New Renewable and Biodegradable Particleboards from *Jatropha* Press Cakes

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ABSTRACT: The influence of thermo-pressing conditions on the mechanical properties of particleboards obtained from *Jatropha* press cakes was evaluated in this study. Conditions such as molding temperature and press cake oil content were included. All particleboards were cohesive, with proteins and fibers acting respectively as binder and reinforcing fillers. Generally, it was the molding temperature that most affected particleboard mechanical properties. The most resistant boards were obtained using 200°C molding temperature. Glass transition of proteins then occurred during molding, resulting in effective wetting of the fibers. At this optimal molding temperature, the best compromise between flexural properties (7.2 MPa flexural strength at break and 2153 MPa elastic modulus), Charpy impact strength (0.85 kJ/m^2) and Shore D surface hardness (71.6°), was a board obtained from press cake with low oil content (7.7%). Such a particleboard would be usable as interlayer sheets for pallets, for the manufacture of containers or furniture, or in the building trade.

KEYWORDS: Jatropha press cake, lignocellulosic fibers, particleboard, proteins, thermo-pressing

1 INTRODUCTION

Jatropha curcas is a drought-resistant shrub or tree belonging to the family *Euphorbiaceae*, which is cultivated in Central and South America, Southeast Asia, India and Africa [1]. It is a plant with many attributes, multiple uses and considerable potential [2–4]. The seed is the part of the jatropha plant with the highest potential for utilization. It contains between 40 and 60% oil, and between 20 and 30% proteins. *J. curcas* oil is regarded as a potential alternative to diesel fuel [5]. The fact that jatropha oil cannot be used for nutritional purposes without detoxification [1, 6], makes its use as an energy source for fuel production very attractive. The use of biodiesel from jatropha oil is a promising alternative to fossil fuel because it is renewable and environmentally friendly, and can also be produced locally.

Conventional industrial technology for the synthesis of biodiesel from vegetable oils, involves isolation of the oil from the seed, refining, and then transesterification. Industrial oil extraction from oilseeds is usually carried out by mechanical pressing, followed by solvent extraction with n-hexane. Over the last twenty years, there has been much focused research concerning continuous oil extraction by mechanical pressing using extrusion technology [7–11]. This process in a single-screw press (or single-expeller press) is widely employed for oilseeds, using a single screw of variable pitch and channel depth, slowly rotating in a cage-type barrel [7]. However, transport of material in this type of press depends mainly on friction between the material and the barrel's inner and screw surfaces during screw rotation. Thus, a solid core component is often necessary to produce this friction, causing overheating, high energy consumption, plus oil and cake deterioration. Furthermore, single-screw presses provide insufficient crushing and mixing if they are not equipped with breaker bars, or other special equipment.

A twin-screw oil press can be expected to solve these problems because of the higher transportation force, similar to a gear pump, and better mixing

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and crushing at the twin-screw interface, improving mechanical lysis of the cells [12]. In addition, energy consumption of the twin-screw press is more efficient [7, 13]. Thus, twin-screw extrusion technology has increasingly been successfully used to undertake mechanical pressing of various oilseeds [7, 13–21].

Mechanical pressing of jatropha oilseed was recently conducted using a co-rotating (Clextral BC 21, France) twin-screw extruder [22]. In this study, the influence of operating conditions, including screw configuration, pressing temperature and screw rotation speed, on oil yield, specific mechanical energy and oil quality, was examined. Generally, it was the screw configuration, or profile, that most affected oil extraction efficiency. The best oil yields, a minimum of 57.5%, were obtained with a trituration zone composed of 10 monolobe and 10 bilobe paddles, and a pressing zone composed of 50 mm long, reverse pitch screws with a −33 mm pitch. In addition, oil extraction yield increased with decreasing temperature and screw rotation speed. Highest oil extraction yield (70.6%) with good press cake quality (residual oil content lower than 8%) was obtained under operating conditions of 153 rpm screw rotation speed, 5.16 kg/h inlet flow rate of jatropha seeds, and 80°C pressing temperature. The corresponding expressed oil was inexpensive to produce (314 W h/kg expressed oil) compared with another continuous technique, i.e., the single expeller press, commonly used for mechanical extraction of jatropha oil (about 1.6 kW h/kg expressed oil) [23]. Its quality was also satisfactory for biodiesel production.

After extraction of oil from jatropha seeds using the twin-screw extruder, the oil content in the press cake is at least 5.9% of the dry matter [22]. Although this can be a disadvantage for direct utilization of the press cake, it could be converted into usable energy by combustion, gasification or pyrolysis [24, 25]. The press cake can also act as reinforcing filler for a biodegradable polymer, i.e., poly(ε-caprolactone) (PCL), and have potential uses in biocomposite applications [26]. Nevertheless, new valorizations of the press cake, as a mixture of proteins and lignocellulosic fibers coming mainly from the shells but from the kernel breakdown process as well, could also be considered [27–39]. In particular, as a natural composite, it could be transformed into biodegradable and value-added agromaterials by thermo-pressing [34, 35, 37–39].

This study was aimed at evaluating the influence of thermo-pressing conditions (molding temperature, oil content in press cake) on mechanical properties (flexural properties, Charpy impact strength and Shore D surface hardness) of particleboards made from jatropha press cakes produced in a twin-screw extruder, inside a mold equipped with vents to allow expression of residual oil during molding.

2 EXPERIMENTAL

2.1 Materials

Molding of particleboards was conducted by thermopressing using five different jatropha press cakes (A to E). The press cakes were obtained after the extraction of oil from ground jatropha seeds using a Clextral BC 21 (France) twin-screw extruder [22]. Their residual oil contents varied from 5.9 (press cake A) to 19.1% of the dry matter (press cake E), depending on the operating conditions (screw configuration, pressing temperature and screw rotation speed) used for mechanical pressing in the twin-screw extruder. Moisture contents of equilibrated press cakes A to E were 7.2±0.0%, 5.8±0.2%, 6.3±0.1%, 6.2±0.0% and 5.9±0.3%, respectively (French standard NF V 03–903).

2.2 Analytical Methods

The moisture contents were determined according to French standard NF V 03–903. The mineral contents were determined according to French standard NF V 03–322. The oil contents were determined according to French standard NF V 03–908. The protein contents were determined according to French standard NF V 18–100. An estimation of the three parietal constituents (cellulose, hemicelluloses, and lignins) contained in the solids was made using the ADF-NDF method from Van Soest and Wine [40, 41]. An estimation of the water-soluble components contained in the solids, was made by measuring the mass loss of the test sample after 1 h in boiling water. All determinations were carried out in duplicate.

2.3 Particle Size Distribution

The press cakes were examined with a Nachet France Z 45 P (France) × 15 binocular magnifier, and six different photographs were taken of each sample and analyzed using the Archimed 4.0 (France) software. Particle size distribution was determined by manually measuring the diameter of all the particles on the six photographs, using the ImageJ (USA) software. The tapped density of the press cakes was also measured in a Granuloshop Densitap ETD-20 (France) volumenometer, and the corresponding apparent density, i.e., before compaction, was determined at the same time.

2.4 TGA Measurements

Thermogravimetric analysis (TGA) of the press cakes was performed with a Shimadzu TGA-50 (Japan) analyzer. Dynamic analysis was conducted under air at a heating rate of 5°C/min, from 20 to 750°C. Before

analysis, the press cakes were equilibrated in a climatic chamber (60% RH, 25°C) for three weeks. For all measurements, the mass of the test sample was around 8 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

$$D = \frac{W_0 - W}{W_0}, \quad (1)$$

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

2.5 DVS Measurements

Dynamic vapor sorption (DVS) of the press cakes was performed with a DVS Advantage automated gravimetric vapor sorption (Surface Measurement Systems Ltd., London, UK) analyzer. DVS measures the uptake of vapor gravimetrically using a Cahn D200 recording ultramicrobalance with a mass resolution of ±0.1 µg. The relative humidity around the sample was controlled by mixing saturated and dry carrier gas streams using mass flow controllers. A constant temperature was maintained (±0.1°C) by enclosing the entire system in a temperature-controlled incubator. Before analysis, the press cakes were stored in a desiccator. For each experiment, the press cake was immediately placed into the DVS analyzer under a continuous stream of dry (<0.1% RH) air. A sample size between 15 and 25 mg was used. Prior to exposure to any water vapor, the samples were dried at 0% RH to remove superficial water present and establish a dry baseline mass. The samples were exposed to the following relative humidity profile: 0%, 15%, 30%, 45%, 60%, 75% and 90% RH. At each stage, the sample mass was allowed to reach equilibrium before the relative humidity was increased. An isotherm was calculated from the complete moisture sorption profile using the DVS Advanced Analysis Suite v3.6 software. All experiments were performed at 25°C.

2.6 DSC Measurements

Differential scanning calorimetry (DSC) of the press cakes was performed from deoiled materials with a Mettler Toledo DSC 1 STARe System (Switzerland) power compensation calorimeter fitted with an intracooler cooling system. The purge gas used was nitrogen of analytical quality at a flow rate of 50 mL/min. Temperature and energy calibration was carried out with zinc (T_f = 419.5°C), indium (T_f = 156.6°C) and distilled water (T_f = 0°C) before the beginning of the tests. All analyses were performed with hermetic 120 µL stainless steel capsules (plus an empty reference capsule) fitted with O-rings resistant to an internal pressure of 20 bar (Mettler Toledo). They were carried out at a heating speed of 5°C/min from 25°C to 250°C. Before analysis, the deoiled press cakes were either equilibrated in a climatic chamber (60% RH, 25°C) for three weeks, or dried in a ventilated oven (60°C, 12 h). Sample mass was around 10 mg and all measurements were made in triplicate. The treatment of data obtained was carried out using the STARe software (Mettler Toledo).

2.7 Thermo-pressing

The press cakes were molded by thermo-pressing inside an aluminum mold, using a 400 ton capacity Pinette Emidecau Industries (France) heated hydraulic press, producing 150 mm square particleboards. The mold was equipped with vents to allow expression of residual oil from press cakes during molding. The press cakes were dried in a ventilated oven (60°C, 12 h) before molding, to minimize vapor generation during thermo-pressing and so restrict the risk of defects such as blisters inside the particleboards. On molding, moisture contents of press cakes A to E were 1.4±0.3%, 1.0±0.2%, 1.4±0.0%, 1.2±0.2% and 1.4±0.3%, respectively. Press cake quantity, pressure applied and molding time for all experiments were 145 g (i.e., 644 mg/cm^2), 297 kgf/cm^2 and 90 s, respectively. At the same time, three molding temperatures were tested for each press cake: 160, 180 and 200°C. Particleboards molded at 160°C from press cakes A to E were referenced A1, B1, C1, D1 and E1, respectively. Likewise, those molded at 180°C were referenced A2, B2, C2, D2 and E2, and those molded at 200°C were referenced A3, B3, C3, D3 and E3. Two particleboards were manufactured for all the thermo-pressing conditions tested (including temperature of the aluminum mold, and press cake). One was used to assess mechanical properties for bending, and the second for measuring Shore D surface hardness, and Charpy impact strength.

Oil expression yield during molding was calculated from the following formulae:

$$R_{L2} = \frac{(m_C \times L_C) - (m_{PB} \times L_{PB})}{m_C \times L_C} \times 100 \quad (2)$$

where R_{L2} is the oil expression yield during molding relative to the residual oil contained in the press

cake (%), m_C the mass of press cake used for thermo-pressing (g), m_{PB} the mass of particleboard (g), L_C the residual oil content in the press cake (%), and L_{PB} the oil content in the particleboard (%).

$$R'_{L2} = R_{L2} \times \frac{100 - R_{L1}}{100} \quad (3)$$

where R'_{L2} is the oil expression yield during molding relative to the total amount of oil in the jatropha seeds (%), and R_{L1} is the oil extraction yield in the twin-screw extruder based on the residual oil content in the press cake (%).

The total oil yield (extraction of oil from jatropha seeds in the twin-screw extruder, and expression of residual oil from press cake during molding) was calculated from the following formulae:

$$\begin{aligned} R_{LT} &= R_{L1} + R'_{L2} = R_{L1} + \left(R_{L2} \times \frac{100 - R_{L1}}{100} \right) \\ &= \left(R_{L1} \times \frac{100 - R_{L2}}{100} \right) + R_{L2} \end{aligned} \quad (4)$$

where R_{LT} is the total oil yield (the difference between the oil contained in the jatropha seeds and the residual oil in the press cake after extraction of oil in the twin-screw extruder, and oil expressed during molding) relative to the total amount of oil that the jatropha seeds contain (%).

$$R'_{LT} = R'_{L1} + R'_{L2} = R'_{L1} + \left(R_{L2} \times \frac{100 - R_{L1}}{100} \right) \quad (5)$$

where R'_{LT} is the total oil yield (oil extracted in the twin-screw extruder, and oil expressed during molding) relative to the total amount of oil that the jatropha seeds contain (%), and R'_{L1} is the oil extraction yield in the twin-screw extruder relative to the total oil that the jatropha seeds contain (%).

2.8 Mechanical Properties for Bending

An 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 with 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 2 mm/min and the grip separation was 100 mm. Test specimens were cut, and equilibrated in a climatic chamber (60% RH, 25°C) for three weeks before being tested. All determinations were carried out four times.

2.9 Charpy 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 60 mm long and 10 mm wide. Their thickness was measured at three points with an electronic digital sliding caliper with a 0.01 mm resolution, and the mean value (t) was recorded to calculate their section. Impact strength measurements were made at 23°C using the three points bending technique, and grip separation was 25 mm. Test specimens were cut and equilibrated in a climatic chamber (60% RH, 25°C) for three weeks before being tested. All determinations were carried out sixteen times.

2.10 Shore D Surface Hardness

A Bareiss (Germany) durometer was used to assess the Shore D surface hardness of the particleboards according to the French standard NF EN ISO 868. Particleboards were equilibrated in a climatic chamber (60% RH, 25°C) for three weeks before being tested. All determinations were carried out 48 times (24 times for each side of the particleboard).

2.11 Colorimetry

A Minolta CR-410 (Japan) spectrocolorimeter was used in reflectance mode to compare the color of the particleboards with that of the corresponding press cake and that of the ground jatropha seeds. The particleboards had been previously crushed using a Foss Cyclotec 1093 (Denmark) mill fitted with a 1 mm screen. The ground materials were equilibrated in climatic chamber (60% RH, 25°C) for three weeks before being tested. The color measurements were made using the CIE L*a*b* referential, which is widely employed for nonluminous objects. The illuminant was D65, and the observer angle was 2°. In the L*a*b* color space, L* is the lightness and it varies from 0 (black) to 100 (white), and a* and b* are the chromaticity coordinates: +a* is the red direction, -a* is the green direction, +b* is the yellow direction, and -b* is the blue direction. The center is achromatic. All determinations were carried out five times.

The L* color values measured were used to estimate the darkening of the press cake compared to the ground jatropha seeds and also to estimate the lightening of the particleboard compared to the corresponding press cake. In addition, the color difference (ΔE*) between the ground jatropha seeds and press cake analyzed, or between the press cake and particleboard analyzed, was calculated using the following formula:

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (6)$$

where ΔL*, Δa* and Δb* are the differences between the ground jatropha seeds and the press cake, or between the press cake and the particleboard, in L*, a* and b*, respectively.

3 RESULTS AND DISCUSSION

3.1 Physicochemical Characterization of Press Cakes

The five press cakes used here (A to E) originated from a previous study on extraction of oil from ground jatropha seeds using a Clextral BC 21 twin-screw extruder [22]. They were more or less rich in lipids, thus their residual oil contents were 5.9, 7.7, 9.0, 13.3 and 19.1% of the dry matter, respectively (Table 1). This led to oil extraction yields (R_{L1}), based on the residual oil contents in the press cakes, of 89.6, 85.0, 82.2, 73.8 and 59.1%, respectively. After elimination of the "foot" (i.e., the solid particles forced through the filter) in the filtrates by centrifugation, oil extraction yields (R'_{L1}) relative to the total oil that the jatropha seeds contained were in fact 53.6, 70.6, 57.5, 46.3 and 29.6%, respectively. As mixtures of proteins (from 18.9 to 23.8% of the dry matter) and lignocellulosic fibers (from 43.2 to 51.3% of the dry matter) (Table 1), the press cakes could also be considered as natural composites. They also contained minerals and hemicelluloses: from 4.9 to 5.9% of the dry matter and from 5.4 to 16.7% of the dry matter, respectively (Table 1). Moreover, the hemicellulose contents were much greater in press cakes B and C that had been produced in the twin-screw extruder with optimized screw profile: 16.7 and 15.6% of the dry matter, respectively, against 5.4–6.8% of the dry matter for the three other press cakes. This screw profile consisted of a trituration zone composed of 10 monolobe and 10 bilobe paddles, and a pressing zone composed of 50 mm long, reverse pitch screws with a -33 mm pitch [22]. It contributed to minimizing the mass content of the foot in the filtrate: 32.3 and 42.4% for press cakes B and

Table 1 Chemical composition of press cakes A to E (% of the dry matter) and corresponding oil extraction yields in the Clextral BC 21 twin-screw extruder (%), color in the CIE L*a*b* referential, and apparent and tapped densities (g/cm³) of the press cakes.

Press cake	A	B	C	D	E
Chemical composition (% of the dry matter)					
Minerals [22]	5.7±0.1	5.9±0.0	5.6±0.0	5.5±0.0	4.9±0.0
Lipids [22]	5.9±0.0	7.7±0.0	9.0±0.1	13.3±0.0	19.1±0.0
Proteins [22]	21.3±0.0	23.8±0.1	21.9±0.0	21.1±0.2	18.9±0.4
Cellulose	47.2±0.1	40.8±0.3	41.9±0.3	43.1±0.5	41.0±0.7
Hemicelluloses	6.8±0.3	16.7±0.4	15.6±0.6	5.4±0.2	5.5±0.6
Lignins	4.1±0.3	3.8±0.2	3.0±0.1	2.2±0.1	2.2±0.2
Water-soluble components	16.3±0.6	16.6±0.3	16.1±0.6	13.4±0.3	13.3±0.2
Color in the CIE L*a*b* referential					
L*	69.4±0.2	68.8±0.2	67.6±0.0	67.7±0.1	66.9±0.0
a*	0.0±0.1	0.4±0.1	-0.1±0.0	-0.3±0.1	-0.6±0.0
b*	1.7±0.2	1.6±0.2	0.5±0.0	0.4±0.1	-0.4±0.0
ΔE*	4.9	5.5	7.0	7.0	8.2
Densities (g/cm³)					
Apparent density	0.580	0.545	0.553	0.575	0.551
Tapped density	0.685	0.618	0.615	0.675	0.650

ΔE is the color difference between the ground jatropha seeds and the press cake. – L*, a* and b* values of the ground jatropha seeds were 73.7±0.2, 0.2±0.0 and 4.0±0.1, respectively.*

C, respectively, instead of at least 54.5% for other press cakes. This could explain the higher hemicellulose contents in press cakes B and C. Finally, water-soluble components in the press cakes varied from 13.3 to 16.6% of the dry matter, and tended to decrease with the increase in residual oil content, i.e., only 13.3% of the dry matter for the least deoiled press cake (E) (Table 1).

Press cakes were all darker than ground jatropha seeds. Indeed, L* color values for press cakes were lower than those of the seeds: 69.4 maximum instead of 73.7 for the seeds (Table 1). Nevertheless, a better reduction in lipids led to a clarification of the press cake, as illustrated by the increase in L* color value: from 66.9 for press cake E to 69.4 for press cake A (Table 1). This resulted in a decrease in the color difference (ΔE*) between the ground jatropha seeds and the press cake (from 8.2 to 4.9), as its residual oil content decreased (from 19.1 to 5.9% of the dry matter). The five press cakes were composed of almost spherical particles, and particle size distribution of press cakes A to E was clearly correlated to their residual oil contents (Figure 1). Indeed, the mean diameter of particles in press cakes A to D, increased from 72 to 100 µm as their residual oil content increased from 5.9 to 13.3%, and it was 238 µm for the least deoiled press cake (E). Apparent densities of press cakes were roughly similar, and this was also the case for tapped densities: between 0.545 and 0.580 g/cm^3 and between 0.615 and 0.685 g/cm^3, respectively (Table 1).

Thermogravimetric analysis of press cakes showed that all TGA degradation curves under air were almost the same (Figure 2). Decomposition temperatures

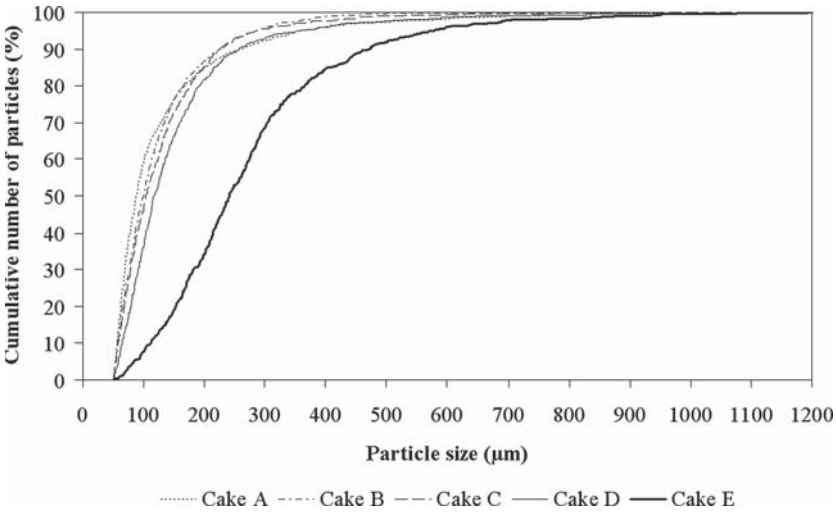

Figure 1 Particle size distribution in press cakes A to E.

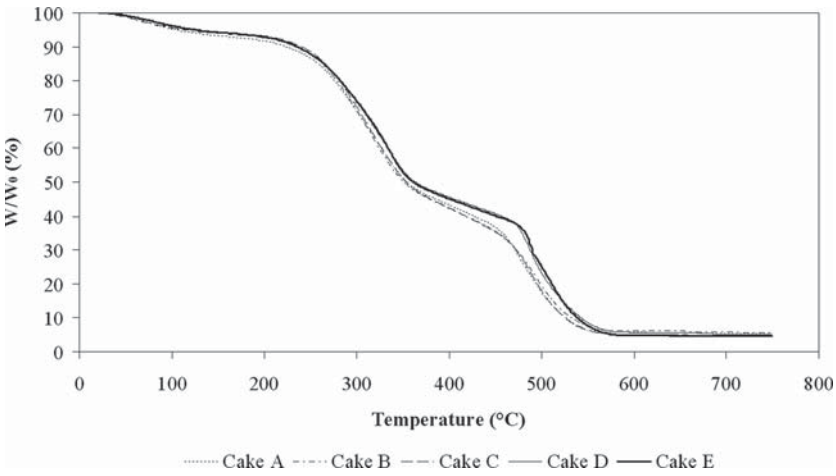

Figure 2 TGA degradation curves under air and at 5°C/min of press cakes A to E.

observed were always the same. An initial mass loss was observed at 100°C corresponding to water evaporation. Moisture content of equilibrated press cakes varied from 5.8 to 7.2%, and the mass loss observed in TGA curves corresponded to approximately the same mass percentage. The thermal degradation of organic compounds occurred in two stages. The first (between 250 and 350°C) led to a loss of more than 45% of the dry matter in the sample. A second degradation phenomenon was also observed between 450 and 550°C but was associated with a lower mass loss (around 30% of the dry matter in the sample).

Considering literature data for thermal degradation of fibers, hemicelluloses degrade first, around 270–330°C, then cellulose, around 320–380°C, and finally lignins, around 420°C [42–45]. Thermal degradation of vegetable proteins from an industrial sunflower cake has also been observed, above 250°C and below 350°C [46]. Moreover, the smoke point of jatropha oil associated with the onset of its thermal degradation is around 250°C, similar to many other vegetable oils (e.g., 232°C in the case of refined sunflower oil).

Consequently, it was reasonable to assume that the first thermal degradation stage (250–350°C) could be associated with the simultaneous degradation of lipids, proteins, and hemicelluloses. The second, situated at around 475°C, would then correspond to the thermal degradation of cellulose and then to that of lignins. At the end of the measurements, the undegraded sample represented between 4.6 and 5.7% of the test sample mass. The undegraded compounds logically corresponded to minerals, whose content in press cakes varied from 4.9 to 5.9% of the dry matter (Table 1). In conclusion, because no thermal degradation occurred before 225°C, this confirmed that the three thermo-pressing molding temperatures chosen (160, 180 and 200°C for each press cake) were appropriate. Indeed, there was no risk of thermal degradation of organic compounds inside press cakes during molding, especially proteins, resulting in the production of particleboards with their mechanical properties preserved.

Water sensitivity of press cakes was estimated by DVS analysis. For all samples, water uptake logically increased with an increase in relative humidity (Figure 3). But, some differences were observed in water uptakes between the five press cakes, and this could be explained by their different chemical compositions. Residual oil content was highest in press cake E, resulting in a lower water uptake along the relative humidity profile, and press cake E was thus the least water sensitive. Conversely, press cake A was the most sensitive to water because its residual oil content was the lowest, hence water uptakes at 60% RH of press cakes A and E were 7.8 and 6.3%, respectively. Similarly, at 90% RH, they were 17.0 and 12.8%, respectively.

The DSC analysis of press cakes was conducted on deoiled materials that were equilibrated in a climatic chamber before being tested. The DSC curves revealed a significant glass transition phenomenon for the five press cakes tested (Figure 4). It was attributed to the glass transition of proteins even if other minor materials inside press cakes like hemicelluloses could also reveal the same phenomenon [47–50]. Moreover, the corresponding glass transition temperature was

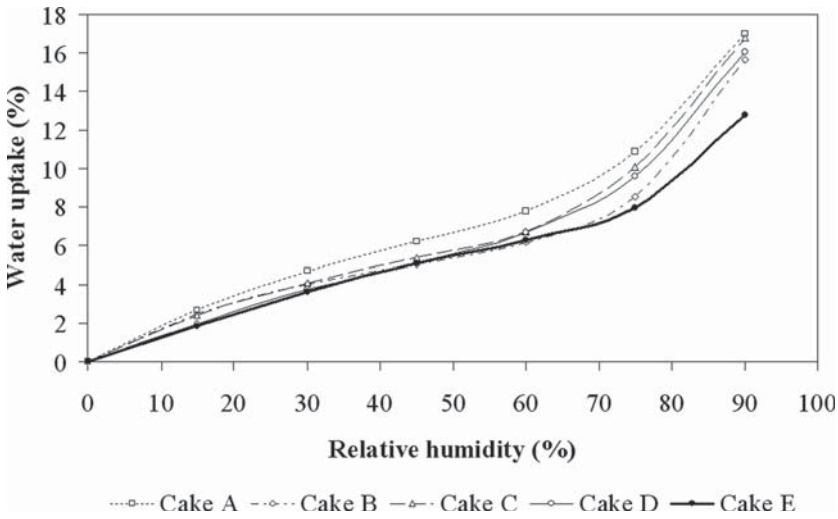

Figure 3 DVS curves for press cakes A to E.

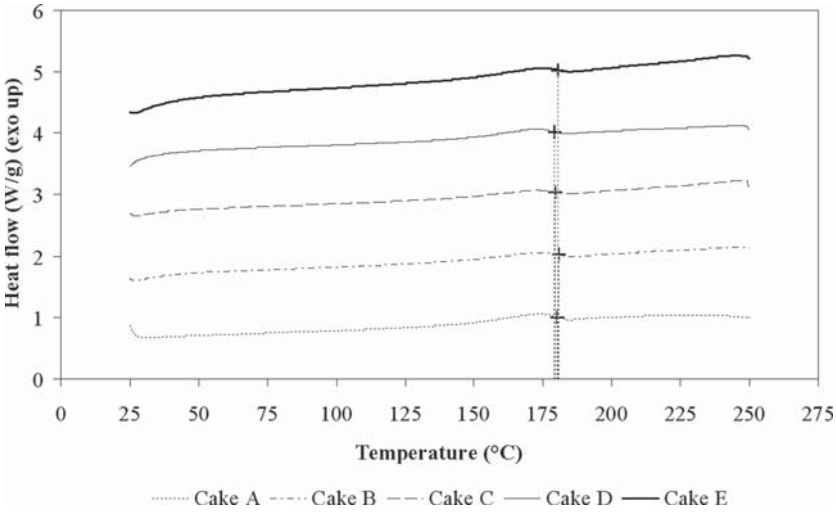

Figure 4 DSC curves in pressure-resistant capsules of deoiled press cakes A to E equilibrated in a climatic chamber (60% RH, 25°C) for three weeks.

Table 2 Glass transition temperatures of proteins in deoiled press cakes A to E equilibrated in a climatic chamber (60% RH, 25°C) for three weeks (°C).

Press cake	A	B	C	D	E
Onset	176.4 (181.8)	176.1 (180.9)	173.9 (179.7)	174.5 (181.0)	175.6 (182.0)
Midpoint	180.1 (186.3)	180.9 (186.4)	179.6 (185.4)	179.3 (185.9)	180.3 (186.2)

The numbers in parentheses correspond to the glass transition temperatures of proteins after drying of deoiled press cakes A to E in a ventilated oven (60°C, 12 h).

mainly independent of the starting material. Indeed, the onset temperature varied from 173.9 to 176.4°C, and the midpoint value was situated between 179.3 and 180.9°C (Table 2). When deoiled press cakes were dried in a ventilated oven (60°C, 12 h) before DSC analysis, a slight increase in the glass transition temperature of proteins was systematically observed (Table 2). This was characteristic of the plasticizing effect of water on jatropha proteins, and such a tendency has been previously observed for sunflower proteins [28, 31], wheat gluten [51, 52], corn zein [53] and soy proteins [54]. Indeed, proteins contain the main biopolymers (starch, pectins, hemicelluloses and other polysaccharides) polar functions (amides) capable of linking the water molecules by hydrogen interactions. The presence of water separates the proteins and facilitates their movement, thus improving their thermoplastic properties [50]. The thermal and rheological properties of proteins are therefore highly dependent on the amount of water, resulting in variations in their glass transition temperature according to their hydratation.

3.2 Influence of Molding Temperature and Press Cake Oil Content on Particleboard Mechanical Properties

Press cakes A to E were dried in a ventilated oven (60°C, 12 h) before thermo-pressing, and their moisture contents were between 1.0 and 1.4% at molding. For all experiments, press cake quantity, pressure applied and molding time were 145 g (i.e., 644 mg/cm^2), 297 kgf/cm^2 and 90 s, respectively. These values were similar to those used in previous studies [34, 35, 37, 38]. For each press cake, three molding temperatures were tested: 160, 180 and 200°C. The fifteen particleboards manufactured using these thermo-pressing conditions (Table 3) were all cohesive, proteins and fibers acting respectively as natural binder and reinforcing fillers. Nevertheless, particleboards molded at 160°C from press cakes A, D and E (i.e., A1, D1 and E1 boards, respectively) were not tested mechanically because they were too fragile. Indeed, cutting test specimens from these boards was not possible without breaking them.

Table 3 Thermo-pressing conditions and mechanical properties of the particleboards manufactured.

Particleboard	B1	C1	A2	B2	C2	D2	E2	A3	B3	C3	D3	E3
Thermo-pressing conditions												
Press cake	B	C	A	B	C	D	E	A	B	C	D	E
Temperature (°C)	160	160	180	180	180	180	180	200	200	200	200	200
Flexural properties												
H_{PB} (%) [a]	7.4±0.0	7.2±0.2	7.4±0.0	6.8±0.1	7.1±0.1	7.4±0.1	7.0±0.1	6.9±0.1	5.9±0.0	6.6±0.1	6.9±0.1	6.7±0.0
t (mm)	5.54±0.13	5.32±0.09	5.23±0.19	4.96±0.08	4.89±0.11	4.71±0.10	4.48±0.12	5.19±0.10	4.84±0.10	4.79±0.23	4.60±0.22	4.37±0.15
d	1.09±0.03	1.16±0.03	1.19±0.03	1.26±0.02	1.26±0.01	1.25±0.02	1.23±0.03	1.21±0.01	1.28±0.02	1.27±0.02	1.26±0.03	1.25±0.03
F (N)	1.6±0.2	3.6±0.4	4.1±0.6	16.0±3.0	15.2±3.2	8.2±1.5	6.0±1.2	36.9±4.2	33.6±3.1	32.0±4.0	29.9±3.7	28.5±3.6
σ_f (MPa)	0.25±0.02	0.63±0.06	0.74±0.12	3.25±0.61	3.18±0.68	1.84±0.34	1.50±0.30	6.85±0.78	7.18±0.66	6.97±0.87	7.08±0.87	7.47±0.94
E_f (MPa)	38±7	124±16	181±41	909±156	1003±203	609±123	602±110	1509±241	2153±265	2022±251	2100±362	2287±432
Charpy impact strength												
W (mJ)	13.6±2.2	11.1±3.7	21.8±5.8	31.4±3.8	34.6±5.1	26.8±7.3	24.7±6.7	42.4±5.7	41.1±4.4	41.4±5.4	37.9±4.8	37.6±6.1
K (kJ/m^2)	0.25±0.04	0.21±0.07	0.42±0.11	0.63±0.08	0.71±0.11	0.57±0.16	0.55±0.15	0.82±0.11	0.85±0.09	0.86±0.12	0.82±0.11	0.86±0.14
Surface hardness												
Shore D (°)	25.9±5.7	31.1±2.4	47.5±6.3	61.5±5.2	61.7±5.0	58.2±4.8	61.0±4.6	58.4±7.1	71.6±5.9	69.8±4.7	71.1±7.7	70.3±6.4

[a] *H_{PB} is the moisture content of the particleboard (%). Particleboards were equilibrated in a climatic chamber (60% RH, 25 °C) for three weeks before moisture measurements.*

For each press cake, thickness of particleboards decreased when molding temperature increased (Table 3). But, the decrease in board thickness was slight between 180 and 200°C molding temperature. Density of particleboards increased at the same time. It was never more than 1.16 at 160°C, and it was at least 1.19 at 180°C and at least 1.21 at 200°C (Table 3). Such an evolution could be correlated to the decrease observed for each press cake in the particleboard moisture content: 7.2–7.4% at 160°C, 6.8–7.4% at 180°C and 5.9–6.9% at 200°C. As an example, for press cake B, moisture contents in B1, B2 and B3 boards were 7.4, 6.8 and 5.9%, respectively. For the two highest molding temperatures, density of particleboards increased slightly when residual oil content in the press cake decreased (to 1.26 for the B2 board and 1.28 for the B3 board, respectively). It resulted in lower moisture contents inside B2 and B3 boards (6.8 and 5.9%, respectively). Such an increase in board density was probably due to higher protein contents in the press cakes poorest in lipids (from 18.9% of the dry matter in press cake E to 23.8% of the dry matter in press cake B) (Table 1), thus confirming the binding ability of proteins inside particleboards. Even if press cake A was the poorest in lipids (only 5.9% of the dry matter), it was an exception, and it generated boards with lower densities (1.19 and 1.21, respectively). This was not only due to a rather low protein content in press cake A (21.3% of the dry matter) compared with press cake B, but also to the excessive shear applied to the material in the twin-screw extruder for such operating conditions [22], leading to degradation of proteins in press cake A, that adversely affected their binding ability in A2 and A3 boards.

Taking into account moisture contents of press cakes at molding (1.0–1.4%), the corresponding protein glass transition temperature was around 180°C (Table 2). Consequently, glass transition did not occur at 160°C molding temperature, and thus thermo-pressing consisted essentially of material densification, with solid particles being squeezed together. Thus, proteins could not act as an effective binder inside boards A1 to E1, leading to materials with unsatisfactory mechanical properties: only 0.6 MPa flexural strength at break, 124 MPa elastic modulus, 0.21 kJ/m^2 resilience and 31.1° Shore D surface hardness for the C1 board (Table 3).

At 180°C molding temperature, shear, i.e., the pressure, applied at molding plus the increase in molding temperature, resulted in the protein glass transition. Consequently, proteins were in a rubbery state during molding, leading to the fiber wetting. Therefore, their binding effect inside boards A2 to E2 allowed them to be much more mechanically resistant than those made at 160°C (Table 3). Moreover, their mechanical properties were clearly correlated to their densities, an increase in board density leading to a more resistant particleboard. Indeed, the two densest boards, i.e., B2 and C2, were also the most resistant: 3.2–3.3 MPa flexural strength at break, 909–1003 MPa elastic modulus, 0.63–0.71 kJ/m^2 resilience and 61.5–61.7° Shore D surface hardness (Table 3). Conversely, the least dense board, A2, was also the most fragile.

At 200°C molding temperature, glass transition of proteins still occurred at molding. Nevertheless, the increase in molding temperature led to a less viscous protein-based resin, and this contributed undoubtedly to improve fiber wetting. Therefore, the binding effect of proteins was clearly improved inside boards A3 to E3, leading to the most resistant particleboards in this study (Table 3). For this molding temperature, resilience and Shore D surface hardness were still correlated to the board density: up to 0.85 kJ/m^2 and 71.6° for the densest board (B3), respectively. However, the Charpy impact strength increase was then quite limited (from 0.82 to 0.86 kJ/m^2). Concerning bending tests, the highest breaking load was obtained with press cake A (36.9 N). But, there was no positive effect on flexural strength at break (6.9 MPa) because board A3 was also the thickest one (5.2 mm); moreover, corresponding elastic modulus was low (only 1509 MPa). For press cakes B to E, breaking load increased linearly (from 28.5 to 33.6 N) with board density (from 1.25 to 1.28). But, since board thickness increased at the same time (from 4.4 to 4.8 mm), all flexural strength at break values were quite similar (between 7.0 and 7.5 MPa), and the same was true for elastic modulus (between 2022 and 2287 MPa).

In conclusion, the best compromise between flexural properties (7.2 MPa flexural strength at break and 2153 MPa elastic modulus), Charpy impact strength (0.85 kJ/m^2 resilience) and Shore D surface hardness (71.6°) was board B3 (Table 3). Board B3 was also the densest board (1.28). Its moisture content was the lowest one in this study (only 5.9%), indicating that both board density and its mechanical properties were sensible with moisture content. Board B3 was obtained at 200°C molding temperature from a press cake (B) with a low residual oil content (7.7% of the dry matter), and that was associated with the best R'_{L1} oil extraction yield (70.6%) [22]. Press cake B was also the richest in proteins (23.8% of the dry matter) (Table 1) and, as effective internal binders, these ensured really good material cohesion inside board B3.

3.3 Oil Expression Yields during Molding

For all particleboards, part of the residual oil in the press cake was expressed during molding through the sidewall vents of the mold, due to the pressure

applied. Such a phenomenon, i.e., oil expression at the same time as molding, had been previously observed starting from a cake produced after biorefinery of sunflower whole plant in a twin-screw extruder [37, 38]. This led to a decrease in residual oil content inside particleboards compared with that in the corresponding press cake (up to 2.8% of the dry matter in the case of board D3 instead of 13.3% in press cake D), and to an increase in total oil yields (up to 95.4% for R_{LT} in the case of board D3) (Table 4).

Apart from particleboards from press cake A, oil expression yield during molding increased with increasing molding temperature. This could be explained by a decrease in viscosity of jatropha oil at higher temperatures, thus it was easier for the oil to escape from the mold. As an example, for press cake B that corresponded to the highest R'_{L1} oil extraction yield in the twin-screw extruder (70.6%) [22], residual oil content decreased from 7.7% of the dry matter in the press cake to 6.2 and 5.3% of the dry matter in boards B1 and B2, respectively (Table 4). And, it was only 4.2% of the dry matter in board B3, the optimal for mechanical properties. Thus, oil expression yield during molding relative to the residual oil contained in the press cake (R_{L2}), logically increased with increasing molding temperature: 26.9, 36.8 and 50.0% for boards B1, B2 and B3, respectively. This also led to a slight increase in the R'_{LT} total oil yield: 74.7, 76.2 and 78.1% for boards B1, B2 and B3, respectively. Furthermore, R'_{LT} total oil yield was highest for board B3 (78.1%), meaning that the study's optimal board for mechanical properties was also associated with the best oil extraction efficiency. At the same time, contents of other constituents in particleboards, apart from lignins, logically increased with increasing molding temperature, due to oil loss during molding (Table 5). As an example, protein contents in boards B1, B2 and B3 were 24.5, 24.9 and 25.5% of the dry matter, respectively, instead of 23.8% of the dry matter in press cake B. Similarly, cellulose contents in boards B1, B2 and B3 were 42.8, 43.3 and 43.7% of the dry matter, respectively, instead of 40.8% of the dry matter in press cake B. Lastly, the moisture content of equilibrated particleboards from press cake B decreased with the increase in molding temperature and so with the increases in board density and mechanical properties. Indeed, it was 7.4%

Table 4 Quantification of the oil expressed during molding of the particleboards.

Particleboard	B1	C1	A2	B2	C2	D2	E2	A3	B3	C3	D3	E3
m_{PB} (g)	142.4	144.7	145.2	142.9	140.6	135.5	126.4	145.6	140.3	137.8	130.7	124.0
L_{PB} (% dry matter)	6.2±0.0	7.2±0.0	3.7±0.1	5.3±0.0	5.3±0.3	5.1±0.2	3.4±0.2	4.0±0.1	4.2±0.0	3.8±0.0	2.8±0.2	3.4±0.1
R_{L2} (%)	26.9±0.5	24.8±0.4	40.2±1.4	36.8±0.3	45.9±1.5	66.2±1.0	85.2±1.0	36.0±0.9	50.0±0.2	61.5±0.0	82.4±1.3	85.7±0.6
R'_{L2} (%)	4.0	4.4	4.2	5.5	8.2	17.3	34.8	3.8	7.5	10.9	21.6	35.1
R_{LT} (%)	89.1	86.6	93.8	90.5	90.4	91.2	94.0	93.3	92.5	93.1	95.4	94.2
R'_{LT} (%)	74.7	61.9	57.8	76.2	65.6	63.6	64.5	57.3	78.1	68.4	67.8	64.7

Table 5 Chemical composition of particleboards from press cake B (% of the dry matter).

Particleboard	B1	B2	B3
Minerals	6.0±0.0	6.1±0.0	6.3±0.1
Lipids	6.2±0.0	5.3±0.0	4.2±0.0
Proteins	24.5±0.1	24.9±0.2	25.5±0.1
Cellulose	42.8±0.1	43.3±0.1	43.7±0.2
Hemicelluloses	14.7±0.0	18.4±0.2	21.3±0.1
Lignins	3.0±0.0	2.9±0.0	0.2±0.0
Water-soluble components	15.6±0.0	16.0±0.1	17.2±0.0

Table 6 Color of the particleboards in the CIE L*a*b* referential, and color differences between the press cake (A to E) and the particleboards produced from them.

Particleboard	B1	C1	A2	B2	C2	D2	E2	A3	B3	C3	D3	E3
L*	68.9±0.0	68.7±0.2	71.4±0.2	68.8±0.2	68.4±0.0	70.9±0.0	71.4±0.1	72.6±0.2	70.1±0.1	71.0±0.2	69.9±0.2	70.9±0.1
a*	0.4±0.0	0.8±0.1	0.6±0.1	1.1±0.1	0.5±0.0	0.4±0.0	0.6±0.0	0.8±0.1	1.3±0.0	1.3±0.1	0.1±0.1	0.3±0.0
b*	1.6±0.0	s1.5±0.2	3.4±0.1	1.5±0.1	1.2±0.0	3.0±0.0	3.5±0.1	4.4±0.2	2.5±0.1	3.4±0.1	2.1±0.2	3.0±0.1
ΔE*	0.1	1.7	2.6	0.7	1.2	4.2	6.1	4.2	1.9	4.6	2.8	5.4

for board B1, 6.8% for board B2 and only 5.9% for board B3 (Table 3), and the same tendency was also observed with particleboards from the four other press cakes (Table 3). This was due to the increase in particleboard density with increasing molding temperature (Table 3). Indeed, during climatic chamber conditioning of particleboards, water uptake was less for denser boards, due to their lower surface porosity.

Oil expression during molding also led to the lightening of particleboards compared to the corresponding press cake, as illustrated by the increase in the L* color value for all boards tested (Table 6). And, as previously observed for the lipid levels, lightening of particleboards was usually more pronounced at higher molding temperatures. As an example, in the case of press cake B, the L* color value was 70.1 for board B3 instead of only 68.8–68.9 for boards B1 and B2. This usually resulted in an increase in the color difference (ΔE*) between the press cake and the particleboard with increasing molding temperature. Thus, in the case of press cake B, ΔE* was only 0.1 for board B1, and it reached 0.7 and especially 1.9 for boards B2 and B3, respectively (Table 6).

Even if the pressure applied during molding led to partial oil expression, particleboards still contained residual oil. As an example, for the 200°C molding temperature that led to the most mechanically resistant panels (Table 3) and to the best oil expression yields during molding (Table 4), residual oil content inside particleboards was between 2.8 and 4.2% of the dry matter. Thus, in spite of their global hydrophilic character, it is reasonable to assume that residual oil in particleboards will contribute slightly to making 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 driven through the vents of the mold during thermo-pressing, and this could then be supplemented by a refining step. Two applications could be 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) [6].

4 CONCLUSION

New renewable and biodegradable particleboards were manufactured by thermo-pressing from press cakes produced after extraction of oil from jatropha seeds using a twin-screw extruder. Particleboards were all cohesive, proteins and lignocellulosic fibers acting respectively as binder and reinforcing fillers. The molding temperature was the factor that most affected mechanical properties (flexural properties, Charpy impact strength and Shore D surface hardness) of particleboards obtained. A 200°C molding temperature was required to give glass transition of proteins during molding and especially to an effective wetting of the fibers inside the boards. The best compromise between flexural properties (7.2 MPa flexural strength at break and 2153 MPa elastic modulus), Charpy impact strength (0.85 kJ/m^2) and Shore D surface hardness (71.6°) was a board molded at 200°C from a press cake with low residual oil content (7.7%). With these mechanical properties, such a particleboard would be usable as an interlayer sheet for pallets, for the manufacture of containers or furniture, or in the building trade (floor underlayers, interior partitions or ceiling tiles). Moreover, thermo-pressing was not only a molding operation to manufacture new renewable and biodegradable particleboards. It also increased the oil extraction efficiency (from 70.6% after extrusion to a maximum of 78.1% after thermo-pressing in the case of the board with optimal mechanical properties).

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