



Catalytic cracking of vegetable oils and vacuum gasoil with commercial high alumina zeolite and halloysite nanotubes for biofuel production



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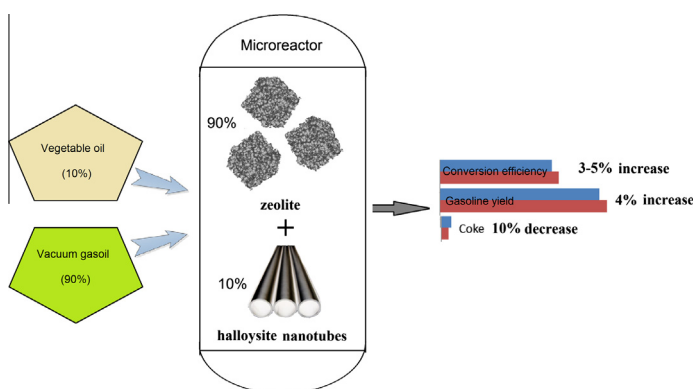
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HIGHLIGHTS

- Catalytic cracking of vegetable oils with vacuum gasoil is an effective way for biofuel production.
- Halloysite nanotube was blended with high alumina Y-zeolite to reduce coke formation.
- Gasoline yield was increased by about 4% while coking decreased by 10% due to a more efficient cracking of large molecules.
- Halloysite yielded more efficient isomerization, causing branched hydrocarbons in gasoline.

GRAPHICAL ABSTRACT



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ABSTRACT

Blends of cottonseed and sunflower oils with vacuum gasoil were catalytically cracked in fixed bed microreactor using commercial high alumina zeolite FCC catalyst and halloysite nanotubes as a catalyst. Halloysite occurs in nature as clay nanotube with large 5–20 nm inner lumen that provides cost-effective way to produce mesoporous cracking catalysts with low environmental footprint. Performance of the cracking catalyst was significantly improved in terms of gasoline yield and coke formation upon addition of halloysite. Hydrocarbon content of the gasoline fraction was analyzed in detail and efficiency of the skeletal isomerization within halloysite pores was observed to be significantly higher than with the FCC catalyst alone, increasing the yield of the branched hydrocarbons in produced gasoline and hence octane rating.

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1. Introduction

Recycled vegetable oils provide renewable source to fulfill the growing demand on diesel and gasoline in automotive industry. In the USA alone over 1.2 billion gallons of biofuel was produced from used vegetable oils recycled from industrial potato fryers,

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snack food factories and restaurants during 2014 [1]. Catalytic cracking of vegetable oils together with vacuum gasoil offers one of the most effective routes for biofuel production as it does not require additional infrastructure to be build. In a typical process 5–10% of vegetable oil is mixed with vacuum gasoil (VGO) and cracked in fluid catalytic cracking (FCC) reactors [2,3]. Catalytic cracking of vacuum gasoil with 5% Sunflower oil was found to be beneficial for increasing gasoline yield to above 50%, whereas cracking vacuum gasoil alone yielded little over 43% of gasoline [3]. Addition of up to 10% palm oil into VGO did not affect the hydrogen consumption reactions and reduced hydrodesulfurization activation energy [2]. Several studies reported catalytic cracking of pure vegetable oils, like cottonseed [4], sunflower [3] and palm oils [5,6] with the yields of gasoline being about 30% in all the cases.

However, feeds with vegetable oils increase coke formation on the catalyst. Large molecules existing in vegetable oils cannot easily penetrate deep within smaller 1–2 nm pores of the catalyst, and therefore cracking effect is limited to the relatively small reaction sites at the catalyst surface. These sites are quickly deactivated by coke formation, causing the total loss of the catalytic activity. The most effective solution to this problem is the introduction larger diameter pores within the catalyst.

In this work we attempted to discover the potential of blending halloysite nanotubes with large lumen diameter into commercial FCC catalyst to introduce mesoporous cracking catalyst. Halloysite nanotubes occur in nature due to hydrothermal alteration of various clay minerals and comprised of submicron size tubes with up to 20 nm diameter inner lumen diameter [7,8]. Hydroxyl groups existing in inner octahedral alumina surfaces of HNT create extremely reactive sites for catalytic cracking [9]. Pure halloysite has been utilized by petroleum industry as a cracking catalyst before the introduction of synthetic zeolites [10]. Nowadays, it is extensively studied as additives for polymer nanocomposites and for controlled drug delivery [11–13]. In our preliminary work we have shown that the utilization of halloysite nanotubes along with high silica Y-zeolite was very efficient in increasing the gasoline yield and lowering the coke formation on the catalyst during catalytic cracking of the vacuum gasoil and cottonseed oil [14]. To best of our knowledge this is the first detailed study with halloysite nanotubes for vegetable oil cracking.

Blend of cottonseed and sunflower oils with vacuum gasoil has been cracked in fixed bed FCC microreactor using commercial high alumina X-zeolite catalyst and halloysite nanotubes for demonstration of its potential for fuel production from renewable resources. Cracking temperature and feed rate were optimized using design of experiments. Composition of the reaction products was analyzed in detail and perspectives of adding halloysite clay nanotubes into commercial FCC catalysts were discussed with emphasis on production of bio-gasoline.

2. Materials and methods

2.1. Materials

Halloysite nanotubes (HNT) were obtained from Imerys Corporation and used as received. Petroleum FCC catalyst with trade name Omnikat-210P (Si/Al = 1) was obtained from H. Aliyev petrochemical refinery (Baku, Azerbaijan) and used as received (later will be denoted as Omnikat). Non-refined sunflower oil (SFO) and cottonseed oil (CSO) were obtained from Azersun Holding Ltd (Azerbaijan). Vacuum gasoil (VGO) was obtained from H. Aliyev petrochemical refinery (Azerbaijan). Pyridine was purchased from Sigma Aldrich.

2.2. Characterization

HNT and Omnikat catalysts were characterized by SEM (Hitachi S 4800 FE-SEM) and TEM (Zeiss EM 912). Elemental composition of the halloysite was determined by SEM-EDX elemental analysis at 25 kV acceleration voltage. Trace elements were detected by ICP-AES spectrometer (PerkinElmer, Optima 2100 DV). Phase composition has been analyzed by X-ray powder diffraction using Cu K α radiation (Bruker, D8 Discover). HNT particle size distribution was determined by dynamic light scattering (Brookhaven Inst). Composition and physical properties of the Omnikat were provided by the supplier. Molecular weight distribution of the vegetable oils and vacuum gasoil were determined using high performance liquid chromatography (Kovo Co, Czech Republic) with RI detector. Chromatographic separations were achieved in 150 mm column (diameter: 3.3 mm) packed with 7- μ m Separon SGX C₁₈ sorbent at 20 °C using dimethylformamide as eluent. Compositions of vegetable oils, vacuum gasoil as well as cracking byproducts were analyzed using gas chromatography (Autosystem XL, Perkin Elmer), FT-IR (InfraLUM, FT-02) and NMR (TESLA, BS-487C) spectrometers. Octane numbers were calculated based on compositions of the gasoline fractions obtained from gas chromatograph (Autosystem XL, Perkin Elmer). Chromatographic separations were achieved using helium gas in Zebron ZB-1 capillary column coated with dimethyl polysiloxane polymer as stationary phase. Densities of the petroleum distillates, cracking byproducts and oils were detected using aerometer (ANT-1, length-500 mm, diameter-22 mm). Distillation fractions were determined using micro distillation apparatus by ASTM D 7345-08 method.

2.2.1. Catalyst surface acidity and area

Surface acidity of the catalysts was tested using pyridine adsorption method as described by Jacobs and Heylen [15]. Briefly catalyst samples were heated at 650 °C for 1 h followed by exposure to the pyridine vapors at 20 °C for 4 h. Samples were heated at 20–700 °C range using STA 449 F3 thermal analyzer (Netzsch, Germany) and weight loss due to the pyridine desorption was recorded.

Specific surface areas of the catalysts were analyzed by Nitrogen adsorption–desorption BET isotherms (NOVA-2200, Quantochrome Inst). About 0.2 g of the catalyst was heated at 300 °C and under vacuum for 1 h to degas the entrapped gases within the pores before each analysis. Then samples were analyzed for nitrogen gas adsorption–desorption. Specific surface area was measured using seven point BET analysis, while pore size distribution was obtained using Monte-Carlo DFT method.

2.2.2. Iodine number oils

About 0.5 g of oil was dissolved in 10 mL of chloroform. 10 mL of iodine solution in ethanol (2.5% by weight) was slowly added and resultant solution is left in dark for 1 hour. Then 170 mL of 2.3% aqueous KI solution is added to the mixture and titrated with 0.1 M sodium thiosulfate solution. Similar procedure was applied to the blank chloroform (without sample). Iodine number was determined as: $1.29 * (V_{\text{sample}} - V_{\text{blank}}) * C/m$, where V (mL) and C (M) are the volume and concentration of the sodiumthiosulfate solution and m (g) is the mass of the oil.

2.2.3. Acid number of oils

About 50 mL of 85% ethanol–water solution is boiled and titrated with 0.05 M ethanolic potassium hydroxide solution using phenolphthazine indicator. Then 5 g of sample was added to the solution and titrated using KOH solution. Acid number was determined using formula: $K = 56 * V * C/m$, where K is the amount of

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