

Optimization and Characterization of Biofuel from Waste Cooking Oil

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Abstract—Waste cooking oil (WCO) is regarded as one of the cheapest feedstock for the production of biodiesel. The waste cooking oil used in this study was prepared in the laboratory by adding 5 wt. % of oleic acid into 95 wt. % of soybeans oil. 10 wt. % of titania-supported-magnesium oxide catalyst (MgO/TiO₂) used was prepared by incipient wetness impregnation and characterized using XRF and XRD. These materials were tested and used as catalyst for the conversion of waste vegetable oil to biodiesel in the presence of methanol and hexane as co-solvents. Methanol to hexane mole ratio of 1:1 was employed in the transesterification process. The effects of reaction time, reaction temperature and hexane co-solvent on the waste vegetable oil conversion have been established. The ¹HNMR analysis was used to estimate the waste vegetable oil conversion and the average molecular formula of fatty acid methyl esters (FAME) produced. It was observed that the oil conversion increased with the increase in reaction time, reaction temperature and use of hexane as co-solvent.

Keywords — Biodiesel, waste cooking oil, MgO/TiO₂, co-solvent, transesterification

I. INTRODUCTION

For centuries, the world had relied on non-renewable crude oil for its energy supply. As a result, the International Energy Agency predicts that from now to 2030, world energy consumption will increase by 45 percent [1]. The world oil production rises exponentially from current levels of about 27 billion barrels per year to a maximum of about 55 billion barrels per year in 2037 [2], hence oil demand is growing exponentially. It has been reported that oil production in 33 out of 48 countries has now peaked and global oil production is approaching an all-time peak. There are various predictions about the decline of oil peaks. The World Energy Forum has predicted less than 10 decades more; all these energy supplies will be exhausted [3]. By the year 2035 crude and other liquid fuels are estimated to provide only 29% of global energy demands. The use of other sources of energy is expected to accelerate. Natural gas and coal consumption will increase by about 50% while Nuclear and renewable energy will grow.

As a solution for these predictions, researchers have identified renewable raw materials which can be processed into liquid fuel as alternatives to keep pace with society's

demand for energy supply. Biodiesel has received most of the interest because 90% of the total world energy is consumed by the transportation sector [4]. Waste cooking oil (WCO) can be used as a biodiesel sources and partially improve the global problems. The use of waste cooking oil as biodiesel feedstock reduces the overall cost of biodiesel production [5]. It also diminishes the problems of contamination thereby reducing the burden of disposing as waste, maintaining public sewers and treating the oil wastewater [6]. Hence, the use of waste cooking oils and non-edible oils should be given higher priority over the edible oils as biodiesel feedstock [7].

In another development, the use of a support to disperse a catalytically active metal phase is receiving widely recognition not only because of its economic benefit (lower preparation costs/longer productive lifetime) but also because the substrate can influence catalyst performance through electronic interactions between the active phase and the support [8]. The activity, selectivity and stability of the catalyst are determined by the correct dispersion and location of the active ingredients. Therefore, the interaction of the active components with the support surface during preparation is determined by the location and dispersion of the active ingredients [9]. Complete heterogeneous catalysts consisting of mixed metal oxide of magnesium and titanium dioxide (MgO/TiO₂) were used to promote the transesterification reaction of waste cooking oil (WCO). While magnesium nitrate hexahydrate (Mg(NO₃)₂·6H₂O) is the raw material to produce MgO catalysts, titanium dioxide is used as a catalyst support. However, the aim of this study is to design titanium-supported-magnesium oxide catalyst (MgO/TiO₂) for biodiesel production from waste vegetable oil and to determine the effect of operating conditions such as hexane co-solvent, reaction temperature, and reaction time on the overall conversion of waste vegetable oils to biodiesel. It also includes using ¹HNMR analysis to characterize the biofuel produced.

II. METHODOLOGY

The materials used to conduct the experiment in this study were magnesium nitrate hexahydrate (Mg(NO₃)₂·6H₂O) (98%), soybean oil (99%) oleic acid (99%) methanol (99%) and titanium (IV) oxide. All reagents were received from Sigma Aldrich South Africa and used exactly as supplied.

Titanium IV oxide support was prepared by mixing 200 g (dry mass) of titanium powder with 100 ml of deionised water. The resulting paste was dried in air at 100°C for 12 hours. The dried support was then calcined in air at 600°C for 12 hours. After calcination, the support was crushed and sieved. The particle sizes of the support ranging between 53 and 106 µm were collected and weighed. About 27 g mass of calcined titanium IV oxide support were obtained. Titanium-supported-magnesium oxide catalyst (MgO/TiO₂)

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was prepared by impregnation method. In this method, 19 g of magnesium nitrate hexa-hydrate was dissolved in 13.5 ml of de-ionized water. The nitrate solution was then poured slowly into a beaker containing 27 g of calcined titanium support. The resulting mixture (Magnesium nitrate and TiO₂) in pasty form was dried in air for 12 hours at 100°C. It was subsequently calcined in air for 12 hours at 600°C.

The calcined TiO₂ support and the prepared TiO₂-supported-MgO catalyst were characterized by X-ray diffraction (XRD) and X-ray Fluorescence (XRF) analyses. Characterization of the catalyst and the support by various methods is to understand the structure of active surface magnesium oxide species and its relation to catalytic properties. The XRD analysis was carried out using Rigaku Ultima IV X-ray diffractometer at measurement conditions of CuK α ($\lambda = 1.54 \text{ \AA}$) radiation source, current and voltage set at 30 mA and 40 KV, scan speed of 1.0000 degree/minutes, 2θ scan range of 5.0 – 90° and step width of 0.01°. The XRF analysis was performed using Rigaku ZSX Primus II equipment to determine the MgO loading on the titania support.

The catalyst testing experiment was conducted using a 300 cm³ Parr reactor, under an inert-nitrogen gas pressure of 24 bar that kept all reactants in liquid phase at different reaction temperatures. This reactor has a fitted stirrer that was operated at 1100 rpm for all the runs. A K-type thermocouple in contact with the reacting medium was connected to a PID controller which controls the reaction temperature to the desired set-point temperatures of 100°C, 150°C and 200°C. The required feedstock which included soybean oil, methanol, oleic acid and catalyst were measured and charged into the reactor. When hexane co-solvent was used, it was charged alongside with other feedstock into the reactor. Sampling was done at 15, 30, 45 and 60 minutes. After sampling, the products were left to cool to room temperature for phase separation. It was therefore separated into two phases, the bottom glycerol plus the unreacted methanol phase and the top oil plus the methyl esters phase. The methanol was removed by heating the samples in a vacuum dryer at 65°C. When hexane was used as a co-solvent, vacuum pump (v-700) was used to remove hexane from the samples. Thereafter, the latter was taken for NMR analysis to determine the waste vegetable oil conversion.

III. RESULT AND DISCUSSION

The XRD diffraction patterns for the blank TiO₂ support and the catalyst (10 wt. % MgO/TiO₂) were generated and plotted as shown in Fig. 1. The pattern a shows the XRD diffraction patterns of 10 wt. % MgO/TiO₂ catalyst while pattern b shows that of the blank TiO₂ support. The two patterns look identical and show major peaks for anatase at 2θ of ca. 20, 32, 43, 48 and 50°.

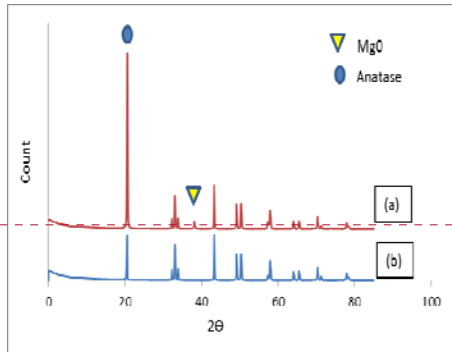


Fig. 1: XRD patterns for (a) TiO₂-supported-MgO catalyst and (b) blank TiO₂

The XRD pattern for the MgO/TiO₂ (pattern a) catalyst has additional diffraction peaks detected at diffraction angles of 37° compared to the calcined blank support. This peak can be attributed to MgO particles stabilized on the titanium support which is in conformity with Corma et al. [10] who reported the XRD diffraction peaks for MgO at $2\theta = 37^\circ, 42.9^\circ, 64^\circ, 67^\circ$ and 78.6° . The most intense peak for the catalyst is at Bragg's angle of 37° and this was used to calculate the average MgO crystallite size (D) using Scherrer equation (i).

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (i)$$

where: k = shape factor, β = FWHM = line broadening at half the maximum intensity, λ = wavelength of x-rays, and θ = Bragg's diffraction angle. The calculated average crystallite size (with $K = 0.9$ and $\lambda = 0.15 \text{ nm}$) was found to be 25.7 nm.

The XRD quantitative analysis shows that the blank calcined TiO₂ support contains 100% anatase. After impregnation and calcination at 600°C, this proportion changes as the catalyst was found to contain 79.32% anatase and 20.7% periclase or MgO without the formation of rutile particles. XRF data are reported in Table I where the MgO content in the catalyst is 10.8% and close to the target value of 10%.

Table I: XRF analysis of samples calcined at 600°C

Component	Calcined support (TiO ₂)	Calcined supported catalyst (MgO/TiO ₂)
Na ₂ O	0.01	0.00
MgO	0.01	10.87
Al ₂ O ₃	0.02	0.00
SiO ₂	0.23	1.06
K ₂ O	0.20	0.25
CaO	0.01	0.00
TiO ₂	99.39	87.66
Fe ₂ O ₃	0.13	0.16

The waste vegetable oil conversion was calculated using NMR analysis data of the biodiesel and unreacted oil phase using equation (ii) [11].

$$C = (2 A_{ME} / 3 A_{\alpha-CH_2}) \times 100\% \quad (ii)$$

Where C is the percentage conversion/yield of methyl, A_{ME} is area from the integration value of the protons of methyl

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ester and $\alpha\text{-CH}_2$ is area from the integration value of the methylene protons. The ^1H NMR spectrum of a sample collected after 60 minutes of reaction at 200°C with the addition of hexane co-solvent is shown in Fig. 2.

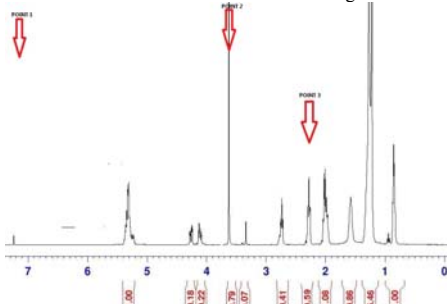


Fig. 2: ^1H NMR spectrum of sample collected after 60 min of reaction at 200°C with hexane as co-solvent.

From the NMR spectra in Fig. 2, point 1, represents the peak for the solvent (CDCl_3) which is at 7.20 ppm, point 2 is the peak for methoxy group of fatty acid methyl ester (FAME) at 3.6 ppm and point 3 is the peak for methylene group of the triglyceride at 2.6 ppm. Using the areas of the peak generated from integration, the sample calculation of the percentage conversion of biodiesel after 60 minutes of reaction at 200°C with hexane co-solvent using equation (ii) was 89.3%. The areas of the generated peaks from integration were also used to estimate the average chain length of methyl-ester produced [12]. The average number of carbon and hydrogen atoms in biodiesel was estimated by using the ^1H -NMR peak assignment proposed by Irmawati et al. [13] and summarized in Table II.

Table II: ^1H -NMR peaks assignment [13]

Functional group	Chemical shift δ (ppm)
Terminal methyl group	0.80 – 1.00
Backbone CH_2	1.22 – 1.42
β -Methylene proton	1.55 – 1.69
α -Methylene group to one double bond	1.93 – 2.10
α -methylene group to ester	2.31
Methyl group to ester	3.67
Olefinic proton	5.27 – 5.41

From the methyl group, we find a factor that divides the area to give 3, since it is known that the area of methylum has three hydrogen atoms; the factor was used to find the number of hydrogen atoms in other groups as shown in Table III.

Table III: Summary estimates of H and C atoms in produced biodiesel

Functional group	Methine: (CH)		Methylene (CH_2)			Total			
	Chemical shift δ (ppm)	(CH)	(CH)	(CH ₂)	(CH ₂)				
Area	5.2-5.4	3.6	0.9	2.3	2	1.5	1.2		
H/C ratio	1	0.79	1.0	0.5	1.08	0.86	5.46		
H	3.8	3	3	2	2	2	2		
C	3.8	3.0	3.8	2.2	4.1	3.3	20.7	40.9	
		3.8	1.0	1.3	1.1	2.1	1.6	10.4	21.2

Using these estimates, the molecular formula for the biodiesel sample was found to be $\text{C}_{21}\text{H}_{41}\text{O}_2$.

The effect of reaction temperature and time on waste vegetable conversion was studied since temperature is known to influence the trans-esterification reaction and yield of the biodiesel product. A high reaction temperature can decrease the viscosities of oils and result in an increased reaction rate and a shortened reaction time [14]. This is the reason why a reaction limited by mass transfer between reactants and catalyst, after 100°C proceeded very fast to give a better biodiesel yields at 150°C and 200°C . The waste soybeans oil conversion with alcohol to oil mole ratio of 18:1 measured over 10 wt% of MgO/TiO_2 catalyst concentration at 100°C is 14.4% after 15 minutes (Fig. 3).

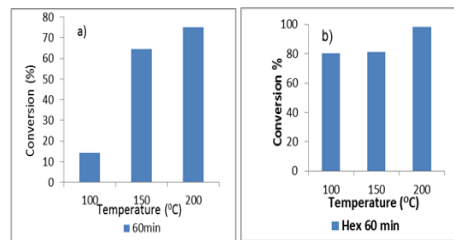


Fig. 3: Effect of temperature on waste oil conversion (alcohol to oil mole ratio of 18:1; Hexane to oil mole ratio of 1:1; catalyst amount of 3 wt% with respect to oil at 60 minutes reaction time). (a) Without hexane co-solvent (b) With hexane co-solvent.

Increasing the reaction temperature to 150°C resulted in an increase in waste oil conversions to 64.6% after 60 minutes. The data increased further to 75.0% after 60 minutes when the reaction temperature was increased to 200°C (Fig. 3a). However, the behaviour is similar to the case involving hexane as co-solvent. With hexane to oil mole ratio of 1:1, oil conversion measured over 10 wt. % of titanium-supported-magnesium oxide catalyst at 100°C is 80.3% after 60 minutes. Increasing the temperature to 150 and 200°C produced an increased oil conversion of 81.3 and 89.3% respectively (Fig. 3b). This result shows that as reaction temperature increased, the waste oil conversion to biodiesel increased over titanium-supported-magnesium oxide catalyst (MgO/TiO_2).

Summarily, the effect of reaction temperature and reaction time showed that as the temperature increased, the viscosity of waste vegetable oil decreased and this improves the mass transfer of reactants to the active sites in the catalyst. This on the other hand means that as more energy was added to the system, the effective number of collisions increased which helped to overcome the activation energy barrier. In the same vein, more waste vegetable oil eventually dissolved in methanol to improve the methanol-oil immiscibility which also improved the mass transfer in the catalyst.

From Fig. 4, it was observed that the conversion to biodiesel yield increases as the reaction time increases. For example, an amount of MgO/TiO_2 catalyst (3 wt. % with respect to waste vegetable oil) at 150°C and methanol to oil

ratio of 18:1 led to waste oil conversion of 46.6, 48.4, 57.0 and 64.6.0% at 15, 30, 45 and 60 minutes respectively (Fig. 4a). The case involving hexane as co-solvent exhibits similar behavior. For the same amount of catalyst as for the example discussed above at 150°C, methanol to oil ratio of 18:1 and hexane to oil mole ratio of 1:1 gives improved oil conversions of 54.8, 72.8, 80.2 and 81.3 % at 15, 30, 45 and 60 minutes respectively (Fig. 4b).

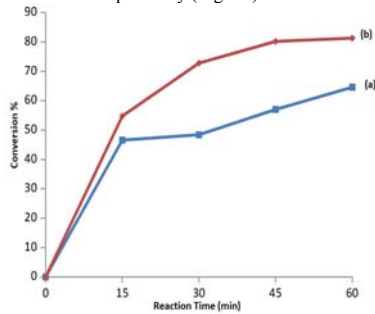


Fig. 4: Effect of reaction time on waste oil conversion (alcohol to oil mole ratio of 18:1, Hexane to oil mole ratio of 1:1; catalyst amount 3 wt.% with respect to oil and reaction temperature of 150°C) (a) Without hexane co-solvent (b) With hexane co-solvent.

However, the reaction time in this study is limited to just 1 hour and to achieve more satisfactory levels of waste oil conversion, extended reaction times must be recommended. Albeit, the measured data show that the waste vegetable oil conversion to biodiesel over TiO_2 -supported-MgO catalyst increases with an increase in reaction time. However, some researchers have conducted transesterification reaction for an extended reaction time. Sadrameli et al. [15] used KOH catalyst loaded on $\gamma\text{-Al}_2\text{O}_3$ support, methanol/oil ratio of 15:1 and varied reaction time from 1 to 5 hours to conduct a transesterification reaction. He reported that there is an increase in biodiesel yield with an increase in reaction time up to 3 hours, but after 4 hours of reaction time the biodiesel yield did not increase significantly.

IV. CONCLUSIONS

In this study, (MgO/TiO_2) catalyst was prepared by impregnation of titanium (TiO_2) support with magnesium nitrate followed by drying and calcination at a higher temperature of 600°C. The catalyst was tested in the transesterification of waste cooking oil with methanol into biodiesel at 100, 150 and 200°C for a reaction time of 1 hour under an inert-nitrogen gas pressure of 24 bar. The conversion was found to increase with the reaction time and temperature. A utilization of hexane co-solvent was found to be of positive effect and increases the rate of transesterification reaction producing higher biodiesel yields in small times of reaction. The analyses of the results showed that when hexane co-solvent to oil mole ratio of 1:1 was used, the synergy of the transesterification reaction resulted to a waste oil conversion of 89.3% at 200°C for reaction time of 1 hour. This result is very promising when compared to 75.0% waste oil conversion obtained when only methanol was used as the solvent/reactant for transesterification under the same reaction conditions. ^1H NMR analysis was used to

produce a spectrum which identified that the average chain length of fatty acid methyl-ester (FAME) produced was $\text{C}_{21}\text{H}_{41}\text{O}_2$.

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