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Supercritical Methanol for Biodiesel Production from Jatropha Oil in the Presence of Heterogeneous Catalysts

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***Abstract*—**The lanthanum and zinc oxide were synthesized and then loaded with 6 wt% over γ-Al_2O_3 using the wet impregnation method. The samples were calcined at 900 °C to ensure a coherent structure with high catalytic performance. Characterization of the catalysts was verified by X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR). The effect of catalysts on biodiesel content from jatropha oil was studied under supercritical conditions. The results showed that ZnO/γ-Al_2O_3 was the superior catalyst for jatropha oil with 98.05% biodiesel under reaction conditions of 7 min reaction time, 1:40 oil to methanol molar ratio, 6 wt% of catalyst loading, 90 bar of reaction pressure, and 300 °C of reaction temperature, compared to 95.50% with La_2O_3/γ-Al_2O_3 at the same parameters. For this study, ZnO/γ-Al_2O_3 was the most suitable catalyst due to performance and cost considerations.

***Keywords*—**Biodiesel, heterogeneous catalyst, Jatropha oil, supercritical methanol, transesterification.

I. Introduction

THERE is a growing interest in the development and application of sustainable energy as one of the means to achieve impressive pioneering energy results that address the global environmental climate from the threat of fossil fuel emissions. In this regard, studies indicate the rise in prices that the petroleum market is currently witnessing as a result of rising global usage and decreasing supplies [1]. Accordingly, there is a necessity to supplement long-term energy requirements through the use of environmentally friendly and renewable fuel resources [2]. So far, biodiesel (fatty acid alkyl ester) from bio-oil such as vegetable oils, animal fats, and algae oil through transesterification with alcohols (such as methanol) has played an important role in reducing dependence on fossil fuels, thus helping to reduce carbon dioxide emissions [3]. Recently, *Jatropha curcas* oil has attracted attention as a vegetable oil [4]. This tropical shrub produces a high-quality inedible oil that contains compounds that are toxic and anti-nutritive to both animals and humans such as curcins and phorbol esters, which has increased its preference (compared to edible oils) in renewable bioenergy production [5]. Indeed, biodiesel production under supercritical methanol conditions (temperatures and pressures greater than 240 °C and 81 bar) demonstrated higher production efficiency without soap formation, and lower reaction time compared to conventional biodiesel production techniques [6]. In this technology, since the reaction of oil and alcohol occurs in a single-phase due to the cross-mixing of oil and alcohol mixture, it reduces the operating cost and pre-treatment of oils containing water and free fatty acids [7], [8]. The presence of heterogeneous catalysts instead of homogeneous catalysts in the transesterification reaction enhances cost reduction and produces biodiesel in a more environmentally friendly manner [9], as well as being used several times [10].

For a decade, the synthesis, efficiency, and activity of several types of heterogeneous catalysts for biodiesel production through transesterification have been studied [11]. In this regard, our previous review discussed in depth the influence of novel heterogeneous catalysts in biodiesel production under supercritical conditions of alcohols [12]. In the following, this paper will discuss the La_2O_3/γ-Al_2O_3 and ZnO/γ-Al_2O_3 characterization and their efficacy in biodiesel production from *Jatropha curcas* oil under supercritical methanol conditions.

II. Experimental

A. Materials

The lanthanum (III) nitrate hexahydrate, zinc (II) nitrate hexahydrate and methanol (99% pure) were purchased from Merck company, Germany. Gama aluminum oxide was from Alfa Aesar materials company, Germany. The seeds of *Jatropha curcas* were hydraulically pre-pressed and the oil was used as received from Sudan.

B. Catalyst Preparation

The 6 wt% load of La_2O_3 and ZnO were synthesized from their metal nitrate of $La(NO_3)_3 \cdot 6H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$, respectively, using incipient wetness impregnation method. The proportions were individually dissolved in 10 ml of deionized water at ambient temperature. The mixtures were added to 10 g of γ-Al_2O_3 and stirred under an ultrasonic water bath for 2 h to ensure that the mixture spread over and into the γ-Al_2O_3. Finally, samples were dried at 105 ºC and then calcined at 900 ºC for 4 hours, after which they were ready for application.

C. Transesterification Reaction

First, the Packed Bed Reactor (PBR) reactor was filled with the synthesized and calcined catalysts as described in Section II *B* one by one, considering the reactor volume and the area

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occupied by different loads of catalysts (2 wt% and 6 wt%). The reactor was connected by two separate feed lines, one representing jatropha oil and the other for methanol under the molar ratios of 1:40. Half the length of the lines were designed to take place inside a muffle furnace with a PBR reactor (which they already connect to), and thus preheated to help the reactants (methanol and oil) to approximately equal reaction temperatures. Since the critical temperature and pressure of methanol are 242.2 °C and 82.2 bar, respectively, the experiments were performed at 240, 250, 265, 280 and 300 °C. The mentioned temperatures were applied to examine the best temperature parameter that could achieve the highest biodiesel production along with other parameters by adjusting each degree individually using a proportional integral derivative controller (PID), while the reaction pressure was set to be constant at 90 bar using a back pressure regulator and monitored by a digital pressure gauge. The reactor feed out connected to shell and tube heat exchanger to bring the elevated product temperature down to the ambient temperature. Finally, samples were collected and subsequently left for 60 min to separate in a separating funnel, where the bottom layer was biodiesel, and the top layer contained an excess of methanol. Subsequently, biodiesel yields were calculated.

III. Results and Discussion

A. Composition of Crude Jatropha curcas Oil

Jatropha oil analysis was performed using quantitative gas chromatography-mass spectrometry (GC-MS) with capillary column dimensions of 30 m x 0.25 mm internal diameter (I.D) x 0.25 µm. The flow rate of He as carrier gas was set at 1.30 ml/min with different temperatures and duration. The results showed that the components mainly include oleic acid and linoleic acid besides myristic, palmitic, palmitoleic, stearic, arachidic and linolenic acids as shown in Table I.

TABLE I
Components of Crude Jatropha Oil Fatty Acid

Fatty Acid	Content (%)
Myristic Acid (C14:0)	0.06
Palmitic Acid (C16:0)	13.93
Palmitoleic Acid (C16:1)	0.74
Stearic Acid (C18:0)	6.46
Oleic Acid (C18:1)	43.25
Linoleic Acid (C18:2)	32.25
Arachidic Acid (C20:0)	0.27
Linolenic Acid (C18:3)	0.12
Other	2.92

B. Catalyst Characterization

1) Fourier-Transform Infrared Spectroscopy (FTIR)

The (Nicolet iS 10) model was used to identify the functional groups of catalysts within frequency waves between 4000-500 cm^{-1} as shown in Fig. 1. First, the major bands of γ-Al_2O_3 appear in the region of 500-800 cm^{-1}. Since the metal oxides (La_2O_3 and ZnO) were synthesized from their nitrates and then impregnated on γ-Al_2O_3, the peaks at 1250 cm^{-1} (La_2O_3/γ-Al_2O_3) and 1320 cm^{-1} (ZnO/γ-Al_2O_3) indicate the stretching vibration of metal oxides, respectively. Pasupulety et al. [13] reported that intense and broad bands of CaO/Al_2O_3 appeared within the 1400-1600 cm^{-1} region. Several studies reported that a broad band around 3500-3000 cm^{-1} indicates O-H stretching vibration, along with the presence of C-H groups in the following small peaks [14]-[18]. Therefore, the absorption peak at 3610 cm^{-1} indicates the O-H bending vibration of the adsorbed H_2O molecules, while the peaks at 2250 cm^{-1} indicate the presence of Al-O bond, as Garba and Usman reported its presence at 2117 cm^{-1} [19].

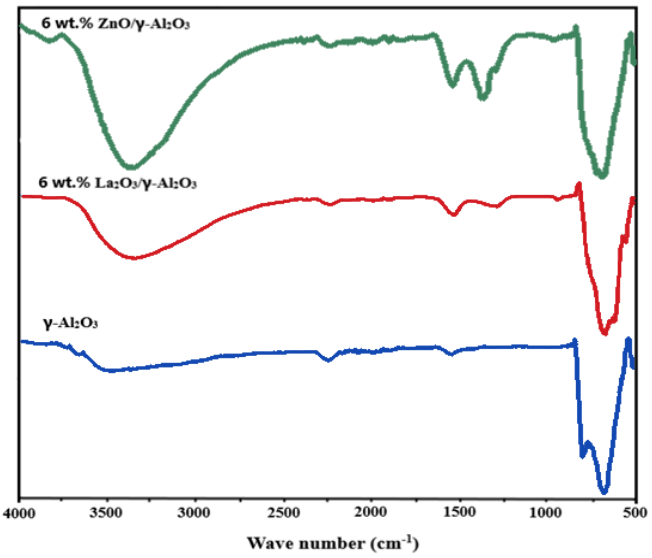


Fig. 1 FTIR spectrum for γ-Al_2O_3, La_2O_3/γ-Al_2O_3 and ZnO/γ-Al_2O_3

2) X-Ray Diffraction

In this part, the γ-Al_2O_3 2θ values of 17.40°, 27.70°, 31.07°, 37.90°, 39.40°, 46.00°, 60.89°, 67.30° and 75.00° were compared with other catalysts as shown in Fig. 2, to ensure the existence of lanthanum and zinc oxides on γ-Al_2O_3. In addition to these values, new 2θ values were observed with 6 wt% catalyst loading of La_2O_3 at (32.70°, 37.02°, 44.53°, 49.60°, 56.40°, 63.40°, 66.30°, 78.52°), and ZnO at (24.30°, 30.93°, 37.05°, 43.53°, 48.90°, 55.38°, 62.30°, 66.40°, 77.50°). In the study of Razali et al. [20], the characterization of La_2O_3 by XRD was reported with different peaks at 2θ values including 27.5°, 28.1°, 29.3°, 30.1°, 39.6°, 46.2° 48.9° and 52°. When La_2O_3 is dispersed as small particles on the γ-Al_2O_3 bulk, the crystallinity of the binary oxides concentration maintains their crystal structure [21], as well as many other peaks may appear in the range between (50° - 80°) 2θ. This point was clearly supported by Shukla et al. [22] by reporting 2θ values of ZnO impregnated on Al_2O_3 at 32°, 34°, 37°, 47.5°, 57°, 62.5°, 68°, 69°, and 77°, which are close if compared with our results.

C. The Effect of Interaction Parameters

1) Effect of Oil/Methanol Molar Ratio on the FAME Content

Various oil to methanol molar ratios of 1:3, 1:10, 1:20, 1:30 and 1:40 mol/mol were applied to investigate the highest FAME yields with catalysts loading at 6 wt% as shown in Fig. 3. Other reaction parameters were performed under reaction temperature

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of 240 °C, reaction pressure of 90 bar and reaction time of 1 min. Sawangkeaw et al. [23] mentioned that the ester content increased with an increase of oil to methanol molar ratio under supercritical conditions from 1:3 to 1:40. To prove it in our study, with γ-Al_2O_3, the ester content increased dramatically from 0.72% at 1:3 molar ratio to 53.7% at 1:40 molar ratio. Moreover, the highest value of ester content using γ-Al_2O_3 is high by 6.57% when compared with no catalyst use. On the other hand, with 1:40 molar ratio, La_2O_3/γ-Al_2O_3 showed a yield of 62.40% as slightly higher by 1% than ZnO/γ-Al_2O_3, compared to the results of 2.57% and 1.23% for mentioned catalysts using 1:3 molar ratio, respectively.

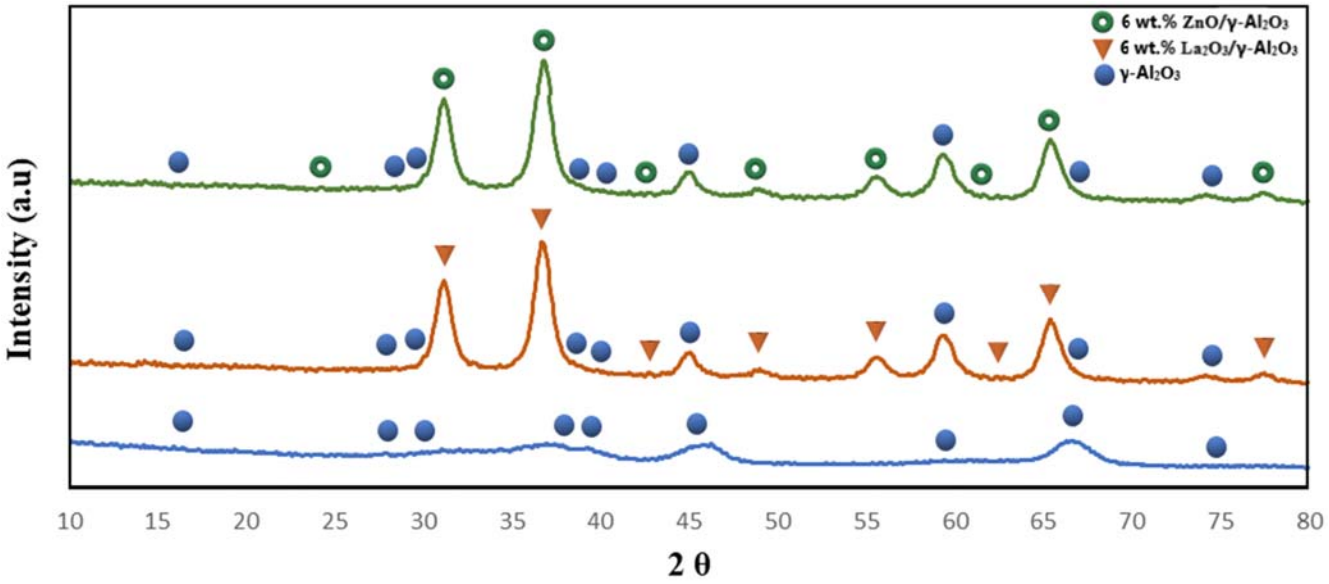


Fig. 2 XRD spectrum of γ-Al_2O_3, La_2O_3/γ-Al_2O_3, and ZnO/γ-Al_2O_3 catalysts

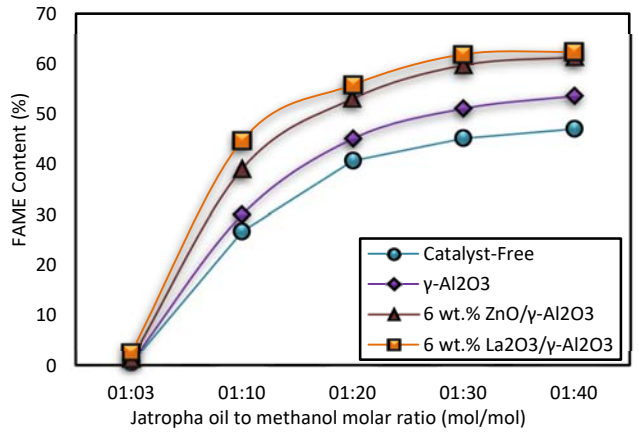


Fig. 3 Effect of oil to methanol molar ratios on FAME content; reaction conditions: 6 wt% of La_2O_3/γ-Al_2O_3 and ZnO/γ-Al_2O_3, 240 °C reaction temperature, 90 bar reaction pressure, 1 min reaction time

2) Effect of the Reaction Temperature on the FAME Content

One of the most important parameters that will affect the rate of transesterification reaction is the reaction temperature [24]. To investigate this effect on the ester content, the parameters of 1:40 oil to methanol molar ratio, 6 wt% catalysts loading, 90 bar reaction pressure and 1 min reaction time were applied against temperature values of 240 °C, 250 °C, 265 °C, 280 °C and 300 °C. The results showed that the esters content increased to 64.12% and 65.22% for ZnO/γ-Al_2O_3 and La_2O_3/γ-Al_2O_3, respectively, with increasing temperature, especially at 300 °C as shown in Fig. 4. Farobie and Matsumura [25] concluded that the ester content increased significantly with increasing temperature from 270-400 °C. Another study reported an increase in biodiesel content from 63.47% to 97.42% with an increasing reaction temperature from 150 °C to 250 °C. The study attributed the shift of the reaction equilibrium towards a higher concentration of FAME due to the positive transesterification enthalpy in the supercritical methanol temperature domain [26].

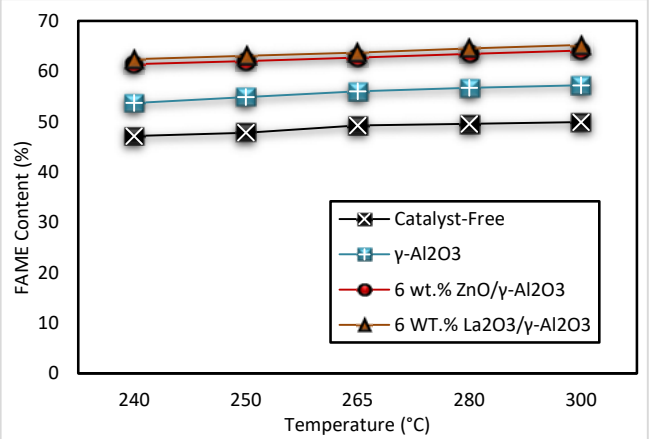


Fig. 4 Effect of reaction temperature on FAME content; reaction conditions: 1:40 oil to methanol molar ratio, 6 wt% catalyst amount, 90 bar reaction pressure, 1 min reaction time

3) Effect of the Reaction Time on the FAME Content

The reaction time parameters of 1 min, 3 min, 5 min, 7 min

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and 9 min were applied to investigate the highest yield of jatropha oil methyl ester through transesterification reaction. Other parameters of reaction temperature, oil to methanol molar ratio, catalyst amount and reaction pressure were kept constant at 300 °C, 1:40 (mol/mol), 6 wt% La_2O_3 or ZnO on γ-Al_2O_3, and 90 bar, respectively. Under these conditions, we observed a significant increase in biodiesel production by 23.18% (from 65.22% to 88.40% with La_2O_3/γ-Al_2O_3) and 26.55% (from 64.12% to 90.67% with ZnO/γ-Al_2O_3) after turning the reaction time from 1 min to 3 min. These results gradually increased with the reaction time from 5 min to 7 min, and the results were reported to increase from 93.20% to 95.50% (with La_2O_3/γ-Al_2O_3) and from 95.82% to 98.05% (with ZnO/γ-Al_2O_3) as depicted in Fig. 5.

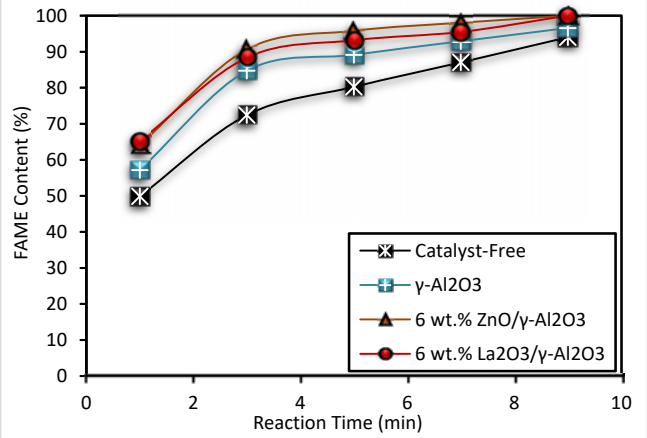


Fig. 5 Effect of reaction time on FAME content; reaction conditions: 1:40 oil to methanol molar ratio, 6 wt% catalyst amount, 300 °C reaction temperature, 90 bar reaction pressure

It was also observed that the number of non/partially transesterified triglycerides could increase in the final product with high reaction time parameters (e.g., 9 min) due to the higher oil mol fraction compared to the methanol mol fraction in the feed. Mazanov et al. [27] highlighted that the yield of rapeseed ethyl ester under supercritical ethanol conditions with a catalytic impregnation of 5 wt% ZnO/Al_2O_3 was 97.45%. Since the high La_2O_3 cost may affect the commercial viability of biodiesel production [12], in this study ZnO/γ-Al_2O_3 was selected to be the best catalyst due to its industrial potential compared to La_2O_3/γ-Al_2O_3.

IV. Conclusion

In this study, the heterogeneous catalysts were successfully synthesized and employed into biodiesel production from *Jatropha curcas* oil under supercritical methanol conditions. Obviously, the increase in the production of FAMEs in the presence of metal oxides confirms their good distribution over γ-Al_2O_3, as well as their high performance to allow better access of the reactants to the catalytically active sites. Among the catalysts, the ZnO/γ-Al_2O_3 showed better results and performance with higher biodiesel yield of 98.05% at the optimum conditions. The system had the potential to increase this percentage with the application of a higher reaction time as 9 min and above, however, an increase in non-transesterified triglycerides was observed and later attributed to a higher oil mol fraction in the feed compared to methanol. In this regard, with a loading of 6wt% ZnO/γ-Al_2O_3, a reaction time of 7 min was selected to be the optimal parameter to achieve highest biodiesel production yield, considering the cost reduction to be in line with industrial and commercial applications.

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