Biodiesel production from Waste Vegetable Oil over \( \text{SnO}_2/\text{ZrO}_2 \) Catalysts

S. Dlambezu, E. Vunain, R. Meijboom, K. Jalama

Abstract— The catalytic properties of \( \text{ZrO}_2 \)-supported \( \text{SnO}_2 \) for the conversion of a modeled waste vegetable oil (5\% oleic acid in soybean oil) into biodiesel have been investigated at 100, 150 and 200\(^{\circ}\)C. The waste oil conversion was found to increase with the reaction temperature and time. The reaction time was limited to 1h in order to operate in low conversion ranges where the effect of temperature on the reaction was clearly determined and allowed the estimation of the apparent activation energy that was found to be ca. 30.18±0.45 kJ/mol.

Index Terms— Apparent activation energy, biodiesel, waste vegetable oil, \( \text{ZrO}_2/\text{SnO}_2 \).

I. INTRODUCTION

The increase of prices of fossil fuels and their global reserve depletion rate have created the need for alternative fuels. Beyond economic priorities, the need for alternative fuels also stretches into health priorities. Fossil fuels emit toxic gases when burnt in conventional engines [1]. Some of these toxic gases have irreversible adverse effects on the environment and the health of living organisms. Various alternative energy sources are central topics of research around the world. These include sun, wind and biomass. Vegetable oils for example, were tried in diesel engines and it was this trial that led to the interest of using vegetable oils as a substitute for diesel fuel in diesel engines [2]. Due to some technical problems associated with vegetable oils in diesel engines such as higher viscosity of the vegetable oil leading to poor fuel atomization, carbon deposition and incomplete combustion leading to engine fouling [2], vegetable oils converted to biodiesel are preferred. Biodiesel is a bio-degradable and non-toxic fuel consisting of fatty acid methyl esters (FAME) which can be synthesized from vegetable oils [2]. It does not contain cancer causing substances, sulphur and aromatics found in the emissions of petrol and diesel engines.

Shahid and Jamal [3] have indicated that over 300 feedstock have been identified for biodiesel production in research with soybean oil being the most commonly used in USA and rapeseed oil in European countries. However, the use of virgin oils constitute a threat as it competes with food production in terms of land and water resources in certain parts of the world. The use of used vegetable oils as feedstock for biodiesel production has become an attractive option as it allows cheap waste materials to be used with no competition with food production while improving environmental conditions at the same time. The use of waste oils also comes with technical problems as they generally contain high contents of free fatty acids (FFA) that lead to soap formation during the biodiesel production process using conventional homogeneous catalysts. Soap formation adversely affects downstream separation processes and must be avoided. For this reasons, solid catalysts have drawn the attention of researchers for application in biodiesel production from waste oils. Because of high contents of FFA in waste oils, the process consists of esterification of FFA to biodiesel and transesterification of triglycerides into biodiesel respectively. A solid catalyst that is active for both esterification and transesterification reactions is required for this application. Tungstated zirconia has been reported to be suitable for both esterification and transesterification [4-7]. Kim et al. [8] have also reported the ability of zirconia supported metal oxides to perform simultaneous esterification and transesterification reactions on FFA-containing oil feedstock for biodiesel production. They used mixed metal oxides (\( \text{ZnO–TiO}_2–\text{Nd}_2\text{O}_3 \) and \( \text{ZnO–SiO}_2–\text{Yb}_2\text{O}_3 \)) respectively supported on \( \text{ZrO}_2 \).

In this study, we intent to investigate catalytic properties of \( \text{ZrO}_2 \)-supported \( \text{SnO}_2 \) for the conversion of waste vegetable oil into biodiesel since good catalytic properties of \( \text{SnO}_2 \) for the transesterification reaction have been reported [9, 10]. In particular, the activation energy for the conversion of waste vegetable oil to biodiesel over the \( \text{SnO}_2/\text{ZrO}_2 \) catalyst system will be estimated.

II. EXPERIMENTAL DETAILS

Zirconia powder from Sigma Aldrich was first mixed with distilled water and dried at 100\(^{\circ}\)C for 2h, and calcined in air at 500\(^{\circ}\)C for 8 h. The sample was then crushed and sieved to keep particles with sizes between 50 and 100\(\mu\text{m} \) as...
catalyst support. An aqueous solution of tin chloride was added to the support in an appropriate proportion to achieve the intended loading of tin in the catalyst. The sample was subsequently dried at 105°C overnight and calcined in air at 500°C for 8h to get the catalyst that was used in this study. The sample was characterized by XRD to respectively study the catalyst structure and determine the SnO₂ content in the catalyst. The biodiesel synthesis reaction was carried out in an agitated batch reactor (Parr reactor, 300ml). The composition of a typical waste vegetable oil was modeled by mixing 154g of soy-bean oil with 8g of oleic acid. This mixture added to 50g of methanol and 1.5g of the catalyst were transferred into the reactor and pressurized with UHP N₂ at an appropriate pressure to keep the methanol in liquid phase at high temperatures. The reaction was performed at different temperatures and a small sample (ca. 5ml) was withdrawn from the reactor after every 15 min and allowed to settle for phase separation. Unreacted methanol and produced glycerol formed one phase separated from the formed biodiesel and the unreacted waste vegetable oil phase. The latter was sent for NMR analysis that was used to determine the waste vegetable oil conversion. The reaction was stopped after 1h to ensure operating in the lower conversion ranges where the effect of reaction temperature was significant and allowed the determination of the reaction activation energy.

III. RESULTS AND DISCUSSION

A. Catalyst characterization

XRD analysis

Fig. 1 below represents XRD data for the ZrO₂-supported SnO₂ catalyst (pattern a) and the calcined blank ZrO₂ support (pattern b).

![XRD patterns for a) ZrO₂-supported SnO₂ catalyst and b) calcined blank ZrO₂ support](image)

The two patterns are almost identical and show the diffraction peaks for ZrO₂ with the most intense peaks at 2θ of ca. 28° and 31° respectively with an exception of an additional peak at 20 of ca. 26° that was only detected in the pattern for the ZrO₂-supported SnO₂ catalyst (pattern a). This peak was attributed to the SnO₂ particles stabilized on the ZrO₂ support and was also used to calculate the average SnO₂ crystallite size using the Scherrer equation below.

\[ D_p = \frac{K\lambda}{\beta \cos \theta} \]  

Where \( D_p \) is the crystallite size in nm;
- \( K \) is the shape factor;
- \( \lambda \) is the X-ray wavelength in nm;
- \( \beta \) is line broadening at half the maximum intensity and
- \( \theta \) is the Bragg angle.
The calculated average crystallite size (with K = 0.9 and λ = 0.15 nm) was found to be ca. 14.6 nm and the SnO\textsubscript{2} content in the catalyst was determined to be ca. 7.5% compared to the intended 10%. This difference was expected considering that XRD is a semi-quantitative technique.

**B. Catalyst testing**

**Effect of reaction temperature and time on waste vegetable oil conversion**

The waste vegetable oil conversion was calculated using NMR analysis data of the biodiesel and unreacted oil phase using the following formulae [11]:

\[
C = 100 \times \left( \frac{2A_{\text{ME}}}{3A_{\text{CH}_2}} \right)
\]

(2)

Where C is the conversion of triacylglycerol feedstock; 
A\text{ME} is the integration value of the protons of the methyl esters; 
A\text{CH}_2 is the integration value of the methylene protons.

An example of the NMR data for a sample collected after 60 min of the reaction performed at 200°C is shown in fig. 2.

![Fig. 2: NMR data for a sample collected after 60 min of the reaction performed at 200°C](image)

The signals at δ 2.3 ppm are due to methylene protons and the signal of the methyl esters protons are represented by the strong singlet at δ 3.6 ppm [11].

Fig. 3 shows the waste vegetable oil conversion data as a function of time and reaction temperature.
Fig. 3: Waste vegetable oil conversion as function of time and reaction temperature.

At 100°C (fig. 3a) the measured waste oil conversions were very low. Conversions of ca. 1.41, 1.59, 1.62 and 2.04% were respectively measured after 15, 30, 45 and 60 min of reaction. These values increased to 2.56, 2.71, 3.19 and 3.81% after 15, 30, 45 and 60 min of reaction respectively when the reaction temperature was increased to 150°C (fig. 3a).

These values of waste oil conversion are still low and below 5%. Increasing the reaction temperature to 200°C resulted in an increase in conversion to 11.11, 12.73, 13.74 and 17.0% after 15, 30, 45 and 60 min of reaction respectively (fig. 3c).

The highest conversion was measured at 200°C after 60 min of reaction. These data show that the waste vegetable oil conversion to biodiesel over ZrO$_2$-supported SnO$_2$ catalyst increases with an increase in temperature and reaction time. The effect of temperature can be explained by the following:

i) As the temperature increases, the viscosity of the waste vegetable oil decreases and improves the mass transfer of reactants to the active sites in the catalyst;

ii) More waste vegetable oil eventually dissolves in methanol and also improves the mass transfer in the catalyst;

iii) More energy is added to the system and helps overcome the activation energy barrier;

iv) More reaction sites become activated at high temperatures.

Higher conversions are required for industrial applications. The conversions measured over ZrO$_2$-supported SnO$_2$ in this study are low because the reaction time was limited to 1h. Higher reaction temperatures and extended reaction times must be used to achieve higher conversions. Other alternatives to increase the waste vegetable oil conversion include the increase in catalyst amounts and methanol to oil ratio, not considered in this study.

**Average reaction rate and apparent activation energy**

As the reaction was done with an excess of methanol, the average reaction rate was expressed in terms of waste vegetable oil as the limiting reagent. It was calculated after 15, 30, 45 and 60 min of reaction as the number of
moles of waste vegetable oil converted to bio diesel divided by the reaction time. Fig. 4 shows the average reaction rates at different reaction time as a function of reaction temperature. They follow an exponential law in temperature. The data also show a decline in the average reaction rate as the reaction time increases. For example an average rate of ca. 0.0013 mol/min was measure after 15 min of the reaction performed at 200°C (fig. 4a) and declined to 0.00076 (fig 4b), 0.00055 (fig 4c) and 0.00051 mol/min (fig. 4d) respectively after 30, 45 and 60 min of the reaction performed at 200°C. This decline can be explained by a decrease in waste vegetable oil concentration in the reactor as the reaction time increases. Fig. 5 shows the dependence of the average reaction rate on 1/T and the estimated apparent activation energy.

Fig. 4: Average reaction rates after a) 15 min, b) 30 min, c) 45 min and d) 60 min of reaction as a function of reaction temperature
The values of the apparent $E_a$ calculated at different reaction times were, within an experimental error, very close. Apparent activation energies of 29.66, 29.84, 30.77 and 30.44 kJ/mol have been obtained after 15, 30, 45 and 60 min of reaction respectively. The apparent activation energy has therefore been estimated as 30.18±0.45 kJ/mol.

IV. CONCLUSION

SnO$_2$/ZrO$_2$ catalyst has been prepared by impregnation of the ZrO$_2$ support with SnCl$_2$ followed by drying and calcinations in air. The average SnO$_2$ crystallite size as determined by XRD was found to be 14.6 nm. The catalyst was tested in the conversion of a modelled waste vegetable oil into biodiesel at 100, 150 and 200°C for up to 1h of reaction. The conversion was found to increase with the reaction time and temperature. The apparent activation energy for the reaction over the SnO$_2$/ZrO$_2$ catalyst system was estimated as 30.18±0.45 kJ/mol.

REFERENCES


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