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Sylviana Sutanto, Alchris Woo Go, Suryadi Ismadji &

2**Yi-Hsu** Ju **Journal of the American Oil Chemists' Society** ISSN 0003-021X **Volume 92**

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2**Taguchi Method and Grey Relational Analysis to Improve in Situ Production of FAME from Sunflower and Jatropha curcas Kernels with Subcritical Solvent Mixture**

Sylviana Sutanto1 · Alchris Woo Go1,3 · Suryadi Ismadji2 · Yi-Hsu Ju1 Received: 21 March 2014 / Revised: 26 June 2015 / Accepted: 17 August 2015 / Published online: 18 September 2015 © AOCS 2015 Abstract

2**This study investigates the possibility of employing in situ (trans)esterification (ISTE) under the subcritical condition (200–250 °C) of the solvent mixture (methanol acetic acid) with a high solid loading and a low solvent to solid ratio (SSR). The Taguchi method + together with grey**

relational analysis was used to improve both FAME yield and productivity. It was found that tem- perature reaction time and SSR were factors which con- tributed the most in obtaining high FAME yields. In addi- tion to the above-mentioned factors the addition of acetic acid also significantly improved the productivity. Employ- ing the following conditions: 250 °C; 8.8 MPa; 3–7 mL/g SSR; 10 % acetic acid was found to provide an improved FAME yield and productivity. A confirmatory test resulted in a FAME yield of 87.5–92.7 % for sunflower kernels and S. Sutanto and A. W. Go have made equal contributions

11**to this work. Electronic supplementary material The online version of this article (doi:10.1007/** s11746 **-015-** 2714-4) **contains supplementary material, which is available to authorized users.**

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88.2–97.22 % for Jatropha curcas L. kernels and produc- tivity up to 37.5 kg/m3/h can be obtained with good repeat- ability. Furthermore, the process developed in this study can tolerate moisture and a free fatty acid content of up to 25 %. The direct application of the method using whole kernels was also investigated. Keywords Biodiesel · Jatropha curcas · Subcritical methanol · Subcritical acetic acid · Sunflower oil · (trans) Esterification Abbreviations FAME Fatty acid methyl ester(s) FFA Free fatty acid(s) AA Acetic acid JCL Jatropha curcas L SF Sunflower ISTE In-situ (trans)esterification SSR Solvent to solid ratio Introduction In-situ (trans)esterification (ISTE) was first employed using sunflower kernels in acidified methanol by Harrington and D'Arcy-Evans in the 1980s [1, 2]. Acid as a catalyst was preferred as it is more tolerant to moisture and

18**high free fatty acid** (FFA) **content. The** main advan- tage **of** ISTE is **the**

elimination of the extraction step and higher yield of fatty acid methyl esters (FAME) compared to conventional methods [1–3]. Depending on the amounts of alcohol and catalyst used, the ISTE reaction usually requires 10–24 h [1–4]. Considering that both extraction and reaction occurred simultaneously, the time required is still shorter than that of the conventional process where oil is firstly extracted before it can be reacted with methanol to produce FAME. Its main disadvantage is the need to use high amounts of solvents, typically with a solvent to solid ratio (SSR) of at least 10 mL/g. Haas et al. first employed a base-catalyzed ISTE using soybean flakes, distillers dried grains and meat and bone meal as feedstock [4]. In their process, the SSR can be lowered down to 2.4 mL/g but feedstock drying to a moisture content of ~2.6 % and long reaction time (~10 h) were required [4, 5]. Although a conventional base catalyst acts as a stronger catalyst, which leads to lower SSR, it should be noted that the amount of solvent required greatly depends on the amount of oil in the solid feedstock. Georgogianni et al. [6] employed a base catalyzed ISTE on sunflower kernels with

10**an SSR of 10 mL/g and** this resulted in **a** high FAME yield **(~95**

%) in just 20 min. The use of high SSR is undesirable as this leads to low productivity, hence a high cost and high energy consumption in recovering the unreacted methanol [4, 5]. Moreover the use of a catalyst also implies additional cost in its removal and treatment. For ISTE the use of a recoverable (heterogeneous/solid) and environmentally benign (enzyme) catalyst would require specially designed reactors. These types of cata- lyst are usually more expensive but can be reused. Unlike conventional biodiesel production ISTE involves solid feedstock, which poses recovery or separation issues when using a solid catalyst. The other possibility is employing supercritical ISTE in which low SSR is required without the need of a catalyst. One of the early attempts to produce biodiesel via ISTE in supercritical methanol and carbon dioxide utilized rice bran as the feedstock [7]. Despite the short reaction time (10 min) it resulted in a low FAME yield, which was attrib- uted to thermal degradation. Factors affecting ISTE of Jat- ropha curcas L. (JCL) in supercritical solvents were exten- sively studied including the effects of pretreating (drying, grinding and particle size) JCL seed kernels [8, 9], choice of co-solvent [8, 10] and other key factors [11, 12]. An optimized process was developed resulting in a high FAME yield (>92 %) by using an SSR of 5.9 mL/g at 300 °C and an initial pressure of 2.0 MPa using CO2 for a reac- tion time of 12.3 min (a heating up time of 80 to 90 min was required) [12]. In most of these studies a high reaction temperature (300 °C) and drying of the kernels (12 h) were required. Moreover high space loadings (30–54 mL/g) were employed [11, 12], implying low utilization of the reactor's effective volume. In our previous works, acetic acid was employed as a co-solvent and as a catalyst [13, 14]. Acetic acid as a catalyst under subcritical condition enhanced extraction rate and allowed the use of feedstock with moisture up to ~10 % which resulted in faster FAME conversion rate [13]. It was also observed that filling the reactor to its maximum allowable capacity resulted in a decrease in FAME yield [13]. Although a lower operat- ing temperature (250 °C) may be employed for a similar reaction duration as those carried out under supercritical methanol conditions, it has disadvantages including: The need to use high SSR of 7 mL/g; the use of high amount of acetic acid (25 % of the solvent mixture); and requiring the addition of carbon dioxide as a co-solvent. In a sepa- rate study utilizing refined oils, it was observed that upon maximizing the utilization of the reactors effective volume, the amount of methanol and acetic acid could be decreased while still achieving high conversion [15]. In this study, the use of high space loading and low SSR at a fixed total reaction volume was investigated. The possibility of using a low acetic acid concentration was also explored. Previous researches only considered FAME yield as the criteria for the process assessment, in this study both FAME yield and productivity were taken as response variables. The Taguchi method coupled with grey relational analysis was carried out for improving the process and identifying the main fac- tors contributing to the process response. Sunflower (SF) kernels were first used as a model feedstock for the ISTE process. The improved conditions were then applied and confirmed for the said feedstock. Furthermore, the robust- ness of the said process was further investigated by apply- ing it to a different feedstock (JCL kernels), moisture con- taining kernels and kernels with lipid containing high FFA. Materials and Methods Materials SF seeds were purchased from a local supplier in Taiwan while JCL seeds were obtained from Muhammadiyah Uni- versity (Malang, Indonesia). Seeds obtained were sun dried and de-hulled manually. Kernels obtained were ground to particle sizes between 0.71 to 1.0 mm and kept at 20 °C prior to use. Standards of fatty acid (FA), acylgly−cerides (AG) such as monoolein, diolein and triolein and fatty acid methyl esters (FAME) were supplied by Supelco (Bella- fonte, PA).

17**All solvents and reagents** used **were either high performance liquid chromatography (HPLC) or analytical reagent grade, obtained from commercial sources.**

Sample Preparation and Characterization Ground kernels (~5 g) were lyophilized to determine their moisture content [13, 14]. To estimate the amount of extractable lipid, a sample (5 g) was extracted using n-hexane in a Soxhlet extractor. Unsaponifiable matter and FFA contents in the extracted lipid was analyzed using AOCS official methods (Method 6b-53 and Method Ca 5a-40, respectively). Saponified lipids obtained after the 1515 determination of unsaponifiable matter were collected for an FA profile and theoretical maximum FAME yield deter- minations. Detailed analysis procedures can be found else- where [14, 15]. Dewaxing and degumming of the extracted crude lipid was carried out before its AG composition was analyzed using high temperature gas chromatography (HTGC) described elsewhere [16, 17]. In-situ Transesterification Ground seed kernels (21–42 g) containing ~5 % moisture were loaded into a glass chamber (190 mL) and placed in a high-pressure reactor (290 mL). The ground ker- nels were mixed and suspended in a mixture of methanol (120–140 mL) and acetic acid (7–35 mL). A detailed reac- tor description and can be found elsewhere [17]. After the sample was put into the reaction chamber, the reactor was sealed and the chamber was purged with N2. The reactor was equipped with external electric heating and the temperature inside the reactor was controlled to within 2 °C.

18**The reaction was carried out at 200–** 250 **°C for**

a predetermined time (0–90 min). The heating rate ± of the reactor was ~5–6 °C/min with a heating period of 40–45 min. The moment the desired reaction temperature was reached in the reactor was taken as the reaction time zero. After the reaction, the reactor was rapidly cooled, pressure inside the reactor was released and the product was collected at room temperature. The reaction product was vacuum filtered using a Buchner funnel with Advantec No.2 filter paper (8 μm pore size) to separate the solid residue from the reac- tion product. The retained solid was washed three times (each time with 30 mL methanol) to recover the FAME produced. Methanol and acetic acid in the filtrate were removed and recovered using a rotary evaporator oper- ated at 60 °C and 13.3 kPa for 30 min. The concentrated organic extract was then redissolved in 100 mL n-hexane and transferred to a separation funnel. Salt solution (5 % NaCl) was added to aid phase separation. To recover the FAME produced the top FAME-rich hexane layer was transferred to another separation funnel, the organic extract in the first funnel was then re-extracted four times (each time using 25 mL n-hexane, with approx. 15 min between extractions). The recovered FAME-rich layers were pooled and washed four times (each using 25 mL, 5 % NaCl solution, approx. 15 min between washings) in the separation funnel to remove non-lipid products co-extracted by methanol. The solution was allowed to clarify in between washings. The upper hexane phase, which contained FAME, was withdrawn. Hexane from the combined extract was evaporated. The recovered product was weighed and analyzed for its FAME, FA and AG contents. Results of the reaction were evaluated in terms of FAME yield, conversion and productivity. The FAME yield

19**is defined as the** mass **of FAME** (MFAME) **produced per** mass **of**

extractable oil (MOil) loaded into the reactor. This was calculated using Eq. 1, where AFAME is the area calculated from the GC analysis and fc is the external calibration fac- tor (slope of the calibration curve) while Cs and Vs are the concentration and volume of the samples prepared and injected to the GC for analysis, respectively. FAME yield (%) = MFAME × 100% MOil = Mproduct × ∑ AFAME MOil CsVs · fc × 100 % (1) Conversion of FAME was calculated using Eq. 2. The theoretical FAME yield was obtained based on the total convertible lipids to FAME from the extracted crude lipid. Conversion (%) = FAME yield × 100 % (2) Theoretical FAME yield while Eq. 3 was utilized to calculate productivity, which

19**is defined as the** amount **of FAME** (MFAME) **produced per**

rineacclutodrinvgotlhuemteim(Verto=he2a4t0upmtLh)e preearcrteoar.ction time (t in h), Pr oductivity L · h Vrt (kg) = MFAME (3) All values reported are the averages of two experimental trials. Gas Chromatography Analysis A 20-mg aliquot of lipid sample was dissolved in ethyl acetate and filtered through a PTFE hydrophobic filter to remove moisture.

7**External calibration curves were** gener- ated **using 0.2–20 mg of pure standards dissolved in**

n-hep- tane or ethyl acetate.

7**Each calibration curve was** gener- ated **by fitting a straight line with the y-intercept passing through zero (R2 > 0.**

99). Qualitative and quantitative analyses of FAME and un- reacted FA in each sample were performed using a Shi- madzu GC2010 instrument (Kyoto, Japan) equipped with a split-injector and

14**a flame ionization detector. Separation was carried out on a** ZB **-5HT (5 % phenyl)-** methylpoly- siloxane **nonpolar column (15 m 0.32 mm i.d.,** 0.1 mm film thickness) (Zebron, Phenomen×ex, Torrence, CA). Both

8**injector and detector** temperatures **were set at 370 °C. The temperature** program **was** set **at 80 °C, increased to 365 °C at**

15 °C/min and held for 8 min. The total analysis time was 29 min. Nitrogen was used as the

8**carrier gas with a** lin- ear **velocity of 30 cm/s at 80 °C.**

Data analyses were carried out by the software “GC Solution version 2.3”, Shimadzu. The method described above was adopted from a previ- ously established protocol [16, 17]. Analysis of recovered solvents was carried out using a Finnigan TSQ-700

4**GC–MS, equipped with a** DB **-5** MS **capillary column (30 m 0.25 mm 0.25 μm)** and mass spectra **detector** (MSD). The sample **was**

injected in split × × mode with a ratio of 20:1 under helium flow at 1.0 cm3/ min. The

4**initial oven temperature was set at 353 K and ramped to** 553 **K at** 8 **K/min and held for 2 min.**

Tempera- tures of the ion source and interface of the detector were set at 473 and 513 K, respectively. Identification of com- ponents in bio-oil was conducted by comparing the mass chromatogram of the sample with standard database from the National Institute of Standards and Technology. Experimental Design In order to develop a good design of the experiment, some preliminary trials were carried out to avoid unnecessary experiments. Previous studies on ISTE of JCL in subcriti- cal solvent (methanol acetic acid) required to use 25 % acetic acid (AA) in the solvent mixture and reacted at + 250 °C [13, 14]. In a separate study utilizing refined soy- bean oil an AA of 6.25 % was sufficient to achieve a high FAME yield (>90 %) and at a lower solvent requirement once a larger reactor space was utilized [15]. Thus in this work, preliminary studies with SF kernels were done by first utilizing acidified methanol solution containing 0, 6.25 and 25 % AA, where reactions were carried out at 250 °C for 0 and 1 h. All experiments were carried out by filling the glass chamber (190 mL) in the reactor to ~87 % of its capacity, which is about ~70 % of the reactor’s effective volume (240 mL). Experiments based on the Taguchi method were carried out and analyzed statistically using analysis of variance (ANOVA). In the Taguchi method it utilizes the

15**signal-to- noise ratio (S/N) to**

evaluate the response of experimental trials [18, 19]. In this study, high FAME yield and produc- tivity were preferred. The S/N ratio with the higher the better function is defined as [14, 18, 19]: S ( ) N = −10 × log 1 ∑n

1 n y (4) i=1 i 2 where yi is the ith quality parameter (yield) and

6**n is the number of** trials. A factorial **design**

of 34 was carried out using the Tagu- chi L9 orthogonal array and the levels of variables are based on the preliminary experiment. Table S1 in the elec- tronic supplementary is a summary of the operating condi- tions and parameters studied together with its correspond- ing responses. The individual experiments were carried out at random. In the

6**Taguchi method the average** S/N ratios **for each parameter** and **level**

are plotted in a response graph. From the response graph, the level resulting in the highest response for each factor investigated is taken as the factor level providing an improvement to the response investigated. With the level for each factor identified, it then assumes that the contribu- tion of each factor to the overall response is additive. ∑q ypred = ym + ȳi − ym (5) i=1 where ypred is the predicted response of the combination of the identified factors to provide an improved response of the process,

12**q is the number of significant processing parameters,** ym **is the** overall mean **of**

all responses and ȳi

12**is the mean response value of the ith level of the significant processing**

parameter. The predicted responses (yield and productivity of FAME) are confirmed by running a confirmatory test employing the optimum factor levels as analyzed. A confi- dence interval can be calculated using the equation: √ (CI = Fα

20**;1,v2 × Ve × neff 1) + 1 r** (6) **where** Fα **:1,v2** is the **F ratio of significant level**

α, α is the sdieggnriefiec-aonf-tfrleevedelo,m1 −of αpoisoltehde ceorrnofirdevnacreianlecvee,l,VVe2 iiss tthhee pooled error variance and r is the number of repeated trials. On the other hand neff

15**is the number of effective measured results defined as:**

neff = total number of experiments sum of degrees of freedom used in estimating the response + 1 (7) The

15**Taguchi method was** first **successfully applied to** improve in situ FAME production from JCL under sub- critical solvent conditions [14] through improving a single quantity characteristic (FAME yield). In most processes more than one process characteristics (FAME yield and productivity) are involved. Generally a pool of data from various processing and operating conditions are collected and analyzed to understand the relationship between qual- ity characteristics, processing parameters and target values, requiring complicated statistical analysis and sophisticated modeling tools for regression. Grey relational analysis has been found to efficiently transform multiple quality responses into a single grade by measuring the correlation degree between factors based on similarity and/or differences between them [19]. A detailed discussion of the method can be found elsewhere [19]. In brief, similar to the Taguchi method, it converts the quan- tity characteristics (FAME yield productivity) measured into grey relational generation (GRG). Since both high yield and productivity are the preferred responses the higher-the-better principle is again adopted and the quality characteristics are first normalized through: xi∗(k) = maxxi(xki)(k−) −mimnxini(xki)(k) (8) where xi can either be the actual characteristic response or the S/N ratio from the Taguchi method. The normal- ized characteristics are further converted into its differ- ence sequence (Δ0,i (k)) to calculate the grey relational coefficient: ?0,i(k) = |x0(k) − xi(k)| (9) Grey relational coefficient (γ) was determined by: γ0,i(k)=γ xi(k),xj(k) = ??0m,i(ikn)++ζζ??mmaaxx ( ) (10) where the identification coefficient (ζ), ranging from zero to one, in general is set to a value of 0.5 and the average value of the grey relational coefficient is the GRG. The GRG is then sorted in a descending order as the evaluation criterion. A summary of the calculated results is provided in Table S2. Results and Discussion Table 1 summarizes the basic characteristics of sunflower and JCL seed kernels used in this study. Kernels utilized in the following experiments were not dried after grind- ing and both kernels have a moisture content of ~5 %. The average extractable lipids from both kernels are within the range reported in the literature [1–7]. Although JCL kernels contain higher amounts of extractable lipid than SF kernels, their theoretical maximum yields are very similar, due to the higher wax/gum and lower AG contents in JCL kernels. Preliminary Evaluation of Process Parameters Product yields at various solvent to solid ratios (SSR) and AA concentrations are presented in Fig. 1. It is evident that with increasing SSR and AA concentrations, extrac- tion yield increases in all cases. This clearly shows that AA acted as a co-solvent and an acid catalyst. Without AA, FAME decreased with increasing SSR, which is probably due to dilution by methanol. In ISTE extraction and transesterification occur simultaneously. During extraction, a large amount of solvent or higher SSR results in faster extraction due to an increased solva- tion capacity and the increased lipid concentration gradi- ent between solid matrix and solvent. In transesterification, the reaction rate depends on the concentration of lipids and methanol. Since excess methanol was used in this study, methanol concentration may be assumed relatively unchanged, leaving lipid concentration as the main driv- ing force for the reaction. The presence of more methanol would result in dilution of the reaction system, specifically in decreasing lipid concentration. Thus the addition of more methanol improved the extraction of other lipid com- ponents but at the same time resulted in a more dilute sys- tem and thus a slower reaction rate. In a previous study with JCL kernels [13], the dilution effect was observed at an SSR above 10 mL/g, which is significantly higher than that used in this study. The main difference lies in the reactor volume utilized. Only ~15 % of the effective reactor volume was initially occupied in the previous study [13], providing a relatively large void for expansion. In this study, ~87 % of the reactor volume was utilized. Although nitrogen gas was previously used to pressurize the system, a significant portion of methanol was still in the vapor phase. By reducing the reactors void space, the space for gaseous methanol was reduced, which in turn resulted in a pressurized system without the need of Table 1 Characteristics of seed kernels used in this study Components Sunflower Jatrophaa Lipid Kernelb Lipid Kernelb Moisture (%)c Lipid content FFA (%) Wax and gum (%) Unsaponifiables (%) AG (%) Hydrolyzable (%) Theoretical FAME yield (%) – – 2.98 0.11 9.86 0.52 ± 1.49 0.15 ± ~85.67 ± 87.68 0.42 ~92.06 ± 5.38 0.03 45.22 .0.44 ± 1.35 ± 4.45 0.67 ~38.74 49.28 ~41.63 –

– 2.16 0.21 13.73 1.07 ± 1.18 0.06 ± ~82.93 ± 87.38 1.61 ~91.74 ± 4.53 0.08 54.42 .0.86 ± 1.16 ± 7.43 0.64 ~44.84 47.25 ~49.61 a Ref [14] b Based on dry weight of the kernel c Wet basis Fig. 1 Product yields and extraction efficiencies for in situ transesterification of sunflower kernels at different SSR and AA concentrations. Reaction mixtures were heated to 250 °C (0 h) and rapidly cooled down once this temperature was reached % Yield (g product/ g extractable lipid) 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 3 5 7 TG 8.6 36.0 42.9 DG 12.0 17.8 19.7 MG 7.1 3.1 2.9 FFA 5.9 3.0 3.4 FAME 24.2 13.7 12.0 Solvent to Solid Ra?o (mL:g) (a) 0% AA adding pressurizing gas and this also kept most methanol initially fed into the reactor in the liquid phase. The same phenomenon was observed in the (trans)esterification of refined soybean oil, which was carried out in a subcritical

2**solvent mixture** of **methanol** and **acetic acid** at **a high** reac- tor **loading**

[15]. Since acetic acid also acted as an acid catalyst, its pres- ence improved FAME yield at a fixed SSR. Without add- ing AA, FAME yield decreased with increasing SSR due to dilution effect of methanol as describe previously. In the presence of AA, FAME yield remained almost the same with increasing SSR. The dilution effect of methanol at higher SSR still occurred, but, when AA was added, FAME yield did not change with increasing SSR possibly due to the catalytic effect of AA, which kept the rate of FAME formation almost constant. With initial experiments carried out by heating the reac- tor to 250 °C (0 h reaction time), it is clear that the addi- tion of AA and more methanol (higher SSR) could substan- tially improve the extraction yield but the yields of FAME are unsatisfactory even after an approximately fourfold increase in the AA added. Upon reaching 250 °C, the reaction was allowed to con- tinue for 1 h and the results of product yield are summa- rized in Table S3. At the end of 1 h, lipids in the SF ker- nels were completely extracted. The addition of 6.25 % AA in the solvent mixture can achieve comparable FAME yield to that of using pure methanol but at a lower SSR (3 vs 7 mL/g). Reactions carried out in the presence of AA resulted in higher FFA in the final product, which sug- gests that TG was converted first to FFA and subsequently % Yield (g product/ g extractable lipid) 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 3 5 7 TG 12.4 14.8 14.4 DG 17.1 28.8 31.9 MG 6.6 6.2 6.0 FFA 5.9 5.1 4.3 FAME 24.6 25.3 26.1 Solvent to Solid Ra?o (mL:g) (b) 6.25% AA 100.0 % Yield (g product/ g extractable lipid) 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 3 5 7 TG 7.9 9.8 9.5 DG 15.2 24.7 31.0 MG 9.3 11.8 9.6 FFA 9.3 7.7 6.2 FAME 34.1 35.6 37.3 Solvent to Solid Ra?o (mL:g) (c) 25.0% AA esterified, in agreement with the previous findings of Go et al. [15]. At the same acetic acid concentration (6.25 %) but at a higher SSR of 7 mL/g, FFA was reduced significantly which resulted in a FAME yield of 92.75 %. From the preliminary experimental runs it was found that both SSR and addition of AA in the solvent improved FAME yield. Addition of AA at 25 % v/v of the solvent used resulted in better extraction efficiency, however at 250 °C prolonged reaction for an hour using 6.25 % AA not only resulted in high extraction efficiency but also high FAME yield. In a practical perspective addition of less amount of AA is preferable. Acetic acid is more expensive and would require more energy to recover after the reaction when compared to methanol. Temperature upper limit was set at 250 °C in order to keep the reaction system within subcritical condition (details are discussed in "Process Evaluation"). With information from the preliminary exper- iments it was decided that improvements to the reaction response would be carried out by varying SSR, % AA, time and temperature. The most common measure or criteria of the perfor- mance of an ISTE process is the FAME yield and/or con- version. Another important parameter in chemical pro- cesses is process productivity, which is often overlooked. Since ISTE reactions are carried out in the same reactor with fixed volume, a decrease in SSR also implies that more oil bearing seed kernels are being processed, leading to more FAME being produced. In the following experi- mental design study both yield and productivity were taken into consideration in improving the ISTE process for pro- ducing biodiesel.

Yield and Productivity of FAME FAME yield and productivity obtained by ISTE of SF kernels are summarized in Table S1. Based on S/N ratios obtained from experiments, the effects of each factor can be calculated and its average response graph is presented

6**in Fig. 2.** In **the** Taguchi **design of** experiments, **the main**

effect is determined by calculating the difference between the maximum and minimum of the average S/N ratio of each factor. In the case of FAME yield, the main contributing fac- tor was found to be the reaction time (C), while results for FAME productivity showed that temperature (D) was the main contributing factor. The factor response graph (Fig. 2) Fig. 2 Response graph of higher-the-better signal-to-noise ratios of FAME yield (a) and productivity (b) from ISTE of SF kernels reveals that improved responses were achieved at factor levels A3, B3, C3 and D3 for yield and A3, B1, C3 and D3 for productivity. To provide a more objective judgment on the effects of the factors investigated, ANOVA was employed to the raw responses (yield and productivity). From the exper- iments carried out in this study an F ratio greater than 4.3 implies a significant contribution of the factor to the response. From Table 2, we can see that for FAME yield all factors were found to have significant contribution except for acetic acid (A), while time (C) has the highest contribution. For productivity, all factors also contributed significantly with temperature (D) having the greatest contribution. 40 35 30 Mean S/N (db) 25 20 15

9**10 5 0 A1 A2 A3 B1 B2 B3 C1 C2 C3 D1 D2 D3**

Levels (a) Average 30 25 Mean S/N (db) 20 15

9**10 5 0 A1 A2 A3 B1 B2 B3 C1 C2 C3 D1 D2 D3**

Levels (b) Average Table 2 Summary of ANOVA analysis on FAME yield and Factor DOF SS SSE F 0 p value Contribution (%) Rank productivity for in situ (trans) esterification of SF kernels FAME yield A (acetic acid) B (SSR) C (time) D (temperature) Error Total Pooled error FAME productivity A (acetic acid) B (SSR) C (time) D (temperature) Error Total Pooled error 2 2 2 2 9 17 11 2 2 2 2 9 17 9 35.10 168.29 3283.80 1895.29 17.569 5400.05 185.86 269.21 555.06 473.84 840.52 22.00 2160.62 22.00 31.19 164.39 3279.90 1891.39 37.335 264.32 550.17 468.95 835.63 41.55 3.76 19.81 395.33 227.97 28.6 59.59 50.79 90.50 1.00 0.06501987 0.00050515 0.00000000 0.00000002 0.00012596 0.00000644 0.00001252 0.00000110 0.58 3.04 60.74 35.03 0.69 100.08 12.23 25.46 21.70 38.68 1.92 100.00 4 3 1 2 4 2 3 1 F0: F ratio, p: p value (Fcrit 4.3 at p 0.05) DOF degrees of freedom, SS sum of squares, SSE sum of square error = = Fig. 3 Response graph of 1 higher-the-better GRG of 0.9 FAME yield and productivity 0.8 from ISTE of SF kernels 0.7 GRG 0.6 0.5 0.4 0.3 0.2 0.1 0 A1 A2 A3 B1 B2 B3 C1 C2 C3 D1 D2 D3 Factors/Levels Average As can be seen from the preliminary investigation AA acted both as a co-solvent and a catalyst. By adding AA, SSR and time required for extraction were reduced through improved solubility [13, 15]; and the reaction rate was increased by the catalytic effect of AA. Thus AA played a more significant role in FAME productiv- ity than in FAME yield. On the other hand, other factors also contributed significantly to both yield and produc- tivity with time and temperature as the main contribut- ing factors. Taguchi analysis on yield and productivity resulted in two different sets of improved process conditions, with yield having a preference in higher SSR while pro- ductivity in lower SSR. To resolve this, grey relational analysis was employed to obtain a single grade response from two different responses simultaneously. From the response graph in Fig. 3, the favored response levels for each factor considering both yield and productivity are A3, B1, C3 and D3. By employing the improved conditions (250 °C, 8.8 MPa, 3 mL/g SSR, 10 % v/v acetic acid), high FAME yield and productivity can be obtained. The required reaction time was about an hour at 250 °C. It took 45 min to heat the reaction mixture from room temperature to 250 °C, thus an overall reaction time of 1.75 h was required. Using Eqs. (5) and (6) the predicted yield and productiv- ity based on the identified factor levels (A3, B1, C3, D3) was found to be 88.69 2.20 % for yield (96.34 % conver- sion) and 40.59 3.2±4 kg/m3/h for productivity. Confor- mational runs carried out in triplicate resulted in an aver- ± age FAME yield of 87.09 0.70 % (S/N 38.79) and a productivity of 37.46 0.4±2kg/m3/h (S/N =31.47). These tests show that impro±ved conditions can be=well predicted by a simple addition model and the results falls within 95 % CI, showing good reliability of the model while measured responses by the conformational runs (n 3) show repeat- ability of the method. = Effects of Water After sun drying, seed kernels retain some moisture. Haas [4, 5, 20] reported that the removal of moisture to <1 % substantially improved the efficiency of alkaline catalyzed ISTE biodiesel production. ISTE of SF oil using kernels with 5.5–6.2 % moisture content [1, 2, 21] for acid cata- lyzed reactions and 4.6–5.6 % for base catalyzed reac- tions [6, 22] required 1 h drying at 85 °C prior to use. A process capable of tolerating high moisture and/or water content in the reaction mixture is important for two main reasons. Firstly, energy required for drying can be saved. Secondly methanol and AA are very hygroscopic, if the presence of water cannot be tolerated it would require to have a specially designed process for recovery and storage of solvents. Figure 4 shows the effect of moisture on the ISTE pro- cess carried out under the previously improved conditions. It can be seen that insignificant decrease in yield and pro- ductivity was observed even up to a moisture content of ~25 %. Kernel from oil seed typically contains moisture less than 6 %, but other potential feedstock for biodiesel like rice bran and biomass of microbial origins mostly con- tain moisture over 10 %. With this process the drying step can be eliminated or the extent of drying feedstock can be greatly reduced. Applicability to JCL Kernels One of the most studied oil seeds is the JCL kernel. A detailed summary of ISTE reactions carried out with JCL kernels is mentioned elsewhere [13]. The use of JCL ker- nels as feedstock is favored due to their high lipid con- tent. The JCL kernels used in this study contained ~54 % extractable lipid and had a potential of producing ~0.5 g FAME per gram of dry kernels. Table S4 summarizes the results of ISTE reactions of JCL kernels using improved reaction conditions adopted from the ISTE of SF kernels. Fig. 4 Effect of moisture con- tent on yield and productivity of FAME (results are average values from duplicate runs) 100.0% 45.0 95.0% % Yield (g FAME/g Oil) 40.0 90.0% 35.0 85.0% 80.0% 30.0 75.0% 25.0 70.0% 20.0 65.0% 15.0 60.0% 10.0 Produc? vity (kg/m3/h) 55.0% 5.0 50.0% 0.0 0.0% 5.0% 10.0% 15.0% 20.0% 25.0% 30.0% Moisture Content Yield Produc?vity Extraction efficiency (99–109 %) and FAME yield (88– 97 %) based on extractable lipids obtained in this study are comparable to those reported in literature, while a lower space loading of 3 mL/g and a higher fraction of reactor volume (~70 %) were utilized leading to higher overall productivity in this study. Compared to SF kernels, JCL kernels gave higher yield despite more oils being required to be extracted and the same amounts of solvents were used. Considering the stoichiometry of reactions involved the amount of methanol used was in great excess which resulted in a high yield. In ISTE the presence of solid will affect the reaction. Since SF and JCL kernels were ground to the same particle size, the composition and properties of the solid matrix involved will have an effect on FAME yield. A difference between the two kinds of kernel is that the lignin content of SF kernels is ~6–12 % (lipid free basis) [23] and JCL kernels contain only ~0.3–0.5 % lignin [24]. Kernels with a lower lignin content require a shorter time to breakdown their solid matrix, which leads to easier penetration of solvent and faster extraction. Maximal utilization of reactor volume allowed a sub- sequent decrease in acetic acid required for the reaction. The need to use carbon dioxide as a co-solvent was also eliminated thus lowering the reaction pressure. The sever- ity of this process being lower than that of the supercritical ISTE [11, 12] may lead to lower costs in terms of energy consumption and process design. Moreover, ISTE was also conducted with JCL kernels which were left at room tem- perature for 9 months (FFA content ~25 %); high FAME yield (89.72 %) can still be achieved. In addition to being flexible to feedstock source, this process also can tolerant feedstock with a high FFA content. The ISTE process developed in this study does not require stirring. From previous studies it was found that stirring significantly improved FAME yield [13], short- ened reaction time [13, 14] and further lowered down SSR required [13, 15]. The effect of stirring was not investigated in this study. Because low space loading and low SSR were used which resulted in high solid loading in the reactor, stirring with a magnetic stir bar was not possible. Process Intensification As discussed in the previous section, the interaction between solid material and reacting solvent plays a role in the ISTE process. If whole kernels can be used in ISTE reaction, the size reduction step could be eliminated. It was reported that subcritical water-pretreated whole JCL ker- nels could be utilized directly without further size reduc- tion [14]. Since the ISTE process developed in this study is relatively water tolerant, the possibility of directly utilizing whole SF kernels was also investigated and results are sum- marized in Table S5. Runs 1 and 2 (R1, R2) show that at a fixed SSR of 3 mL/g, an increase in AA concentration from 10 to 25 % did not result in higher FAME yield due to a decrease in methanol content in the reaction system. Compared to R3 and R6, an increase in AA concentration resulted in an increase in FAME yield, this is due to the difference in the SSR (7 mL/g) employed. Even at 7 mL/g SSR and 25 % AA, FAME yields (R6 to R9) were still lower than the maximum FAME yield (~88– 92 %) achieved with ground kernels. Addition of CO2 (R4), and prolonged reaction time (1.5 h, R5, R9) had very little effect on FAME yield despite an additional 0.5 h of reac- tion time. Without extra water addition (R8) resulted in the lowest FAME yield at 7 mL/g SSR and 25 % AA. Adding 1.0 mL/g kernel water (R7) also resulted in a lower yield than R6. At a water to kernel ratio of 0.3 mL/g kernel (R6), a reasonably high FAME yield (77.68 %) can be achieved in 1 h when whole kernels were utilized. Apart from lower FAME yield, extraction efficiencies were also lower. The dried solid residue after the reaction was re-extracted with hexane in a Soxhlet extractor for 4 h. Results of ISTE and Soxhlet extraction of the residual solids are sum- marized in Table S6. Compared to ground kernels a significant amount of lipid components was left in the solid residue. Sur- prisingly, extract from the solid residue contained a significant amount of FAME, resulting in an overall FAME yield of over 85 %. This results suggest that the reaction not only take place with the extracted oil but also with oil trapped in solid matrix. This phenomenon was also observed in alkaline catalyzed ISTE of rapeseed by Zakaria and Harvey [25], which they supported with stained microscopic images of the solids. Although lower FAME yield was obtained by using whole SF kernels, the solid residues were easier to separate after the reaction. The use of higher SSR resulted in a similar overall FAME yield to that of ground kernels. Despite the lower pro- ductivity due to higher SSR required, the direct use of whole kernel eliminated the size reduction step. Although further opti- mization on the washing step to fully recover all products from spent kernels and detailed economic analysis on the process are required, this approach offers certain advantages which might be compensated for the lower productivity in the reaction step. Process Evaluation From the Constantinou and Gani method of group contri- butions [26] and the pseudo-triglyceride model proposed by Espinosa et al. [27], critical temperature (Tc) and criti- cal pressure (Pc) of SF were found to be 698.3 °C and 0.34 Mpa, respectively; and for JCL Tc and Pc were found to be 704.1 °C and 0.36 MPa, respectively. For simplicity it is assumed that the system is mainly composed of oil, metha- nPmocelt=h(Ta5nc.o=8l–Mo2i4Pl0am) °.iCxF,tuiPgruecr=eob5t8a.si1nheoMdwPsbay)thLaenodpresAenutAzd–o(BTTecrct=haen3ldo1t9Ptcy°Cpoef, mixing rules [10, 28]. It indicates that with increasing sol- vent content, Tc decreases while Pc increases. The addition of AA on the other hand resulted in an increase in Tc and a decrease in Pc. The temperature employed in this study (250 °C) is below the predicted Tc (265–272 °C). The oper- ating pressure of 8.5 to 11.0 MPa are much higher than the psoreliddicatreed tPack.eInf iwnatoterco(nTscid=er3a7ti3o.n9, °tChePmci=xtu2r2e.s1 pMsePuad)oanTdc Fig. 5 Pseudo-critical tem- perature and pressure of metha- nol–

oil mixture estimated by Lorentz–Berthelot type mixing rules [10, 28] should be much higher and thus it is safe to assume that the system is under subcritical conditions. The use of AA as a catalyst and a co-solvent in this pro- cess offers certain advantages. Less severe operating tempera- ture and pressure are required to achieve high FAME yield than that required for reactions carried out under supercritical conditions. Unlike conventional acid and base catalyst (Table S7), AA maybe recovered easily by distillation or evaporation under vacuum since its boiling point (~118 °C) is lower than that of mineral acids such as sulfuric acid. Compared to other processes, the subcritical ISTE devel- oped in this study requires less solvent but still achieves comparable conversion without using strong alkali or acid. Although it requires much higher temperature and longer reac- tion time than those of alkaline catalyzed reactions, the process can tolerate high FFA and water contents, which are common characteristics of potential non-edible feedstock for biodiesel production. For conventional acid catalyzed process, high yield can also be achieved with kernels containing ~5 % moisture in 1 h reaction time and at a relatively low SSR; however it requires the use of large amount of strong acid (100 % H2SO4 based on oil) [21]. The use of co-solvent allows the reduction in SSR [22], but requires higher amount of catalyst and the cost of co-solvent like DEM may offset the advantage of reducing the amount of methanol. While stirring was not required in this study, most other studies on ISTE required stirring or sonica- tion [6] to promote contact between reacting materials. GC–MS analysis of the recovered methanol revealed the presence of methyl acetate, which was the product of esteri- fication of AA and methanol. This leads to the possibility of simultaneously producing methyl acetate, which is easier to recover than AA due to its lower boiling point (56.9 °C). The use of refined SF oil to verify the catalytic effect of AA was carried out by adding 6.25 % AA or methyl acetate to the solvent mixture and

10**at a solvent to** oil **ratio of** 1 **mL/g**

based on previous study [15]. Reactions were then carried out at 250 °C for 1 h. The use of AA resulted in a FAME yield of 88.5 % while using methyl acetate only resulted in 44.4 %. Methyl acetate may not have the same catalytic effect as AA, but it 700 650 Temperature (°C) 600 550 500 450 400 350 300 250 0 5 10 15 Solvent:Oil (v:m) Methanol 10ª 25ª 8.0 Cri?cal Pressure (MPa) 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 0 5 10 15 Solvent:Oil (v:m) Methanol 10ª 25ª may have acted as a co-solvent since reactions between refined SF oil and methanol only resulted in yield less than 34 %. Conclusion In this study, an improvement in FAME productivity (37.46 kg/m3/h) and FAME yield (87.47 %) in the ISTE of SF oil in subcritical solvent was successfully carried out by

6**using the Taguchi method and grey relational analysis. The** improved **process**

allowed the use of low SSR (3–7 mL/g) and space loading as low as 6 mL reactor space per gram of solid. CO2 as a co-solvent was not required. Maximizing utiliza- tion of reactor volume allowed the use of a lower amount of AA. The developed method can tolerate the presence of water (~25 %) and FFA (~25 %). Its applicability to other oil-bearing seeds like J. curcas L. was tested and resulted in a high FAME yield (88–97 %). Direct utilization of whole seed kernels was also looked into and preliminary results seem encouraging. Acknowledgments The authors would like to acknowledge the

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