REDUCTION OF FREE FATTY ACIDS IN CRUDE *JATROPHA CURCAS* OIL VIA AN ESTERIFICATION PROCESS

Azhari[1], M. Faiz[1], R. Yunus[1*], T.I Mohd. Ghazi[1], and T.C.S Yaw[1]
[1]Department of Chemical and Environmental Engineering, Faculty of Engineering, Universiti Putra Malaysia
43400, Serdang, Selangor, Malaysia.
Email: robiah@eng.upm.edu.my

ABSTRACT

An important consideration in the feedstock selection for biodiesel production is the content of free fatty acid (FFA) in the oil. In this project, the Jatropha curcas oil (JCO) was used as the feedstock for producing biodiesel. To be used as a feedstock, the JCO should contain a low percentage of FFA so that the oil can directly be utilized in a transesterification reaction with methanol in the presence of an alkaline catalyst. Since, the free fatty acid contents in the JCO were found to vary from 2.5% to 65%, the FFA content in the oil was reduced via esterification of JCO with methanol and sulphuric acid as a catalyst. In this study, the effects of esterification parameters namely the time of reaction, temperature, catalyst-to-JCO ratio and methanol-to-JCO ratio on the final free fatty acid content of JCO were studied. The final FFA content of JCO was successfully lowered to 0.5% at 60°C under atmospheric pressure, using 1.0% of catalyst-to-JCO ratio, 60% w/w of methanol-to-JCO ratio, and 180 minutes of reaction time. Without prior removal of FFA, a large quantity of fatty soap was formed in the reaction and the entire products become gel-like materials. However, after using two-steps reaction consisting of the esterification followed by transesterification, the yield and quality of product are markedly enhanced.

Keywords: *free fatty acid, transesterification, jatropha curcas oil*

INTRODUCTION

In the biodiesel production, to obtain Jatropha curcas methyl esters (JME), the *jatropha curcas* oil (JCO) was subjected to a chemical reaction termed transesterification. In that reaction, the JCO was reacted in the presence of an alkaline catalyst with methanol to give the corresponding methyl esters. Berchmans and Hirata [1] reported that the alkaline base catalyzed transesterification depended on several basic variables. One of them was the level of FFA in the feedstock should be less than 1% [2-3]. Therefore, to be used as a feedstock in biodiesel production, the JCO should contain a low percentage of free fatty acids (FFA) so that the oil can directly be utilized in a transesterification reaction with alcohol as an excess reactant in the presence of an alkaline catalyst. Otherwise, the saponification shall occur and the separation of products shall be exceedingly difficult, and as a result, the yield of biodiesel product would be low. The free fatty acid values in the JCO were found to vary from 2.5 to 65%.

Some researchers also (Marchetti and Errazu) [4] reported that if the feedstock has a high amount of free fatty acids, much higher than the maximum amount suitable to be used with basic homogeneous catalyst, high amount of soap would be produced simultaneously with the transesterification reaction. Therefore, to avoid this reaction, alternative technology should be used for example with a homogeneous acid catalyst, solid resins, enzymes or in supercritical process [4-5]. Chung et al. [6] stated that due to the corrosion problem, these homogeneous catalyst-based processes involved elaborate process steps for removal of FFA and water from the feedstock and catalyst from the products.

In many cases, *jatropha curcas* oil (JCO) quality deteriorates gradually due to improper handling and inappropriate storage condition. It was known that improper handling of the oil would cause the moisture content of the JCO to increase. In addition, exposing the oil to open atmospheric air and sunlight for long time would cause the concentration of FFA to increase significantly. The FFA content of the oil would vary and depend on the quality of feedstock [1]. Furthermore, other researchers have worked with raw materials having higher FFA levels using alternative processes, which included pretreatment step to reduce the FFA of these raw materials [2].

In order to reduce the content of FFA in the JCO, a preliminary treatment of the oil must be done through the esterification reaction process. Marchetti and Errazu [4] reported that the direct esterification reaction of the FFA in the presence of TGs was studied using a model acid oil. Sulphuric acid was used as catalyst and ethanol was used as alcohol instead of methanol since ethanol was safer to handle. Besides the esterification reaction using sulphuric acid, Ni and Meunier [7] stated that the esterification of FFA found in vegetable oils with methanol using a solid catalyst was another promising method to convert FFA into valuable fatty acid.

The measurement of FFA content was a relatively simple test to evaluate the quality of the frying fat or oil. The test however, did not provide complete information about the adequacy of lipids for further use [8]. In this study, the determination of FFA was very important to determine the degree of deterioration, as it evaluates the extent of hydrolysis. Osawa et al. [9] reported that the FFA determination was also a measurement intimately linked to the nature and quality of the raw material, quality and degree of purity of the oil. It was calculated as the percentage of a specific FFA predominant present in the sample, for example, oleic acid or palmitic acid. The procedure involves sample dilution in a neutralized solvent, followed by titration with a standard NaOH solution, in the presence of phenolphthalein as indicator.

In this study, the effects of esterification parameters on the final free fatty acid content of JCO were studied. Among the parameters considered in this study were the time of reaction, temperature, catalyst-to-JCO ratio and methanol-to-JCO ratio. JCO with high and low FFA content were both transesterified to determine the effect of FFA content on the yield and quality of biodiesel (JME).

MATERIALS AND METHODS

Materials

Jatropha curcas oil was obtained through the following steps: firstly the *jatropha curcas* seeds were dried, de-shelled and crushed by using a crusher. The crushed seeds were extracted in an extractor using a non polar solvent, hexane (96% purity). The resulting oil was filtered and evaporated to separate the oil from the solvent. Fatty acid composition of JCO was given in Table 1. The isopropanol of 99.7% purity, phenolphthalein of 1% and NaOH of 99% purity were used for the determination of free fatty acids content of JCO. The JCO used in this study contained 25.3% of FFA. While for the esterification reaction, methanol of 99.8% purity and sulphuric acid of (H_2SO_4) 95-98% purity were employed. Potassium hydroxide (KOH) of 85% purity was utilized as catalyst in the transesterification reaction.

Equipment

Experiments were conducted using the following apparatus namely the three neck flask, graham condenser, thermometer, heater completed with stirrer, separator funnel, burette, and other related glass wares.

Table 1: Fatty acid composition of jatropha curcas oil[*]

Fatty acid	Formula	Systemic name	Structure	Weight (%)
Myristic	$C_{14}H_{28}O_2$	Tetradecanoic	14:0	0-0.1
Palmitic	$C_{16}H_{32}O_2$	Hexadecanoic	16:0	14.1-15.3
Palmitoleic	$C_{16}H_{30}O_2$	*cis*-9-Hexadecanoic	16:1	0-1.3
Stearic	$C_{18}H_{36}O_2$	Octadecanoic	18:0	3.7-9.8
Oleic	$C_{18}H_{34}O_2$	*cis*-9-Octadecanoic	18:1	34.3-45-8
Linoleic	$C_{18}H_{32}O_2$	*cis*-9,*cis*-12-Octadecedianoic	18:2	29.0-44.2
Linolenic	$C_{18}H_{30}O_2$	*cis*-6,*cis*-9,*cis*-12-Octadecatrienoic	18:3	0-0.3
Arachidic	$C_{20}H_{40}O_2$	Eicosanoic	20:0	0-0.3
Behenic	$C_{22}H_{44}O_2$	Docosanoic	22:0	0-0.2

[*] Source from [10].

Experimental procedure

In this study, the pre-treatment step was carried out by following the esterification reaction. Firstly, the JCO was heated in the three neck flask reactor. The solution of sulphuric acid (H_2SO_4) in methanol at various concentrations ranged from 0.5 to 1.5% w/w was heated at the specified temperature, and then added into the reactor containing the heated JCO. The ratio of methanol to JCO ratio was varied at 50%, 60% and 70% w/w and the time of reaction was varied at 60, 120 and 180 minutes. After the reaction was completed, the mixture was allowed to settle down for 2 hours and the methanol water fraction at the top layer was removed. The optimum condition having the lowest acid value was utilized as the feedstock for transesterification reaction.

Analytical procedure

The free fatty acids content of the sample was determined using acid base titration technique. A standard solution of 0.1N sodium hydroxide (NaOH) solution was used. The titration method involved the following method. The neutralized isopropanol was prepared by placing 50 ml isopropanol in a flask and bring the solution to boil on a hot plate. Added about 0.5 ml of phenolphthalein and neutralized by drop-wise addition of 0.1N sodium hydroxide till a faint, but permanent pink colour was obtained. To prepare sample for analysis, weighed the specified amount of sample into an Erlemeyer flask. In this study, the weight of sample was taken around 2.5 g. Added 50 ml of the neutralized solvent. Placed the flask on the hot plate and regulate the temperature to about 40 ºC. Shake the sample gently while titrating with standard alkaline to the first permanent colour. The colour must persist for 30 minutes [11].

RESULTS AND DISCUSSIONS

FFA content in JCO

After the *jatropha* seed was extracted, JCO was stored for a long time prior to utilization. The quality of JCO would deteriorate due to the improper handling and storage. Berchmans and Hirata [1] reported that various chemical reactions such as hydrolysis, polymerization and oxidation caused the deterioration of oil quality. Therefore, the chemical and physical properties of JCO changed during handling and storing. The value of FFA has been found to increase due to the hydrolysis of triglycerides in the presence of moisture and oxidation.

Table 2: The FFA content of JCO, RBDPO and CPO

No.	Oil	FFA (%)
1	*Jatropha curcas* oil (JCO)	25.3
2	Refined bleached deodorized palm oil (RBDPO)	0.031
3	Crude palm oil (CPO)	6.1

The FFA content of some oils is given in Table 2 for comparison. JCO contains higher value of FFA when compared to RBDPO and CPO. This is because of poor handling and storage of the *jatropha* seed. The degradation of the oil in the nuts could occur through hydrolysis of oil in the presence of humid air. Canakci [12] reported that the possible oxidation of the unsaturated fatty acids component in JCO occurred easily and it could also lead to degradation of the oil. The reason for auto oxidation is due to the double bonds in the chains of unsaturated fatty acids compounds.

Esterification of *jatropha curcas* oil

The main purpose of this study was to reduce the FFA content of *jatropha curcas* oil (JCO) to the acceptable level of below than 1%. This was achieved via esterification of JCO with methanol and sulphuric acid as a catalyst. Important variables affecting the FFA content in the esterification process were the reaction time, methanol to JCO ratio, the acid to JCO ratio, and reaction temperature. In this experiment, the initial free fatty acids (FFA) content in JCO was 25.3%.

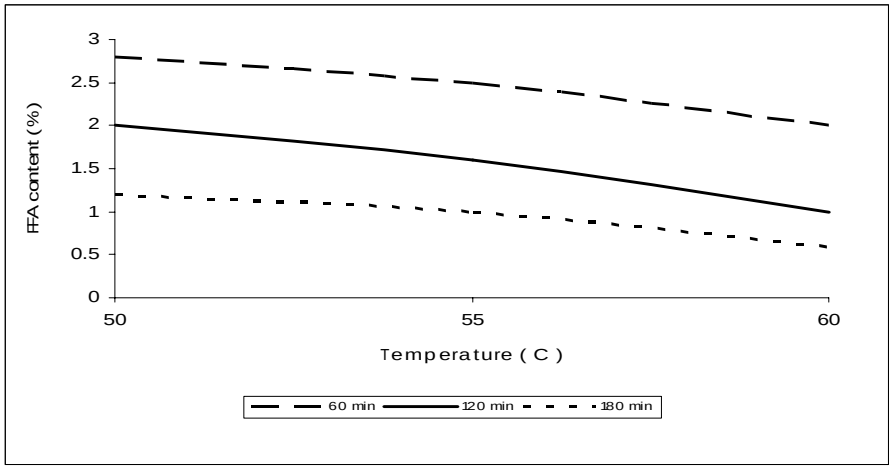

Figure 1: Effect of temperature on esterification reaction at various reaction times (catalyst to JCO ratio, 1% w/w and methanol to JCO ratio, 60% w/w)

Effect of reaction temperature

In order to determine the effect of temperature on the percentage value of FFA in JCO, the esterification reaction was carried out at 50, 55 and 60 °C with variable amount of sulphuric acid (H_2SO_4). The aim was to observe the effect of temperature change on the concentration of FFA in JCO. The effect of temperature on the esterification reaction of *jatropha curcas* oil (JCO) with methanol is shown in Figure 1. As expected, the lowest FFA content in the JCO was achieved at the highest temperature, 60 °C. Below this temperature, the FFA content in JCO was still higher than 1%. Even though, the reaction time was extended to 180 minutes.

Effect of sulphuric acid concentration

Previous study on esterification reaction of *jatropha curcas* oil (JCO) had clearly suggested that the FFA concentration could be affected by the amount of sulphuric acid as catalyst. Ghadge and Raheman, [13] reported that the esterification of some vegetable oils could be carried out at reaction temperature of 50ºC, 60 minutes reaction time, and sulphuric acid to oil ratio of 1% w/w. In this study, the variation of sulphuric acid to JCO ratio was fixed at 0.5, 1 and 1.5% w/w.

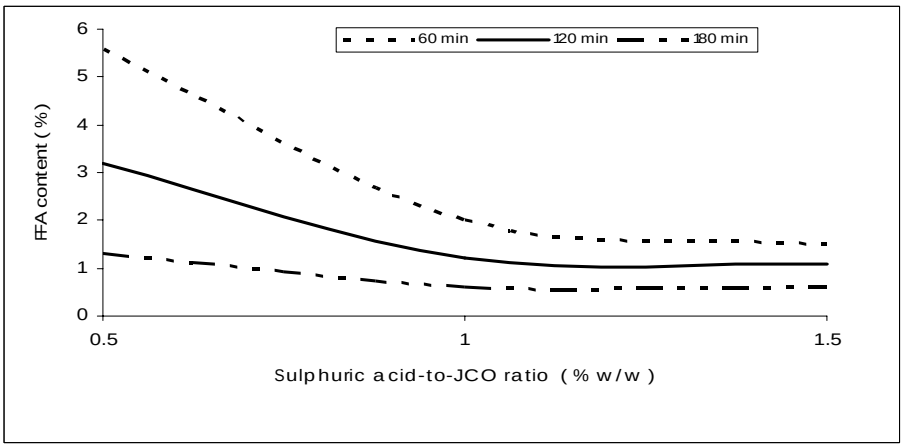

Figure 2: Effect of sulphuric acid to JCO ratio on esterification reaction at various reaction times (reaction temperature, 60 °C and methanol to JCO ratio, 60% w/w)

The effect of sulphuric acid to JCO ratio on the FFA concentration in JCO is shown in Figure 2. From the initial FFA concentration of 25.3%, the FFA content was markedly reduced to less than 1%. However, at low sulphuric

acid concentrations, the decrease in FFA content was marginal compared to higher concentration. As the sulphuric acid concentration increases, the FFA content decreases. Similar trend was observed at different reaction times such as 60, 120 and 180 minutes. However, the effect of sulphuric acid concentration on FFA content was marginal when the reaction was longer. Thus, the optimum concentration of sulphuric acid chosen for subsequent experiments was fixed at 1% w/w.

Effect of methanol to JCO ratio

The ratio of methanol to *jatropha curcas* oil (JCO) (w/w) is one of the important variables affecting the concentration reduction of FFA in JCO.

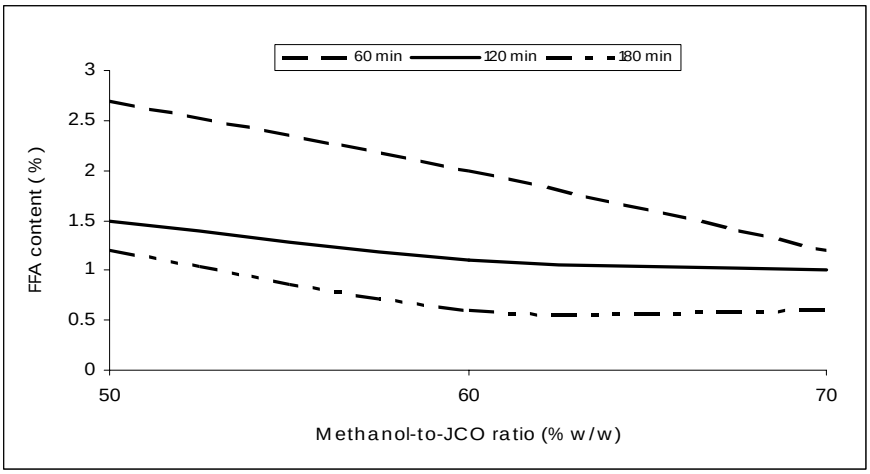

Figure 3: Effect of methanol to JCO ratio on esterification reaction at various reaction times (reaction temperature, 60 °C and catalyst to JCO ratio, 1% w/w)

The effect of methanol to JCO ratio on the FFA content is shown in Figure 3. After 60 minutes of reaction time, the FFA concentration decreased sharply to 2.7% at 50% w/w of methanol to JCO ratio, and then decreased gradually to 2% at 60% w/w of methanol. However, when the esterification was prolonged to 180 minutes, increasing the methanol to JCO ratios has no significant effect on FFA concentration. This could be due to the effect of water produced during the esterification, which prevented the reaction to advance in the forward direction. Esterification is a reversible reaction of which favour forward reaction to produce methyl esters if excess methanol is present in the reaction. However, the presence of water promotes backward reaction thus stabilized the overall reaction. Berchmans and Hirata [1] reported that the esterification process could be improved by water removal in the mixture continuously. The optimum weight percentage of methanol to oil ratio was selected at 60% w/w for 180 minutes of esterification. Under this condition, the FFA concentration was reduced to less than 1%.

Effect of reaction time

The reduction of FFA in JCO depends clearly on the time of reaction. Although other parameters played important roles in reducing the FFA concentration, the esterification reaction time seems to have a substantial effect on the final FFA content as shown in Figure 4. From the figure, it is observed that at lower catalyst concentration, FFA content decreases with increasing reaction time. This is expected since longer reaction time allows for higher conversion of free fatty acids to methyl esters thus reduces the FFA content in JCO. However, at 180 minutes of reaction, the levels of FFA in JCO are similar for both 1 and 1.5% of catalyst concentrations. Adding more catalyst did not increase the conversion. This was could be due to the attainment of reaction equilibrium at the specified temperature.

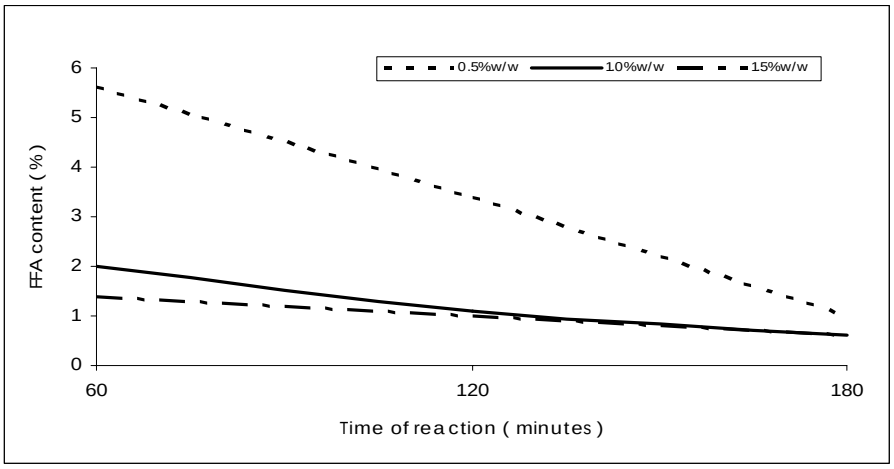

Figure 4: Effect of reaction time on esterification reaction at various catalysts to JCO ratio (reaction temperature, 60 °C and methanol to JCO ratio, 60% w/w)

In this study, the lowest FFA content in JCO that can be achieved was 0.6%. It is an acceptable FFA content of the JCO for the subsequent transesterification reaction to produce biodiesel.

EFFECTS OF FFA IN FEEDSTOCK ON TRANSESTERIFICATION

The effect of free fatty acids on the transesterification of JCO to biodiesel (*jatropha* oil methyl ester) was examined. The transesterification of JCO was carried out using methanol as excess reactant in the presence of alkaline catalyst. Three JCO feedstocks with different percentages of FFA content were transesterified and the effect of FFA content on percent yield is shown in Figure 5. The effect of FFA on the conversion is significant, since for the JCO with FFA content of 25.3%, there is almost no conversion to *jatropha* methyl esters (JME). This is probably due to the reaction between free fatty acid in the feedstock with the alkaline catalyst to produce soap, thus minimize the amount of alkaline catalyst available for the transesterification reaction. At low dosage of alkaline catalyst, lower conversion to methyl ester is expected as shown in samples with 25.3% and 3% FFA. The soap formation also reduced the yield of biodiesel product since the separation of products would be exceedingly difficult. The highest percent yield of JME is 90% for feedstock with FFA content of 0.5%.

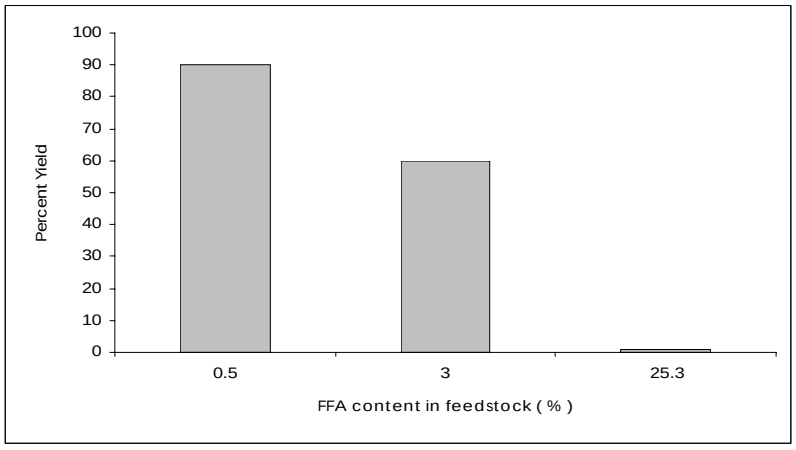

Figure 5: Effect of FFA content in feedstock on percent yield

CONCLUSIONS

The concentration of FFA in the *jatropha curcas* oil (JCO) (25.3% w/w) was reduced to less than 1% through a pre-treatment method via esterification with 60% w/w methanol using 1% w/w of sulphuric acid (H_2SO_4) as catalyst, at 60°C and 180 minutes of reaction time. The treated JCO was then used in the transesterification reaction with methanol in the presence of an alkaline catalyst to produce *jatropha curcas* methyl ester (JME).

ACKNOWLEDGEMENT

This work was done under financial support of FRGS (Fundamental Research Grant Scheme) from Higher Education Ministry, Malaysia.

REFERENCES

[1] Berchmans, H.J. and Hirata, S. (2008) Biodiesel production from crude *jatropha curcas L.* seed oil with a high content of free fatty acids. Bioresource Technology 99: 1716-1721.

[2] Tiwari, A. K., Kumar, A. and Raheman, H. (2007) Biodiesel production from jatropha oil (*Jatropha curcas*) with high free fatty acids: An optimized process. Biomass & Bioenergy 31: 569-575.

[3] Foidl, N., Foidl, G., Sanchez, M., Mittelbach, M. and Hackel, S. (1996) *Jatropha curcas L.* as a source for the production of biofuel in Nicaragua. Bioresource Technology 58: 77-82.

[4] Marchetti, J.M. and Errazu, A.F. (2008) Esterification of free fatty acid using sulphuric acid as catalyst in the presence of triglycerides. Biomass and Bioenergy: 1-4.

[5] Kelkar, M.A., Gogate, P.R. and Pandit, A.B. (2008) Intensification of esterification of acids for synthesis of biodiesel using acoustic and hydrodynamic cavitation. Ultrasonic Sonochemistry 15: 188-194.

[6] Chung, K., Chang, D. and Park, B. (2008) Removal of free fatty acid in waste frying oil by esterification with methanol on zeolite catalysts. Bioresource Technology: 1-6.

[7] Ni, J. and Meunier, F.C. (2007) Esterification of free fatty acids in sunflower oil over solid acid catalysts using batch and fixed bed-reactors. Applied Catalysis A: General 333: 122-130.

[8] Berger, K.G. (1984) *The practice of frying*. PORIM Technology, Malaysia.

[9] Osawa, C.C., Gonçalves, L.A.G. and Ragazzi, S. (2007) Correlation between free fatty acids of vegetable oils evaluated by rapid tests and by the official method. Journal of Food Composition and Analysis 20: 523-528.

[10] Gubitz, G.M., Mittelbach, M. and Trabi, M. (1999) Exploitation of tropical oil seed plant *Jatropha curcas* L. Bioresource Technology 67: 73-82.

[11] Lin, S.W., Sue, T.T. and Ai, T. Y. (1995) *PORIM test methods.* Palm Oil Research Institute of Malaysia, Ministry of Primary Industries, Malaysia.

[12] Canakci, M. (2007) The potential of restaurant waste lipids as biodiesel feedstocks. Bioresource Technology 98(1): 183-190.

[13] Ghadge, S.V., and Raheman, H. (2005) Biodiesel production from mahua (*Madhuca indica*) oil having high free fatty acids. Biomass Bioenergy 28: 601-605.