



Full Length Article

Biodiesel from batch and continuous oleic acid esterification using zeolite catalysts



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ARTICLE INFO

Keywords:

Biodiesel

Oleic acid esterification

Zeolite

Continuous fixed-bed reactor

ABSTRACT

The esterification of oleic acid with ethanol was studied in both batch and continuous conditions in a fixed-bed reactor over FAU-type zeolites prepared from shale rock. The addition of Co-Ni-Pt to the zeolite increased the catalyst activity over the entire reaction temperature range. Experiments confirmed that esterification follows pseudo first-order kinetics. Thermodynamic analysis and Thiele modulus calculations show that the reaction is kinetically controlled in batch conditions, while diffusional limitations occur at higher flow rates when conducted in continuous mode. The maximum oleic acid conversions were recorded as 93% for batch and 89% for continuous, which exceed those of any analogous studies.

1. Introduction

Biodiesel is a carbon neutral fuel source that has the potential to provide almost unlimited renewable energy. Untreated biodiesel (natural oils) e.g. sunflower oil, typically consists of fatty acids that require (trans)esterification to produce methyl or ethyl esters that have appropriate viscosity and burning rate (cetane number) for use in existing diesel compression engines thereby making them suitable as fuels. Biodiesel is traditionally prepared using homogeneous catalysts e.g. sulfuric acid. Heterogeneous catalysts have the advantage of being easily removed from the biodiesel produced so it is not surprising that more recent research efforts have focussed on the development and testing of such heterogeneous systems.

Oleic acid is present in natural oils and its acid catalysed esterification has become a model reaction in the study of biodiesel formation. Most of the literature around oleic acid esterification reports its reaction with methanol. Homogenous systems using mineral acid/base catalysts have been well studied so recent innovations in this area tend to focus on increasing the product yield by additional reaction treatment. Examples include the use of a water adsorption apparatus, which increases the reaction yield via water removal to enhance the oleic acid:methanol equilibrium towards the ester [1], and the application of ultrasound during reaction [2]. Heterogeneously catalysed oleic acid:methanol reactions have been reported over the following catalysts; Amberlyst-46 [3]; sulfonated carbon [4]; acid ion-exchange polymer

resin [5]; titanium dioxide supported on natural phosphate [6]; 12-tungstophosphoric acid supported on mesoporous silica [7]; and solid acid catalysts prepared from Amazon flint kaolin [8]. Ethyl esters have superior properties to their methyl counterparts, evidenced by higher oil solubility, calorific value, cetane number, cold filtering plugging point, cloud point and pour point. The catalysis of the oleic acid:ethanol reaction has been examined using; sulfonated cation exchange resin [9]; organophosphonic acid-functionalised silica [10]; sulfonated carbonised bamboo ash [11]; Amberlyst-15 [12] niobic acid [13]; calcium ferrite [14]; and zirconia supported 12-tungstophosphoric acid [15].

Zeolites are high surface area solid acids that have been widely used for water treatment and purification, humidity control, and heterogeneous catalysis [16]. Zeolite acidity originates from the charge imbalance between silica and alumina units bound within the stable crystalline aluminosilicate framework; these properties makes zeolites suitable to the acid-catalysed esterification of free fatty acids in biodiesel production, and a number of reviews have been published [17–22]. In addition to their preparation from laboratory based silicate/aluminosilicates reagents, zeolites may also be prepared from a variety of natural/waste materials; the compositions of silicon and aluminium based minerals in these materials is similar to those of aluminosilicate zeolites, and the literature describes examples of zeolites prepared from fly ash [23–33], kaolin [34–45], fly ash-kaolinite [46] and shale [47–51]. There are few reports in the literature on zeolite catalysed oleic acid esterification reactions, and the majority use

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methanol; zeolite beta [52,53]; mordenite, ZSM-5 and FAU-type zeolite [54]; and ZSM-5 modified with citric acid [55]. Oleic acid esterification with ethanol was studied in batch conditions over zeolite Y [56] and zeolite beta [57], and via pervaporation-assisted continuous esterification over Amberlyst-15 [58] and NaA zeolite membrane [59].

We recently reported the preparation of pure FAU- zeolite from shale rock, and demonstrated that its catalytic activity was comparable to that of commercial Y zeolite in the esterification of oleic acid with ethanol [51]. Here, we expand on our previous experiments using FAU-type zeolite as a catalyst in both batch and continuous conditions, in which the maximum conversion is enhanced by the straightforward addition of Co-Ni-Pt metals. Kinetic and thermodynamic parameters are also presented.

2. Experimental

2.1. Materials

The following is a list of the materials' source/supplier and purity; shale rock was collected from the surface of a tilled field on a working farm in county Wexford, Ireland, washed with water to remove all soil residue and dried at 120 °C for three hours; sodium hydroxide (NaOH) pellets, extra pure, Scharlau; sodium silicate (Na₄SiO₄), 99% purity, BDH Chemicals Ltd.; ammonium chloride (NH₄Cl), Sigma Aldrich; absolute ethanol (C₂H₅OH) Sigma Aldrich; phenolphthalein, 2% in ethanol, Sigma-Aldrich; cobalt (II) nitrate hexahydrate, Co (NO₃)₂·6H₂O, Sigma Aldrich; nickel (II) nitrate hexahydrate, Ni (NO₃)₂·6H₂O, Sigma Aldrich; platinum (IV) oxide hydrate, PtO₂·xH₂O, Sigma Aldrich.

2.2. Catalyst preparation

The zeolite was prepared using a procedure based on our previous paper [51]. The washed shale was crushed in a ball mill apparatus, sieved to < 90 μm and calcined in air at 800 °C for 4 h to remove organic matter. 10 g of calcined shale was then refluxed with 40 cm³ of 5 M HCl at 85 °C for 4 h (to remove Fe) and the product recovered by filtration. 1 part (by mass) of calcined shale was mixed with 1.5 parts (by mass) of 40 wt% aqueous NaOH solution, heated at 850 °C in air for 3 h in a furnace to get fused shale, which was crushed to powder form after cooling to ambient temperature. 2 g of fused shale, 1 g sodium silicate and 16 g distilled water were added to a polypropylene bottle, stirred at room temperature for 3 h, then aged under static conditions at room temperature for 18 h, and finally hydrothermally treated at 100 °C for 24 h. The product was recovered by filtration.

To convert the prepared zeolite from Na⁺ to NH₄⁺ form, 90 g of zeolite were added to 250 cm³ of 2 M ammonium chloride and stirred in a round bottom flask at room temperature for 2 h. The solid was recovered by filtration, washed with distilled water and the ion-exchange procedure was repeated a further two times using 60 g and 30 g, respectively. The solid was again recovered by filtration, washed with distilled water, dried for 12 h at 120 °C and calcined in air at 500 °C for 4 h to give zeolite in H⁺ form, hereafter labelled H-FAU.

Before metal loading, the zeolite was dried in an oven at 110 °C for 2 h to remove any absorbed water. Precious metals were added to the zeolite using incipient wetness; solutions were prepared by dissolving the appropriate masses of Co, Ni, and Pt metal precursors in 0.1 M HCl, which were then added to the zeolite to give loadings of 1 wt% of each metal. After impregnation, the catalysts were dried overnight at ambient temperature, heated for 24 h at 120 °C, and calcined in air at 500 °C for 4 h to give Co-Ni-Pt-FAU.

2.3. Characterization

Nitrogen adsorption/desorption measurements were carried out using a Micromeritics ASAP 2020 Surface Analyser at -196 °C.

Samples were degassed under vacuum ($p < 10^{-5}$ mbar) for 12 h at 350 °C prior to analysis. BET surface areas of the samples were calculated in the relative pressure range 0.05–0.30. Microscopic images were recorded using a JEOL JSM-5600LV scanning electron microscope (SEM). Semi-quantitative chemical analysis was performed by energy-dispersive X-ray spectroscopy (EDAX) using a detector from Oxford Instruments.

2.4. Catalyst testing

2.4.1. Batch reactor

The esterification reaction of oleic acid with ethanol was performed by reflux in a 500 ml batch reactor placed in a thermostatic oil bath under stirring. The desired amount of catalyst was dried before reaction at 130 °C for 2 h. The reactor was loaded with 50 ml (44.75 g) of oleic acid and the desired amount of pre-heated ethanol was then added to give an ethanol to oleic acid molar ratio of 6. Esterification was carried out at reaction temperatures 40, 50, 60 and 70 °C. 5 ml samples were withdrawn from the reaction mixture at 15 min intervals, and centrifuged for 10 min at 3000 rpm to separate the solid zeolite from the liquid phase.

The supernatant layer was purified by rotary evaporator to remove excess ethanol and water generated during reaction and analysed by titration with 0.1 M KOH, using phenolphthalein indicator, to calculate the acid value (AV) as shown in the following equation;

$$AV = \frac{\text{ml of KOH} \times N \times 56}{\text{Weight of Sample}} \quad (1)$$

From the acid value, the conversion of oleic acid was calculated for each amount of catalyst as shown in the following equation;

$$\text{conversion \%} = \frac{AV_{t_0} - AV_t}{AV_{t_0}} \times 100\% \quad (2)$$

where:

AV_{t₀} (acid value of the reaction product at time 0)

AV_t (acid value of the reaction product at time t)

2.4.2. Continuous fixed-bed reactor

Oleic acid esterification was conducted in continuous mode using a vertical fixed-bed quartz reactor (Fig. 1) with internal diameter 10 mm and height 650 mm. 6.35 g of catalyst pellets were prepared by compressing the catalyst powder at 2 tonnes for 1 min in a hydraulic press, followed by crushing and sieving to the size range 355–500 μm. Ethanol and oleic acid were mixed and preheated (using the same quantities as in the batch reaction), and delivered upwards to the reactor using a Perkin Elmer LC pump. The reaction temperature was controlled by circulating water from a bath. Different flow rates were employed to obtain sufficient residence times between the reactants and catalyst inside the reactor column (30, 60, 90, 120, 150 and 180 mins). The product stream was collected in an accumulation tank, during which 10 ml samples were taken for analysis at each flow rate and temperature. The product was purified and analysed in the same manner as that used in the batch reaction.

3. Results and discussion

3.1. Characterisation

The XRD patterns for H-FAU prepared from shale rock confirm the faujasite structure; these were discussed in detail by the authors in Ref. [51] so will not be repeated here. The BET surface area of H-FAU decreased from 571 m² g⁻¹ to 490 m² g⁻¹ after the addition of Co, Ni and Pt metal salts by incipient wetness, and subsequent heating and calcination in air. A decrease in surface area is expected as the Co-Ni-Pt-FAU has undergone twice the period of calcination as H-FAU, thereby

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