



Transesterification of Waste Cooking Oil to Biodiesel using γ -alumina Coated on Zeolite Pellets

M. Hassani, G. D. Najafpour and M. Mohammadi*

Faculty of Chemical Engineering, Noshirvani University of Technology, 47148 Babol, Iran

Received 23 Apr 2015, Revised 15 Oct 2015, Accepted 17 Oct 2015

*Corresponding author: E-mail: m.mohammadi@nit.ac.ir

Abstract

In this work, a cheap and environmentally friendly heterogeneous catalyst was developed to catalyze the transesterification of waste cooking oil to fatty acid methyl ester (FAME), commonly known as biodiesel. Nano γ -alumina powder was synthesized through sol-gel method and loaded on the zeolite support, which was synthesized from natural aluminosilicate minerals. The successful synthesis of nano γ -alumina powder was confirmed by XRD, FTIR and BET analyses. To produce biodiesel, waste cooking oil was purified and used as the substrate. The influence of catalyst loading, methanol to oil mass ratio, reaction temperature and time on the conversion of triglyceride to FAME was investigated. Maximum triglyceride conversion of 86.43% was achieved at the catalyst loading of 2.2% (ww^{-1}), methanol to oil ratio of 60% (ww^{-1}), reaction temperature of 338 K and reaction time of 4 h.

Keywords: Biodiesel, Heterogeneous catalyst, Transesterification, Waste cooking oil, γ -alumina coated zeolite

1. Introduction

Increasing importance of renewable energy in the world in one hand and the environmental problems caused by nonrenewable fossil fuels on the other hand, have directed worldwide attention on biofuel production. In this regard, especial interest has been concentrated on biodiesel production as a source of alternative fuel due to characteristics like high degradability, no toxicity, low emission of carbon monoxide and renewability [1].

Biodiesel is directly used without any alteration in the engines or burners and can create super properties by mixing this fuel with diesel. Use of biodiesel results in a considerable reduction in the amount of unburned hydrocarbons, carbon monoxide and particulate emission. The presence of oxygen (about 11% by weight) in biodiesel leads to relatively complete combustion. Also the absence of sulfur compounds in the biodiesel is another reason for its environmentally friendly character [1-3].

The biodiesel fuel is made from oil resources such as plant oil, animal fat, waste cooking oil and seaweed oil. Utilization of this fuel has attracted considerable attention due to its plant and animal origin [4-9]. Biodiesel is produced by transesterification of vegetable oils or animal fats with short chain alcohols in the presence of a catalyst. The production of biodiesel from crude vegetable oils will increase the final price of the product. Therefore, use of non-edible oils and used edible animal fats as low-value oils will reduce the cost of biodiesel production. However, a high concentration of free fatty acids (FFAs) in such oils decreases the amount of biodiesel produced by conventional homogeneous acid or basic catalysts like sulfuric acid and sodium hydroxide. The reaction between free fatty acid and alkaline catalysts produces soap as byproduct. Homogeneous acid catalysts need high operating temperatures and oppose corrosion problems. Moreover, the major drawback of homogeneous catalysts is the difficulty in recovery and reuse of them. Therefore, a process which employs solid catalysts (heterogeneous reaction) is more favorable for the production of biodiesel. They can be easily recovered from the effluent stream by simple filtering; lower need of water for cleaning, compatibility with the environment and reduction of the manufacturing cost by elimination of expensive process steps such as separation and purification of biodiesel are considered as the main advantages of heterogeneous reaction [10, 11].

Various types of heterogeneous catalysts (acidic or basic catalysts) have been implemented for biodiesel production. Metal alkoxides have been suggested as heterogeneous catalysts instead of hydroxides as

homogeneous alkaline catalysts [12]. The basic catalysts that have been used include oxides, alkaline metal hydroxide, alumina composite consisting of a gamma or eta substrate coated with a film of alkali metal salts, alkaline zeolite and hydro catalysts [13]. The surveys show that heterogeneous alkaline catalysts are less active than homogeneous ones [14]. The suitable acidic heterogeneous catalysts for biodiesel production should have moderate to strong acid sites, large cavities and hydrophobic surfaces. Presence of crystalline phases, appropriate pore size and good acidity factor are essential for the esterification to improve the performance of catalysts in the transesterification reaction. Replacement of homogeneous acid catalysts by acidic heterogeneous catalysts is effective toward eliminating the corrosion problems and environmental pollution [13-15].

Heterogeneous acid catalysts could be classified as Brönsted and Lewis catalysts [16]. This character of catalyst defines the transesterification reaction rate. Zeolites are known as efficient solid catalysts for industrial applications; nevertheless, their usage for biodiesel production is restricted by their hydrophilic nature [17]. To overcome this issue, Costa et al. [18] incorporated tungsten oxide (WO₃) onto a zeolite surface through which, the hydrophobicity of the catalyst enhanced considerably. Borges et al. [19] examined the feasibility of increasing the catalytic stability of zeolite by reducing the number of acid sites through cerium doping; they reported that the stability and activity of the zeolite catalyst increased. The zeolite (with large amount of silicon and alumina) coated with γ -alumina shows a progressive replacement of strong Lewis acid site with medium strength Brönsted acid sites [20].

In this work attempts were made to explore new routes to make a boehmite sol from aqueous solution of aluminum chloride. An accurate neutralization was carried out by ammonia solution and the produced stable boehmite sol was sedimented on developed zeolite pellets. The synthesized γ -alumina coated zeolite pellets were tested for their ability to catalyze the transesterification of waste cooking oil to biodiesel. The influence of several operation parameters on transesterification of triglyceride to FAMS was studied.

2. Materials and methods

2.1. Pretreatment of waste cooking oil

2.1.1. Physical pretreatment

The waste cooking oil which was collected from restaurants was filtered using filter paper to remove the large particles and impurities. Then for the removal of small particles, the oil was centrifuged at 12000 rpm for 5 min to obtain oil without solid impurities and particulates.

2.1.2. Chemical pretreatment

In order to remove the water content, sodium sulfate as dehumidifier was used. First, sodium sulfate was poured into the physically treated oil, then it was left for a period of time to absorb the water content of the oil. After 72 h, sodium sulfate which was deposited at the bottom was slowly removed. Finally, in order to remove other impurities which were not removed by these purification methods, n-hexane was used. Thereafter hexane was separated by rotary evaporation. In the next step, to determine the fatty acids present in the oil gas chromatography-mass spectrometry (GC-MS) analysis was performed. This sample contained three saturated fatty acids, four unsaturated fatty acids and high amount of FFA as summarized in Table 1. A photo of waste cooking oil before and after purification is illustrated in Figure 1.

Table 1: Fatty acid, FFA and water content of WCO

Compound	Fatty acid	wt %
1	C _{14:0}	0
2	C _{16:0}	28.91
3	C _{16:1}	1.45
4	C _{18:0}	0.93
5	C _{18:1}	26.51
6	C _{18:2}	27.44
7	C _{18:3}	4.6
8	C _{20:0}	0.33
9	FFA	9.85
10	water	0.03



Figure 1: Waste cooking oil before (left) and after (right) treatment

2.2. Preparation of catalysts

2.2.1. Zeolite catalyst pellets

The zeolite catalyst pellets were prepared by mixing a sample of red soil with kaolin powder (10% based on dry soil) and polyvinyl alcohol (PVA, 15% based on dry soil) as binder. The chemical composition of red soil and kaolin powder were determined by X-ray Fluorescence (XRF) analysis using a Philips PW 1480 spectrometer and the results are presented in Table 2. Analysis of the compounds in the red soil and kaolin showed the high level of silica content in both samples which indicates the presence of free quartz in the samples. Details of zeolite pellet preparation procedure are described elsewhere [21].

Table 2: Chemical composition of natural aluminosilicate minerals

Chemical composition (wt %)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	Na ₂ O	TiO ₂	MgO	K ₂ O	P ₂ O ₅	SO ₃	MnO	LOI
Kaolin	77.02	16.3	0.47	0.06	0.04	0.1	0.04	0.54	0.08	0.02	0.01	4.2
Red soil	85.3	6.92	0.90	0.75	0.74	0.48	0.47	0.21	0.029	0.003	0.001	78

2.2.2. Zeolite catalyst pellets coated with γ -alumina

The catalyst synthesized in this work was γ -alumina coated zeolite. The method used for the preparation of this catalyst was as follows: first, hydrated aluminum chloride was dissolved in water at 25 °C to create a clear aqueous solution. In this step, the solution pH was 1.1. Ammonia was added little by little to increase the pH value of the solution to 6.2. At this stage, formation of a white colloidal precipitate was observed. The resulting mixture was placed in a water bath at 80 °C and mildly stirred for 16 h, then nitric acid (65%) was slowly added to the solution by a micro-pipette for peptization. This solution was then kept at 80 °C in water bath for about 12 h under reflux condition; a solution of polyvinyl alcohol (prepared with 1.5 g of PVA in 50 ml of H₂O) was then poured into the boehmite sol at the room temperature. The PVA was used as a drying control chemical additive and binder. The pre-developed zeolite pellets were deposited into the sol and placed in the oven at 45 °C for 7 days to form thick gel. The coated pellets were dried in the oven and calcined in muffle furnace at 750 °C for 3 h.

2.3. Characterization techniques

The crystal structure of the synthesized γ -alumina powder was investigated by X-ray diffraction (XRD) analysis using a Philips 1830 diffractometer equipped with Cu K α radiation at 40 kV and 30 mA in the scanning angle (2 θ) of 10–90°. The surface functional groups of the γ -alumina powder were determined using Fourier Transform Infrared Spectroscopy (FTIR) analysis (Shimadzu FTIR-8300). Moreover, N₂ adsorption-desorption isotherms were recorded at 77 K using Micromeritics Gemini series surface area analyzer. The surface area was measured from the adsorption-desorption isotherm using Brunauer-Emmett-Teller (BET) equation. The pore size distribution was determined using the Barrett-Joyner-Halenda (BJH) method. Scanning Electron Microscopy (SEM) analysis was employed to investigate the surface morphology of the γ -alumina coated zeolite catalyst using the EM3200KYKY scanning electron microscope.

2.4. Synthesis of biodiesel using the developed catalyst

The pretreated waste cooking oil, methanol and the prepared catalyst were mixed and stirred thoroughly. Based on some experiments on stirring speed, the speed of 600 rpm was selected. The transesterification of waste cooking oil containing 9.85 wt% FFA with γ -alumina coated zeolite particles was carried out in a round-bottom

flask equipped with a temperature controller and mechanical stirrer under reflux condition. The transesterification times of 1.5, 2.5, 4, 5.5 and 7 h were examined; the temperature was controlled by fixing the reaction flask in a water bath in the range of 328–358 K. The reaction was performed with 25 g of waste cooking oil while the amount of catalyst was 0.1, 0.25, 0.4, 0.55 and 0.7 g in different experiments. Several methanol to oil mass ratios of 36, 48, 60, 72 and 84% (ww⁻¹) were used.

After completion of the transesterification reaction, the catalyst was filtered from the reaction vessel and the produced mixture was centrifuged. Upon the centrifugation, fatty acid methyl ester (FAME) was separated from glycerol; the upper layer contained FAME and glycerol was in the lower layer. Finally, the water washing method was employed to separate the glycerol from the FAME–glycerol mixture and to achieve pure FAME. The products were analyzed using GC-MS spectrometer. The used GC-MS was an Agilent 5973 spectrometer equipped with an Agilent 6890N gas chromatograph equipped with a capillary column (HP-5); Wiley library was used as reference database. A summary of the transesterification reaction condition is presented in Table 3.

Table 3: Transesterification experiments with γ -alumina coated zeolite catalyst

Number of experiment	Reaction temperature (K)	Reaction time (h)	Catalyst loading (g in 25 g oil)	Methanol to oil ratio (% , ww ⁻¹)
1	328	4	0.55	60
2	338	4	0.55	60
3	348	4	0.55	60
4	358	4	0.55	60
5	338	1.5	0.55	60
6	338	2.5	0.55	60
7	338	5.5	0.55	60
8	338	7	0.55	60
9	338	4	0.1	60
10	338	4	0.25	60
11	338	4	0.4	60
12	338	4	0.7	60
13	338	4	0.55	36
14	338	4	0.55	48
15	338	4	0.55	72
16	338	4	0.55	84

3. Results and discussion

3.1. Characterization of synthesized materials

3.1.1. XRD analysis

The successful synthesis of γ -alumina was confirmed by the XRD analysis. The XRD pattern of the synthesized γ -alumina powder is depicted in Figure 2. Three major peaks observed at $2\theta = 67, 45$ and 38° correspond to the cubic structure of γ -alumina. Using the XRD pattern, the size of the crystalline grain can be expressed by means of the width of the maximum peak in half height and other parameters using the Scherrer formula [22]:

$$D = \frac{0.9 \times \lambda}{B_p \cos \theta} \quad (1)$$

In this equation, D is crystalline grain size, λ is the wavelength of X-ray and B_p is the width of the maximum peak in half height. The grain size was calculated using Equation (1) and the data in Figure 2; the results are presented in Table 4.

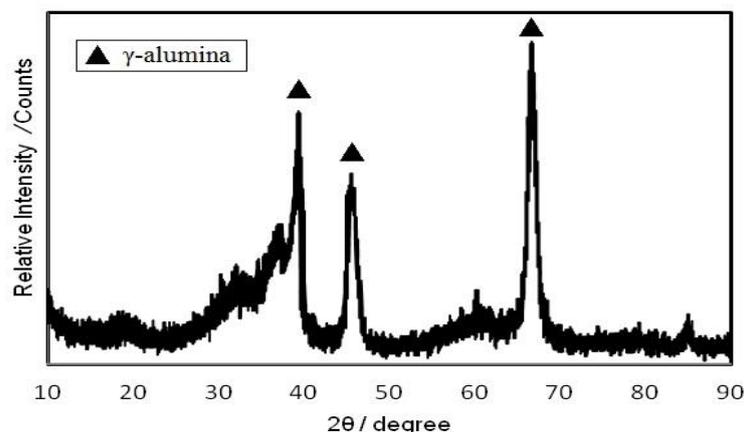


Figure 2: XRD pattern of the synthesized γ -alumina powder

Table 4: Scherer equation parameters for γ -alumina powder

Peak no.	Peak location (2θ)	Corresponding element	$B_p (2\pi)$	D (nm)
1	39.39	γ -alumina	0.0212	6.3
2	45.65	γ -alumina	0.023	6.56
3	66.70	γ -alumina	0.0287	5.775

As could be inferred from the XRD results, nano size γ -alumina powder was well synthesized. The deposition of this nano powder on the porous zeolite base could effectively increase the active site for transesterification reaction.

3.1.2. FTIR analysis

The FTIR spectrum of the prepared γ -alumina powder at the frequencies of 400 to 4000 cm^{-1} is illustrated in Figure 3. In the spectrum of this material, three peaks with very high intensities appeared at the frequencies of 609, 851 and 3460 cm^{-1} , three moderate peaks were observed at the frequencies of 1420, 1522 and 1641 cm^{-1} and finally a peak with very low intensity was seen at 2106 cm^{-1} .

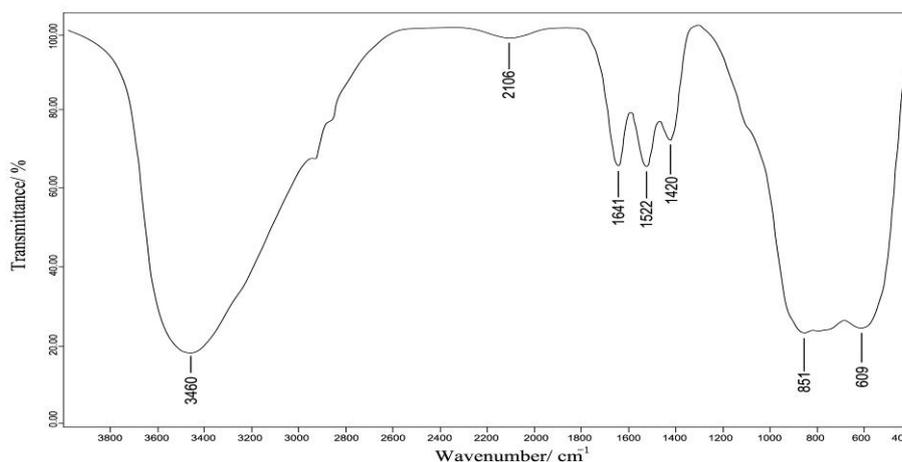


Figure 3: FTIR spectrum of γ -alumina powder

The very sharp peak located at 609 cm^{-1} is related to Al–O coordinates octahedral bonds . The next intense peak which appeared at 851 cm^{-1} is due to the vibrating bond in O–Al–O [23]. The third intense peak at 3460 cm^{-1} is due to the presence of stretching vibration in OH which is formed by the presence of water in boehmite, vaporized due to calcination and the remainder of it is set on the surface of alumina [24]. The mean peak at 1420 cm^{-1} probably represents the stretching vibration of NH group [25]. The vibration band at 1522 cm^{-1} is related to

the N = O bond; result of nitrate group decomposition [26, 27]. Another main peak located at 1641 cm^{-1} is pertained to H–O–H bending vibrations of the absorbed water on the surface [28]. The peak observed at 2106 cm^{-1} probably corresponds to carbon monoxide bond [29].

3.1.3. BET analysis

The N_2 adsorption-desorption isotherms of the synthesized γ -alumina powder is illustrated in Figure 4. It showed a type IV isotherm which is a characteristic of mesoporous materials. The feature of this isotherm is that in low concentrations, the absorbent surface has a high tendency to the adsorbate, while the rate of absorption is reduced with increasing the concentration of the adsorbate [30]. The phenomenon of ‘hysteresis’ observed in the adsorption-desorption isotherm is an inherent property of a cavity which indicates the presence of semi-stable liquid states. Hysteresis occurs when desorption from the mesopores takes place at pressures lower than the capillary condensation pressure. The hysteresis loop fully corresponds to type H3 which is caused by the presence of mesopores [30, 31].

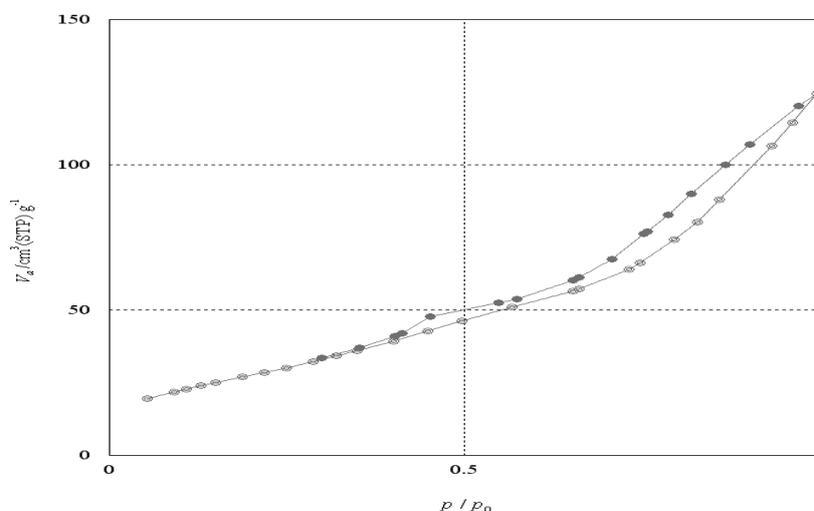


Figure 4: N_2 adsorption-desorption isotherms of the synthesized γ -alumina powder

The surface area of the developed γ -alumina powder was measured from the adsorption-desorption isotherm using BET equation. Based on the analysis results, a BET surface area of $115.37\text{ m}^2/\text{g}$ and pore volume of $0.1901\text{ cm}^3/\text{g}$ was achieved based on BJH method. Pore size distribution was obtained from BJH method and the results are illustrated in Figure 5.

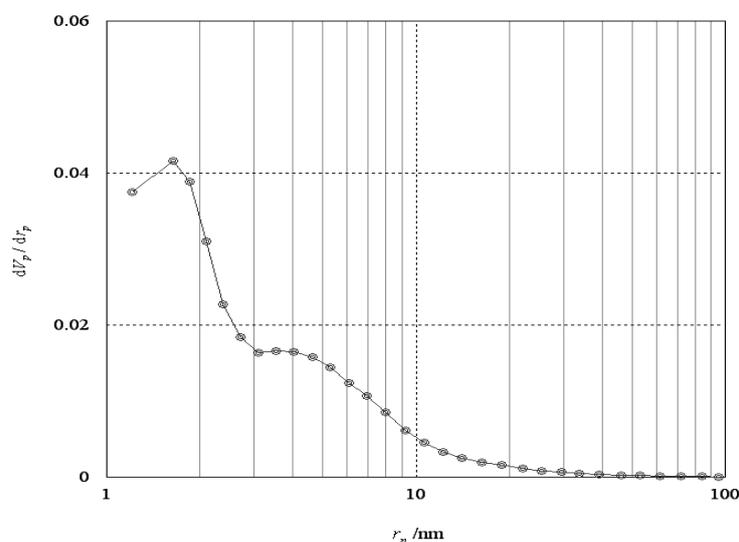


Figure 5: Pore size distribution of the developed γ -alumina powder

3.1.4. SEM analysis

The SEM micrograph of γ -alumina coated zeolite pellets is presented in Figure 6. The boehmite sol was coated on the external surface of zeolite support. Due to the inability of boehmite sol for wetting the surface of zeolite, γ -alumina particles sedimented on the surface and the subsequent heat treatment enhanced the coating of alumina. After the calcination of the sample in the furnace at 700 °C, a relatively uniform layer was created on the porous substrate as observed in the SEM image.

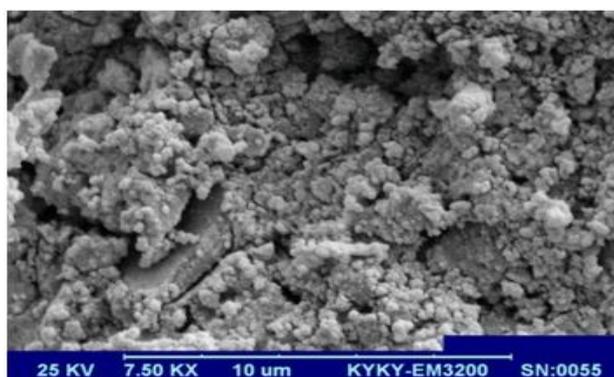


Figure 6: SEM image of γ -alumina powder coated on zeolite

3.2. Synthesis of biodiesel using γ -alumina coated zeolite catalyst

3.2.1. Effect of reaction temperature

This investigation was carried out at the temperature range of 328 to 358 K with fixed values of 25 g oil, 0.55 g catalyst and methanol to oil mass ratio of 60% (ww^{-1}); the experiment duration was 4 h. The results of this study are presented in Figure 7. The highest triglyceride conversion was 86.43% gained at 338 K. It is well understood that higher temperatures increase the rate and speed of the transesterification reaction. Increase of temperature increases the energy of molecules to move faster, therefore breakage of the carbon bonds in triglycerides by alcohol and catalyst is easier, leading to greater production of methyl ester in a shorter reaction time due to intensification in reaction kinetics. However, as the temperature exceeds to above the boiling point of methanol, it vaporizes and bubbles form. Therefore, the reaction in the alcohol-oil interface is restricted [32]. Moreover, at high temperatures, the rate of formation of glycerol byproduct increases. As a result, the solubility of glycerol in the fatty phase enhances which intensifies the glycerolization of methyl ester. It should be noted that the mass transfer between two liquid phases is the rate determining step that temperature has small effect on it [33].

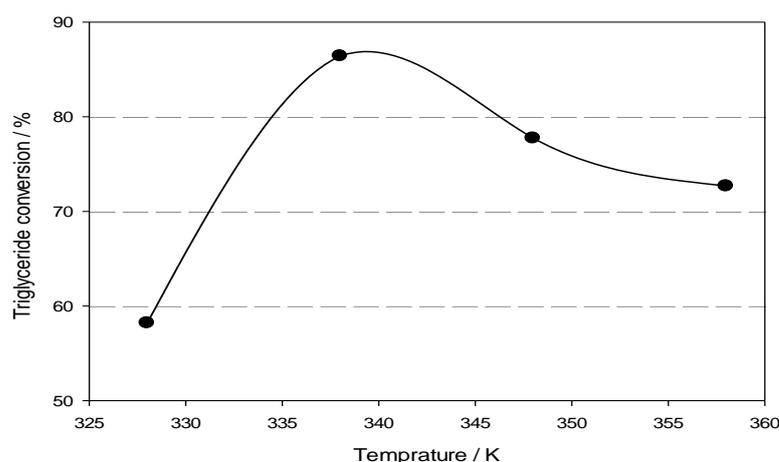


Figure 7: Effect of reaction temperature on the conversion of triglyceride at 60% (ww^{-1}) methanol to oil, 0.55 g catalyst and reaction time of 4 h

3.2.2. Effect of reaction time

Figure 8 shows the effect of transesterification time on the conversion of triglycerides to methyl ester with reaction time in the range of 1.5 to 7 h. As inferred from this figure, by increasing the reaction time to 4 h, the

triglycerides conversion considerably increased to approximately 86.43%. Further increase in the reaction time did not lead to any significant effect on the conversion of triglycerides. This fact may be due to deactivation, resulting from accumulation of byproducts during the reaction and the change in the structure of catalyst. These lead to the loss of active sites on the catalyst's surface, resulting in the reduction of catalyst activity and stability [34].

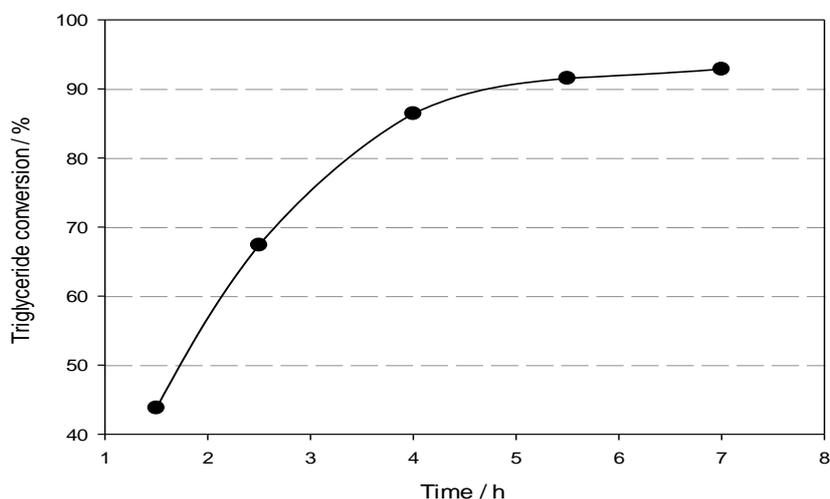


Figure 8: Effect of reaction time on the conversion of triglyceride at 60% (ww⁻¹) methanol to oil, 0.55 g catalyst and temperature of 338 K

3.2.3. Effect of catalyst loading

Figure 9 shows the effect of catalyst loading on the conversion of triglyceride in the range of 0.1 to 0.7 g of catalyst; the amount of oil was fixed at 25 g. As shown in the figure, by increasing the amount of catalyst from 0.1 to 0.55 g, the conversion increased from 34 to 86%. Further increase of the catalyst amount to 0.7 g did not have considerable effect on the production of methyl ester.

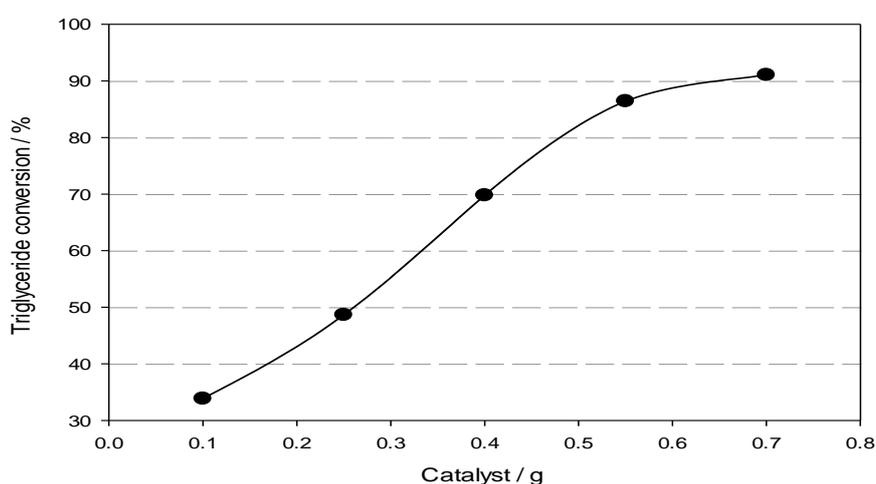


Figure 9: Effect of catalyst loading on the conversion of triglyceride at 60% (ww⁻¹) methanol to oil, temperature of 338 K and reaction time of 4 h

At lower amounts of catalyst, there are not enough active sites for the reaction. Also, since the solubility of methanol in oil is limited, transesterification can occur at the interface of the two phases in lower amounts of the catalyst. However, use of excess amount of catalyst did not pronouncedly improve the conversion. This is due to the fact that by an increase in the amount of catalyst, the proton concentration at the interface enhances and more FAME will be formed. Since FAME will act as a bilateral solvent, the reactants will be placed in a single-phase, so the effect of catalyst enhancement will not be significant [35, 36].

3.2.4. Effect of methanol to oil mass ratio

In a stoichiometric transesterification reaction, one mole of triglyceride reacts with three moles of alcohol to produce three moles of FAME and one mole of glycerol. Since the transesterification reaction is reversible, usually an excess amount of alcohol is needed to shift the equilibrium towards product formation [17]. Thus, the ratio of alcohol to oil has a significant effect on biodiesel production yield. The influence of mass ratio of methanol to oil on the conversion of triglyceride was investigated by examining different ratios of methanol to oil, from 36 to 84% (ww^{-1}); the results are depicted in Figure 10. Since oil is immiscible in alcohol, the reaction is limited by diffusion and thermodynamic processes and remains incomplete, so excess methanol should be used to shift the equilibrium towards the formation of ester and result in complete conversion [37, 38] However, at the methanol to oil ratios higher than 60%, the excess amount of methanol will not have a major impact on the conversion of triglyceride. Conversely, very long time is required to isolate and separate the glycerol from ester substrates because methanol can increase the solubility between the glycerol and ester, causing an emulsion between them. This causes that some portion of the dilute glycerol remains in the ester phase [39].

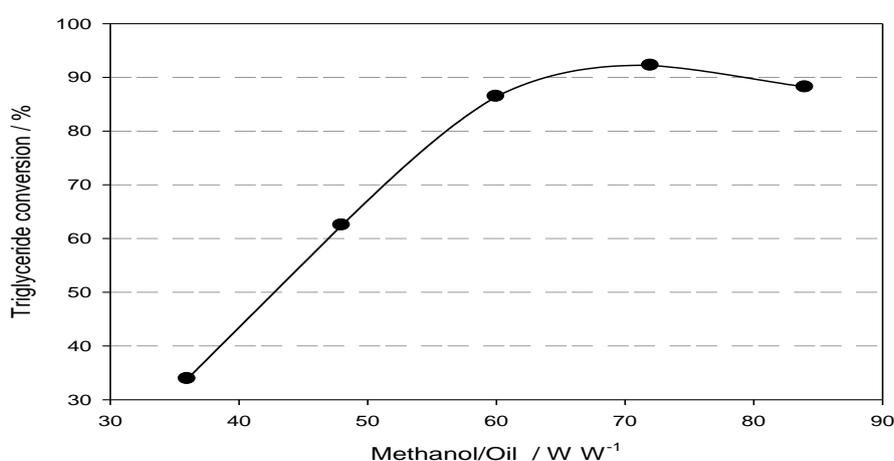


Figure 10: Effect of mass ratio of methanol to oil on the conversion of triglyceride at 0.55 g catalyst, temperature of 338 K and reaction time of 4 h

3.3. Analysis of FAME

The product of the transesterification reaction at the optimized condition i.e., the reaction temperature of 338 K, reaction time of 4 h, 60% (ww^{-1}) methanol to oil mass ratio and 0.55 g catalyst in 25 g oil (corresponding to 2.2% (ww^{-1})), was analyzed using GC-MS and the results are summarized in Table 5.

Table 5: Analysis of biodiesel produced from waste cooking oil

NO.	Biodiesel components	Linear formula	wt %
1	Hexadecanoic acid, methyl ester, methyl palmitate	$\text{C}_{17}\text{H}_{34}\text{O}_2$	30.85
2	9,12-Octadecadienoic acid (Z,Z), methyl ester	$\text{C}_{19}\text{H}_{34}\text{O}_2$	29.91
3	8-Octadecenoic acid, methyl ester, methyl oleate	$\text{C}_{19}\text{H}_{36}\text{O}_2$	16.96
4	Methyl dihydromalvalate	$\text{C}_{19}\text{H}_{36}\text{O}_2$	7.71
5	9-Octadecenoic acid (Z), methyl ester	$\text{C}_{19}\text{H}_{36}\text{O}_2$	9.32
6	α -Linolenic acid, methyl ester, methyl alpha-linolenate	$\text{C}_{19}\text{H}_{32}\text{O}_2$	4.38
7	4,4-Dimethyl-1,1:3,1-terphenyl -2-carboxylic acid, methyl ester	$\text{C}_{22}\text{H}_{20}\text{O}_2$	0.87

Conclusion

γ -alumina powder was prepared from hydrated aluminum chloride, ammonia, nitric acid and PVA and coated on zeolite pellets by sol-gel method. The synthesized γ -alumina powder was characterized by the XRD, FTIR and BET techniques. Results of analyses represented the successful development of γ -alumina catalyst with reasonable textural properties that cannot be deactivated by water and could be active at low temperatures. The developed catalyst was used to catalyze the conversion of waste cooking oil to biodiesel. The reaction condition was optimized in terms of catalyst loading, methanol to oil mass ratio and reaction time and temperature. At the

optimized condition, a high triglyceride conversion of 86.43% was attained. The achieved results were promising where a cheap heterogeneous catalyst with high specific area was synthesized and a high conversion of waste cooking oil, containing high amount of FFA, to FAME was achieved.

References

1. Atadashi I., Aroua M., Aziz A.A. *Renewable Sustainable Energy Rev.* 14 (2010) 1999.
2. Szybist J.P., Song J., Alam M., Boehman A.L. *Fuel Process. Technol.* 88 (2007) 679.
3. Murillo S., Miguez J., Porteiro J., Granada E., Moran J. *Fuel* 86 (2007) 1765.
4. Georgogianni K., Katsoulidis A., Pomonis P., Manos G., Kontominas M. *Fuel Process. Technol.* 90 (2009) 1016.
5. Hameed B., Lai L., Chin L. *Fuel Process. Technol.* 90 (2009) 606.
6. Phan A.N., Phan T.M. *Fuel* 87 (2008) 3490.
7. Huang G., Chen F., Wei D., Zhang X., Chen G. *Appl. Energy* 87 (2010) 38.
8. Halder S., Sakthivel S., Jayaraj K., Gupta P. *Chem. Eng. Commun.* 201 (2014) 88.
9. Chanchaochai P., Boonnoun P., Laosiripojana N., Goto M., Jongsomjit B., Panpranot J., Mekasuwandumrong O., Shotipruk A. *Chem. Eng. Commun.* 200 (2013) 1542.
10. Amini G., Najafpour G.D., Rabiee S.M., Ghoreyshi A.A. *Chem. Eng. Technol.* 36 (2013) 1708.
11. Endalew A.K., Kiros Y., Zanzi R. *Biomass Bioenergy* 35 (2011) 3787.
12. Helwani Z., Othman M., Aziz N., Kim J., Fernando W. *Appl. Catal. A* 363 (2009) 1.
13. Hassani M., Amini G., Najafpour G., Rabiee M. *Int. J. Eng. C* 26 (2012) 563.
14. Carrero A., Vicente G., Rodríguez R., Linares M., Del Peso G. *Catal. Today* 167 (2011) 148.
15. Tahira F., Hussain S.T., Ali S.D., Iqbal Z., Ahmad W. *Int. J. Energy Power* 1 (2012) 31.
16. Chouhan A., Sarma A. *Renewable Sustainable Energy Rev.* 15 (2011) 4378.
17. Avhad M., Marchetti J. *Renewable Sustainable Energy Rev.* 50 (2015) 696.
18. Costa A.A., Braga P.R.S., de Macedo J.L., Dias J.A., Dias S.C.L. *Micropor. Mesopor. Mat.* 147 (2012) 142
19. Borges L.D., Moura N.N., Costa A.A., Braga P.R.S., Dias J.A., Dias S.C.L., de Macedo J.L., Ghesti G.F. *Appl. Catal. A* 450 (2013) 114.
20. Kulkarni M.G., Gopinath R., Meher L.C., Dalai A.K. *Green Chemistry* 8 (2006) 1056.
21. Hassani M., Najafpour G.D., Mohammadi M., Rabiee M. *J. Sci. Ind. Res.* 73 (2014) 129.
22. Jellinek M., Fankuchen I. *Ind. Eng. Chem.* 37 (1945) 158.
23. Zou J., Dai Y., Tian C., Pan K., Jiang B., Wang L., Zhou W., Tian G., Wang X., Xing Z. *Environ. Sci. Technol.* 46 (2012) 4560.
24. Sakka S. *Handbook of sol-gel science and technology. 1. Sol-gel processing*: Springer, 2005.
25. Cheng X., Zhao H., Huo L., Gao S., Zhao J. *Sens. Actuators, B* 102 (2004) 248.
26. Baluja S., Solanki A., Kachhadia N. *J. Iran. Chem. Soc.* 3 (2006) 312.
27. Patra A.K., Ray M., Mukherjee R. *Inorg. Chem.* 39 (2000) 652.
28. Dickinson G.H., Vega I.E., Wahl K.J., Orihuela B., Beyley V., Rodriguez E.N., Everett R.K., Bonaventura J., Rittschof D. *J. Exp. Biol.* 212 (2009) 3499.
29. Mallick K., Scurrill M.S. *Appl. Catal. A* 253 (2003) 527.
30. Chang S.-S., Clair B., Ruelle J., Beauchêne J., Di Renzo F., Quignard F., Zhao G.-J., Yamamoto H., Gril J. *J. Exp. Bot.* 60 (2009) 3023.
31. Galarneau A., Cambon H., Di Renzo F., Fajula F. *Langmuir* 17 (2001) 8328.
32. Hayyan A., Alam M.Z., Mirghani M.E., Kabbashi N.A., Hakimi N.I.N.M., Siran Y.M., Tahiruddin S. *Bioresour. Technol.* 101 (2010) 7804.
33. Shu Q., Yang B., Yuan H., Qing S., Zhu G. *Catal. Commun.* 8 (2007) 2159.
34. Komintarachat C., Chuepeng S. *Ind. Eng. Chem. Res.* 48 (2009) 9350.
35. Boz N., Kara M., Sunal O., Alptekin E., Degirmenbasi N. *Turk. J. Chem.* 33 (2009) 433.
36. Jacobson K., Gopinath R., Meher L.C., Dalai A.K. *Appl. Catal. B* 85 (2008) 86.
37. Ma F., Hanna M.A. *Bioresource technology* 70 (1999) 1.
38. Schuchardt U., Sercheli R., Vargas R.M. *J. Braz. Chem. Soc.* 9 (1998) 199.
39. Hossain A., Boyce A., Salleh A., Chandran S. *Afr. J. Agric. Res.* 5 (2010) 1851.

(2016); <http://www.jmaterenvirosnci.com>