Biodiesel Production from Simarouba glauca Oil using CaO and KOH Catalysts: A Comparative Study

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Abstract: Biodiesel was prepared from the crude oil of Simarouba glauca by transesterification with methanol in the presence of KOH as catalyst. A maximum conversion was achieved using a 1:6 molar ratio of oil to methanol at 650C i.e. 92% (oil to methyl ester). Otherwise addition of 8% Solid base catalyst CaO using 1:6 molar ratio of oil to methanol at 650C was also used as cata-lyst for this transesterification and conversion exceeds 95%. Important fuel properties of methyl esters of Simarouba oil (Biodiesel) was compared with ASTM and DIN EN 14214. The viscosity was found to be 4.68 Cst at 400C and the flashpoint was 1650C.

Keywords: *Biodiesel, CaO catalyst, KOH Catalyst, Simarouba Glauca, Transesterification*

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1 Introduction

Due to the increase in cost, rapid depletion of world fossil fuel reserves and increasing concern for environmental pollution, research is increasingly directed towards the environmen-tally friendly materials or the alternative fuel that have potential to substitute mineral oil in vari-ous applications. India's demand for diesel fuel is roughly six times that of gasoline, hence, seek-ing alternative to diesel is a more pressing concern [1]. Alternative fuels should be at low cost, environment friendly and easily available. Among various possible options, fuels derived from triglycerides (vegetable oils/non edible oils/waste oils/animal fats) are promising for substitutes of fossil fuels because some of their physical, chemical and combustion related properties are nearly similar to that of fossil fuel. Now, biofuels are getting a renewed attention because of global stress on reduction of green house gases and clean environment.

Biodiesel, consisting of methyl esters of fatty acids produced by transesterification of oils and fats with methanol, has attracted considerable recent attention because of its environmental benefits and the fact that it comes from renewable resources. It is superior to diesel in terms of sulfur content and aromatic content, as well as safety and biodegradability [2]. A number of stud-ies of the preparation of biodiesel by the transesterification of vegetable oils have been reported using a variety of oil or alcohol precursors and different reaction conditions [3], [4], [5].

Transesterification of vegetable oils to biodiesel with metha-nol can be carried out using both homogeneous (acid or base) and heterogeneous (acid, base and enzymatic) cata-lysts. Trans-esterification of vegetable oil was reported to complete in 1 hour of reaction by using the solu-tion of NaOH [6]. Although sulfuric acid can catalyze the transester-ification, the acid-catalyzed transesterification is seriously slow as compared to the base-catalyzed one [7]. Homogene-ous base catalysts provide much faster reaction rates than heterogeneous catalysts in transesterifica-tion. But in homo-geneous alkali-hydroxide catalyst, massive wastewater was discharged from the process to wash the dissolved alkali-hydroxide off the produced biodiesel and also it invites the soap formation causing considerable loss of the transesteri-fied product. Many researchers have studied to develop dif-ferent processes producing biodiesel without using alkali-hydroxide rather devoted to heterogeneously catalysed methanolysis of vegetable oils.

Heterogeneous catalysis is an economically and ecologically and also much easier to separate from liquid products and they can be designed to give higher activity, selectivity and longer catalyst lifetimes [8]. As a result, a great variety of catalysts such as alkaline-earth metal oxides and hydroxides [9], alkali metals (Na and K) hydroxides or salts supported on γ-alumina [10],[11], [12] as well as some acid solids [13] have been checked to date at very different reac-tion condi-tions and with a variable degree of success and also catalyst-free transesterification utilizing supercritical methanol was studied [14] and it was reported that the conversion of rape-seed oil into biodiesel took only 4 min at 3500C under 30 MPa with a molar ratio of oil to methanol of 1:42. The trans-esterification catalyzed by solid base is a bright technology due to the fast reaction rate under the mild reaction condi-tions. Transesterification of soybean oil at reflux of methanol in the presence of alumina supported potassium was carried out [15]. The anion-exchange resin with porous texture can be utilized as the solid base catalyst in their process in-cluding regeneration step of the catalyst with aqueous solu-tion of alkali hydroxide [16]. The solid base catalyst calcium oxide was quite active in transesterification of soybean oil with re-fluxing methanol [17]. CaO.MgO provided higher catalytic activity than CaO powder to trans-form rapeseed oil

to biodiesel, but MgO caused soap formation in the reaction process. The ad-vantage of CaO as a catalyst in the methanalysis reaction is a possibility of its reuse without a significant deactivation [18]. CaO catalytic activity was a result of the existing basic sites, the amount was strongly influenced by the calcination temperature [19]. The methanolysis of sunflower oil catalyzed by CaO was studied using the molar ratio of methanol to oil of 6:1 at 600C [20].

A few studies have been reported on non-edible oils. There are a number of other non-edible tree-based oil seeds available in India with a great potential for biodiesel production. Si-marouba glauca (Family – Simaroubaceae quasia) is o ne of such non-edible oils, which have an estimated annual production potential of 1000 – 200 0 kg/ha/year [21] in India and it can be grown in waste land. It is used for industrial purposes in the manufacture of Biofuels, Soaps, Detergents and Lubricants etc. It is wise to cultivate oilseed bearing trees like Simarouba with high productivity to meet the Industrial and biofuel oil needs of the world as renewable source for long term gains [22].

This paper reports the catalytic activity of calcium oxide was compared with homogenous KOH. For the details of the process of base catalyzed transesterification of crude Simarouba oil with methanol and KOH and also using CaO as solid base catalyst wherein the progress of trans-esterification was monitored by G.C. and also the influence of variables such as alcohol to oil molar ratio, different molar ratio at different temperature and reaction temperature on transesteri-fication were studied. The fuel properties of Simarouba oil methyl esters (Biodiesel) on compari-son with those of accepted Biodiesel standards indicate that transesterification of oil does im-prove its properties making it similar to diesel.

2   Methods
2.1 Materials and apparatus

All the chemicals used were analytical reagent grade and reference standards were pur-chased from Sigma-Aldrich (New Delhi) for chromatographic analysis. The apparatus used for transesterification was designed and fabricated [5]. It consists of oil bath, reaction flask with condenser and digital rpm controller with mechanical stirrer. The volume is about 1 L and con-sists of three necks. A digital temperature indicator was used to measure the reaction tempera-ture. It has an open valve to obtain the outputs. Fatty acid methyl ester content in the transesteri-fied oil was determined by Gas Chromatograph (Chemito CERES 800 plus G.C) equipped with a FID detector.

2.2 Transesterification of crude oil of Simarouba glauca

2.2.1 Transesterification of crude Simarouba oil using KOH

A two-step transesterification process is developed to convert the high FFA oils to its mono-esters. The first step, acid catalyzed esterification reduces the FFA content of the oil to

less than 2%. The second step, alkaline catalyzed transesterification process converts the prod-ucts of the first step to its mono-esters and glycerol.

2.2.1.1 Acid Esterification

One liter of crude Simarouba oil requires 250 ml of methanol for the acid esterifi-cation process. The Simarouba oil is transferred into the flask and heated to about 50 °C. The methanol is added with the preheated Simarouba oil and stirred for a few minutes followed by addition of 1% of sulphuric acid. Heating and stirring is continued for 1 hour at atmospheric pressure. On completion of this reaction, the product is poured into a separating funnel for sepa-rating the excess alcohol. The excess alcohol, with sulphuric acid and impurities moves to the top surface and removed. The lower layer is separated for further processing (alkaline transesteri-fication).

2.2.1.2   Alkaline Transesterification

750ml Simarouba oil was measured and charged into the re-actor. The KOH/CH3OH solution was added (before pre-pared by removing the moisture from the CH3OH) to the closed reac-tion vessel and the system was total closed to the atmosphere to prevent any loss of CH3OH. The mixture was heated to the required reaction temperature 60-650C for about 2 hours with continu-ous stirring.

After the completion of the reaction, the products were trans-ferred into the separating funnel and allowed to stand undis-turbed for about 24 hours and the glycerin separates simply drawn off from the bottom layer of the separating funnel. The final Biodiesel layer required washing with tap water in order to remove the excess catalyst and the methanol. After washing the final product was heated to remove the mois-ture.

2.2.2. Transesterification of crude Simarouba oil using solid base catalyst at 650C (oil to methanol molar ratio 1:12)

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 un-der mag-netic stirring. Then, the Simarouba oil was added into the mixture and heated by water circula-tion. In the end, the excess methanol was distilled off under vacuum. After the products were centrifugated, it formed three phases, the upper layer was biodiesel, the middle layer was glyc-erol, and the lower layer was a mixture of solid CaO and a small amount of glycerol. The bio-diesel was collected for analysis. The water wash can remove all CaO basically. However, lit-tle CaO has not any effect on the GC analysis of biodiesel yield in the experiments.

3 RESULTS AND DISCUSSIONS

3.1 Effect of molar ratio of oil:methanol and tem-

perature on transesterification of Sima-rouba oil

3.1.1 Using KOH as catalyst

Transesterification of Simarouba oil is studied at two different molar ratios of oil:methanol (1:3 and 1:6) at 45^0C (Fig.1). At a molar ratio of 1:3 a maximum conversion 80% was observed whereas at 1:6 molar ratio the conversion was 83% with an initial lag time. The initial lag phase is usually attributed to transport effects required to transfer the methanol into the oil phase [23], [24]. At a molar ratio of 1:6 (oil:methanol), increasing the reaction temperature from 450C to 650C resulted in a significant increase in conversion from 83% to 92% (Fig. 2).

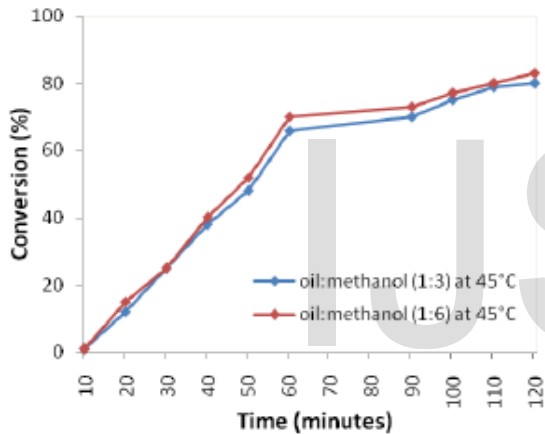Therefore, the optimum molar ratio of oil to methanol was 1:6 (Fig. 3).

Fig. 3. Influence of molar ratio on transestrification of simarouba oil. Cao/oil mass ratio is 8%. KOH is 0.6%. Reaction temperature is 650C. Reaction time: 120 min-utes

3.1.2 Using CaO as catalyst

As per the experimental results (Fig. 4), the biodiesel yield increased from 62% to 95% when the molar ratio was increased from 1:3 to 1:12. However, the yields were slightly reduced when the ratio of oil to methanol was higher than 1:12 and the biodiesel yield was only 87% at 1:18. The reason is that the catalyst content decreased with increase of methanol content. There-fore, the optimum molar ratio of oil to methanol was 1:12.

3.3 Effect of reaction temperature

The influence of reaction temperature is one of the important factors that affect the reac-tion. In this work, CaO/oil mass ratio 8%, KOH/Oil mass ratio 0.6%, Oil/methanol molar ratio 1:6 and Reaction time 120 minutes was taken. A graph was plotted between conversion (%) of Biodiesel versus temperature and shown in Fig.4. in the presence of KOH and CaO cata-lyst, the reaction rate was slow at low temperature, the yield first increased and then decreased with the increase in temperature. The reaction temperature above boiling point of alcohol is avoided as methanol is vaporized and formed a large number of bubbles, which inhibits the reac-tion and tends to accelerate the saponification of glycerides. Hence, the optimum reaction tem-perature was 650C.

Fig. 1. Conversion of Simarouba oil to Fatty acid methyl esters using KOH catalyst at two differ-ent molar ratio of. 1:6 and 1:3 (oil:methanol) at 450C.
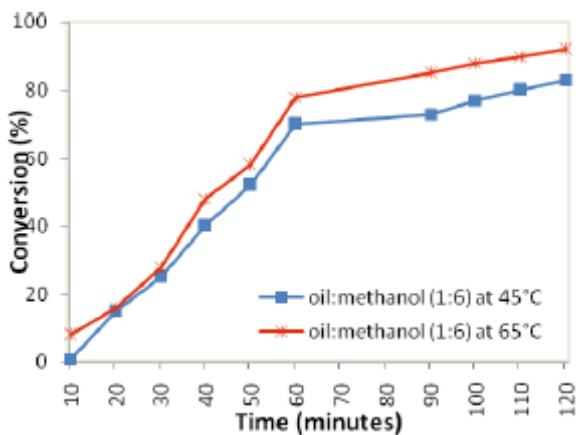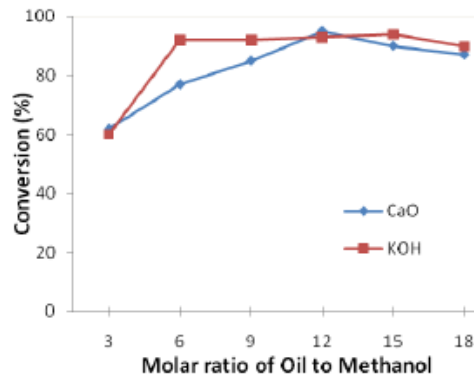
Fig.2. Conversion of Simarouba oil to Fatty acid methyl esters at two different temperatures 450C and 650C at 1:6 (oil:methanol) molar ratiousing KOH catalyst.
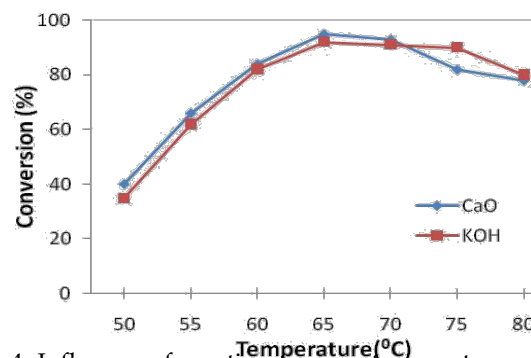
Fig. 4. Influence of reaction temperature on transestrification of Simarouba oilCaO/oil mass ratio is 8%. KOH/Oil mass

ratio is 0.6%. Oil/methanol molar ratio is 1:6. Reaction time is 120 min-utes.

4 Fuel properties of fatty acid methyl ester (fame) of simarouba

The two important fuel properties viz, viscosity and flash point of methyl esters of Simarouba oil were found to be 4.68 Cst (400C) and 1650C (Table-1) respectively. Simarouba oil itself has a high viscosity of 17.3 Cst (400C) which drops down dramatically on estrification followed by transesterifi-cation to 4.68 Cst (400C). Both these properties meet the spec-ifications of ASTM and DIN EN 14214.

5. Conclusion

Crude Simarouba oil was transesterified using KOH as cata-lyst and methanol to form Biodiesel. The conversion was 92% at 650C with 1:6 molar ratio (oil:methanol) for KOH (0.6% by wt) catalyzed transesterification. CaO also catalyze the trans-esterification of Simarouba oil and the conversion is 95%. The fuel properties especially viscosity (4.68 Cst @ 400C) and flash point (1650C) of the transesterified product (biodiesel) compare well with accepted biodiesel stan-dards i.e. ASTM and DIN EN 14214.

References

Fuel parameters of Simarouba FAME, ASTM and DIN EN 14214

Parameters	Simarouba FAME	ASTM standard for B100	DIN EN 14214
Viscocity (Cst)	4.68	$1.9 - 6.0$	$3.5 - 5.0$
Flash point (^{0}C)	165	130 min	>120
Calorific value (kJ/kg)	38500	-	-
Acid value (mg KOH/g)	0.7	≤0.8	≤0.8
Iodine value (gI$_2$/100g)	83.4	≤115	≤115

[1] D. Agarwal and A.K. Agarwal, Performance and emission character-istics of Jatropha oil (preheated and blends) in a direct compression igni-tion engine, Applied Thermal Engineer-ing, Vol. 27, No. 13, pp.2314–2323, 2007.

[2] F. Ma, M. A. Hanna, Biodiesel production: a review. Bioresour Tech-nol, vol. 70, pp 1–15, 1999.

[3] X Lang, AK Dalai, NN Bakhshi, MJ Reaney, PB Hertz, Preparation and characterization of bio-diesels from various bio-oils. Bioresour Technol, vol. 80, pp 53–63, 2001.

[4] M.K Mohanty, S.R Mishra, N.Panigrahi, Biodiesel Production from Various Tree-Borne Oils, Journal of Biofuels, Vol.-3 Issue-1, pp 10-16, January-June, 2012.

[5] S.R.Mishra, M.K.Mohanty, S.P.Das and A.K. Pattanaik, Production of Bio-diesel (Methyl Ester) from Simarouba glauca oil, Research Journal of Chemical Sciences, vol. 2(5), pp 66-71, 2012.

[6] B Freedman, EH Pryde, TL Mounts. Variables affecting the yields of fatty esters from transesterified vegetable oils. J Am Oil Chem Soc, vol.61, pp 1638–43, 1984.

[7] H Fukuda, A Kondo, H Noda. Biodiesel fuel production by trans-esterification of oils. J Bio sci Bioeng, vol.92, pp 405–16, 2001.

[8] S.Gryglewicz, Rapeseed oil methyl esters preparation using hetero-geneous catalysts. Biore-sour Technol, vol. 70, pp 249–53, 1999.

[9] T.F. Dossin, M.-F. Reyniers, G.B. Marin, Kinetics of heterogeneously MgO-catalyzed transesterification, Appl. Catal. B., vol. 62, pp 35–45, 2006.

[10] J. Jitputti, B. Kitiyanan, P. Rangsunvigit, K. Bunyakiat, L. Attanatho, P. Jenvanitpanjakul, Transesterification of crude palm kernel oil and crude coconut oil by different solid cata-lysts, Chem. Eng. J., vol. 116, pp 61–66, 2006.

[11] H.-J. Kim, B.-S. Kang, M.-J. Kim, Y.M. Park, D.-K. Kim, J.-S. Lee, K.-Y. Lee, Transesteri-fication of vegetable oil to biodiesel using heteroge-neous base catalyst, Catal. Today, vol. 93–95, pp 315–320, 2004.

[12] W. Xie, H. Peng, L. Chen, Transesterification of soybean oil cata-lyzed by potassium loaded on alumina as a solid base catalyst, Appl. Catal. A, vol. 300, pp 67–74, 2006.

[13] S. Ramu, N. Lingaiah, B.L.A. Prabhavathi Devi, R.B.N. Prasad, I. Suryanarayana, P.S. Sai Prasad, Esterification of palmitic acid with methanol over tungsten oxide supported on zir-conia solid acid cata-lysts: effect of method of preparation of the catalyst on its structural stability and reactivity, Appl. Catal. A, vol. 276, pp 163–168, 2004.

[14] S Saka and D Kusdiana. Biodiesel fuel from rapeseed oil as prepared in supercritical metha-nol. Fuel, vol.80, pp 225–31, 2001.

[15] W Xie, H Peng, L Chen. Transesterification of soybean oil catalyzed by potassium loaded on alumina as a solid-base catalyst. Appl Catal A: Gen, vol. 300, pp 67–74, 2006.

[16] N Shibasaki-Kitagawa, H Honda, H Kuribayashi, T Toda, T Fuku-mura, T Yonemoto. Bio-diesel production using anionic ion exchanged resin as heterogeneous catalyst. Bioresour Technol, vol. 98, pp416–21, 2007.

[17] M Kouzu, M Umemoto, T Kasuno, M Tajika, Y Aihara, Y Sugimoto, J Hidaka. Biodiesel production from soybean oil using calcium oxide as a heterogeneous catalyst. J Jpn Inst En-ergy, vol.85, pp 135–41, 2006.

[18] ML Granados, MD Zafra Poves, D Martin Alonso, R Mariscal, F Cabelo Galisteo, R Mo-reno-Tost, Biodiesel from sunflower oil by using activated calcium oxide. Appl Catal B, vol.73, pp 327–36, 2007.

[19] Y-W Chen, H-Y Chen, W-F Lin. Basicities of alumina-supported alkaline earth metal ox-ides. React Kinet Catal L, vol.65, pp 83–86, 1998.

[20] V. B. Veljkovic, O. S. Stamenkovic, Z. B. Todorovic, M. L Lazic, D. U. Skala, Kinetics of sunflower oil methanolysis catalyzed by calcium oxide, Fuel, vol. 88, pp 1554–1562, 2009.

[21] S.Joshi and S.Hiremath, Simarouba oil tree. University of Agricul-tural Science, Bangalore and National Oil Seeds and Vegetable Oils and Development Board, Gurgaon, India, 2001.

[22] S. R. Mishra, M. K. Mohanty, S. P. Das & A. K. Pattanaik, Optimisation of base-catalysed transesterification of Simarouba glauca oil for biodiesel production, International Journal of Sustainable Energy, 2013, DOI:10.1080/14786451.2013.796942

[23] B. Freedman, E. H. Pryde, and R. O. Butterfield, Transestrification kinetics of soybean oil. J. Am. Oil Chem. Soc., vol. 63, pp 1375-1380, 1986.

[24] H. Noureddini and D. Zhu, Kinetics of transesterification of Oyabean oil J. Am. Oil Chem. Soc., vol. 74, pp 1457-1463, 1997.

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