

Full Length Research Paper

# Evaluation of homogeneous catalysis and supercritical methodology for biodiesel production from *Jatropha curcas*, *Azadirachta indica* and *Hevea brasiliensis* oil seeds

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The present study investigated the production of biodiesel from *Jatropha curcas*, *Azadirachta indica*, *Hevea brasiliensis* oil seed via transesterification methods: base catalysed and supercritical methanol, a catalyst-free process, as a cleaner alternative to conventional chemically catalyzed process. In biodiesel production using base catalyzed transesterification, temperature, methanol: oil molar ratio, catalyst type, catalyst concentration and agitation were found to have significant role on ester conversion. For supercritical transesterification method, reaction was performed in a tubular reactor, at 250°C, with 200 rpm, varying the pressure in the range from 1 to 100 bars. The results obtained showed that non-catalytic supercritical methanol technology required 3, 4, 5 min reaction time to produce 98, 97.17 and 87.1% biodiesel from *J. curcas*, *A. indica* and *H. brasiliensis* seed oil, respectively. Compared to conventional catalytic methods, which required at least 1 h reaction time to obtain similar yield, supercritical methanol technology has been shown to be superior in terms of time and energy consumption. Apart from the shorter time, it was found that separation and purification of the products were simpler since no catalyst is involved in the process. Hence, formation of side products such as soap in catalytic reactions does not occur in the supercritical methanol method.

**Key words:** Biodiesel, *Jatropha curcas*, *Azadirachta indica*, *Hevea brasiliensis*, supercritical.

## INTRODUCTION

Developing alternative energy source to replace traditional fossil fuels has recently become more and more attractive due to the high energy demand, the limited resource of fossil fuel and environmental concerns (Ramadhas et al., 2005). Biodiesel fuel derived from vegetable oils or animal fats is one of the promising possible sources to be substituted for conventional diesel fuel and produces favorable effects on the environment (Shieh et al., 2003). However, in spite of favorable impact, the economic aspect of biodiesel production is still a barrier for its development, mainly due to the lower price of fossil fuels (Antolin et al., 2002). The cost of biodiesel production is dependent on two factors; the

costs of feedstocks and production process cost. Although, the cost of biodiesel production is highly dependent on the costs of feedstock which affect the cost of the finished product up to 60 to 75% (Cetinkaya and Karaosmanoglu, 2004). The 25 to 40% cost of production also dependent on the production process using catalyzed transesterification including homogeneous and heterogeneous catalyst. The transesterification reaction is affected by alcohol type, molar ratio of glycerides to alcohol, type and amount of catalyst, reaction temperature, reaction time and free fatty acids and water content of vegetable oils or animal fats (Vieitz et al., 2008). Nevertheless, the usage of catalyst complicates the transesterification reaction mainly in the need to separate the catalyst from the product mixture.

Recently, new production processes have been developed among which supercritical process is one, an alternative catalyst-free method for transesterification

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which uses supercritical methanol at high temperatures and pressures. Although, high temperatures and pressures are required for this process, however, energy costs of production are similar to catalytic production routes. In studies, it has been reported that with methanol at supercritical stage, a single phase of methanol-oil mixture can be obtained instead of two phase methanol-oil mixture observed at room conditions. This is because at supercritical stage, the dielectric constant of liquid methanol and enables the transesterification reaction to complete in a very short reaction time. Since catalyst is not being used, this process is much simpler and superior as compared to conventional catalytic transesterification process in terms of cost saving and purification of the product mixture (Demirbas, 2006).

Currently, partially or fully refined and edible-grade vegetable oils, such as soyabean, rapeseed and sunflower, are the predominant feedstock for biodiesel production (Hass, 2005), which obviously results in the high price of biodiesel. Therefore, exploring ways to reduce the cost of raw materials is of much interest in recent biodiesel research.

With the foregoing information, in the present study, *Jatropha curcas*, *Azadirachta indica*, and *Hevea brasiliensis* seed oil, was chosen as the raw material to produce biodiesel using supercritical condition of methanol. The process can tolerate water in the feedstock, free fatty acids are converted into fatty acid methyl esters with similar or higher rates than the corresponding triglycerides, and therefore, the process can use high FFA, cheaper feedstocks such as rubber seed oil. Also, the catalyst removal step is eliminated making this process as environmental friendly.

## MATERIALS AND METHODS

Dried *J. curcas* and *A. indica* seeds were obtained from the National Research Institute for Chemical Technology, Zaria (Nigeria), while the dried *H. brasiliensis* seeds were obtained from the Rubber Research Institute Benin Nigeria. The seeds were cleaned by removing debris using hand picking method, dried to constant mass in an oven at 50°C for 72 h, dehauled to remove the seed coat (with little or no oil), and the seeds dried at 50°C for another 48 h. The oil was extracted by oil expeller. The seeds were fed to a series of expellers to receive a mild pressing on continuous basis, as each screw press gradually increased the pressure on the incoming material through the interior of a closed barrel.

The extracted oil were drained out through a small gap between positioned hardened steel bar in the barrel cage. The oils were dark Yellow colour, with neem oil being more viscose and denser. The oils were filtered using muslin cloth to remove dirt and other inert materials. The oils were heated in flasks up to near boiling point to remove water contaminant, allowed to cool to room temperature (27°C) and taken for biodiesel production.

### Esterification of seed oil

The free fatty acid (FFA) content of the biodiesel was determined

using ASTM standard methods by initially determination of acid value by neutralization reaction using 0.1 M KOH, hence the FFA is evaluated by dividing the acid value by 2. The *Jatropha* and neem oil had 0.62 and 0.78% free fatty acid (FFA) content respectively and were found suitable for direct transesterification. The rubber seed oil had high FFA content of 16.58% and was refined, as the yield of esterification process decreases considerably where FFA value > 2% (Ramadhas et al., 2005). The FFA of rubber seed oil was reduced below 2% using paratoluene sulphonilic acid as catalyst prior to transesterification. A round bottom flask was used as laboratory scale reactor vessel, and a hot plate with magnetic stirrer was used for the heating. The reaction/heating time, agitation speed and temperature were measured for the test runs of combination of reactants and process conditions.

### Homogeneous catalyzed transesterification (alkaline esterification)

The homogeneous catalyzed transesterification of *jatropha*, neem and rubber oil was carried out using methanol with potassium hydroxide (KOH) catalyst to obtain monoesters of fatty acids. The controlling parameters for the alkaline esterification were methanol to oil molar ratio (3:1 to 12:1), catalyst concentration (0.25 to 1.50% wt/wt of oil), reaction temperature (50 to 65°C) and rate of agitation (150 to 450 rpm). The wide range of reaction conditions were selected to obtain higher conversion to optimize the parameters. Each experiment was carried out in duplicate.

### Supercritical transesterification

The reaction of transesterification of triglycerides with methanol is carried out in supercritical conditions by adopting reaction temperature of 250°C, higher than the critical temperature of methanol (240°C) and agitation of 200 rpm. The effect of molar ratio of supercritical methanol to rapeseed oil (Kusdiana and Saka, 2001) and cottonseed oil (Demirbas, 2006) has been investigated and it was determined that the ratio of 42:1 and 41:1, respectively, was the optimum ratio for the conversion to methyl esters. Therefore, a molar ratio of 40:1 for alcohol to oil was chosen in this study. The initial amounts of methanol and oil were chosen such that when the desired reaction temperature (250°C) was reached, the pressure in the system was 1 to 100 bar. The oil and methanol were in a single phase, and reaction occurred spontaneously and rapidly. When the desired temperature was reached, the process remained for a set time. The temperature of the reaction vessel was measured with a thermocouple. Then, the vessel was transferred to an ice water bath to quench the reaction.

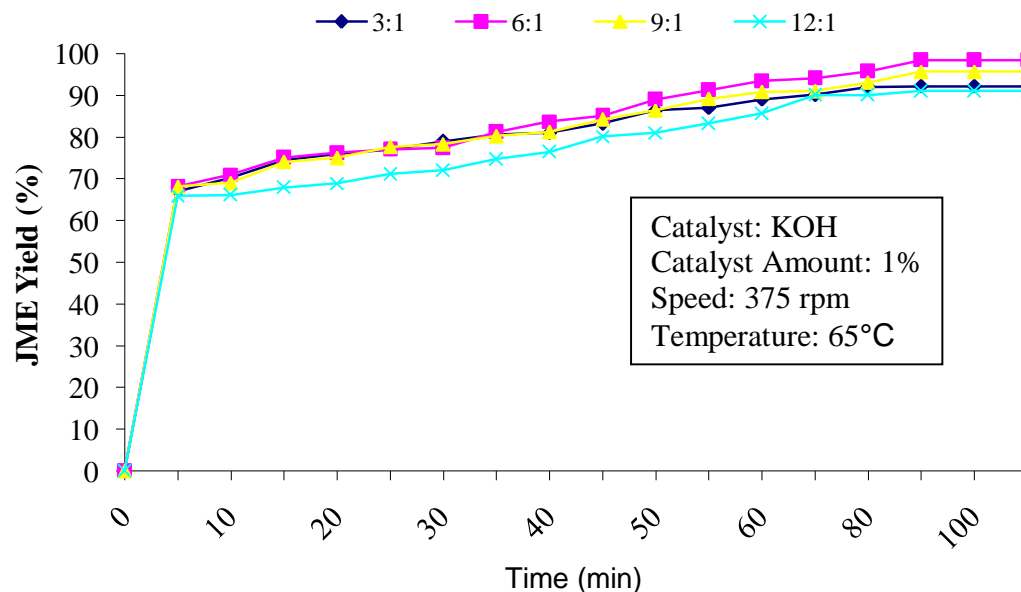
Although, some initial experimental work was carried on biodiesel production at elevated pressure in this study. During the reaction, the effect of pressure on reaction time was studied for all three feedstocks. A Shimadzu (Kyoto, Japan) gas chromatograph, GCMS-QP2010 PLUS, coupled with a flame ionization detector (FID) was used to analyze the fatty acid composition and ester content of the oils and biodiesel obtained from the transesterification reaction.

## RESULTS AND DISCUSSION

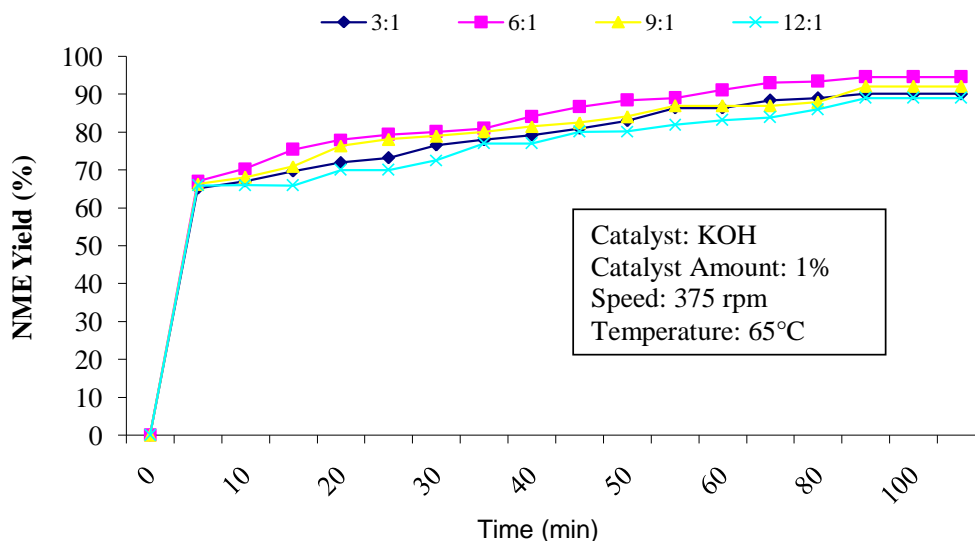
### Homogeneous catalyzed transesterification (alkaline esterification)

#### *Effect of molar ratio of methanol to oil*

Figures 1 to 3 show the effect of alcohol/oil molar ratio on



**Figure 1.** Effect of molar ratio on methyl ester yield for based catalysed transesterification of *Jatropha curcas* oil at varying reaction time showing 6:1 the best.

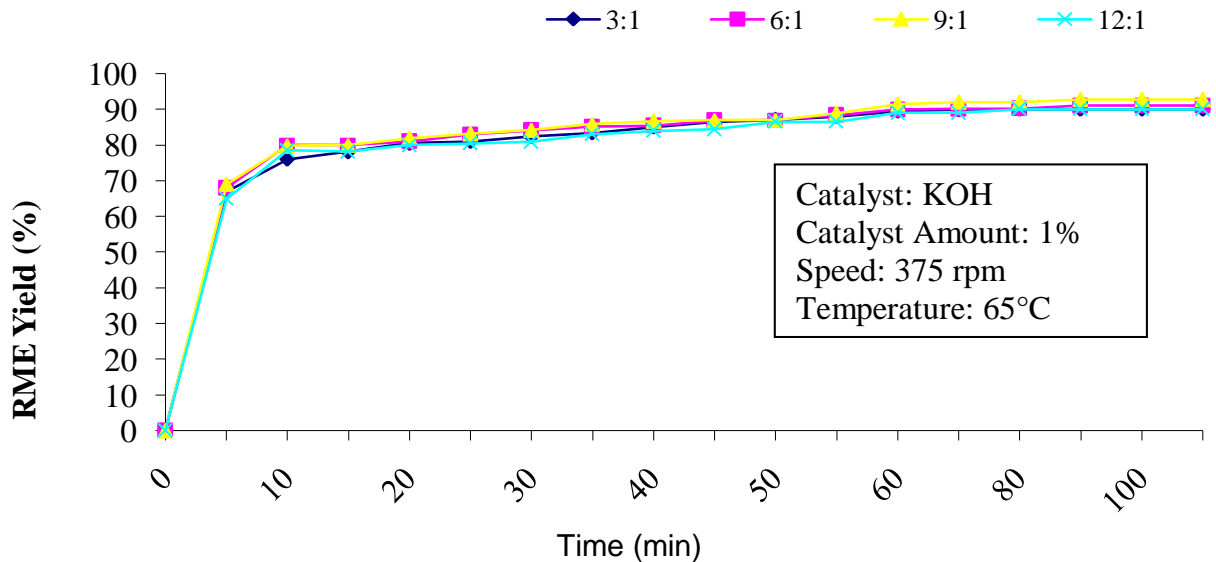


**Figure 2.** Effect of molar ratio on methyl ester yield for based catalysed transesterification of *Azadirachta indica* seed oil at varying reaction time showing 6:1 the best.

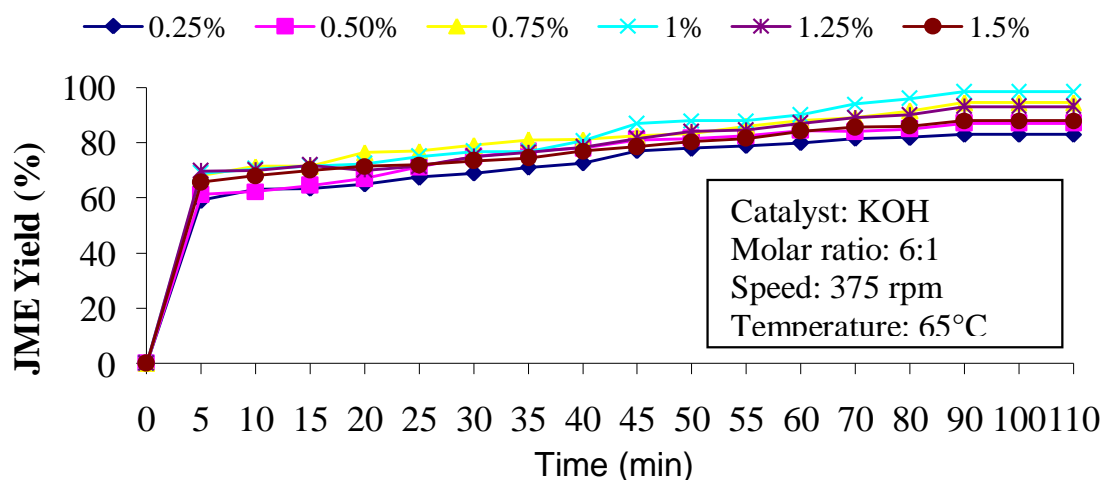
*J. curcas* methyl ester (JME), *A. indica* methyl ester (NME) and *H. brasiliensis* methyl ester (RME) yield, respectively using KOH as a catalyst. Concentration of catalyst, speed and the temperature were maintained constant. From the graph, highest yield for JME and NME was observed with respect to a molar ratio of 6:1 whereas that for the RME was 9:1. Analysis of variation the yield at 6:1 and 9:1 when compared to other molar ratio using SPSS version 17 showed no significant ( $p > 0.05$ ) among the yields. This indicates that despite the

highest yield of JME and NME at 6:1 and JME at 9:1 was not significantly different from 3:1 and 12:1. However, the higher molar ratios than the stoichiometric value of 3:1 resulted in a greater ester conversion and could ensure complete reaction (Leung and Guo, 2006). This result obtained for JME and NME is in line with reports of many investigations based on Canola oil (Leung and Guo, 2006; Zhang et al., 2003; Boocock et al., 1996).

For RME, the larger ratio 9:1 indicated that more methanol were required for achieving the maximum yield



**Figure 3.** Effect of molar ratio on methyl ester yield for based catalysed transesterification of *Hevea brasiliensis* seed oil at varying reaction time showing 9:1 the best.



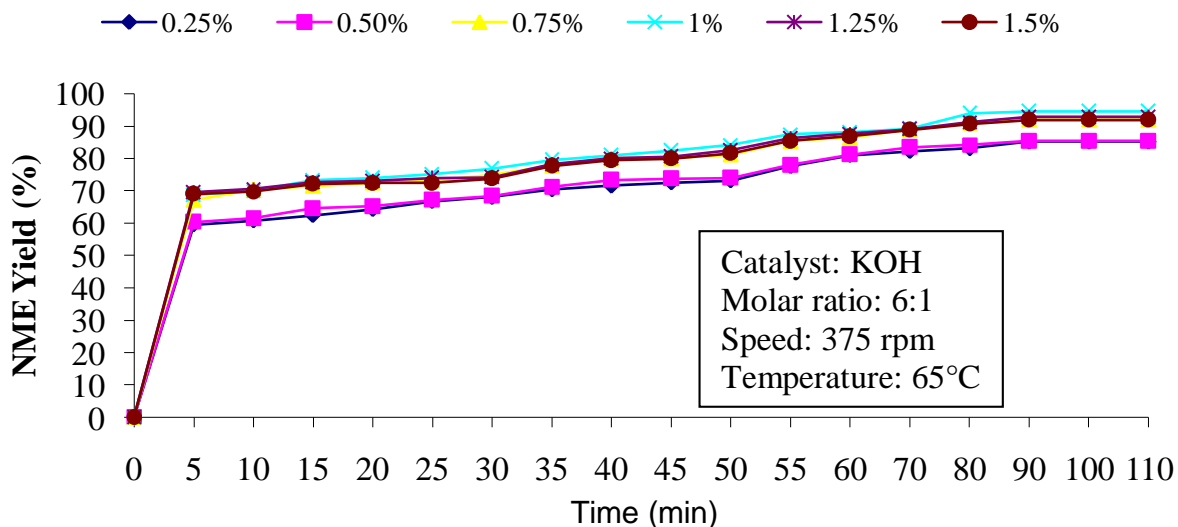
**Figure 4.** Effect of catalyst concentration on methyl ester yield for base catalyzed transesterification of *Jatropha curcas* seed oil at varying reaction time showing 1% is the best.

in the transesterification of rubber oil. The reason for this difference is likely due to the fact that *H. brasiliensis* oil was more viscous than the *J. curcas* and *A. indica* oils. More methanols increase the solubility of the oil in the methanol and improves the contact between oil and methanol molecules, thereby maximizes the conversion.

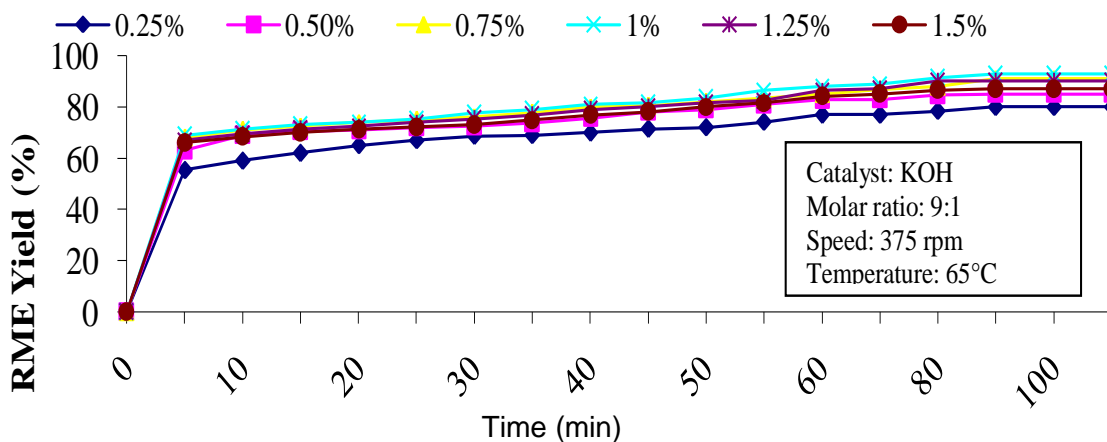
#### Effect of catalyst concentration

Figures 4 to 6 show the effect of catalyst concentration on JME, NME and RME yield, respectively using KOH as a catalyst. Transesterification reaction was carried out

under optimal conditions obtained in the previous section (that is, 6:1 methanol/oil molar ratio for JME and NME and 9:1 methanol/oil molar ratio for RME) while temperature, rate of agitation and alcohol/oil molar ratio were kept constant. From the graphs, highest yield of all the biodiesel fuel has been observed with respect to catalyst concentration of 1%. Analysis of variation among the yield for different catalyst concentration showed no significant difference ( $p > 0.05$ ). It was observed in the course of the experiment that addition of excess amount of catalyst leads to the formation of emulsion, which increased the viscosity of the mixture and led to the formation of gel. It was also observed that excess



**Figure 5.** Effect of catalyst concentration on methyl ester yield for base catalyzed transesterification of *Azadirachta indica* seed oil at varying reaction time showing 1% is the best.



**Figure 6.** Effect of catalyst concentration on methyl ester yield for base catalyzed transesterification of *Hevea brasiliensis* seed oil at varying reaction time showing 1% is the best.

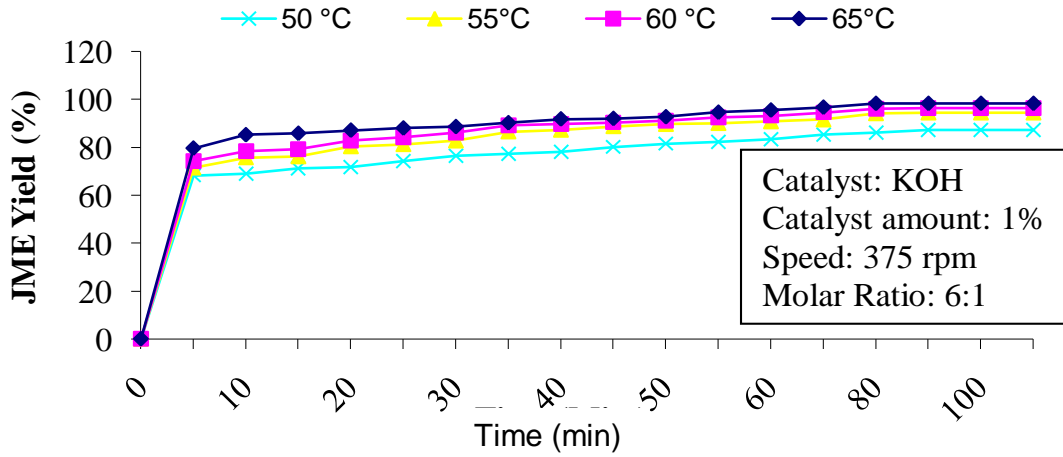
catalyst also reduced the total yield.

### Effect of reaction temperature

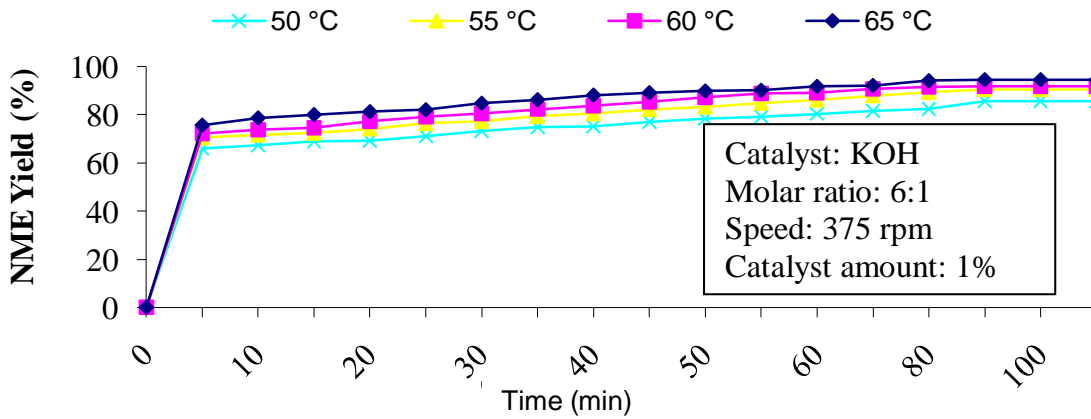
Figures 7 to 9 show the effect of temperature on JME, NME and RME yield, respectively using KOH as a catalyst. Transesterification reaction was carried out under optimal conditions obtained in the previous section (that is, 6:1 methanol/oil molar ratio and 1% catalyst for JME and NME, and 9:1 methanol/oil molar ratio and 1% catalyst for RME) while speed maintained constant. As showed in the graph, highest yield of all biodiesel fuels were observed with respect to reaction temperature of 65°C, though, analysis of variation among the yield for

different temperature showed no significant difference ( $p > 0.05$ ). The results indicated that the transesterification reaction could proceed within the temperature range studied but the reaction time to complete the reaction varied significantly with reaction temperature. The result in this study was however different from previous studies on optimization of *Jatropha* oil in which 55°C was reported as optimal temperature (Eevera et al., 2008).

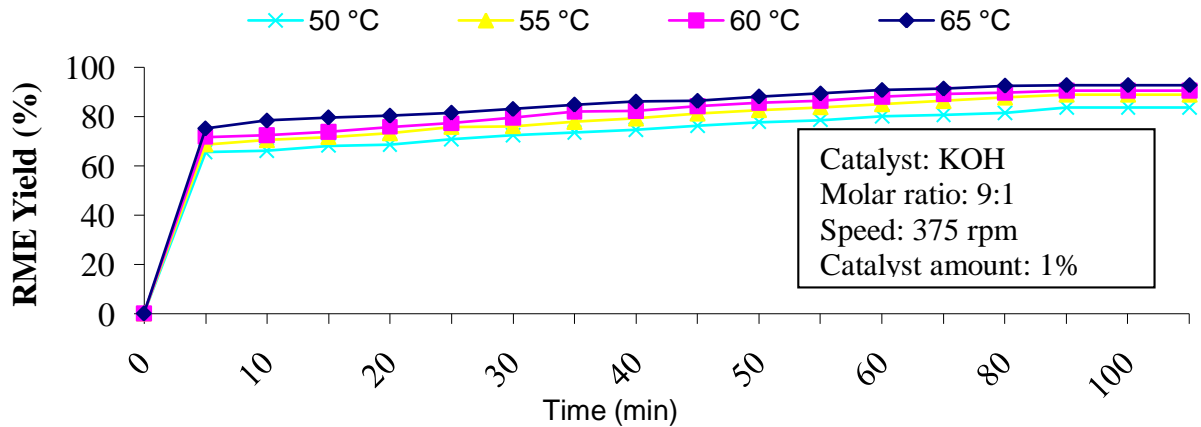
According to Leung and Guo (2006), higher temperature could accelerate the saponification of triglycerides, and have negative effect on the product yield, it could also lead to a drastic decrease in viscosity of the oil that is favourable to increase the solubility of the oil in the methanol and improve the contact between oil and methanol molecules, thereby reaching a better



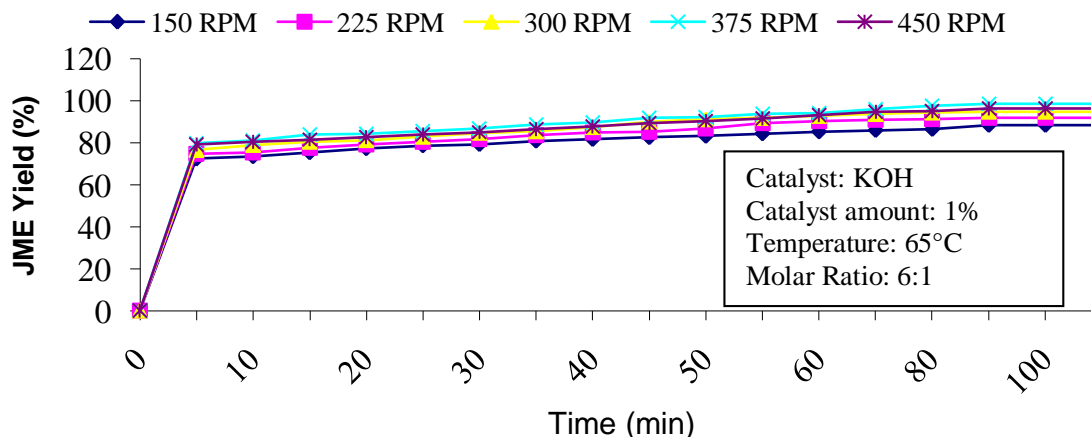
**Figure 7.** Effect of temperature on methyl ester yield for base catalyzed transesterification of *Jatropha curcas* oil at varying reaction time showing 65°C is the best.



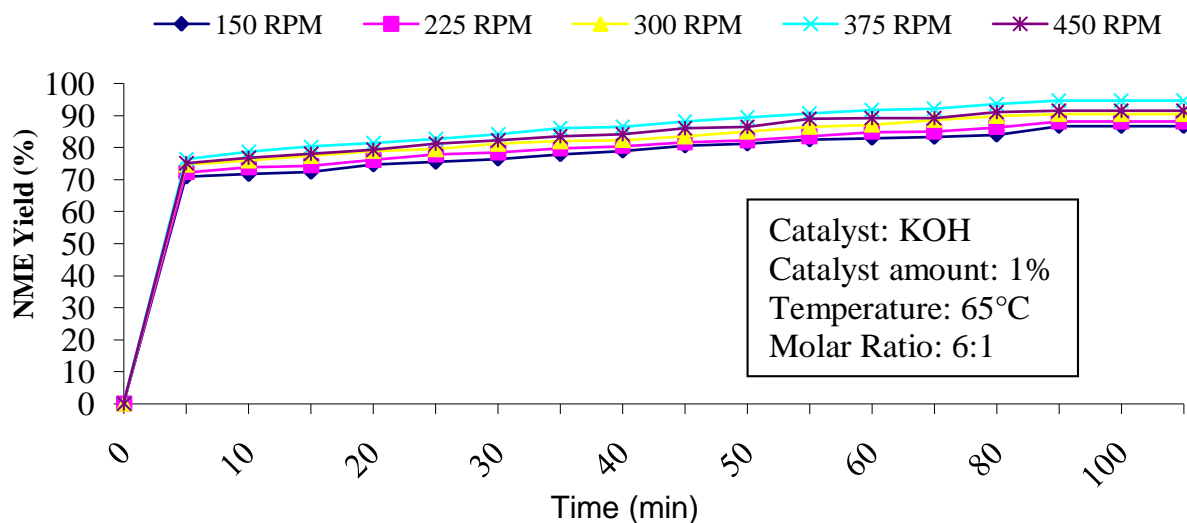
**Figure 8.** Effect of temperature on methyl ester yield for base catalyzed transesterification of *Azadirachta indica* seed oil at varying reaction time showing 65°C is the best.



**Figure 9.** Effect of temperature on methyl ester yield for base catalyzed transesterification of *Hevea brasiliensis* seed oil at varying reaction time showing 65°C is the best.



**Figure 10.** Effect of stirring speeds/mixing intensity on methyl ester yield for base catalyzed transesterification of *Jatropha curcas* oil at varying reaction time showing 375 rpm is the best.



**Figure 11.** Effect of stirring speeds/mixing intensity on methyl ester yield for base catalyzed transesterification of *Azadirachta indica* seed oil at varying reaction time showing 375 rpm is the best.

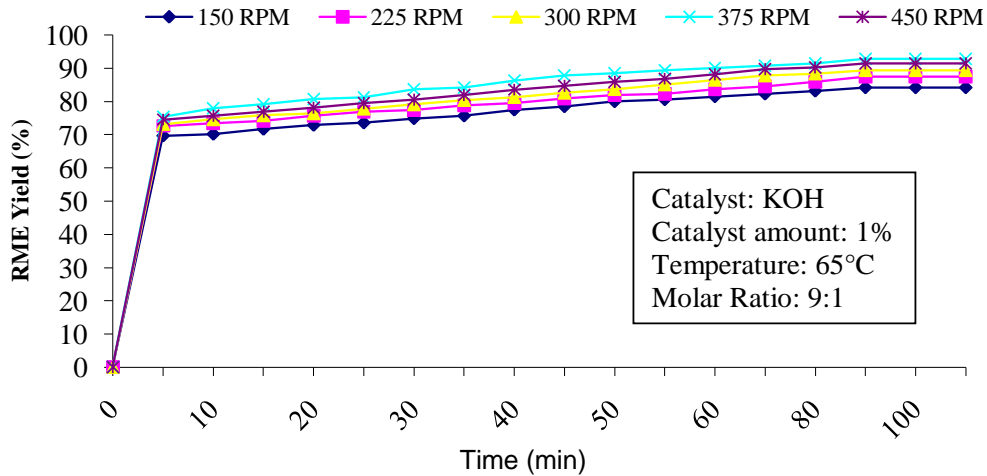
conversion of triglycerides. This implies that optimal temperature of 65°C obtained in this study could be as a result of the competition between the main transesterification reaction and the side saponification reaction.

#### Effect of rate of agitation

Transesterification reaction was carried out under optimal conditions obtained in the previous section (that is, 6:1 methanol/oil, 1% catalyst and 65°C temperature for JME and NME, 9:1 methanol/oil molar ratio, 1% catalyst and 65°C temperature for RME) while rate of stirring was varied. It was observed from Figures 10 to 12 that the

ester yield for all studied oil increased with increase in rate of stirring. Results obtained from the present experiments with *J. curcas*, *A. indica* and *H. brasiliensis* seed oils reveal that 375 rpm was sufficient for the completion of the catalyzed transesterification. Analysis of variation among the yield for different catalyst concentration showed no significant difference ( $p < 0.05$ ).

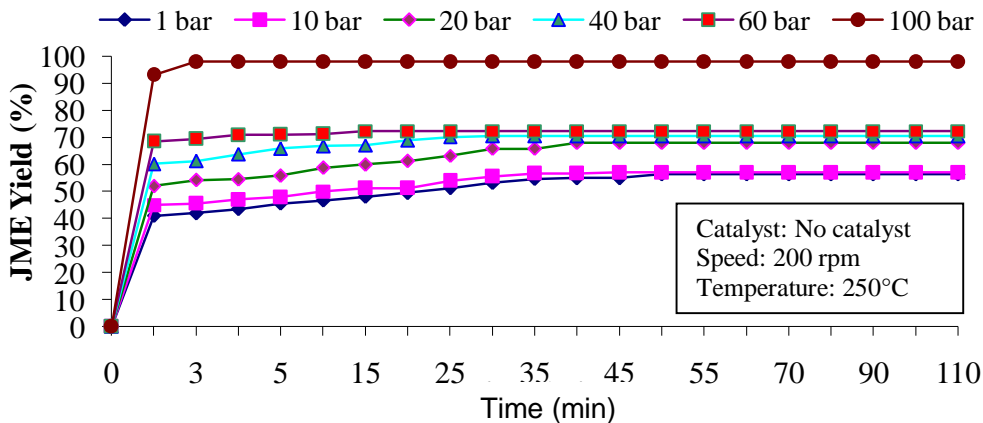
Table 1 summarized the optimal conditions of the biodiesel produced from jatropha, neem and rubber seed oil. The present optimization studies on the transesterification of the oils showed that highest conversion might be achieved at 6:1 methanol/oil molar ratio, 1% catalyst 65°C temperature and 375 rpm for *J. curcas* methyl and *A. indica* 9:1 methanol/oil molar ratio 1% catalyst 65°C,



**Figure 12.** Effect of stirring speeds/mixing intensity on methyl ester yield for base catalyzed transesterification of *Hevea brasiliensis* seed oil at varying reaction time showing 375 rpm is the best.

**Table 1.** Optimized process parameters for base catalyzed transesterification process.

Methyl ester	Alcohol to oil molar ratio	Catalyst (%)	Temperature	RPM	Yield (%)
Jatropha	6:1	1	65	375	98.4
Neem	6:1	1	65	375	94.6
Rubber	9:1	1	65	375	92.8



**Figure 13.** Variation of reaction time with increase in pressure for JME.

and 375 rpm temperature for *H. brasiliensis* seed oil. However, the maximum yield of biodiesel revealed the following trends; JME (98.4%) > NME (94.6%) > RME (92.8%).

**Supercritical transesterification**

An alternative, catalyst-free method for transesterification

uses supercritical methanol at high temperatures and pressures. The process can tolerate water in the feedstock, free fatty acids are converted into fatty acid methyl esters with similar or higher rates than the corresponding triglycerides, and therefore, the process can use high FFA, cheaper feedstocks such as rubber seed oil. Also, the catalyst removal step is eliminated making this process environmental friendly. Some initial experimental work was carried out on biodiesel



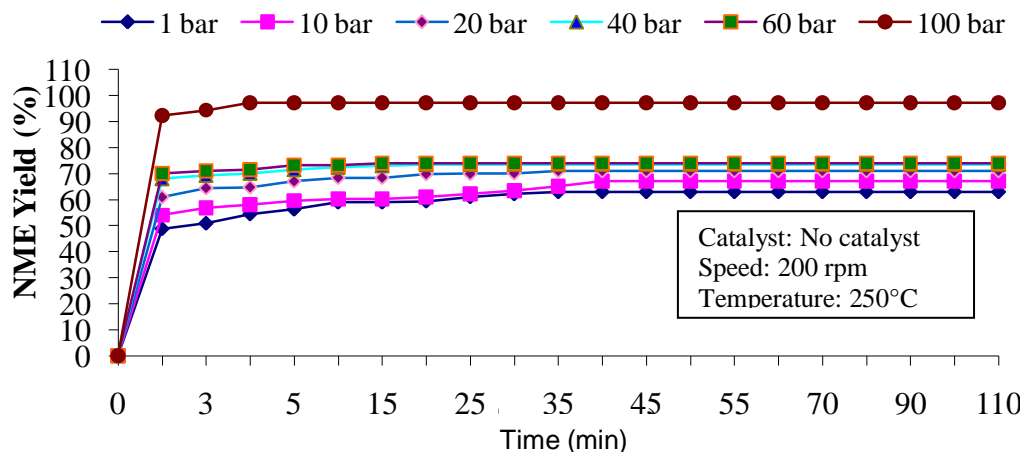


Figure 14. Variation of reaction time with increase in pressure for NME.

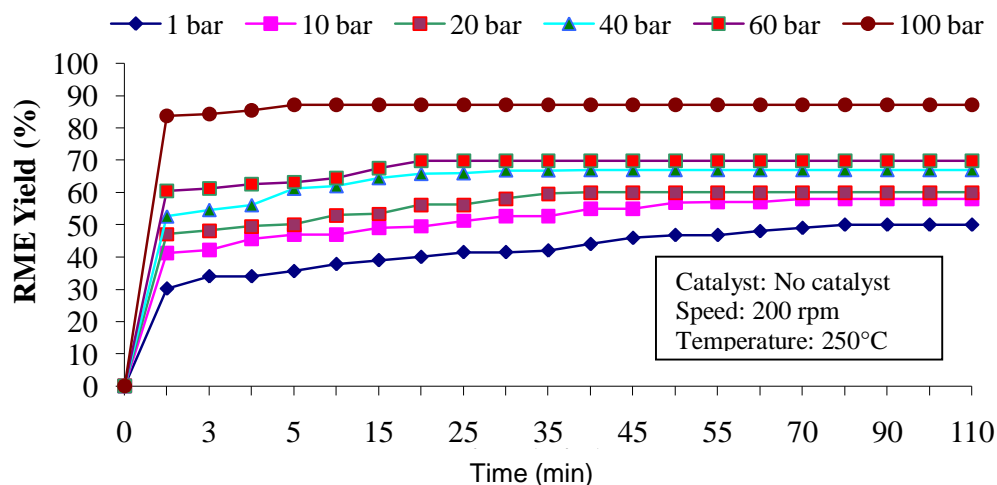


Figure 15. Variation of reaction time with increase in pressure for RME.

production at elevated pressure in this study. The effect of pressure on reaction time was studied for all three feedstocks which are summarized in Figures 13 to 15.

As shown in the figures, the effect of increase in pressure on reaction time of JME, NME and RME yield without using any catalyst. Speed and temperature were maintained constant. As can be seen in the figures, the highest yield of 98% for JME was observed at a pressure of 100 bar in 3 min, yield of 97.1% for NME was observed at a pressure of 100 bar in 4 min and highest yield of 87.1% for RME at a pressure of 100 bar in 5 min. The variation in time could be due to different FFA content of the oil.

#### Comparison between supercritical methanol treatment with catalytic methods

Table 2 shows the comparison between supercritical

methanol treatment with catalytic methods in terms of reaction conditions and biodiesel yield. As can be seen, supercritical methanol is superior to catalytic methods because no catalyst is needed and a relatively lower reaction time is required to obtain a very high yield of 98, 97.1 and 87.1% for JME, NME and RME. On the other hand, a longer reaction time of 65 and 120 min are necessary to obtain similar results for homogeneous and heterogeneous reactions, respectively. Apart from these, the presence of catalyst in the reaction mixture makes the purification and separation process complicated and energy consuming (Cao et al., 2005). Hence, these processes become unreactive in terms of time and economic consideration.

In another study (Kusdiana and Saka, 2004), it was observed that the presence of free fatty acids and water in palm oil did not affect the yield of biodiesel in the supercritical methanol method as no unwanted saponified product was produced as in catalytic reactions. In fact,

**Table 2.** Comparison between supercritical methanol with catalytic transesterification reaction.

Parameter	Catalytic	Supercritical methanol
Reaction time	> 1 h	3-5 min
Reaction pressure and temperature	1 bar, 338 K	100 bar, 523 K
Catalyst	NaOH, KOH	None
Effect of presence of FFA	Soapy products with problems of separation	No separation problems
Yield	<100%	100%
Purification needs of removal of	Methanol, catalyst	Methanol only
Process	Complicated	Simple

the free fatty acids were also esterified during the transesterification reaction and subsequently increased the total yield of biodiesel. Such studies have shown that non-catalytic supercritical methanol transesterification technology has been superior to conventional catalytic reactions in terms of cost and energy consumption. The amount of insignificant reaction time needed and the absence of a catalyst make this technology very attractive compared to other processes. Hence, it has huge potential to be explored and developed in the near future in order to fulfill the escalating demand of renewable energy sources in the world.

## Conclusion

Results obtained through the study suggest that supercritical methanol method has a high potential for transesterification of triglycerides to biodiesel fuel.

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