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The use of underwater high-voltage discharges to improve the efficiency of *Jatropha curcas* L. biodiesel production

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Abstract.

Underwater high-voltage discharges (3.5 kV) resulting in 4.9 kJ shock waves (50–60 MPa) were studied at the laboratory scale as a *Jatropha curcas* L. seed disintegration method. Grinding and macerating in an excess of methanol (3.5:1) was advantageous because methanol acts both as a liquid carrier for the pressure shock waves and as a solvent that increases the efficiency of oil extraction while remaining usable for esterification. The influence of the number of shock waves and the intensity of methanol maceration on the heat values of the pressed cake are stated in detail. Soxhlet extraction demonstrated that a greater than 94% oil extraction was achieved. The increased disintegration of vacuoles rich in oil was documented by surface area analysis, mineralization kinetics analysis, and electron microscopy. The working volumes were small, and the proportion of energy inadequate compared to the yields released; however, much can be improved by upgrading the process.

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1. Introduction

Holistic utilization of the seeds of *Jatropha curcas* L. has been reviewed many times [1–4]. High yields from oil extraction processes are negated by costly apparatus and high demands for energy, water, and chemicals [5–11]. The alternatives to environmentally promising enzymatic extractions require long reaction times [12], which may be sped up by the use of *t*-butanol and ammonium sulfate [13] or ultra-sonication [14]. However, these modifications represent additional demands not only for costly enzymes, but also for additional chemicals and energy, which undermines the *Jatropha* oil business [6].

The profitability of *Jatropha* utilization can be markedly increased by finding a method that significantly reduces the cost of oil extraction before esterification. Previous experiments in the field of plant utilization showed that cavitations caused by sudden pressure changes might open up inner phytomass structures and significantly disrupt the microfibrils that form the walls of plant cells [15].

The scope of the presented work is to verify the hypothesis that the shock waves caused by underwater high-voltage discharge [16–19] may disrupt the *J. curcas* L. cell walls, especially the walls of vacuoles rich in oil, and thus compensate for the lower solvent efficiency of methanol, which could subsequently be used for oil transesterification into biodiesel. A similar technique has been already described by Lee et al. [20], who underlined the importance of shock wave energy in sludge treatment. There have been no previous reports of underwater shock wave use in oil extraction.

2. Material and methods

2.1. Substrate properties

The *J. curcas* L. seeds were obtained from Central Thailand, province of Nakornpathom. After the harvest in 2010, the seeds were dried and stored in an opened perforated plastic bag in a dry, shady place (weight per 1,000 seeds: 622.3 g; bulk laid: 355 g L^{-1}; dry weight: 92.3%, 21.193 MJ kg^{-1}). The husks represented 44.3% of the dry weight (15.207 MJ kg^{-1}), whereas the kernels with vacuoles rich in oil represented the main proportion of the heating value (25.954 MJ kg^{-1}).

Fresh manure [$pH_{20^\circ C}$: 6.83, 1.26 kg L^{-1}, 24.5% total solids (TS)] from stabled cows on a grass and hay diet was used as inoculate for mineralization kinetics analysis of the press cake.

Abbreviations: alpha, probability value; *n*, number of samples; SS, stereo scan; TS, total solids; WD, wide.

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Fig. 1. Side view (A) and view from above (B) on lockable strengthened metallic vessel for high-voltage underwater discharges causing pressure 50–60 MPa shock waves, prototype number 4, with an inner spherical volume of 2 L, a minimal vessel thickness of 2 cm, and copper electrodes.

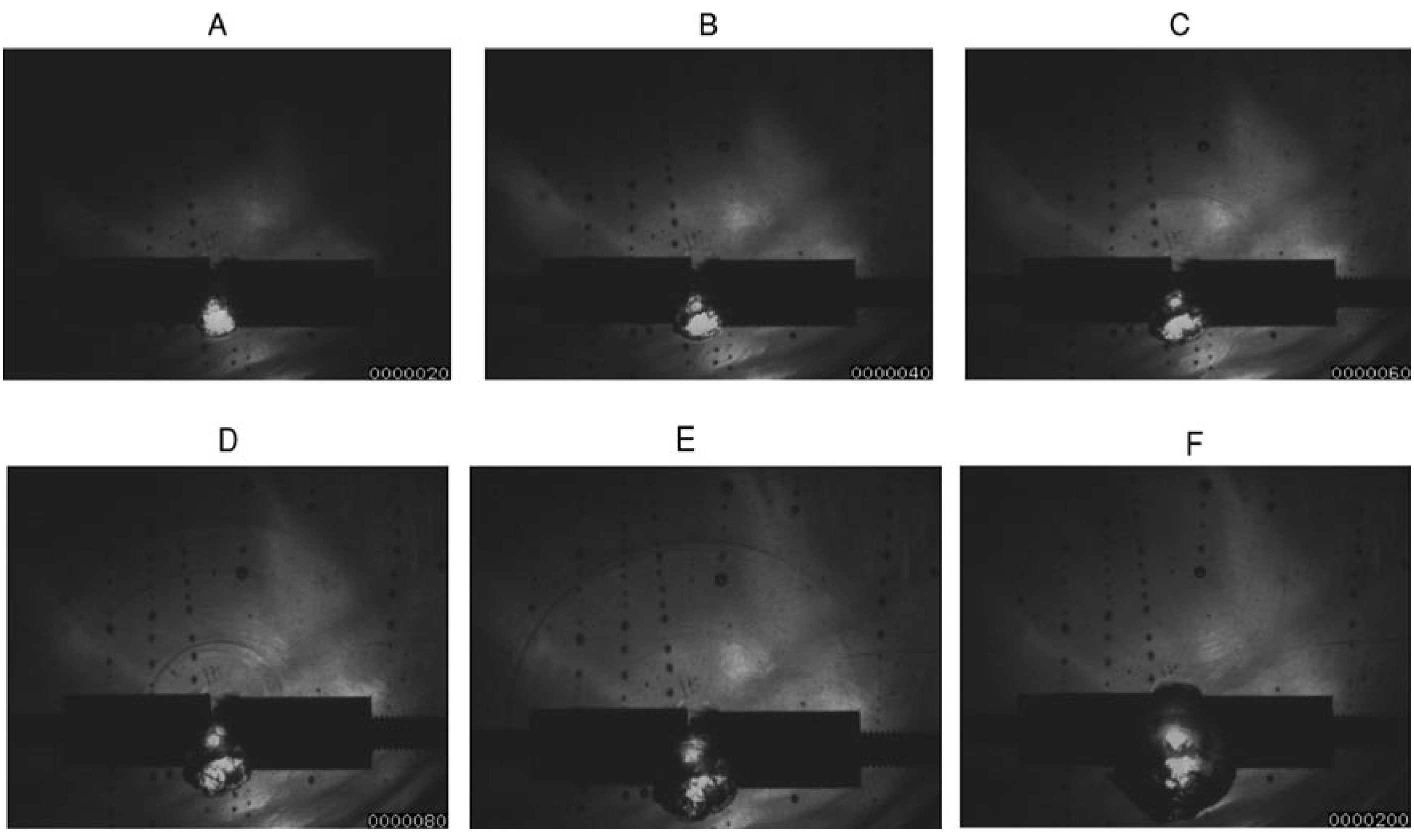

Fig. 2. A slow motion of shock wave at 20 (A), 40 (B), 60 (C), 80 (D), 100 (E), and 200 (F) μSec.

2.2. Chemicals

Methanol (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, Osaka, 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).

2.3. Apparatus

The circuit of a high-voltage generator prototype [21] 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) 50–60 MPa pressure shock waves (4.9 kJ, 1,500 m s^{-1}).

2.4. Heat value of the press cake

Electronic weighing scales (AUX 320; Shimadzu, Kyoto, Japan) and a constant-temperature oven (FSS-S; Hirasawa, Tokyo, Japan) were used for TS determination according to the method developed by the USEPA [22]. The dried seeds were subjected by 30 g to 10 s of grinding in a Labo Milser crusher (IFM-800; Osaka Chemical, Osaka, Japan). The obtained fragments of approximately 3 mm and all of the finest particles were carefully swept into the in I-BOY 200 mL plastic bottles (AS-ONE, Osaka, Japan) and screwed shut to avoid any contact with oil-absorbing material (such as paper) and to minimize microbial degradation. For 10 days, the samples were macerated (1:3, 1:4, and 1:5 by weight in methanol) and gently shaken in a 55°C water bath (BZ-100; Yamato, Akashi, Japan) with a CU-120 temperature control unit (Sibata, Soka-City, Japan) or macerated in methanol 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, Matsumoto, Japan) with a 19.6 cm^2 free piston, whereas the performance was set at 1,400 kg (7.143 MPa) because the amount of oil pressed out decreased sharply at this pressure. An autocalculating bomb calorimeter CA-4AJ equipped with a calorimetric calculator (P-202; Shimadzu) was used for heating value (MJ kg^{-1}) analysis. The data obtained were plotted by online curve and surface fitting software (Zunzun.com); the lowest sum of squared absolute error reached and lowest root mean squared error were the main fitting criteria.

2.5. Oil yield

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

2.6. Mineralization kinetics

Grade 2 (8 μm) filter paper (Advantech, Tokyo, Japan) and a 55-mm Büchner funnel (Sibata) were used for the cold-water (20°C) filtration of fresh cow manure (200 mL of filtrate from 50 g in fresh weight). Thirty grams of press cake residues (obtained according to a previously described procedure, except that water was used instead of methanol) was subjected to 5 Sec of grinding in a Labo Milser IFM-800 crusher (Osaka Chemical) 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, Tokyo, Japan) in 1,000-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.

2.7. Surface area

The single-point surface area at $P/P_0 = 0.2$, Brauner–Emmett–Teller 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 analyzer (Micromeritics, Tokyo, Japan) after 24 H of degassing at 200°C and 1 H of degassing at 300°C.

2.8. 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, Tokyo, Japan). A JSM-6510 LA analytical scanning electron microscope (JEOL) was used to observe the inner structures of the phytomass from the upper electron detector (SEI) at an acceleration voltage of 10 kV.

3. Results and discussion

The amount of pressed oil is usually difficult to measure exactly at a small scale (a considerable amount of oil is always lost on the surface of the piston of the molding machine) and the quality (water and solid residuals) of oil must be taken into account in determining oil yield. The heating value (MJ kg^{-1}) of the press cake was therefore chosen as an indicator of oil yield, with the assumption that a lower heating value of the press cake represents higher oil yields.

On the basis of the trials, it was concluded that the combination of both pretreatments, grinding and macerating (18.312 ± 0.035 MJ kg^{-1}, $n = 6$, $\alpha = 0.05$), synergistically enhances the effect of the shock waves, whereas grinding alone (18.550 ± 0.021 MJ kg^{-1}, $n = 6$, $\alpha = 0.05$) or macerating (18.547 ± 0.039 MJ kg^{-1}, $n = 6$, $\alpha = 0.05$) alone is almost similar to samples with no pretreatment (18.554 ± 0.041 MJ kg^{-1}, $n = 6$, $\alpha = 0.05$). We assume that this mechanism can be explained as follows: the rigid husks must be opened first, and then the liquid must penetrate inside the kernels to allow the pressure shock waves to be transmitted more effectively.

On the basis of these observations, all of the subsequent experiments were carried out in a liquid environment, more precisely, in methanol. The use of methanol for the *J. curcas* L. oil extraction is already well known [6],[7]; however, thus far this application has been effective only in exacting supercritical conditions. Therefore, it is more economical to use stronger solvents such as *n*-hexane (extraction efficiency 98%) [23] even though use of *n*-hexane as a solvent is not recommended because of its environmental impact [1]. It is therefore necessary to determine whether the disintegration caused by the pressure shock waves has the potential to compensate for the lower solvent efficiency of methanol, which could subsequently be used for oil transesterification into biodiesel.

The manifestations of the number of shock waves to the amount of methanol used during less intensive maceration (2 H

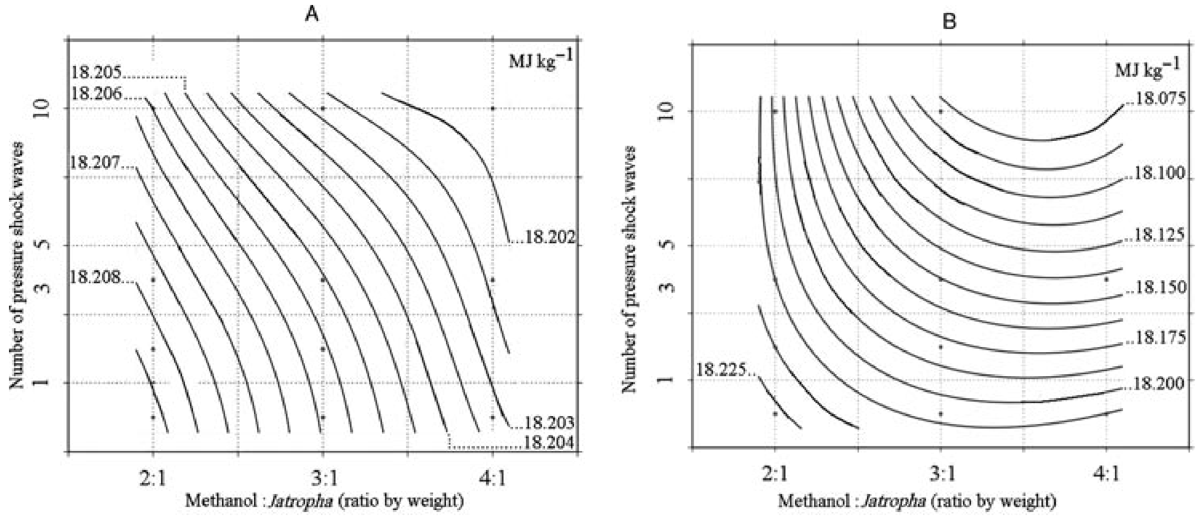

Fig. 3. (A) The manifestation of the number of underwater high-voltage discharges (3.5 kV) and the ratio of methanol to *Jatropha* (by weight) after 2 H of maceration in 99.7% methanol at 20°C on the *Jatropha* seed press cake heat value (MJ kg^{-1}). The dynamics are plotted as a polynomial function; the sum of squared absolute error = 0.004 and the root mean squared error = 0.002. (B) The effect of the number of high-voltage (3.5 kV) discharges and the ratio of methanol to *Jatropha* (by weight) after 10 days of maceration in 99.7% methanol at 55°C on the *Jatropha* seed press cake heat value. The dynamics are plotted as a polynomial function; the sum of squared absolute error = 0.004 and the root mean squared error = 0.006.

of maceration in 99.7% methanol at 20°C) plotted in Fig. 3A led to the conclusion that higher numbers of shock waves and higher amounts of methanol are preferable; however, the dynamics of intensification are not linear.

Intensive methanol maceration (10 days of maceration in 99.7% methanol at 55°C), the results of which are plotted in Fig. 3B, gave higher yields with different dynamics of interdependencies. On the basis of the detailed observation of the plotted manifestations, it can be stated that the economically important impact is that further increasing the proportion of methanol to ground seeds to ratios greater than 3.5:1 may be less profitable.

The most intensive maceration conditions, the highest number of shock waves, and a higher proportion of methanol provided the highest oil extraction yield of 94 ± 0.5% ($n = 6$, $\alpha = 0.05$) established with Soxhlet extraction.

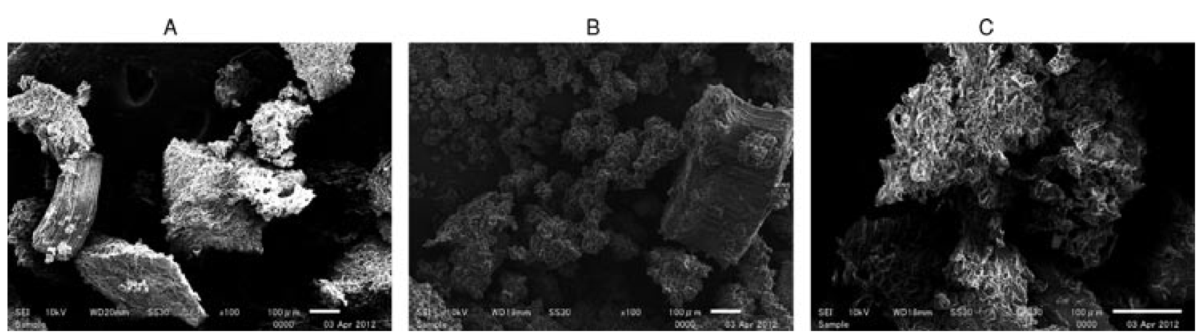

Fig. 4. (A) A press cake (7.143 MPa) of the ground, intensively methanol macerated (4.1 by weight, 10 days, 55°C) and 10 times shock waved (5% to 60 MPa) *Jatropha* seeds. We assume that the greater flattening of the cells was due to greater removal of oil, which was due to the intensified vacuole disintegration (coated with 10 nm of white gold, accelerating voltage of 10 kV, wide (WD) 20 mm, SS30). (B) The ground seeds of *J. curcas* L. were further disintegrated by 10 underwater discharges (3.5 kV) in water (4:1 by weight). The horizontally striped block on the right side of the screen is a lignocellulose-based block of the *Jatropha* husk, which was almost untouched by the pressure shock wave. In the rest of the image, there are fine fragments of the kernels, which were significantly dispersed (coated with 10 nm of white gold, accelerating voltage of 10 kV, WD20 mm, SS30). (C) Mechanical disintegration of *J. curcas* L. by grinding. The vertically striped object on the left side of the image is a fragment of the *Jatropha* husk (brownish shells of the seed) composed mainly of rigid crystal cellulose (stripes) and lignin. The rest of the fragments represent the kernels (white inside parts) of the seeds, which are rich in oil (coated with 10 nm of white gold, accelerating voltage of 10 kV, WD20 mm, SS30).

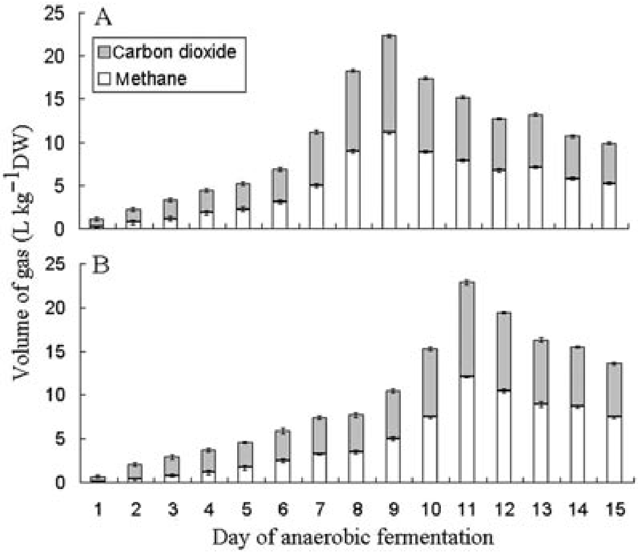

Fig. 5. (A) The mineralization kinetics of 10 times shock waved and intensively water-macerated *Jatropha* seed press cakes in anaerobic fermentation (10% TS, 40°C) expressed by the daily production of methane and carbon dioxide (converted to 0°C and 101,325 Pa). (B) The mineralization kinetics of *Jatropha* seed press cakes without the shock wave pretreatment carried out under similar conditions. The amount of cumulative biogas production at 15 days was almost the same (A: 154 L kg^{-1} TS, B: 148.5 L kg^{-1} TS, a 3.6% increase); however, the daily maximum was 2 days earlier in (A). The bars indicate the standard deviations ($n = 6, \alpha = 0.05$).

According to a review by Achten et al. [1], the oil yields of mechanical extraction methods are in the range of 62.5%–80%, and pretreatments such as cooking of the seeds can increase the oil yield of screw pressing up to 89% after single pass and 91% after dual pass extraction. Winkler et al. [23] obtained a 38% yield using only water and 86% using several cell-wall-degrading enzymes (alkaline protease).

Compared with these, the 94% yield achieved with 10 pressure shock waves and intensive methanol maceration in addition to grinding is outstanding. However, the review by Achten et al. [1] also states that the use of solvents such as *n*-hexane gives oil yields of 95%–99%. Very surprising are the results of Lim et al. [7], who report yields of 105.3% (exceeding theoretical maximum yield); however, the use of 200 mL of methanol and 50 mL of hexane per 20 g of blended seeds at 300°C and under 240 MPa can hardly be profitable.

Here, it must be remembered that in our case the methanol was chosen because of its further use in transesterification.

The slow motion (Fig. 2) shows that the high-voltage discharge occupies at its maximum approximately a volume close to a tennis ball (140 cm^3). Although it was not our task to examine the physical nature of the process, we believe that the pressure waves are formed because of a temporary increase in the density of the liquid, as the outer volume and weight remain the same. By comparing the electron microscope scan of the press cake (7.143 MPa) of the ground, most intensively methanol macerated and 10 times shock waved sample (Fig. 4) to scans of the press cakes obtained by less intensive treatments, we assume that the greater flattening of the plant cells following the intensive methanol maceration was due to higher removal of the oil, as a result of vacuole disintegration.

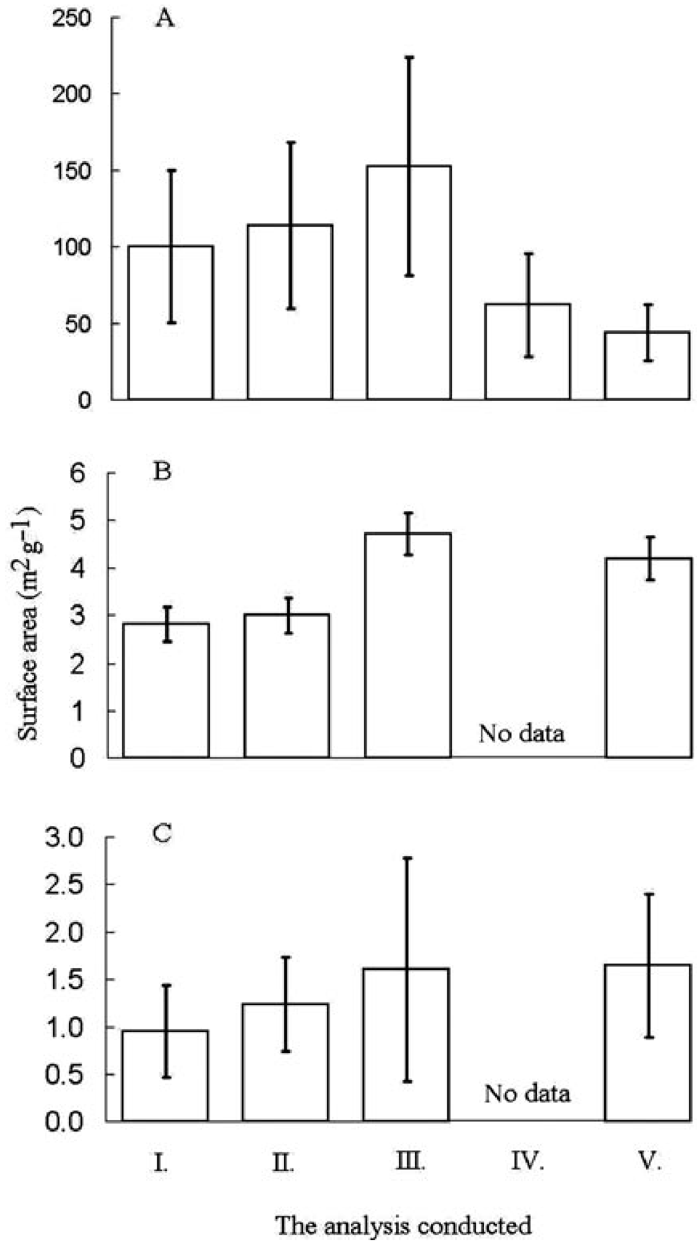

Fig. 6. Results of the surface area analysis. (A) Press cake subjected to intensive maceration in methanol and 10 shock waves; (B) press cake subjected to water maceration and 10 shock waves; (C) press cake that was not subjected to any maceration or shock waves, where I: single point surface area at P/P_0 0.2 (m^2 g^{-1}), II: Brauner–Emmett–Teller 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 bars indicate standard deviations ($n = 6, \alpha = 0.05$).

Indirect comparison of the particle size with the speed of mineralization (Fig. 5) also supports the hypothesis that the shock waves disintegrated cell vacuoles. The amount of cumulative biogas production in 15 days was almost the same (154 L kg^{-1} TS after 10 pressure shock waves and 148.5 L kg^{-1} TS from the blind sample, only a 3.6% difference); however, the daily maximum of biogas yield was 2 days earlier in the case of 10 pressure shock waves ($n = 6, \alpha = 0.05$).

However, methane yields obtained in this study (73.6 L kg^{-1} for 40°C corresponding to 76 L kg^{-1}) were much lower than the yields mentioned by Achten et al. [1], which was 355 L of biogas containing 70% of methane, thus approximately 312.2 L kg^{-1}. After repeated verification of the mineralization experiment, we were about to formulate concerns over whether the results reported by Achten et al. [1] had not been overestimated; however, we later found that a mistake was made in the review: the original authors [24] had stated that the discussed yield referred to 1 kg of degraded chemical oxygen demand.

The increase in the surface area measured by the gas adsorption technique is the most significant evidence of the improved efficacy of plant cell disintegration (plotted in Fig. 6).

Although we have ample evidence of the efficacy of the disintegration effect of the pressure shock wave on *Jatropha* oil extraction, the prototype we used [21] is still very far from operational use. The 2 L vessel can actually handle bottles with a maximum volume of 200 mL, that is, approximately 40 g of seeds per 2 Min. However, the prototype development is heading in the right direction; only 2.2 W are needed per spark (4 kW) [17].

The current energy balance is not ideal. By neglecting the energy intensity of maceration (which may be solved by use of the waste heat from press cake utilization), 49 kJ is used to release 10 high-voltage underwater discharges. However, only 9.68 kJ is actually released in the best case.

4. Conclusions

The application of pressure shock waves produced by underwater high-voltage discharges on unground and inadequately soaked seeds of *J. curcas* L. has a negligible impact on oil extraction. However, the impact increases after husks are ground and intensively macerated in an excess of an organic solvent such as methanol. The depth of penetration of the solvent and the number of shock waves seem to be very important and may increase the oil yield up to 94%.

If the solvent can be effectively replaced by enzymes, it is hypothesized that the press cakes will remain usable for biogas production.

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