Activity assays of calcinated sarulla natural zeolite (snz-cal) in catalytic hydrocracking rubber seed oil

J L Sihombing1,2, S Gea2*, A Kembaren1, Sabani3, A N Pulungan1, A A Wibowo1, B Wirjosentono2

1 Department of Chemistry, Universitas Negeri Medan, Medan, Indonesia
2 Department of Chemistry, Universitas Sumatera Utara, Medan, Indonesia
3 Department of Physics, State Universitas Medan, Medan, Indonesia

*E-mail: s.gea@usu.ac.id

Abstract. The aim of this research was to produce a fuel fraction from catalytic hydrocracking process using Calcinated Sarulla Natural Zeolite (SNZ-Cal) as catalyst and Rubber seed oil as a feed. The methods used were the preparation and calcination of Sarulla Natural Zeolite (SNZ-Cal), catalytic hydrocracking using SNZ-Cal at 400 °C, 450°C and 500 °C with a variation of catalyst and rubber seed oil comprising of 1:2, 1:4 and 1:6 respectively. Finally, the liquid product was analyzed with Gas Chromatography. The result of this research shows that the optimum liquid product was treated at 400 °C (1:2), 450 °C (1:6) and 500 °C (1:2) were 18.00%, 64.60% and 80.60% respectively. Moreover, the highest selectivity of bio-gasoline occurred at 400 °C (1:2), 450 °C (1:2) and 500 °C (1:6) which were 78.16%, 76.46% and 82.57% consecutively. In essence, each temperature depicted a different amount of bio-gasoline with the highest result at 500 °C (1:6).

1. Introduction
An energy crisis causes a human to change their mindset to intensify research related to renewable energy. Biofuel is a liquid, solid and gas product from the conversion of biology materials which is abundant and affordable. One of the raw material which can be used as a sources is vegetables oil for both edible and non-edible one. Rubber tree produce a large volume of rubber seed in which 75% of it did not use and became a waste. Indonesia is one of countries which have a large area of rubber plantation around 3,672 Million Hectares [1]. This plantation can produce a rubber seed of about 1500 kg/ha/year which potential to become a source of bio-fuel. Rubber seed oil contains 40-50% oil [2], 92.22% dried materials, 19.20% protein, 6.00% crude fiber [3] and a large content of it consist linoleic and oleic acid of around 39.657% and 23.524% respectively [4].

Rubber seed oil can be converted to bio-fuel using cracking system comprising thermal cracking, catalytic cracking, and catalytic hydrocracking [5]. Cracking is a process to cut hydrocarbon chain from high-weight molecules to be a low-weight molecule through the cutting of carbon chain (C-C) [6]. Thermal cracking or pyrolysis is a reaction in terms of cutting hydrocarbon chain using high temperature and create a free radical to form a final product. Furthermore, catalytic cracking is a process to cut hydrocarbon chain using material catalyst to accelerate reaction until reaching the stability and producing a liquid product through mechanism of ion carbanion forming. Moreover, catalytic hydrocracking is a process to cut hydrocarbon chain using material catalyst and hydrogen...
gases [7]. In the first step of this reaction, sample is heated and mixed with hydrogen gas after which it send to the first reactor, where catalyst converts sulfur and nitrogen to be hydrogen sulfide and ammonia. In the final step, a gas product is liquified to be liquid product. In catalytic hydrocracking, there are tree types of catalyst are used in the process which are metal, nonmetal and inserted metal such as zeolite with nickel metal.

In Indonesia, the natural zeolite deposit is quite large and its purity is quite high. Zeolite minerals are generally obtained in tuffs formed from volcanic dust sedimentation that has undergone alteration, diagenesis and hydrothermal processes. [8]. Indonesia is in the area of a series of volcanoes ranging from Sumatra, Java, Nusa Tenggara, to Sulawesi. One product of a volcano of tuff is widespread following the path of a volcano and some or all of it has undergone diagenesis into a zeolite. Therefore, geologically Indonesia has great potential to produce zeolites such as those found in North Sumaera, Lampung, West Java, Central Java, East Java, East Nusa Tenggara and Sulawesi with resources of 447,490,160 tons [9].

According to data from the National Non-Metal Mineral Resource in 2008, there are zeolites in Simangumber Village, Pahae Jae District, North Tapanuli Regency, North Sumatra Province with 16,200,000 tons. Therefore, there is Sarulla natural zeolite in Indonesia which indicates the composition of SiO$_2$ and Al$_2$O$_3$ with 80.3% and 14.19%, respectively [10]. Based on the physical and chemical properties of the zeolite, the zeolite can be utilized as an absorber, ion exchanger, molecular filter and catalyst [11].

2. Materials and methods
2.1. Materials
The materials used in this research were aquabidest, Sarulla Natural Zeolite (SNZ), HCl (c) Nitrogen gas, Hydrogen gas, glasswall, AgNO$_3$ and rubber seed oil. These materials were obtained from Department of Chemistry Laboratory at State University of Medan.

2.2. Procedure
2.2.1. Preparation of Sarulla Natural Zeolite – Calcination (SNZ-Cal). Sarulla natural zeolite (SNZ) was crushed and smoothed with 100 mesh sieve. Then, it was soaked in aquabidest for overnight at room temperature. After that, SNZ was filtered and dried at 120 °C. The dried SNZ was refluxed at 90 °C using 3M HCl for 30 minutes. Then, SNZ was cleaned using aquabidest to eliminate the excess of HCl until reached a neutral (pH – 7). Furthermore, the SNZ was dried at 120 °C for around 3 hours. Finally, the SNZ was calcinated using a nitrogen gas at 500 °C for about 2 hours and induced with hydrogen gas for reduction process. Finally, calcinated sarulla natural zeolite (SNZ-Cal) was produced.

2.2.2. Activity Test of SNZ-Cal. The activity assay of SNZ-Cal in hydrocracking system using rubber seed oil as a feed was conducted to know the ability of catalyst to crack a hydrocarbon chain to be a light fuel fraction. The process was performed in various temperature at 400 °C, 450 °C and 500 °C and with the ratio of catalyst and rubber seed oil were 1:2, 1:4 and 1:6 respectively. The process was conducted for 3 hours. Then, the liquid product was analyzed using gas chromatography.

3. Result and discussion
The activity of the catalyst can be seen from the conversion percentage of the liquid product. In Figure 1, it can be seen that the highest conversion percentage of liquid product is owned by SNZ-Cal
catalyst at 400 °C (1:2) and followed by SNZ-Cal catalyst treated at 450 °C (1:6) and 500 °C (1:2) with total conversion of 18.00% 64.60% and 80.60%, respectively.

![Conversion of catalytic hydrocracking using SNZ-Cal](image)

**Figure 1** Conversion of catalytic hydrocracking using SNZ-Cal

In the Hydrocracking process, it was only producing liquid and gas but also cokes. Where according to Alenazey et al (2009), coke formation process begins with the process of chemisorption of hydrocarbon compounds then dehydrogenation of hydrocarbons forming an unsaturated aliphatic compound on the surface of the solid which is then forwarded with dehydropolimerization to form a coke deposit [12].

The catalysts that already play a role in a chemical reaction, during which the process may involve organic compounds and form carbon residues on the surface of the catalyst [13]. In the cracking process used catalysts with acidic carrier (solid acid) have a greater tendency to produce coke than non-acid carrier. Zeolite is a very acidic type of carrier, so the chances of coke formation are very large. The formation of coke will result (deactivate) the ability of the catalyst so as to catalyze the reaction will decrease. This is because the coke deposited inside the catalyst will cover the active site [14].

Selectivity describes the tendency of a catalyst to produce a particular component. In the Catalytic Hydrocracking reaction of rubber seed oil, it is expected to produce a large fraction of gasoline. The gasoline fraction is a hydrocarbon compound with the number of C5-C11 atoms while the diesel has an amount of C12-C20 atoms and heavy oil C>20. Figure 2 shows the hydrocracking GC of rubber seed oil at 500 °C. Based on the figure it can be seen that Atom C12 is in retention time of 13.746 min which indicates that peak that appeared at retention time before 13.757 min is gasoline fraction. While C20 is in retention time of 22.664 min, so it can be seen that diesel fraction occurs between 13.757 min and 22.664 min. While the fractions that occurred at the retention time above 22.664 are heavy oil fraction.
The temperature and number of catalysts are one of the factors that can increase the rate of reaction. In the catalytic reaction occurring on the solid surface, the reaction rate will be directly proportional to the amount of reactant adsorbed. Therefore, to obtain the maximum conversion product, the reaction temperature optimization process must be conducted and the number of catalysts variation as well, as displayed in Figure 3.

Based on Figure 3, it can be seen that the increase in temperature and the number of catalysts have an effect on the selectivity of the catalyst on the gasoline fraction. Increasing the temperature and the number of catalysts show a significant trend toward the percentage of the gasoline fraction where the
higher the temperature and the amount of catalyst, the greater the gasoline fraction produced. It can be explained that the higher the reaction temperature, the greater the available energy for the vibration, rotation and translation of the reactant molecules, the greater the possibility of collisions between reactants. This leads to a greater chance of reactions, resulting in the conversion of liquid products and the selectivity of catalysts as well. Likewise, with the number of catalysts, the greater the amount of catalyst used, the greater the chance of reactants to contact and react with the catalyst so that the catalyst selectivity to the gasoline fraction will be greater (figure 4). However, on the catalyst which actually decreases the liquid product with increasing temperature of reaction, this is because at high temperature cause the happening of very active movement of reactant. This highly active movement resulted in the obstacles of reactivating the active side of the reactant molecule with the active site of the catalyst, resulting in mass transfer restrictions.

![Figure 4. The percentage of bio-gasoline fraction](image)

Based on Figure 3 and 4, the optimal selectivity happened at temperature 400 °C with the ratio of 1:2 catalysts with gas fraction equals to 78.16%. The best selectivity is at 450 °C occurred in 1:2 catalyst variation with the amount of gasoline fraction of 76.46% and at the temperature of 500 °C, the best selectivity occurred on the variation of catalyst 1:6 with the total gasoline fraction of 82.57%.

4. Conclusion
Variation of temperature and number of catalyst affect the product which have different result in each treatment. The pattern shows that at 500 °C it will give a significant result in a total conversion which gave more than 50% among three variation of temperatures. However, the highest selectivity product of bio-gasoline is identified at temperature of 400 °C which are 70.95% (1:6), 67.56% (1:4) and 78.16% (1:2). Moreover, based on variation of weight catalyst, the trend shows that variation of 1:2 have a significant result comprising in total conversion and selectivity in bio-gasoline.

Acknowledgement
The Author would like to address a gratitude to General Directorate of The Higher Education for the research funding via “Scheme Hibah Penelitian Terapan Pendanaan 2017” and also for the Research Institution of State University of Medan.
References
[1] Directorate General of Estate Crops 2017 *Three Crop Estate Statistics of Indonesia* (Ministry of Agriculture)
[2] Setyawardhani D A et al 2010 *Seminar Rekayasa Kimia dan Proses* (Semarang: Indonesia)
[3] Wizna N et al 2000 *Pemanfaatan Produk Fermentasi Biji Karet (Hevea brasiliensis) dengan Rhizopus oligorpus dalam Ransum Syam Noiler* (Bogor: Puslitbang)
[4] Wibowo A A et al 2014 *Proc.1st Int. Seminar on Trends in Science and Science Education* (Medan: Indonesia) p 132
[5] Pulungan A N et al 2014 *The first International Seminar on Trend in Science and Science Education, State University of Medan* (Medan: Indonesia) p 148
[6] Trisunaryanti W et al 2013 *Journal of Chemistry and Chemical Engineering* 7 175
[7] Ghosh U et al 2015 *Chemical and Process Engineering Research* 34 51
[8] Kusdanto K 2008 *Jurnal Zeolit Indonesia* 7 78
[9] Trisunaryant W et al 1996 *Journal of Japan Institute of Petroleum* 39 20
[10] Gultom F et al 2016 *Procedia Chemistry* 19 1007
[11] Mgbemere H E et al 2017 *International Research Journal of Environmental Science* 10 45
[12] Alenazey F et al 2009 *Catalyst. Communication* 10 406
[13] Hughes R 1984 *Deactivation of Catalyst* (London: Academic Press Inc.)
[14] Gates B C et al 1995 *Chemistry of Catalytic Proses* (New York: McGraw-Hill Book Company)