SODIUM ALUMINATE AS HETEROGENEOUS CATALYST FOR BIODIESEL PRODUCTION

A

Thesis submitted

in partial fulfilment of the requirement

for the degree of

Master of Science in Chemistry

Submitted by :	Supervised by :
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July 2010

Acknowledgement

I would like to express my gratitude to all those who gave me any kind of possible support to complete this project.

I am deeply indebted to my supervisor Assistant Professor **Dr. Satnam Singh** from the **Thapar University, Patiala** whose help, stimulating suggestions and encouragement helped me in all the time of work for and writing of this report.

Especially I am obliged to the laboratory staff of chemistry department for their support and help. Also, I am very thankful to research scholar **Mr. Vishal Mutreja** for their guidance and offering suggestions for improvement.

All these thanks are, however, only fraction of what is due to almighty for granting me an opportunity and strength to successfully accomplish this assignment.

Date: 15 July 2010

Baldish Kaur

Candidate's Declaration

I hereby declare that the work presented in the thesis entitled, "**Sodium Aluminate as Heterogeneous Catalyst for Biodiesel Production**", in partial fulfilment of the requirement for the award of the degree of **Masters of Science in Chemistry and being submitted to Thapar University, Patiala,** in my own work during the period of January 2010 to June 2010, under the supervision of **Dr. Satnam Singh**, Assistant Professor, School of Chemistry and Biochemistry, Thapar University, Patiala. I have not submitted the contents embodied in this thesis for the award of any other degree.

Patiala

Date: 15 July 2010

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This is to certify that the above statement made by the candidate is correct and true to the best of our knowledge.

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This is to certify that the thesis entitled "**Sodium Aluminate as Heterogeneous Catalyst for Biodiesel Production**" being submitted by Ms. Baldish Kaur to **Thapar University, Patiala**, in partial fulfilment of the requirement for the award of the degree of Master of Science in Chemistry, is a bonafide work carried out under my supervision, and that no part of this thesis has been submitted for the award of any other degree.

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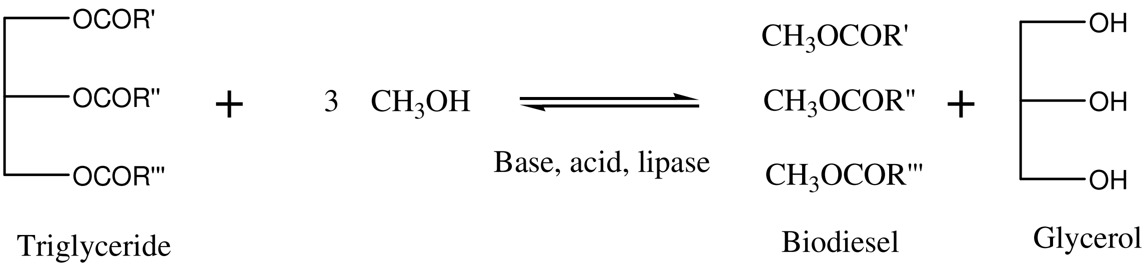
ABSTRACT

Sodium aluminate has been found to catalyse complete transesterification of used cotton seed oil. At optimum reflux conditions of methanol, for 0.5 wt % of the catalyst with 1: 22 molar ratio of oil and methanol, time required for completion of reaction was 1h 45 min. With higher oil: methanol molar ratio of 1:54, the catalyst showed tolerance of moisture upto 8 wt %. Sodium aluminate with calcination in the range of 250-850°C was also evaluated for transesterification of used cotton seed oil with methanol. Both sodium aluminate and calcinied sodium aluminate (250-850°C) were characterized by Powder XRD, Hammett indicators and TEM.

INTRODUCTION

The limited and fast diminishing resources of mineral oil, increasing price of crude oil and environmental concerns have been the diverse reasons for exploring the use of triglycerides (vegetable oils and animal fats) as alternative fuels [1]. It was on August 10, 1893 when a prime model of Rudolf Diesel, a single 10 ft (3m) iron cylinder with a flywheel at its base, ran on its own power for the first time in Augsburg, Germany, running on nothing but peanut oil. In remembrance of this event, August 10 has been declared "International Biodiesel Day". On August 31, 1937, G. Chavanne of the University of Brussels (Belgium) was granted a patent for a "Procedure for the transformation of vegetable oils for their uses as fuels"[2]. This patent described the transesterification of vegetable oils using ethanol and methanol in order to separate the fatty acids from the glycerol by replacing the glycerol with short linear alcohols. This appears to be the first account of the production of today's "biodiesel". Hence, the idea of using vegetable oil as fuel for diesel engines was over a century old when Rudolph Diesel, inventor of Diesel engine, himself demonstrated the performance of his engine using peanut oil as fuel. However, their direct use has not been satisfactory because of high viscosity and poor ignition quality [3].

Treatments that could overcome the major problems associated with the high viscosity of vegetable oils when used as diesel engine fuels are its dilution, micro emulsification, pyrolysis and transesterification with alcohols of short chain length [4]. Transesterification of the triglycerides(TGs) with alcohols in the presence of catalyst (acid, alkali or enzymes) lead to the formation of less viscous fatty acid alkyl esters, known as biodiesel, an alternative fuel for diesel engines and heating systems[5] as shown in scheme 1.



Scheme 1: Reaction of triglyceride with methanol to from biodiesel

Biodiesel can be produced from variety of vegetable oils as feedstocks, viz., sunflower oil, rapeseed oil, rubber seeds, jatropa, karanja, soy bean oil, animal fats or even recycled greases from food industry. Biodiesel has become very attractive diesel fuel substitute as it is derived from renewable resources, is less air polluting, contains more energy per unit than diesel, nontoxic and is biodegradable. Biodiesel can be used either in pure form or in the form of blends with conventional diesel fuel in most modern compression ignition engines [6]. Blends of biodiesel and petroleum diesel are designated by "B" followed by the vol % of biodiesel e.g. B5 and B20, consisting of 5 and 20% biodiesel respectively. Biodiesel with the conventional diesel fuel doesn't require any modification in present diesel engines.

Although the use of homogeneous base catalyst for transesterification of high quality feedstocks gives the excellent result but in case of low grade feedstock leads to serious limitation viz., formation of soap, deactivation of catalyst (in the presence of high free fatty acid and moisture content) contamination of biodiesel and glycerol (by-product) with soap and homogeneous catalyst which requires additional step of neutralization by acid [1].

Homogeneous acid catalysts have the potential to replace base catalysts, since they do not show measurable susceptibility to free fatty acids (FFAs) and can catalyze esterification of FFAs and transesterification of triglycerides simultaneously. However, slow reaction rate and requirement of high molar ratio of oil and alcohol, separation of the catalyst, serious environmental and corrosion related problems, make their use non-practical for biodiesel production at industrial scale [7].

LITERATURE REVIEW

Sustainable energy management is the major concern of modern society. The increasing energy demand makes the implementation of sustainable fuels is a crucial issue worldwide. Biodiesel has become increasingly attractive because it is made from renewable sources and its higher cetane number, meaning better and safer performance than petroleum diesel.

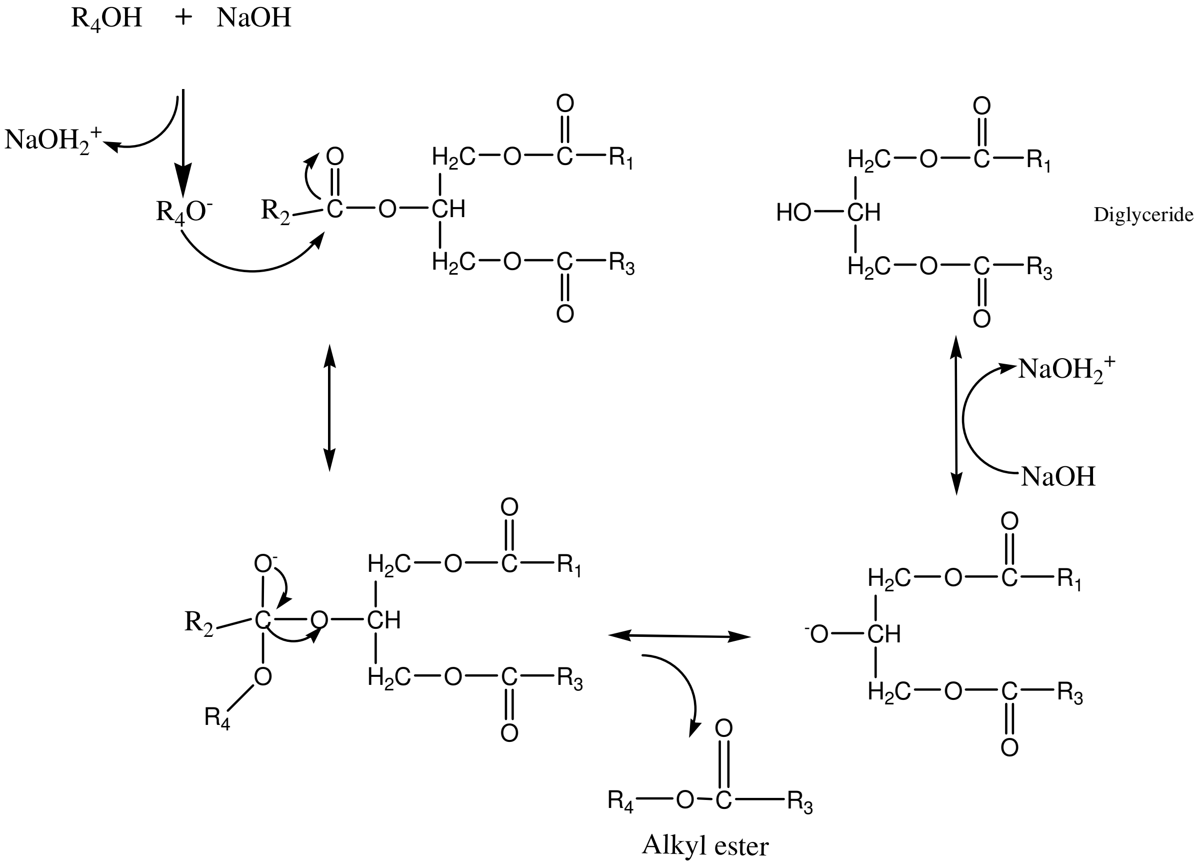
Use of biodiesel is more significant over mineral diesel due to properties[8] based on American Society for Testing and Materials (ASTM) which are tabulated below in table 1.

Table 1: Comparisons of the standards for diesel and biodiesel

Properties	**Diesel**	**Biodiesel**
Standard Number	ASTM D975	ASTM D6751
Composition	Hydrocarbon (C_{10}–C_{21})	Fatty acid methyl ester (C_{12}-C_{22})
Specific gravity (g/ml)	0.85	0.88
Flash point (K)	333–353	373–443
Cloud point (K)	258–278	270–285
Pour point (K)	243–258	258–289
Water (vol %)	0.05	0.05
Carbon (wt %)	87	77
Hydrogen (wt %)	13	12
Oxygen (wt %)	0	11
Sulphur (wt %)	0.05	0.05
Cetane number	40–55	48–60

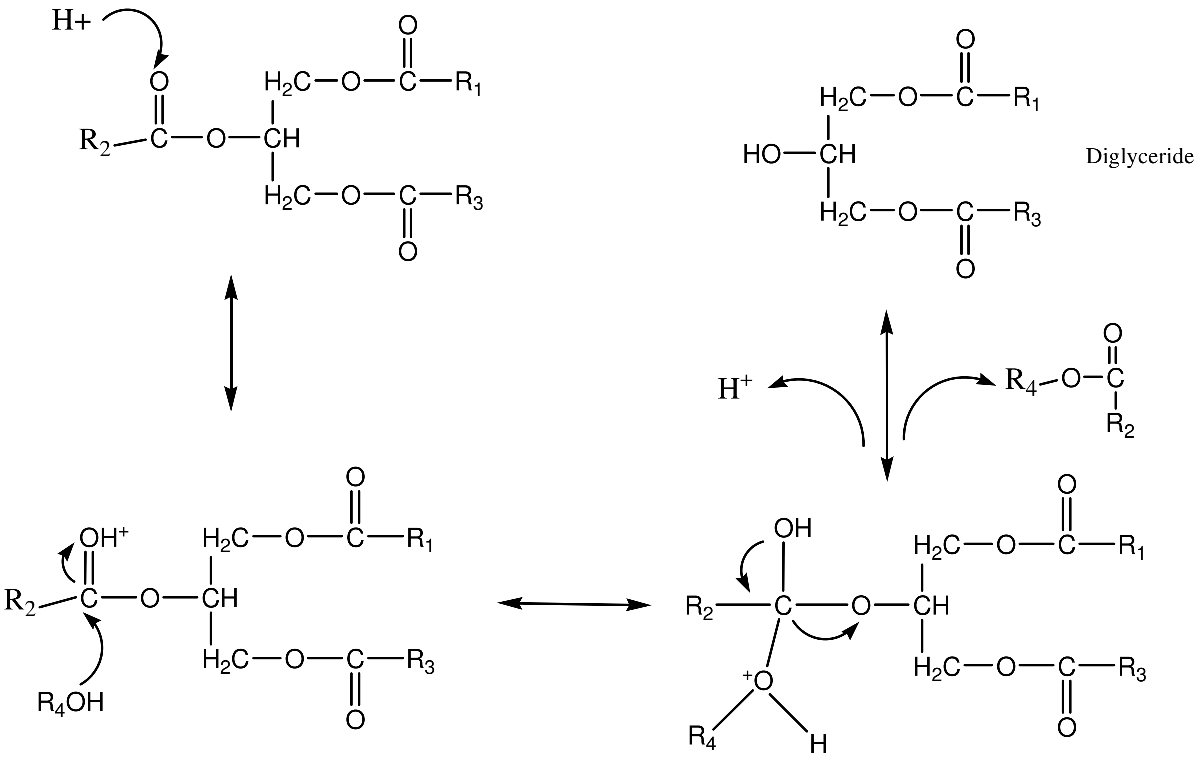
The homogeneous alkali – catalyzed tranesterificaion is approximately 4000 times faster than acid-catalyzed and hence used most often at commercially level using sodium hydroxide. The catalyst selection for the transesterification is based upon free fatty acid content of oil/fat. If the FFA content of oil is high, acid catalyzed esterification is followed by transesterification. If the FFA content is low, base catalyzed tranesterification is most desirable. Despite the industrial applicability, homogeneous catalyst has their own limitations.

The catalyst dissolves fully in the glycerine layer and partially in biodiesel. Heterogeneous catalyst, on the other hand, makes product separation easier and catalyst reusable. With the use of solid catalysts, the refining steps in the purification processes can be reduced. On the other hand the transesterification with heterogeneous catalyst occurs at harsher conditions. i.e., at higher temperatures and pressure.The mechanism of base catalyzed transesterification is shown below in scheme 2 [9].



Scheme 2: Base catalyzed transesterification

The mechanism of Acid catalyzed transesterification reaction is in scheme 3 [10].



Scheme 3: Acid catalyzed transesterification

Oils and Fats are water insoluble hydrophobic substances made up of one mole of glycerol and three moles of fatty acids and are commonly referred to as triglycerides [11]**.** Fatty acids vary in carbon chain length and in the number of unsaturated bonds. The fatty acids composition of vegetable oils is given in table 2.

Table 2: Fatty acids composition of vegetable oils (wt %)

FATTY ACID	SOYBEAN	COTTON SEED	PALM	COCONUT
Lauric	0.1	0.1	0.1	46.5
Myristic	0.1	0.7	1.0	19.2
Palmitic	10.2	20.1	42.8	9.8
Stearic	3.7	2.6	4.5	3.0
Oleic	22.8	19.2	40.5	6.9
Linoleic	53.7	55.2	10.1	2.2
Linolenic	8.6	0.6	0.2	0.0

Literature review on biodiesel produced by using different catalysts (homogeneous and heterogeneous) and enzymes is discussed below.

Homogeneous Catalyzed Transesterification

Homogeneous base catalysts [12] used for the methanolysis of lipids include alkaline metal compounds such as NaOH, KOH, Na_2CO_3, K_2CO_3, CH_3ONa and CH_3OK [13]. Alkaline metal alkoxides such as CH_3ONa are the most effective catalysts for transesterification. But generally alkaline hydroxides catalysts (NaOH and KOH) are preferred because they are cheaper and easier to handle than alkaline alkoxides [14]. In the alkali catalytic methanol transesterification method, the catalyst is dissolved into methanol by vigorous stirring in a small reactor.

Homogeneous acid catalysts [10], such as sulphuric acid, phosphoric acid, hydrochloridric acid and organo sulphonic acids can be used to catalyze the transesterification of TGs and the esterification of FFAs to produce biodiesel type monoesters [11]. Freedman et al. compared the transesterification of soybean oil with methanol, ethanol and butanol using 1% concentrated sulphuric acid based on the weight of oil. Later on Mohamad et al. reported H_2SO_4 as superior to HCl commonly used as acid catalyst for transesterification of used vegetable oils [15]. Biodiesel is produced in the presence of homogeneous catalyst but the soap formation lowers biodiesel yield and requires the separation of ester and glycerol is difficult.

Biocatalysis for Biodiesel Production

Pure lipase or lipase supported catalyst system are a recently growing field of research for biodiesel production [12]. Enzyme catalysis on transesterification of renewable oil is safe and clean without by products. When free enzymes are used in a bio-diesel process, the enzymatic activity can be partially recovered in the glycerol phase. In enzyme-catalyzed transesterification methods, oils with high acid content can be used and glycerol formed as the by product can be recovered easily. Also, there are no side reactions produced in this case. But, Practical use of lipase in transesterification reaction systems presents several technical difficulties such as contamination of the product with residual enzymatic activity and economic cost. However, high cost of enzymes discourages its use on commercial scale [16].

Heterogeneous Catalyzed Transesterification

The work was carried out for bio-diesel production from various feedstocks under different conditions using heterogeneous acid and base catalyst [12] is shown in table 3(a) and 3(b).

Table 3(a): Heterogeneous base catalyzed transesterification of vegetable oil with methanol

Catalyst	Catalyst amount wt % of oil	Oil	Molar ratio	Optimum reaction condition	Ester conversion%
Mg/La (magnesium–lanthanum Mixed oxide)	5	Sunflower	53:1	65°C,30 min	100
Mg/La (magnesium–lanthanum Mixed oxide)	5	Sunflower	53:1	Room temperature, 2.2 h	100
(Calcium ethoxide) $Ca(OCH_2CH_3)_2$	3	Soybean	12:1	65 °C, 1.5 h	95.0
(Calcium ethoxide) $Ca(OCH_2CH_3)_2$*	-	Soybean	12:1	75 °C, 3 h	91.8
Li/CaO	2	Karanja	12:1	65 °C, 8 h	94.8
KF/Al2O_3	4	Palm	12:1	65 °C, 3 h	90.0
KNO_3/Al_2O_3	6.5	Soybean	15:1	65 °C, 7 h	87
KNO_3/Al_2O_3	6.0	Jatropha	12:1	70 °C, 6 h	84
KF/Eu_2O_3	3	Rapeseed	12:1	65 °C, 1 h	92.5
Eu_2O_3/Al_2O_3	10	Soybean	6:1	70 °C, 8 h	63.0
KI/Al_2O_3	2.5	Soybean	15:1	65 °C, 8 h	96.0
Mg–Al hydrotalcites	7.5	Soybean	15:1	65 °C, 9 h	67.0
KOH/NaX zeolite	3	Soybean	10:1	65 °C, 8 h	85.6
CaO	8	Soybean	12:1	65 °C, 3 h	95

*Alcohol used is ethanol.

Table 3(b): Heterogeneous base catalyzed transesterification of vegetable oil with methanol

Catalyst	Catalyst amount (wt % of oil)	Oil	Molar ratio	Optimum reaction condition	Ester conversion%
S–ZrO_2 sulphated zirconia	5	Soybean	20:1	120 °C, 1 h	98.6
(ZS/Si) zinc stearate immobilized on silica gel	3	Waste Cooked Oil	18:1	200 °C, 10 h	98.0
SO^{-4}_2 /TiO_2–SiO_2	3	Waste oil	9:1	200 °C, 5 h	92.0

Solid Acid Catalysts for Biodiesel Production

Zeolites are solid acid catalysts that are generally more suitable for the biodiesel synthesis process in comparison to ion-exchange resins due to poor thermal stability and swelling behaviour, except for a few commercially available, high-cost ion-exchange resins like Nafion and Amberlyst-15[17] . The different characteristics of zeolites make them excellent catalysts for acid-base catalyzed reactions like zeolites can be synthesized with different crystal structures, pore sizes, framework Si/Al ratios, and proton-exchange levels [17]. In addition, zeolites provide the possibility to choose among different pore structures and surface hydrophobicities, according to the substrate's size and polarity.

MCM-41 supported heteropoly acids (HPAs) have been used as catalysts in the gas-phase esterification of acetic acid and 1-butanol, and these catalysts showed good activity at 383 K (95% conversion of 1-butanol)[18] . MCM-41 supported HPA was more active than pure HPA. The enhanced activity was ascribed to the high dispersion of the HPA on the MCM-41 internal surface, giving rise to the higher population of available acid sites than in pure HPA.

Yadav and Murkute [19] reported different synthetic routes to prepare SO^{2-}_4/ZrO_2 with improved sulphate loadings and resistance to leaching of sulphate by hydrolysis. Sulphated zirconia (SO^{2-}_4/ZrO_2) was shown to be active for several acid catalyzed reactions. Sulphate groups can leach out as H_2SO_4 and HSO_4^-, which in turn can give rise to homogeneous acid catalysis.

Solid Base Catalysts for Biodiesel Production

Alkali metal salt-loaded alumina solid base catalysts have also been used [20]. Ebiura et al. [21] studied the selective transesterification of triolein with methanol to methyl oleate and glycerol using alumina loaded with alkali metal salt as a solid base catalyst. Among the catalysts, alumina loaded with K_2CO_3, KF, $LiNO_3$, and NaOH gave methyl oleate and glycerol in high yield over 1 h at 333 K.

Watkins et al. studied the Li-CaO solid base catalyst for transesterification reaction [22] and they chose the glyceryl tributyrate as a model substrate for testing the catalytic activity in the presence of different amounts of lithium doped calcium oxide material. A series of $LiNO_3$ was impregnated with CaO by the wet impregnation method at theoretical Li contents in the range of 1-20 wt %. An optimum Li content of 1.23 wt % gave maximum activity for formation of methyl butanoate, and lithium incorporation in CaO increases the base strength of catalyst.

Recently Basic zeolites were also used [8]. The base strength of the alkali ion exchanged zeolite increases with increasing electropositive nature of the exchanged cation. Systems like ETS-10, a microporous inorganic lithium containing zeolite has been shown to be a new generation solid base catalyst for transesterification. Most of these catalysts contain the basic sites (cation) generated by thermal decomposition of the supported salt. It has been shown that the conversion to methyl ester over NaX faujasite zeolite that was ion exchanged with more electropositive cation was higher than that of the parent zeolite.

Hydrotalcites (HT) [8] are another class of anionic and basic clays with the formula $Mg_6Al_2 (OH)_{16}CO_3.4H_2O$. It presents a positively charged brucite-like layers ($Mg(OH)_2$) in which some of Mg^{2+} are replaced by Al^{3+} in the octahedral sites of hydroxide sheets. Decomposition of Mg–Al HT yields a high surface area Mg–Al mixed oxide, which presumably exposes strong Lewis base sites. The basic properties of these sites depend on the Mg–Al ratio in the precursor hydrotalcite. The decomposed– rehydrated Mg–Al HT with Bronsted base sites exhibited higher catalytic activity than the decomposed Mg–Al HT with Lewis base sites for the transesterification of oleic acid methyl ester with glycerol.

Bio-diesel production using solid heterogeneous base catalysts could potentially lead to cheaper production costs because of reuse of the catalyst and the possibility for carrying out both transesterification and esterification simultaneously [24]. Though, homogenous catalysts give good results but due to its limitations they are being replaced by heterogeneous catalysts. Hence the use of solid heterogeneous base catalysts showed very high catalytic activity in transesterification reaching above quantitative yield under optimal reaction conditions. Heterogeneous catalysts have several other advantages including easier operational procedures, catalyst separation and reduction of environment pollutants, among others.

Because of the versatility of its technological applications, sodium aluminate (SA) is an important commercial inorganic chemical. It is formulated as $NaAlO_2$, $Na_2O \cdot Al_2O_3$ or $Na_2Al_2O_4$. SA is mainly in demand for use in effective water treatment systems. It is also used by producers of paper, paint pigments, alumina-containing catalysts, dishwasher detergents, ingot molds and molecular sieves, concrete, and so on [23]. It is generally believed that $NaAlO_2$ is water soluble and shows strong basicity in water, insoluble in alcohol.

Recently, Wan et al [24] showed the use of sodium aluminate as heterogeneous catalyst for biodiesel production from soybean oil. Hence it was thought worthwhile to study the use of sodium aluminate for biodiesel production from used cotton seed oil.

Objective: To study sodium aluminate as heterogeneous catalyst for biodiesel production from used cotton seed oil.

MATERIALS, METHODS AND EXPERIMENTAL PROCEDURE

This chapter deals with the materials used in the transesterification reaction, various methods and techniques used for the characterisation of catalyst, reaction products and the procedure of the reactions performed.

MATERIALS AND METHODS

Hexane, ethyl acetate, fat, methanol, silica gel, nitric acid, Hammett indicators viz., 2, 4-dinitroaniline, Alizarin and 4-nitroaniline of GR grade were obtained from Loba Chemicals Pvt. Ltd and used as such without further purification. Sodium aluminate of AR grade was obtained from Sigma-Aldrich. Methanol (> 99%) was obtained from MERK, India. Cotton seed oil was purchased from departmental store located in Patiala (Punjab) India. It was used for frying then it was taken for the reaction.

Calcinations of Catalyst and its Characterization

Sodium aluminate was calcined at different temperatures (150^oC-950^oC) and calcined catalysts were characterized by powder XRD and TEM. Basic strengths of the catalysts were measured by Hammett indicators using literature reported procedure [25].

Basic Strength

The Hammett indicator was used to determine the basic strength of the solid bases ($H\_$) [25]. About 200 mg of sample was shaken with 10 ml methanolic solution of the Hammett indicator and kept for 1 h to achieve equilibration. The concentrations of 0.02 mol/L Alizarin ($H\_$= 11.0), 2, 4-dinitroaniline ($H\_$= 15.0) and 4-nitroaniline ($H\_$= 18.4) were used for Hammett indicators. Methanol was used as a solvent. Basic strength of the catalyst was determined from the change in colour of respective Hammett indicators.

Powder XRD Patterns

Powder XRD patterns of the prepared catalysts were recorded on analytical X'pert using Ni-filtered Cu Kα radiation. The measurements were recorded in steps of 0.0170°, with a scan step time of 15.5 s and a 2θ range of 10–80°.

^{1}H NMR Spectra

^{1}H NMR Spectra was recorded on 400 MHz FT-NMR Cryo Spectrometer (Bruker) from Sophisticated Analytical Instrumentation Centre (SAIF), Punjab University, Chandigarh.

EXPERIMENTAL WORK

Reactions with used Cotton Seed Oil

In a typical reaction, 10 g of used cotton seed oil, 10 g of methanol and 0.5 % of catalyst (50mg Sodium Aluminate) was taken in round bottom flask and refluxing was carried out till the completion of reaction. Completion of reaction was monitored by TLC (Solvent system: hexane and ethyl acetate 24:1 (v/v)). With the view to find out the influence of temperature, moisture content, methanol and the catalyst amount, various sets of reactions were performed by varying single parameters at a time.

To study the percentage of Catalyst amount varied from 0.5% to 2.25% in one set of reactions. Similarly, effect of amount of methanol (1:22 to 1:43) on the completion time was studied. For study of effect of temperature, reactions performed at three different temperatures, 55°C, 60°C and 65°C. Methanol content taken was high in this case (1:43), as the reaction did not go to completion at low methanol content. Similar findings were observed with addition of moisture. Sodium aluminate calcined at different temperatures was used for transesterification of used cotton seed oil to find out effect of calcination temperature on catalytic activity.

Reactions with Calcined Sodium Aluminate

To study the effect of calcination, a series of transesterification reactions were performed with 10g of used cotton seed oil, 10g of methanol, 0.5% catalyst and varying the temperatures of calcinations of sodium aluminate from 250°C-850°C at an interval of 100°C.

Determination of Acid value of used Cotton Seed Oil

Acid value indicates the age and quality of oil. It is the number of milligrams of KOH required to neutralize the free fatty acid present in 1 g of oil. During storage, oil may undergo peroxide formation at the double bonds by atmospheric oxygen and subsequent hydrolysis by micro-organisms leads to the liberation of free acid. Hence, presence of free fatty acid gives information about the purity of oil.

To study the acid content, 10 g of used cotton seed oil (one that has stood for several days at room temperature) was taken as sample and 1 ml of phenolphthalein was added to it. The contents were mixed thoroughly and titrated with 0.1 M of KOH. Titrated until the pink colour persists for 20-30s. The number of millilitres of standard alkali required was calculated for the acid value of oil and is given by the equation:

$$\text{Acid value} = \frac{\text{Number of ml of KOH used}}{\text{Weight of the oil take}} \times 5.6$$

Acid value found was 0.380 ~ 0.4

Determination of Iodine value of Used Cotton Seed Oil

Halogens add across the double bonds of unsaturated fatty acids to form addition compounds. Iodine monochloride (ICl) was allowed to react with oil in the dark. The amount of iodine consumed was determined by titrating the iodine released (after the addition of KI) with standard thiosulphate and comparing with a blank (without oil).

The reaction mixture was kept at dark and the titration was carried out as quickly as possible since halogens could be oxidised in the presence of light.

In 10ml of oil, added 25 ml of the ICl solution mixed thoroughly (oil + ICl) and kept it in dark for 1 h. In a blank set up, the used cotton seed oil solution was replaced by 10 ml of chloroform (ICl + chloroform). Added 10ml of KI solution and titrated the released iodine with the standard thiosulphate. When the solution was pale straw colour, added 1 ml of starch solution and continued titrating until the blue colour disappeared. The contents were stirred vigorously during titration to ensure that all the iodine was removed from the chloroform.

Difference in the reading between blank and test (Bl-T) gives the number of 0.1 mol/litre thiosulphate needed to react with the equivalent volume of iodine. Since two molecules of thiosulphate were needed for each iodine, so now it became (Bl-T)/2.

The molecular weight of iodine is 2x127 so the weight of iodine in (Bl-T)/2ml of 0.1mol/litre iodine was:

$$\frac{(\text{Bl-T}) \times 0.1 \times 2 \times 127}{2 \times 1000} \text{ g}$$

The amount of oil taken is 0.2 g so the iodine number was:

$$\frac{(Bl-T) \times 12.7 \times 100}{0.2 \times 1000} \text{ g}$$

Iodine number = (Bl-T) x 6.35 g per 100 g of fat.

Iodine value was found to be 89.40

RESULTS AND DISCUSSION

This chapter deals with the characterisation of catalyst and optimization of amount of reactants and catalyst.

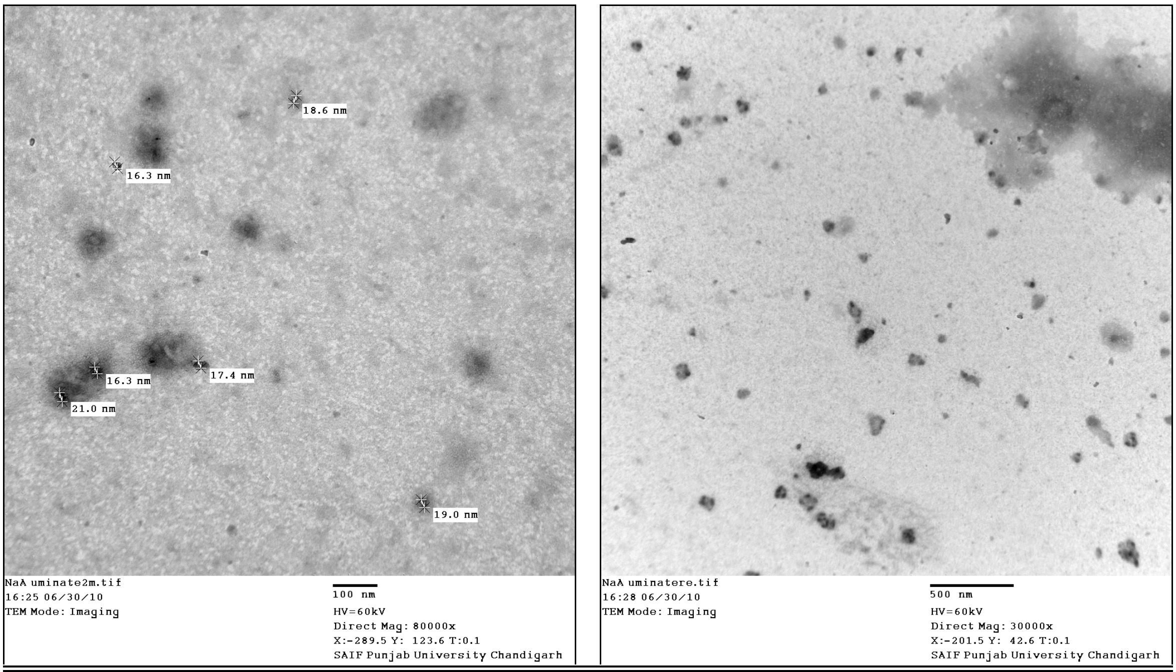
Catalytic Characterisation

The catalyst was characterized by TEM, Hammett indicators and X-ray diffraction (XRD).

TEM

Nano crystalline sodium aluminate is shown in TEM images (fig .1). Particle size of Sodium Aluminate catalyst was found to be in range between 16-21 nm. Smaller particle size of sodium aluminate might be the reason for greater catalytic activity with very less amount.

Fig 1: TEM images of Sodium aluminate



Basic Strength

Sodium aluminate was calcined at different temperature and basic strength was studied with Hammett indicators as shown in table 4. With sinteration at higher temperature, particle size increases and surface area decreases hence catalytic activity decreases. Similar results were obtained with sodium aluminate [24]. Calcination at higher temperature decreases the basic strength.

Table 4: Basic strengths of Sodium aluminate calcined at different temperatures

Sr. No.	**Sodium aluminate calcined at different temperatures (^oC)**	**Basic Strength**	**Hammett Indicator with Higher Basic Strength Showing Colour Change**
1	Without calcination	$15<H\_<18$	2,4-dinitroaniline ($H\_= 15.0$)
2	250	$15<H\_<18$	2,4-dinitroaniline ($H\_= 15.0$)
3	350	$15<H\_<18$	2,4-dinitroaniline ($H\_= 15.0$)
4	450	$15<H\_<18$	2,4-dinitroaniline ($H\_= 15.0$)
5	550	$15<H\_<18$	2,4-dinitroaniline ($H\_= 15.0$)
6	650	$15<H\_<18$	2,4-dinitroaniline ($H\_= 15.0$)
7	750	$11<H\_<15$	Alizarin ($H\_= 11.0$)
8	850	$11<H\_<15$	Alizarin ($H\_= 11.0$)

The catalyst (without calcination) and calcined catalyst (upto 650^oC) showed the colour change (yellow to orange) with 2, 4-dinitroaniline ($H\_= 15.0$). The catalyst calcined at or above 750^oC doesn’t show the colour change with 2, 4-dinitroaniline but showed change in colour (orange to brown) with alizarin ($H\_= 11.0$).

XRD Analysis

Powder XRD of sodium aluminate without calcination and calcined at various temperatures (250^oC-850^oC) are shown in fig 2.

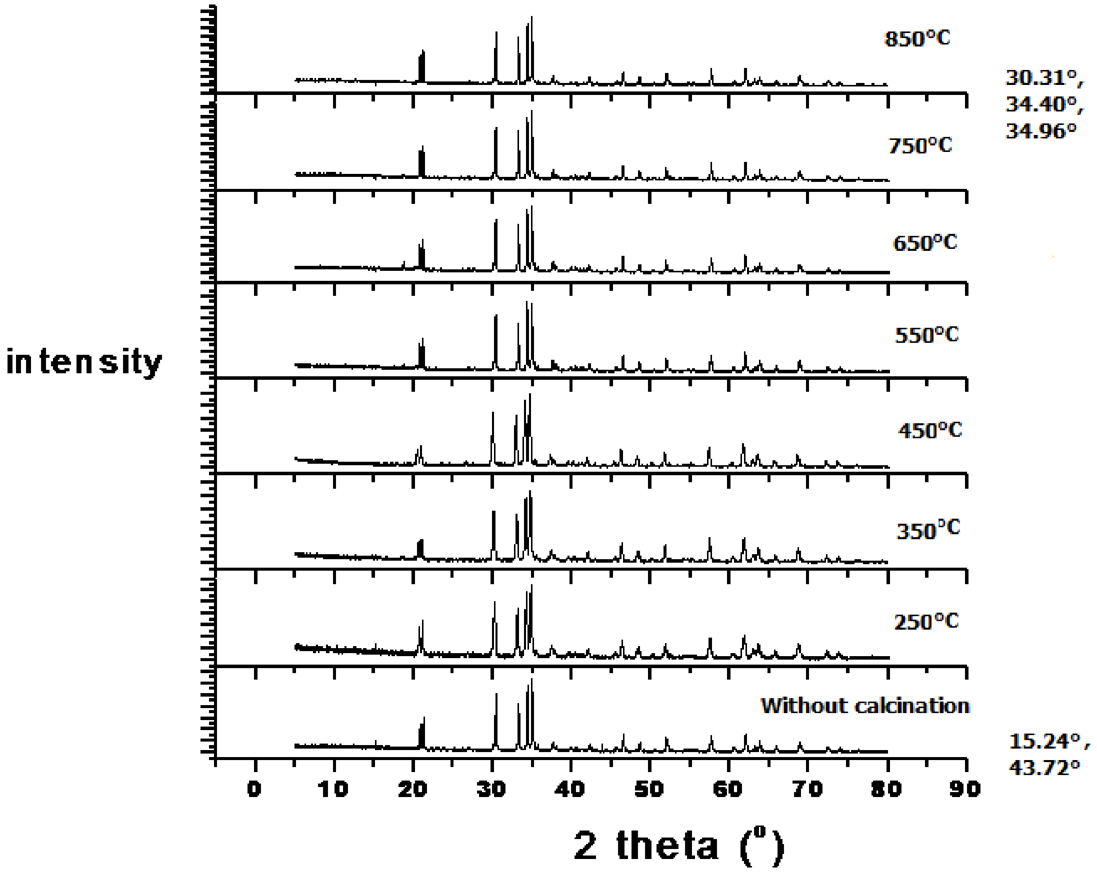


Fig 2: XRD patterns for Sodium Aluminate calcined at different temperatures (a) without calcination (b) sample calcined at 250°C (c) sample calcined at 350°C (d) sample calcined at 450°C (e) sample calcined at 550°C (f) sample calcined at 650°C (g) sample calcined at 750°C (h) sample calcined at 850°C

Sodium aluminate (without any thermal treatment) showed phases corresponding to sodium Dawsonite NaAl $(OH)_2$ CO_3, hydrated sodium aluminate $NaAlO_2 \cdot xH_2O$ (PDF 41-638) and sodium aluminte $NaAlO_2$ (PDF 33-1200) as shown in fig 2(a). Sodium aluminate calcined at high temperature (850°C) lost the phase correspond to Sodium Dawsonite and attained the phase correspond to sodium aluminate with Powder Diffraction file pattern (PDF 33-1200) (2θ = 20.7, 21.1, 30.3, 33.2, 34.3, 34.9, 37.6, 42.2, 46.4, 48.5, 52.0, 57.6, 61.9, 63.1, 63.8, 65.9, 68.8, 72.4) as shown in fig 4(h). The catalytic activity of sodium aluminate without calcination seems to be due to presence of Sodium Dawsonite.

Analysis of Biodiesel by ^{1}H NMR

Biodiesel prepared from used cotton seed oil was characterized by ^{1}H NMR. The proton NMR spectrum of used cotton seed oil shows a multiplet at 4.1 and 5.3 ppm due to the presence of glyceridic protons along with other hydrocarbon peaks. Appearance of new peak at 3.6 ppm due to the $-OCH_3$ protons and disappearance of glyceridic protons support the formation of biodiesel as shown in fig 3(a) and 3(b).

$$C = \frac{100 \times (2 \times I_{M.E})}{3 \times I_{\text{Methylene proton}}}$$

C = percentage conversion of oil into the corresponding methyl ester.

$I_{M.E}$ = integration value of the protons of the methyl esters (at 3.6 ppm).

$I_{\text{Methylene protons}}$ = integration value of the methylene protons (at 2.3 ppm).

From fig 3(b) **% Conversion = 96.2%**

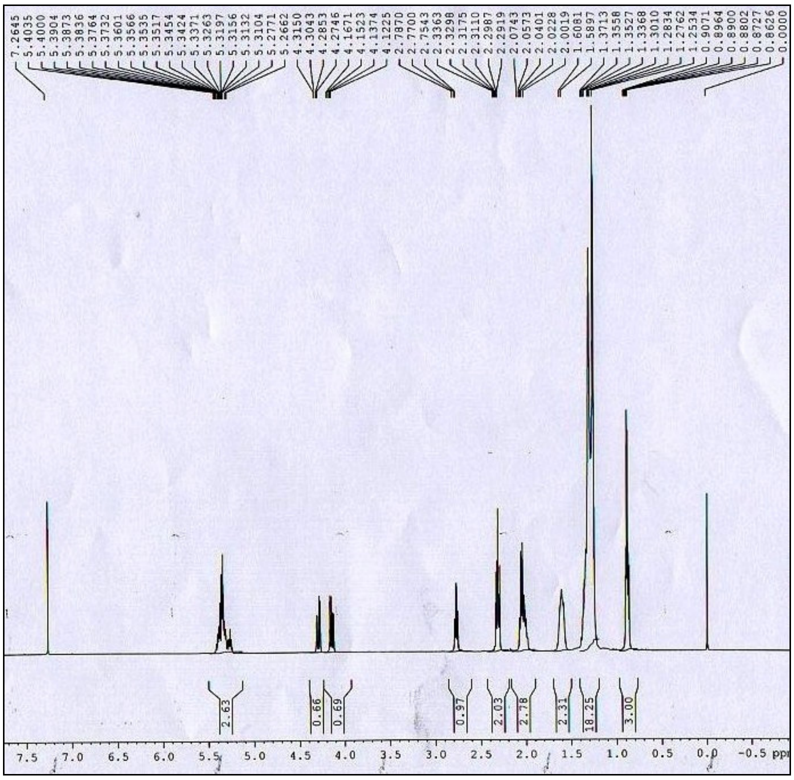


Fig 3(a): ^{1}H NMR of used cotton seed oil

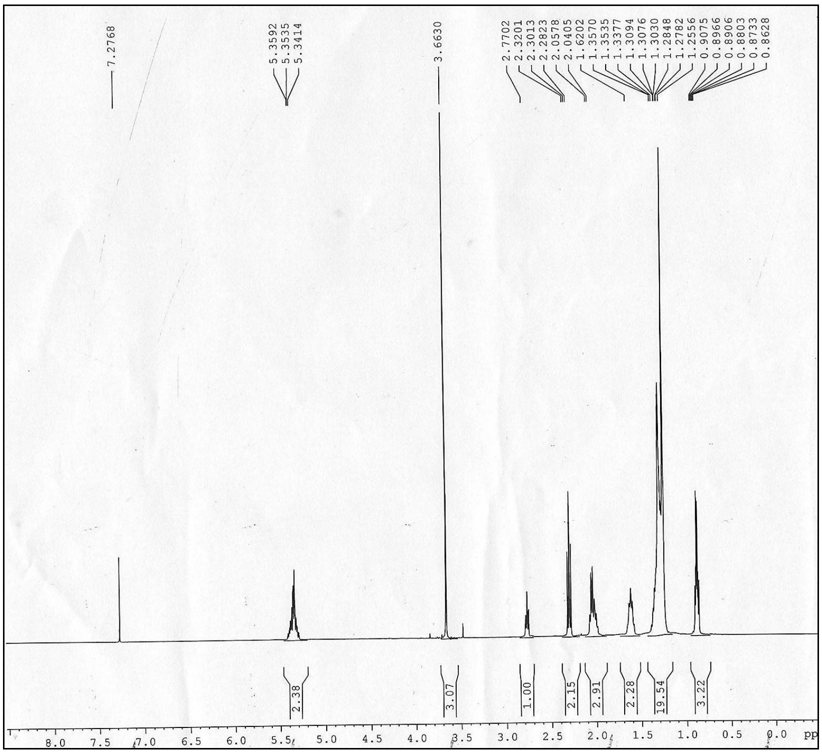


Fig 3(b): ^{1}H NMR of biodiesel

Transesterification Reactions

Various parameters optimised for the transesterification reactions are:

(i) Amount of catalyst
(ii) Amount of methanol
(iii) Temperature and
(iv) Moisture content

Used Cotton Seed Oil

Effect of Catalyst Amount

For studying the effect of catalyst amount, a set of transesterification reactions were carried out by using 10g of used cotton seed oil with 10g of methanol in the presence of varying amount of sodium aluminate as catalyst from 0.5 to 2.25 wt% at 65°C. Time taken for completion of reaction is shown in table 5(a) and fig 4(a).

Table 5(a): Effect of weight % of catalyst

Sr. No.	weight % of Catalyst	Time taken (h)
1	0.50	1.75
2	1.00	0.75
3	1.25	0.62
4	1.50	0.50
5	1.75	0.38
6	2.00	0.32
7	2.25	0.25

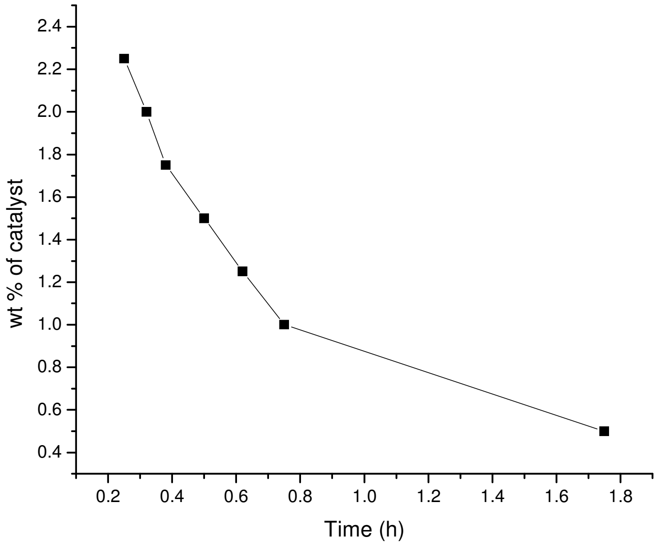


Fig 4(a): Effect of weight % of catalyst

Time required for the completion of reaction decreases with the increase in wt % of the catalyst and reaction completes with in 15 min (0.25 h) with 2.25 wt % of catalyst. With 0.5

wt % of catalyst reaction completes in 1h 45 min, hence, further parameters were optimized with 0.5 wt% of catalyst.

Effect of Oil to Methanol Molar Ratio

To study the effect of oil/methanol ratio, a series of transesterification reactions were carried out by varying oil to methanol molar ratio (1:22 to 1:43) in the presence of 0.5wt % of catalyst at 65^{o}C. Reaction time increases from 1h 47 min to 8 h when oil to methanol molar ratio decrease from 1:43 to 1:22. Oil to methanol ratio of 1:27 was found to be optimum because further increase in oil to methanol ratio doesn't lead to any marked reduction in reaction time of completion as shown in table 5(b) and fig 4(b).

Table 5(b): Effect of oil to methanol molar ratio

Sr. No.	**Oil to methanol molar ratio**	**Time taken (h)**
1	1:22	8
2	1:27	1.75
3	1:32	1.65
4	1:37	1.58
5	1:43	1.47

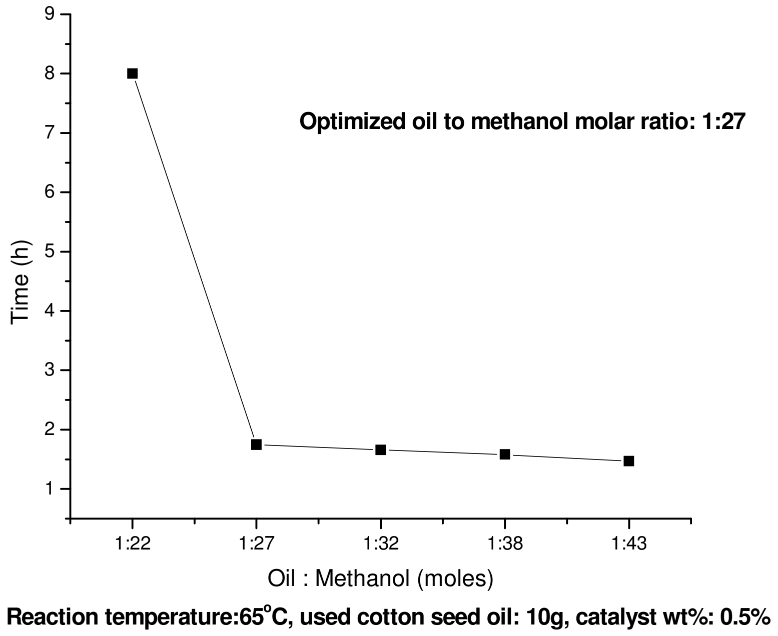


Fig 4(b): Effect of Oil: Methanol molar ratio

Effect of Temperature

Transesterification reactions of cotton seed oil with methanol (1:43 molar ratio) in the presence of 0.5 wt % were carried out at different temperatures (55°-65°C) as shown in table 5(c) and fig 4(c). Higher molar ratio of oil to methanol was found to have positive effect on transesetrification performed at lower temperatures, so 1:43 molar ratio of oil: methanol was selected for studying the effect of temperature. Reaction performed at 55°C took 5.3 h for the complete conversion. Reaction performed at 45 °C did not complete even upto 12 h.

Table 5(c): Effect of temperature on transesterification reaction

Sr. No.	**Temperature (°C)**	**Time taken (h)**
1	55	1.75
2	60	3
3	65	5.3

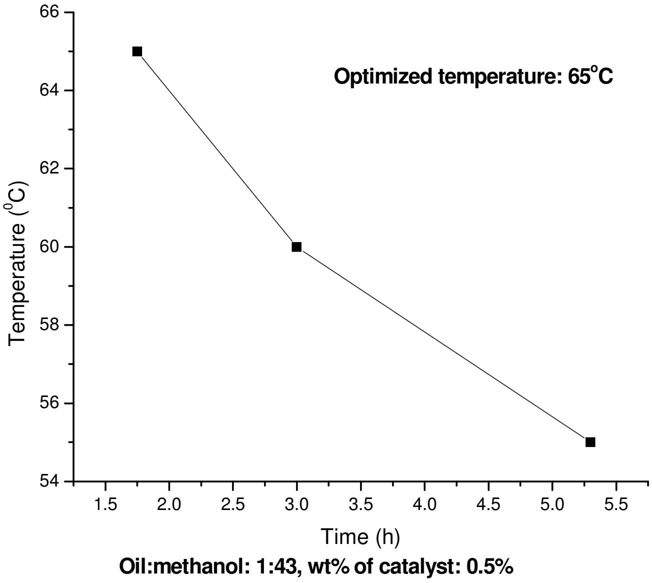


Fig 4(c): Effect of temperature

Effect of Moisture

To test the moisture resistance of the catalyst, transesterification reactions were carried out in the presence of added moisture content as shown in table 5(d) and fig 4(d). Higher molar ratio of oil to methanol have positive effect on transesetrification performed in the presence of added moisture, hence 1:54 molar ratio of oil: methanol was selected for the study of effect of moisture addition. Other reaction conditions used were 5 wt% of catalyst and 65^{o}C temperature. A slight decrease in time for the completion of reaction was observed in the presence of 4 wt % of the moisture. Sodium aluminate is water soluble and shows strong basicity in water [24] that seems to be the reason for increase in catalytic activity in presence of upto 4 wt % of moisture. It was found that similar reaction conditions (5 wt % catalyst, 65^{o}C temperature, oil: methanol molar ratio of 1: 54) can tolerate upto 8 wt % of moisture but time taken for the completion increase and marginally from 1.47 h to 2 h.

Table 5(d): Effect of addition of moisture (weight %)

Sr. No.	Wt.% of Moisture	Time taken (h)
1	2	1.66
2	4	1.33
3	6	1.5
4	8	2.0

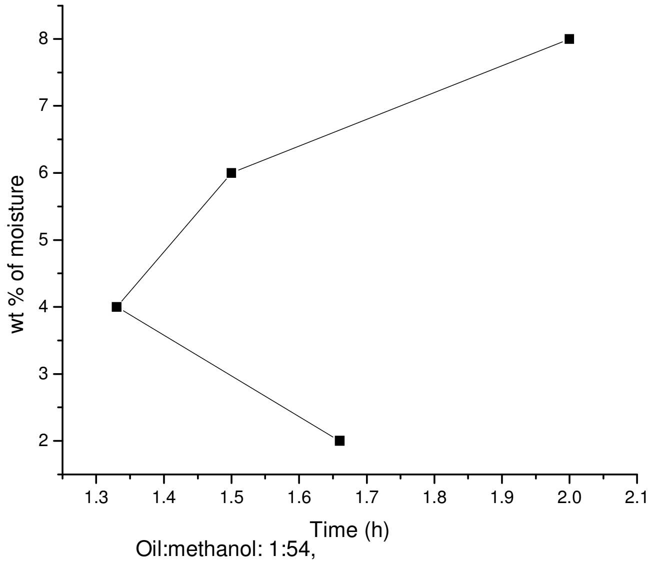


Fig 4(d): Effect of addition of moisture (weight %)

Effect of Calcination Temperature

Calcination of sodium aluminate was carried out at different temperatures from 250°C-850°C and same were used as catalysts (1.5 wt %) with oil to methanol molar ratio of 1:22 at 65°C. Sodium aluminate heated upto 350°C was found to complete the reaction with extended reaction time of completion as shown in table 6. Loss of water absorbed on the surface of sodium aluminate may be the cause of extended reaction time of completion. Further increase in the calcination temperature of sodium aluminate beyond 350^{o}C losses its catalytic nature for transesterification. Probably the increase in calcination temperature increases its particle size and decreases the number of basic sites which seems to be the cause for the loss of catalytic activity.

Table 5: Time taken for transesterification reactions with calcined sodium aluminate

Sr. No.	**Calcination temperature (^{o}C) of sodium aluminate**	**Time taken (h)**
1	250	7
2	350	15
3	450	Not completed
4	550	Not completed
5	650	Not completed
6	750	Not completed
7	850	Not completed

CONCLUSION

Sodium aluminate (0.5 wt%) was found to catalyse the complete transesterification of used cotton seed oil in a time period of 1 h 45 min at 65°C when molar ratio of oil and methanol was 1:27. Presence of moisture content effects the completion of transesterification reaction. Higher oil: methanol molar ratio increases moisture tolerance of the catalyst. Same amount of catalyst (0.5 wt %) was found to complete the transesterification in the presence of 8 wt % of moisture with higher amount of methanol i.e. 1:54 molar ratio of oil: methanol at 65°C. The calcined catalysts do showed the effect of calcination temperature towards transesterification of used cotton seed oil. Calcination at higher temperature deactivates the catalyst.

REFERENCES

[1] C. Lingfeng, X. Guomin, *Energy & Fuels,* 2007**, 21,** 3740.

[2] G. Knothe, *Trans. ASAE*, 2001, **12**, 7.

[3] G. R. Peterson, W. P. scarrah, *J. Am. Oil Chem. Soc.,* 1984**, 61**, 10.

[4] C. R. Reddy, R. Oshel, J. G. Verkade, *Energy & Fuels,* 2006, **20**, 1310.

[5] S. M. P. Meneghetti, M. R. Meneghetti, C. R. Wolf, E. C. Silva, *Energy & Fuels,* 2006, **20**, 2262.

[6] D. Bajpai, V. K. Tyagi, *J. Oleo Sci.*, 2006, **55**, 487.

[7] M. Canakci, J. V Gerpen, *Trans. ASAE*, 1999, **42**, 1203.

[8] Z. Helwani , M. R. Othman, N. Aziz , J. Kim , W. J. N. Fernando, *Applied Catalysis A: General*, 2009, **363**, 1.

[9] I. K. Mbaraka, B. H. Shanks, *J. Am. Oil Chem. Soc.,* 2006, **83***,* 79.

[10] E. Li and V. Rudolph*, Energy & Fuels,* 2008, **22***,* 145.

[11] E. lotero, J. G. goodwin, D. A. bruce, K. suwannakarn, Y. liu and D. E. lopez, *Catalysis*, 2006, **19**, 41.

[12] A. P. Vyas, J. L. Verma, N. Subrahmanyam, *Fuel*, 2010**, 89**, 1.

[13] Y. C. Bak, J. H. Choi, S. B. Kim, D. W. Kang, *Korean J. Chem.Engl.,* 1996, **3**, 242.

[14] V. Gemma, M. Mercedes, A. Jose, *Bioresour Technol.,* 2004, **92**, 297.

[15] Al-Widyan Mohamad I, Al-Shyoukh Ali O. *Bioresour Technol.*, 2002, **85**, 253.

[16] G. Hillon, R. Stloukal, J. Machek, *Fats and Lipids*, 2003, **100**, 636.

[17] S. P. Chavan, Y. T. Subbarao, S. W. Dantale, R. Sivappa, *Synth. Commun.,* 2001, **31**, 289.

[18] M. J. Verhoef, P. J. Kooyman, J. A. Peters, H. V. Bekkum, *A Microporous Mesoporous Mater.,* 1999, **27**, 365.

[19] G. D. Yadav, A. D. Murkute, *J. Catal.*, 2004, **22**, 218.

[20] R. Jothiramalingam, and M. K. Wang**,** *Ind. Eng. Chem. Res.,* 2009*,* **48***,* 6162.

[21] T. Ebiura, T. Echizen, A. Ishikawa, K. Murai, T. Baba, *Appl Catal A Gener.,* 2005, **283,** 111.

[22] R. S. Watkins, A. F. Lee, K. Wilson, *Green Chem.,* 2004, **6**, 335.

[23] V. Rayzman, I. Filipovich, L. Nisse, Y. Vlasenko, *JOM,* **1998**, *50*, 32.

[24] T. Wan, P. Yu, S. Wang, Y. Luo, *Energy & Fuels*, 2009, **23**, 1089.

[25] A. P. Oliveira, R. D. Villa, K. C. P. Antunes, *Fuel*, 2009, **88**, 764.

[26] G. Knothe, *Trans. ASAE*, 2001, **44**, 193.