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Catalytic conversion of jojoba oil into biodiesel by organotin catalysts, spectroscopic and chromatographic characterization

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HIGHLIGHTS

- Synthesis of jojoba seed oil biodiesel by base and organotin catalysts.
- Effect of various parameters on % conversion of biodiesel.
- Determination of physical and fuel properties.
- Spectroscopic (FTIR and NMR) characterization.
- Identification of fatty acid methyl esters by GC–MS.

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ABSTRACT

The transesterification of jojoba oil with methanol has been studied in the presence of various catalysts i.e., sodium hydroxide (NaOH), potassium hydroxide (KOH), dibutyltin diacetate $(C_4H_9)_2Sn\ (OOCCH_3)_2$, dioctyltin diacetate $(C_8H_{17})_2Sn\ (OOCCH_3)_2$, dibutyltin oxide $(C_4H_9)_2SnO$, dioctyltin oxide $(C_8H_{17})_2SnO$, diphenyltin oxide $(C_6H_5)_2SnO$, monobutyltin chloride dihydroxide ($(C_4H_9)Sn(OH)_2Cl$) and monobutyltin hydroxide oxide hydrate ($(C_4H_9)Sn(=O)OH{\cdot}xH_2O$), with % age conversion of oil into biodiesel was 84.5%, 61.3%, 92.6%, 25.4%, 22.0%, 23.3%, 12.0%, 2.15% and 1.05%, respectively. The optimization of experimental parameters was established to achieve maximum yield of the product by using dibutyltin diacetate $(C_4H_9)_2Sn\ (OOCCH_3)_2$. The physical and fuel properties of jojoba biodiesel like density, dynamic viscosity, kinematic viscosity, pour point, cloud point, flash point, and acid number were determined by ASTM procedures and were found to be comparable to ASTM standards for diesels. The synthesis of jojoba seed oil biodiesel (JSOB) was confirmed by FT-IR and NMR (^1H and ^{13}C) analyses of both oil and biodiesel. Chemical composition of fatty acid methyl esters (FAMEs) in jojoba biodiesel was established by GC–MS analysis and verified by retention time data and mass fragmentation pattern.

1. Introduction

The world wide increase in the consumption of petroleum oil has caused economic and environmental problems. In order to reduce dependence on petroleum oil, development of renewable fuel such as biodiesel is very important [1]. The main advantages of biodiesel fuel include renewability, high biodegradability, high flash point and low emission of pollutants [2]. American Society for Testing and Material (ASTM) defines biodiesel as a fuel comprising of monoalkyl esters of long chain fatty acids derived from vegetable oil or animal fats [3]. Biodiesel synthesis from various edible and non edible vegetable oils like rice bran [4], rapeseed [5], soybean [6], sunflower [7], palm [8], and rocket seed [9], has been reported in literature but no extensive information is available regarding the synthesis of biodiesel from jojoba oil.

Jojoba (*Simmondsia Chinensis*) is a perennial shrub that grows naturally in the Sonora desert (Mexico) and in the south west of USA. Jojoba is now being cultivated in some countries such as Argentina, Israel, Pakistan and Africa. The jojoba seeds are nut shaped and round, 1–2 cm long, with red brown to dark brown color. Jojoba wax is a golden liquid that can be obtained by cool pressing or solvent extraction [10]. The direct use of vegetable oil and its blend with mineral diesel caused several operational problems i.e. poor atomization, carbon deposits due to incomplete combustion, oil ring sticking, lubricating problems, etc., because vegetable oil have high viscosity (about 10–20 times than that of diesel fuel) [11], acid composition and free fatty acid contents [12]. Different methods are being used to reduce the viscosity of vegetable oils such as dilution, pyrolysis, microemulsification, catalytic cracking and

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transesterification [13]. Among all these methods transesterification seems to be the best method, as the physical characteristics of fatty acid alkyl esters are similar to the existing diesel fuel.

In the present study, cheaper, easily available and non edible jojoba oil was used for biodiesel production by based catalyzed transesterification as well as with some newly synthesized organotin catalysts. Various parameters such as catalyst concentration, oil methanol molar ratio, time and temperature for the transesterification of oil, were optimized followed by the physical and spectroscopic characterization of jojoba biodiesel.

2. Experimental

2.1. Materials

Jojoba seeds were obtained from oil seeds program of National Agricultural Research Center, Islamabad, Pakistan. The chemicals used for the synthesis, physicochemical characterization of biodiesel and for the synthesis of catalysts were methanol (CH_3OH), sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium sulfate (Na_2SO_4), isopropyl alcohol (C_3H_7OH) and acetic acid (CH_3COOH) obtained from Merck (Germany). Toluene ($C_6H_5CH_3$), diphenyltin oxide (($C_6H_5)_2SnO$), monobutyltin chloride dihydroxide (($C_4H_9)Sn(OH)_2Cl$) and monobutyltin hydroxide oxide hydrate (($C_4H_9)Sn(=O)OH{\cdot}xH_2O$), were obtained from Aldrich, oxalic acid ($C_2O_4H_2.2H_2O$), dibutyltin oxide (($C_4H_9)_2SnO$) from Fluka and chloroform ($CHCl_3$) from Lab-Scan.

2.2. Instrumentation

The oil was expelled by using electric oil expeller (KEK P0015, 10127, Germany). After an average of 5–6 turns, the oil was fully extracted from seeds. The oil obtained was filtered to remove the suspended particles and stored in an air tight glass container till required. Density was determined by using specific gravity bottle. Acid number was determined by acid base titration method. Dynamic and kinematic viscosities were determined by an Ubbelohde viscometer. Biodiesel was analyzed by FT-IR, using a Nicolet 6700 Model FTS 3000 MX in the range 4000–400 cm^{-1}. NMR spectra (^1H, ^{13}C) were recorded in $CDCl_3$ as internal reference by using a Bruker ARX-300MHz FT-NMR. GC–MS analyses were perform by using a GC 6890N coupled to MS 5973MSD. 0.1 μL biodiesel in hexane was injected in DB-5MS column. The carrier gas was helium. The column temperature was programmed from 120 to 300 °C at the rate of 10 °C min^{-1}. The mass spectrometer was set to scan in the range of m/z 50–600 and ionization potential of 70 eV.

2.3. Synthesis of catalysts

All the catalysts were purchased except those of dibutyltin diacetate and dioctyltin diacetate. For the synthesis of dibutyltin diacetate, 1:2 M solutions of dibutyltin oxide or dioctyltin oxide and glacial acetic acid in dry toluene were refluxed in a Dean and Stock apparatus. For the synthesis of dibutyltin diacetate the reflux time was two hours, whereas for dioctyltin diacetate the reflux time was seven hours. The chemical reactions may be represented as:

$$(C_4H_9)_2SnO + 2CH_3COOH \xrightarrow{\text{Toluene}} (C_4H_9)_2Sn(OOCCH_3)_2 + H_2O$$

$$(C_8H_{17})_2SnO + 2CH_3COOH \xrightarrow{\text{Toluene}} (C_8H_{17})_2Sn(OOCCH_3)_2 + H_2O$$

2.4. Methods

2.4.1. Transesterification

Methyl esters were prepared by transesterification according to conditions reported in literature [9,14]. The vegetable oil was heated on a hot plate to remove moisture before reaction. Two methods were adopted for the synthesis of biodiesel. In first method NaOH or KOH were used as catalyst. The sodium or potassium methoxide was prepared by dissolving 6.5 g NaOH or KOH in 200 mL methanol in separate beakers and stirred for half an hour. The resultant methoxide solution was put into one liter of vegetable oil, the mixture was heated at 60 °C and with stirring for 60 min at 500 rpm. The reaction mixture was cooled to room temperature and allowed to settle down, resulting in the separation of two phases. The upper phase contained biodiesel and the lower phase contained glycerin byproduct, which were separated by simple decantation. The biodiesel layer also contains the excess methanol, remaining catalyst, soap formed and partly reacted glycerides. After separation biodiesel was purified by distilling the residual methanol at 60 °C. The remaining catalyst was removed by successive washing with distilled water at pH 4.5 by adding 1–2 drops of acetic acid. Anhydrous Na_2SO_4 was then added to remove water followed by filtration.

For the second method, experimental conditions were adjusted according to the literature [15] using different tin compounds as catalysts. The transesterification reactions were conducted at various oil methanol ratios of 1:5, 1:7, 1:9, 1:11, 1:13, 1:15, 1:17, 1:19, 1:21, 1:23, 1:25, 1:27, 1:33 and 1:43, the catalyst concentrations were 0.5, 1.0, 1.5 and 2.0 w/w of oil whereas the temperatures were ranged from 50 to 90 °C at an interval of 10 °C. The product formed was washed three times with distilled water. Anhydrous Na_2SO_4 was added to remove water followed by filtration.

The biodiesel yield was calculated by using the expression:

$$\%\ \text{Yield} = \frac{\text{Grams of methyl ester produced}}{\text{Grams of oil used for reaction}} \times 100 \quad (1)$$

3. Result and discussion

The synthesis of biodiesel from jojoba oil was investigated by transesterification of oil with methanol. Various catalysts were tested for the synthesis of biodiesel to get maximum yield by optimizing different parameters. Detailed discussion of the optimization is as under.

3.1. Optimization of physical and spectroscopic parameters

Various physical parameters such as oil–methanol ratio, catalyst's concentration, reaction temperature and reaction time were optimized for the conversion of jojoba oil into its biodiesel. The criterion for the optimization was the selection of parameters which produce maximum product. The quantification of the product formed was checked by using Eq. (1). The tested catalysts include sodium hydroxide (NaOH), potassium hydroxide (KOH), dibutyltin diacetate ($(C_4H_9)_2Sn(OOCCH_3)_2$), dibutyltin oxide ($(C_4H_9)_2SnO$), dioctyltin diacetate ($(C_8H_{17})_2Sn\ (OOCCH_3)_2$), dioctyltin oxide ($(C_8H_{17})_2SnO$), diphenyltin oxide ($(C_6H_5)_2SnO$), monobutyltin chloride dihydroxide ($C_4H_9Sn(OH)_2Cl$) and monobutyltin hydrooxide oxide hydrate (($C_4H_9)Sn(=O)OH{\cdot}xH_2O$). The results of percentage conversion into biodiesel are shown in Table 1. Among the tested catalysts maximum conversion of oil into biodiesel was observed from di-*n*-butyltin (IV) diacetate (DBD), therefore, the optimization of different parameters was done with this catalyst and is discussed in the following paragraphs.

3.1.1. Effect of oil–methanol ratio

The effect of oil–methanol molar ratio on the conversion of jojoba seed oil into biodiesel was checked with oil methanol ratios of 1:5, 1:7, 1:9, 1:11, 1:13, 1:15, 1:17, 1:19, 1:21, 1:23, 1:25, 1:27,