

# Waste Vegetable Oils to Biodiesel over $\text{Al}_2\text{O}_3$ – Supported $\text{SnO}_2$ Catalyst: Effect of Support Pore Size

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**Abstract**—The main aim of this study was to investigate the catalytic properties of  $\text{Al}_2\text{O}_3$ -supported  $\text{SnO}_2$  for the conversion of waste vegetable oil into biodiesel. The effect of support pore size on waste oil conversion was investigated at 100 and 200 °C by using  $\alpha$ -alumina (with larger pore size) and  $\gamma$ -alumina (with smaller pore size) respectively as support for  $\text{SnO}_2$ . The effect of pore-size on conversion was found to depend on the operating temperature. At low temperature, i.e. 100 °C, higher conversion for waste vegetable oil was measured on  $\text{SnO}_2$  catalyst supported on  $\alpha$ - $\text{Al}_2\text{O}_3$  than the catalyst supported by  $\gamma$ - $\text{Al}_2\text{O}_3$ . This effect became less significant at 200 °C. It was also observed that the oil conversion increased with an increase in reaction temperature and reaction time.

**Index Terms**—Biodiesel,  $\text{SnO}_2/\text{Al}_2\text{O}_3$ , Support pore size, Waste vegetable oil

## I. INTRODUCTION

THE global energy requirements are currently primarily supplied by fossil fuels, nuclear fuels and hydroelectric sources with fossil fuels being the major sources [1]. However, there are problems associated with the current fossil fuel sources. Some of these energy problems include the limited availability of fossil fuels such as petroleum oil, natural gas and coal due to the increased demand. According to Balat [2] the demand for these energy sources is estimated to increase radically in future. The current used fossil fuels are classified as non-renewable sources, that is, after they are consumed they cannot be replaced in a meaningful time frame [2]. This implies that an increase in the use of non-renewable fossil fuels results in larger emissions of greenhouse gases and higher prices of fuels due to the limited availability of these energy sources. Because of these problems, there is a need of alternative

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sources which are renewable, economic and environmental friendly.

Biodiesel is one of the most researched renewable energy sources. It is a form of diesel fuels; it is safe, biodegradable and produces less air pollutants than petroleum-based diesel [3]. It is produced from vegetable oils, animal fats or recycled restaurant greases [3]. However, the feedstock used for biodiesel production has limited availability, and is expensive, thus representing a challenge to the fuel industry. For this reason, the use of waste vegetable oils can be an effective way of reducing production costs, since waste oils are cheaper than virgin vegetable oils. However, this feedstock usually contains an amount of free fatty acids that leads to undesirable saponification in the presence of homogeneous base catalysts such as NaOH, KOH, etc. To avoid these drawbacks, our study will use  $\text{SnO}_2/\text{Al}_2\text{O}_3$  as a solid, heterogeneous catalyst for the production of biodiesel from waste vegetable oils. The effect of  $\text{Al}_2\text{O}_3$  support pore size on the waste oil conversion will be evaluated.

## II. EXPERIMENTAL

### A. Catalyst Preparation

Gamma ( $\gamma$ - $\text{Al}_2\text{O}_3$ ) and alpha ( $\alpha$ - $\text{Al}_2\text{O}_3$ ) alumina purchased from Sigma-Aldrich were used to first prepare the catalyst supports with different pore sizes. Alumina (50 g) was mixed with distilled water (ca. 40 g) to form a paste that was dried in air at 120 °C for 18 hours. The dried sample was subsequently calcined in air at 500 °C for 11 hours. After calcination, the material was sieved to retain particles with sizes 100 - 150  $\mu\text{m}$  for use as catalyst support. The calcined support was impregnated with an aqueous solution of tin chloride ( $\text{SnCl}_2$ ) and dried in air at 120 °C overnight, followed by calcination in air at 500 °C for 11 h. The amount of tin chloride solution was determined so that 10% by mass loading of tin oxide in the catalyst after calcination in air was achieved.

### B. Catalyst Characterization

The  $\text{SnO}_2$  loading in the catalyst after calcination was determined by X-ray fluorescence (XRF) analysis performed using a MAGIX PRO XRF spectrometer. The surface area and pore size distribution of the two blank supports ( $\gamma$ - and  $\alpha$ - $\text{Al}_2\text{O}_3$ ) and the  $\text{SnO}_2/\text{Al}_2\text{O}_3$  catalysts were measured by  $\text{N}_2$  sorption experiments at a temperature of 77 K using a Micromeritics Tristar 3000 apparatus, using the Brunauer-Emmett-Teller (BET) analysis. X-ray diffraction (XRD) analysis was used to determine the structure of the catalyst system and that of the blank

calcined supports on a Philips PW 3040/60 using a CuK $\alpha$  radiation. Samples were scanned over a  $2\theta$  range of 4–90° with a 0.02° step size and a scan speed of 0.04 s/step.

### C. Catalyst Evaluation

The prepared Al $_2$ O $_3$ -supported SnO $_2$  catalyst samples were evaluated for the *trans*-esterification of a waste oil that was represented by a mixture of soybean oil (95 wt.%) and oleic acid (5 wt.%) in a 300 cm $^3$  Parr batch autoclave reactor under a nitrogen pressure that was selected to keep all the reactants in liquid phase at the selected reaction temperatures. The stirring speed of the reactor was set at 1100 rpm for all the runs. The reactions were performed at 100 and 200 °C using the synthesized SnO $_2$  catalyst supported on  $\alpha$ - and  $\gamma$ -Al $_2$ O $_3$  respectively. Small samples were drawn from the reactor on 15 minute intervals and allowed to cool. The top layer of the sample, containing biodiesel and unreacted oil, was analysis on a Master Dani GC using TRB-biodiesel column: 30 m x 0.3 mm x 0.25  $\mu$ m connected to an FID to determine the oil conversion.

## III. RESULTS AND DISCUSSION

### A. Catalyst Characterization

**XRD analysis.** Fig.1 shows the XRD pattern for the calcined blank  $\gamma$ -Al $_2$ O $_3$  support and SnO $_2$ / $\gamma$ -Al $_2$ O $_3$  catalyst respectively.

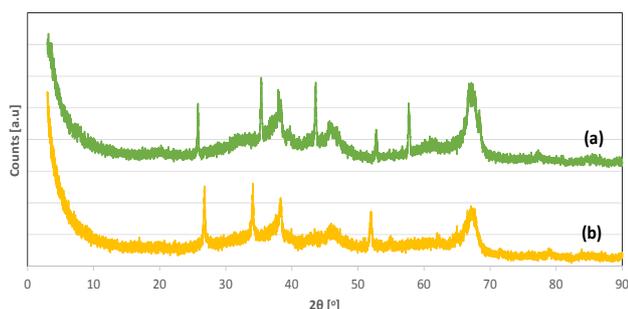


Fig. 1. XRD pattern of (a) calcined blank gamma Al $_2$ O $_3$ ; (b) calcined SnO $_2$ /Al $_2$ O $_3$  (gamma) catalyst.

No diffraction peak for SnO $_2$  was detected probably because they overlapped with the  $\gamma$ -Al $_2$ O $_3$  peaks or the crystallite size for SnO $_2$  in the sample was too small.

The XRD data for calcined blank  $\alpha$ -Al $_2$ O $_3$  support and SnO $_2$ / $\alpha$ -Al $_2$ O $_3$  are reported in figure 2.

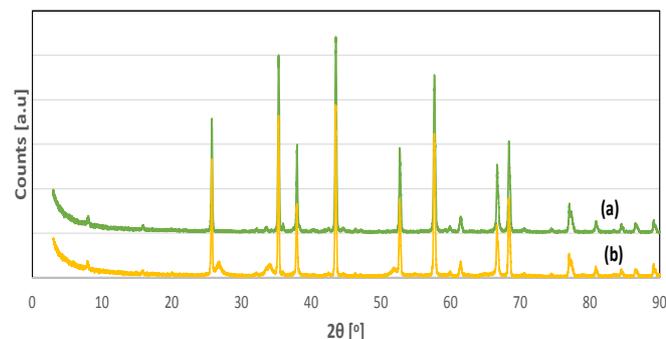


Fig. 2. XRD pattern of (a) calcined blank alpha Al $_2$ O $_3$ ; (b) calcined SnO $_2$ /Al $_2$ O $_3$  (alpha) catalyst.

An additional peak was detected for the SnO $_2$ / $\alpha$ -Al $_2$ O $_3$  sample at a diffraction angle  $2\theta$  of ca. 27°. This was attributed to SnO $_2$  crystallites.

**XRF analysis.** XRF analysis was performed in order to determine the SnO $_2$  loading in the catalysts. The results are summarized in table 1.

TABLE I: XRF ANALYSIS RESULTS FOR THE PREPARED CATALYSTS

Catalyst	Target % SnO $_2$	Obtained % SnO $_2$
SnO $_2$ / $\gamma$ -Al $_2$ O $_3$	10	8
SnO $_2$ / $\alpha$ -Al $_2$ O $_3$	10	12

The measured SnO $_2$  loadings in SnO $_2$ / $\gamma$ -Al $_2$ O $_3$  and SnO $_2$ / $\alpha$ -Al $_2$ O $_3$  were found to be ca. 8 and 12% respectively. These values were within the error range expected from an XRF analysis and therefore were found satisfactory for this study.

**BET data.** The surface area and pore size for the calcined blank  $\alpha$ - and  $\gamma$ -Al $_2$ O $_3$  supports, and calcined SnO $_2$ / $\alpha$ -Al $_2$ O $_3$  and SnO $_2$ / $\gamma$ -Al $_2$ O $_3$  samples are summarized in table 2. Calcined blank  $\gamma$ -Al $_2$ O $_3$  had a surface area of ca. 132.2 m $^2$ /g and an average pore diameter of 5.8 nm. These values did not practically change as they respectively became 132.1 m $^2$ /g and 6.0 nm for surface area and pore diameter when the support was loaded with SnO $_2$  after calcination. The  $\alpha$ -Al $_2$ O $_3$  had a surface area of 0.39 m $^2$ /g, which is significantly lower than that of  $\gamma$ -Al $_2$ O $_3$  and a pore diameter of 142.9 nm, which is much larger. Upon SnO $_2$  loading, the surface area for SnO $_2$ / $\alpha$ -Al $_2$ O $_3$  increased to 1.4 m $^2$ /g and the pore size significantly decreased to 21.6 nm. This suggest that most of the loaded SnO $_2$  stabilized inside the pores of the  $\alpha$ -Al $_2$ O $_3$  support.

TABLE II: SUMMARY OF BET DATA

	Calcined blank $\gamma$ -Al $_2$ O $_3$	Calcined blank $\alpha$ -Al $_2$ O $_3$	SnO $_2$ / $\gamma$ -Al $_2$ O $_3$	SnO $_2$ / $\alpha$ -Al $_2$ O $_3$
Surface area (m $^2$ /g)	132.2	0.4	132.1	1.4
Pore size (nm)	5.8	142.9	6.0	21.6

### B. Catalyst evaluation

Reactions with catalysts of different pore sizes were performed at 100 °C and 200 °C. Fig. 3 shows the waste oil conversion to biodiesel as a function of reaction time at 100 °C as catalyzed by 10% SnO $_2$  loaded on  $\alpha$ - and  $\gamma$ -Al $_2$ O $_3$  supports respectively.

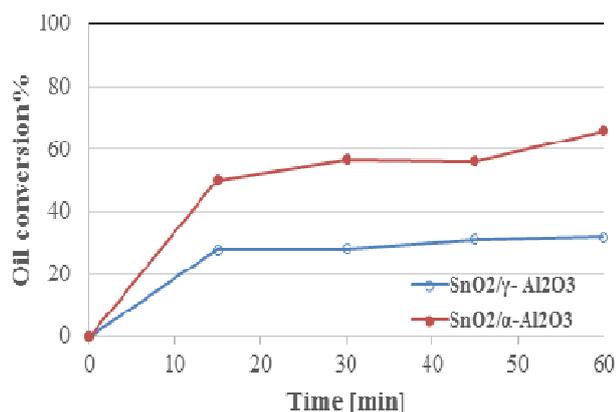


Fig. 3. Waste oil conversion versus reaction time over SnO<sub>2</sub>/α-Al<sub>2</sub>O<sub>3</sub> and SnO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalysts at 100 °C

The following were observed when the reaction was performed at 100 °C:

- i) The waste oil conversion increased with reaction time for both α- and γ-Al<sub>2</sub>O<sub>3</sub>-supported SnO<sub>2</sub> catalysts. Waste oil conversions of ca. 50, 56, 57 and 66% were measured after 15, 30, 45 and 60 min of reaction over SnO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalyst respectively. A similar trend was observed for the reaction using SnO<sub>2</sub>/α-Al<sub>2</sub>O<sub>3</sub> catalyst.
- ii) Higher conversions were measured over SnO<sub>2</sub>/α-Al<sub>2</sub>O<sub>3</sub> catalyst compared to SnO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalyst which had values approaching half the conversions measures on SnO<sub>2</sub>/α-Al<sub>2</sub>O<sub>3</sub> catalyst after the same reaction time.

These data unveil a correlation between catalyst pore size and waste vegetable oil conversion. Higher conversions were measured on the catalyst with larger pore size (ca. 21.6 nm for SnO<sub>2</sub>/α-Al<sub>2</sub>O<sub>3</sub> catalyst). This suggests increased mass transfer within the catalyst particles with increasing pore size.

The data for reactions conducted at 200 °C are presented in fig. 4 and show higher waste vegetable oil conversions than the reactions conducted at 100 °C. For example, conversions of ca. 88, 95, 94 and 97% were measured after 15, 30, 45 and 60 min over SnO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalyst at 200 °C compared ca. 28, 28, 31 and 32 after 15, 30, 45 and 60 min of reaction respectively at 100 °C.

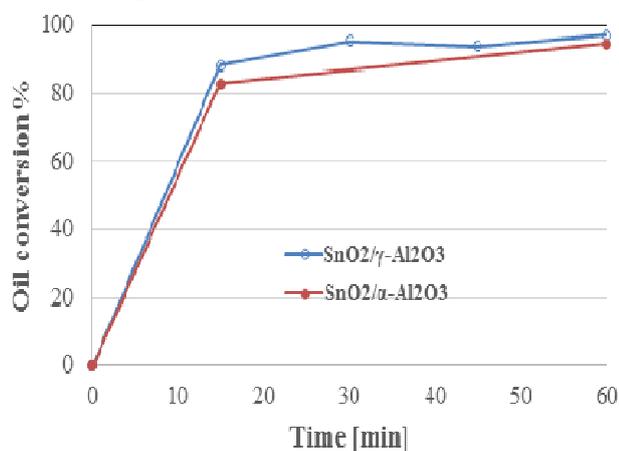


Fig. 4. Waste oil conversion versus reaction time over SnO<sub>2</sub>/α-Al<sub>2</sub>O<sub>3</sub> and SnO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalysts at 200 °C

This increase in oil conversion with an increase in reaction temperature can be explained by improved mass transfer in the catalyst as a result of increased oil solubility in methanol and a decrease in oil viscosity with temperature. It is also possible that the strength of the basic sites is also affected by the reaction temperature.

The data in figure 4 also show that at 200 °C, there is no significant difference between the levels of oil conversions measured on both SnO<sub>2</sub>/α-Al<sub>2</sub>O<sub>3</sub> and SnO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalysts, suggesting that the effect of catalyst pore size is less significant at higher reaction temperatures. This indicates that catalyst pore size plays a significant role in reactions that are mainly mass-transfer controlled.

#### IV. CONCLUSION

The effect of catalyst support pore size on the conversion of waste vegetable oil to biodiesel was investigated at 100 and 200 °C using SnO<sub>2</sub>/α-Al<sub>2</sub>O<sub>3</sub> and SnO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalysts with comparable SnO<sub>2</sub> loading. It was found that catalyst pore size has a significant effect at low temperature (100 °C) where the reaction seems to be significantly mass-transfer controlled. Higher oil conversions were measured on the catalyst with larger pores. This effect was not significant at a higher reaction temperature (200 °C).

#### REFERENCES

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