Innovative Process for Continuous Esterification of Cottonseed Oil for Synthesis of Biodiesel

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ABSTRACT

Due to the predicted shortness of conventional fuels and environmental concerns, a search for alternative fuels has gained recent significant attention. Biodiesel is well known as the replacement for the traditional mineral diesel fuel . It is characterized by excellent properties as diesel engine fuels and thus can be used in compression-ignition (diesel) engines with little or no modifications. Besides, it also affects a decrease in emissions of SOx, CO, unburnt hydrocarbons and particulate matter during the combustion process when compared with fossil fuels. The techno-economic analysis of biodiesel production has indicated that cost of biodeisel will vary from Rs. 25.70 to Rs. 56.70 per liter with cost of oil ranging from Rs. 25/- to 55/- per Kg compared to Rs.36.5/- per liter for diesel. With further availability of cheap oils and taking into consideration the carbon credits earned due to green fuel under CDM mechanism, the biodiesel costs will further reduce and be more competitive with diesel. In the present paper an overflow system for continuous esterification of cottonseed oil using an economical process was developed using a continuous stirred tank reactor (CSTR). Continuous production compared to batch production at the same condition had higher product purity. The optimum condition for the esterification process was obtained and the free fatty acid (FFA) content in the cottonseed oil were reduced by optimum esterification. The components and properties of fatty acid methyl ester (FAME) could meet the standard requirements for biodiesel fuel. Eventually the production costs were calculated to disclose its commercialization.

Keywords: biodiesel, cottonseed oil, continuous esterification, economical process, transesterification

1. INTRODUCTION

Due to continuous increase in petroleum prices throughout the world, there is a renewed interest in vegetable oils and their derivatives as alternative fuels for diesel engines. The reasons for the attraction towards vegetable oils are that the vegetable oils are environmentally beneficial and they are obtained from renewable resources. Vegetable oil is potentially inexhaustible source of energy with an energetic content close to diesel fuel. Diesel boiling range material is of particular interest because it has been shown to significantly reduce particulate emissions relative to petroleum diesel (Giannelos et al., 2002). There are more than 350 oil bearing crops which has been identified for biofuels production, but cottonseed , peanut and rapeseed oils are considered as potential alternative fuels for diesel engines(Goering et al., 1982, Pryor et al., 1982).

Vegetable oils have about 88% energy content of petroleum diesel fuel (Demirbas, 1998). Both vegetable oils and their esters (biodiesel fuels) are promising alternatives as fuel for diesel engines. Because of their high viscosity, drying with time and thickening in cold conditions, vegetable oil fuels still have problems, such as flow, atomization and heavy particulate emissions (Altin et al., 2001). Transesterification is the process of using methanol or ethanol, in the presence of a catalyst to chemically break the molecule of the raw bio-oil into methyl or ethyl esters of the bio-oil with glycerol as a by-product. The purpose of the transesterification process is to lower the viscosity of the oil. The viscosity and flash point values ofcottonseed oil methyl and ethyl esters highly decrease after transesterification process. A novel process of biodiesel fuel production has been developed in this paper by using continuous stirred tank reactor.

The vegetable oils of choice for biodiesel production are those which occur abundantly in the region of testing. India contributes about 6-7% of the world oilseeds production. Export of oilmeals, oilseeds and minor oils has increased from 5.06 million Tones in the financial year 2005-06 to 7.3 million tons in the financial year 2006-07. In terms of value, realization has gone up from Rs. 5514 crores to Rs.7997 crores. India accounted for about 6.4% of world oilmeal export. INDIA is the third largest cottonseed producing country, next only to China and the US. Traditional method of cottonseed processing is adversely affecting the export of by-products and losses of extra oil. There is approximately an estimated loss of over Rs.5380 crores annually due to adoption of traditional processing of cottonseed.

Cottonseed oil is rich in palmitic acid (22-26%), oleic acid (15-20%), linoleic acid (49-58%) and 10% mixture of arachidic acid, behenic acid and lignoceric acid. It also contains about 1% sterculic acids and malvalic acids in the crude oil.

Table.1 Cottonseed availability in India (State wise): (lakhs metric tonnes)

Sr. no.	Particulars	2008-09 Quantity	2009-10 Quantity	% of each state 2009-10
1	Gujarat	29.97	32.63	33.60
2	Mahaarshtra	20.65	20.3	20.90
3	Andhra pradesh	17.65	16.65	17.10
4	Punjab	5.83	5.08	5.20
5	Haryana	4.66	4.91	5.00
6	Karnataka	3	3.16	3.2
7	Tamilnadu	1.67	1.67	1.70
8	All other states	13.14	12.84	13.20
	TOTAL	96.57	97.24	

Less seeds retained for direct consumption cultivation
4.99 4.00
Seeds available for processing
91.58 93.24
(Data from AICOSA)

Cottonseed oil is one of the cheapest vegetable oils in India and it is produced in most parts of the country. The process to produce biodiesel is called transesterification or alcoholysis, is the displacement of alcohol from an ester (glycerol from triglyceride) by another alcohol (for instance methanol, so the process also called methanolysis). The transesterification reaction is represented by :

$$\begin{array}{ccccccc} H_2COCOR_1 & & & & H_2COH & & R_1COOCH_3 \\ | & & & & | & & \\ H\,COCOR_2 & + & 3\,CH_3OH & \leftrightarrow & H\,COH & + & R_2COOCH_3 \\ | & & & & | & & \\ H_2COCOR_3 & & & & H_2COH & & R_3COOCH_3 \\ \text{triglyceride} & & \text{methanol} & & \text{glycerol} & & \text{methyl ester} \end{array} \quad (1)$$

In this reaction, a catalyst is needed in order to improve the reaction rate. Conventionally, alkaline metal alkoxides are the most effective methanolysis catalyst compared to the acidic catalyst. Sodium alkoxides are the most efficient catalyst used for it, although KOH and NaOH can also be used (Meher, et.al., 2006). Methanolysis occurs faster in the presence of a alkaline catalyst than that catalysed by the same amount of acid catalyst.

Many researchers have concluded that vegetable oils hold promise as alternative fuels for diesel engines. However, using raw vegetable oils for diesel engines can cause numerous engine-related problems. However, these effects can be reduced or eliminated through transesterification of vegetable oil to form methyl ester. Transesterification is the process of reacting a triglyceride with an alcohol in the presence of a catalyst to produce glycerol and fatty acid esters.

In the present investigation, an innovative process in which continuous biodiesel production was undertaken by using continuous stirred tank reactors using potassium hydroxide catalyst. Cottonseed oil has energy per unit volume than diesel fuel. This means that more than one gallon of cotton seed oil will be required to replace one gallon of petro-diesel. India's cottonseed production is estimated to be around 35% of its cotton output of over 4.5 million tons. Nearly 80% of the cottonseed is crushed for oil while the rest goes for feed. Major producers of cotton in the country are Maharashtra, Gujarat, Andhra Pradesh, Punjab, Haryana, Rajasthan, Madhya Pradesh, Tamil Nadu and Karnataka. So, there is an enormous scope for biodiesel manufacture from cottonseed oil in India. Different parameters for biodiesel production have been investigated. The effect of reaction temperature; catalyst percentages, alcohol percentages and reaction time for optimum biodiesel production have been studied.

2. EXPERIMENTAL

2.1. Materials:

- ***Feedstock oil***: The cottonseed oil used in for this experiment was refined edible grade oil. The oil was purchased in local market in Amravati, India.
- ***Methanol: Methanol*** used was technical grade (99.5% purity). The methanol density at 30 ^{o}C was 0.785 g/mL.
- ***Catalyst:*** The catalyst KOH was purchased in local chemical store at Amravati, India.

2.2. Apparatus: The apparatus used for carrying out the above reaction was 500 mL three necks flask equipped with a mechanical stirrer, reflux condenser, thermometer, heating mantle and sampling device.

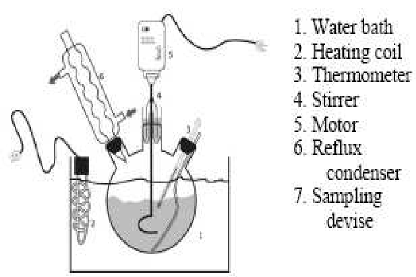

Fig. 1. Diagram of Methanolysis Equipment

3. PROCEDURE

The experimental procedure was as follows. Initially, the reactor was charged with 100 mL of cottonseed oil, and then it was heated to the selected temperature. At the same time, but in another flask, certain amount of methanol was charged and heated. When the selected oil temperature was achieved, the catalyst and the hot methanol were added to the hot oil under stirring and heating. The attainment of the selected temperature of the mixture determined the start of the reaction time. The system was maintained under the certain conditions during the reaction. Ten milliliters of sample was taken every 20 minutes until 2 hours. The reaction in the sample was stopped by immersing it in the cold water. After the reaction is completed at the end of the process, the mixture left was poured into a separating funnel, allowing the glycerol and the catalyst to separate from the biodiesel. The glycerol layer and the biodiesel layer were drained separately and collected prior to purification processes.

4. RESULTS AND DISCUSSIONS

4.1. Effect of catalyst concentration:

The effect of catalyst concentration (% weight of catalyst in the oil) in methanolysis process was studied in four sets of reactions.The studies on the effect of KOH on methanolysis of vegetables oils were done at concentration ranging from 1% to 4 % oil weight. The reactions were conducted using catalyst ranging from 1% to 4 %, while the methanol-oil equivalent ratio, temperature and stirring speed were maintained constant and equal to respectively, 6 : 1, 50^{o}C and 250 rpm. The results were summarized in Figure 2

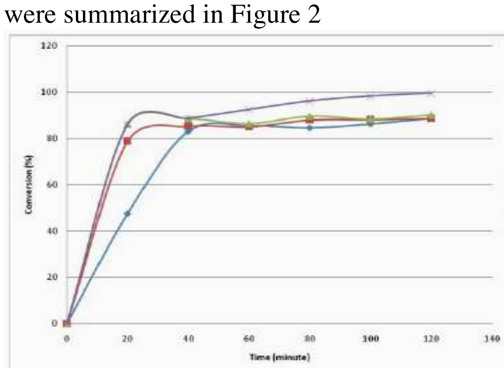

Fig.2. Effect of catalyst concentration on % conversion of oil (50 ^{o}C, N= 500 rpm)

Figure 2 shows, the oil conversion increases at increasing catalyst concentration, especially for the first 20 min reaction time. The methanolysis using 1 % catalyst shows only 50% oil conversion, while 3 and 4 % catalyst show higher values. When the reactions are conducted for more than 40min no significant changes in conversion was observed for all sets of reactions. The oil conversion that will fulfill the standard biodiesel is usually more than 95 %. This conversion is achieved by using 4 %catalyst for more than 80 min reaction time. So, 4 % catalyst is the optimum catalyst concentration in this experiment..

4.2 Effect of molar ratio of methanol to oil

Methanolysis is a reversible reaction. In order to shift the reaction to the right, it is necessary to use either a large excess of alcohol or to remove one of the products from the reaction mixture. The second option was preferred, whenever feasible, since in this way, this reaction can be driven to completion. Freedman (1984), Mittelbach and Remschmidt (2004) and Encinar (2005) recommended the ratio of alcohol to oil was at least 3:1, and a molar ratio of 6 : 1 is normally used in industrial processes to obtain oil conversion higher than 98%. Figure 3 shows the results, oil conversions increase on increasing % methanol.

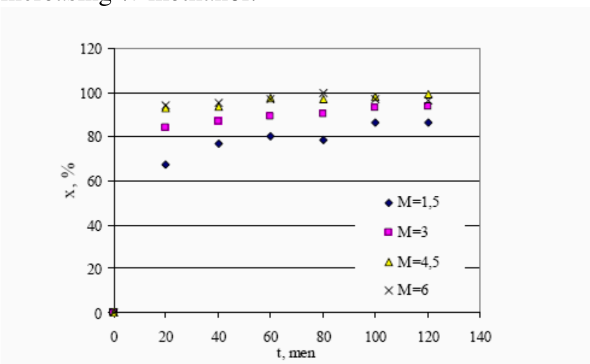

Fig.3. Effect of molar ratio of methanol to oil on% conversion (T=50 ^{o}C, C=4 %, N= 500 rpm)

4.3 Effect of stirring speed

The effect of stirring speed is studied ranging from 250 rpm to the maximum speed of the equipment. (Fig4).The faster stirring speed, the higher molecule collision frequency, the more reaction occurred, then the higher oil conversion achieved. Slower stirring speed needs longer time to reach equilibrium oil conversion. At 250 rpm, the equilibrium conversion was achieved after 60 min, while at 500 rpm or above, the equilibrium starts at 40 min or less. This results show that the rate of reaction is influenced by stirring speed. Even though, the effect is not significantly showed at stirring speed more than 500 rpm. So, 500 rpm is the optimum stirring speed with maximum equilibrium conversion 99 %.

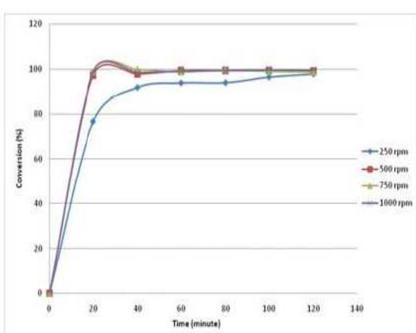

Fig. 4. Effect of stirring speed (rpm) on % conversion of oil (50 ^{o}C, M=4.5, C= 4 %)

4.4 Effect of Reaction Temperature: The cottonseed oil methanolysis results which were conducted at various temperatures ranging from 30 to 60^{o}C, are presented in Figure 5. In each run, the catalyst 4 %, stirring speed 500 rpm and methanol 450% are constant. It was observed that the oil conversion increase at increased temperature.

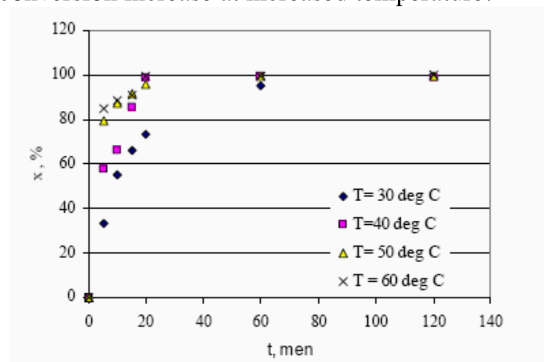

Fig 5. Effect of temperature on % conversion of oil (M = 4.5, C=4 %, N= 500 rpm)

Table .2.Fuel properties of cottonseed oil and cottonseed oil biodiesel

Sample	Viscositymm^2/s at (311K)	Density (Kg.m^3 at 288K)	Flash point K
Cottonseed oil	35.42	904	502
Cottonseed oil biodiesel	3.7	873	432

5. CONCLUSIONS

According to the cottonseed oil transesterification results which were conducted at various catalyst concentration, various stirring speed, various methanol/oil equivalent ratio and temperature,

1. The optimum conditions are achieved by using KOH catalyst as much as 4 % (wt) of oil, stirring speed of 500 rpm, methanol to oil ratio of 9:2 and reaction temperature of 50^{o}C. At these conditions, 99% of oil was converted within 60 min.
2. It was observed that the oil conversion increase at increased temperature.
3. It is recommended to take samples within shorter periodic time so that the concentration change with time can be observed better before equilibrium condition is achieved.
4. Thus biodiesel synthesis from cottonseed oil using the above process is more economical than

conventional process. Continuous production compared to the batch production at the same condition had higher product purity. Thus, this process can be an innovative process for synthesis of biodiesel from cottonseed oil and can be worked out and scaled up for commercial production of biodiesel.

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