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Esterification of sludge palm oil using trifluoromethanesulfonic acid for preparation of biodiesel fuel

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Abstract−Trifluoromethanesulfonic acid (TFMSA) was used to reduce the high free fatty acids (FFA) content in sludge palm oil (SPO). The FFA content of SPO was converted to fatty acid methyl ester (FAME) via esterification reaction. The treated sludge palm oil was used as a raw material for biodiesel production by transesterification process. Several working parameters were optimized, such as dosage of catalyst, molar ratio, reaction temperature and time. Less than 2% of the FFA content was the targeted value. The results showed that the FFA content of SPO was reduced from 16% to less than 2% using the optimum conditions. The yield of the final product after the alkaline transesterification was 84% with 0.07% FFA and the ester content was 96.7%. All other properties met the international standard specifications for biodiesel quality such as EN 14214 and ASTM D6751.

Key words: Biodiesel, Esterification, Free Fatty Acids, Transesterification, Sludge Palm Oil, Trifluoromethanesulfonic Acid

INTRODUCTION

Biodiesel is a promising environmental and alternative fuel for petroleum diesel fuel [1,2]. It is biodegradable, non-toxic and can reduce the CO_2 emission [3,4]. It can be produced via acidic or alkaline catalyzed reactions [5,6]. Esterification and transesterification are the typical reactions to convert the free fatty acid (FFA) and triacylglycerols (TAG) to fatty acid methyl ester (FAME), respectively [7-9]. The raw material is the main cost effective factor in the biodiesel production [10]. Many studies have used low grade oils or fats for preparation of biodiesel such as trap grease [11], soybean soapstock [12], waste cooking palm oil [13], industrial low grade palm oil (LGCPO) [14], acidic crude palm oil (ACPO) [15], and palm fatty acid distillate (PFAD) [16]. Recently, sludge palm oil (SPO) with FFA content of 22.33% was used as agro-industrial raw material for biodiesel production [6]. SPO is generated from oil palm mills in large amounts [17]. Due to the high FFA content in SPO, the biodiesel cannot be produced via the alkaline transesterification reaction. Therefore, strong acidic catalysts were used in the reduction of FFA content such as in PFAD, LGCPO, ACPO and SPO and converted it into FAME. Thus, it is of great importance to investigate the use of a proper catalyst for the production of biodiesel from SPO [15,18]. Many types of catalysts are used for biodiesel production such as homogeneous (sulfuric acid) and heterogeneous (tri-potassium phosphate) [19]. Ferric sulfate, as a heterogeneous catalyst, has been used in the treatment of waste cooking oil, and results show high activity and high conversion of FFA to FAME [20]. Other studies have used biocatalysts such as lipase for biodiesel production via enzymatic esterification reaction [1,21]. Recently, ionic liquids (ILs) were used as a catalyst for the preparation of biodiesel from crude palm oil (CPO) [22]. The main problem behind commercial application of heterogeneous, biocatalyst and ILs in biodiesel production is their high cost compared to homogeneous catalyst. *p*-toluenesulfonic acid (PTSA), sulfuric acid, and methanesulfonic acid (MSA) are the catalysts commonly used for esterification reaction [6,17,18]. Table 1 shows the recent publications related to treatment of high acidity in oils using homogeneous and heterogeneous catalysts. However, very limited studies have used trifluoromethanesulfonic acid (TFMSA) as a catalyst for the pre-treatment of acidic oils. Hashim et al. [23] reported the optimum conditions for pre-treatment of crude palm oil (CPO) using TFMSA. The former study applied two-step processes (esterification and transesterification) to reduce the FFA content in CPO. TFMSA, also known as triflic acid, is one of the strongest acids used in the esterification reaction [23, 24]. There is a need for more studies on TFMSA in terms of catalytic activity for pre-treatment of high FFA content of acidic oils. There is also a need to study the use of TFMSA in the esterification of acidic oils having high content of FFA such as SPO. Therefore, our main goal was to investigate the use of TFMSA in the esterification of SPO to reduce the FFA content to the acceptable limit for biodiesel production. In addition, the effect of main operating parameters was evaluated.

MATERIALS AND EXPERIMENTAL METHODOLOGY

1. Raw Material and Chemicals

SPO was obtained from a local mill, Selangor Darul Ehsan, Malaysia. Methanol 99.8% and potassium hydroxide (KOH) pellets 85% were purchased from R&M Chemicals. TFMSA (CHF_3O_3S) 98%

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Table 1. Literature review summarization of biodiesel production by esterification using acidic catalysts

Feedstock	Initial FFA or AV	Type and concentration of acid catalyst	Optimum conditions of esterification process	Final FFA% or AVmgKOH/g	References
Coconut oil	FFA=12.8%	Sulfuric acid=0.7% v/v	Molar ratio=0.35 v/v Temperature=60 °C, Reaction time=60 min	0.6%	[30] Nakpong et al. (2010)
Waste cooking oil	FFA=38%	Ferric sulfate=2 wt%	Molar ratio=10 : 1 Temperature=95 °C, Reaction time=4 hr	1%	[31] Wang et al. (2007)
Palm fatty acid distillate	FFA=93%	Sulfuric acid=1.834 wt%	Molar ratio=8 : 1 Temperature=70 °C Reaction time=1 hr	<2%	[32] Chongkhong et al. (2007)
Rapeseed deodorizer distillate oil	AV=97.60 mgKOH/g	Cation exchange resin D002 catalyst packed dosage=18 wt%	Molar ratio=9 : 1 Temperature=60 °C Reaction time=4 hr	1.129 mgKOH/g	[33] Lin et al. (2009)
Low grade crude palm oil	FFA=9.3%	Phosphonium-based deep eutectic solvent=1%	Molar ratio=10 : 1 Temperature=60 °C Reaction time=30 min	0.88%	[14] Hayyan et al. (2013)
Low grade crude palm oil	FFA=9.5%	Ammonium-based deep eutectic solvent=0.75%	Molar ratio=8 : 1 Temperature=60 °C Reaction time=30 min	<1%	[34] Hayyan et al. (2013)

was purchased from Sigma-Aldrich.

2. Methods

TFMSA at different acid dosages (0.1-3.5%wt/wt) was added into 30 ml of pre-heated SPO in the presence of methanol. After each run the sample was transferred to a rotary evaporator to evaporate the excess methanol. The sample was then washed with warm distilled water for further purification. FFA content was measured after purification of treated SPO. The esterification of SPO was conducted using lab-scale batch multiunit reactor system with methanol reflux. The mixing intensity for all experimental runs was fixed at 300 rpm. The SPO amount for each experimental run was 20 g. Biodiesel fuel was produced from the SPO via the esterification and transesterification reactions. Single factor optimization was used to design the experiments. Treated SPO was further transesterified using 1% KOH as alkaline catalyst, 10 : 1 molar ratio, 60 min reaction time and 300 rpm stirrer speed. Transesterification reaction forms crude biodiesel, excess methanol and crude glycerol. After reaction the mixture of FAME, methanol and glycerol was transferred to a rotary evaporator to remove the excess methanol while the glycerol was separated via gravity settling for 24 h using a separating funnel. Two layers were formed in the separating funnel, and the upper layer was collected, washed, dried and analyzed for FAME and other characterization.

3. Chemical Analysis

To study the fatty acid composition, GC/MS (Agilent Technologies 7890A gas chromatograph equipped with 5975C mass spectrometer) was used; the capillary column was DBwax 122-7032 with a length of 30 m, film thickness of 0.25 μm and an internal diameter of 0.25 mm. Helium was used as carrier gas with a flow rate of 1 ml/min, measured at 50 °C; the run time was 35 min. One micro liter (1.0 μL) of neat sample was diluted in hexane prior injection into GC. Ester content was analyzed using GC/FID (Perkin Elmer Clarus 500), split-splitless mode of injector, capillary column-polyethylene glycol wax phase, isotherm oven at 250 °C. Monoacylglycerols (MAG), diacylglycerols (DAG, triacylglycerols (TAG), free and total glycerol content were determined using GC/FID (Perkin Elmer Clarus 500). An on-column injector, a high temperature column with polysiloxydivinyl benzene phase (DB-HT type), a mega bore type column, and the temperature program of the oven up to 350 °C setting were used to detect trace compounds. Free fatty acid (FFA) was determined according to the American oil Chemist's Society (AOCS) official method Ca 5a-40 commercial fats and oils [25]. Experiments related to the characterization of SPO were measured according to the Malaysian Palm Oil Board (MPOB) test methods [26]. Catalyst consumption (C.C) is defined as the mass of catalyst consumed per mass of treated SPO after esterification reaction with unit (mg/gm) [6]. Treated SPO yield is defined as the weight percentage of the final product relative to SPO weight at the beginning of experiment. Conversion was calculated is defined as the converted FFA (%) divided by the initial content of FFA (%) [6].

RESULTS AND DISCUSSION

1. SPO Characterization

FFA content in SPO was 16% and according to saponification value the average molecular weight was calculated and found to be 818 g/mol. The main fatty acids composition of SPO was palmitic, stearic, oleic, linoleic acid. The concentration of saturated and unsaturated fatty acid was 47.55% and 52.45%, respectively.

2. Effect of Catalyst

From the esterification reaction it is clear that the molar ratio and the catalyst are the main factors affecting the pre-treatment process. The TFMSA catalyst (CHF_3O_3S) was used to reduce FFA content to less than 2%. Esterification reaction as shown (Fig. 1) used TFMSA catalyst to convert FFA content to FAME. TFMSA catalyst has SO_3H group, which is the main chemical group that reacts with FFA content

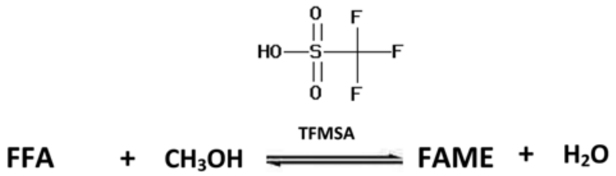

Fig. 1. Esterification of SPO using trifluoromethanesulfonic acid (TFMSA).

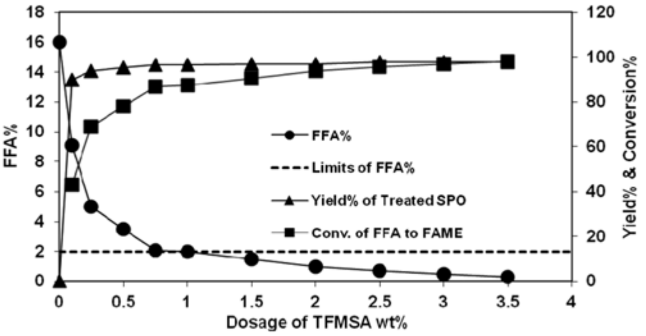

Fig. 2. Effect of dosages of TFMSA on reduction of FFA content, yield of treated SPO and conversion of FFA to FAME at 10 : 1 molar ratio, 60 °C, 30 min reaction time and 300 rpm.

and converts it to FAME. TFMSA is also known as a super acid and one of the strongest acids due to its structure [24]. Dosage of TFMSA to SPO was examined in the range of 0.10 to 3.5%. According to Fig. 2 the FFA content was reduced from 16% to less than 2% using 0.75% or above of TFMSA to SPO. Results of this study showed that 1% of catalyst to SPO reduced the FFA content to slightly less than 2%; therefore, 0.75% of TFMSA was selected to be the optimum dosage for esterification reaction. Hashim et al. [23] found that 0.5% is the optimum dosage of TFMSA which can reduce the FFA content of CPO from 8.3% to around 1%. The optimum dosage of this study is close to that reported by Hashim et al. [23] because the FFA content in SPO was twice the value in CPO. This means that every 0.53% acid value can be converted to FAME at 1 min reaction time. Table 2 shows the effect of dosages of TFMSA on yield of treated SPO and catalyst consumption (C.C). Based on the optimum conditions the yield, C.C and FAME conversion using 0.75% TFMSA were 96%, 7.80 mg/gm (weight of catalyst per weight of prepared treated SPO) and 90%, respectively.

According to the official website of Sigma-Aldrich (2011), the cost of 1 ml of sulfuric acid is RM 5.288, while the cost of TFMSA is RM 15.696, which means that TFMSA costs about three-times more than sulfuric acid. The high cost of TFMSA can be attributed to the sophisticated procedure of TFMSA synthesis and limited applications, among other factors. Additionally, this type of acid is not widely used and is still limited to R&D work only. The main drawback in using TFMSA in the chemical process is the presence of fluorine atoms in their chemical structure. The three fluorine atoms react with air and form white hazardous fumes. The TFMSA may lose its activity due to change of physical properties; therefore, it should be handled carefully and kept in the fume hood. This study is considered as early stage of laboratory work, and according to cost, storage and handling issues, industrially the sulfuric acid is more acceptable compared to TFMSA. Future studies may improve the physical properties of TFMSA and make it more acceptable in a wide range of chemical industrial applications.

Table 2. Effect of dosages of TFMSA on catalyst consumption

TFMSA dosage (wt%)	Catalyst consumption (mg/gm)
0.25	3.21
0.50	5.35
0.75	7.80
1.00	10.33
1.50	19.12
2.00	22.68

3. Effect of Molar Ratio

Molar ratio of methanol to oil is the main factor that increases the total cost of the pre - treatment process of acidic oils or fats; therefore, the optimization of molar ratio is very useful to reduce the cost of pre-treatment process. According to the stoichiometry of esterification reactions (Fig. 1) a molar ratio of 1 : 1 is required. Based on the literature 1 : 1 molar ratio is not enough to reduce FFA content and to produce FAME [6,15]. Thus, a higher molar ratio is needed. In this study, therefore, the reduction of FFA content was optimized using different ratios of methanol to SPO as shown in Fig. 3. As can be seen, a low reduction of FFA content when low loading of molar ratio (5 : 1) is applied while 10 : 1 successfully reduced the FFA content to 2%. Higher molar ratio did not cause significant reduction in the FFA content. The high amount of methanol requires high energy to evaporate and consequently will increase the total cost of biodiesel production. Thus, 10 : 1 was selected to be the optimum molar ratio for esterification of the SPO. When 10 : 1 was added to SPO without addition of TFMSA, 1-2% of FFA content was converted to FAME. In the literature, molar ratios of 8 : 1 and 10 : 1 are the optimum for reduction of FFA in SPO and ACPO [17,18].

4. Effect of Reaction Temperature

Reaction temperature was varied in the range of 40 °C to 70 °C using fixed reaction time (60 min). Fig. 4 shows the effect of reaction temperature on the reduction of FFA content in SPO using TFMSA. The low temperature (40 °C) reduced the FFA content to 3% while 50 °C and 60 °C can reduce the FFA content to 2% and 1%, respectively. On the other hand, higher reaction temperature (70 °C) reduced

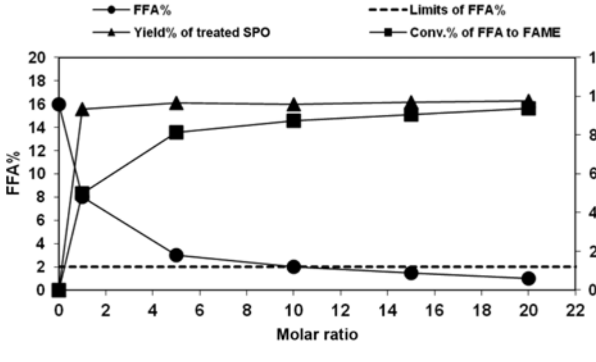

Fig. 3. Effect of molar ratio on reduction of FFA content, yield of treated SPO and conversion of FFA to FAME at 0.75% dosage of TFMSA to SPO, 60 °C reaction temperature, 30 min reaction time and 300 rpm.

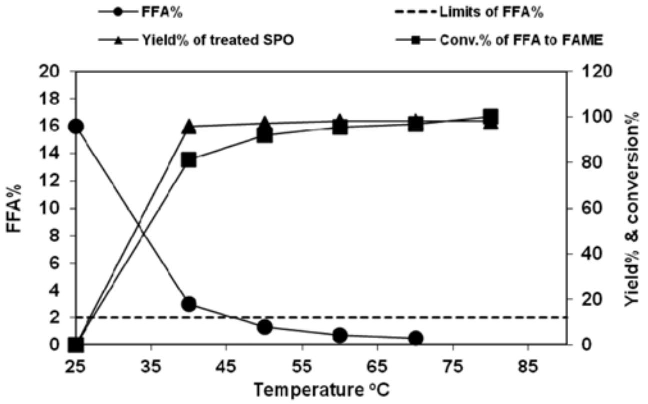

Fig. 4. Effect of reaction temperature on reduction of FFA content, yield of treated SPO and conversion of FFA to FAME at 0.75% dosage of TFMSA to SPO, 10 : 1 molar ratio, 30 min reaction time and 300 rpm.

the FFA content to less than 1%. To save energy and to confirm the treated SPO can be transesterified, a reaction temperature of 60 °C is the optimum reaction temperature. This is in agreement with that reported by Hayyan et al. [6,17] for the pre-treatment of SPO.

5. Effect of Reaction Time

Reaction time is one of the main factors usually studied in the field of esterification of acidic oils [3,5,27,28]. Here, the reaction time was increased up to 120 min. Fig. 5 shows the effect of reaction time on the reduction of FFA content, yield of treated SPO and FAME conversion. It can be seen that the esterification reaction is very responsive to the reaction time and after 30 min 10% of FFA content was reduced. At 40 min the value of FFA was 2%. After 40 min there was no significant change in the FFA reduction. The results of this study are comparable to the previous studies dealing with SPO. It was noted that the reaction time of using TFMSA is shorter than reaction time carried out using PTSA and sulfuric acid [6,17]. This may be due to the chemical structure of TFMSA and its high acid dissociation constant (pKa), which is reported to be −15 mol/kg [24]. The result of this study supports the claim that TFMSA is one of the known strongest acids [23].

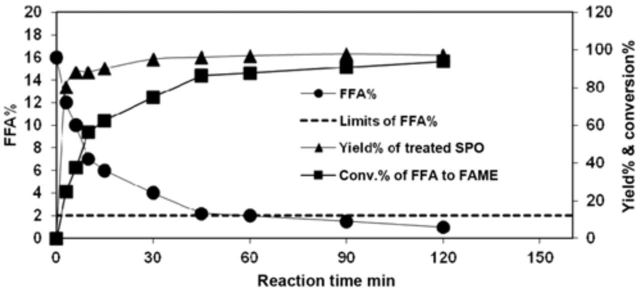

Fig. 5. Effect of reaction time on reduction of FFA content, yield of treated SPO and conversion of FFA to FAME at 0.75% dosage of TFMSA to SPO, 10 : 1 molar ratio, 60 °C reaction temperature and 300 rpm stirrer speed.

Using fixed experimental conditions we found that both acids (TFMSA and sulfuric acid) show high catalytic activity. TFMSA can enhance the reaction and may reduce the time of the reaction compared to sulfuric acid, but sulfuric acid is cheap and available in bulk quantities. Consequently, the process using sulfuric acid is more economically acceptable compared to that using TFMSA. The reaction rate was determined in this study. The results showed that the esterification reaction using TFMSA is a second-order reaction. The value of R^2 (0.98) indicated that the theoretical FFA content obtained from the corresponding regression equation was fitted with actual values. The pretreatment of SPO by the esterification reaction via TFMSA catalyst has rate constant $k=0.0075\ \mathrm{min}^{-1}$.

6. Transesterification of Treated SPO

In the course of esterification reaction the FFA content is converted to FAME using an acidic catalyst such as TFMSA. It was shown in this study that not all FFA content is converted to FFA. There was about 2% of FFA content still in the treated SPO. Transesterification reaction using alkaline catalyst was used to convert the TAG to FAME as well as neutralize the rest of FFA content or convert them to FAME. We found that 2% of FFA in treating SPO was

Table 3. Specifications of biodiesel from SPO

Properties	Biodiesel from SPO	EN 14214 Limits	ASTM D6751 Limits
Ester content	96.7	96.5% mol mol^{-1} min (EN 14103)	-
Monoacylglycerol content	0.055%	0.80% mol mol^{-1} max (EN 14105)	-
Diacylglycerols content	0.02%	0.20% mol mol^{-1} (EN 14105)	-
Triacylglycerols content	<0.012%	0.20% mol mol^{-1} max (EN 14105)	-
Free glycerol content	<0.02%	0.02% mol mol^{-1} max (EN 14105)	0.020% (w/w) max (ASTM D 6584)
Total glycerol content	0.05%	0.25% mol mol^{-1} max (EN 14105)	0.240% (w/w) max (ASTM D 6584)
water content	<400	500 mg kg^{-1} max (EN ISO 12937)	0.050% (v/v) max (ASTM D 2709)
K content	1	5.0 mg kg^{-1} max (EN 14108)	5.0 mg kg^{-1} max (UOP 391)
P content	7.11	10.0 mg kg^{-1} max (EN 14107)	0.001% (w/w) max (ASTM D 4951)
Density (15 °C)	877	860-900 kgm^{-3} (EN ISO 3675)	-
Flash point	182.95	120 °C min (EN ISO 3679)	130 °C min (ASTM D 93)
Sulphated ash	<0.005%	0.02% (w/w) max (ISO 3987)	0.020% (w/w) max (ASTM D 874)
Total contamination	0.009	24 mg kg^{-1} max (EN 12662)	-
Acid value	0.06	0.50 mg KOH g^{-1} max (EN 14104)	0.50 mg KOH g^{-1} max (ASTM D 664)
Copper strip corrosion (3 hours at 50 °C)	Class 1	Class 1 rating (EN ISO 2160)	No. 3 max (ASTM D130)

converted to FAME and some impurities. Therefore, the two-step process is a very useful technique to produce high quality of FAME (biodiesel fuel) [3]. We used KOH as a catalyst in this study in the transesterification reaction with 1% dosage of catalyst. While the molar ratio methanol to oil was 10 : 1, reaction time 60 min, 300 rpm stirrer speed and 60 °C reaction temperature [29]. The final yield of biodiesel fuel produced from treated SPO was 84% with 96.7% of FAME content.

7. Characterization of SPO Biodiesel

The main fatty acid compositions of biodiesel from SPO were C18:1, C16:0, C18:2, C18:0. The palmitic acid and oleic acid were the highest fatty acid concentration in FAME of SPO. The fatty acid composition of palm oil and SPO was compared and the two types of oils shared the same fatty acid compositions. The two types of fatty acids (palmitic acid and oleic acid) were the highest concentration in the two types of oils. A saturated fatty acid such as palmitic acid shows an unfavorable property to be used in the cold countries due to crystallization phenomena of fuel during storage in cold conditions. In contrast, palmitic acid and other saturated fatty acids possess useful properties for hot countries and can increase the cetane number and reduce oxidation [3,5]. Table 3 shows the specifications of biodiesel from SPO, and the results meet the international standards for qualification of biodiesel fuel (EN 14214 and ASTM D6751).

CONCLUSION

Sludge palm oil can be considered as a cheap and promising feedstock for biodiesel production. TFMSA shows very high catalytic activity to reduce the FFA content in SPO compared to other types of acids. The optimum results using TFMSA as a super acid catalyst in the esterification of SPO were 0.75% TFMSA to SPO (wt/wt) with 10 : 1 molar ratio (methanol to SPO), 60 °C reaction temperature and 40 min reaction time. After the determination of the optimum conditions, the FFA content was reduced from 16% to less than 2% using TFMSA. The FFA content of the biodiesel produced from treated SPO was 0.07% using two-step processes. The ester content of biodiesel was about 96.7% after transesterification reaction and the yield was 84%. Further studies are needed to investigate the possibility of using this catalyst in pilot plant scale process. In addition, the mechanism and kinetics of the reactions are also important to determine the rate and order of reaction.

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REFERENCES

1. L. A. Nelson, T. A. Foglia and W. N. Marner, *JAOCS*, **73**, 1191 (1996).
2. A. Demirbas, *Biodiesel a realistic fuel alternative for diesel engines*, Springer, London (2008).
3. M. Canakci and V. J. Gerpen, *Trans. ASAE*, **44**, 1429 (2001).
4. S. Mori, *Environ. Eng. Manage. J.*, **19**, 67 (2009).
5. M. Canakci, *Bioresour. Technol.*, **98**,183 (2007).
6. A. Hayyan, Md. Z. Alam, M. E. S. Mirghani, N. A. Kabbashi, N. I. N. M. Hakimi, Y. M. Siran and S. Tahiruddin, *Bioresour. Technol.*, **101**, 7804 (2010).
7. A. S. Ramadhas, S. Jayaraj and C. Muraleedharan, *Fuel*, **84**, 335 (2004).
8. Y. C. Sharma, B. Singh and S. N. Upadhyay, *Fuel*, **87**, 2355 (2008).
9. X. Hou, Y. Qi, X. Qiao, G. Wang, Z. Qin and J. Wang, *Korean J. Chem. Eng.*, **24**, 311 (2007).
10. F. Ma and M. A. Hanna, *Bioresour. Technol.*, **70**, 1 (1999).
11. J.-Y. Park, J.-S. Lee, Z.-M. Wang and D.-K. Kim, *Korean J. Chem. Eng.*, **27**, 1791 (2010).
12. Z.-M. Wang, J.-S. Lee, J.-Y. Park, C.-Z. Wu and Z.-H. Yuan, *Korean J. Chem. Eng.*, **24**, 1027 (2007).
13. A. Buasri, B. Ksapabutr, M. Panapoy and N. Chaiyut, *Korean J. Chem. Eng.*, **29**, 1708 (2012).
14. A. Hayyan, M. A. Hashim, F. S. Mjalli, M. Hayyan and I. M. AlNashef, *Chem. Eng. Sci.*, **92**, 81 (2013).
15. A. Hayyan, F. S. Mjalli, M. A. Hashim, M. Hayyan, I. M. AlNashef, S. M. Al-Zahrani and M. A. Al-Saadi, *Bioresour. Technol.*, **102**, 9564 (2011).
16. S. Hong, H. Cho, S. Kim and Y. Yeo, *Korean J. Chem. Eng.*, **29**, 18 (2012).
17. A. Hayyan, Md. Z. Alam, M. E. S. Mirghani, N. A. Kabbashi, N. I. N. M. Hakimi, Y. M. Siran and S. Tahiruddin, *Fuel Process. Technol.*, **92**, 920 (2011).
18. A. Hayyan, F. S. Mjalli, M. A. Hashim, M. Hayyan, I. M. AlNashef and S. M. Al-Zahrani, *Chem. Pap.*, **66**, 39 (2012).
19. G. Guan, K. Kusakabe and S.Yamasaki, *Fuel Process. Technol.*, **90**, 520 (2009).
20. S. Gan, H. K. Ng, C. W. Ooi, N. O. Motala and M. A. F. Ismail, *Bioresour. Technol.*, **101**, 7338 (2010).
21. G. K. Khor, J. H. Sim, A. H. Kamaruddin and M. H. Uzir, *Bioresour. Technol.*, **101**, 6558 (2010).
22. Y. A. Elsheikh, Z. Man, M. A. Bustam, S. Yusup and C. D. Wilfred, *Energy Convers. Manage.*, **52**, 804 (2011).
23. M. A. Hashim, A. Hayyan, F. S. Mjalli, M. Hayyan and I. M. AlNashef, *Int. J. Sus. Water Env. Syst.*, **3**, 19 (2011).
24. R. D. Howells and J. D. McCown, *Chem. Rev.*, **77**, 69 (1977).
25. American Oil Chemists' Society (AOCS), *Ca 5a-40: free fatty acids, Official Methods and Recommended Practices of the AOCS*, 5th Ed. American Oil Chemists' Society Press, Champaign, IL (1997).
26. A. Kuntom, S. W. Lin, T. Y. Ai, N. A. Idris, M. Yusof, T. T. Sue and N. A. Ibrahim, *Malaysian Palm Oil Board (MPOB) Test Methods*, MPOB, Bangi-Malaysia (2005).
27. X. Deng, Z. Fang and Y. H. Liu, *Energy Convers. Manage.*, **51**, 2802 (2010).
28. F. F. P. Santos, J. Q. Malveira, M. G. A. Cruz and F. A. N. Fernandes, *Fuel*, **89**, 275 (2010).
29. M. Hayyan, F. S. Mjalli, M. A. Hashim and I. M. AlNashef, *Fuel Process. Technol.*, **91**, 116 (2010).
30. P. Nakpong and S. Wootthikanokkhan, *Renew. Energy*, **35**, 1682 (2010).
31. Y. Wang, S. Ou, P. Liu and Z. Zhang, *Energy Convers. Manage.*, **48**,

184 (2007).

32. S. Chongkhong, C. Tongurai, P. Chetpattananondh and C. Bunyakan, *Biomass Bioenergy*, **31**, 563 (2007).
33. Y. Lin, L. Wang and Y. Yan, *Fuel Process. Technol.*, **90**, 857 (2009).
34. A. Hayyan, M. A. Hashim, M. Hayyan, F. S. Mjalli and I. M. AlNashef, *Ind. Crops Products*, **46**, 392 (2013).