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Preparation of Biodiesel from Crude oil of *Simarouba glauca* using CaO as a Solid Base Catalyst

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Abstract

The purpose of the work is to study biodiesel production by transesterification of Simarouba oil with methanol in a heterogeneous system, using CaO as a solid base catalyst. The reaction variables such as the molar ratio of methanol to oil, reaction temperature, mass ratio of catalyst to oil and the reaction time was studied. At 65^{0}C, 12:1molar ratio of methanol to oil, 180 minutes reaction time and 8% catalyst in oil, the conversion was over 95%.

Keywords: biodiesel, CaO catalyst, transesterification, *Simarouba glauca.*

Introduction

Biodiesel (fatty acids methyl esters, FAME) has recently become very attractive, because of its environmental benefits due to its production from renewable sources[1]. Biofuels have become a matter of global importance because of the need for an alternative energy at a cheaper price and with less pollution[2]. Nowadays, most biodiesel is produced by the transesterification of triglycerides of edible oils, non edible oils, and waste vegetable oils using methanol with alkaline catalyst NaOH or NaOMe[1-5]. Homogeneous alkali-catalyzed transesterification is much faster than acid-catalyzed transesterification[6]. A number of studies have been conducted on biodiesel processes, such as acid-catalyzed process[7,8], supercritical process[9,10], enzymatic process[11,12] and heterogeneous catalytic process[13,14]. Due to noncorrosive, environmentally benign and easily separated from the liquid products the heterogeneous base catalysts can be designed to give higher activity, selectivity and longer catalyst lifetimes[13,14].

The heterogeneous catalytic process is expected to be an effective biodiesel production process with low cost and minimal environmental impact because of the possibility of simplifying the production and purification processes under mild conditions. Therefore, many heterogeneous catalysts for the transesterification of oils have been developed. The conversion in excess of 90% was achieved at a temperature of 100^{0}C in the transesterification reaction of soybean oil with ETS-10 zeolite[15]. It has also been reported that the conversion to methyl ester reaches 87% with the potassium-loaded alumina catalyst, when a mixture with a molar ratio of methanol to oil of 15:1 is refluxed for a reaction time 7 hours[16]. Besides these, there have been several other reports on heterogeneous catalysts for the transesterification of oils to biodiesel[17-21]. Under room-temperature, for soybean oil and poultry fat to biodiesel using Nanocrystalline Calcium Oxides, the rate of reaction was slow and it required 6–24 hours to obtain high conversion with the most active catalyst and it was also observed that the deactivation of catalyst after eight cycles with soybean oil and after three cycles with poultry fat[22]. A 93% conversion of *Jatropha curcas* oil was obtained using CaO as a catalyst, but the catalyst must be treated with ammonium carbonate solution and calcinated at high temperature[23].

In this work, we intend to examine a heterogeneous base catalyst in order to develop an effective biodiesel process catalyst with high activity and durability; hence the catalytic efficiency of CaO in the transesterification reaction of Simarouba oil is evaluated with respect to the conversion of Simarouba oil to methyl esters. The effects of various reaction variables such as the molar ratio of methanol to oil, reaction temperature, mass ratio of catalyst to oil and the reaction time on the conversion to methyl esters are investigated.

Material and Methods

All chemicals were Analytical Reagents and bought locally. Methanol was dried and distilled before use. The apparatus used for transesterification was designed and fabricated (figure-1). It consists of oil bath, reaction flask with condenser and digital rpm controller with mechanical stirrer. The volume is about 1 L and consists of three necks. A digital temperature indicator was used to measure the reaction temperature. It has an open valve to obtain the outputs. Fatty acid methyl ester content in the transesterified oil was determined by Gas Chromatograph (Chemito CERES 800 plus G.C) equipped with a FID detector.

Extraction of oil: Simarouba seeds were obtained from different parts of Odisha, India and decorticated manually. The oil was extracted from the kernel by mechanical expeller and Soxhlet extraction. In the process of mechanical expeller, a screw press oil expeller was used[3]. For Soxhlet extraction, the

kernels were crushed using a mechanical blender and for Soxhlet extraction procedure, 50 g of crushed kernel was packed in a thimble and the oil was extracted with n-hexane for 2 h. In Soxhlet extraction methods, the oil was isolated from n-hexane by rotary evaporator. The oil after mechanical extraction was subjected to filtration and neutralization. The acid value of the oil was high and by esterification to reduce the acid value to 1.1 mg KOH/g.

Transesterification of crude oil of Simarouba glauca: As shown in figure-1, transesterification reactions were carried out in a 1000 ml glass reactor with a condenser. The reaction procedure was as follows: First, the catalyst was dispersed in methanol under magnetic stirring followed by the addition of Simarouba oil into the mixture and heated by water circulation. The mixture was vigorously stirred and refluxed for the required reaction time, then the reaction mixture was allowed to settle down to separate into three phases in a separating funnel. The upper layer was biodiesel consists of methyl esters and unreacted triglycerides, the middle layer was glycerol and the lower layer was a mixture of solid CaO and a small amount of glycerol. The biodiesel, after water wash and subsequent heating (to remove the moisture) was collected for chromatographic analysis. The residual methanol was separated from the liquid phase by distillation. Experiments were carried out by changing different parameters like methanol to oil molar ratio, reaction time, catalyst amount and temperature.

Results and Discussion

Properties of Biodiesel: The properties of Simarouba oil, its Biodiesel were studied and compared with ASTM D6751 (table-1). The oil contains primarily eight fatty acids viz. stearic acid ($C_{18:0}$), oleic acid ($C_{18:1}$), palmitic acid ($C_{16:0}$), linoleic acid ($C_{18:2}$), arachidic acid ($C_{20:2}$), erucic acid ($C_{22:2}$), linolenic acid ($C_{24:0}$), eptadecanoic acid ($C_{17:2}$). Out of these, the four which were commonly found in most oils, including simarouba, are the saturated acids, palmitic (hexadecanoic acid) and stearic (octadecanoic acid); the unsaturated acids, oleic (Octadec-9-enoic acid) and linoleic (9, 12-octadecadienoic acid).

Effect of molar ratio of oil: methanol on transesterification of Simarouba oil: The alcohol to oil molar ratio is one of the important factors that affect the reaction. As by the addition of excess amount of methanol to shift the equilibrium to right so that the alcohol to oil molar ratio varied from 3:1 to 18:1. The yield of methyl esters versus different molar ratio of methanol to oil, such as, 3:1, 6:1, 9:1, 12:1, 15:1, 18:1 are shown in figure-2. The yield of methyl esters for methanol to oil molar ratio of 12:1 after 3 h was 95% whereas the yield was slightly reduced on increasing molar ratio because the catalyst content decreased with the increase in methanol. Hence the optimum molar ratio is 12:1.

Table -1
Fuel properties of Diesel, Simarouba oil and biodiesel

Fuel properties	Diesel	Simarouba oil	Biodiesel	ASTM D6751
Kinematic Viscosity (at40^{0}C) Cst	2.8	17.3	4.8	1.9–6.0
Density at 15^{0}C, kg m^{-3}	812	860	830	-
Acid value, mg KOH g^{-1}	-	8.4	0.75	<0.80
Flash Point, ^{0}C	52	225	165	>130
Pour Point, ^{0}C	-20	-	14.2	-15–10
Cloud Point, ^{0}C	-8	-	19	-3–12
Calorific value, MJ kg^{-1}	42.50	-	39.8	-

Effect of reaction temperature on transesterification of Simarouba oil: Studies were carried out at different temperatures from 50 - 80°C with 8% CaO as catalyst and methanol to oil molar ratio of 12:1. The conversion (%) of SOME (Simarouba oil methyl ester) versus different reaction temperature was plotted as shown in figure-3. It was observed that temperature has positive influence on methanolysis of Simarouba oil. The reaction rate was slow at low temperature due to the diffusion resistance, as the heterogeneous catalyst forms a three phase system, oil-methanol-catalyst. The reaction temperature above boiling point of alcohol is avoided since at high temperature it tends to accelerate the saponification of glycerides by the catalyst before completion of the alcoholysis[24]. Hence the optimum temperature is 65^{0}C.

Effect of mass ratio of catalyst to oil on transesterification of Simarouba oil: Alcoholysis of Simarouba oil was carried out with CaO as a catalyst at a concentration of 1-12% wt. of oil at 65°C with methanol/oil molar ratio of 12:1. Figure-4 shows the yield of methyl esters versus time at different catalytic concentrations. The lower catalytic concentration was insignificant to catalyze the reaction to completion. However, 8% CaO was optimal in the reaction with a yield of 95% in 180 minutes. With the increase in the concentration of catalyst, there was decrease in the yield of methyl esters. This was in accordance with the result obtained by Dorado et al[24].

Effect of reaction time on transesterification of Simarouba oil: In figure-5, the conversion versus reaction time was presented. It can be seen that the conversion was increased in the reaction time ranges between 60 minutes and 180 minutes, and thereafter remained nearly constant as a representative of a nearly equilibrium conversion. The nearly equilibrium conversion was found to be about 95% at 180 minutes of reaction time.

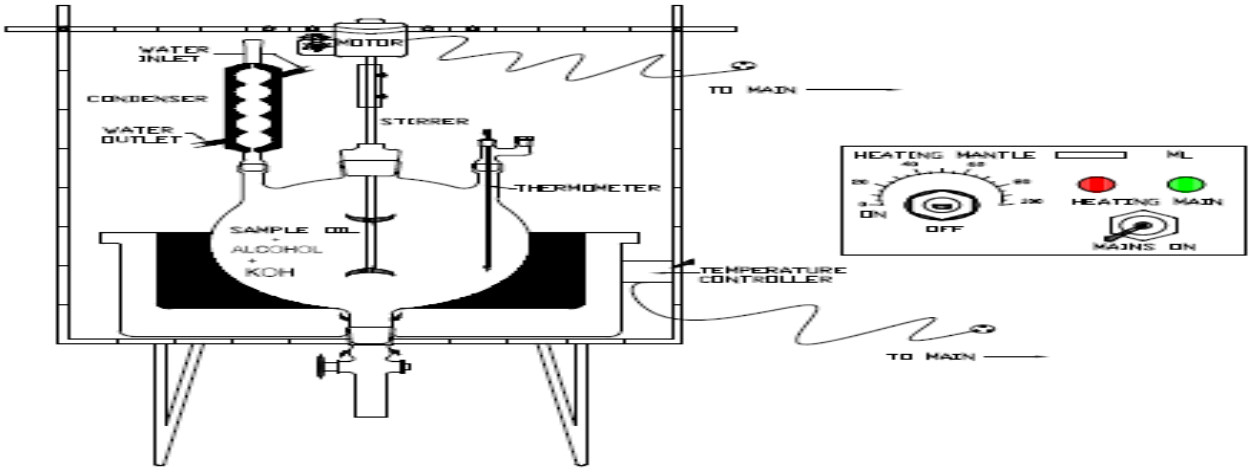

Figure-1
Schematic diagram of a transestrificator (from Mishra et.al., 2012)[3]

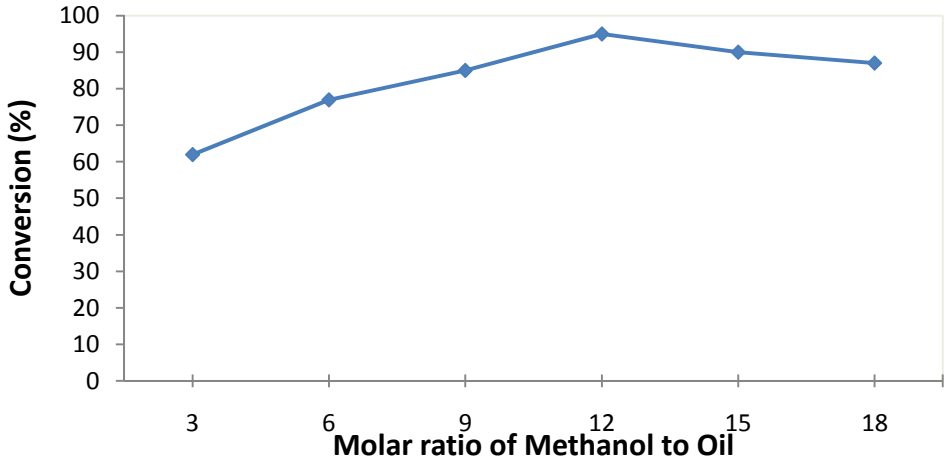

Figure-2
Influence of molar ratio on transestrification of simarouba oil, Cao/oil mass ratio is 8%, Reaction temperature is 65^{0}C, Reaction time: 180 minutes

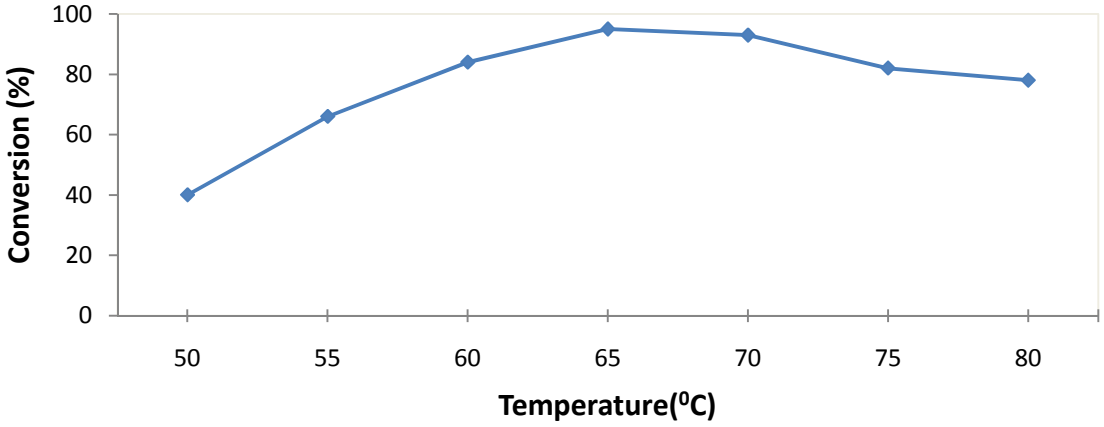

Figure-3
Influence of reaction temperature on transestrification of Simarouba oil, CaO/oil mass ratio is 8%, Oil/methanol molar ratio is 1:12, Reaction time is 180 minutes

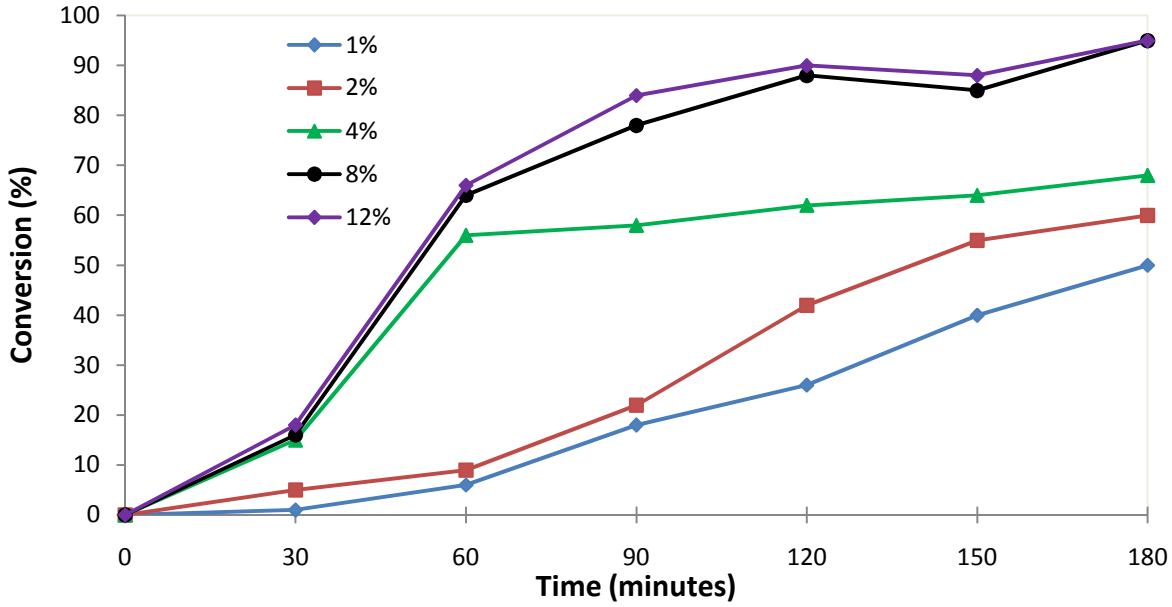

Figure-4
Influence of mass ratio of CaO concentration on transestrification of simarouba oil, Oil/Methanol molar ratio is 1:12, Reaction temperature is 65^0C

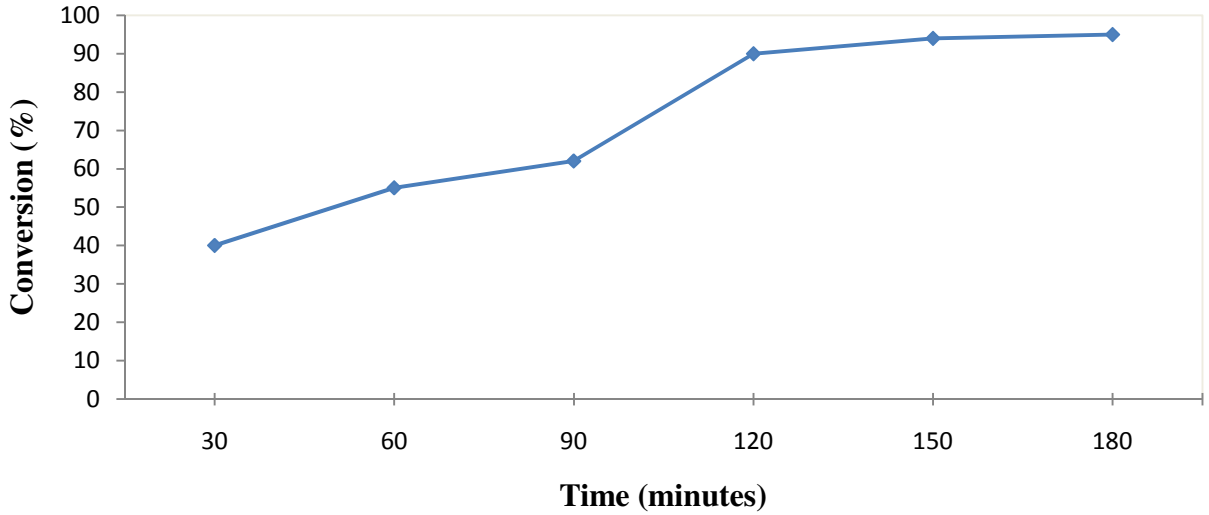

Figure-5
Influence of reaction time on transestrification of simarouba oil, CaO/oil mass ratio is 8%. Oil/methanol molar ratio is 1:12, Reaction temperature 65^0C

Conclusion

According to the experimental studies, the optimum reaction conditions for alcoholysis of Simarouba oil is 8% of catalyst in oil, methanol to oil molar ratio 12:1, reaction temperature 65^0C for a period of 180 minutes. The yield of methyl ester is more than 95%. The conversion of transesterification of oil is 90 – 95% and almost complete at higher molar ratio of methanol to oil within 150 minutes.

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References

1. Frangrui M. and Hanna M.A., Biodiesel production: a review, *Bioresour. Technol*., **70**, 1-15 **(1999)**

2. Okoro L.N., Belaboh S.V., Edoye N.R. and Makama B.Y., Synthesis, Calorimetric and Viscometric Study of Groundnut oil Biodiesel and Blends, *Research Journal of Chemical Sciences,* **1(3),** 49-57 **(2011)**

3. Mishra S.R., Mohanty M.K., Das S.P. and Pattanaik A.K., Production of Bio-diesel (Methyl Ester) from Simarouba Glauca Oil, *Research Journal of Chemical Sciences,* **2(5)**, 66-71 **(2012)**

4. Loreto E., Liu Y., Lopez D.E., Suwannakaran K., Bruce D.A., Goodwin Jr. J.G., Synthesis of biodiesel via acid catalyst, *Ind. Eng. Chem. Res*., **44**, 5353-5363 (**2005)**

5. Ananadhi P.M.R. and Shaleesha A.S., Microalgae as an Oil Producer for Biofuel Applications, *Research Journal of Recent Sciences,* **1(3)**, 57-62 **(2012)**

6. Vicente G., Martinez M. and Aracil J. Integrated biodiesel production: a comparison of different homogeneous catalysts systems, *Bioresour Technol,* **92,** 297–305 **(2004)**

7. Edgar L., Liu Y., Lopez D.E., Kaewta S., Bruce D.A. and Goodwin J.G., Synthesis of biodiesel via acid catalysis, *Ind. Eng. Chem. Res*., **44**, 5353–5363 **(2005)**

8. Freedman B., Pryde E.H. and Mounts T.L., Variables affecting the yields of fatty esters from transesterified vegetable oils, *J. Am. Oil Chem. Soc*., **61**, 1638–1643 **(1984)**

9. Minami E. and Saka S., Kinetics of hydrolysis and methyl esterification for biodiesel production in two-step supercritical methanol process, *Fuel,* **85**, 2479–2483 **(2006)**

10. Demirbas A., Biodiesel production via non-catalytic SCF method and biodiesel fuel characteristics, *Energy Convers. Mgmt.,* **47,** 2271–2282 **(2006)**

11. Shimada Y., Watanabe Y., Sugihara A. and Tominaga Y., Enzymatic alcoholysis for biodiesel fuel production and application of the reaction to oil processing, *J. Mol. Catal. B: Enzym*., **17**, 133–142 **(2002)**

12. Nie K., Xie F., Wang F. and Tan T., Lipase catalyzed methanolysis to produce biodiesel: optimization of the biodiesel production, *J. Mol. Catal. B: Enzym*. **43**, 142–147 **(2006)**

13. Gryglewicz S., Rapeseed oil methyl esters preparation using heterogeneous catalysts, *Bioresour Technol*, **70**, 249–53 **(1999)**

14. Tanabe K. and Holderich W.F., Industrial application of solid acid–base catalysts, *Appl Catal A*, **181**, 399–434 **(1999)**

15. Suppes G.J., Dasari M.A., Doskocil E.J., Mankidy P.J. and Goff M.J., Transesterification of soybean oil with zeolite and metal catalysts, *Appl. Catal. A: Gen*., **257**, 213–223 **(2004)**

16. Xie W., Peng H. and Chen L., Transesterification of soybean oil catalyzed by potassium loaded on alumina as a solid-base catalyst, *Appl. Catal. A: Gen*. **300**, 67–74 **(2006)**

17. Gryglewicz S., Rapeseed oil methyl esters preparation using heterogeneous catalysts, *Bioresour. Technol*. **70**, 249–253 **(1999)**

18. Suppes G.J., Bockwinkel K., Lucas S., Botts J.B., Mason M.H. and Heppert J.A., Calcium carbonate catalyzed alcoholysis of fats and oils, *J. Am. Oil Chem. Soc*., **78**, 139–145 **(2001)**

19. Kim H.J., Kang B.S., Kim M.J., Park Y.M., Kim D.K., Lee J.S. and Lee K.Y., Transesterification of vegetable oil to biodiesel using heterogeneous base catalyst, *Catal. Today* **93–95**, 315–320 **(2004)**

20. Cantrell D.G., Gillie L.J., Lee A.F. and Wilson K., Structure reactivity correlations in MgAl hydrotalcite catalysts for biodiesel synthesis, *Appl. Catal. A: Gen*. **287**, 183–190 **(2005)**

21. Jitputti J., Kitiyanan B., Rangsunvigit P., Bunyakiat K., Attanatho L. and Jenvanitpanjakul P., Transesterification of crude palm kernel oil and crude coconut oil by different solid catalysts, *Chem. Eng. J*. **116**, 61–66 **(2006)**

22. Reddy C.R.V., Oshel R. and Verkade J.G., Room-temperature conversion of soybean oil and poultry fat to biodiesel catalyzed by nanocrystalline calcium oxides, *Energy Fuels*, **20**, 1310–4 **(2006)**

23. Zhu H., Wu Z., Chen Y., Zhang S., Duan S. and Liu X., Preparation of biodiesel catalyzed by solid super base of calcium oxide and its refining process, *China J Catal,* **27**, 391–6 **(2006)**

24. Dorado M.P., Ballesteros E., Lopez F.J. and Mittelbach M., Optimization of alkali-catalyzed transesterification of *Brassica carinata* oil for biodiesel production, *Energ. Fuel,* **18(1),** 77–83 **(2004)**