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PRESSURE SHOCKWAVES TO ENHANCE OIL EXTRACTION FROM *JATROPHA CURCAS* L.

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ABSTRACT

Kinetic data regarding the intensity of maceration and subsequent pretreatment with pressure shockwaves (50 MPa to 60 MPa) are described in detail and evaluated statistically. Mass balances as well as the study on liquid environment are reported, allowing further process optimization according to financial aspects. It was verified on a laboratory scale by Soxhlet apparatus that oil extraction over 94 % may be reached. Achieving such a high level of disintegration opens wide options for application of hydrolysis in order to break apart the remaining lignocellulose cell walls and access the last oil remaining in the vacuoles.

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Keywords: oil, extraction, maceration, pressure shockwaves

Introduction

Extraction technology significantly affects the final price of vegetable oil, and furthermore biodiesel (18). The most common extraction technology is the use of mechanical presses or different molding machines (7, 12, 15). According to the review by Achten et al. (1), the oil yields of mechanical extraction methods are in the range of 62.5 % to 80 %. Higher results may be obtained by the second direction represented by the use of solvents, often in combination with other chemicals, high energy inputs and water demands (4, 17, 18, 19, 25, 27, 28). The last widely used method represents the use of hydrolytic enzymes (mostly cellulases) which enhance the oil extraction by disruption of the lignocellulose cell walls (22). However, such methods are extremely slow and require huge reactors. Therefore, other costly methods including addition of other chemicals or increased energy inputs are applied to increase the rate the hydrolysis (23).

Based on work by Higa et al. (9), the hypothesis considered was that the pressure shockwaves may also enhance the yields of extracted oil. Other papers (2, 5, 10, 11, 14, 16, 21) reinforced this assumption.

Materials and Methods

Substrate properties

Jatropha School – Kasetsart University, Kamphaeng Sean Campus (Nakhon Pathom, Thailand) donated the *Jatropha curcas* L. seeds. After the harvest in 2010, the seeds were dried and stored in an opened perforated plastic bag in a dry, shady place (weight per 1000 seeds: 622.3 g; bulk laid: 355 $g \cdot L^{-1}$; dry weight: 92.3 %, 21.193 $MJ \cdot kg^{-1}$). The husks represented 44.3 % of the dry weight (15.207 $MJ \cdot kg^{-1}$), while the kernels with vacuoles rich in oil represented the main proportion of the heating value (25.954 $MJ \cdot kg^{-1}$).

Fresh manure ($pH_{20°C}$ = 6.83, 1.26 $kg \cdot L^{-1}$, 24.5 % TS) from stabled cows on a grass and hay diet was used as inoculate for mineralisation kinetics analysis of the press cake.

Chemicals

Ethanol (99.7 %) was used as the macerating reactant, and 99.7 % hexane and 99.7 % *2*-propanol were used as solvents in the control analysis with the Soxhlet extractor (Wako Pure Chemicals, Ltd., Japan). Helium and liquid nitrogen for surface area analysis were prepared with helium liquefier L-140 and liquid nitrogen generator LINIT-25 (Linde Group, München, Germany).

Apparatus

The circuit of a high voltage generator prototype (9) releasing 3.5 kV discharges was linked to a lockable strengthened metallic vessel with an inner spherical volume of 2 L, which was filled with distilled water (**Fig. 1**). The high voltage discharge released (**Fig. 2**) 50 MPa to 60 MPa pressure shockwaves (4.9 kJ, 1500 $m \cdot s^{-1}$).

Heat value of the press cake

Electronic weighing scales (AUX 320, Shimadzu) and a constant temperature oven (FSS-S, Hirasawa) were used for TS determination according to the method developed by the USEPA (29). The dried seeds were subjected by 30 g to 10 s of grinding in a Labo Milser crusher (IFM-800, Osaka Chemical). The obtained fragments of approximately 3 mm and all of the finest particles were carefully swept into I-BOY 200 mL plastic bottles (AS-ONE Ltd., Japan) and screwed

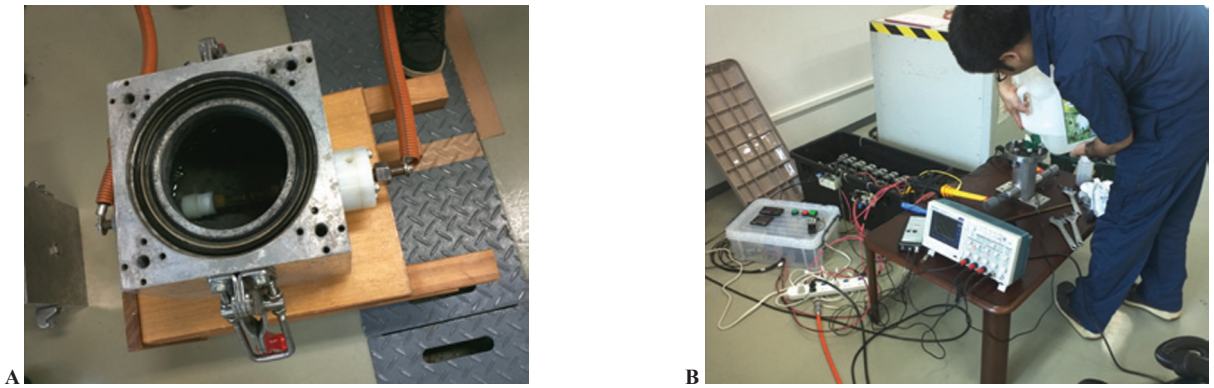

Fig. 1. Pressure chamber. View from above (**A**) – the chamber generating the pressure shockwaves (50 MPa to 60 MPa) by discharges of high voltage (3.5 kV). Setting the electrical equipment associated to the pressure chamber (**B**).

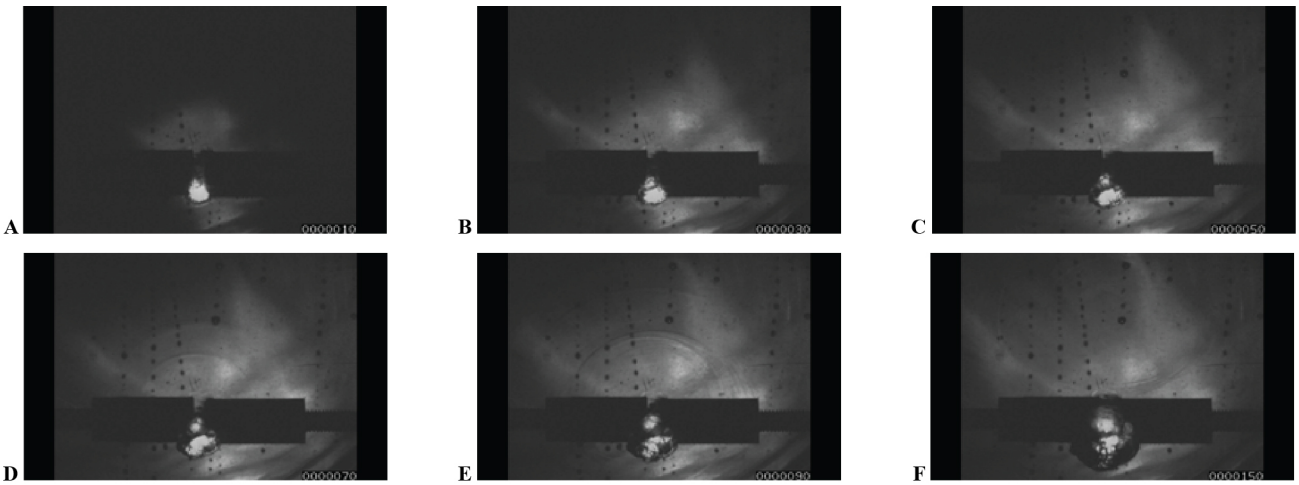

Fig. 2. Evolution of the high voltage discharge generating pressure shockwave: 10 microseconds (**A**), 30 µs (**B**), 50 µs (**C**), 70 µs (**D**), 90 µs (**E**), and 150 µs (**F**).

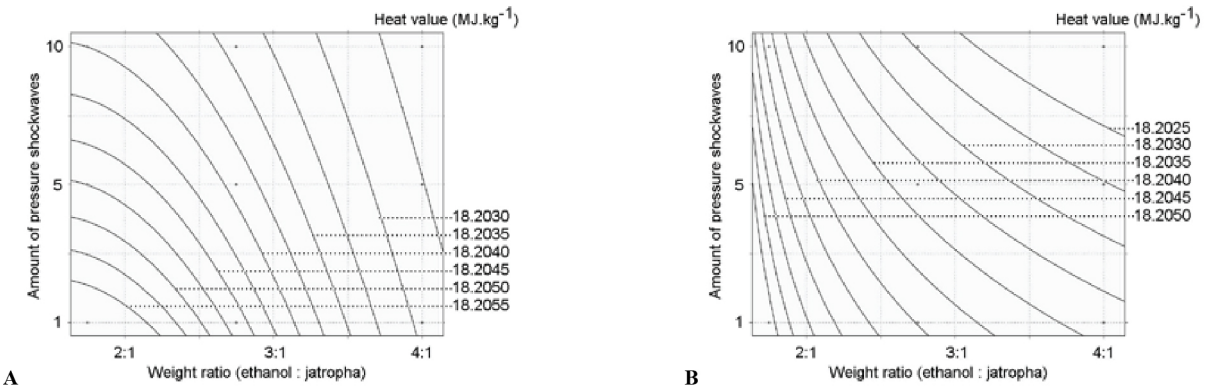

Fig. 3. Plotted dynamics of loss on the heat value in relation to the amount of ethanol and number of pressure shockwaves after less intensive maceration (**A**). Manifestation of loss on the heat value (as in **A**), with the only difference that the maceration was more intensive (**B**).

shut to avoid any contact with oil-absorbing material (such as paper) and to minimise microbial degradation. For 10 days, the samples were macerated (1:3, 1:4, 1:5 by weight in ethanol) and gently shaken in 55 °C water bath (BZ-100, Yamato) with a CU-120 temperature control unit (Sibata, Japan) or macerated in ethanol for 2 h at 20 °C. Underwater discharges (1, 3, 5 and 10; 3.5 kV) were performed on macerated and bottled dry material. After the underwater discharges were applied, the samples were kept under the same conditions for another 3 days and subsequently dried to TS in a constant-temperature oven at 65 °C. Molding was performed by a computer-controlled molding machine (D02, Marutani) with a 19.6 cm^2 free piston, while the performance was set at 1400 kg (7.143 MPa) because at this pressure, the amount of oil pressed out decreased sharply. An auto-calculating bomb calorimeter CA-4AJ equipped with a calorimetric calculator (P-202,

Shimadzu) was used for heating value ($MJ \cdot kg^{-1}$) analysis. The data obtained were plotted by online curve and surface fitting software (Zunzun.com, New Jersey, USA); the lowest sum of squared absolute error reached and lowest root mean squared error were the main fitting criteria.

Oil yield

The oil residue in the press cake was determined by a 24-hour Soxhlet extraction (Sibata, Japan) at 65 °C, with 50 mL of hexane and 50 mL of *2*-propanol used per extraction.

Mineralisation kinetics

Grade 2 (8 μm) filter paper (Advantech, Japan) and a 55 mm Büchner funnel (Sibata, Japan) were used for the cold-water (20 °C) filtration of fresh cow manure (200 mL of filtrate from 50 g in fresh weight). Thirty-gram press cake residues (obtained according to a previously described procedure, except that water was used instead of ethanol) were subjected to 5 s of grinding in a Labo Milser IFM-800 crusher to loosen the pellet from the molding machine and were then subjected to 15 days of monitored anaerobic digestion (20:1 substrate to inoculum by TS) in FV801 sealed (Hakko, Japan) in 1000 mL plastic bags with sealed plastic outlets, creating inverted measuring cylinders (submerged in diluted H_2SO_4, pH = 2) that allowed measurement of the quantity of biogas. The quality of the biogas was evaluated by a 350-XL gas measuring system (Testo, Yokohama, Japan), and only methane and carbon dioxide were taken into account after conversion to 0 °C and 101 325 Pa.

Surface area

The single point surface area at $P/P_0 = 0.2$, BET surface area, Langmuir surface area, micropore area, and external surface area were detected using the technique of helium gas adsorption using a TriStar3000 surface area analyser (Micromeritics Ltd., Tokyo, Japan) after 24 hours of degassing at 200 °C and 1 hour of degassing at 300 °C.

Visual observations

To prevent charging up of the surface, samples were coated with approximately 10 nm of white gold (Au + Pb) with the vacuum evaporation method using a JFC-1600 sputtering device (JEOL, Japan). A JSM-6510 LA analytical scanning electron microscope (JEOL, Japan) was used to observe the inner structures of the phytomass from the upper electron detector (SEI) at an acceleration voltage of 10 kV.

Results and Discussion

Comparison of the yields was not carried out by the volumes of oil extracted because such a method may be highly inaccurate due to the varying quality of oil (seed residues, lumps of protein, water, etc.) as well as practical difficulties in detecting low volumes. For these reasons, the loss on the heating value ($MJ \cdot kg^{-1}$) of the seedcake was chosen as the main comparative criteria. Stand-alone grinding (18.550 $MJ \cdot kg^{-1} \pm 0.04$ $MJ \cdot kg^{-1}$, $n = 6$, $\alpha = 0.05$) or maceration (18.537 $MJ \cdot kg^{-1} \pm 0.025$ $MJ \cdot kg^{-1}$, $n = 6$, $\alpha = 0.05$) followed by 5 pressure shockwaves did not provide satisfactory results in comparison to samples without

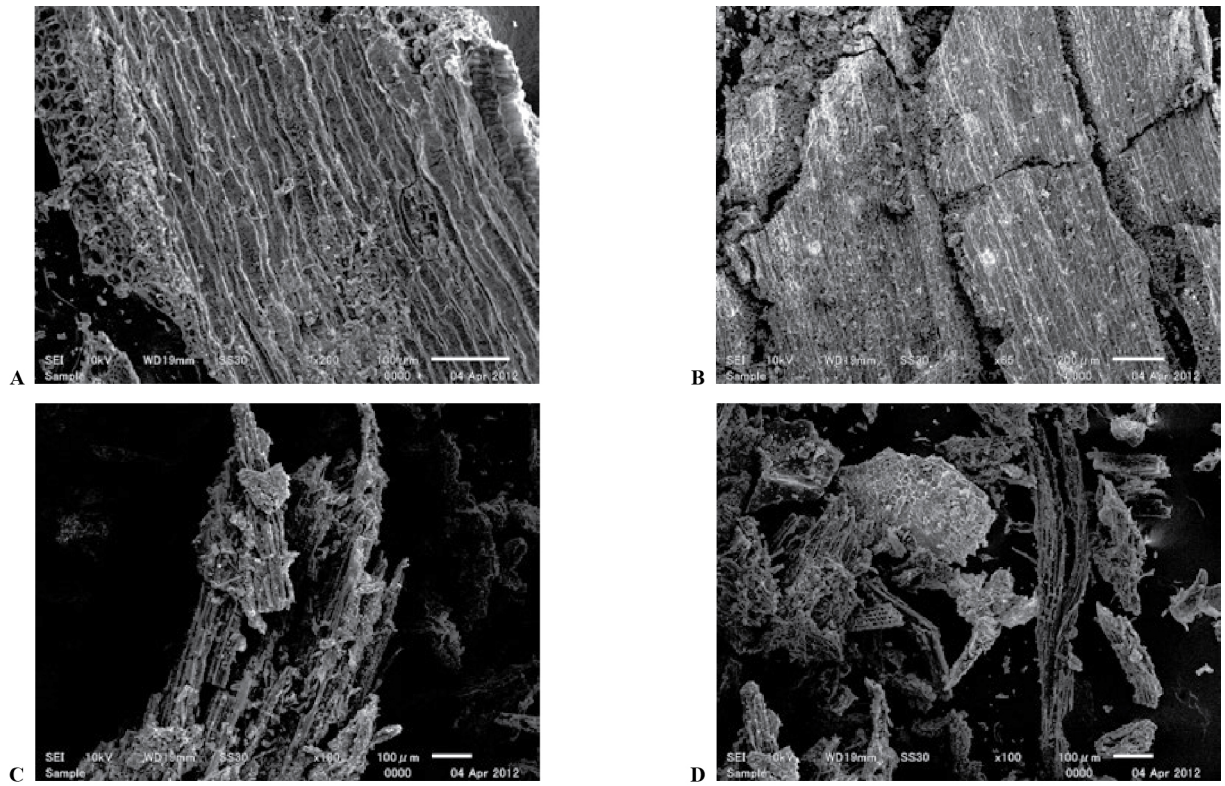

Fig. 4. Solid cell walls (**A**, **B**) formed by lignocellulose constitute a major obstacle for mechanical expellers. The pressure shockwaves may splinter the cell walls (**C**, **D**) if the phytomass is appropriately pretreated.

any kind of pretreatment (18.553 MJ·kg^{-1} ± 0.044 MJ·kg^{-1}, n = 6, α = 0.05) followed by 5 pressure shockwaves. Based on these findings it was decided that it will be beneficial to combine both procedures. Preferably, in the order of grinding followed by maceration, so the liquid medium may better soak into the phytomass which was previously grinded. Based on experimental work conducted by Campbell and Pitcher (3), who observed that the amount of liquid is in a strong relation with the speed of the pressure shockwave, it was decided that the amount of the liquid must be observed in detail. Methanol (17, 18) or *n*-hexane (extraction efficiency 98% [30]) are most frequently used solvents; however, there are concerns about the environmental impacts (1). Safe ethanol is generally a weak solvent, but its application accelerated by microwaves (8), reverse osmosis or ultrafiltration (6, 13) is well known. The use of commercial-grade ethanol is compatible with enzyme-based process (20, 24). According to the methods described above, the loss on heat value (MJ·kg^{-1}) to the amounts of pressure shockwaves and the weight ratio of ethanol to jatropha were studied. The robust amounts of data obtained were plotted as a polynomial function in two different conditions of maceration. Maceration for 2 h in 99.7 % ethanol at 20 °C (the less intensive pretreatment) is shown in **Fig. 3A** (approximated by polynomial function, sum of squared absolute error = 0.021, root mean squared error = 0.005). In comparison to more intensive maceration which took 10 days in 99.7 % ethanol at 55 °C, which is presented in **Fig. 3B** (approximated by polynomial function, sum of squared absolute error = 0.013, root mean squared error = 0.007). Based on both graphs, it can be assumed that more severe maceration conditions as well as higher volumes of liquid allow steeper manifestation of the pressure shockwaves. No definitive conclusion can be made regarding the optimal process conditions; however, it can be assumed that increasing the intensity of maceration may allow to reduce the number of the pressure shockwaves. Conditions, with maximal loss on the heat value (MJ·kg^{-1}) were subjected to detailed analysis by Soxhlet. A high yield of 94 % ± 0.7 % (n = 6, α = 0.05) was confirmed by repeated extraction. Achten et al. (1) review that mechanical procedures achieve oil yields between 62.5 % and 80 %. However, additional cooking may boost the yields of oil to 89 % after the first and 91 % after the second pass through the expeller. Other authors (7, 12, 15) discuss similar values. Winkler et al. (30) reported a yield of 38 % when there are no chemicals used. However, yields of 86 % may be achieved with hydrolysing enzymes (alkaline protease). The yield of 94 % achieved after intensive maceration and 10 pressure shockwaves in abundance of ethanol is above the average values found in the literature. Although, Achten et al. (1) has demonstrated that with solvents like *n*-hexane yields of 95 % or even 99 % may be achieved, application of such solvents is economically wasteful and environmentally undesirable.

The scans from the electron microscope showed that the cell walls of *Jatropha Curcas* L. are formed of a solid composite of lignocellulose (**Fig. 4A, B**) and grinding does not help to break the rigid structures. However, treatment with the pressure shockwaves preceded by maceration allows the cell walls to be broken down (**Fig. 4C, D**).

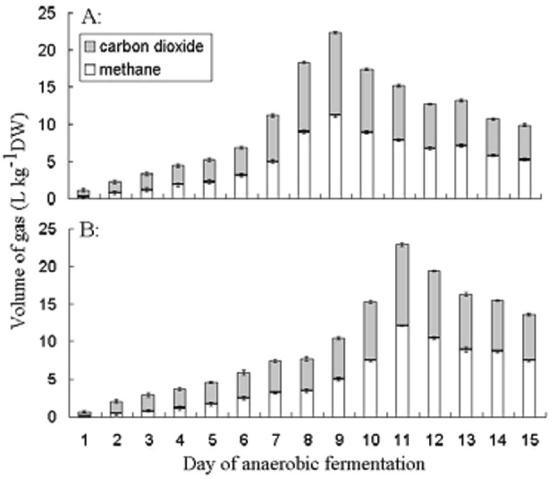

Fig. 5. Speed of biogas production simplified to methane and carbon dioxide converted to 0 °C and 101 325 Pa; bars indicate the standard deviations (n = 6, α = 0.05). The intensively water-macerated substrate subjected to 10 pressure shockwaves (**A**). Cumulative biogas production of the reference sample without pretreatment with pressure shockwaves (**B**).

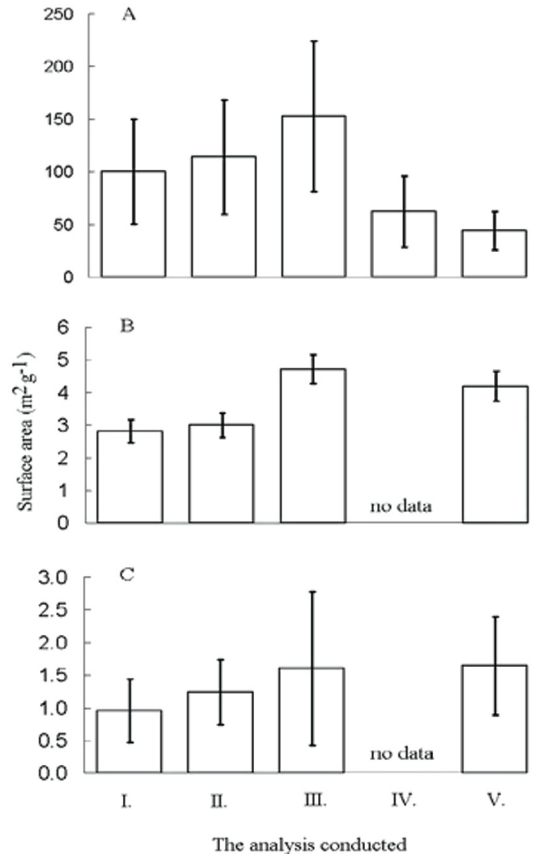

Fig. 6. Surface area of the presscakes by the gas adsorption technique, the bars indicates standard deviations (n = 6, α = 0.05). Intensive maceration in ethanol and 10 shockwaves (**A**); water maceration and 10 shockwaves (**B**); reference sample, not pretreated (**C**). I.: Single Point Surface Area at P/Po 0.2 (m^2·g^{-1}); II.: BET Surface Area (m^2·g^{-1}); III.: Langmuir Surface Area (m^2·g^{-1}); IV.: Micropore Area (m^2·g^{-1}); V.: External Surface Area (m^2·g^{-1}).

The speed of biogas production (simplified to methane and carbon dioxide), understood also as the mineralization kinetics, may serve as another assessment of the cell walls disintegration level. The data (**Fig. 5**) showed that the yields of methane were nearly equal (157.1 $L \cdot kg^{-1} \pm 9.7$ $L \cdot kg^{-1}$ VS after 10 pressure shockwaves, $n = 6$, $\alpha = 0.05$) compared to the reference sample (149.4 $L \cdot kg^{-1} \pm 12.3$ $L \cdot kg^{-1}$ VS without any pretreatment, $n = 6$, $\alpha = 0.05$). The methane yields achieved were low in comparison to Staubmann et al. (26), which could possibly be due to the smaller size of the laboratory equipment. The key point is that the peaks of daily methane production were identical 2 days earlier in comparison to the reference samples.

One of the most powerful tools to compare the level of phytomass disintegration is the measurement of the surface area by the gas adsorption technique. For this reason, these measurements (**Fig. 6**) were considered with the greatest importance.

Although the assessment of all the methods gave clear evidence that a significant level of seed disintegration was achieved, the prototype is still in the early stage of development. The device still works only on a batch principle, allowing utilization of 200 mL volumes at most. Thus, the future development may take different directions, e.g. whether to work more on the electrical facilities, on the principle of a continuous prototype, or whether to focus on other structural changes.

Conclusions

There has been large progress in the development of the device for pressure shockwave pretreatment of the *Jatropha Curcas* L. seeds. However, much work remains. It has been demonstrated that a significant level of disintegration, which implies subsequent 94 % oil extraction, may be achieved. It was found that grinding, followed by maceration may enhance the effect of following pressure shockwaves. Maceration may decrease the effect of soaking of the oil into the husks. In addition, it was observed that the amount of liquid plays an important role in the overall dynamics of the process. Reported mass balances allow further development of the device as well as technology optimisation.

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