

## Synthesis of homogeneous and heterogeneous base catalysts for the esterification of soybean oil

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### ABSTRACT

*Studies using soybean oil and alkali and alkaline metal alkoxides have been conducted using  $\text{CH}_3\text{ONa}$ ,  $\text{CH}_3\text{OK}$ ,  $(\text{CH}_3\text{O})_2\text{Ca}$ , and  $(\text{CH}_3\text{O})_2\text{Mg}$ . However, the Na and K metal alkoxides were found to be most active during the methanolysis reaction. The influence of Na loading on a  $\gamma\text{-Al}_2\text{O}_3$  support was investigated. Surface area monotonically decreases with increasing NaOH loading. A 10 wt % Na solution optimum was found for the methanolysis reactions. This catalyst has been found to have a few optimum parameters. A catalyst concentration of 3.5 g per 100 g of soybean oil provided the best results when varying the amount of catalyst. A study of the effect of methanol to oil ratio also found that the yield increases as methanol to oil ratio increases.*

**Key words:** Biodiesel, methanolysis, alkoxides, Na /  $\gamma\text{-Al}_2\text{O}_3$

### INTRODUCTION

Biodiesel refers to lower alkyl esters of long chain fatty acids, which are synthesized by transesterification with lower alcohols [5]. Chemically, the oil/fats consist of triglycerides molecules of three long chain fatty acids that are ester bonded to a single glycerol molecule. The stoichiometric reaction for biodiesel production requires 1 mol of a triglyceride and 3 mol of the alcohol.

Most of the commercial biodiesel is produced from plant oils by using very effective homogeneous base catalysts containing NaOH or KOH dissolved in methanol. The homogeneous catalyst thus made favours the formation of stable emulsion making separation of methyl ester more difficult. Glycerol is also obtained as an aqueous solution of relatively low purity. The reaction is sensitive to the presence of water and free fatty acids.

These problems can be alleviated with the use of heterogeneous transesterification catalysts. Solid base catalysts have been considered as an alternative to homogeneous base catalysts due to several advantages: the catalysts are not dissolved or consumed in the reaction and therefore can be easily separated from the product, regenerated and reused and the catalyst also can be applied in a continuous process. Therefore, there is an increasing interest in the possibility of replacing the homogeneous base catalysts by heterogeneous solid catalysts that could potentially lead to easier refining of the produced biodiesel and glycerol, recycling of the catalysts and hence, lower production costs.

Transesterification is a reversible catalytic reaction. However, an excess of the alcohol is used to increase the yields of the alkyl esters and to allow its phase separation from the glycerol formed. Several aspects, including the type of catalyst, alcohol, edible/non-edible oil, purity of the reactants (mainly water content) and free fatty acid content have an influence on the course of the transesterification reaction [5].

In this work, the transesterification of soybean oil is studied using several homogeneous and heterogeneous base catalysts. The catalytic activity of the methanol solution of the hydroxides of sodium, potassium, and calcium and methoxide of sodium, potassium, magnesium and calcium, for the transesterification of soybean oil has been investigated. The heterogeneous catalyst is prepared with basic solids consisting of NaOH supported on gamma alumina [11]. The transesterification reaction has been carried out to find the effect of the concentration of catalyst, methanol/oil and catalyst/methanol molar ratios. Also in this regard, the performance of the heterogeneous catalysts has been compared with that of conventional homogeneous NaOH [12].

## EXPERIMENTAL PROCEDURE

The experiment was performed with 100 gm of oil placed in a reactor and then heated to the desired temperature (60 °C). Measured amounts of methanol (6:1 molar ratio) and NaOH (1.5 % w/w) of oil were mixed separately at room temperature to make a homogeneous solution [10]. This solution was then added to the bottom of an agitated reactor (750 rpm) to avoid the loss of methanol. In the case of heterogeneous catalyst the transesterification reaction was carried out at 60 °C with 250 gm grams of soybean oil, the required amount of supported catalysts and the volume of methanol required to obtain a alcohol/oil molar ratios of 6:1, 12:1, 24:1 were added into the reactor and samples (about 20 ml) were withdrawn at various intervals for intermediate yield analysis [7]. The sample was then allowed to settle for 12 hours followed by the washing of the upper biodiesel containing layer with 70°C heated distilled water and mild shaking to remove the NaOH catalyst and excess methanol. The waste was removed from the bottom of the separating funnel [2]. The upper ester layers of the samples were analysed with  $H^1$  NMR spectroscopy for the calculation of conversion/yield using published procedures [3]. The same steps were followed for different catalysts and alcohol with the corresponding molar ratios.

## Heterogeneous Catalyst Preparation

A series of heterogeneous base catalysts ( $Na/Al_2O_3$ ) were prepared by the incipient wetness impregnation (IWI) method. Prior to catalyst preparation, the support was pretreated by mixing with incipient wetness volumes of water [6]. The paste of the support was dried in a desiccator for 8 hr followed by heated through a pre-defined temperature cycle and finally calcined at 500°C for 6 hr. The pretreated support was loaded with required amounts of NaOH solution in incipient wetness volumes and followed by the same pre-defined temperature cycle and calcinations [1]. The reaction with the prepared catalyst was done in the same reactor using the reagents in the same ratios as the homogeneous catalyst.

## Equipment used

A 2.0 litre batch reactor (AmAr Equiprnents Ltd, Mumbai, India) was used in this study for transesterification studies. The reactor is equipped with a PID controller, RTD-PT100 temperature sensor, electrically heated jacket, a cooling water circulation system, magnetic stirrer and a reflux condenser with other valves and gauges. Valve at the bottom was used for sampling [8].

## Catalyst Characterization

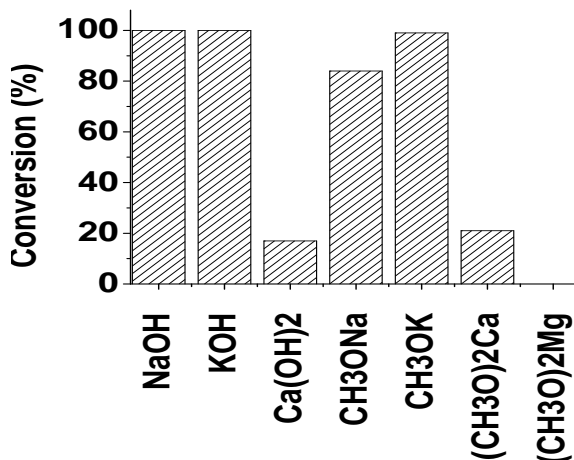
The prepared catalysts were characterized by different techniques such as BET surface area measurement and X-ray diffraction (XRD).

The surface area of the catalysts samples were measured using SMART SORBS 92/93, which was based on the BET single point equation using nitrogen absorption.

The XRD patterns of the selected samples were obtained with 180 Debye Flex-2002 X-ray diffractometer [9]. Nickel filtered  $K_{\alpha}$  radiation of copper target ( $\lambda=1.541841 \text{ \AA}$ ) was employed covering  $2\theta$  angles of up to  $90^{\circ}$ , data were recorded in the step mode at  $2\theta$  sweep of  $3^{\circ} \text{ min}^{-1}$  and a time constant of 3.0 s was maintained. The data were collected in the range of 10 to  $75^{\circ}$ .

## RESULTS AND DISCUSSION

Comparing the different homogeneous catalysts it was observed that sodium hydroxide, sodium methoxide, potassium hydroxide and potassium methoxide showed high and comparable conversion (90-100%). In contrast, calcium hydroxide and calcium methoxide showed less conversion (15-20%) and magnesium methoxide showed no conversion in soybean oil methanolysis at  $60^{\circ}\text{C}$ . The results of this study are shown in Figure 1.



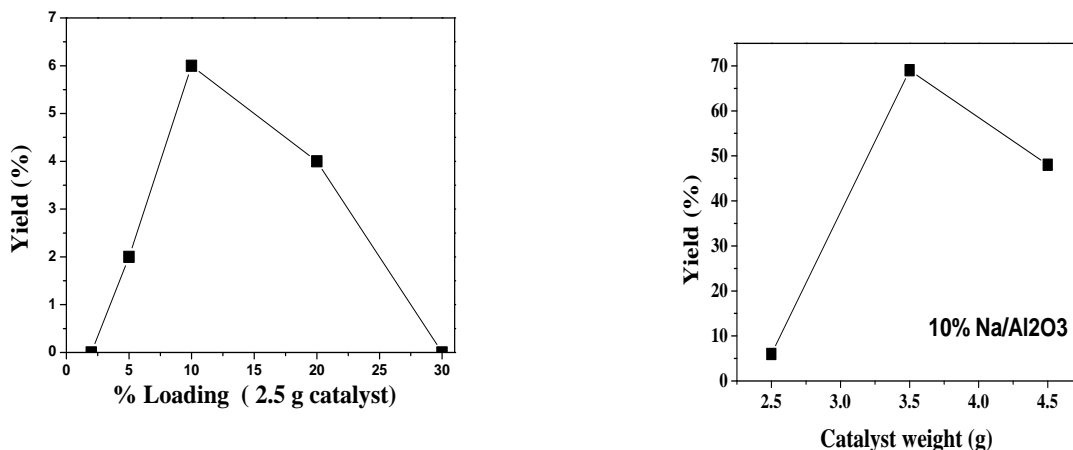
**Figure 1-** Effect of type of homogeneous catalyst on the conversion at  $60^{\circ}\text{C}$

The effect of using ethanol instead of methanol was also studied. The conversion results were compared with methanol and ethanol for the same experimental procedure using homogeneous catalyst (NaOH) and are shown in Table 1. During the course of the transesterification reaction emulsions are usually formed. In the case of methanolysis these emulsions quickly and easily break down to form a lower glycerol-rich layer and upper methyl ester-rich layer. In ethanolysis, these emulsions were more stable and severely complicate the separation and purification of esters.

S.No.	Alcohol	Yield (%)
1	CH <sub>3</sub> OH	100
2	C <sub>2</sub> H <sub>5</sub> OH	65

**Table 1-** Effect of alcohol on transesterification reaction at 60 °C

Therefore, NaOH is considered for making the heterogeneous catalyst. Different NaOH percentage loadings on Al<sub>2</sub>O<sub>3</sub> were tried as catalysts and the results are shown in Figure 2. It was observed that the conversion increase and then decrease as the NaOH % increased. The optimum percentage loading of catalyst was 10% Na/γ-Al<sub>2</sub>O<sub>3</sub>. Furthermore the optimum amount of catalyst (10% Na/γ-Al<sub>2</sub>O<sub>3</sub>) was 3.5 g per 100 g of catalyst.



**Figure 2-** Optimum % loading of Na on Al<sub>2</sub>O<sub>3</sub> using 2.5 g catalyst and the amount of catalyst for 10% Na/Al<sub>2</sub>O<sub>3</sub>

To understand the reason for this optimum loading the surface area of the catalyst were determined and presented in Table 2. From Table 2 it is observed that the surface area monotonically decreases with an increase in NaOH loading. It appears that the increase in the amount of Na in heterogeneous catalysts is not necessarily beneficial since the surface area

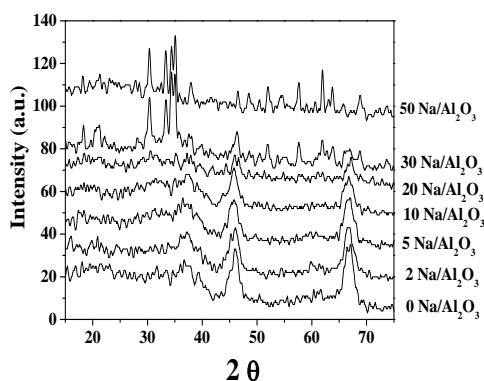
available for the reaction decreases. Combination of these two factors may give rise to the optimum NaOH loading.

Sample Code	Na/ Al <sub>2</sub> O <sub>3</sub> (% loading)	BET Area (m <sup>2</sup> /g)	%Yield (2.5 g Catalyst)
0 Na/Al <sub>2</sub> O <sub>3</sub>	0	145	0
2 Na/Al <sub>2</sub> O <sub>3</sub>	2	137	0
5 Na/Al <sub>2</sub> O <sub>3</sub>	5	110	2
10 Na/Al <sub>2</sub> O <sub>3</sub>	10	86	6
20 Na/Al <sub>2</sub> O <sub>3</sub>	20	12	4
30 Na/Al <sub>2</sub> O <sub>3</sub>	30	3	0

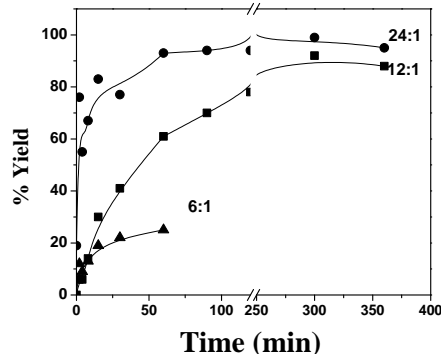
**Table 2-** Effect of Na loading on BET Area and Yield.

Homogeneous NaOH is clearly more active than the heterogeneous catalysts. This is, of course, a primary consequence of the fact that the solid catalysts are insoluble in methanol. Though almost all pure NaOH added in the homogeneous process does react to form sodium methoxide, the amount of active species formed in the heterogeneous reaction depends critically on the surface properties and texture of the solid catalysts.

XRD analyses of selected samples were performed to obtain more information about the catalysts structure. Figure 3 shows the XRD patterns of the prepared catalysts. The patterns of the treated support and the prepared catalysts reveal some differences. Several additional diffraction peaks are clearly visible showing the presence of NaOH and Na<sub>2</sub>O<sub>2</sub>, both as hydrated compounds, and sodium aluminate (NaAlO<sub>2</sub>). These results indicate that some of the NaOH has reacted with the support giving rise to the formation of aluminates.



**Figure 3-** XRD patterns of the support and the catalysts



**Figure 4 -** Time scale study of the transesterification reaction for various methanol /oil

In order to study the effect of the methanol/oil ratio in the reaction mixture, three molar methanol/oil ratios, 6:1, 12:1 and 24:1, were considered. These set of experiments were performed with the optimum loading catalyst, 10 Na/Al<sub>2</sub>O<sub>3</sub> and the results are shown in Figure 4. As shown in Figure 4 the performance of the NaOH /  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts depends on the methanol/oil molar ratio. An oil yield of 25% is reached at 1hr with a 6:1 methanol/oil ratio; it increase up to 60 % at a 12:1 ratio and is almost complete at a Methanol/oil ratio of 24:1. It appears that with an increase in methanol/oil ratio additional methoxide species are formed on the catalyst surface, thus, favouring the transesterification reaction. Initial studies reveal that the heterogeneous catalyst (NaOH/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>), however is inactive for ethanolysis.

## CONCLUSIONS

In the present study several methanol solutions of alkali and alkaline hydroxide and alkali and alkaline methoxides were studied for the transesterification reaction. The sodium and potassium hydroxide solutions or methoxide were found to be the most active. A series of supported sodium on Al<sub>2</sub>O<sub>3</sub> heterogeneous catalyst were also tested for the transesterification reaction. An optimum sodium loading was obtained. The influence of the molar methanol/oil and catalyst/methanol ratios was also considered. It was observed that the performance significantly depends on the methanol/oil molar ratio. This behaviour can be interpreted in terms of a more favoured methoxide formation as the methanol/oil ratio is increases due to an increased driving-force for methanol adsorption. The result also shows that the transesterification rate depends on the catalyst/methanol ratio and a higher than stoichiometric catalyst/methanol ratio is favoured. Additional studies are required for understanding the effect of sodium loading and effects of leaching, if any.

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