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Transesterification of jojoba oil, sunflower oil, neem oil, rocket seed oil and linseed oil by tin catalysts

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ABSTRACT

The methanolysis of jojoba oil has been studied in the presence of tin powder, 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 $(C_6H_5)_2SnO$, dibutyltin chloride dihydroxide $(C_4H_9)_2Sn(OH)_2Cl$, butyltinhydroxide hydrate $(C_4H_9)Sn(=O)OH.xH_2O$, Ni nanoparticles and Pd nanoparticles act as catalysts. Among these, 1 weight % of dibutyltin diacetate shows the maximum conversion. Then, methanolysis of sunflower oil, neem oil, rocket seed oil and linseed oil into methyl esters studied in the presence of 1% dibutyltin diacetate as a catalyst and was compared their percentage conversions. The experimental yield for the conversion of jojoba oil, sunflower oil, neem oil, rocket seed oil and linseed oil into biodiesel was found to be 71%, 51%, 50.78%, 40.90% and 39.66%, respectively. The experimental yield of the conversion of jojoba oil into methyl esters was found to be increased up to 96% by increasing reaction time, without emulsion formation. The synthesis of jojoba seed oil biodiesel (JSOB), soybean oil biodiesel (SOB), neem oil biodiesel (NOB), rocket seed oil biodiesel (RSOB) and linseed oil biodiesel (LSOB) was confirmed by NMR (^1H & ^{13}C) and FT-IR analyses of biodiesel.

1. Introduction

The worldwide increase in the extraction and consumption of fossil fuel has caused economic and environmental problems. In order to reduce dependence on fossil fuel, recent research has been directed to the development of renewable fuel such as biodiesel [1]. American Society for Testing and Material (ASTM) define biodiesel as a fuel comprises of monoalkyl ester of long chain fatty acids derived from vegetable oil or animal fats [2]. The biodiesel has advantages of high biodegradability, renewability, low toxicity, high flash point and low pollutant emissions [3]. In addition, it can be used in diesel engines alone, or blended with diesel oil [4]. Notably, the composition of different oils is different but generally they are composed of triglycerides, free fatty acids, monoglycerides, and diglycerides [5]. In this context, numerous efforts have been devoted to the conversion of various edible and non-edible vegetable oils to biodiesel [6–14]. For example, transesterification of soybean oil with methanol under

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homogeneous condition can be achieved by using metal complexes of M (3-hydroxy-2-methyl-4-pyrone)$_2$(H_2O)$_2$ as a catalyst (M = Sn, Zn, Pb and Hg). Note that the Sn complex shows high activities, and yields without emulsion formation [15]. Recently, it has been reported the synthesis of jojoba biodiesel from jojoba oil by transesterification of various organotin and base catalysts with methanol [16]. Canoira et al. [17] have developed a method of jojoba oil wax transesterification with methanol in the presence of sodium metal and acetyl chloride. The use of vegetable oil and its blend with diesel caused several operational problems i.e. poor atomization, carbon deposits due to incomplete combustion, oil ring sticking, lubricating problems, etc., because vegetable oil has high viscosity [18], poly unsaturation and free fatty acid contents [19]. Different methods are being used to reduce the viscosity of vegetable oils such as dilution, microemulsion and transesterification [20]. Among these transesterification is the key and foremost important step to produce the cleaner and environmentally safe fuel from vegetable oils. In the present study different catalysts have been used for the production of biodiesel from jojoba oil. The catalyst which showed the best performance for the production of biodiesel from jojoba oil was used for the production of biodiesel from sunflower oil, neem oil, rocket seed oil and linseed oil with methanol, and percentage conversion of different oils was also compared.

2. Experimental

2.1. Materials

Jojoba, sunflower, neem, linseed and rocket seeds were obtained from oil seeds program of National Agricultural Research Center, Islamabad, Pakistan. The chemicals used for the synthesis and characterization of biodiesel, and for the synthesis of catalysts were methanol (CH_3OH), sodium sulfate (Na_2SO_4), sodium hydroxide (NaOH), Palladium acetate Pd(OAc)$_2$ and acetic acid were obtained from Merck (Germany). Toluene ($C_6H_5CH_3$), tin powder, dibutyltin chloride dihydroxide (($(C_4H_9)_2Sn(OH)_2Cl$), butyltinhydro oxide hydrate (C_4H_9 Sn(=O)–OH·xH_2O), diphenyltin oxide ($(C_6H_5)_2SnO$, Nickel chloride, Hydrazinium hydroxide ($NH_2NH_2·H_2O$), ethylene glycol ($HOCH_2CH_2OH$), dioctyl sulfosuccinate sodium salt, and isooctane were obtained from Aldrich, 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, 10,127, Germany). The oil is fully extracted from seeds, after an average of 5–6 turns. The oils obtained were filtered to remove the suspended particles and stored in air tight glass containers till required. Biodiesel produced from different oils were 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 $CDCl_3$ using tetramethyl silane as internal reference on Bruker ARX-300 MHz FT-NMR spectrometer. GC-MS analyses were performed 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. The mass spectrometer was set to scan in the range of *m*/z 50–600 and ionization potential of 70 eV.

3. Methods for the synthesis of catalysts and biodiesel

For the synthesis of dibutyltin diacetate, 1:2 M solutions of dibutyltin oxide and glacial acetic acid in dry toluene were refluxed in a Dean-Stock apparatus. For the synthesis of dibutyltin diacetate the reflux time was 2 h, whereas for dioctyltin diacetate 7 h of reflux were required. Ni and Pd nanoparticles were prepared according to the method in literature [21,22].

Fatty acid methyl esters were prepared by the transesterification of vegetable oil with methanol in the presence of catalysts, according to the method suggested in the literature [23,24]. Two methods were adopted for the synthesis of biodiesel. In first method calculated amount of catalyst was dissolved in 200 mL methanol in separate beakers and stirred for half an hour. The vegetable oil was heated on a hot plate to remove moisture before reaction. The catalyst methanol solution was put into 1 L of vegetable oil; the mixture was heated at 60 °C and with stirring for required time 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, 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.

While in the second method the calculated amounts of oil, methanol and catalyst were put together in round bottom flask and refluxed for a given time at particular temperature. The reaction mixture was allowed to settle down into two phases. The upper phase contained biodiesel and the lower phase contained glycerin byproduct and catalyst, which were separated by simple decantation. After separation biodiesel was purified by distilling the residual methanol at 60 °C.

4. Result and discussion

The synthesis of biodiesel from jojoba oil, sunflower oil, neem oil, rocket seed oil and linseed oil was investigated by transesterification of oil with methanol. Tin catalysts show no conversion for 1st method. Various tin and nano catalysts were tested for the transesterification of jojoba oil with methanol by using 2nd method. Various catalysts such as tin powder, 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 $(C_6H_5)_2SnO$, dibutyltin chloride dihydroxide $(C_4H_9)_2Sn(OH)_2Cl$, butyltinhydroxide hydrate $(C_4H_9)Sn(=O)OH.xH_2O$, Ni and Pd nanoparticles were used for biodiesel production from jojoba oil

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