



Differential Studies of Alkali Catalysed Production of Biodiesel from Sorghum Oil

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Abstract

Conventional energy sources that is petroleum fuel reserve are depleting day by day which has led the world to think about non-conventional fuels and other major concerning issue is about eco-friendly environment and it pull the search for eco-friendly renewable fuel. Biodiesel is non-toxic, biodegradable and contributes a minimal amount of net greenhouse gases. A study was conducted to produce biodiesel from sorghum oil by transesterification process. The volumetric ratio, catalyst type NaOH, KOH and concentration are some important parameters that affect the quality and yielding of biodiesel that also fulfil the ASTM D6751 standard. For yielding highest percentage (92.9) of biodiesel, the ideal condition were 5:1 molar ratio of sorghum oil to ethanol, 1.0% NaOH catalyst, reaction time 90 minutes, temperature 60°C and 300 rpm stirring speed. While using 1.0% of NaOH and KOH as catalyst, higher amount of biodiesel was yielded in NaOH as comparing to KOH catalyst and biodiesel yielding were maximum in 1.0% NaOH catalyst as compared to 0.5% and 1.5% NaOH catalyst. At different parameters a minor difference in viscosity, acid value, and saponification value was observed. The detailed study has revealed that efficient biodiesel can be produced from sorghum oil under optimized conditions and appropriate catalyst concentration.

Keyword: Sorghum oil, biodiesel, transesterification, viscosity, acid value.

Introduction

To meet the rising demand for energy resources and the need to protect the environment, renewable biofuels are needed to replace petroleum-derived transport fuels. Biodiesel, from sources such as edible, non-edible oils, animal fats and microalgae, has received extensive attention in recent years, owing to its biodegradability, renewability, and lack of toxicity, among other advantages. However, technical and economic barriers must be overcome to realize the potential of this energy source¹⁻³. Biodiesel reduces levels of global warming gases such as CO₂, CO and SO_x. As plants like edible, non-edible oil plants and *Jatropha curcas* grow, they take CO₂ from the air during photosynthesis reaction. After the oil is extracted from edible, non-edible and *Jatropha curcas*, it is refined into biodiesel and, when burned, produces CO₂ and other emissions, which are returned to the atmosphere. However, this cycle does not add to the CO₂ level in the air because the next edible, non-edible oils and *Jatropha curcas* crops will use the CO₂ they grow⁴. Biofuels have become a matter of global importance because of the need for an alternative energy at a cheaper price and with less pollution⁵. Biodiesel is a domestic, renewable fuel for diesel engine comprised of mono-alkyl esters of long chain fatty acids derived from edible and non-edible oils designated as biodiesel, which meets the of ASTM D6751 or BIS ISI5607:05. It was obtained by transesterification of renewable materials composed of C₁₄-C₂₀ fatty acid triglycerides with short chain alcohol such as methanol or ethanol in the presence of catalyst, usually a base like NaOH or KOH.

Biodiesel production by transesterification reaction of edible, non-edible oils or animal fats with ethanol or methanol in the presence of alkali, acid or enzyme catalyst to form alkali ester and glycerol which is removed. Biodiesel consists of long-chain fatty acid ester produced by transesterification reaction of vegetable oils with short-chain alcohols^{6,7}. In Indian scenario many efforts have been made for producing biodiesel by chemical transesterification of *Jatropha curcas*⁸ and some other edible oils such as soybean oil⁹, sunflower oil¹⁰ and palm oil¹¹, have been studied for preparation of biodiesel by alkali catalytic process. However, it is felt that alternative starting oils also need to be studied¹². Sorghum constitutes one such potential alternative source for biofuel. Sorghum (*Sorghum bicolor*) belongs to *Poaceae* family and popularly called as jowar, jondhri, jundi, chari, is most extensively grown grain in country. The crop is environmentally-friendly as it is water-efficient, requires little or no fertilizer or pesticides and biodegradable⁸. The sorghum grown in two major seasons, viz kharif and rabi. The decline in area is mostly in kharif and at present, area of both kharif and rabi is more or less equal. As far as the productivity is concerned, the kharif crops yield higher when compared with rabi crops¹³. Sorghum crops are genus comparing many species growing in tropical and subtropical countries; eight species are reported to occur in India. Sorghum grain is crop plant, which grown in several parts of India. The food, feed and fodder needs of farmers will not be affected, by the oil extraction. The seed kernel of sorghum is comprised of 30-50% oil. The fatty composition of sorghum oil consist of palmitic acid 10-14%, stearic acid 3-6%, oleic acid 3-47%,

lenolic acid 40-55% and lenolenic acid 0-1%¹⁴, while composition of the oil is similar to other oil, which are edible and non-edible in purpose. Thus it is good choice as the starting oil for the production of biodiesel.

This paper investigates the optimum conditions of biodiesel production using NaOH and KOH catalyst and concentration and potential use of sorghum oil. Fulfil the requirement of ASTM the obtained biodiesel investigated the standard quality (ASTM standard) such as viscosity, acid value; saponification value is also useful for diesel engine.

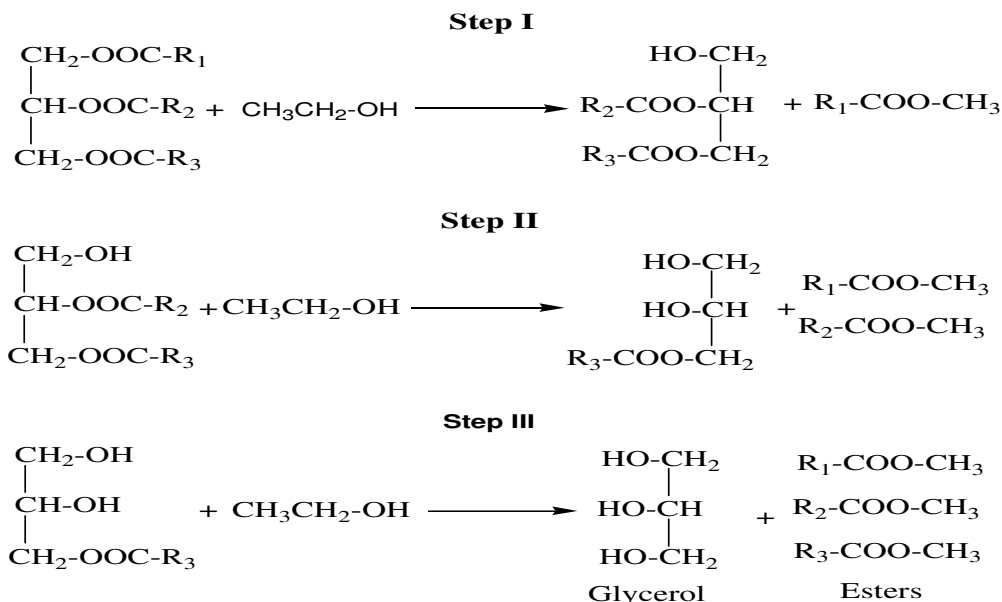
Material and Methods

Preparation of Sodium and Potassium Alkoxides: In a 500 ml measuring flask was poured an appropriate amount of alcohol after the measurement. Pellet form of catalyst was weighed and mixed with alcohol. The mixture was shaken for about 1 hour till the complete dissolution of catalyst. In order to prevent the alcohol from evaporation during shaking, the flask was kept covered with aluminium foil, covering of flask also prevent alkoxides from absorbing moisture present in the environment.

Transesterification of Edible and non-edible oil: In the presence of catalyst, a triglyceride reacts with three molecule of alcohol that produces of mixture of fatty acid alkyl ester and glycerol, in transesterification process of edible and non-edible oil which is shown scheme 1. The overall process is a sequence of three consecutive reactions, in which di and monoglycerides are formed as intermediates. Transesterification is a reversible reaction thus; excess alcohol is used to increase the yields of the alkyl esters and to allow its phase separation from the glycerol formed.

Conversion of edible and non-edible oil to biodiesel is affected by several parameters namely: i. Time of reaction, ii. Type of catalyst, iii. Temperature of reaction, iv. Amount of catalyst, v. Reactant ratio (Molar ratio of alcohol to edible and non-edible oils).

Preparation of Biodiesel: In a typical experiment a known amount of sorghum oil was charged to a round bottom flask. A known amount of catalyst based on weight percent of oil was mixed in excess mole percent of alcohol. The mixture of catalyst in alcohol was added to the sorghum oil in the round bottom flask, while stirring the material. Required temperature was maintained by controlling the electrical heating till the reaction. After complete addition of alcohol, catalyst solution, samples were drawn at regular interval (5-10minutes) to confirm the formation of alkyl ester (biodiesel) and thin layer chromatography (TLC) technique was used for monitoring biodiesel formation. After the completion of biodiesel formation, a known amount of sulphuric acid in alcohol was added to the biodiesel to neutralize the catalyst present in the biodiesel. The excess alcohol present in the biodiesel was recovered by distillation with electrical heating and constant stirring. A sample of sorghum oil biodiesel was analyzed for acid value and then refined with catalyst solution to remove the free fatty acid. In the transesterification reaction temperature was maintained at 60° for 90 minutes keeping the molar ratio of alcohol to sorghum oil was kept as 5:1 and catalyst concentration was 1.0 weight percentage of sorghum oil and percentage of excess alcohol was used. The refined sample was further cooled and centrifuged to remove residual soap. The pH level of the organic layers was measured and neutralized separately.



Scheme-1
Transesterification reaction of triglyceride

The washed samples were further dried. Under optimal condition the yield of sorghum oil biodiesel from sorghum oil which was found to 92.9%. The reaction parameters such as alcohol to oil molar ratio percentage of excess alcohol, reaction time, temperature and concentration of catalyst were optimized for the production of sorghum oil biodiesel. Table 1 shows fixed parameters and variables that are used in this study. Various fuel properties of sorghum oil and sorghum oil biodiesel were determined experimentally to ascertain their suitability as diesel.

Table-1

Variable and fixed parameters used in this study

Variable Parameters	Fixed Parameters
Alcohol to oil molar ratio 1:3 1:5 1:6	Type of alcohol: Ethanol Types of catalyst: NaOH Amounts of catalyst: 1.0% Reaction time: 90 minutes Mixing intensity: 300rpm
Types of catalyst NaOH KOH	Alcohol to oil molar ratio: 1:5 Types of alcohol: Ethanol Amount of catalyst: 1.0% Reaction time: 90 minutes Mixing intensity: 300rpm
Amounts of catalyst 0.5% 1.0% 1.5%	Alcohol to oil molar ratio: 1:5 Types of alcohol: Ethanol Types of catalyst: NaOH Mixing intensity: 300rpm

Results and Discussion

The Effect of different Molar Ratio of Sorghum Oil and Ethanol on Biodiesel Production: The molar ratios of sorghum oil to ethanol like 5:1, 6:1 and 3:1 were carried out using 1.0% NaOH catalyst for reaction time 90 minutes at reaction temperature 60°C. The yield of biodiesel from sorghum oil by using different types of molar ratio of sorghum oil to ethanol shows in figure 1. The produced amount of biodiesel was increased with increasing ethanol to oil molar ratio. The higher amount of biodiesel (92.9%) was obtained by 5:1 molar ratio of sorghum oil to ethanol compared to 3:1 and 6:1 molar ratio of sorghum oil to ethanol.

The result showed that higher yield of biodiesel is obtained by 5:1 molar ratio of sorghum oil to ethanol. The 3:1 and 6:1 molar ratio of sorghum oil and ethanol gave the lowest percentage of biodiesel. If alcohol amount is elevated with increasing sorghum oil to ethanol molar ratio the ethyl ester (biodiesel) increased. It is necessary to drive the transesterification reaction to shift to the product which is biodiesel and glycerol, it maximize the fatty ester yield. However, increasing the reactant concentration would be more favourable condition to produced biodiesel yield. Many researches proved that lower amount of alcohol will cause the transesterification reaction to incomplete. If other reaction conditions are optimum, one can get higher yield of ester with the molar ratio of oil to alcohol. However, the high molar ratio of alcohol to vegetable oil interferes with separation of glycerine because; there is an increase in solubility. When

glycerol remains in solution, it helps drive the equilibrium to back to the left, lowering the yield of esters¹⁵.

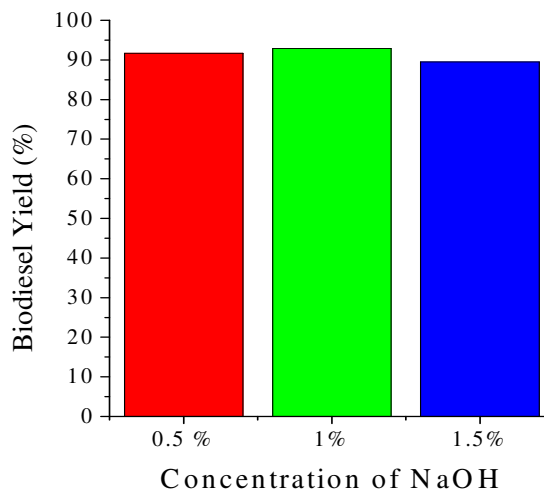


Figure-1

The effect of sorghum oil to ethanol molar ratio on biodiesel production

The Effect of Different Catalyst Types on Biodiesel Production: Production of biodiesel can be influenced by NaOH and KOH as catalyst used in the experiment. Two catalysts NaOH and KOH were used in this experiment. The reaction were carried out by using 1.0% of catalyst 5:1 to sorghum oil to ethanol molar ratio for reaction time 90 minutes, reaction temperature 60°C. Figure shows the comparison of yield of biodiesel using NaOH and KOH. The result showed that NaOH gave the better yield than KOH. Higher biodiesel yield (92.9%) was obtained by using NaOH as catalyst whereas lower biodiesel yield (89.5%) was obtaining by using KOH as catalyst.

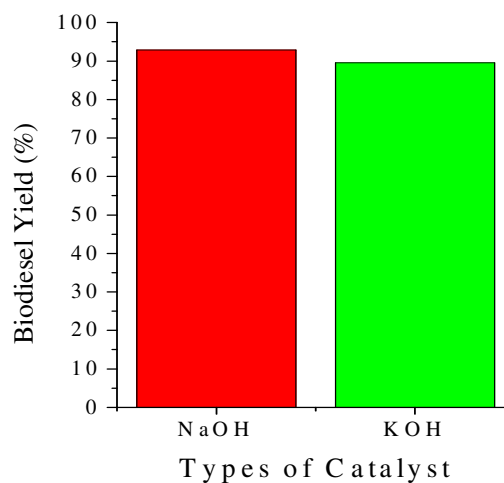


Figure-2

The effect of catalyst types and yield of biodiesel production

When NaOH is used as catalyst in transesterification reaction it gave much better result comparing with KOH as catalyst for biodiesel production. Types of catalyst performance and reaction conditions influence the transesterification reaction of biodiesel production.

The Effect of Catalyst Concentration on Biodiesel Production: Biodiesel production was influence by type and amount of catalyst using in the process. In this reaction NaOH was used as catalyst with different concentration as 0.5%, 1.0% and 1.5%. The reaction were carried out using ethanol with 5:1 molar ratio of sorghum oil to ethanol and required reaction time and temperature were 90 minutes and 60°C respectively. Different concentration of NaOH as catalyst and molar ratio of sorghum oil to ethanol for biodiesel production is shown in figure 3. It is clear from the figure that 1% NaOH concentration is optimum for maximum production of biodiesel that is 92.9% of biodiesel.

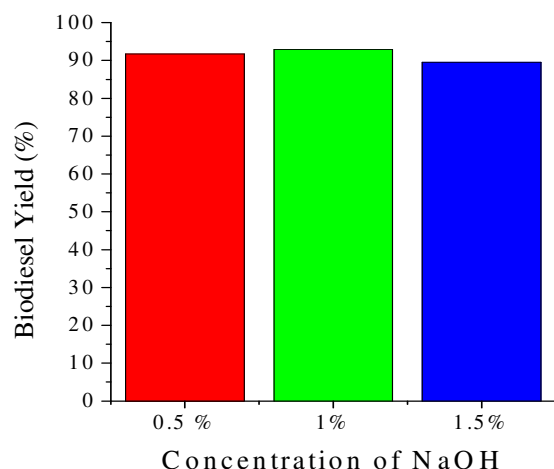


Figure 3
Effect of catalyst concentration on biodiesel production

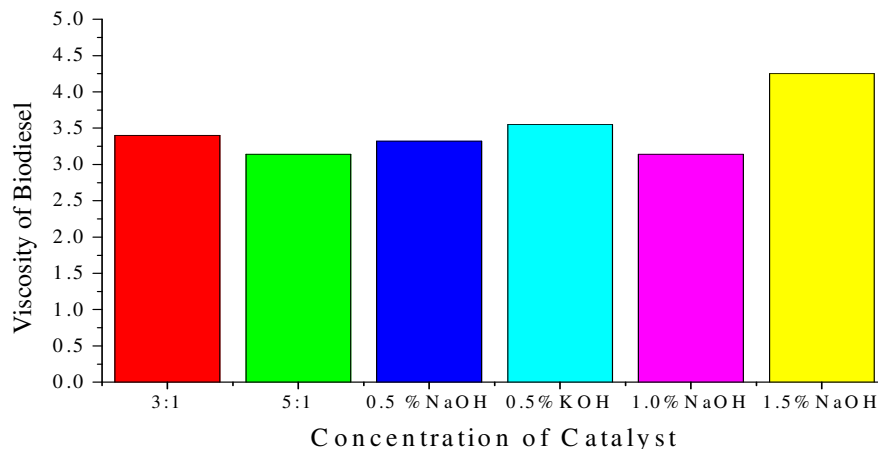


Figure 4
Effect of different parameters on biodiesel viscosity

Among various concentration (0.5%, 1.0% and 1.5% wt) of NaOH, the obtained result showed 1.0% wt of NaOH gave the best yielding of biodiesel. The biodiesel yielding was increasing with catalyst concentration till 1.0% and above this value the biodiesel yielding started to drop. Mostly, increasing the catalyst amount help to fasten the reaction for giving result and every reaction has optimum catalyst concentration value. We found, excessive catalyst amount (NaOH) reduced the biodiesel production because of it will take place in saponification which react with triglyceride to form soap and water.

Viscosity Measurement of Biodiesel: Mostly, viscosity of oil is reduced by transesterification reaction that changes the properties which is convert oil to biodiesel fuel. The ASTM D6751 standard norms for viscosity rang of biodiesel were 1.9-6.0 mm²/s at 40°C. Different ratio and concentration of catalyst gave different viscosities of biodiesel that shown in figure 4. The viscosity was maintained the ASTM D6751 standard. The lowest viscosity was obtained in 5:1 molar ratio of sorghum oil to ethanol and 1.0% concentration of catalyst.

The result showed obtained biodiesel viscosities follow ASTM standards. Average of biodiesel viscosities that produced were maximum 4.4 cst at 55°C. However, the ASTM D6751 standard limit is 1.9-6.0mm²/s or cst/s at 40°C. Higher viscosity may be due to the long storage time. There are few researcher found that longer the storage time of biodiesel, higher the viscosity value. During the storage the viscosity of biodiesel increases owing to formation of oxidize polymeric compound that can lead to the formation of gums and sediments that clog filters¹⁵ and eventually, it increases the viscosity of biodiesel in stored condition. It was reported that kinetic viscosity of biodiesel from sorghum oil was 3.14 and 1.9-4.1mm²/s at 40°C commercial biodiesel fuels¹⁶.

Conclusion

The result showed required condition for highest yielding that was 92.9% of biodiesel was 5:1 molar ratio of sorghum oil to ethanol, 1.0% catalyst NaOH using reaction time 90 minutes and temperature 60°C. Physical and chemical properties affect the maximal conversion of sorghum oil to biodiesel for achieving optimal values of these parameters. To complete the conversion of sorghum oil to sorghum oil biodiesel based on higher yield, 1.0% concentration of NaOH can be recommended. Conclusively results showed that sorghum oil could be used to production of biodiesel from sorghum oil.

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References

1. Pienkos P.T. and Darzins A., The promise and challenges of microalgal-derived biofuel, *Biofuel Bioprod. Bior.*, **3(4)**, 431-400 (2009)
2. Chist Y., Biodiesel from microalgae beats bioethanol, *Trends Biotechnology*, **26(3)**, 126-131 (2008)
3. Mata T.M., Martins A. and Caetano N.S., Microalgae for biodiesel production and other applications: A review, *Renewable Sustainable Energy Rev.*, **14(1)**, 217-232 (2010)
4. Ramadhas A.S., Jayaraj S. and Muraleedharan C., Use of vegetable oils as IC engine fuel- A review, *Renewable Energy*, **29**, 727-742 (2004)
5. Okoro L.N., Belaboh S.V., Edoye N.R. and Makama B.Y., Synthesis Calorimetric and Viscometric Study of groundnut oil Biodiesel and Blend, *Research Journal of Chemical Sciences*, **1(3)**, 49-57 (2011)
6. Nouredin H., Harkey D. and Medikonduru V.A., Continuous process for the conversion of vegetable oil into methyl esters of fatty acid, *Journal of the AOCS*, **75**, 1775-1783 (1998)
7. Encinar J.M., Gonales J.F., Rodriguez J.J. and Tejedor A., Biodiesel fuels from vegetables oils: Transesterification of *Cynara cardunculus* L. oils with ethanol, *Energy and Fuel*, **19**, 443-450 (2002)
8. Francis G., Edinger R., and Becker K., A concept for simultaneous wasteland reclamation, fuel production, and socio-economic development in degraded areas in India: Need, potential and perspectives of *Jatropha* plantations, *Nat. Resource Forum*, **29**, 12-24 (2005)
9. Schwab A.W., Dykstra G.J., Selke E., Sorenson S.C., and Pryde E.H., Diesel fuel from thermal decomposition of soybean oil, *J. Am. Oil Chem. Soc.*, **65**, 1781-1786 (1988)
10. Belafi Bako K., Kovacs F., Gubicza L., and Hancsok J., Enzymatic biodiesel production from sunflower oil by *Candida antarctica* lipase in a solvent-free system, *Biocatal. Biotransform.*, **20**, 437-439 (2002)
11. Abigor R.D., Uadia P.O., Foglia T.A., Hass M.J., Jones K.C., Okpefa E., Obibuzor J.U. and Bafor M.E., Lipase-catalyzed production of biodiesel fuel from some Nigerian lauric oils, *Biochem. Soc. Trans.*, **28**, 979-981 (2000)
12. Srivastava A., and Prasad R., Triglycerides-based diesel fuels, *Renewable and Sustainable Energy Reviews*, **4**, 111-133 (2000)
13. Samukawa T., Kaieda M., Matsumoto T., Ban K., Kondo A., Shimada Y., Noda H., and Fukuda H., Pretreatment of immobilized *Candida Antarctica* lipase for biodiesel fuel production from plant oil, *J. Biosci Bioeng.*, **90**, 180-183 (2000)
14. www.chempro.in/Fatty acid.htm (2013)
15. Bouaid A., Martinez M., and Jose A., Production of biodiesel from bioethanol and *Brassica carinata* oil: Oxidation stability study, *Bioresource Technology*, **100** (7), 2234-2239 (2009)
16. Demirbas A., Biodiesel from waste cooking oil via base-catalytic and supercritical methanol transesterification, *Energy Conversion and Management*, **50**, 923-927 (2009)