LITHIUM DOPED SILICON DIOXIDE AS HETEROGENEOUS CATALYSTS FOR TRANSESTERIFICATION OF NON-EDIBLE OILS

A

Thesis submitted

in partial fulfilment of the requirement

for the degree of

Master of Science in Chemistry

Submitted by:

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Tajbir

Date: 14/7/11

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Candidate's Declaration

I hereby declare that the work presented in the thesis entitled, "**Lithium doped silicon dioxide as heterogeneous catalysts for transesterification of non-edible oils**", 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 2011 to June 2011, 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.

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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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Certificate

This is to certify that the thesis entitled "**Lithium doped silicon dioxide as heterogeneous catalysts for transesterification of non-edible oils**", being submitted by Ms. Tajbir Kaur Minhas 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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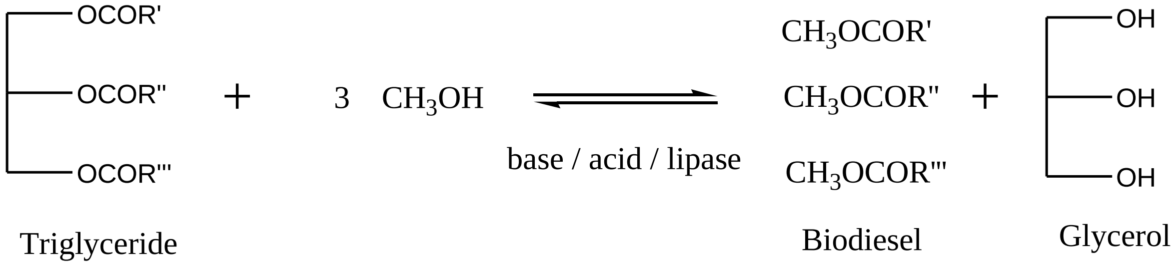
ABSTRACT

Lithium doped SiO_2 catalysts having 2:1 to 5:1 Li: Si molar ratio were prepared and used for the transesterification of jatropha and karanja oil with methanol. Transesterification of jatropha oil resulted in 96 % conversion within 45 min by using 6 wt % of the catalyst (Li: Si:: 3:1 molar ratio) and 1: 60 molar ratio of oil to methanol at $65^{o}C$. Moisture tolerance of the catalyst was also evaluated by performing the transesterification of jatropha oil in the presence of added moisture content and it was found that reaction can be completed within 5 h in the presence of 20 wt % of added moisture content with optimized reaction parameters viz., 6 wt % catalyst amount and 1:60 oil to methanol molar ratio at $65^{o}C$. Transeseterification of karanja oil resulted in 40 % of methyl esters by using 6 wt % of the catalyst (Li: Si:: 3:1 molar ratio) and 1: 80 molar ratio of oil to methanol at $65^{o}C$.

INTRODUCTION

Due to the concern on the availability of recoverable fossil fuel reserves and the environmental problems caused by the use of fossil fuels, considerable attention has been given to biodiesel production as an alternative to petrodiesel. However, as the biodiesel is produced from vegetable oils and animal fats, there are concerns that biodiesel feedstock may compete with food supply in the long-term. Hence, the recent focus is to find oil bearing plants that produce non-edible oils as the feedstock for biodiesel production. Hence, the contribution of non-edible oils such as jatropha and karanja will be significant as a non-edible plant oil source for biodiesel production. 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 system as shown.



Scheme: Reaction of triglyceride with methanol to form methyl esters

Biodiesel has become more attractive recently because of its environmental benefits and the fact that it is made from renewable resources. Biodiesel is a mixture of monoalkyl esters of long chain fatty acids derived from renewable feed stock like vegetable oils and fats [1], mainly made of fatty acid glycerides. It is biodegradable and nontoxic, and has low emission profiles compared to petroleum diesel [2].

The alkaline catalysts show high performance, providing biodiesel fuel of high quality, but the oils often contain significant amounts of free fatty acids, which are turned into soap by reaction with the alkali catalyst. In addition, the outflow of the alkaline catalysts with the biodiesel fuel product is a serious problem that requires the addition of further washing and separation steps to the process.

An alternative way to process these oils is to use an acid catalyst. However, homogeneous acids such as hydrochloric acid and sulfuric acid require a long reaction time; one or more order of magnitudes larger than that required by the alkali catalysts, and this becomes a serious problem. The use of liquid acids and bases as catalysts presents not only environmental threats, but also causes difficulties in their separation from the products.

Enzymatic reactions involving lipases can be an excellent alternative to produce biodiesel. Protein engineering can be useful in improving the catalytic efficiency of lipases as biocatalysts for biodiesel production. In addition, the enzymatic approach is environmentally friendly, considered a “green reaction and requires mild operating conditions compared with chemical methods. But there are two main problems in enzymatic approaches for biodiesel production: one is the relatively high cost of lipase and second is its short operational life caused by the negative effects of excessive methanol and by-product glycerol.

LITERATURE REVIEW

The petroleum fuels play a very important role in the development of industrial growth, transportation, agricultural sector and to meet many other basic human needs. The increasing energy demand, reducing harmful emissions, and depletion of fossil fuel resources inevitably necessitate for the optimum utilization of exhaustible fossil fuel and non-renewable energy resources. Hence, there is a great need for alternative fuels and biodiesel is one of the best available sources to fulfill the energy demand of the world. Biodiesel exhibits characteristics that are comparable to the traditional diesel fuel as given in Table 2.1 where the ASTM standards for both these fuels are given.

Table 2.1: Comparisons of the standards for diesel and biodiesel [3]

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

Transesterification can be done with homogenous as well as heterogeneous catalysts. Though homogenous catalysts i.e. acid and base require milder conditions (low temperature and low pressure) for the reaction to occur but like heterogeneous catalysts they can't be separated from the reaction products. The catalyst dissolves fully in the glycerine layer and partially in biodiesel. With heterogeneous catalysts it is easy to separate the product and also the catalyst can be reused.

The homogeneous alkali – catalyzed transesterification is approximately 4000 times faster than acid catalysts. Mechanism of acid catalyzed and base catalyzed reaction is shown in Figure 2.1 and 2.2 respectively. Generally, the mechanism of the base-catalyzed transesterification involves four steps. The first step is the reaction of the base with the alcohol, producing an alkoxide and the protonated catalyst. The second step is the nucleophilic attack of the alkoxide at the carbonyl group of the triglyceride generating a tetrahedral intermediate. The third step involves the formation of the alkyl ester and the corresponding anion of diglyceride. The final step involves deprotonating the catalyst, thus regenerating the active species, which is now able to react with a second molecule of the alcohol, starting another catalytic cycle. Diglycerides and monoglycerides are converted by the same mechanism to a mixture of alkyl esters and glycerol.

The acid catalyzed transesterification involves protonation of the carbonyl group of the ester leads to the carbocation which after a nucleophilic attack of the alcohol produces the tetrahedral intermediate. This in turn eliminates glycerol to form the new ester, and to regenerate the catalyst. The mechanism can be extended to *di*- and triglycerides. Carboxylic acids can be formed by reaction of the carbocation with water present in the reaction mixture. This suggests that an acid-catalyzed transesterification should be carried out in the absence of water, in order to avoid the competitive formation of carboxylic acids, which reduce the yield of alkyl esters.

2.1. Acid catalysts

Homogeneous acid-catalyzed transesterification reaction can be carried out using Bronsted acids like HCl, BF_3, H_3PO_4, H_2SO_4 and sulphonic acids. Preferably, sulphonic and sulphuric acids are mostly used. These catalysts give very high yields in alkyl esters, but the reactions are slow, requiring typically, temperatures above 100^oC and from 3-48 h to reach complete conversion [4]. This procedure seems to be more suitable when the feedstock is of low grade with relatively high FFA [5, 6] and/or moisture contents and when ethyl esters of fatty acids are to be obtained [7].

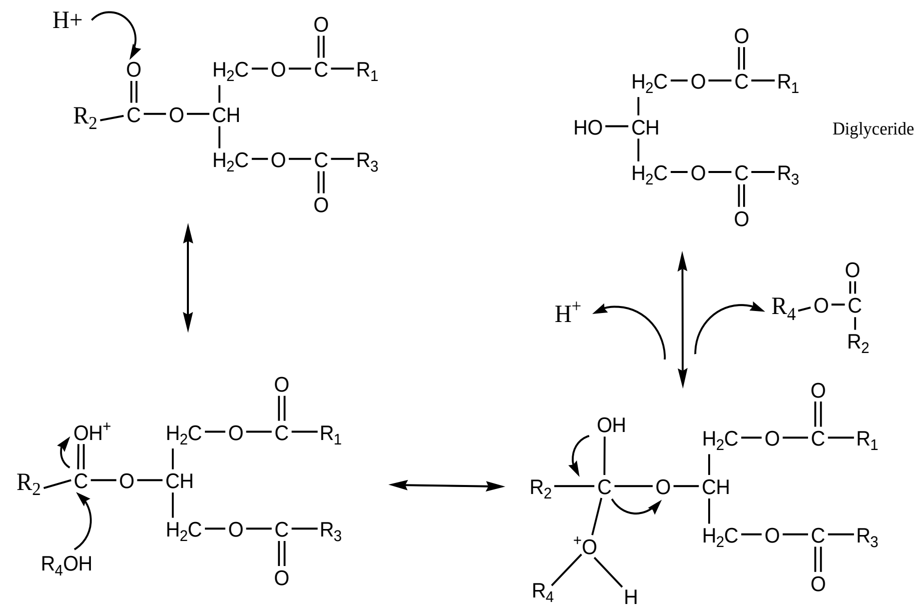


Figure 2.1: Acid Catalysed Reaction Mechanism

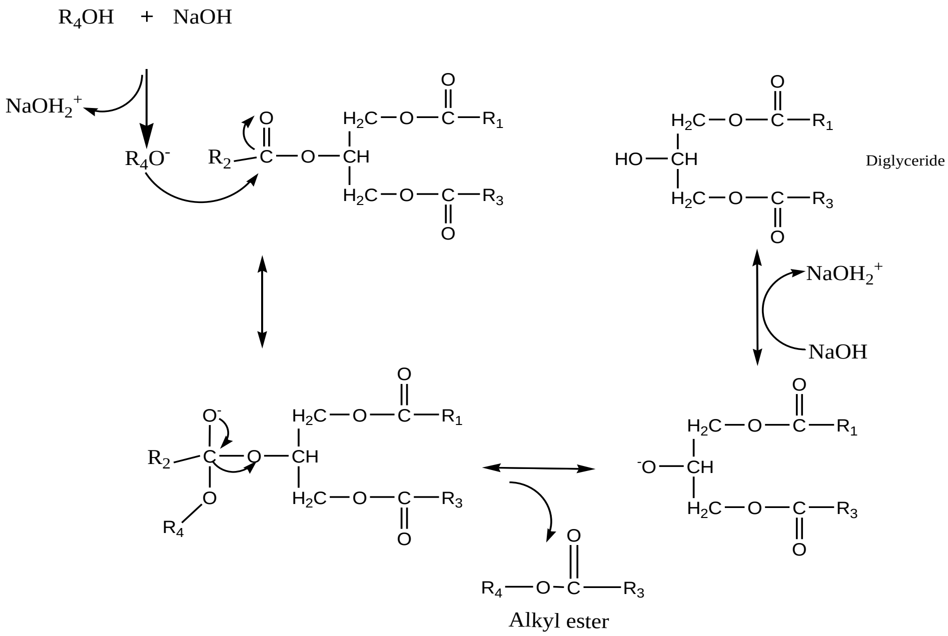


Figure 2.2: Base Catalysed Reaction Mechanism

The development of solid acid catalysts has recently gained attention in view of their ease of separation and lack of corrosion or toxicity problems [8, 9, 10]. Unfortunately, in the inorganic-oxide solid acids such as zeolites, the active sites are protons and they are inside the pores (pore size < 8 Å), and so the pore size places restriction on the shape and size of the molecule that can enter it. Bulky molecules cannot enter these pores. Therefore zeolites are useful in reactions involving either only small molecules or a mixture of different-sized molecules with the same functional group, where only the reaction of the smaller sized molecules is desired. They also readily lose their activities under harsh conditions. Although strong acidic ion-exchange resins such as amberlyst and nafion have abundant sulphonic acid groups ($-SO_3H$) which act as strong acid sites but these resins are expensive and their catalytic activities are still much lower than that of sulfuric acid. In addition, such resins show low operational stability and their catalytic activity is lost after a few cycles of re-use [11, 12, 13]. Sulfated zirconia, on the other hand, is an efficient solid acid catalyst [14, 15] but is expensive because zirconium is a rare and costly metal.

2.2. Basic catalysts

The base-catalyzed transesterification are reported to proceed faster than the acid-catalyzed reactions. Because of this and the fact that the alkaline catalysts are less corrosive than acidic compounds, industrial processes usually favour base catalysts, such as alkaline metal alkoxides and hydroxides as well as sodium or potassium carbonates. Alkaline metal alkoxides are the most active catalysts. They give yields greater than 98% in a relatively short reaction time of 30 min. even at low molar concentrations of about 0.5 mol%, but their requirement of the absence of water makes them inappropriate for typical industrial processes in which water cannot be avoided completely[4]. Also homogenous alkali catalysts generally react with FFAs to form unwanted soap by-products leading to the deactivation of the catalyst [16].

The fuel properties of the esters produced from the transesterification can vary depending on the types of oil used. Table 2.2 enlists fuel properties of karanja and jatropha oil and derived methyl esters.

Table 2.2: Fuel properties of karanja and jatropha oil and derived methyl esters [17]

Properties	karanja oil (Raw)	karanja oil (Derived Biodiesel)	jatropha oil (Raw)	jatropha oil (Derived Biodiesel)	Diesel
Viscosity(cST) at 30°C	29.65	8.73	53.79	7.2	2.5
Calorific value (kj/kg)	-	35879	-	42640	43500
Flash point (°C)	241	217	261	248	52
Fire point (°C)	253	223	302	295	63
Cloud point (°C)	7	6	7	6	5
Pour point (°C)	3	3	4	4	4
Specific gravity(at 30°C)	0.912	0.882	0.902	0.876	0.835

Apart from these catalysts, biocatalysts are also being used for biodiesel production.

2.3. Enzymatic catalyst

Lipases are able to catalyze the transesterification of triglycerides in either aqueous or non-aqueous systems [18]. Although the lipases are non-polluting and require mild operating conditions the reaction yields as well as the reaction times are still unfavorable compared to the base- catalyzed reaction systems and are usually expensive. Moreover, methanol was found to denature the enzyme decreasing its activity [19-25]. It has been reported that as methanol is insoluble in vegetable oils, it inhibits the immobilized lipases and thereby decreases the catalytic activity of the transesterification reaction. Further, the hydrophilic by-product glycerol is also insoluble in the oil, so it is easily adsorbed onto the surface of the immobilized lipase leading to a negative effect on lipase activity and operational stability [4].

Heterogeneous catalysts

More recently, there has been an increased research activity directed towards the development of heterogeneous catalyst systems for biodiesel production as they are easy to separate after the completion of the reaction, yield pure product and by product, easy to reuse, reduced corrosion problems and has low sensitivity to FFAs and water .With the use of heterogeneous catalysts, the refining steps in the purification process can be reduced.. Different heterogeneous catalysts used for transesterification are given in table 2.3.

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 [26]. 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. Na/NaOH/ γ-Al_2O_3 showed almost the same catalytic activity as NaOH under the optimum reaction conditions [27]. When commercial CaO was used as a catalyst, the conversion rate of vegetable oil achieved was up to 95.5% after 300 min of reaction [28]. KF/CaO showed a higher activity in transesterification of vegetable oil with methanol as compared to CaO. CaO, dipped in an ammonium carbonate solution becomes a solid super-base and leads to 93% conversion in optimal conditions [29]**.** Most of these catalysts lose their activity on recycle and/or require pretreatment of the feedstock to remove the FFAs and water.

Table 2.3: Different heterogeneous catalysts used for transesterification of oils

Oil	Catalyst	Molar ratio MeOH/Oil	Rxn time (h)	Temp (^oC)	Conversion (%)	Ref.
Jatropha	CaO	9:1	2.5	70	93	30
Jatropha	Na/SiO_2	15:1	0.75	65	99	31
Karanja	CaO/Li	12:1	8	65	94.9	32
Soyabean Oil	$MgO.MgAl_2O_4$	3:1	10	65	57	33
Palm oil	$Mg–Al–CO_3$ (Hydrotalcite)	30 :1	6	100	86.6	34,35
Rapeseed oil	$CaTiO_3$, $CaMnO_3$,$Ca_2Fe_2O_5$, $CaZrO_3$,CaO-CeO_2	6:1	10	60	90	36

Jatropha oil contains about 14% free fatty acid (FFA) content, which is far beyond the limit of 1% FFA level that can be converted into biodiesel by transesterification using an alkaline catalyst [25]. The homogeneous catalyst-based processes thus involve elaborate process steps for removal of FFAs and water from the feedstock and catalyst from the products. When FFAs are present, they react with the homogeneous alkali catalysts and form unwanted soap by-product and deactivate the catalyst. In addition water, sometimes present in non-edible, unrefined or waste vegetable oils also leads to the deactivation of homogeneous catalysts. Na/SiO_2 catalyst with a Na/Si ratio of 50: 50, calcined at 600^oC, yielded maximum biodiesel production from jatropha oil when compared with any reported solid catalyst [25].

Keeping the above facts in mind, the present work has been undertaken with the following **objectives:**

1) To prepare Li impregnated SiO_2 catalyst of various Li/Si molar ratios.

2) To study the transesterification reactions of jatropha and karanja oil with the prepared catalysts

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.

3.1 Materials

Hexane, ethyl acetate, ethanol, deionised water, silica gel and lithium nitrate were obtained from Loba Chemicals Private Limited and used without much purification. Pluronic P123 was obtained from sigma aldrich. Methanol (> 99%) was obtained from MERK, India. Jatropha oil and karanja oil were purchased from Medors Biotech Pvt. Limited, Delhi.

3.2 Preparation of catalyst

Lithium doped SiO_2 catalysts were prepared with Li: Si molar ratio 2:1, 3:1, 4:1, and 5:1. In a typical preparation desired amount of $LiNO_3$ (3.3g, 0.090 mol to 12.6g, 0.225 mol) was added to a mixture of 18.7 ml ethanol and 18.7 ml distilled water. To this 9.34 g (0.001 mol) of pluronic P123 was added and mixed thoroughly for 1 h. Tetraethylorthosilicate (10 ml, 0.045 mol) was added drop wise to the above mixture and was stirred for 1 hr 30 min. The transparent sol obtained was dried at $80^{o}C$ for 48 h. Calcination was carried out at $600^{o}C$ for 4 h. Lithium doped SiO_2 catalysts are designated as Li-SiO_2-X (where X is the molar ratio of Li with respect to 1 mole of Si)

3.3. Catalyst characterisation

The physicochemical properties of all the prepared catalysts having different molar ratios of Li: SiO_2 were studied by powder XRD, BET (Surface area analyser) and SEM.

Powder XRD. Powder XRD pattern were recorded using **Panalytical X'pert** with Ni-filtered Cu Kα radiation in steps of 0 .0170 with a scan step time of 15.5 sec in the 2Θ range of 10-80^{o}

BET surface area. Single point BET surface area was recorded on **Smartsorb 92/93** using calibrated gas mixture of 29.74 % N_2 and 70.26% He.

Scanning electron microscope (SEM). JEOL JSM-6510LV Scanning electron microscope from Research & Development Centre of Thapar University, Patiala.

3.4.1. Transesterification with jatropha oil

In a typical reaction, 5 g jatropha oil, 1:60 molar ratio of oil: methanol (5g: 11.03g) and 6 wt% (300mg) of catalyst were taken in round bottom flask (50 ml) and refluxing was carried out till the completion of reaction at 65°C. Completion of reaction was monitored by TLC (Solvent system:: hexane and ethyl acetate 24:1 (v/v)). With a view to find out the influence of temperature, moisture content, methanol and the catalyst amount, various sets of reactions were performed by varying single parameter at a time.

3.4.2 Transesterification with karanja oil

In a typical reaction, oil (5g) and methanol in 1: 80 molar ratio and 6 wt. % of catalyst were stirred in a round bottom flask (50 ml) at 65°C. The contents were refluxed till the completion of reaction. Progress of the reaction was monitored by TLC (solvent system:: hexane: ethyl acetate 24:1(v/v)). Various reaction conditions were optimized viz., the catalyst amount, oil to methanol molar ratio and the reaction temperature, by varying one parameter at one time.

3.5 Analysis of oil

Determination of acid value of oil

Acid value is the number of milligrams of KOH required to neutralize the free fatty acid present in 1 g of oil. It was used to know the age and quality of oil.

When oil is stored, it may undergo peroxide formation at the double bonds by atmospheric oxygen and hydrolysis by micro-organisms with liberation of free acid. Thus by calculating the free fatty acid present, we came to know about the purity of oil.

In order to study the acid content of karanja oil, a mixture of 2.646 g (0.002964 moles) of oil, 25 ml ethanol and 25 ml diethyl ether was taken as sample and 1 ml of phenolphthalein was added to it. This was thoroughly mixed and titrated with 0.1 M of KOH until the pink colour persisted for 20-30 s. For studying the acid content of jatropha oil, a mixture of 3.14 g (0.0036092 moles) of oil, 25 ml ethanol and 25 ml diethyl ether was taken as sample and was titrated against 0.25 M of KOH using phenolphthalein as indicator. The number of millilitres of standard alkali required was calculated for the acid value of oil, given by the equation:

$$\text{Acid value} = \frac{\text{No. of ml of KOH used}}{\text{Wt. of oil taken}} \times \text{Amount of KOH present in 1 ml of sol.}$$

Acid Value was found to be 22.39 mg of KOH/g of oil for karanja oil

and it was found to be 11.18 mg of KOH/g of oil for jatropha oil

RESULTS AND DISCUSSION

4.1 Catalyst characterization

4.1.1 Hammett indicator

Basic Strength of catalysts viz., Li-SiO_2-X (X=2, 3, 4, 5; X being molar ratio of Li w.r.t. Si) was determined by Hammett indicators. It was observed that all the four catalysts show sharp colour change from yellow to orange with 2,4-dinitroaniline (H_15). This shows that all these catalysts have almost the same basicity. The basic strength of these catalysts is shown in table 4.1.

Table 4.1: Basic strength of catalysts

S.No.	Catalyst	Hammett indicator(with Highest possible basic Strength) showing change of colour	Basic strength
1	Li-SiO_2-2	2,4-dinitroaniline	15<H_<18.0
2	Li-SiO_2-3	2,4-dinitroaniline	15<H_<18.0
3	Li-SiO_2-4	2,4-dinitroaniline	15<H_<18.0
4	Li-SiO_2-5	2,4-dinitroaniline	15<H_<18.0

4.1.2 Power XRD pattern of prepared catalysts

Powder XRD pattern of Li impregnated SiO_2 catalysts at different Li: SiO_2 molar ratios

Powder XRD pattern of Li-SiO_2-X catalysts (X= 2 to 5) are shown in fig.4.1. Peaks at 18^o, 26.9^o and 33.1^o in all the prepared catalysts showed the presence of Li_2SiO_3 (PDF 70-0330, 72-1140). But there is emergence of new peaks at 24.808^o and 23.7^o which correspond to the presence of $Li_2Si_2O_5$ (72-0102) and new peak at 22.288^o which corresponds to the presence of Li_4SiO_4 (37-1472, 86-0551) as we increase the amount of Li in case of Li-SOP-X (X= 3 to 5)

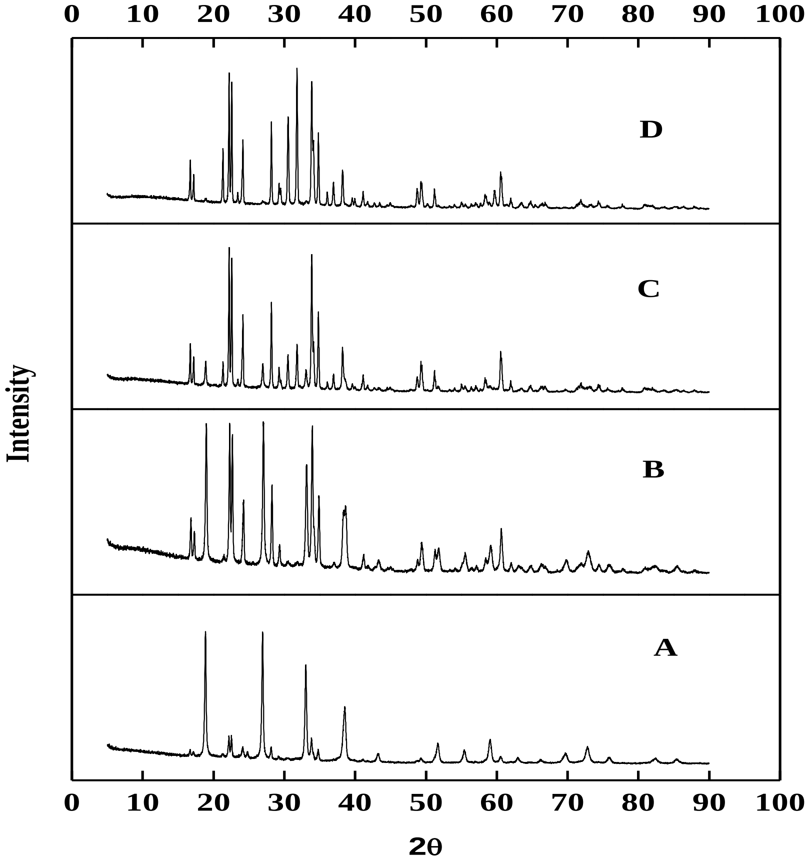


Fig. 4.1 Powder XRD patterns of Li-SiO_2-X catalyst A) Li-SiO_2-2 B) Li-SiO_2-3 C) Li-SiO_2-4 D) Li-SiO_2-5

4.1.3 BET surface area measurement

The BET surface area of Li-SiO_2-2, Li-SiO_2-3, Li-SiO_2-4 and Li-SiO_2-5 (Table 4.1) are found to be 3.44, 1.62, 0.55, and 0.86m^2/g, respectively. The surface areas of the catalysts decreased with an increase in the concentration of Li content except for Li-SiO_2-5 where surface area is more than Li-SiO_2-4.

Table 4.2: Surface area of Li-SiO_2-X catalysts

S.No.	Catalyst	Surface area (m^2/g)
1	Li-SiO_2-2	3.44
2	Li-SiO_2-3	1.62
3	Li-SiO_2-4	0.55
4	Li-SiO_2-5	0.86

4.1.4 SEM image of Li-SiO_2-3 catalyst

The SEM image of Li-SiO_2-3 is shown in figure 4.2. The same study reveals that the catalyst exists in spherical shape of 1 µm.

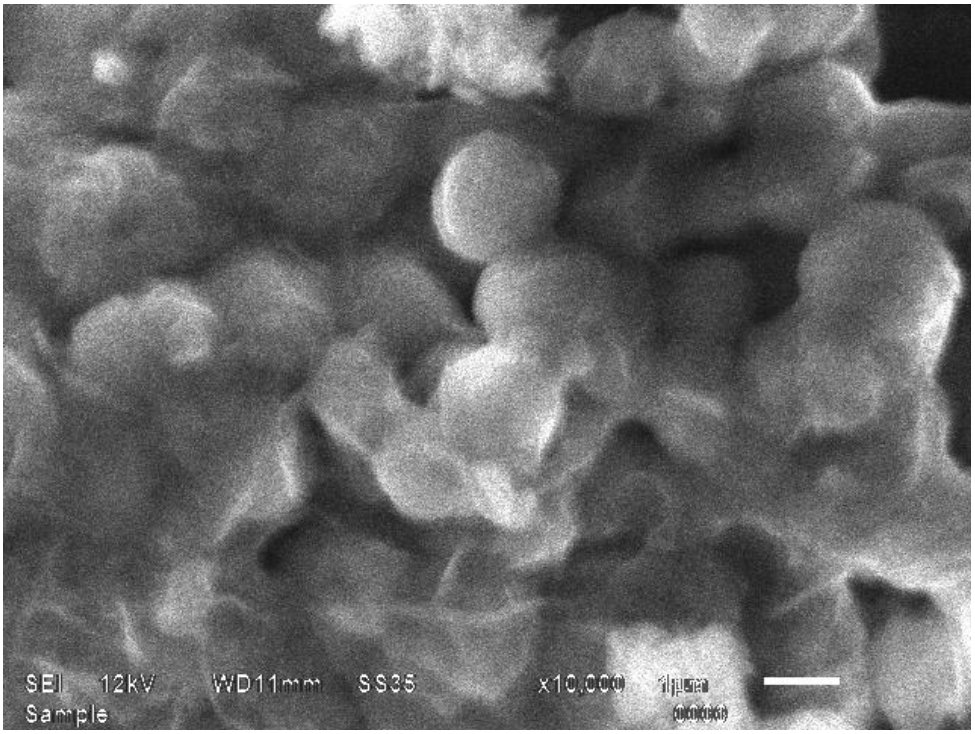


Fig.4.2 SEM image of Li-SiO_2-3 catalyst

4.2 Catalytic activity

In order to observe the catalytic activity of Li-SiO_2-2, Li-SiO_2-3, Li-SiO_2-4, Li-SiO_2-5 catalysts, a series of reactions were carried out by treating jatropha oil (5g) with methanol (10g) at 65^oC in the presence of 6 wt% (300 mg) of the catalyst and time taken for complete transesterification is shown in the table 4.3.

Table 4.3: Reaction time for completion of reaction by different Li-SiO_2-X catalysts

Catalyst	Time taken for completion of reaction (h - min)
Li-SiO_2-2	1 - 15
Li-SiO_2-3	0 - 45
Li-SiO_2-4	1 - 15
Li-SiO_2-5	3 - 00

Li-SiO_2-3 catalyst took least time among all Li/SiO_2 catalysts for complete transesterification. Further Li-SiO_2-3 catalyst was used for optimizing other parameters viz., the amount of catalyst, amount of methanol and the temperature.

The catalytic activity of the catalyst, Li-SiO_2-3 has been studied for preparation of methyl esters from two different oils viz., jatropha and karanja oil.

4.2.1 Jatropha oil

Effect of catalyst amount

For studying the effect of catalyst amount, a set of transesterification reactions were carried out by using 5g of jatropha oil with 11 g of methanol (oil and methanol in 1:60 molar ratio) in the presence of varying amount of the catalyst from 2 to 8 wt% (100 to 400mg) at 65^oC. Time taken for the completion of reaction decreases with the increase in wt % of catalyst as shown in table 4.4 and fig 4.4. Lowest reaction time of 45 min was observed with 6 wt % of the catalyst; hence other reaction parameters were optimized with same amount of catalyst.

Table 4.4: Effect of weight % of Li/SiO_2 catalyst on the reaction time

Sr. No.	Weight % of catalyst	Time taken (h - min)
1	2.00	5 - 30
2	3.00	4 - 00
3	4.00	1 - 15
4	5.00	1 - 00
5	6.00	0 - 45
6	7.00	0 - 45
7	8.00	0 - 45

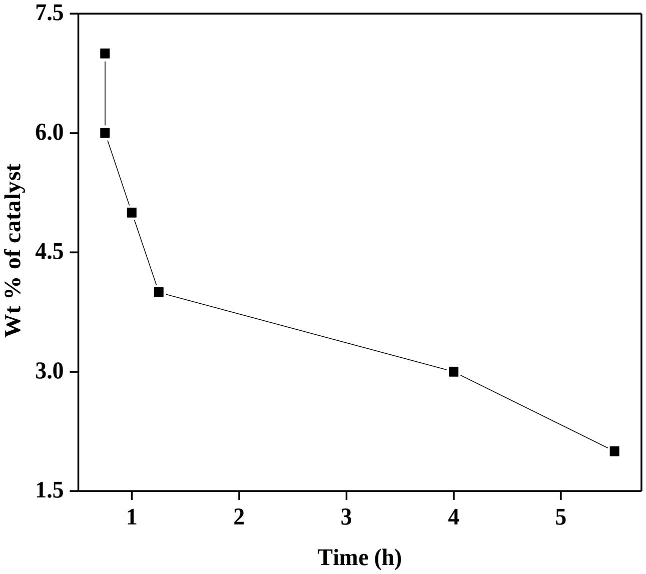


Fig 4.4: Effect of wt % of the catalyst on reaction time

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 from 1:30 (5g: 5.5g) to 1:100 (5g: 18.4g) in the presence of 6 wt % (300mg) of the catalyst at 65°C. Reaction time increases from 45 min to 1 h 15 min when oil to methanol molar ratio decreases from 1:100 to 1:30. Oil to methanol ratio of 1:60 (5g: 11g) was found to be optimum because further increase in oil to methanol ratio did not lead to any marked reduction in reaction time of completion as shown in table 4.5 and fig 4.5.

Table 4.5: Effect of oil to methanol molar ratio on reaction time

Sr. No.	Oil to methanol molar ratio	Time taken (h - min)
1	1:30	1 - 15
2	1:40	1 - 15
3	1:60	0 - 45
4	1:80	0 - 45
5	1:100	0 - 45

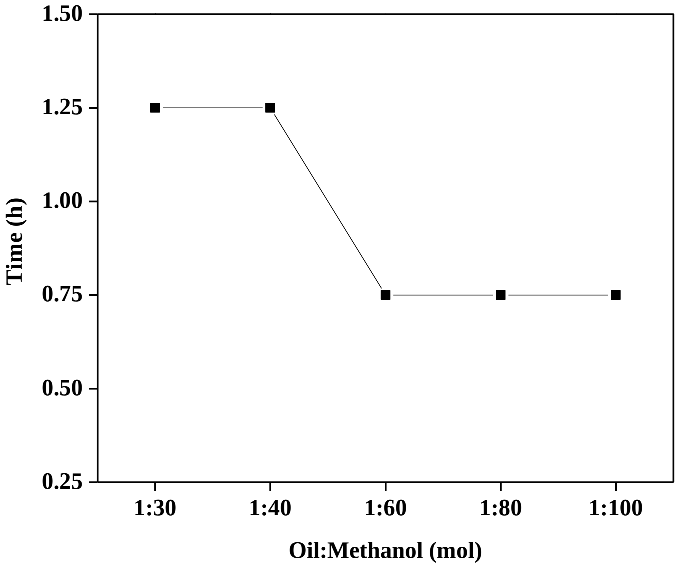


Fig 4.5: Effect of oil to methanol molar ratio on reaction time

Effect of temperature

Transesterification reactions were carried out at different temperatures by using 1:60 molar ratio of oil to methanol and 6 wt% of the catalyst. Lowest reaction time of completion of reaction was 45 min at 65 ^{o}C. Time taken for completion of reaction is shown in table 4.6 and fig 4.6.

Table 4.6: Effect of temperature on reaction time

Sr. No.	Temperature (^{o}C)	Time taken (h - min)
1	45	2 - 15
2	50	2 - 00
3	55	1 -15
4	60	1 - 15
5	65	0 - 45

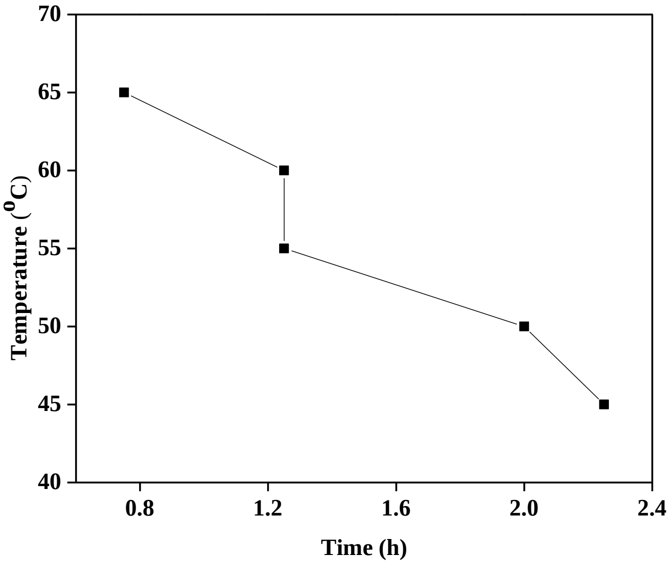


Fig 4.6: effect of temperature on reaction time

Effect of moisture

To test the moisture resistance of the catalyst, transesterification reactions were carried out in the presence of added moisture content. These results are shown in table 4.7 and fig 4.7. Reaction conditions used were 6 wt% (300mg) of the catalyst and oil to methanol molar ratio of 1:60 (5g: 11g) at 65°C. It was found that these reaction conditions can tolerate up to 20 wt % of moisture but time taken for the completion increased from 1 h to 5 h when moisture content was increased from 5 to 20%.

Table 4.7: Effect of addition of moisture (weight %) on reaction time

Sr. No.	Wt.% of moisture	Time taken (h - min)
1	5	1 - 00
2	10	1- 30
3	15	3 - 00
4	20	5 - 00

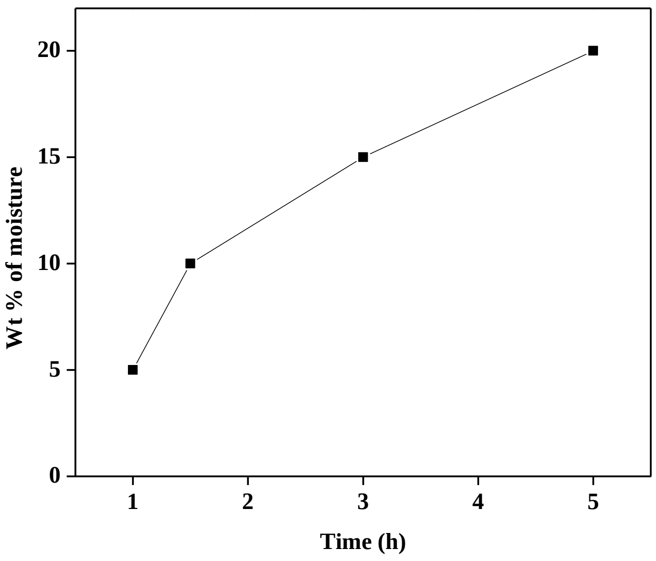


Fig 4.7: Effect of wt % of moisture on reaction time

4.2.2 Karanja oil

Tranesterification reactions of karanja oil with methanol were performed in the presence of Li- SiO_2-3. In a typical reaction, oil and methanol in molar ratio 1: 80 (5g: 14.3g) were stirred with 6 wt% of catalyst at 65°C till the disappearance of oil spot on thin layer chromatography plate (Solvent system: hexane and ethyl acetate:: 24 : 1). Various reaction parameters optimized on the basis of TLC are; amount of catalyst (4 -8 wt %), oil: methanol molar ratio (1:40 to 1:100), and temperature (45-65°C).

Effect of catalyst amount

A series of transesterification reactions were carried out by using oil and methanol in 1:80 molar ratio in the presence of varying amount of Li-SiO_2-3 catalyst, from 4 to 8 wt% at 65°C. Time taken for completion of reaction decreases with increase in wt % of catalyst as shown in table 4.8 and fig 4.8.

Table 4.8: Effect of weight % of catalyst on the completion of reaction

Sr. No.	Wt % of catalyst	Time taken (h - min)
1	4.00	3 - 15
2	5.00	2 - 00
3	6.00	1 - 15
4	7.00	1 - 15
5	8.00	1 - 00

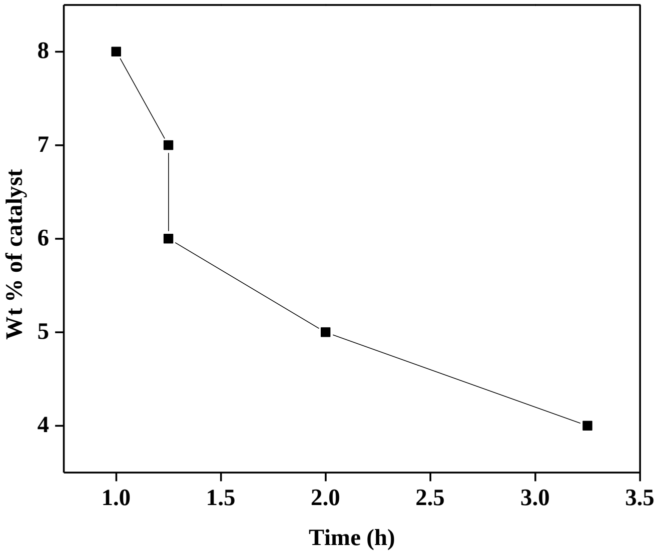


Fig 4.8: effect of wt % of catalyst on reaction time

Effect of oil to methanol molar ratio

Transesterification reaction was carried by using different oil to methanol ratio from 1: 40 to 1: 100 (7.2 g to 17.9 g of methanol for 5 g of oil) in the presence of 6 wt% of catalyst at 65^{o}C. Reaction time for the disappearance of oil spot on TLC plate increased from 1 h 15 min to 3 h when oil to methanol molar ratio was decreased from 1:100 to

1:40. Oil to methanol ratio of 1:80 (5g: 14.3g) was found to be optimum because further increase in oil to methanol ratio did not lead to any marked reduction in reaction time of completion as shown in table 4.9 and fig 4.9.

Table 4.9: Effect of oil to methanol molar ratio on reaction time

Sr. No.	Oil to methanol molar ratio	Time taken (h - min)
1	1:40	3 - 00
2	1:60	3 - 00
3	1:80	1 - 15
4	1:100	1 - 15

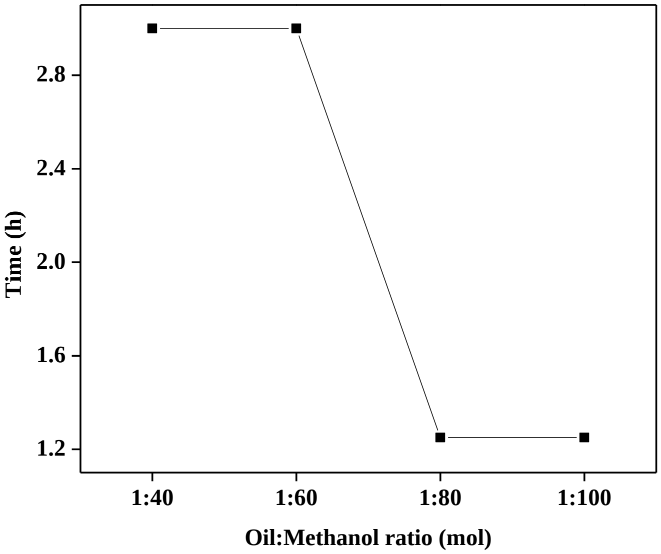


Fig 4.9: Effect of oil to methanol molar ratio on reaction time

Effect of temperature

Transesterification reactions of karanja oil with methanol were performed by using 1:80 (5g: 14.3g) molar ratio of oil: methanol in the presence of 6 wt % (300mg) at different temperatures (45°-65°C). Reaction times for the disappearance of oil spot from TLC plate are shown in table 4.10 and fig 4.10. There is no disappearance of oil spot in case of reaction performed at 45°C.

Table 4.10: Effect of temperature on reaction time

Sr. No.	Temperature (°C)	Time taken (h - min)
1	50	2 - 30
2	55	2 - 00
3	60	2 - 00
4	65	1 - 15

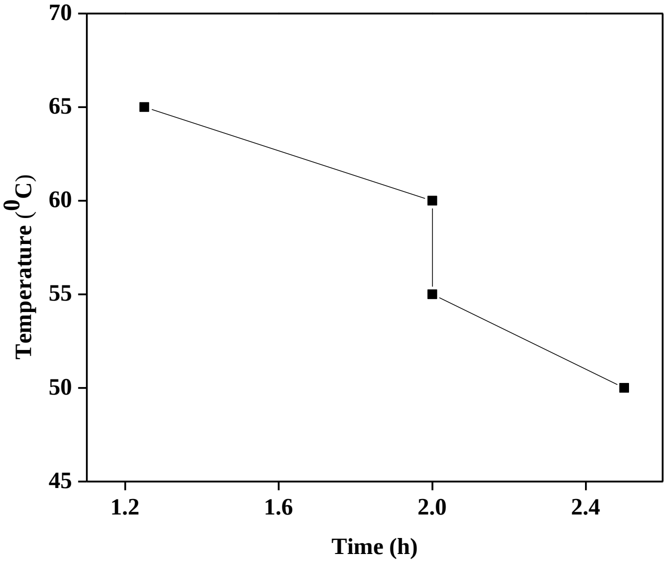


Fig 4.10: Effect of temperature on reaction time

Identification and quantification of methyl esters

Methyl esters prepared from jatropha oil were characterized by ^1H NMR. The ^1H NMR spectra of jatropha and karanja oil are shown in fig.4.11 (a) and 4.12 (a) which show a multiplet at 4.1 and 5.3 ppm due to the presence of glyceridic protons along with other hydrocarbon peaks.

The ^1H NMR spectrum of transesterified product of jatropha oil is shown in fig. 4.11(b). The appearance of a new peak at 3.6 ppm due to the 'OCH_3' protons and disappearance of peaks due to glyceridic protons supports the formation of biodiesel and it is quantified as 96 % by reported method [37].

The ^1H NMR spectrum of transesterified product of karanja oil is shown in fig. 4.12(b). The methyl esters are quantified as 40 % by reported method [37].

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

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

$I_{\text{M.E}}$ = integration value of the protons of the methyl esters

$I_{\text{Methylene protons}}$ = integration value of the methylene protons

The factors 2 and 3 derive from the fact that the methylene carbon possesses two protons and the alcohol (methanol–derived) carbon has three attached protons.

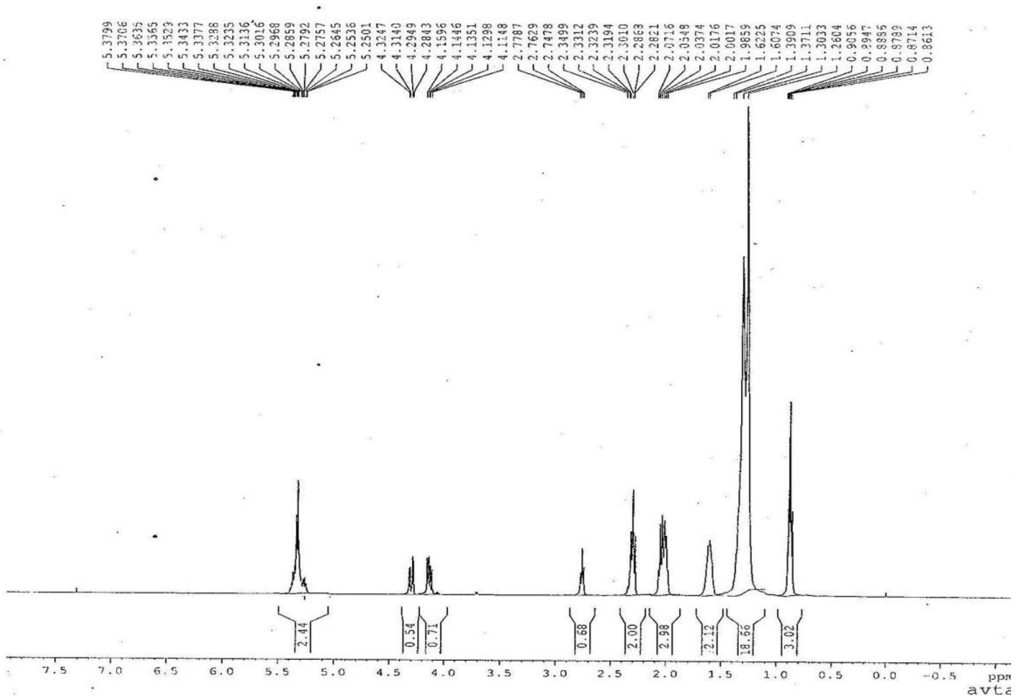


Fig 4.11(a): ^{1}H NMR of jatropha oil

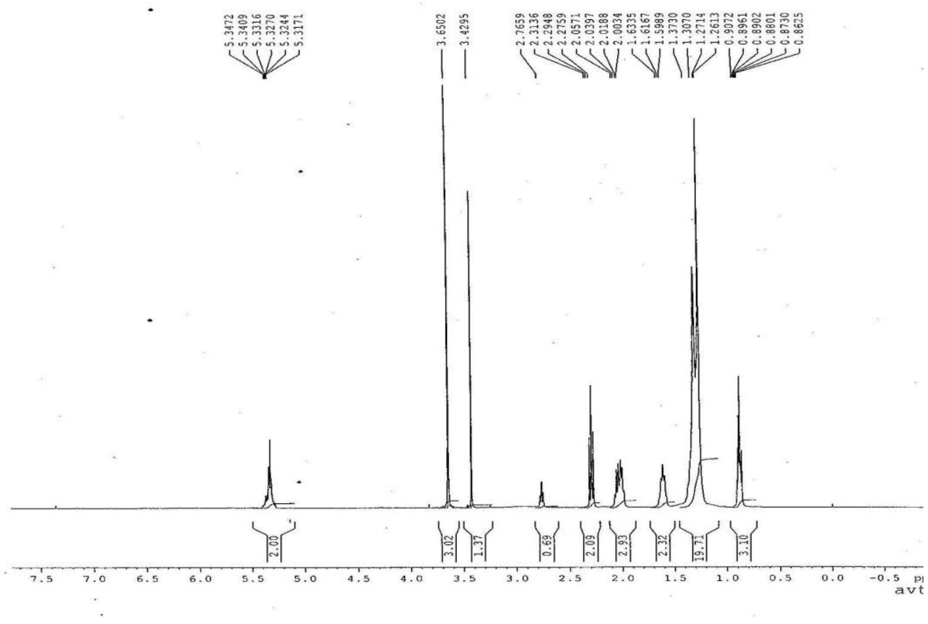


Fig 4.11(b): ^{1}H NMR of transesterified product of jatropha oil

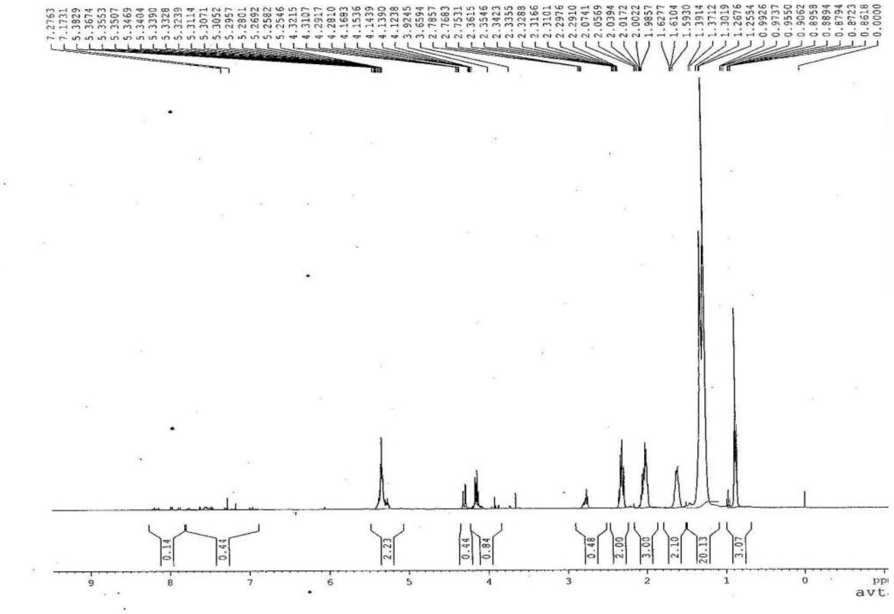


Fig 4.12(a): ^{1}H NMR of karanja oil

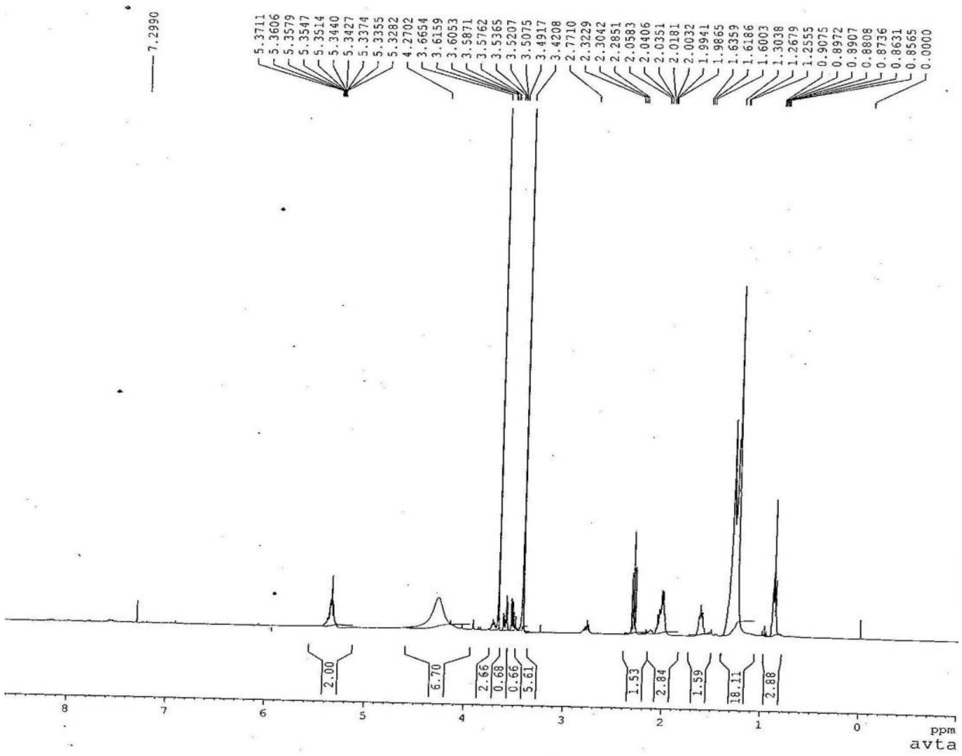


Fig 4.12(b): ^{1}H NMR of transesterified product of karanja oil

CONCLUSION

Li/SiO_2 (6 wt %) having Li: Si molar ratio of 3:1 has been found to catalyse the transesterification reactions of both jatropha oil and karanja oil. Transesterification of jatropha oil resulted in 96% conversion within 45 min by using 1:60 molar ratio of oil to methanol with 6 wt% of the catalyst at 65°C. Same amount of catalyst (6 wt %) was found to be effective for complete transesterification in the presence of 20 wt % of moisture with 1: 60 oil to methanol molar ratio within 5 h. The major advantages of the present system include operational simplicity, mild reaction conditions, low reaction time and high conversion, insensitive to moisture. However, transesterification of karanja oil with methanol by using 6 wt% of catalyst and 1:80 molar ratio of oil to methanol resulted in 40% methyl esters at 65°C.

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