



Co-solvents transesterification of cotton seed oil into biodiesel: Effects of reaction conditions on quality of fatty acids methyl esters



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ABSTRACT

Solvent Technology, is gaining the interest of researchers in improving transesterification process recently. Transesterification of cotton seed oil into biodiesel using different mixtures of methanol with Diethyl Ether (DEE), Dichlorobenzene (CBN) or Acetone (ACT) co-solvent systems was conducted. Potassium hydroxide (KOH) was used as the catalyst all through. The reaction conditions optimized include; the molar ratio of co-solvent in methanol, reaction temperature and time. The catalyst concentration was also optimized. The optimization was based on the percentage yields of Fatty Acids Methyl Esters (FAMES) produced. In addition, the effects of co-solvent systems on physico-chemical properties (Acid value and fatty acids composition) and fuel properties (viscosity, density and calorific value) were investigated as well. The result obtained, indicated 10% (v/v) addition of co-solvents CBN and ACT in methanol was the optimal volume. The optimal reaction temperature was 55 °C for 10 min when the catalyst concentration of 0.75% (w/w) weight of oil was used. Fuel properties were within the acceptable limit of ASTM and not significantly affected by the co-solvent systems except for the calorific value. It was concluded that the addition of co-solvent reduced the reaction time and improved some fuel properties of the biodiesel produced.

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1. Introduction

Biodiesel is a monoalkyl ester produced by the transesterification of triglyceride or FAs of vegetable oil or animal fat with short chain alcohols and has met the ASTM D6751 standard. It can be used directly on conventional diesel engines without further modifications [1–4]. Recently, biodiesel has also been produced using other bioresources such as waste cooking oil [5,6], sludge waste [7] and algal oil [8,9]. Authors have reported different conversion technologies for converting feedstocks such as triglycerides of vegetable oils, biomass or algal oils and fats into their corresponding FAMES otherwise known as biodiesel.

Biomass or oil can be converted into low molecular weight products and liquid fuels via a number of conversion routes available. In general, biodiesel conversion technologies are classified as either chemical/thermo-chemical or thermal conversion processes. Notable thermal conversion technologies reported include pyrolysis. Pyrolysis is a thermal conversion process of

heating organic matter in the absence of oxygen and supported by a catalyst. This results in formation of bio-char, pyrolysis oil and some gases as major products. The ratio of the final products depends on the extent of heating, residence time and other conditions while other by-products such as chemicals are also produced in the process [10–12]. Thermal conversion processes are known to be faster and pollution free but on the contrary, these processes are expensive and high technology is required. Chemical conversion processes on the other hand are slow, require low technology and products of high quality are obtained. Dickerson and Soria [10], proposed different conversion routes for biomass materials which depend on the quality of the end product(s) as well as the technology available.

The most widely employed chemical process for producing biodiesel is transesterification [1–5]. Transesterification has been described as a chemical reaction between triglycerides and an alcohol in the presence of a catalyst to produce monoesters of FAs. Transesterification reaction using conventional acid/base catalyzed [5,6], enzymatic [13] catalyzed and supercritical [14] conditions have been investigated. Three molecules of an alcohol are required to completely react with one molecule of the triglyceride in the reversible reaction as shown below.

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Nomenclature

ASTM	American Standard for Testing and Materials	FA	Fatty Acids
COME	Cotton seed Oil Methyl Esters	OSI	Oxidation Stability Index
GC	Gas Chromatography	EN	European Standards
FAMES	Fatty Acids Methyl Esters	DEE	Diethyl Ether
FAEE	Fatty Acids Ethyl Esters	ACT	Acetone
FFA	Free Fatty Acids	CBN	Chlorobenzene
AV	Acid Value	BTE	Brake Thermal Efficiency
CFFP	Cold Filter Plugging Point		

Solvent Technology is recently gaining the interest of researchers in their efforts towards improving the transesterification process. Methanol is one of the best solvents for transesterification of vegetable oils into their corresponding FAMES. Although, the reaction occurs when there is complete bond cleavage between the carbon atom from the parent chain and the carbon atom from the alkyl substituent in the triglyceride. This is the rate determining step of the reaction. Substantial improvements in this nucleophilic substitution reaction mechanism upon the addition of another solvent into methanol (co-solvent system) have been reported.

For example, Soriano et al. [15] investigated the homogenous Lewis acid-catalyzed transesterification of Canola seed oil using Methanol-Tetrahydrofuran co-solvent system. The progress for the reaction monitored by ^1H NMR revealed an improved biodiesel yields due to the presence of THF as co-solvent. The authors attributed the increase in the yields to significant reduction in mass transfer resistance between phases of oil and reacting methanol. Mohammed-Dabo et al. [16] also conducted co-solvent transesterification of *Jatropha curcas* seed oil into biodiesel. The effect of THF addition as co-solvent was optimized for the production process as well. The authors also confirmed the increasing percentage yields with an optimal addition of 1:1% (v/v) of co-solvent/methanol ratio. A conversion of 98% was recorded under the stated conditions. Finally, Thanh et al. [17] developed a room temperature homogenous transesterification of different vegetable oils using methanol-acetone co-solvent system. Acetone-methanol molar ratio of 4.5:1 was found suitable for converting the oils investigated using 1% (wt) KOH in less than 30 min reaction time.

Biodiesel is said to be a replacement for petroleum based diesel and can be used on diesel engines without any major engine modification. However, its fuel properties such as viscosity, cetane number, density, flash points and other important properties must meet some International Standards. Vegetable oils differ in their molecular structures, as well as in their physical and chemical properties. Therefore, the resulting biodiesel from each vegetable oil may differ in its properties and compositions [18]. In addition, other properties of biodiesel are affected by nature of feedstocks and efficiency of conversion process employed during its production [6]. During applications, fuel and physico-chemical properties of biodiesel affect its combustion and storage properties. This complex interaction necessitated formulation of some International standards like the ASTM D6751 to ensure safety of engines and environment [2–6,19,49]. Therefore, evaluating the physico-chemical and fuel properties of biodiesel becomes an integral part of any research work on biodiesel production.

In this research work, transesterification of Cotton seed oil using methanol-cosolvent systems was conducted. The effect of adding CBN, ACT or DEE in Methanol (MeOH) was evaluated based on yield and quality of final biodiesel produced. Optimization of reaction time, temperature, methanol-co-solvent ratio and catalyst concentration ratio were conducted also. Finally, the quality of COMEs produced was also evaluated using standard methods of analyses.

2. Materials and methods

2.1. Materials

Cotton seed oil was purchased from a local vendor in New Delhi, India. All materials and reagents used were analytical grade (AnalaR) chemicals except otherwise stated. Glassware, containers and other tools were initially washed with liquid detergent, rinsed with 20% (v/v) nitric acid and finally rinsed with distilled water. CBN, ACT and DEE were BDH products purchase from a chemical supplier in Delhi. The physical and chemical properties of the solvents are presented in Table 1 below.

2.2. Biodiesel production and optimization

The AV of pure vegetable oil used was 0.78 (mg KOH/g) initially. Because of this, transesterification of cotton seed oil was conducted in one-step reaction. Potassium methoxide solution was prepared by dissolving calculated amount of KOH in a given volume of methanol. The molar ratio between oil and methanol used was 1:6, whereas catalyst concentration used was 0.75% (w/w) of the oil. An average reaction temperature of 60 ± 1 °C was used all through the experiments. The experiments were conducted in a 250 ml capacity batch reactor made up of three neck round bottom flask immersed in magnetic stirrer water bath with condenser unit. Transesterification of known volume of vegetable oil and methanol-cosolvent was conducted in the reactor. The reaction time, temperature and catalyst concentration ratio were varied over different range of values under constant stirring. After the reaction was completed, glycerol layer was separated in a separating funnel over night and drawn separately afterwards.

The ester layer was severally washed with warm water mostly about three to four times. Thereafter, excess methanol-cosolvent system was evaporated using rotary evaporator. The percentage yield for each batch produced was calculated from results of the chromatogram obtained after samples were analyzed using GC by the following equation [35].

$$\% \text{ Yield} = \frac{\text{Weight of biodiesel produced (g)} \times \text{Area of component}}{\text{Weight of oil used (g)}} \times 100\%$$

The same reaction set-up was used for the optimization studies. Catalyst concentration (w/v) was varied from 0.25%, 0.5%, 0.75%, 1.0% and 1.25%. The reaction temperature was varied from $45 \text{ °C} \pm 1 \text{ °C}$, $50 \text{ °C} \pm 1 \text{ °C}$, $55 \text{ °C} \pm 1 \text{ °C}$, $60 \text{ °C} \pm 1 \text{ °C}$ and $65 \text{ °C} \pm 1 \text{ °C}$. The methanol to co-solvent ratio (v/v) was varied from 10%, 20%, 30%, 40% and 50% increasing co-solvent.

In order to critically evaluate the influence of methanol-cosolvent systems on biodiesel yield and quality, percentage glycerol recovery from the transesterification was recorded. Finally, the reaction time (minute) was varied from 45 min, 75 min, 105 min, 135 min and 165 min. However, after significant

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