Renewable Energy 85 (2016) 759–765

Contents lists available at ScienceDirect

Renewable Energy

journal homepage: www.elsevier.com/locate/renene

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

Alchris Woo Go [a, d], Sylviana Sutanto [a], Siti Zullaikah [b], Suryadi Ismadji [c, *], Yi-Hsu Ju [a, **]

[a] Department of Chemical Engineering, National Taiwan University of Science and Technology, 43, Keelung Rd., Sec. 4, Taipei 106-07, Taiwan
[b] Department of Chemical Engineering, Institut Teknologi Sepuluh Nopember, Kampus ITS Keputih Sukolilo, Surabaya 60111, Indonesia
[c] Department of Chemical Engineering, Widya Mandala Surabaya Catholic University, Kalijudan 37, Surabaya 60114, Indonesia
[d] Department of Chemical Engineering, University of San Carlos – Talamban Campus, Nasipit, Talamban, Cebu City 6000, Philippines

ARTICLE INFO

Article history:
Received 10 September 2014
Received in revised form
8 June 2015
Accepted 29 June 2015
Available online xxx

Keywords:
Jatropha curcas
Supercriticritical 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 fatty acid methyl ester (FAME) yield of 96.56% could be achieved at a solvent (water: acetic acid: methanol = 1:5:15, v/v/v) to solid ratio of 7 cm^3 g^{-1}. The reaction mixture was pressurize 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.

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 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 %–80 % 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

---

Abbreviations: AG, acylglyceride; AOCS, American Oil Chemist Society; FA, 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; TLC, thin layer chromatography.

[*] Corresponding author.

[**] Corresponding author.

E-mail addresses: suryardiismadji@yahoo.com (S. Ismadji), yhju@mail.ntust.edu.tw (Y.-H. Ju).

http://dx.doi.org/10.1016/j.renene.2015.06.073

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)*esterication 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 transesterification. 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-picryhydrazyl (DPPH) and Fast Blue were acquired from Sigma Aldrich (St. Louise, MO). All solvents and reagents used were either high performance liquid chromatography (HPLC) or analytical reagent 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 n−hexane for 12 h in a Soxhlet extractor.

The FFA content 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). Details 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 was 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 allowed to settle until 2 phases were formed. The upper layer was extracted with hexane and further reacted with BF_3-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 into 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. At a reaction temperature of 523 K, a final system pressure of ~11.5–12.5 MPa was achieved. Heating rate of the reactor was kept at 5 K min^{-1} with a heating period of 40–45 min. When the desired temperature was reached, this was noted as the start time of the reaction. After the desired reaction time was achieved, reactor was rapidly cooled. Pressure inside the reactor was released and products in the reactor were collected at room temperature.

The cooled reaction mixture was vacuum filtered using a Buchner funnel with Advantec No.2 filter paper (8 μm pore size) to separate the spent kernels from the reaction products. The retained solids were washed three times. Each washing was with 30 cm^3 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 cm^3 n-hexane and 25 cm^3 water. The upper layer (hexane fraction) was separated and collected in a flask. The remaining organic phase was re-extracted twice, each with 25 cm^3 hexane. This was done to recover the available FAME. The pooled hexane layers were then washed three times, with 25 cm^3 5% NaCl solution to remove impurities like glycerol. After washing, hexane from the combined extract was evaporated under vacuum using a 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 μm pore size), then fractioned with equal volume of solvents into ethyl acetate fraction (EAF), butanol fraction (BF) and water fraction (WF-2). The un-dissolved organics were then washed and extracted with methanol (50 cm^3). 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

Ultimate analysis was performed with a CHNS analyzer (Elementar Vario EL Cube, Germany) to 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.

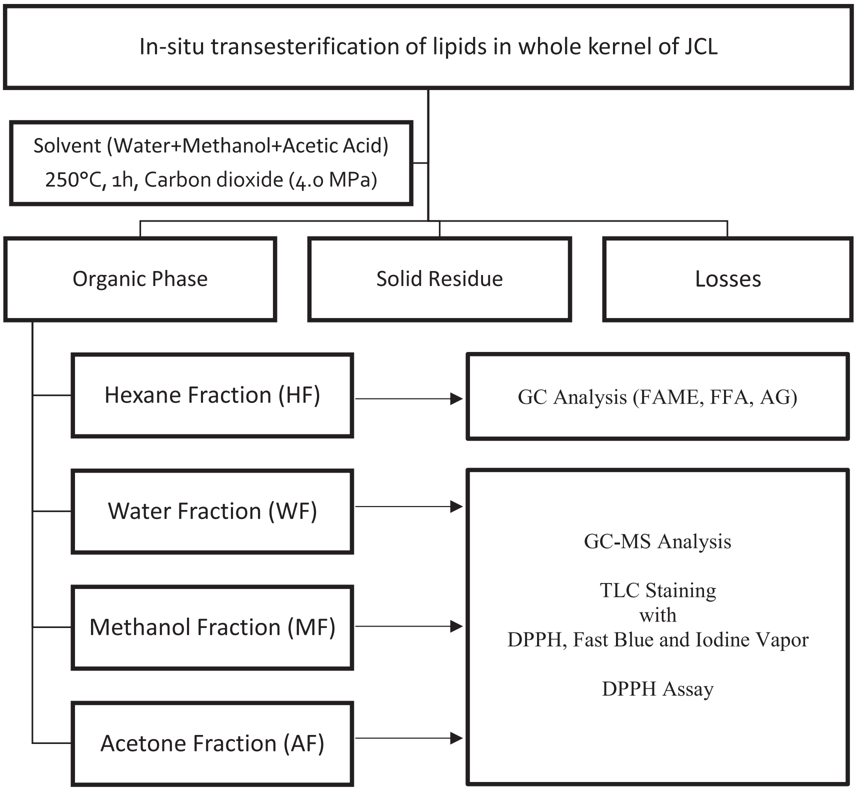

Fig. 1. Schematic flow of the in-situ transesterification process carried out in this study.

3. Results and discussion

Ground *Jatropha* kernels contained about 5% moisture. The hexane extractable crude lipid in the dry solid was 54.08 ± 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 cm^3 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 a mixture of acetic acid, water and methanol were employed as the solvent, solvent to solid ratio (SSR) of 3.3 and 7.0 $cm^3\ g^{-1}$ 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 $cm^3\ g^{-1}$, in situ transesterification of whole kernels resulted in very low FAME yield of about 15%. At an SSR of 7 $cm^3\ g^{-1}$, 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

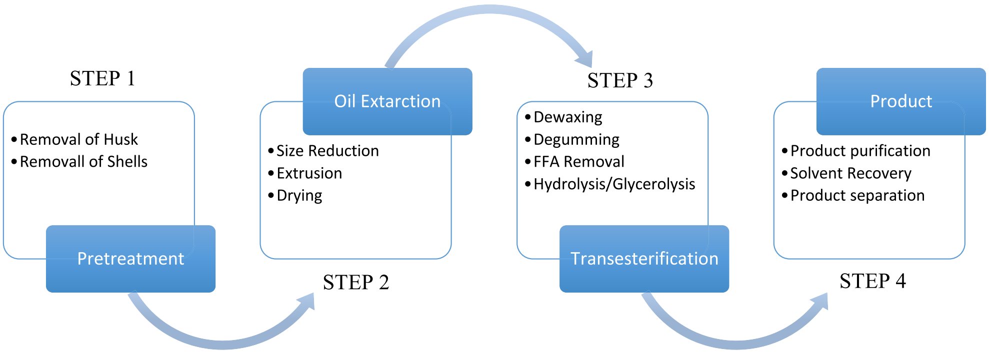

Fig. 2. Steps in biodiesel production.

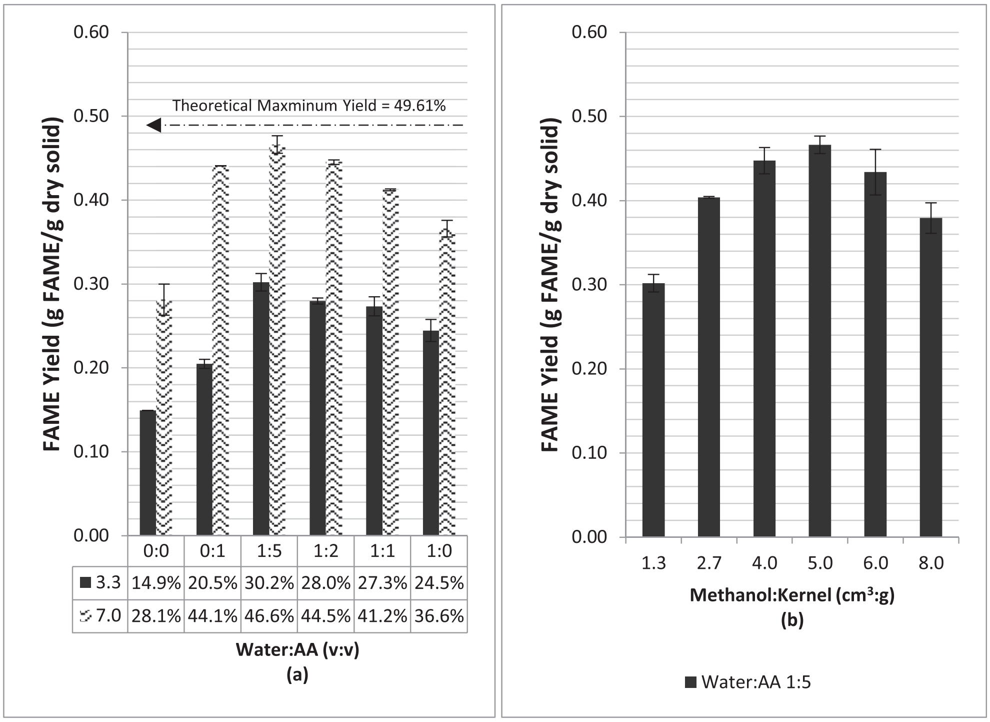

Fig. 3. (a) Effects of ratio of acetic acid to water and SSR on FAME yield, kernel to acetic acid solution fixed at 0.5 g cm^{-3}, with a total SSR of 3.3 or 7 cm^3 g^{-1}. (b) Effect of methanol loading (cm^3 per gram kernel) on FAME yield, kernel to acetic acid solution fixed at 0.5 g cm^{-3} and water 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 cm^3 g^{-1} (SSR = 7 cm^3 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 supercritical 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 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 11–12.5 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.

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 cm^3: 5 cm^3: 15 cm^3).

Gas/Stirring	Final pressure (MPa)	% Yield[b]
Nitrogen without stirring	11.5	46.6 ± 1.0 (86.21)[a]
Nitrogen with stirring	11.5	49.4 ± 1.1 (91.35)
Carbon dioxide without stirring	12.5	48.5 ± 0.2 (99.01)
Carbon dioxide with stirring	12.5	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.

Compared to non in-situ supercritical methanol transesterification the amount of methanol utilized for in-situ process is higher by almost 7 times. Since non in-situ transesterification requires 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 transesterification 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 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] ($cm^3 g^{-1}$)	Temp (K)	Pressure (MPa)	Time (h)	Yield (%)	Ref.
Acid catalyzed (H_2SO_4 21.8%, w/w)	54.6	10.5	333	~0.1	10	98.1[c] (53.53)[d]	[17]
Two-step acid/base with ethanol as solvent (H_2SO_4 7.5%, w/w/5N KOH in ethanol)	32.4	10.5 – Step 1 8.2 – Step 2	Microwave	–	0.76	~90	[18]
Supercritical methanol (process intensification)	66.8	5.0	573	9.5	0.5 (2.0)[b]	99.67 (66.6)	[19]
Supercritical methanol co-solvent (CO_2 50 bars)	64.6	5.0	573	20.0	0.5 (2.0)	102.3 (66.1)	[20]
Supercritical methanol, co-solvent (CO_2 40 bar)	66.8	5.8	568	20.0	0.125 (1.63)	87.1 (58.2)	[11]
Supercritical methanol, co-solvent (CO_2 20 bar)	66.8	5.9	573	20.0	0.21 (1.71)	92.0 (61.5)	[11]
Subcritical methanol – acetic acid (7.5:2.5), co-solvent (CO_2 20 bar)	58.1	7.0	523	21.0	1.0 (1.75)	94.43 (54.72)	[16]
Whole kernels (~5% water content), subcritical methanol - acetic acid-water (15:5:1), co-solvent (CO_2 40 bar)	54.08	7.0	523	12.5	1.0 (1.75)	96.56 (52.2)	This Study

[a] SSR = solvent (methanol + acetic acid + 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.

FAME[a]	Ref [21]	Ref [24]	Ref [25]	This study	
				Before reaction	After reaction
Methyl palmitate (C16:0)	18.2	14.2	14.1–15.3	13.2	13.6
Methyl stearate (C18:0)	5.1	7.1	3.7–9.8	6.8	7.6
Methyl oleate (C18:1)	28.5	43.2	34.3–45.8	48.9	53.5
Methyl linoleate (C18:2)	48.1	34.9	29.0–44.2	30.3	24.6
Saponification value (SV)[b]	200.9	200.3	–	199.6	199.8
Iodine value (IV)[c]	112.7	102.1	–	98.8	92.7
Cetane number (CN)[d]	48.6	50.6	–	51.08	52.5
Cold filter plugging point (CFPP)[e]	−3.2	−2.7	–	−2.8	−1.7

[a] wt. fractions (%) of methyl ester per 100 g sample.
[b] $SV = 560 \sum (w_i/MW_i) \times 100$ [26].
[c] $IV = 254 \sum (D_i\ w_i/MW_i) \times 100$ [26].
[d] $CN = 1.068 \sum (CN_i\ w_i) - 6.747$ [27].
[e] CFPP = 37.02–46.55 MO - 56.16 ML [24].

significantly differs from that of the unreacted lipid. A decrease in methyl linoleate and an increase in both methyl strearate 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 IC_{50} of 7.22 and 2.28 mg/mL for the extract from methanol and water fraction, respectively, suggesting the presence of antioxidant compounds.

Table 4
Product distribution for in situ production of FAME from whole JCL seed kernels. Reaction conditions: 3 g whole kernels, 21 cm^3 solvent mixture (water:methanol:acetic acid = 1:15:5, volume ratio), reaction temperature 523 K, initially pressurized with CO_2 gas to 4.0 MPa, reaction time 1 h.

Whole kernel	Product distribution
Organic phase[a]	**92.20 ± 0.68**[a]
Hexane fraction[a,*] *(HF)*[b]	*57.5*[a] *(62.4)*[b]
FAME[c]	91.6[c]
FFA	5.3
Others	3.1
Water fraction (WF)	*27.0 (29.8)*
Methanol fraction (MF)	*6.7 (7.3)*
Acetone fraction (AF)	*0.96 (1.0)*
Solid residue	**8.75 ± 0.52**
Losses	**(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.

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 compound 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 column temperature. It is possible that some compounds were not detected by GC-MS. Most compounds detected by GC-MS from the

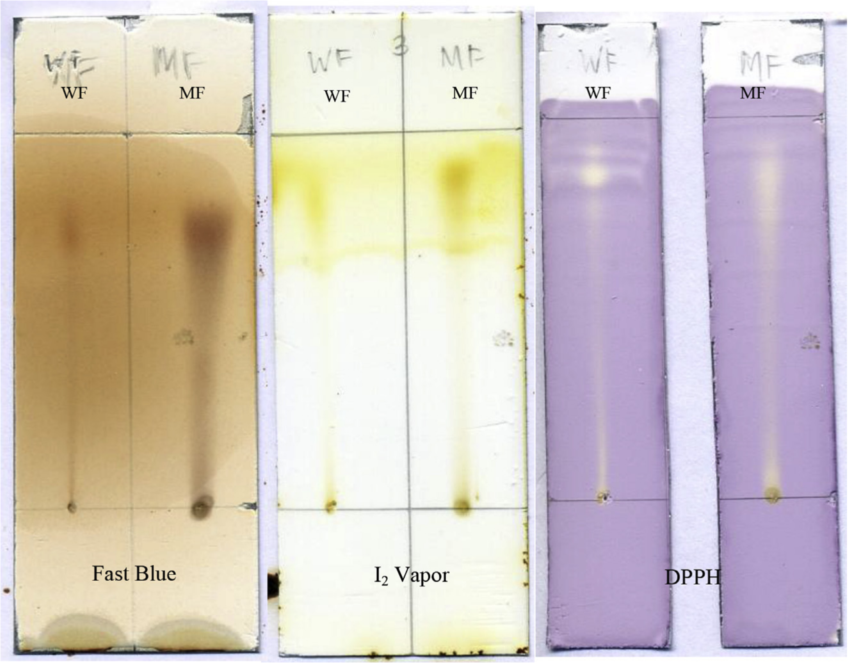

Fig. 4. TLC elution and staining results of water and methanol fractions.

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. DPPH radical scavenging activity of bioactive compounds from the organic extract of methanol and water fraction showed an IC_{50} 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.

Acknowledgments

The authors would like to acknowledge the financial supports of the National Science Council of Taiwan (NSC 101-ET-0-E-011 -003 -ET) and National Taiwan University of Science and Technology (101H451403). Improvement in technical writing by Dr. Fred Quarnstrom is greatly appreciated.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.renene.2015.06.073.

References

[1] B.P., Statistical review of world energy 2013, in: B.S.R.o.W. Energy, British Petroleum, 2013.
[2] C. Martín, A. Moure, G. Martín, E. Carrillo, H. Domínguez, J.C. Parajó, Fractional characterisation of jatropha, neem, moringa, trisperma, castor and candlenut seeds as potential feedstocks for biodiesel production in Cuba, Biomass Bioenergy 34 (2010) 533–538.
[3] S. Karaj, J. Müller, Optimizing mechanical oil extraction of *Jatropha curcas* L. seeds with respect to press capacity, oil recovery and energy efficiency, Ind Crops Prod. 34 (2011) 1010–1016.
[4] A.P. Vyas, N. Subrahmanyam, P.A. Patel, Production of biodiesel through transesterification of Jatropha oil using KNO_3/Al_2O_3 solid catalyst, Fuel 88 (2009) 625–628.
[5] C.-H. Chen, W.-H. Chen, C.-M.J. Chang, S.-M. Lai, C.-H. Tu, Biodiesel production from supercritical carbon dioxide extracted Jatropha oil using subcritical hydrolysis and supercritical methylation, J. Supercrit. Fluids 52 (2010) 228–234.
[6] A. Zarei, N.A.S. Amin, A. Talebian-Kiakalaieh, N.A.M. Zain, Immobilized lipase-catalyzed transesterification of Jatropha curcas oil: optimization and modeling, J. Taiwan Inst. Chem. E 45 (2014) 444–451.
[7] M.K. Lam, K.T. Lee, A.R. Mohamed, Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking

oil) to biodiesel: a review, Biotechnol. Adv. 28 (2010) 500–518.

[8] T. Pinnarat, P.E. Savage, Noncatalytic esterification of oleic acid in ethanol, J. Supercrit. Fluids 53 (2010) 53–59.

[9] J. Lee, S. Kim, H. Yoo, Y. Suh, G. Kang, W. Jang, J. Kang, C. Park, S. Kim, Biodiesel production by enzymatic process using Jatropha oil and waste soybean oil, Biotechnol. Bioproc. E 18 (2013) 703–708.

[10] S. Lim, S.S. Hoong, L.K. Teong, S. Bhatia, Supercritical fluid reactive extraction of *Jatropha curcas* L. seeds with methanol: a novel biodiesel production method, Bioresour. Technol. 101 (2010) 7169–7172.

[11] S. Lim, K.T. Lee, Optimization of supercritical methanol reactive extraction by response surface methodology and product characterization from *Jatropha curcas* L. seeds, Bioresour. Technol. 142 (2013) 121–130.

[12] P.L. Tran Nguyen, A.W. Go, L.H. Huynh, Y.-H. Ju, A study on the mechanism of subcritical water treatment to maximize extractable cellular lipids, Biomass Bioenergy 59 (2013) 532–539.

[13] L. Rajam, D.S. Kumar, A. Sundaresan, C. Arumughan, A novel process for physically refining rice bran oil through simultaneous degumming and dewaxing, J. Am. Oil Chem. Soc. 82 (2005) 213–220.

[14] A. Go, Y.-T. Liu, Y.-H. Ju, Applicability of subcritical water treatment on oil seeds to enhance extractable lipid, Bioenergy Res. 7 (2013) 711–719.

[15] A.W. Go, S. Sutanto, P.L. Tran-Nguyen, S. Ismadji, S. Gunawan, Y.-H. Ju, Biodiesel production under subcritical solvent condition using subcritical water treated whole Jatropha curcas seed kernels and possible use of hydrolysates to grow *Yarrowia lipolytica*, Fuel 120 (2014) 46–52.

[16] A.W. Go, S. Sutanto, Y.-T. Liu, P.L.T. Nguyen, S. Ismadji, Y.-H. Ju, In situ transesterification of *Jatropha curcas* L. seeds in subcritical solvent system, J. Taiwan Inst. Chem. E 45 (2014) 1516–1522.

[17] S.H. Shuit, K.T. Lee, A.H. Kamaruddin, S. Yusup, Reactive extraction of *Jatropha curcas* L. seed for production of biodiesel: process optimization study, Environ. Sci. Technol. 44 (2010) 4361–4367.

[18] H. Jaliliannosrati, N.A.S. Amin, A. Talebian-Kiakalaieh, I. Noshadi, Microwave assisted biodiesel production from *Jatropha curcas* L. seed by two-step in situ process: optimization using response surface methodology, Bioresour. Technol. 136 (2013) 565–573.

[19] S. Lim, K.T. Lee, Process intensification for biodiesel production from *Jatropha curcas* L. seeds: supercritical reactive extraction process parameters study, Appl. Energy 103 (2013) 712–720.

[20] S. Lim, K.-T. Lee, Influences of different co-solvents in simultaneous supercritical extraction and transesterification of *Jatropha curcas* L. seeds for the production of biodiesel, Chem. Eng. J. 221 (2013) 436–445.

[21] S. Hawash, N. Kamal, F. Zaher, O. Kenawi, G.E. Diwani, Biodiesel fuel from Jatropha oil via non-catalytic supercritical methanol transesterification, Fuel 88 (2009) 579–582.

[22] S. Sayyar, Z.Z. Abidin, R. Yunus, A. Muhammad, Extraction of oil from Jatropha seeds-optimization and kinetics, Am. J. Appl. Sci. 6 (2009) 1390.

[23] N. Niza, K. Tan, Z. Ahmad, K. Lee, Comparison and optimisation of biodiesel production from Jatropha curcas oil using supercritical methyl acetate and methanol, Chem. Pap. 65 (2011) 721–729.

[24] Y.-H. Chen, J.-H. Chen, Y.-M. Luo, N.-C. Shang, C.-H. Chang, C.-Y. Chang, P.-C. Chiang, J.-L. Shie, Property modification of jatropha oil biodiesel by blending with other biodiesels or adding antioxidants, Energy 36 (2011) 4415–4421.

[25] G.M. Gübitz, M. Mittelbach, M. Trabi, Exploitation of the tropical oil seed plant *Jatropha curcas* L, Bioresour. Technol. 67 (1999) 73–82.

[26] P. Kalayasiri, N. Jeyashoke, K. Krisnangkura, Survey of seed oils for use as diesel fuels, J. Am. Oil Chem. Soc. 73 (1996) 471–474.

[27] D. Tong, C. Hu, K. Jiang, Y. Li, Cetane number prediction of biodiesel from the composition of the fatty acid methyl esters, J. Am. Oil Chem. Soc. 88 (2011) 415–423.

[28] H.-Y. Shin, J.-H. Ryu, S.-Y. Park, S.-Y. Bae, Thermal stability of fatty acids in subcritical water, J. Anal. Appl. Pyrolysis 98 (2012) 250–253.