to the loss of more than 55% of the dry matter in sample. Another degradation phenomenon was also observed around 425 °C but it was associated with a lower mass loss (no more than 10% of the dry matter in sample).

Considering data mentioned by a few researchers in previous studies dealing with the thermal degradation of fibers, hemicelluloses would degrade first, around 270–330 °C, and then cellulose, around 320–380 °C, and finally lignins, around 420 °C [23–26]. Thermal degradation of sunflower proteins from an industrial cake was also observed, above 250 °C and under 350 °C [19]. Moreover, the smoke point of the refined sunflower oil, associated with the beginning of its thermal degradation, is 232 °C. As oil was expressed during molding, residual oil content in fiberboard from trial 5 was less important than in cake: about 13.2% of the dry matter (Table 6).

Consequently, it was reasonable to think that the main thermal degradation stage (200–375 °C) could be associated to the degradations of lipids, proteins, hemicelluloses, and cellulose at the same time. The second one, situated at around 425 °C, could then correspond to the thermal degradation of lignins only. Because no thermal degradation occurred before 200 °C, it confirmed that the temperature chosen for the aluminium mold in the heated hydraulic press during molding was appropriate. Moreover, when used under 200 °C, fiberboards will not degrade, and their mechanical properties will be logically preserved.

At the end of the measurement, the undegraded sample represented more than 23% of the test sample mass, meaning that the undegraded compounds were not only minerals (5.85 ± 0.06% of the dry matter in that case) but contained also some organic biomolecules from the test sample. It was probably due to a too high heating rate (10 °C/min) that resulted in a partial thermal degradation of organic compounds inside the analyzed sample.

Table 5
Thermal conductivity (λ) and thermal resistance (R) of three of the nine fiberboards manufactured by thermo-pressing and of the bulk cake.

Trial	1	3	5	Bulk cake[a]
λ (mW/m K)	135.7	128.3	103.5	63.1
R (m^2 K/W)	0.040	0.063	0.099	0.792

[a] 0.20 for bulk density.

3.3. Oil expression yields during molding

For all fiberboards, part of residual oil in the cake was expressed during molding through the side walls vents of the mold. This led to the decrease of residual oil content in fiberboards (up to 8.7% of the dry matter for the highest pressure applied), and to the increase of total oil yield (at least 64.6% instead of 50.0% for oil extraction yield in the twin-screw extruder, and up to 79.3%) (Table 6).

Oil expression during molding was more difficult with an increasing cake quantity (from 46.2 to 29.1% for oil expression yield according to the oil content in the cake), due to the increase of the fiberboard thickness. The mass of residual oil in the cake inside the mold before thermo-pressing increased with the cake quantity. The molding duration (120 s) became then insufficient to allow the same efficiency for oil expression through the defined number of vents. Obviously residual oil content in the fiberboard from trial 5 was higher (13.2% of the dry matter) than the others because it corresponded to the fiberboard manufactured from the highest cake quantity and with the highest thickness. This led to a total oil yield of only 64.6% instead of 73.1% for the best trial (trial 2).

When the pressure applied during molding was 360 kgf/cm^2, oil expression yield reached 58.5% according to the oil content in the cake. Consequently, the corresponding fiberboard (fiberboard from trial 6) was the poorest board in lipids (only 8.7% of the dry matter) of this study, leading to the most important total oil yield (79.3%). As for the pressure applied, the increase of molding time from 60 to 150 s also contributed to an increase of oil expression yield: from 35.8 to 52.5% according to the oil content in the cake. A decrease of

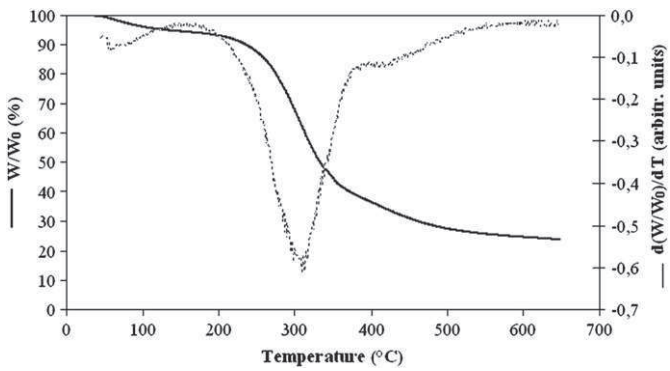

Fig. 3. TGA degradation curve under air and at 10 °C/min of the fiberboard from trial 5.

Table 6
Quantification of the oil expressed during molding for the nine fiberboards manufactured by thermo-pressing.

Trial	1	2	3	4	5	6	7	8	9
m_{FB} (g)	109.8	128.3	158.7	179.8	201.6	99.7	116.6	113.2	99.3
H_{FB} (%)[a]	6.95(±0.05)	7.51(±0.09)	7.21(±0.01)	7.17(±0.06)	7.37(±0.17)	7.75(±0.18)	7.80(±0.20)	6.80(±0.03)	6.96(±0.21)
L_{FB} (% dry matter)	11.20(±0.02)	10.52(±0.09)	12.55(±0.05)	12.98(±0.17)	13.22(±0.05)	8.72(±0.16)	11.55(±0.06)	10.89(±0.05)	9.94(±0.05)
R_{L2} (%)	40.9(±0.1)	46.2(±0.5)	31.8(±0.3)	30.0(±0.9)	29.1(±0.3)	58.5(±0.8)	35.8(±0.3)	40.6(±0.3)	52.5(±0.3)
R_{L2}' (%)	20.4(±0.1)	23.1(±0.2)	15.9(±0.1)	15.0(±0.4)	14.6(±0.1)	29.3(±0.4)	17.9(±0.2)	20.3(±0.1)	26.3(±0.1)
R_{LT} (%)	70.4(±0.3)	73.1(±0.5)	65.9(±0.4)	65.0(±0.7)	64.6(±0.4)	79.3(±0.6)	67.9(±0.4)	70.3(±0.4)	76.3(±0.4)

[a] Fiberboards were equilibrated in a climatic chamber (60% RH, 25 °C) during three weeks before moisture measurements.

the residual oil content in fiberboards from 11.5 to 9.9% of the dry matter was also observed, and total oil yield increased from 67.9 to 76.3%. Nevertheless, the increase of molding time had a lesser effect on oil expression during molding than the increase of pressure applied. Indeed, oil expression was lower in the case of trial 9 (320 kgf/cm^2 during 150 s) than in the case of trial 6 (360 kgf/cm^2 during 120 s): 52.5% instead of 58.5% for oil expression yield according to the oil content in the cake, and 76.3% instead of 79.3% for total oil yield. So, residual oil content in the fiberboard from trial 9 was a bit higher than in the fiberboard from trial 6: 9.9% of the dry matter instead of 8.7% of the dry matter.

Even if the pressure applied during molding led to a partial oil expression, residual oil content in fiberboards was not negligible (Table 6). It was at least 8.7% of the dry matter (case of the highest pressure applied), and it was more than 10% of the dry matter in most cases (up to 13.2% of the dry matter for trial 5 that was conducted with the highest cake quantity). Thus, in spite of their global hydrophilic character, it is reasonable to think that residual oil in fiberboards will contribute to make them less water-sensitive and more durable than deoiled thermo-pressed agromaterials.

Oil expressed during molding could be collected. Firstly, its filtration would eliminate small solid particles that were driven through the vents of the mold during thermo-pressing. Then, its refining would make it a vegetable oil usable for human feeding. Two other applications can be also considered for such refined oil: its use as a biolubricant or its transformation into biodiesel after transesterification of triglycerides with methanol to produce fatty acid methyl esters (FAME).

4. Conclusion

The use of the cake generated during the biorefinery of sunflower whole plant in a twin-screw extruder makes possible the manufacture of renewable and biodegradable fiberboards by thermo-pressing. Their mechanical and heat insulation properties depend on the thermo-pressing conditions used during molding: up to 3.9 MPa for flexural strength at break, 6.5 kJ/m^2 for Charpy impact strength, 52.6° for Shore D surface hardness, and 103.5 mW/m K for thermal conductivity. Moreover, thermo-pressing is not only a molding operation to manufacture cohesive fiberboards. It also favours the oil extraction efficiency (reaching 79.3% for total oil yield). Such fiberboards would be potentially usable as inter-layer sheets for pallets, for the manufacture of biodegradable containers (composters, crates for vegetable gardening) by assembly of fiberboards, or as heat insulating materials in building industry.

Fiberboards with a low thickness (less than 6 mm) would be suitable for their use as inter-layer sheets or for the manufacturing of containers because their flexural properties are better (at least 3.2 MPa for flexural strength at break, and up to 3.9 MPa). In particular, the fiberboard molded with the highest pressure (360 kgf/cm^2) is a good compromise to have at the same time high mechanical properties in bending (3.5 MPa for flexural strength at break, and 728.6 MPa for elastic modulus), a high value for Shore D surface hardness (52.6°), and also an efficient expression of residual oil in the cake during molding (79.3% for total oil yield). On the contrary, the thickest fiberboards (more than 8 mm) reveal not only the highest values for Charpy impact strength (at least 3.0 kJ/m^2 for resilience, and up to 6.5 kJ/m^2) but also the lowest thermal conductivities (no more than 128.3 mW/m K, and up to 103.5 mW/m K). They are also the fiberboards with the highest residual oil contents (at least 12.5% of the dry matter, and up to 13.2% of the dry matter). They would be suitable for their heat insulation properties in the building industry.

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References

[1] Isobe S, Zuber F, Uemura K, Noguchi A. A new twin-screw press design for oil extraction of dehulled sunflower seed. J Am Oil Chem Soc 1992;69(9):884–9.
[2] Rosenthal A, Pyle DL, Niranjan K. Aqueous and enzymatic processes for edible oil extraction. Enzym Microb Technol 1996;19(6):402–20.
[3] Galvin JB. In: Technology and Solvents for Extracting Oilseeds and Nonpetroleum Oils. Toxicity Data for Commercial Hexane and Hexane Isomers. AOCS Press; 1997. pp. 75–85.
[4] Hagenmaier RD. Aqueous processing of full-fat sunflower seeds: yields of oil and protein. J Am Oil Chem Soc 1974;51(10):470–1.
[5] Southwell KH, Harris RV. Extraction of oil from oilseeds using the hot water flotation method. Trop Sci 1992;32(3):251–62.
[6] Evon P, Vandenbossche V, Pontalier PY, Rigal L. Direct extraction of oil from sunflower seeds by twin-screw extruder according to an aqueous extraction process: feasibility study and influence of operating conditions. Ind Crops Prod 2007;26(3):351–9.
[7] Evon P, Vandenbossche V, Pontalier PY, Rigal L. Aqueous extraction of residual oil from sunflower press cake using a twin-screw extruder: feasibility study. Ind Crops Prod 2009;29(2-3):455–65.
[8] Evon P, Vandenbossche V, Pontalier PY, Rigal L. The twin-screw extrusion technology, an original and powerful solution for the biorefinery of sunflower whole plant. Ol Corps Gras Li 2010;17(6):404–17.
[9] Maréchal V, Rigal L. Characterization of by-products of sunflower culture: commercial applications for stalks and heads. Ind Crops Prod 1999;10(3):185–200.
[10] Leyris J, Silvestre F, Rigal L, Gaset A. Procédé de fabrication d'objets à partir de matière première végétale par formage ou thermoformage. European Patent EP 0 987 089; 2000.
[11] Rouilly A, Orliac O, Silvestre F, Rigal L. DSC study on the thermal properties of sunflower proteins according to their water content. Polymer 2001;42(26):10111–7.
[12] Orliac O, Rouilly A, Silvestre F, Rigal L. Effects of additives on the mechanical properties, hydrophobicity and water uptake of thermo-moulded films produced from sunflower protein isolate. Polymer 2002;43(20):5417–25.
[13] Rouilly A, Orliac O, Silvestre F, Rigal L. Thermal denaturation of sunflower globulins in low moisture conditions. Thermochim Acta 2003;398(1-2):195–201.
[14] Orliac O, Rouilly A, Silvestre F, Rigal L. Effects of various plasticizers on the mechanical properties, water resistance and aging of thermo-moulded films made from sunflower proteins. Ind Crops Prod 2003;18(2):91–100.
[15] Rouilly A, Orliac O, Silvestre F, Rigal L. New natural injection-moldable composite material from sunflower oil cake. Bioresour Technol 2006;97(4):553–61.
[16] Rouilly A, Mériaux A, Geneau Sbartaï C, Silvestre F, Rigal L. Film extrusion of sunflower protein isolate. Polym Eng Sci 2006;46(11):1635–40.

[17] Humbert J, Makoumbou U, Rigal L, Chelle R, Rouilly A, Geneau Sbartaï C. Matériau plastique composite sous la forme de granulats issus de matières protéiques végétales et son procédé de fabrication. French Patent FR 2 940 297; 2010.
[18] Evon P, Vandenbossche V, Pontalier PY, Rigal L. Thermo-mechanical behaviour of the raffinate resulting from the aqueous extraction of sunflower whole plant in twin-screw extruder: manufacturing of biodegradable agromaterials by thermopressing. Adv Mater Res 2010;112:63–72.
[19] Geneau C. Manufacturing process of agromaterial natural composite by twin-screw extrusion and injection moulding from sunflower cake. Ph.D. thesis, INP, Toulouse, France; 2006.
[20] Zhang J, Mungara P, Jane J. Mechanical and thermal properties of extruded soy protein sheets. Polymer 2001;42(6):2569–78.
[21] Van Soest PJ, Wine RH. Use of detergents in the analysis of fibrious feeds. IV. Determination of plant cell wall constituents. J AOAC Int 1967;50:50–5.
[22] Van Soest PJ, Wine RH. Determination of lignin and cellulose in acid detergent fiber with permanganate. J AOAC Int 1968;51:780–4.
[23] Schaffer EL. Effect of pyrolytic temperatures on the longitudinal strength of dry Douglas-fir. J Test Eval 1973;1(4):319–29.
[24] Beaumont O. Pyrolyse extractive du bois. Ph.D. thesis, Ecole Nationale Supérieure des Mines de Paris, Paris, France; 1981.
[25] Lalou A. Mise au point d'un procédé d'extraction des hémicelluloses à partir d'un substrat végétal ligno-cellulosique: application au cas des coques de tournesol. Ph.D. thesis, INP, Toulouse, France; 1995.
[26] Hatakeyama T, Hatakeyama H. Thermal properties of green polymers and biocomposites. Dordrecht: Kluwer Academic Publishers; 2004.