Modification of Ni/Zn-HZSM-5 Double Promoted Catalyst for Biofuel Production from Cerbera Manghas Oil

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Abstract

Renewable energy sources have been necessary recently because the use of fossil energy sources is no longer preferable for the future. This is caused by its scarcity and CO2 emission that is not good for the environment. One of the other promising alternatives is biofuel. Biofuel is an environment-friendly renewable energy source. This research aims to study the effect of Ni/Zn-HZSM-5 double promoted catalyst modification and hydrocracking temperature of Cerbera manghas oil on biofuels selectivity. The variables of the catalysts were Ni/Zn ratio and metal content/total catalyst mass ratio. The maximum selectivity of gasoline and kerosene were 52.42% at 350 °C and 86.72% at 400 °C, respectively. These results were reached in the use of Ni/Zn-HZSM-5 catalyst with Ni/Zn as 1:1 and 2 wt% metals content. Ni and Zn were recommended to be impregnated to HZSM-5 catalyst in biofuel production.

Introduction

Fossil energy resources are still commonly used nowadays, nevertheless they affect the environment badly because of their emission. Additionally, the fossil energy resources become scarce and they are unrenewable. This phenomenon leads to deficiency of fossil energy resources, such as petroleum. Based on the consumption of petroleum data, it can be estimated that petroleum will no longer be used in 50 years later. The evidences of this case are the increasing price in petroleum market and also the instability in its international trade. Hence, a new alternative renewable energy resource is needed to be found and developed furthermore.

Before using fossil energy resources, humans have used biomass as energy resources, such as firewood. Later humans found petroleum so that biomass energy resources became less useful. Recently, biomass energy resources have been considered to be substitution of petroleum and other fossil resources. Modern development of biomass shows that environment-friendly fuels can be produced from biomass through several chemical processes, such as biofuel and biodiesel.

Biofuel is fuel produced from biomass in liquid or gas form by chemical conversion. Since biomass energy resources have been abundant, cheap, renewable, and low emission-contributed, biofuel is promising to substitute fossil resources. Biodiesel is one of biofuels that is solar-like. Biodiesel also produces low carbon dioxide and low sulphur emission. Biodiesel also has low smoke number and high octane number, so that it is beneficial to be produced.

The production of biofuel using zeolite-based catalyst in hydrocracking process has been widely studied. But it was the first time for Cerbera manghas oil to be studied as raw material of biofuel. HZSM-5 zeolite has good performance in cracking process. Zeolite has advantages in terms of providing main surface area and active site. They control the activity and selectivity of the catalyst. On the other hand, this catalyst has a disadvantage, i.e., the selectivity is low. The catalyst can be improved by Ni and Zn impregnation into HZSM-5 catalyst. The results showed that an increase in gasoline selectivity caused a decrease in kerosene and diesel yield. The use of these double promoted catalysts gives the highest selectivity of 52.42% gasoline and 86.72 % kerosene. The use of Ni and Zn is assumed to give better selectivity because noble metals are good to be used as promoter.

Impregnation of Ni and Zn have been selected because they have a lot of electrons which are easily delocalized. It can be used to influence the reaction, especially to break covalent bonds such as cracking. This research aims to study the effect of temperature and Ni and Zn impregnation into HZSM-5 catalyst on the catalytic properties. Thus, two kinds of variables are set for the catalyst, i.e. Ni/Zn mass ratio and metal content/total catalyst mass ratio. The formation of biofuel from Cerbera manghas oil by hydrocracking process was carried out in a batch reactor. The reaction temperature was set from 300°C to 400 °C, with the increase of 25 °C. The success of this research...
will give a very important contribution to the process of the production of cracking catalyst and proper operating temperature in the production of biofuel.

Methodology

The raw material for hydrocracking process was Cerbera manghas oil. Cerbera manghas oil was extracted from Cerbera manghas fruit by compression method. Later, Cerbera manghas oil composition was analysed using Gas Chromatography-Mass Spectrometry method. The catalyst support used was a synthetic zeolite. The raw materials for making Ni/Zn-HZSM-5 catalyst were NiCl₂·6H₂O, ZnSO₄·7H₂O, NH₄Cl and distilled water. Other materials were nitrogen gas and hydrogen gas.

Preparation of Catalyst

NaZSM-5 catalyst was converted to HZSM-5 by ion exchange process. The NH₄Cl solution was added to NaZSM-5 catalyst with ratio of 1:10 until three times, each of the runs takes time up to 12 hours. After NH₄ZSM-5 was formed, the catalyst was calcined for 5 hours at temperature of 550 °C [1]. The calcination process released NH₃ vapour so that HZSM-5 was formed [2]. HZSM-5 was later impregnated by the solution of nickel oxide and zinc sulphate [3]. Ni/Zn-HZSM-5 catalysts were dried in an oven at 110 °C for 14 hours, then they were oxidized at temperature of 550 °C for 4 hours and reduced at temperature of 450 °C for 3 hours, and finally they were cooled in a desiccator [4].

Hydrocracking Process

Hydrocracking was done in a batch reactor with a diameter of 7.5 cm, 20 cm long and filled with 0.6 gram of catalyst. Figure 1 shows the equipment used to produce biofuel from Cerbera manghas oil by hydrocracking process. After oxygen purging process using nitrogen gas was done, Cerbera manghas oil was streamed into the reactor. Hydrogen gas was also streamed into the reactor to start hydrocracking process [5]. The reactor temperature was set from 300 °C to 400 °C with increase of 25 °C. Biofuel products were analysed by FID Gas Chromatography method. The operating conditions of gas chromatography, i.e., column temperature of 50-250 °C, flow rate of nitrogen gas in the GC of 30 ml/min, temperature rise of 5 °C·min⁻¹, initial time of 2 min, detector temperature of 250 °C, injector temperature of 250 °C. Chromatogram of biofuel was compared to the chromatogram of gasoline, kerosene and diesel commercial based on retention time similarity.

Results and Discussion

Cerbera manghas oil composition

Chromatogram of Cerbera manghas oil is shown in Figure 2. This chromatogram is resulted from GCMS analysis. from Figure 2, it is known that the main constituents of Cerbera manghas oil are oleic acid of 73.47%, palmitic acid of 20.29%, margaric acid of 4.29% and tridecylic acid of 1.95%.

Characterization of Catalyst
The impregnated catalysts were analysed using X-Ray Diffraction method. XRD was used to make sure the type of the catalysts. Figure 3 shows the diffractogram of Ni/Zn-HZSM-5 with Ni/Zn as 1:1 and 2 wt% metal content as a sample. The existence of Ni, Zn and HZSM-5 in the catalysts can be determined. The results show that Ni, Zn and HZSM-5 exist in the catalyst. Henceforth, the catalyst was Ni/Zn-HZSM-5.

![Figure 2. Chromatogram of Cerbera manghas oil](image)

![Figure 3. Diffractogram of Ni/Zn-HZSM-5 catalyst with Ni/Zn as 1:1 and 2 wt% metal content](image)

### Biofuels Analysis Results

Biofuels produced were analysed using Gas Chromatography method. The main constituents of biofuels are gasoline, kerosene and solar. Figure 4 and 5 shows the results of biofuels analysis.

![Figure 4. Graph of Selectivity vs. Temperature for Ni/Zn as 1:1 and metal content of 2wt%](image)
Figure 5. Graph of Selectivity vs. Temperature for Ni/Zn as 1:1 and metal content of 4wt%

The highest selectivity of gasoline was 52.42% at temperature of 350 °C using 1:1 Ni/Zn ratio and 2 wt% metal content catalyst. The highest selectivity of kerosene was 86.72% at temperature of 400 °C using same catalyst. The best temperature for the hydrocracking was in range of 350-400 °C. Ni/Zn-HZSM-5 was recommended for biofuel production by hydrocracking process.

Conclusions

It is recommended to synthesize Ni/Zn-HZSM-5 catalyst with Ni/Zn ratio as 1:1 and 2 wt% metal content since it gave highest selectivity of gasoline and kerosene. The highest selectivity of gasoline and kerosene was 52.42% and 86.72% respectively. The ideal hydrocracking temperature range was 350-400 °C. Further research that can be developed is hydrocracking of vegetable oil with more catalyst and higher temperature.

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