Proceedings of the World Congress on Engineering 2014 Vol II,
WCE 2014, July 2 - 4, 2014, London, U.K.

Biodiesel Production from Waste Vegetable Oils over MgO/ZrO_2 Catalyst

Thembi Sithole, Kalala Jalama, Reinout Meijboom

***Abstract*—MgO was loaded on ZrO_2 using the incipient wetness impregnation method. The catalyst was characterized using FTIR, XRD, XRF and BET. The effects of reaction temperature, reaction time and MgO loading on waste vegetable oil conversion to biodiesel were investigated. Biodiesel yield was observed to increase with the reaction temperature and the reaction time. The effect of MgO loading in the catalyst on oil conversion was found to be influenced by the reaction temperature.**

***Index Terms*—Biodiesel, MgO/ ZrO_2, waste vegetable oil**

I. INTRODUCTION

Biodiesel production is among the most researched topics as it offers a renewable alternative to fossil fuel. However the cost of the feedstock is still among the major factors that make the biodiesel production cost more expensive. In this study, waste vegetable oil (WVO) has been used as feedstock because: i) used vegetable oils are cheap compared to virgin oils and their supply don't compete with food production; ii) the conversion of used vegetable oils will reduce/eliminate their disposal into waste drainage posing environmental problems. Around 379 million litres of waste cooking oil are produced per day in USA [1] and 1.9 – 2.6 million gallons/day in Europe [2]. The amount of waste cooking oil available in South Africa on a monthly basis is in excess of 30 million litres [3]. WVO usually contain significant amounts of free fatty acids which lead to the formation of soap during the conversion of WVO in an alkaline catalysed process. This can be avoided by using a solid catalyst. The catalytic properties of various solid catalysts for the transesterification reaction have been reported in literature.

In this study the catalytic properties of the MgO/ZrO_2 system will be investigated for the conversion of WVO into biodiesel. In particular the effect of reaction temperature, reaction time and catalyst loading on the overall WVO conversion will be investigated.

II. EXPERIMENTAL DETAILS

A. Catalyst Preparation

The catalyst preparation was performed in two steps: i) ZrO_2 pre-treatment and ii) MgO stabilization on ZrO_2 support. ZrO_2 from Sigma Aldrich (Aldrich, < 5 μm powder) was pre-treated by mixing it with distilled water in a 1:1 weight ratio, dried in air at 120°C overnight and calcined in air at 500°C for 10 hours. The pre-treated ZrO_2 was subsequently crushed and sieved to retain the particles with sizes between 50 and 150 μm for use as catalyst support. MgO was stabilized on the support by incipient wetness impregnation of the ZrO_2 support with an aqueous solution of $Mg(NO_3)_2.6H_2O$ (Sigma Aldrich) followed by drying in air overnight at 120°C and calcination in air at 500°C for 8 hours. Catalyst samples with MgO loadings of 10 and 20 wt.% were successfully prepared by using an appropriate amount of $Mg(NO_3)_2.6H_2O$.

B. Catalyst Characterization

MgO loading in the prepared catalyst samples was verified by using XRF analysis that was performed using a MAGIX PRO XRF spectrometer. Fourier Transform Infrared spectroscopy was used to determine functional groups in the catalyst samples after drying and after calcination. The analysis was performed using a Bruker Tensor 27 with a Pike Golden Gate ATR attachment in the range of 4000-400 cm^{-1}. The surface area and pore size distribution of the prepared catalyst samples were measured using BET analysis by N_2 adsorption at a temperature of 77 K on a Micromeritics ASAP 2000 apparatus. Finally x-ray diffraction (XRD) analysis was used to determine the structure of the catalyst system on a Philips PW 3040/60 X-ray diffraction apparatus with a CuK_α ($\lambda = 1.54$) radiation. Samples were scanned over a 2θ range of 4–130° with a 0.02° step size and a scan speed of 0.04 s/step.

C. Catalyst Testing

The waste vegetable oil that was used in this study was obtained from local frying houses and had an acid value of 11.1 mg of KOH/g and a moisture content of 0.12 wt.%. It was reacted with methanol (methanol to oil molar ratio of 18:1) in a 300 cm^3 stainless steel batch reactor (PARR 4842 series reactor) fitted with a pitched blade stirrer in presence of varying masses of catalyst. The reaction was performed at 60, 150, 175, 200 and 225°C under appropriate N_2 pressure to keep methanol in liquid form. A sample was collected from the reactor after every 15 min up to 1h of reaction. The product sample was cooled to room temperature and the

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Manuscript received April 8, 2014. This work was supported by the University of Johannesburg Research Committee.

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catalyst was removed from the products by centrifugation. Methanol was removed from the sample by evaporation at 65 °C under vacuum. The products that remained after evaporation were glycerol, unreacted oil and methyl esters. These products separate into two phases: glycerol as the bottom phase and oil and methyl esters as the top phase. The top phase was used to determine the oil conversion to methyl esters using NMR data and the following equation:

$$\%Conversion = \frac{2A_{ME}}{3A_{\alpha-CH_2}} \times 100 \qquad (1)$$

where A_{ME} is the integration value of the protons of the methyl esters; $A_{\alpha\text{-}CH2}$ is the integration value of the methylene protons.

III. RESULTS AND DISCUSSION

A. *Catalyst characterization*

FTIR analysis:

The FTIR data for both dried and calcined catalyst samples with 20%MgO loading are reported in fig. 1. For the dried sample (spectrum a), the O-H transmittance peak was observed at 3370.03cm^{-1} and 1633.01cm^{-1}, the NO_3^- at 1342.69cm^{-1}, $Mg(OH)_2$ at 816cm^{-1}, and the presence of ZrO_2 was observed at transmittance peaks between 562 and 558cm^{-1}.

After calcination at 500°C, it was observed that the O-H bending and stretching vibration modes present in the dried catalyst sample (fig. 4a) disappeared on the 20% MgO/ZrO_2 (Fig. 4b) due to the removal of the dissociated water. The NO_3^- also disappeared from the 20% MgO/ZrO_2 spectrum a suggesting complete decomposition of $Mg(NO_3)_2$ into MgO after calcination.

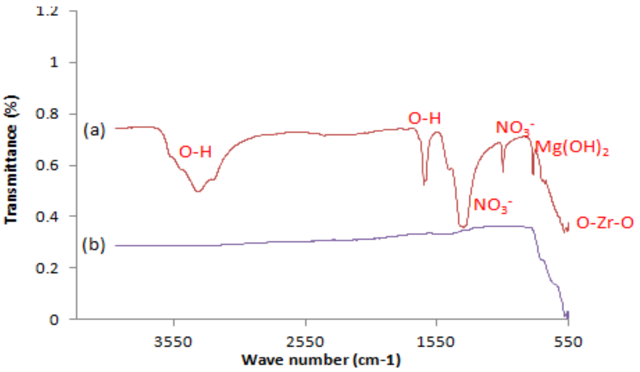

Fig. 1. FTIR spectrum of (a) dried catalyst ; (b) 20% calcined MgO/ZrO_2

XRD analysis:

Fig. 2 shows the XRD data for blank ZrO_2 after calcination (pattern b) and calcined MgO/ZrO_2 catalyst sample (pattern a). Both patterns are similar except that two additional diffraction peaks at 42.0 and 62.3° were observed on the pattern for the calcined MgO/ZrO_2 catalyst sample and are ascribed to MgO. The crystallite sizes of MgO in 10% and 20% MgO/ZrO_2 were calculated from XRD data using the Scherrer equation and were found to be 30.3 and 28.3 nm respectively.

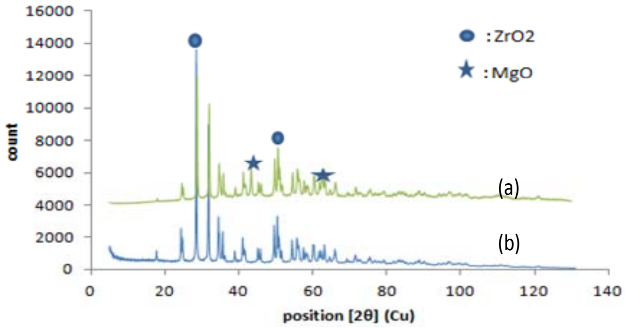

Fig. 2. XRD pattern of (a) 20% calcined MgO/ZrO_2, (b) calcined blank ZrO_2

A comparison of XRD data for the calcined MgO-ZrO_2 catalyst before and after the *trans*-esterification reactions was performed to investigate whether the catalyst underwent any structural change during the reaction. The data are shown in fig. 3 where patterns a, b and c respectively represent the data for the catalyst before reaction, after reaction at 150 and after reaction at 225°C. All three patterns are similar and suggest that no significant structural change took place in the catalyst during reaction.

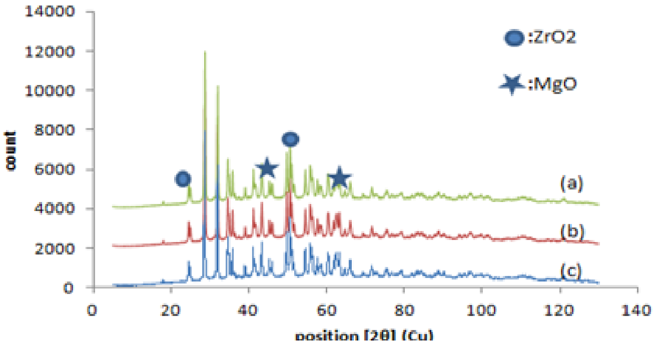

Fig. 3. XRD pattern of calcined MgO/ZrO_2 (a) before reaction; (b) after transesterification reaction at 150°C and (c) after transesterification reaction at 225 °C

XRF analysis:

XRF results for the prepared MgO/ZrO_2 catalysts are summarized in table 1 below:

TABLE I: TARGET MGO LOADING ON ZRO_2 AND ACTUAL XRF DATA

Target %MgO on ZrO_2	%MgO by XRF
10	10.3
20	21.0

The measured MgO loading was satisfactorily closer to the

ISBN: 978-988-19253-5-0
ISSN: 2078-0958 (Print); ISSN: 2078-0966 (Online)

target loading for all the samples.

BET analysis:

The surface area and pore size diameter for the calcined blank ZrO_2 support, 10% MgO/ZrO_2 and 20% MgO/ZrO_2 are summarized in the table 2.

TABLE II: SURFACE AREA AND PORE SIZE DIAMETER FOR CALCINED BLANK ZrO_2 SUPPORT AND 10 AND 20% MGO-LOADED CATALYST

	Calcined blank Al_2O_3	10% MgO/ Al_2O_3	20% MgO/ Al_2O_3
Surface area (m^2/g)	6.6	3.9	2.5
Pore size (nm)	21.9	39.2	41.2

The blank zirconia support had a surface area of ca. 6.6 m^2/g which decreased to ca. 3.9 m^2/g for 10% MgO and to ca. 2.5 m^2/g for 20% MgO-loaded catalysts respectively. This could be due to some pores obstruction by the MgO loaded in the catalyst. The decrease in zirconia surface area upon MgO loading was also observed by Jiang *et al.* [4]. Unexpectedly the data show an increase in pore sizes with an increase in MgO loading. Pore sizes of 21.9, 39.2 and 41.2 nm have been measured on the calcined blank ZrO_2 support, the 10 and 20%MgO-loaded catalyst samples respectively. This could suggest that some pores collapsed in the ZrO_2 support upon MgO addition and calcination of the MgO-loaded samples.

B. Catalyst testing

Fig. 4 and 5 show the waste oil conversion as function of reaction temperature, time and MgO loading in the catalyst.

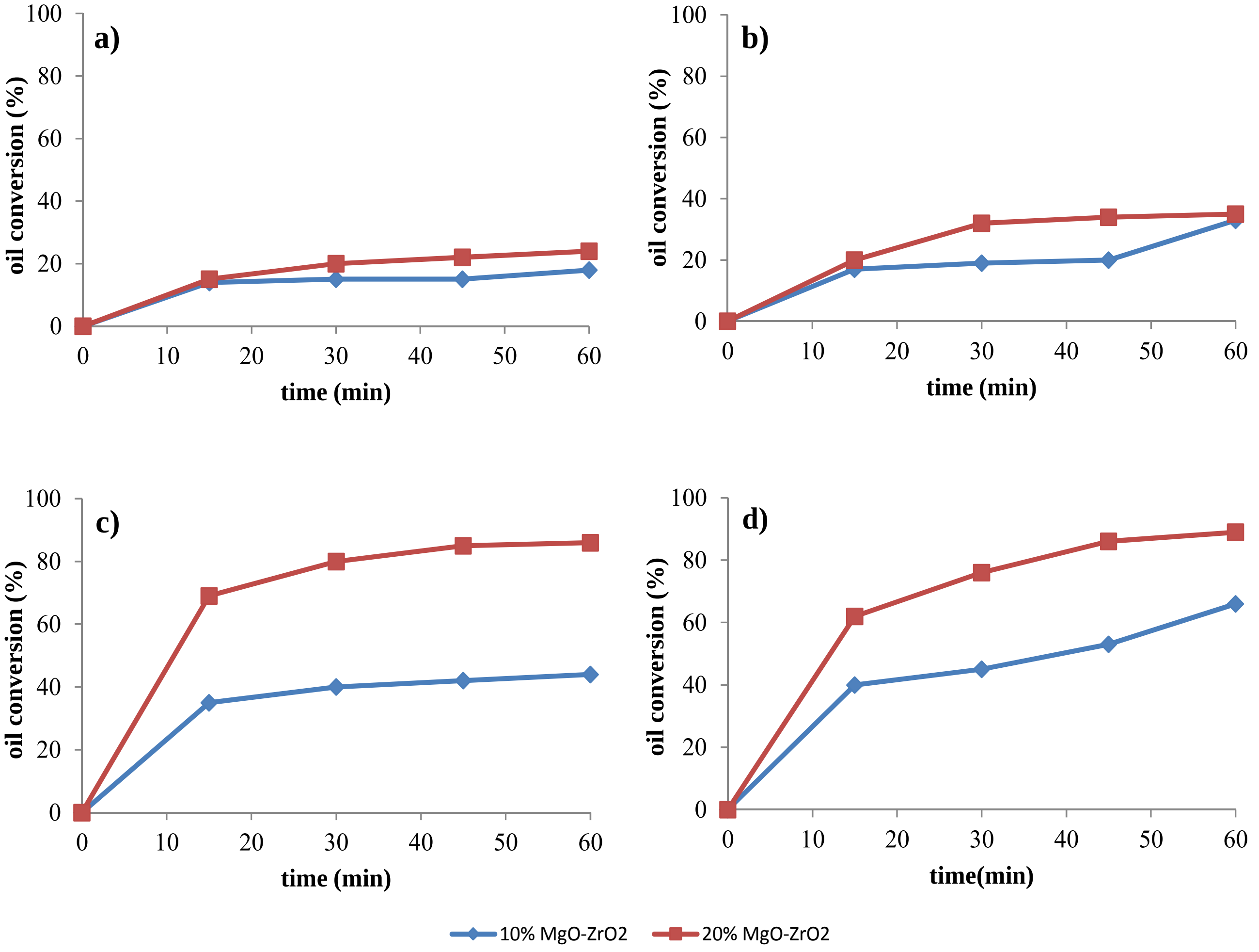

Fig.4. Effect of temperature: a) 60°C, b) 150°C, c) 175°C and d) 200°C, time (0 to 60 min) and MgO loading (10 and 20%MgO) on waste oil conversion to biodiesel (catalyst amount 3wt.%)

The waste oil conversion increased with the increase in reaction temperature. For example, waste oil conversions of ca. 24, 33, 86 and 89% were measured at 60, 150, 175 and 200°C respectively for 20% MgO loading after 60 min (Fig. 4. a-d). This effect of temperature on the reaction rate can be explained through the theory of chemical reaction kinetics. An increase in temperature will result in increasing fraction of molecules that have a high kinetic rate [5].

As the reaction time increases, the waste oil conversion to biodiesel also increases. For example, waste oil conversions over the 10wt.% MgO catalyst were respectively 36, 38, 40, and 42% after 15, 30, 45 and 60 min of reaction at 175°C (Fig. 4c).

The effect of MgO loading in the catalyst on the conversion of the waste vegetable oil to biodiesel was found to depend on the operation temperature. No significant difference in waste oil conversion was observed between 10 and 20% MgO loaded catalysts for the reactions performed at 60 and 150^{o}C. This could suggest that at these reaction temperatures the limiting factor was the mass transfer resistance. When the reaction temperature was increased to 175 and 200^{o}C, the effect of MgO loading was evident and a higher waste oil conversion was measured on the catalyst with a high MgO loading. This can be explained by the fact that the increase in reaction temperature decreased the reactants viscosity and reduced mass transfer resistances in the catalyst. In this case the reaction rate is more controlled by the MgO active sites density in the catalyst which is proportional to the MgO loading. No significant effect of MgO loading was observed for the reaction performed at 225^{o}C as shown in Fig. 5 where the waste oil conversion in the absence of the catalyst and over the blank zirconia support are also reported. The data show a significant contribution of the blank zirconia support to the waste oil conversion to biodiesel (ca. 25, 35, 48 and 50% after 15, 30, 45 and 60 min respectively) making the assessment of the effect MgO loading difficult.

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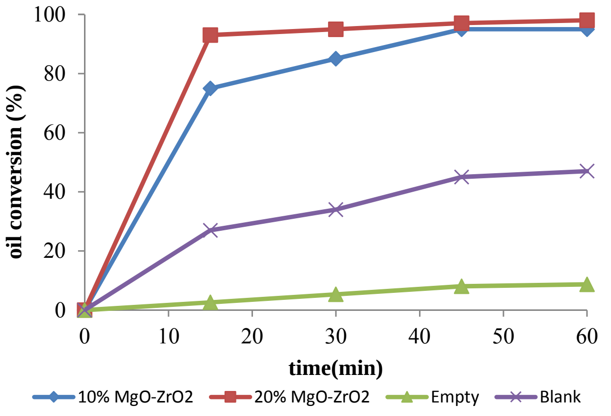

Fig. 5. Waste oil conversion to biodiesel at 225^{o}C as function of time in the absence of catalyst, over blank ZrO_2 support, 10%MgO/ZrO_2 and 20%MgO/ZrO_2 respectively (alcohol to oil molar ratio 18:1, catalyst amount 3 wt.%).

IV. CONCLUSION

The conversion of waste oil to biodiesel over MgO/ZrO_2 catalyst has been assessed at 60, 150, 175 and 200 and 225^{o}C and at reaction times of 15, 30, 45and 60 min. It has been found that the conversion increases with the reaction temperature and the reaction time. The effect of MgO loading in the catalyst on the oil conversion has also been assessed and found to also be influenced by the reaction temperature. Below 175^{o}C the reaction was more mass transfer-controlled and the effect of MgO loading was not significant. Higher oil conversions were measured on the catalyst with the highest MgO loading for the reactions performed at 175 and 200^{o}C. At 225^{o}C the effect of MgO loading could not be evaluated because of a significant contribution of the blank ZrO_2 to the oil conversion.

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