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Solute and gas assisted mechanical expression for green oil recovery from rapeseed hulls

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ABSTRACT

This work aims at evaluating the alternative technologies of solvent (liquid) and gas assisted mechanical expression to recover oil from rapeseed hulls and comparing these technologies with conventional solute extraction (SE). First, SE and solute assisted mechanical expression (SAME) have been applied using hexane and green solvents (water, ethanol, water/ethanol mixture) to extract efficiently oil and other bioactive compounds (polyphenols, and proteins). In order to avoid the use of organic solvents, oil extraction yield was compared to that of gas assisted mechanical expression (GAME) technology after optimizing the extraction parameters (effective pressure, CO_2 flow, and the impact of pre-treatments (grinding and/or cooking)). Results show that the highest extraction yield (65%) with GAME was obtained using 35 MPa effective pressure, 8.5 kg/h CO_2 flow, and without pre-treatment. Although similar extraction yields have been recorded between the three extraction processes, the use of GAME technology allowed the recovery of oil without subsequent purification steps (removing the extraction solvent, meal desolvation), and without pre-treatment.

1. Introduction

Rapeseed (cultivated in France) and canola (cultivated in Canada) constitute two of the most important oilseed crops worldwide. Their seeds contain about 40–45% oil, 13% crude fiber and 30–35% proteins. After oil extraction, the resulting meal contains high amount of proteins (38–43%) with excellent nutritional quality (Tzeng et al., 1988). However, the presence of anti-nutritional compounds (e.g. glucosinolates, phytates and phenolic compounds) constitutes a bottleneck for using rapeseed and rapeseed meals as protein sources in food products. This limitation led agronomists to develop new varieties with lower glucosinolates content like 00 rapeseed variety commercialized since 1989. Moreover, food technologists proposed different pre-treatments of rapeseeds before oil extraction, improving thus the meal quality for food and feed purposes. Among the tested pretreatments, dehulling, heating, and enzymatic digestion were the most effective (Mulder et al., 2012). According to Carré et al. (2016), French rapeseeds contain about 18,2% ± 1,3 hulls (w/w). Dehulling, which involves the removal of the fibrous seed envelopes, is rarely practiced in rapeseed due to several technical issues, including small seed size and the close gap between cotyledon and hulls. Nevertheless, several dehulling techniques were described in the literature for rapeseed and canola seeds. They include CETIOM dehuller developed in the 1970s, abrasive dehullers, roll dehullers, infrared and microwaves equipment, and tail-end hull separators (Mulder et al., 2012). Despite the improve of oil and meal quality, seed dehulling leads to the loss of the oil remaining in the hulls, which can decrease the economical profitability of the process (Carré et al., 2015; Ikebudu et al., 2000). Consequently, it has been suggested to recover the oil remaining in hulls in order to make this pretreatment economically beneficial (Carré et al., 2015). To the best of our knowledge, the methods of oil recovering from rapeseed hulls were insufficiently studied. They should be therefore better explored.

Sequential process of mechanical expression and hexane extraction is conventionally used for oil recovery from rapeseeds. Mechanical expression is generally considered as the most efficient technique to recover virgin oil from seeds with high oil content (>20%) (Carr, 1995). The resulting press cake is usually defatted meaning hexane extraction, by dissolving the remaining oil and generating a low oil-content meal. Nowadays, hexane is the most widely used solvent at industrial scale, and approved for this

Abbreviations: SE, solute expression; SAME, solute assisted mechanical expression; GAME, gas assisted mechanical expression; sc-CO_2, supercritical carbon dioxide.

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kind of application. However, due to the health and environmental related issues associated with its use, some other alternative (green) organic solvents have been proposed in the literature (e.g. isopropanol, ethanol) (Johnson and Lusas, 1983), the application of enzyme-based aqueous extraction (Rosenthal et al., 1996), and the use of supercritical fluid (sc-CO_2) extraction (Temelli, 2009). Rapeseed oil extraction using sc-CO_2 technology has been reported as promising alternative method for hexane extraction replacement (Cvjetko et al., 2012; Dunford and Temelli, 1996; Moquin et al., 2006; Pederssetti et al., 2011; Przybylski et al., 1998; Uquiche et al., 2012). The interest to this technique is mainly related to the low operational temperature, cheapness and the renewable character of CO_2 (Kazmi, 2012). Despite these advantages, the application of sc-CO_2 for oil extraction is limited due to the high CO_2 consumption and the long extraction duration. Recently it was proposed to combine supercritical fluid extraction with mechanical expression (Willems and de Haan, 2011). This technology called gas assisted mechanical expression (GAME) has been successfully applied to recover oil from oilseed crops (Müller and Eggers, 2014; Pietsch and Eggers, 2011; Rombaut et al., 2014; Venter, 2006; Venter et al., 2006; Willems and de Haan, 2011; Willems et al., 2008), showing higher yields, shorter extraction time, and less consumed CO_2. In GAME technology, injected CO_2 in the pressing chamber is dissolved into the seed oils, which leads to the increase of oil extraction yield (Willems et al., 2008), whereas by using sc-CO_2 without pressing, oil is dissolved in CO_2. Similarly, solute assisted mechanical expression (SAME) consists of soaking (impregnation) the raw material with a liquid solvent to improve its softness and improve the expression yield. This process was successfully applied for sugar beet juice recovery (Almohammed et al., 2015). The use of this technology for oil seed recovery has not been reported in the literature.

Recovering oil from rapeseed hulls could be performed by hexane extraction, and other solvents (e.g. mixture of benzene and chloroform (Liu et al., 1996)). However, it has been demonstrated that the heat energy required to remove hexane from hulls is higher than that used for dehulled oilseed meal (Yuan, 2014). Consequently, the aim of this work is to evaluate the use of alternative methods for oil recovery from rapeseed hulls using GAME and SAME technologies. The potential of these alternative technologies was compared to that of conventional extraction by solute extraction (SE).

2. Materials and methods

2.1. Chemicals

Hexane, methanol, ethanol (96%), Folin-Ciocalteu reagent and sodium bicarbonate ($NaHCO_3$) were obtained from Fisher Scientific (Illkirch, France). Tween was purchased from Sigma-Aldrich (France).

2.2. Plant materials

Rapeseed hulls were provided by the Technical center for oilseeds "CETIOM" (Pessac, France) after dehulling of rapeseeds. According to the supplier, rapeseeds being dehulled contain an average of 18.2% ± 1.3% hulls (w/w). Oil content in rapeseed hulls was determined using hexane for 24 h according to Soxhlet's method, and was estimated to 15.7% dry matter basis. Moisture content in rapeseed hulls was determined using an infrared desiccator (Scaltec) and was estimated to 14.7 ± 0.3%.

2.3. Experimental set-up and extraction processes

Rapeseed hulls were subjected to *i*) solute extraction (SE), *ii*) solute assisted mechanical expression (SAME), and *iii*) gas assisted mechanical expression (GAME) (Fig. 1).

2.3.1. Pre-treatments of rapeseed hulls

Rapeseed hulls were pre-treated (grinding and/or cooking) before extraction. Grinding was performed using a coffee grinder giving an average particle size of 450 μm, determined using a "Malvern Mastersizer 2000" granulometer. Cooking was performed using a laboratory oven at a temperature range of 80–130 °C, during 30 min.

2.3.2. Solute extraction (SE)

Untreated or pre-treated (cooked, grinded) hulls were mixed with different solvents in a glass beaker. All experiments were conducted at 200 rpm during 30 min using a mechanical stirrer (VELP Scientifica, Italy) (Fig. 1). The impact of pre-treatments (cooking, grinding), type of solvent (hexane, water, ethanol, and ethanol/water mixture), extraction temperature (20, 35, and 50 °C), and liquid/solid ratio (3/1, 5/1, 10/1) on the extraction yield were studied. For each experiment, oil, proteins, and polyphenols were quantified.

2.3.3. Solute assisted mechanical expression (SAME)

Mechanical expression was performed using a hydraulic press (Creusot-Loire, France). Preliminary experiments showed that no oil was expressed by pressing rapeseed hulls for 4 h at 10 MPa. In order to soften the tissue texture, it was decided to impregnate hulls with solvents before pressing. For this purpose, 100 g solvent (hexane, ethanol, water, and ethanol/water (v/v)) was mixed with 100 g hulls (1:1). The resulting mixture (200 g) was pressed (Fig. 1) for 1 h at either 20 °C or 50 °C and 10 MPa using the hydraulic press described above. Emulsion of solvent and oil was recovered for each experiment. A centrifugation step for 10 min at 6000 rpm was performed when required in order to separate the organic and the aqueous phases.

2.3.4. Gas assisted mechanical expression (GAME)

GAME process was performed using a pilot scale equipment (insert in Fig. 1) (SEPAREX, France) as described by Koubaa et al. (2015a,b). In brief, 150 g of rapeseed hulls were introduced into the extractor, pre-heated at 50 °C. The CO_2 pressure was maintained in the extractor at 10 MPa, and in the separators at 6 MPa, meaning a backpressure regulator. The CO_2 recirculation valve allowed the recycling of CO_2 in the system. The CO_2 flow was maintained first at 8.5 kg/h and rapeseed hulls were pressed by piston at different pressures (20, 25, 30, 35, and 40 MPa). After mechanical pressure optimization, based on the final extraction yield of oil, the CO_2 flow was changed to 5 kg/h then to 12 kg/h. The optimal extraction conditions were then tested using pre-treated materials as described above. The extracted oil was collected during the different experiments from two separators, maintained at 30 °C.

2.4. Quantification of rapeseed hull components

2.4.1. Quantification of lipids

Oil content in rapeseed hulls was determined using Soxhlet's method as previously reported (Norme AFNOR (NF EN ISO 659), 1998), with slight modifications. Briefly, 5 g of grinded hulls were washed with 250 ml hexane for 8 h. After extraction, hexane was removed using a rotary evaporator system in a vacuum at 60 °C until constant weight. Oil content was determined by measuring