



Feasibility of modified bentonite as acidic heterogeneous catalyst in low temperature catalytic cracking process of biofuel production from nonedible vegetable oils

Abdelrahman M. Rabie, Eslam A. Mohammed, Nabel A. Negm*

Egyptian Petroleum Research Institute, 1-Ahmed El Zommer Street, Nasr city, Cairo, Egypt

ARTICLE INFO

Article history:

Received 25 December 2017

Received in revised form 14 January 2018

Accepted 19 January 2018

Keywords:

Heterogeneous catalyst

Catalytic cracking

Biofuel

Oil

ABSTRACT

Acidic bentonite clay was obtained through surface modification of bentonite clay using hydrochloric acid as acidic precursor to increase the acidity of the bentonite. The modified catalyst was examined via X-ray fluorescence (XRF), XRD analysis, Brunauer Emmett and Teller surface area (BET), FTIR analysis and temperature-programmed desorption (TPD) analysis. XRF analysis showed that the acid modification of bentonite clay results in an increase in the silica content and lower abundance of metal oxides, due to the dissolve of Fe_2O_3 , MnO , CaO , Na_2O . Ca^{2+} , Na^{+} cations from the interlayer and octahedral sheets. FTIR spectroscopy showed that the acid activation decreased the intensity of the absorption bands at 915 , 875 and 836 cm^{-1} which arise from the binding modes of OH groups. NH_3 -TPD analysis showed a considerable increase in the moderate and strong Bronsted acid sites on the modified bentonite compared to the native clay. The modified bentonite was evaluated as economic and efficient heterogeneous catalyst in catalytic cracking process of two nonedible vegetable oils to obtain the corresponding biofuels at moderate processing temperature of 250 – 280°C . It was observed that the catalytic conversion was preceded under mild temperature and obtained efficient biofuels with approved physical and fuel properties according to ASTM specifications. The role of the catalyst ratio was considerable on the yield percent and the properties of the obtained biofuels. The catalytic activity-reaction mechanism was discussed based on NH_3 -TPD analysis.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

The demand for crude oil was raised rapidly due to the increase of industrialization activities around the world. The economic development led to huge demand of energy, where its major part is derived from fossil fuel, i.e., petroleum, coal and natural gas. However, the limited reserve of fossil fuel has drawn the attention of several research trends to find alternative renewable energy resources which can be used to produce energy [1]. Biofuel researches are of growing interest recently and have been strongly recommended according to the environmental regulations as alternative for petroleum fuel. Biofuels including biodiesel and biogasoline are generally blended by petroleum fuel due to their similar fuel properties with less hazardous effect on the environment [2]. Biofuels are mainly produced from renewable and sustainable sources such as edible and nonedible vegetable oils and fats. There are four primary methods to produce biofuels: catalytic hydrogenation, microemulsion, pyrolysis (thermal or catalytic) and transesterification. In catalytic hydrogenation process, unsaturated oils are converted into saturated hydrocarbons throughout consumption a large amounts of

hydrogen [3,4]. The beneficial characteristic of catalytic transesterification process is the reduction of the corrosiveness of biofuels occurred due to the contaminated free fatty acids in the raw materials, but it accompanied by the depression of the energetic values of the produced biofuels [5,6]. Pyrolysis includes treatment of oils and fats under influence of heat either from thermal agitation or microwave treatment [7–9]. Microwave heating offers a promising approach for the conversion of biomass into biofuel products with improved properties [10,11]. Comparable to these techniques, the flow catalytic cracking process consumes zero hydrogen and has the potential of converting biomass into biofuels compatible with existing petroleum products [12,13]. Flow catalytic cracking is a key process in biofuel production, which use the fossil fuels as the feedstock and breaks low economic molecules (higher molecular weights and refineries residuals) into smaller ones with high economic value [14–17]. The approved environmental regulations aim to reduce CO_2 emission according utilization of renewable energy sources and biofuels. The proportion of fuel obtained from renewable sources in the total gasoline pool and diesel pool in the European Union is supposed to be at least 10% by 2020 [18]. Thus, it is a challenge to substitute JCO for fossil fuels in the future. Catalyst is the key technology of flow catalytic cracking process; it is a target to design a suitable and effective catalyst towards high gasoline/diesel yield, high

* Corresponding author.

E-mail address: nabelnegm@hotmail.com (N.A. Negm).

octane number of gasoline and low coke formation (i.e. low CO₂ emission). The ideal catalyst is expected to include mesoporus and microporus systems. Mesoporus system enhances the accessibility of active sites when the large molecules are involved in the reaction; while microporus system enhances the selectivity of the process and aliphatic chains carbon distribution [19,20]. In this study, bentonite clay was chemically modified via reaction by hydrochloric acid to enhance its activity and produce more acidic heterogeneous catalyst. The prepared catalyst was characterized using FTIR, XRF, XRD, NH₃-TPD and N₂-adsorption desorption measurements. The prepared catalyst was evaluated as heterogeneous catalyst in catalytic cracking of two nonedible oils at moderate temperature of 250–280 °C. The catalyst activity was determined and the properties of the obtained biofuels were measured and compared to the ASTM standard specifications.

2. Materials and methods

2.1. Catalysts

Acidic bentonite was used in this study as catalysts for cracking of castor oil and jatropha oil to obtain the corresponding biofuels.

2.1.1. Preparation of modified bentonite

Modification of bentonite was performed by adding 50 g of bentonite clay to 1 M HCl (500 mL) and the medium was refluxed at 110 °C for 4 h under atmospheric pressure in a round-bottom flask equipped with a reflux condenser. The resulting clay suspension was rapidly quenched by adding 500 mL ice-cold water. The reaction matrix was then filtered, repeatedly washed with distilled water until chloride ions disappeared (using AgNO₃ as indicator) [21]. The modified bentonite then dried in an oven at 100 °C, calcined at 550 °C for 4 h and finally ground in a mortar pastel to powder form.

2.1.2. Characterization of catalysts

XRD analysis of pure bentonite sample as well as acid treated samples were carried out using a Philips PW-1050-25 diffractometer fitted with PW-1965-40 and PW-2100-00 using goniometers employing Ni-filtered Cu. Ka radiation at 500 KV and 30 mA, in order to confirm the crystal structure. The scans were taken at $2\theta = 4-80^\circ$. X-ray fluorescence (XRF) was recorded using a Bruker (S4 EXPLORER) operated at 20 mA and 50 kV. The Brunauer, Emmett, and Teller (BET) surface area of the catalysts was measured using Quanta chrome AS1Win, Quanta chrome Instrument v2.01. Prior to such measurements, all samples were perfectly degassed at 200 °C for 6 h before experiments. The specific surface area (ABET) was determined from the linear part of the adsorption curve. The pore diameter distribution was calculated from the desorption branch using BJH formula. FTIR analysis was performed using Nicolet IS-10 FTIR over the wave number 4000–400 cm⁻¹. Temperature-programmed desorption (TPD) studies were obtained using an adsorption unit Micromeritics, (Chemisorb-2705) equipped with TCD detector. 500.0 mg catalyst sample was pretreated under helium flow at 500 °C for 30 min and allowed it to cool up to 100 °C, and at this temperature the gas was switched to 5% NH₃ in helium with a flow rate of 20 mL/min for 30 min and subsequently purged with helium gas at 100 °C for 1 h to remove the physically adsorbed NH₃. NH₃-TPD curves were obtained at temperature range of 100–800 °C with a ramping rate of 10 °C/min and hold at 800 °C for 30 min. Thermogravimetric analysis (TGA) was performed using thermogravimetric analyzer (TG-DSC TAQ600).

2.2. Oils

2.2.1. Extraction of oils

Native castor and jatropha oils were obtained by cold hydraulic pressing of dried Jatropha and castor seeds. After pressing, the oils

were centrifuged to remove any solid contaminants and water, and used without further purification or treatment.

2.2.2. Oils characterization

The oils were characterized for their fatty acids profile and their physical properties. The fatty acids profile of the obtained Jatropha oil and castor oil were determined using GC-Chromatographic analysis using GC-7890A instrument equipped with DB-23 column, 60 mm × 0.25 mm, i.d. of 0.25 μm. The physical properties of the different oils were determined including the following properties: viscosity, density, specific gravity, sulfur content, pour point, cloud point, acid value, fatty acid composition, iodine value, saponification value, and oxidation stability.

2.3. Preparation of biofuels using the modified catalysts

2.3.1. Catalytic cracking process

Catalytic cracking procedures were performed as follows [22]: 150 mL of the different oils were charged in 500 mL two necked flask equipped by mechanical stirrer and distillation tail connected to a glass reservoir. Modified bentonite was added in different ratios of 0.2, 0.4, 0.6, 0.8 and 1% by weight relative to the used oil. The mixture was mixed and allowed to thermal agitation for 4 h at 280 °C. The reaction setup was connected to nitrogen flow (5 mL/min) and stirring rate at 150 rpm. The reaction products were collected and their volumes were determined. The obtained biofuels were settled in a separating funnel to separate the produced water and then centrifuged to remove any contaminated or dispersed water. The obtained vapors during the reactions were also collected to determine the efficiency of the reaction conversion.

2.3.2. Biofuel specification

The obtained biofuels from the catalytic cracking reactions of the different oils using different ratios of the modified bentonite as catalyst were characterized by determining the following properties: viscosity, density, specific gravity, carbon residue, ash content, sulfate content, pour point, flash point, and fire point according to the following specifications: ASTM D-4052 [23], ASTM D-445 [24], ASTM D-4530 [25], ASTM D-482 [26], ASTM D-4294-16 [27], ASTM D-97 [28], and ASTM D-93 [29].

2.4. Reusability of catalysts

The reusability of the used catalyst was determined by repeating the catalytic cracking reaction of the oils using one portion of the catalysts for several rounds and the properties of the obtained biofuel were determined after each round [30]. Before each experiment, the catalyst was washed by benzene and dried to remove the formed contaminations on its surface and the loss in weight was compensated. The reactions were stopped after drawback the properties of the obtained biofuels.

3. Results and discussion

3.1. Characterization of bentonite and modified bentonite

For effective examination of the impacts of acid activation by mineral acids on the crystalline structure and acidity of the bentonite clay (Montmorillonite), the following characterizations were done.

3.1.1. XRF analysis

XRF analysis of the natural bentonite and acid-activated bentonite powders are given in Table 1. It is clear that SiO₂ and Al₂O₃ are the main constituents of the bentonite, with trace amounts of other metal oxides. As it is evident from the changes in chemical composition represented in Table 1, acid activation modifies the bentonite chemistry. HCl

Download English Version:

<https://daneshyari.com/en/article/7843033>

Download Persian Version:

<https://daneshyari.com/article/7843033>

[Daneshyari.com](https://daneshyari.com)