USE OF CERAMIC MATERIAL (CEMENT CLINKER) FOR THE PRODUCTION OF BIODIESEL

SUNNY SONI*, MADHU AGARWAL

*Department of Chemical Engineering,
Malaviya National Institute of Technology Jaipur,
J.L.N. Marg, Jaipur-302017, India*

Author e-mail: sunny.soni371@gmail.com, madhunaresh@gmail.com.

Biodiesel is a renewable liquid fuel made from natural, renewable biological sources such as edible and non edible oils. Over the last years, biodiesel has gained more market due to its benefits and because it appears as the natural substitute for diesel. Reasons for growing interest in biodiesel include its potential for reducing noxious emissions, potential contributions to rural economic development, as an additional demand center for agricultural commodities, and as a way to reduce reliance on foreign oil. Biodiesel was prepared from soybean oil by transesterification with methanol in the presence of cement clinker. Cement clinker was examined as a catalyst for a conversion of soybean oil to fatty acid methyl esters (FAMES). It can be a promising heterogeneous catalyst for the production of biodiesel fuels from soybean oil because of high activity in the conversion and no leaching in the transesterification reaction. The reaction conditions were optimized. A study for optimizing the reaction parameters such as the reaction temperature, and reaction time, was carried out. The catalyst cement clinker composition was characterized by XRF. The results demonstrate that the cement clinker shows high catalytic performance & it was found that the yield of biodiesel can reach as high as 84.52% after 1 h reaction at 65°C, with a 6:1 molar ratio of methanol to oil, 21 wt% KOH/cement clinker as catalyst.

Keywords: cement clinker; biodiesel; transesterification; soybean oil.

Introduction

The world energy demand is increasing rapidly due to increase in population and industrialization that limited reservoirs will soon be depleted at the current rate of consumption. Diesel fuel has an essential function in the industrial economy of a developing country and is used in transports, industrial and agricultural goods, etc. Interest in renewable fuels has increased substantially in recent years¹. An alternative fuel should be easily available, environment friendly and techno-economically competitive. One of such fuels is triglycerides and their derivatives². Biodiesel, as renewable and biological origin alternative diesel fuel, has been receiving a lot of concern throughout the world due to the energy needs and environmental awareness³. Therefore the alternative fuel diesel engines have gained attention all over the world. Biodiesel is defined as the mono alkyl esters of long chain fatty acids derived from renewable feed stock, such as vegetable oil or animal fats, for use in compression ignition engines⁴. The

plant oils usually contain free fatty acids, phospholipids, sterols, water, odorants and other impurities. Because of these the oil cannot be used as fuel directly. To overcome these problem the oil requires slight chemical modification mainly transesterification, pyrolysis and emulsification. Among these, Transesterification is one of the most commercially useable methods to produce biodiesel and the process involves a reaction between ester (here triglyceride) and alcohol to form new ester and alcohol. Different types of alcohols such as, methanol, ethanol, propanol and butanol have been used. However, methanol and ethanol are the most widely used, particularly methanol owing to its low price and availability⁵. In the transesterification of triglyceride to fatty acid alkyl esters three reversible reactions take place consecutively in which diglycerides and monoglycerides are major intermediate products (Fig. 1)³.

Figure 1. Transesterification of triglyceride to fatty acid alkyl esters³

Transesterification reaction can be either carried out via non-catalytic or catalytic processes. Catalyst used for the transesterification of triglycerides is classified as alkali, acid, enzyme or heterogeneous catalysts. Enzymatic base production of biodiesel has attracted many attention in recent years since enzymes tolerate free fatty acid and water contents in the oil to avoid soap formation and thus purification of biodiesel and glycerol is easier^{7, 8}. However, enzymes are expensive to be used in a commercial production of biodiesel. Significant amounts of work have been carried out on homogeneous acid and base catalysis transesterification of vegetable oils. If the oil has high free acid content and more water, acid catalyst is suitable. Sulphuric acid and hydrochloric acid are normally used as acid catalysts since these catalysts are capable to handle esterification and transesterification of triglyceride simultaneously. Nonetheless, the process requires a high molar ratio of alcohol to oil and long reaction time⁹. Besides that, under these conditions all the equipment need to withstand against corrosion due to an acidity environment¹⁰. Alkali metal alkoxides are most effective Transesterification catalyst compared to the acid catalyst. Sodium alkoxides are the mostly efficient catalysts, although KOH and NaOH can also be used^{11, 12}. Trans methylation occurs approximately 4000 times faster in presence of an alkaline catalyst than the same amount of acidic catalyst¹³. As they are less corrosive to industrial equipments, alkaline catalysts are preferred in industrial processes. The concentration in the range of 0.5–1.0% (w/w) has found to yield 94–99% conversion of vegetable oils into ester and further increase of catalyst concentration does not affect the conversion but add to extra cost, as the catalyst needs to be removed from the reaction mixture after completion of reaction^{14–16}. The transesterification can be performed in a shorter reaction time and relatively modest operation conditions¹⁷. In spite

of this, the water and free fatty acids content in the oil need to be very low because of the probability of soap formation which can consume catalyst thus reducing the methyl ester yields. Conventional synthesis techniques rely on soluble sodium and potassium hydroxide catalysts; however, removal of these catalysts is technically difficult and brings extra cost to the final product¹⁸. Besides, the process is not environmentally friendly because a large amount of waste water is produced in the separation step¹⁹. However, the cost of biodiesel could certainly be lowered by improving the production processes²⁰. The first step in this direction could be represented by the use of heterogeneous catalysts instead of homogeneous ones. Heterogeneous catalysts can be more easily separated and give place to higher quality of ester products and glycerol by product. Pure high grade glycerol can be obtained, in this case, without expensive refining operations. For these reasons, many heterogeneous catalysts, based on Metal hydroxides²¹, metal complexes²², metal oxides such as calcium oxide²³, magnesium oxide²⁴, zirconium oxide²⁵ and supported catalysts²⁶ have been investigated as solid catalysts. The catalysts are not consumed or dissolved in the reaction and therefore can be easily separated from the products. As a result, the products do not contain impurities of the catalyst and the cost of final separation could be reduced. The catalysts can also be readily regenerated and reused and it is more environmentally benign because there is no need for acid or water treatment in the separation step²⁷. Studies have been carried out to synthesize and develop new solid catalysts for transesterification reaction in order to overcome disadvantages of use of homogeneous catalyst and more likely to reduce the cost of biodiesel production.

In the present work the catalytic performances of cement clinker catalyst in the transesterification reaction of soybean oil with methanol have been studied. Methanolysis of soybean oil was carried out with 21wt% KOH/cement clinker as a catalyst at 65 °C with MeOH/oil molar ratio of 6:1. The reaction yield in the temperature range 65°C was about 85% in 1 h.

Experimental

Materials

Soybean oil used for the preparation of biodiesel was purchased from jaipur. CH₃OH, KOH & all the chemicals were purchased from companies Ranbaxy fine chemicals (Renkem) Laboratory, Hi-media Laboratory Limited & MERCK Limited. The Cement clinker was collected from J.K. Lakshmi Cement Ltd., Jaykaypuram-Sirohi (Rajasthan). The quality of oil is expressed in terms of the physicochemical properties such as acid value, Specific gravity, Kinematic viscosity, etc. These properties of soybean oil (without further treatment) were determined as per Bureau of Indian Standard which have shown in Table 1.

Table 1. Characterization of soybean oil

S.NO.	Parameters	Soybean oil
1	Acid value (mg KOH/g)	2.4
2	Free fatty acid(mg KOH/g)	2.09
3	Kinematic viscosity (cSt at 40 ⁰ C)	31.6
4	Density (kg/l)	0.843
5	Specific gravity (at 26 ⁰ C)	0.9125
6	Pour point (⁰ C)	-8
7	Cloud point (⁰ C)	-2
8	Flash point (⁰ C)	265
9	Fire point (⁰ C)	270

Catalyst preparation

The characterization of cement clinker has been done by XRF at JK Lakshmi Cement Ltd., which have shown in Table 2. The clinker was first dried at 100 °C for 12 hrs to remove moisture. After that, it was crushed with a grinder and sieved to a particle size of 1.8–2.8 mm. 15gm of clinker were taken in a beaker & 4gm of aq. KOH solution was mixed drop by drop while stirring and heating continuously for making paste. This paste was dried in oven at 100⁰C for a night. Thereafter, the dried powder was calcinated at 650⁰C for 3 hrs. The catalyst, thus, obtained with KOH loading as 21wt% KOH/Clinker.

Table 2. Characterization of cement clinker

S.NO.	Content	%
1	Na ₂ O	0.37
2	MgO	3.03
3	Al ₂ O ₃	5.72
4	SiO ₂	20.99
5	SO ₃	1.29
6	Cl [⊖]	-
7	K ₂ O	0.69
8	CaO	63.98
9	TiO ₂	-
10	Fe ₂ O ₃	3.71
11	A/F	1.54
12	S/R	2.23
13	LSF	94
14	F/CaO	1.84
15	Tricalcium Silicate (Ca ₃ SiO ₅), C ₃ S	46.11
16	Dicalcium Silicate (Ca ₂ SiO ₄), C ₂ S	25.4
17	Tricalcium Aluminate (Ca ₃ Al ₂ O ₆), C ₃ A	8.87
18	Tetracalcium Aluminoferrite (Ca ₂ AlFeO ₅), C ₄ AF	11.3
19	Liquid	28.1

Reaction procedure

The transesterification was carried out in a batch reactor, equipped with thermostat, mechanical stirrer, condensation systems and a beaker of capacity 500 ml on hot plate with magnetic stirrer. Soybean oil (100ml) was preheated to the desired temperature before starting the reaction. The KOH doped cement clinker-methanol solution was prepared freshly in order to maintain the catalytic activity and to prevent moisture absorbance. The methanolic solution was added to Soybean oil in the reaction flask and the measurement of time was started at this point. Experiment was allowed to prolong for 1 h at 65°C conduct to ensure the completion the conversion of the fatty acid into fatty acid methyl esters (FAMES). The reaction mixture was allowed to cool down and equilibrate which resulted in separation of two phases. The upper phase consisted of alkyl esters, and the lower phase contained the glycerol.

Figure 2. Schematic representation of biodiesel production

Process description

Schematic representation of biodiesel production has been shown in figure 2. The Esterification step is required if the oil is above 2.5% FFA. The production of biodiesel is divided into three processing:

- A transesterification section where the vegetable oil is subject to chemical transesterification in order to produce fatty acid methyl esters (biodiesel) and co-product glycerol.
- A biodiesel purification section where the methyl esters are refined to meet the biodiesel specifications.
- A glycerol recovery section.

Results and Discussion

Transesterification of soybean oil was carried out with 21 wt% KOH/ Cement clinker as a catalyst at the Reaction temperature of 65°C with MeOH/oil molar ratio of 6:1. It was found that by using of KOH doped cement clinker catalyst, the reaction yield was of $\leq 85\%$ in 1 h. With the increase in the concentration of catalyst, there was decrease in the yield of methyl esters. The characterization of biodiesel has shown in Table 3.

Table 3. Characterization of biodiesel

S.NO.	Parameters	Biodiesel
1	Kinematic viscosity (cSt at 40°C)	13
2	Density (kg/l)	0.812
3	Specific gravity (at 26°C)	0.875
4	Pour point (°C)	-10
5	Cloud point (°C)	-6
6	Flash point (°C)	170
7	Fire point (°C)	175
8	Yield (%)	84.6

Conclusions

The present study clearly showed that the KOH doped cement clinker is non-toxic, inexpensive, recyclable and promising eco-friendly catalysts. Cement clinker loaded with potassium hydroxide was found to be strong solid base catalyst for the transesterification of soybean oil with methanol. The catalyst with 21 wt% KOH loaded on cement clinker and calcined at 650°C for 3 h. When the reaction was carried out at 65°C, with a molar ratio of methanol to soybean oil of 6:1, a reaction time 1 h and an agitation speed of 600 rpm, the highest conversion reached $\leq 85\%$. The catalyst was recycled to study the reusability. Catalyst may be used at least for three times.

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