



Biodiesel from mutton fat using KOH impregnated MgO as heterogeneous catalysts

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ABSTRACT

The use of MgO impregnated with KOH as heterogeneous catalysts for the transesterification of mutton fat with methanol has been evaluated. The mutton fat (fat) with methanol (1:22 M ratio) at 65 °C showed > 98% conversion to biodiesel with 4 wt% of MgO–KOH-20¹ (MgO impregnated with 20 wt% of KOH) in 20 min. The reaction conditions optimized were; the amount of KOH impregnation (5–20 wt%), the amount of catalyst (1.5–4 wt%, catalyst/fat), the reaction temperature (45–65 °C), fat to methanol molar ratio (1:11–1:22) and the effect of addition of water/oleic acid/palmitic acid (upto 1 wt%). Although, transesterification of fresh fat (moisture content 0.02 wt% and free fatty acids 0.002 wt%) with methanol in the presence of KOH (homogenous catalyst) resulted in the complete conversion to biodiesel, but in the presence of additional 1 wt% of either free fatty acid or moisture content, formation of soap was observed. The MgO–KOH-20 catalyst was found to tolerate additional 1 wt% of either the moisture or FFAs in the fat.

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1. Introduction

The limited and fast diminishing resources of mineral oil, increasing prices of crude oil and environmental concerns have been the diverse reasons for exploring the use of triglycerides (vegetable oils and animal fats) as substitute of mineral based fuel. However, direct use of triglycerides has not been satisfactory because of their high viscosity and poor ignition quality [1,2]. Treatments that could overcome the major problems associated with the high viscosity of vegetable oils when used as diesel engine fuels are its dilution, micro emulsification, pyrolysis, and transesterification with alcohols of short chain length [3]. Transesterification of triglycerides with alcohols in the presence of catalyst (acid, alkali or enzymes) lead to the formation of less viscous fatty acid alkyl esters, commonly known as biodiesel. Acid catalysts are normally used when FFAs content in feedstock is higher, however, the rate of reaction is relatively slow and higher molar ratios of Triglyceride/methanol are required to attain the maximum conversion. Transesterification reactions are usually catalyzed by homogenous base catalysts when free fatty acid contents (FFAs) and moisture contents are < 0.5 and 0.1 wt% respectively in feedstock [4] and such reactions lead to the formation of biodiesel and glycerol contaminated with catalyst. Catalyst removal from the biodiesel required further purification steps which leads to increase the overall production cost of biodiesel. Further if moisture and FFAs

in feedstocks are present in higher amount, catalyst leads to the formation of soap instead of biodiesel. Heterogeneous catalysis has the potential to overcome the problems associated with homogeneous catalysts. Benefits of using heterogeneous catalysts include ease of separation and purification of the reaction products, easy reuse of the catalyst in the reactor, reduced corrosion problems and low sensitivity towards FFAs and moisture contents [5–8]. At present biodiesel is not cost competitive with conventional diesel fuel owing to its high production cost which could be attributed to high feedstock cost and high energy consumption during the transesterification and purification process. In order to decrease the cost of biodiesel production, cheap feedstocks viz., animal fat and greases could be used with the catalysts that could convert the feedstock into biodiesel at relatively faster rate to reduce the energy demand for the reaction.

In literature significant reports are available which deals with conversion of fat into biodiesel using homogeneous or heterogeneous catalysts. Ma et al. [4] used 0.3 and 0.5 wt% of NaOH and NaOCH₃ respectively for the transesterification of beef tallow and maximum conversion was obtained within 15 min of reaction time. Potassium hydroxide as catalyst has been reported for biodiesel production [9] from bovine and beef fat [10] as feedstock. Mixtures of vegetable oils (virgin and waste) and lard in different compositions have also been reported for the biodiesel production using NaOH as catalyst [11]. A report by Ngo et al. [12] have shown the preparation of biodiesel from greases in two steps by using a series of diarylammonium catalysts as homogeneous catalyst as well as heterogeneous (immobilized on polymer support) catalyst, for the esterification of the FFA (12–40 wt%) present in greases. Resulting

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¹ MgO–KOH-X (X = wt% of KOH impregnation over MgO).

ester-glyceride mixtures were completely converted to esters by base-catalyzed transesterification. Canoria et al. [13] investigated the production of biodiesel from the different mixtures of animal fat and soybean oil in two steps. In first step, esterification was carried out with *p*-toluenesulfonic acid and then transesterification of the same was performed with methanol using sodium methoxide as catalyst. Nanocrystalline CaO were reported by Reddy et al. [3] as heterogeneous catalysts for the transesterification of poultry fat at room temperature with fat to methanol ratio 3:10 (v/v) and requires 6 h for the maximum conversion of fat. Goodwin Jr. et al. [14] used the heterogeneous base catalysts derived from Mg–Al hydrotalcite for the transesterification of poultry lipids into biodiesel in the temperature range of 60–120 °C and varying methanol to lipid molar ratios from 6:1 to 60:1. High temperature (120 °C), high methanol to fat ratio (60:1) and use of co-solvent (hexane, toluene, THF) were found to show the positive effect for the same reaction.

It is manifested from the literature review, that most of the heterogeneous catalysts require high fat to methanol ratio, high reaction temperature, higher pressure and in most cases, their use requires longer time and addition of co-solvents during reaction for the maximum conversion of fat to biodiesel. All these factors directly or indirectly are expected to increase the production cost of biodiesel, which is a major hurdle for the commercialization of the biodiesel. In order to develop a heterogeneous catalyst that could catalyze the transesterification of fat under ambient conditions, here we report the preparation, characterization and use of KOH impregnated MgO catalysts for the transesterification of mutton fat.

2. Materials and methods

2.1. Materials

Potassium hydroxide, magnesium oxide, ethyl alcohol, hydrochloric acid, sodium hydroxide, silica gel, Hammett indicators viz., neutral red, bromthymol blue, phenolphthalein, 2,4-dinitroaniline, and 4-nitroaniline of GR grade were obtained from Loba Chemicals Pvt. Ltd and used as such without further purification. Methanol (>99%) was obtained from MERK, India. Mutton fat was purchased from a meat shop located in Patiala (Punjab) India.

2.2. Feed stock's characterization

FFAs content in fat was determined by reported method [15] and was found to be 0.514 and 4.95 mg KOH/g for the fresh and six months old fat respectively. Moisture content in fat was determined by Karl Fisher method using AF7LC Orion Coulometric autotitrator and found to be 0.02 wt%.

2.3. Catalyst preparation and characterization

KOH impregnated MgO catalysts were prepared by wet impregnation method [16]. In a typical preparation, MgO (10 g) was suspended in 100 ml of deionized water followed by addition of 10 ml aqueous solution of KOH of appropriate concentration. The slurry was stirred for 2 h, heated to 120 °C for 16 h followed by calcination at 550 °C for 5.5 h. MgO was impregnated with 5–20 wt % of KOH and designated as MgO–KOH-*X* (*X* being the wt% of KOH impregnated over MgO). Catalysts were characterized by FT-IR, powder XRD, TEM and DTA. Basic strengths of the catalysts were measured by Hammett indicators [17].

The catalysts (25 mg) were shaken with 5 ml methanolic solution of each Hammett indicator (0.02 M) to observe the colour change. Hammett indicators used were: neutral red ($H_- = 6.8$), bromthymol blue ($H_- = 7.2$), phenolphthalein ($H_- = 9.8$), 2,4-dinitroaniline ($H_- = 15.0$), and 4-nitroaniline ($H_- = 18.4$).

FT-IR attenuated total reflectance spectra were recorded on Perkin Elmer (BX-II) spectrophotometer in the range of 4000–500 cm^{-1} . Powder XRD were carried on Panalytical X'pert using Ni-filtered Cu K α radiation in steps of 0.0170° with a scan step time of 15.5 s in the 2θ range of 10–80°. DTA of the catalysts were recorded on Perkin Elmer Diamond TGA/DTA under nitrogen atmosphere with a heating rate of 10 °C/min upto 1000 °C. Transmission electron micrographs were recorded on Hitachi (H-7500) 120 kW.

2.4. Transesterification of fat

In a typical transesterification reaction, fat and methanol (1:22 M ratio) and 4 wt% of the catalyst (catalyst/fat) were stirred at 65 °C till the completion of the reaction. Progress of the reaction was monitored on TLC (solvent system; hexane: ethyl acetate: 24:1 v/v; $R_f = 0.2$, fat; $R_f = 0.36$, biodiesel). The reaction conditions were optimized by varying: the amount of KOH impregnation, amount of the catalyst, reaction temperature, fat/methanol molar ratio, moisture content and the FFAs (addition of oleic acid and palmitic acid). Pure MgO (4 wt%) and KOH (0.8 wt%, an equivalent amount of KOH present in 4 wt% of MgO–KOH-20) were also used as catalysts for transesterification to compare the results obtained with MgO–KOH-20.

2.5. Analysis of biodiesel

Quantification of methyl esters was carried out by ^1H NMR [18]. Concentrations of potassium ions in samples of biodiesel (obtained from KOH and MgO–KOH-20) were determined by reported method [19]. In a typical procedure, biodiesel (0.5 g) in silica crucible was heated at 250 °C for 1 h followed by slow increase in temperature upto 600 °C and further maintaining the temperature for 4 h. The resulting content was dissolved in dilute nitric acid and analyzed for K^+ ions on Flame photometer. Biodiesel samples (5 g) from both homogenous and heterogeneous catalyzed reactions were stirred with 25 ml of deionized water for half an hour to study pH and the leaching behavior of K^+ ions from the catalysts into biodiesel.

3. Results and discussion

3.1. Catalyst characterization

Basic strengths for MgO–KOH-*X* (*X* = 5–15) were similar to calcined MgO (Table 1). An increase in basic strength was observed for MgO–KOH-20.

FT-IR spectra of MgO–KOH-*X* (*X* = 5–20) are shown in Fig. 1. MgO–KOH-20 showed a weak and broad band at $\sim 3400 \text{ cm}^{-1}$ due to the presence of –OH group. Another peak at 1430 cm^{-1} indicated the presence of CO_3^{2-} [20,21] probably formed during calcination.

Powdered XRD patterns of calcined MgO and MgO–KOH-*X* (*X* = 5–20) are shown in Fig. 2. The impregnated catalysts showed peaks at 37.0°, 43.0° and 62.3° due to the presence of MgO crystalline phases (PDF 78-0430). Another peak at 31.3° due to

Table 1
Basic strengths of KOH impregnated MgO.

Catalyst	Hammett Indicator with Higher Basic Strength Showing Colour Change	Basic strength
MgO ^a	Phenolphthalein ($H_- = 9.8$)	$7.2 < H_- < 9.8$
MgO–KOH-05	Phenolphthalein ($H_- = 9.8$)	$7.2 < H_- < 9.8$
MgO–KOH-10	Phenolphthalein ($H_- = 9.8$)	$7.2 < H_- < 9.8$
MgO–KOH-15	Phenolphthalein ($H_- = 9.8$)	$7.2 < H_- < 9.8$
MgO–KOH-20	2,4-Dinitroaniline ($H_- = 15.0$)	$9.8 < H_- < 15.0$

^a Without impregnation with KOH.

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