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Effects of Temperature and Natural Zeolite/Spirituous Ratio to the Yield of Gasoline from Spirituous at Two Stages Fixed Bed Reactor Using Iron Sulfate as the Catalyst

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Abstract – Generally, gasoline is produced abundantly from crude petroleum refinery. Its compound contains paraffins, naphthenes, olefins and aromatics which the amount of carbon atoms from C4 to C11. The decreasing of petroleum reservoirs will influence the gasoline reservoirs as the famous fuel so the synthetic gasoline with high quality is needed to obstruct the rate of crude petroleum exploration in Indonesia. The objective of this research is how to produce gasoline from bagasse as the alternative fuel using iron sulfate as the catalyst at proper temperature. Reaction process occurred in the fixed bed reactor with two zones, first zone was thermal cracking and the second one is catalytic cracking. The effect of various temperature from 2000°C to 3000°C and effect of methanol concentration as the solvent varied from 10% to 30% were observed in this research while it occurred at constant solvent volume, mass of bagasse, and mass of catalyst. The gasoline product of this research has better characteristic than conventional gasoline from Pertamina with octane number 90 and heating value 19,872 Btu/lb while the highest yield was obtained at temperature 2500°C, solvent concentration 20% for 100 minutes. The gasoline was analyzed in Laboratory of Pertamina UP III Plaju, Palembang – South Sumatera, Indonesia.

Keywords – Bagasse, gasoline, hydrocarbons, thermal cracking, catalytic cracking.

1. INTRODUCTION

Experts had developed many experiments to get fuel from bagasse. In spite of the process to produce methanol as an intermediate compound before the production of biofuel, there are also processes that were invented to produce biofuel directly by using methanol as raw material. Further research is needed to get the competitive process. Based on the literature review, the process to produce gasoline from methanol is Methanol to Gasoline process or known as MTG process. MTG process was developed by Mobil’s company in 1975, by converting methanol using catalyst ZSM-5 in fluidized bed reactor at 415°C and 217 kPa[1,2]. It produced dimethyl ether as an intermediate compound then changed into olefins, paraffines (alkanes), and aromatic, the conversion is about 34.4%.

The study made by Chang (1978) used ZSM-5 zeolite in fluidized bed reactor at 450°C and 221 kPa.

Carbon monoxide compound as free radicals will break the methyl groups of methanol and methyl polymerization. But the difficulty to produce free radicals from carbon monoxide compound became the main problem in this research and hydrocarbon as products still contain impurities. As the results, the yield reached 35% [3].

Meisel and Meyer (1978) produced the alliance of propane, butane and iso-butane with very high yield from MTG process. This process was at fluidized bed reactor, 430°C, 219 kPa, and ZSM-5 zeolite[4]. Jayamurthy (1995) made the innovation of MTG process by using ZSM-5 of catalyst that is known as Surface Reaction Temperature Program (TPSR) technique. This technique observed two steps of the process[4]. First, the dehydration of methanol generating oxonium ion and oxonium methyl is in CSTR reactor at 420°C, 30 kg/cm². Second, the polymerization of oxonium methyl to form gasoline compounds in fluidized bed reactor for 4.5 hours of the resident time. This process produced the yields of gasoline about 40%. A long resident time will influence the needs of energy and cost.

Based on this literature review, the weakness of the previous researches is caused by the high utilization of energy, the non-optimize of heat transfer, long residence time, the low percentages of gasoline product (especially Meisel and Meyer research) and the high cost. From these weaknesses, the main factor as promoter is the reactor type that can give good effect to heat and mass transfer process and ZSM-5 zeolite as catalyst that is very sensitive to the operational condition.

Based on those weaknesses, the problem of this research is how to obtain high yield of biofuel and find the proper temperature by using cheap zeolite as the catalyst in a simple reactor[5].
Chang extended the model using the following autocatalytic over ZSM-5. 2 discovered that the oxygenate disappearance is

Zeolite are water-containing crystalline, porous 2 can add : CH

ethers, which can dehydrate to form olefins and which

insertion into C–H bonds, forming higher alcohols or

intermediates. The intermediates then undergo sp

concerted bimolecular process involving carbonoid

formation from methanol–DME. They have supposed a

Silvestri have postulated a mechanism of hydrocarbon

studies of methanol conversion to gasoline. Chang and

methanol–DME disappearance in process and pilot plant

lumped kinetic model which described the rate of

equilibrium. Thus the equilibrium oxygenate mixture

subsequent olefin-forming step, and is essentially at

range of temperatures, pressures and feed compositions. It was found in the

1970s that over a wide range of conversions the initial

step of ether formation is much more rapid than the

subsequent olefin-forming step, and is essentially at

equilibrium. Thus the equilibrium oxygenate mixture

can be conveniently treated as a single kinetic

order in oxygenates.

(4) Olefins can be treated as a single kinetic

species.

(5) Disappearance of olefins is first order in olefins.

In the range between 115 and 200°C the kinetics

of methanol conversion followed the rate law

$$r = k_{\text{rate}} / (1 + k_{\text{rate}} P_{\text{methanol}})$$

(1)

Zeolite are water-containing crystalline, porous

aluminosilicates composed of SiO$_4$ and AlO$_4$ edge-

sharing tetrahedral interlinked through common oxygen

atoms giving rise to three-dimensional networks of

channels, cages and rings. These structural attributes

account for the different physical properties of

individual zeolites. Since silicon is balanced by four

surrounding oxygen atoms, in a pure silicate, a zeolite is

charge neutral. However, when one substitutes silicon

atoms by aluminum the charge balance of the network is

upset creating strong Brønsted acid sites. Zeolites are

thus very good solid-acid catalysts. Two important

industrially relevant processes involving zeolites include

the conversion of methanol to gasoline (MTG) and

methanol to olefin (MTO) which were developed by


The major products of the MTG reaction are

hydrocarbons and water. Hence, any unconverted

methanol will dissolve into the water phase and recovery

of this methanol would entail adding a distillation step to

process the very dilute water phase. Thus, essentially

complete conversion of methanol is sought [11]. Finally,

the yield that obtained in the research was calculated as

the formulation below:

$$\text{Yield} = \frac{\text{desired product (gasoline)}}{\text{reactant input (methanol)}} \times 100$$

(2)

3. EXPERIMENTAL

Type of reactor will influence the quality and quantity of

reaction because the type of reactor can influence

hydrodynamics and thermodynamics process in the

reactor. These processes are connected to the mass and

heat transfer that will affect the conversion of reaction.

The catalyst fluidization has few disadvantages such as

the need of the minimum velocity of fluidization.

This research used different types of reactor and

zeolite than the previous one. It used one unit of reactor

which was completed with the other equipments to

increase the operation and process such as reactor,

extruder, condenser, separator, pump, valve, check

valve, heater, TIC, PI, flow meter, tank, and pipe. The

description of the process is figured out at Fig.1.

![Fig. 1. Scheme of Processing of Gasoline Productions](image)

The feeds were spirituous, hydrogen which is in

gas phase, and natural zeolite. Natural zeolite was from

Lampung, Indonesia. It contained 85% Klinoptilolit,

$\text{H}_2\text{[Al}_2\text{Si}_3\text{O}_8\text{]}\cdot\text{74 H}_2\text{O}$.

The innovation of this research varied the reaction

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temperature; 250 °C, 300 °C, 350 °C and 400 °C, the weight of zeolite are 300 gr, 400 gr and 500 gr, and the reaction time in the isothermal reactor for 1 hours, 2 hours and 3 hours.

The process started from zeolite calcination at 400 °C. After the calcinations process, zeolite were put into the reactor for 300 gr (varied from 300 to 500 gr). All the valves were closed, and then valve for spirituous feed (V-01) was opened. Spirituous was pumped (P-01) into the reactor through V-01 for 2.5 L. The heater was turned on to obtain the temperature of reactor for 250 °C (varied from 250 °C to 400 ºC). After the temperature was in set point, V-03 was opened to flow hydrogen gas for achieving absolute pressure for 5 kg/cm². While the process was taking place, V-02 was opened to recycle the vapor product. The reaction occurred for 1 hour (1 hour to 3 hours). After the reaction time (for example 1 hour), the reaction process was stopped by changing the temperature settling at 30 °C, while the hydrogen gas flow (V-01) was closed. If the temperature was 30 °C, heater was turned off and all the electric current were switched off. All the products from the inside of reactor was taken by opening valve (V-05) for separation between gasoline and water. The crude gasoline from the process was distillated by distillation process in a laboratory scale to obtain pure gasoline. Then the gasoline product could be analyzed in laboratory.

4. RESULTS AND DISCUSSION

The process variables which were observed in this research consist of the operational temperature, and the ratio of natural zeolite/spirituous. As the results, the conversion of spirituous to gasoline in the fixed bed reactor using recycled product from bottom reactor and the addition of zeolite gave prospective condition at ratio of zeolite/spirituous as 0.13 (v/v) and 0.17 (v/v), the yield is 55.97% and 57.12%.

Fig. 2. Effect of Temperature and Zeolite/Spirituous Ratio to the Yield of Gasoline for 3 Hours

Fig. 3. Effect of Temperature and Zeolite/Spirituous Ratio to the Yield of Gasoline for 2 Hours

The increasing ratio of zeolite/spirituous 0.03 (v/v) under the prospective condition affected the yields which were achieved about 56.76%. The effect ratio of zeolite gave significant effects at high temperature (350 °C and 400 °C), and this condition caused by the mechanism of Brønsted active center in catalyzing reaction with hydrocarbon synthesis mechanism reaction worked well. Besides that, zeolite gave the protons to methanol to form active carbonium ion. This reaction happened at endothermic condition so the increasing ratio of natural zeolite/spirituous would increase the activated energy so the constant of reaction equilibrium and the reaction rate of spirituous conversion into gasoline will be higher significantly. The results of this research were compared with the characteristics of gasoline that was produced by Pertamina (Indonesia State Owner Enterprise).

4. CONCLUSION

This research results in the proportional condition to convert spirituous into gasoline at 350 °C, the reaction time for 3 hours, the ratio of zeolite/spirituous is 0.17 (V/V), and the yield achieved is 56.69%. Gasoline product from this research gives better characteristics than Pertamina that is shown by the octane number and the heat value. The PONA composition that is dominated by hydrocarbon groups, such as 64.18% of paraffins, 24.01% of olefins, 10.02% of aromatics, and 0.55% of Naphthenes, add the peculiarity of this research.

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