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8A new approach in maximizing and direct utilization of whole Jatropha curcas L. kernels in biodiesel production e Technological improvement

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Jatropha curcas Supercritical methanol Subcritical water Subcritical acetic acid (Trans)esterification abstract The direct (trans)esterification of whole Jatropha curcas L. (JCL) kernels in subcritical solvent mixture of water, methanol and acetic acid was explored. A high

4fatty acid methyl ester (FAME) yield of 96.56% could be achieved

at a solvent (water: acetic acid: methanol 1/4 1:5:15, v/v/v) to solid ratio of 7 cm³ g 1. The reaction mixture was pressurized with carbon dioxide and reacted for 1 h at 523 K and 12.5 MPa. Qualitative tests on the recovered polar fractions of the product were found to have radical scavenging activities. The characteristics of the spent kernel residues were also studied. The method employed in this study provides an alternative approach to better utilize JCL kernels and cut down the number of production steps. © 2015 Elsevier Ltd. All rights reserved. 1. Introduction Renewable and environmental friendly alternatives to petroleum as an energy source, like hydroelectric, wind, solar power and biofuels have been utilized to ease our dependence on the depleting oil reserves. Based on the available reserves and production rates our existing crude oil will last about 52 years [1]. Biofuels like bioethanol and biodiesel are alternative fuels that can be utilized to partly replace fossil fuels. In 2012 biodiesel production grew 2.7% over the previous year and has doubled that of five years ago, contributing up to 31% of the global biofuel supply [1]. Jatropha curcas L. (JCL) seed with its high oil content is a Abbreviations: AG, acylglyceride; AOCS, American Oil Chemist Society;

9FA, fatty acid; FAME, fatty acid methyl ester; FFA, free fatty acid; HTGC, high temperature gas chromatography;

JCL, Jatropha curcas L.; PM, phospholipid membrane; SCW, subcritical water; SSR, solvent to solid ratio; DPPH, 1,1-diphenyl-2-picryhydrazyl;

9TLC, thin layer chromatography. * Corresponding author.

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promising feedstock for biodiesel production. Utilization of all fractions and by-products from the biomass of this feedstock in a biodiesel production process is required for its economic sustainability [2]. Oil is first extracted from seed or kernel before it is reacted with methanol to produce fatty acid methyl ester (FAME). Typical methods require drying and/or flaking of seeds or kernels. Mechanical extraction (50 ± 0 % recovery) [2,3] is preferred as a primary extraction method as it does not require separation and recovery of solvents from extracted lipids. An optimized screw press design and operation was capable of recovering 89.3% lipid but it required high pressure (9.0 MPa) and temperature (413 K) [3]. Solvent extraction is normally employed as a second step to recover lipids from extruded pressed cakes; but, still results in a lipid loss of about 10% [2,3]. A three-phase extraction process, requiring only 2 h with an 85% oil recovery was proposed by Vyas et al. [4]. Although a short extraction time was needed, it involved several intermediate steps and required the separation and recovery of solvents. Supercritical carbon dioxide has been employed for easier solvent separation, with a better oil recovery of about 95% than that of mechanical expeller and comparable extraction time (5 h) to that of classical solvent (n-hexane) extraction. It operates at a low temperature of 333 K but at very high operating pressure (up to 35.0 MPa) [5]. Low quality feedstock such as JCL oil for biodiesel production is associated with high free fatty acid (FFA) and high moisture contents.

(Trans)esterification of oil extracted from JCL seeds in the presence of acid-base catalyst typically requires multistage reactions to obtain FAME. To overcome problems associated with feedstock impurities and provide easier product recovery and separation, enzyme-catalyzed processes have been explored [6], but the high cost of enzyme has hindered its commercialization [7]. The use of supercritical alcohols as a reaction medium has been found to be capable of tolerating high FFA content and high moisture content in the feedstock. A well-engineered process is required to efficiently recover the enormous energy spent in the process [8]. In-situ (trans)esterification of JCL seeds has been extensively studied employing different catalysts and modes of trans-esterification. Acid-based catalyzed approaches require post treatment to remove and neutralize the catalyst, which accumulates as by-product in the wastewater stream [9]. Lim et al. [10] avoided using catalyst by employing supercritical methanol reactive extraction process. The high temperature (573 K) and pressure (20.0 MPa) required in the process were justified by recovering high value by-products to help lowering down the cost of biodiesel production [11]. In this study a new approach to maximize the utilization of JCL seeds was developed along with the direct utilization of whole kernels. Subcritical solvent mixture (methanol, acetic acid and water) was used as an extracting and reacting medium. Satisfactorily high yields of FAME were achieved and size reduction of the kernels was avoided. Results of preliminary studies on fractional distribution and qualitative analysis of organic by-products are also presented.

2. Materials and methods JCL seeds were obtained from Muhammadiyah University (Malang, Indonesia). The seeds obtained were sun dried and kept at 253 K prior to use. Standards of fatty

acid (FA), acylglycerides (AG) such as monoolein, diolein and triolein and FAMEs were obtained from Supelco (Bellefonte, PA). Thin layer chromatography (TLC) plates were supplied by Merck (Germany). Indicators 1,1-diphenyl- 2-picrylhydrazyl (DPPH) and Fast Blue were acquired from Sigma Aldrich (St. Louise,

11MO). All solvents and reagents used were either high performance liquid chromatography (HPLC) or analytical re- agent grade, obtained from commercial sources.

This study investigated the direct in-situ transesterification of JCL lipids in whole kernels was investigated. A simplified schematic of the process is depicted in Fig. 1. 2.1. Sample preparation and characterization Sun-dried JCL seeds were de-shelled manually. Whole kernels were kept under 253 K for later use. Extractable crude lipid was determined by extracting dried ground kernels (5 g) with nehexane for 12 h in a Soxhlet extractor. The FFA

3content in the crude lipid was determined by the titrimetric method following the AOCS official methods (Method Ca 5a-40)

and by high temperature gas chromatography (HTGC). De- tails of the analysis condition were described by Tran et al. [12]. Before the AG composition of the extracted crude lipids was determined, dewaxing and degumming

6was carried out following the method of Rajam et al.

[13]. Unsaponifiable matter content in the lipid sample was analyzed using the AOCS official methods (Method 6b-53). Saponified lipids obtained after the determination of unsaponifiable matter were collected and acidified to pH 2 with concentrate sulfuric acid at 333 K until the solution was clear. The solution was then

5allowed to settle until 2 phases were formed. The upper layer was

extracted with hexane and further reacted with BF3-methanol for later analysis of FA profile using HTGC.
2.2. In-situ transesterification and product separation Whole kernels (~3 g) containing about 5% moisture were loaded

4into a glass chamber and placed in a high-pressure reactor.

A detailed description of the reactor can be found elsewhere [14]. A mixture of methanol, acetic acid and water was added into the glass chamber. The reactor was sealed and the chamber was purged with nitrogen

gas. Prior to heating, the chamber was pressurized using nitrogen or carbon dioxide to ensure that the solvent mixture was under subcritical state.

5At a reaction temperature of 523 K, a final system pressure of

~11.5e12.5 MPa was achieved. Heating rate of the reactor was kept at 5 K min with a heating period of 1 40e45 min. When the desired temperature was reached, this was noted as the start time of the reaction. After the desired reaction time was achieved,

15reactor was rapidly cooled. Pressure inside the reactor was

released and products in the reactor were collected at

5room temperature. The cooled reaction mixture was vacuum filtered using a Buchner funnel

with Advantec No.2 filter paper (8 mm pore size) to separate the spent kernels from the reaction products. The retained solids were washed three times. Each washing was with 30 cm³ of methanol to recover the FAME produced. Methanol and acetic acid in the filtrate were removed and recovered using a rotary evaporator (BUCHI Labortechnik AG in Flawil, Switzerland) operated at 313 K and a pressure of 13.3 kPa. The residual acetic acid and water was further removed by heating the mixture at 353 K and a pressure of 13.3 kPa. The obtained organic fraction obtained was fractioned using 25 cm³ n-hexane and 25 cm³ water. The upper layer (hexane fraction) was separated and collected in a flask. The remaining organic phase was re-extracted twice, each with 25 cm³ hexane. This was done to recover the available FAME. The pooled hexane layers were then washed three times, with 25 cm³ 5% NaCl solution to remove impurities like glycerol. After washing, hexane from the combined extract was evaporated under vacuum using

4a rotary evaporator. The recovered product was weighed and

analyzed for its FAME, FA and AG contents using HTGC. The water fraction was filtered through Advantec No.2 filter paper (8 mm pore size), then fractioned with equal volume of solvents into ethyl acetate fraction (EAF), butanol

6fraction (BF) and water fraction (WF- 2). The un-dissolved organics were then washed and

extracted with methanol (50 cm³). The fractions were further analyzed using stains, Fast blue, DPPH and Iodine vapor. The constituents of each fraction were identified using GC-MS. All analyses/experiments were at least carried out in duplicates. 2.3. Characterization of kernel residues

12Ultimate analysis was performed with a CHNS analyzer

(Ele- mentar Vario EL Cube, Germany)

12to determine the percentage of carbon, hydrogen, nitrogen and sulfur.**Oxygen**

content was determined using an elemental analyzer (Thermo Flash 2000, Italy). The residue remaining after complete combustion for elemental analysis was taken as ash. Ash content was also verified by heating 1 g of dry solid samples in a muffle furnace (873 K) for 3 h. Moisture (M) and volatile matter (VM) were analyzed using a thermogravimetric analyzer (Diamond TG/DTA, Perkin Elmer, Japan). The difference of the sample weight and that of the moisture, VM and Ash, was used to estimate the fixed carbon content.

Fig. 1. Schematic flow of the in-situ transesterification process carried out in this study. 3. Results and discussion Ground Jatropha kernels contained about 5% moisture. The hexane extractable crude lipid in the dry solid was $54.08 \pm 0.74\%$ by weight. The theoretical FAME yield that can be produced from the extracted lipids is 91% (49% if based on dry kernels). Reducing production steps in a process would contribute to cutting down production costs. Fig. 1 shows the different schemes in biodiesel production. As described earlier, conventional biodiesel production (Fig. 2) requires several intermediate steps and strict requirements on feedstock quality. In situ (trans)esterification eliminates the extraction of oil and the pretreatment of extracted lipids (Step 3 of Fig. 2). In this study de-shelled JCL seeds were directly utilized eliminating the need for drying and size reduction (Step 2 of Fig. 2), which further simplifies the process. 3.1. Direct in-situ transesterification of whole kernels Previous studies showed that SCW pretreatment of whole JCL kernels allowed the complete extraction of the lipids [14]. Optimized pretreatment required at least 2 cm³ of water per gram of kernel at 584 K [14,15]. In the following investigation a fixed kernel to acetic acid and a water solution (1:2, g cm⁻³) was employed but the relative amounts of acetic acid and water was varied. When

15a mixture of acetic acid, water and methanol were employed as the

solvent, solvent to solid ratio (SSR) of 3.3 and 7.0 cm³ g⁻¹ was used in order to understand the role of each solvent involved. Fig. 3(a) shows that when pure methanol was used at an SSR of 3 cm³ g⁻¹, in situ transesterification of whole kernels resulted in very low FAME yield of about 15%. At an SSR of 7 cm³ g⁻¹, the use of pure acetic acid and water as co-solvent improved the FAME yield from 28% to 44.1% and 36.6%, respectively. Optimum FAME yield of Fig. 2. Steps in biodiesel production. Fig. 3. (a) Effects of ratio of acetic acid to water and SSR on FAME yield, kernel to acetic acid solution fixed at 0.5 g cm⁻³, with a total SSR of 3.3 or 7 cm³ g⁻¹. (b) Effect of methanol loading (cm³ per gram kernel) on FAME yield, kernel to acetic acid solution fixed at 0.5 g cm⁻³ and water to acetic acid ratio fixed at 1:5 (volume ratio). Reaction at 523 K, initially pressurized with nitrogen gas to 4.0 MPa with a reaction time of 1 h. 46.6%, which is 93.9% of the theoretical maximum yield, was achieved at a water to acetic acid ratio of 1:5 (v/v). Fig. 3(b) shows that at a methanol to kernel ratio of 5 cm³ g⁻¹ (SSR 1/7 cm³ g⁻¹), the highest FAME yield was obtained. The effects of stirring and the use of carbon dioxide on the direct transesterification of whole kernels were investigated and the results are summarized in Table 1, which indicates that stirring, and carbon dioxide addition resulted in higher FAME yields. The use of acetic acid and the presence of water allowed the

hydrolysis of the kernel. This was supported by the observation that the solid matrix has collapsed upon recovery of the reaction products. Stirring resulted in breaking down of solid matrix into fine powder. The addition of carbon dioxide, which was in super- critical state at the operating conditions employed. This greatly enhanced the overall solubility and extraction efficiency. 3.2. Comparison with other transesterification technologies Table 2 presents comparisons of maximum FAME yields obtained by various investigators in the in-situ transesterification of JCL seed kernels. This study used a lower SSR when compared to Table 1 Direct in situ transesterification of whole kernels (3 g), initially pressurized to 4.0 MPa and reacted at 523 K for 1 h. Kernel:Water:Acetic acid:Methanol (3 g: 1 cm³: 5 cm³: 15 cm³). Gas/Stirring Final pressure % Yield^b (MPa) Nitrogen without stirring Nitrogen with stirring Carbon dioxide without stirring Carbon dioxide with stirring 11.5 11.5 12.5 12.5 46.6 ± 1.0 (86.21)^a 49.4 ± 1.1 (91.35) 48.5 ± 0.2 (99.01) 52.2 ± 0.5 (96.56) a Mass fraction (%) of FAME based on the hexane extractable lipid. b Mass fraction (%) of FAME based on the dry kernel. conventional acid catalyzed reaction or with two step acid/base in- situ process. Although higher SSR was required when compared to supercritical methanol processes, less severe conditions (523 K and 11e12.5 MPa) were employed with a comparable overall reaction time. High water contents and the presence of FFA can be tolerated in this study. This study directly used whole JCL kernels without the need of drying and size reduction of kernels, compared to the previously developed process utilizing methanol and acetic acid as the media [16]. The proposed method does not require the use of mineral acid. This could potentially reduce problems associated with the waste water generated during washing. Acetic acid used in the process could easily be recovered through distillation due to its lower boiling point when compared to sulfuric acid. Compared to non in-situ supercritical methanol trans- esterification the amount of methanol utilized for in-situ process is higher by almost 7 times. Since non in-situ transesterification re- quires oil extraction prior to the reaction, the in-situ approach might still provide certain advantages. Hawash et al. [21] reported the study of non-catalytic supercritical methanol trans- esterification of Jatropha oil at 593 K, which is much higher than 523 K used in this study, using hexane for extraction. An optimized extraction of Jatropha oil using hexane required 8 h and

3 at a solvent to solid ratio of 6 mL g

1 [22]. Taking these into consideration the amount of solvent utilized may just be similar. The indirect method required a reaction time of 4 min [21]. This did not include the heating time required to reach 593 K and the extraction time. A study by Niza et al. [23] on the optimization of biodiesel production using either supercritical methanol or methyl acetate reported that a reaction time of 27 and 32 min at 633 K and 673 K were required, respectively. As shown in Table 3 the fatty acid profile of JCL lipids obtained in this study agrees with those reported in the literature. The iodine value (IV) and cetane number (CN) all meet the ASTM/EN stands for biodiesel. The fatty acid profile of the product Table 2 Comparison of different in-situ transesterification of JCL seed kernel. In-situ (trans)esterification method Oil content (%) SSR^a (cm³ g⁻¹) Temp (K) Pressure (MPa) Time (h) Yield (%) Ref. Acid catalyzed (H₂SO₄ 21.8%, w/w) Two-step acid/base with ethanol as solvent (H₂SO₄ 7.5%, w/w/5N KOH in ethanol) Supercritical methanol (process intensification) Supercritical methanol co-solvent (CO₂ 50 bars) Supercritical methanol, co-solvent (CO₂ 40 bar) Supercritical methanol, co-solvent (CO₂ 20 bar) Subcritical methanol e acetic acid (7.5:2.5), co-solvent (CO₂ 20 bar) Whole kernels (~5% water content), subcritical methanol - acetic acid-water (15:5:1), co-solvent (CO₂ 40 bar) 54.6 10.5 32.4 10.5 e Step 1 8.2 e Step 2 66.8 5.0 64.6 5.0 66.8 5.8 66.8 5.9 58.1 7.0 54.08 7.0 333 Microwave 573 573 568 573 523 523 ~0.1 10 e 0.76 9.5 0.5 (2.0)^b 20.0 0.5 (2.0) 20.0 0.125 (1.63) 20.0 0.21 (1.71) 21.0 1.0 (1.75) 12.5 1.0 (1.75) 98.1c (53.53)d ~90 99.67 (66.6) 102.3 (66.1) 87.1 (58.2) 92.0 (61.5) 94.43 (54.72) 96.56 (52.2) [17] [18] [19] [20] [11] [11] [16] This Study a SSR solvent

(methanol acetic acid β $\frac{1}{4}$ β water) to solid ratio. b Total reaction time including the heat up time for the reaction to reach the desired temperature. c Mass fraction (%) of FAME based on the hexane extractable lipid. d Mass fraction (%) of FAME based on the dry kernel. Table 3 Comparison of Jatropha curcas fatty acid profile. FAMEa Ref [21] Ref [24] Ref [25] This study Before reaction After reaction

16Methyl palmitate (C16:0) Methyl stearate (C18:0) Methyl oleate (C18:1)
Methyl linoleate (C18:2)

Saponification value (SV)b Iodine value (IV)c Cetane number (CN)d Cold filter plugging point (CFPP)e 18.2
14.2 5.1 7.1 28.5 43.2 48.1 34.9 200.9 200.3 112.7 102.1 48.6 50.6 3.2 2.7 14.1e15.3 3.7e9.8 34.3e45.8
29.0e44.2 e e e e 13.2 6.8 48.9 30.3 199.6 98.8 51.08 2.8 13.6 7.6 53.5 24.6 199.8 92.7 52.5 1.7 a wt.
fractions (%) of methyl ester per 100 g sample. b SV $\frac{1}{4}$ 560 (wi/MWi) 100 [26]. P c IV $\frac{1}{4}$ 254 P 100 [26]. d
CN $\frac{1}{4}$ 1.068 P(Di wi/MWi) (CNI wi) e 6.747 [27]. e CFPP $\frac{1}{4}$ 37.02e46.55 MO - 56.16 ML [24]. significantly
differs from that of the unreacted lipid. A decrease in methyl linoleate and an increase in both methyl
stearate and oleate were observed (Table 3). Decomposition was unlikely based on the mass balance of
hexane soluble fatty acids. Fatty acids were fully recovered and are slightly more than the initial amount of
hexane extractable lipids. This might be caused by the reaction of some structural lipids (phospholipids,
glycolipids) to produce FAME. Another possibility is the hydrogenation of the double bonds in the presence
of SCW [28]. The change in composition did not substantially affect the CN but significantly decreased the
IV. This means lesser double bonds are present and more importantly could improve the oxidative stability of
the biodiesel. The CFPP on the other hand increased after the reaction but still meets the ASTM and EN
specifications. 3.3. Qualitative analysis of reaction products A product distribution is shown in Table 4 which
summarizes the reaction products (FAME and by products) from in-situ (trans) esterification of whole JCL
seed kernel. The organic phase was separated into various fractions and the TLC analysis results of water
and methanol fractions are shown in Fig. 4. Both water and methanol fractions showed distinct purple band
when fast blue reagent was sprayed on the TLC plate. This indicated the presence of phenolic compounds.
Moreover DPPH staining resulted in inhibitory zones. The radical scavenging assay resulted in an IC₅₀ of
7.22 and 2.28 mg/mL for the extract from methanol and water fraction, respectively, suggesting the presence
of antioxidant compounds. Results of the GC-MS analysis of different organic fractions are summarized in
Table S1 of the Electronic Supplementary. Contrary to TLC results, GC-MS analysis did not find any
antioxidant com- pound present in the fractions analyzed. This is because in GC analysis the elution of
compounds in an injected sample greatly depends on temperature. Most antioxidant compounds have high
boiling points (>553 K), which are higher than the maximum col- umn temperature. It is possible that some
compounds were not detected by GC-MS. Most compounds detected by GC-MS from the Table 4 Product
distribution for in situ production of FAME from whole JCL seed kernels. Reaction conditions: 3 g whole
kernels, 21 cm³ solvent mixture (water:methanol:acetic acid $\frac{1}{4}$ 1:15:5, volume ratio), reaction temperature
523 K, initially pressurized with CO₂ gas to 4.0 MPa, reaction time 1 h. Whole kernel Product distribution
Organic phasea HeFxAaMneEfraction a,* (HF)b FFA Others Water fraction (WF) Methanol fraction (MF)
Acetone fraction (AF) Solid residue Losses 92.20 \pm 0.68a 5971..56ac (62.4)b 5.3 3.1 27.0 (29.8) 6.7 (7.3)
0.96 (1.0) 8.75 \pm 0.52 (Negligible) *Fractions of the organic phase. a Mass fraction (%) with respect to dry
kernel. b Mass fraction (%) with respect to organic phase. c Mass fraction (%) with respect to hexane
fraction. Fig. 4. TLC elution and staining results of water and methanol fractions. water fraction were found
to be amino acids and their derivatives. The methanol fraction was found to contain methylesters. A more
detailed characterization of byproducts is required. Preliminary results suggest a new approach to the use of
JCL seed kernels producing a low-value high volume product (FAME) and a wide spectrum of high-value low

volume by-products. 3.4. Characteristics of hydrochar The spent solids may be used as solid fuel. Hydrolyzed and spent kernels (hydrochars) recovered after the reaction were collected and analyzed. Table S2 summarizes the elemental analysis and proximate analysis of the solid residue. For application as solid fuel the mineral and moisture free energy content (23.65 MJ kg⁻¹) falls under the ASTM D388-12 specification for sub bituminous B coal. Taking into consideration the ash content (~49%), which is about 4.43% of the native dry kernel. The high mineral content of the solid residue may well be utilized for soil amendments. The pH of the residual solid and ash were found to be 7.53 and 9.99, respectively. The solids became more basic when other components aside from ash were removed. Residual solids like most ash from a biomass tend to be basic. These could be utilized as a low cost base catalyst or sorbent. The energy input for its activation could possibly be self-generated by the other components in the original residual solids making it more economically favorable. Further testing should be done to optimize its application.

4. Conclusion Acetic acid and water acted as catalyst or hydrolyzing agents and improved the reaction yield. Addition of carbon dioxide and stirring of the reaction mixture further improved the FAME yield through increasing contact between reactants and increasing solubility. Results show that high FAME yield, 96.5%, can be achieved by using a subcritical solvent mixture of water, methanol and acetic acid with carbon dioxide as a pressurizing gas. The resulting FAME has a fatty acid profile similar to that of conventional processes.

6DPPH radical scavenging activity of bioactive compounds from the organic extract of methanol and

water fraction showed an IC₅₀ of 7.22 and 2.28 mg/mL, respectively. These compounds could potentially be recovered as high value products. Spent kernel residues may be utilized as solid fuel or as basic catalyst.

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7is greatly appreciated. Appendix A. Supplementary data Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.j...>.

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