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STUDY OF RUBBER SEED OILS HYDROCRACKING INTO BIOGASOLINE AND DIESEL FRACTION OVER THE COMBINATION Y-ZEOLITE AND Ni CATALYST

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ABSTRACT

The purpose of this research is producing fuel fraction which is equal with gasoline by MEFA Catalytic Hydrocracking process of rubber seed oil. The research will be done through these following phases: 1) Rubber seed oil production, 2) Preparation and Characterization of ZY and Ni/ZY catalysts, 3) Esterification and Transesterification, and 4) Catalytic Hydrocracking process of MEFA to obtain equal fractions of gasoline fuels by Fixed Bed reactor systems at 400°C, 450°C, and 500°C with catalyst : decoy ratio 1:2, 1:4, 1:6 (b/b). The result of characterization shows ZY and Ni/ZY catalyst have specific surface area which are 342.651 m²/g and 539 m²/g, pore volume 2.362 x 10⁻¹ cc/g and 3.213.10⁻¹ cc/g, and pore radius average 13.783 Å and 11.918 Å . The result of volumetry analysis of Free Fatty Acid and conversion value of MEFA shows that the optimal process of esterification done on 2% (v/v) catalyst at 60°C producing 72.43% (b/b) with composition 30,60% of 9,12-Octadecanoic Methyl Ester. The result products are liquid, cocas, gas, and residue. Optimal liquid product conversion occurs on Ni/ZY catalyst in catalyst : decoy ratio 1:2 (b/b) at process temperature 450°C with 87.37% liquid product conversion by 74.24% gasoline fraction selectivity (C6-C11) and 25.76% Diesel (C12-C20).

Keywords: *Biogasoline, Catalytic Hydrocracking, Ni/ZY Catalyst, MEFA, Rubber Seed Oil*

INTRODUCTION

Along with globalization increment, the demands of energy getting higher. Besides that, fossil fuel energy which is the world's primary energy source dwindling. It is characterized by the scarcity of liquid fuel and accompanied by a rise in crude oil prices. Meanwhile pollutant compounds resulting from the process of burning fossil fuels (CO_x, NO_x, SO_x) causing air pollution and global warming effects. To anticipate this, Indonesian government has issued a national energy management blueprint for 2005-2025, as outlined in the Energy Sector Public Policy (KUBE) by National Energy Coordinating Agency (BAKOREN) consists of five basic principles, namely: energy diversification, intensification of energy, energy conservation, market mechanisms and environmental policy.

Indonesia is one of the largest natural rubber producing countries in the world. Based on data from the Directorate General of Plantation (2013), in 2012 Indonesia has a total area of 3,484,073 ha of rubber plantation with the proportion of rubber trees that produce is 2,815,163

ha (81%). In addition to produce latex, rubber plantations also produce rubber seed 1080 kg/ha/year that has not been utilized optimally. Of acreage owned plant, it will be produced rubber seed approximately 3,456,128 tons per year. If we assume 25 percent of rubber seed produced is used for seed, the rubber seed that has not been used optimally approximately 2,592,096 tons per year. With a view to the high content of vegetable oils in the rubber seed meat is equal to 45-50% (Hardjosuwito&Hoesnan 1976 in Gita NoveliaAndayani, 2008), then from rubber seed will be produced as much rubber seed oil 1.166.443,2 tons annually.

Rubber seed has ellipsoidal shape, with a length of 2.5-3 cm, which has a weight of 2-4 g/seed. Rubber seed consists of 40-50% of hard brown skin, and 50-60% creamy kernel. Kernel rubber seed consists of 45.63% oil, 2.71% ash, 3.71% water, 22.17% carbohydrate, and 24.21% protein, so that the rubber seed has the potential to be used as a source of oil. However, the water content of a sizable portion of the rubber seed can lead to hydrolysis of triglycerides into fatty acids. Therefore, rubber seed needs to be dried first before pressed to take the oil. The composition of fatty acids in the rubber seed oil consists of 18.9% saturated fatty acids (10.2% palmitic acid and stearic acid 8.7%) and 80.5% unsaturated fatty acids (24.6% oleic acid, 39, 6% linoleic acid and linolenic acid 16.3%) (Ardiana, 2010).

Biodiesel is the monoalkyl esters of long chain fatty acids and consists of a methyl or ethyl ester which is the result of free fatty acid esterification and transesterification of trialkyl glycerides (TG) which contains almost no sulfur and is biodegradable (environmentally friendly) so it can be used as an alternative diesel fuel (Ma, 1999). Catalytic processes of Hydrocracking produce methyl esters of fatty acids (MEFA) will produce liquid fuel fraction commensurate biogasoline.

Esterification process aims to convert free fatty acids into esters by treating the oil with methanol. The catalyst used is sulfuric acid with a reaction time of 60 minutes will produce esters with a low acid value and good for the process of making biodiesel (Suratnoet al, 2007) and continued with the process of transesterification of triglycerides that is processing the base catalyst and the reaction is reversible (Wijaya, 2009). Sudrajat R et al (2010) have done a optimization of billowing oil transesterification reaction in the process of making biodiesel by varying methanol and KOH. Best Biodiesel is produced in 20% methanol and 1% KOH catalyst. It is the basis for the transesterification process to be conducted in this study.

Cracking process on vegetable oil and animal fats, natural fatty acids and methyl esters fatty acids (MEFA) at high temperatures produces hydrocarbon light fraction (light hydrocarbons) which fuel with a greater percentage of biogasoline than the percentage of Biodiesel (Style, 2003). Wiratini (2010) in her research report stated that the process of Catalytic Cracking palm oil methyl ester (MEPO) with catalyst Ni/Zeolite generated conversion of 29.46% biogasoline fraction.

Based on the research results of Adrianus et al (2013) concluded that the cracking of cooked oil using best zeolite/nickel catalyst is the products with ratio 10:40 w/w which is indicated by the abundance (%) of the compound produced pentadecane and nonane larger of the two types other variations. Meanwhile based on the research of Akbar et al (2012) on the palm fatty acid cracking with catalyst Ni/zeolite produces yield of 45.60% with a weight of 5% and a catalyst at 400°C. Wijarnako et al, (2006) was to convert palm oil by catalytic cracking using γ -alumina catalyst, produce hydrocarbons (C6-C11) biogasoline at 45.35% at the reaction temperature operating conditions of 1.5 hours.

The availability of rubber seed and the abundant of oil and high fats content (45-50%) been the main source of raw material of alternative energy. In this study will be done the process of esterification and transesterification of rubber seed oil, followed by a catalytic hydrocracking process which is expected to be generated fraction of Biodiesel and biogasoline with better quality and cheap and easy to use. Fraction of liquid fuels produced from rubber seed oil is expected to meet the needs of alternative energy is environmentally friendly and has the ability to answer the problem of substitute fuels as a result of depletion of fossil fuel energy sources.

The purpose of this study was to determine how much yield biogasoline produced from catalytic hydrocracking process of Rubber Seed Oil in a fixed bed system using a nickel catalyst that falls in zeolite-Y.

METHODOLOGY

Time and Place of The Research. This research was conducted at the Chemistry Laboratory, State University of Medan, Jln. Willem Alexander V Medan Estate Market and implemented in January to July 2014.

Material. Material support in the form of research: Synthetic Zeolite Y, aquabidest, HCl, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Oxygen gas, Nitrogen Gas, Hydrogen gas, Methanol, n-hexane, NH_3 , NaOH, H_2SO_4 , Glycerin, and anhydrous Na_2SO_4 .

Tools. The tools used to support this research is 1 Set of PresHidrolik Tool, 1 Set hydrothermal reactor, 1 Set Tool Reflux, Glass Measure 10 mL and 1000 mL 1 pc, Beaker 250 mL 1 pc and 500 mL 1 pc, Burette 25 mL 1 Pc, 250-ml Erlenmeyer 2 Pcs, Funnel Farewell 1000 mL of 1 pc, the balance of O-Haus 1 Pc, Pumpkin Measure 100 mL 1 Pc, thermometer 150°C 1 Pc, Heating 1 Pc, Glass Funnel 2 Pc, Ovens & Furnaces 1 Pc, Pipette drops 15 Pc, Glass Bottles 10 mL 10 pc 20 3 Pc, 250 mL Plastic Bottle 2 Pc, Analytical Balance 1 Pc, Desiccator 1 Pc, and Glass Tubes 1 Pc.

Rubber Seed Oil Extraction. A total of 1 kg of rubber seed which has been sorted and peeled dried at 100°C for 60 minutes and then crushed and pressed with a hydraulic press to produce oil. Then determined the levels of Free Fatty Acid (FFA) rubber seed oil with acid-base titration method (SNI 01-3555-1998).

Rubber Seed Oil Degumming. Degumming process aims to eliminate the sap on oil, by adding H₃PO₄ of 0.2% oil weighed at a temperature of 56°C within 30 minutes reflux.

Production Process of Catalyst Ni/ZS-Y. The catalyst was prepared by mixing 100 g ZS-Y with 1.6070 g of Ni (NO₃)₂.6H₂O which has been dissolved by aquabidest, after the mixture was refluxed and stirred with a magnetic stirrer for 5 hours at a temperature of 80°C. It is Calcined for 2 hours at a temperature of 500°C with flowing N₂ gas (± 5 mL /sec) obtained catalyst Ni / ZS-Y. Solids Ni / ZS-Y Oxidised During the next 2 hours at 500°C with flowing O₂gas (± 5 mL/sec). ZY catalyst and Ni / ZY later being analyzed by BET, IR and XRD.

Esterification and Transesterification of Rubber Seed Oil. Degumming results of rubber seed oil are heated at a temperature of 100°C and esterified in 3-neck flask with methanol: oil (6: 1) supported catalysts H₂SO₄ (0.5% v/v of the total volume of methanol + rubber seed oil, heated to a temperature of 60°C with speed stirring 100 rpm and record the reaction time, samples were taken every 15 minutes for FFA rate calculated in accordance with SNI 01-3555-1998.

Followed by a transesterification reaction by adding NaOH 1% w/w at a temperature of 60°C for 60 min with a stirring speed of 100 rpm. Once the reaction is complete, added 0.6 N HCl and as much as 3-5 drops of glycerin ± 2.5 mL to obtain methyl ester layer (top) and glycerin (bottom). The bottom layer was drained and the upper layer was evaporated at a temperature of 74°C and then washed with distilled water several times. Methyl ester was dried with anhydrous Na₂SO₄, analyzed by GC and GC-MS.

Catalytic Hydrocracking of Rubber Seed Oil MEFA. Hydrocracking process is carried out with variations of the ratio of catalyst: feed (1: 2, 1: 4 and 1: 6). The catalyst and feed were weighed, and the catalyst is placed in bait containers. Both are included in a fixed-bed reactor made of stainless steel. Then put in a furnace reactor with temperature variation 400°C, 450°C, and 500°C, the feed is vaporized and fed into the reactor. The product is passed through a silicone hose to pass through the condenser and liquid fuel products were analyzed by GC and GC-MS.

RESULTS AND DISCUSSION

Rubber Seed Oil and MEFA. Rubber Seed Oil obtained by hydraulic pressing, quantitative analysis of the results obtained that the oil content of the sample used by 33.32%

and by GC analysis of known high content of rubber seed oil consists of linoleic acid by 39.657% and 23.524% of Oleic Acid . From the results of the analysis of the initial FFA content of rubber seed oil was obtained by 39%. Canacki et al (1999) and ramadhas et al (2005) mentions that the oil has contain higher fatty acid (> 2% -FFA) is not suitable for use as raw material in the transesterification reaction. Based on the process of formation of rubber seed oil MEFA in this study conducted in two phases, namely the reaction of esterification and transesterification followed. Esterification reaction aims to reduce the fatty acid content of <2% (ramadhas et al.2005). The content of free fatty acids (FFA) are high in oil, if used as a raw material in the transesterification reaction with alkaline catalyst, the free fatty acid will react with the catalyst to form soap through the saponification reaction, so the effectiveness of the catalyst will decrease because some catalyst reacts with acid fat (Canacki et al, 1999). Moreover, according to Sudrajat R et al (2010) the condition will reduce the yield of ester and complicate the process of separation. In this study the methanol was used as the type of alcohol reactant. This is because methanol is the shortest carbon chain alcohols and polar (Suratnoet al, 2007), So it can react faster with fatty acids and can dissolve all types of catalysts (either alkaline or acidic) and more economical (Ma et al. 1999). MEFA rubber seed formation rate in the esterification process can be seen from the decline in the value of FFA in Figure 1.

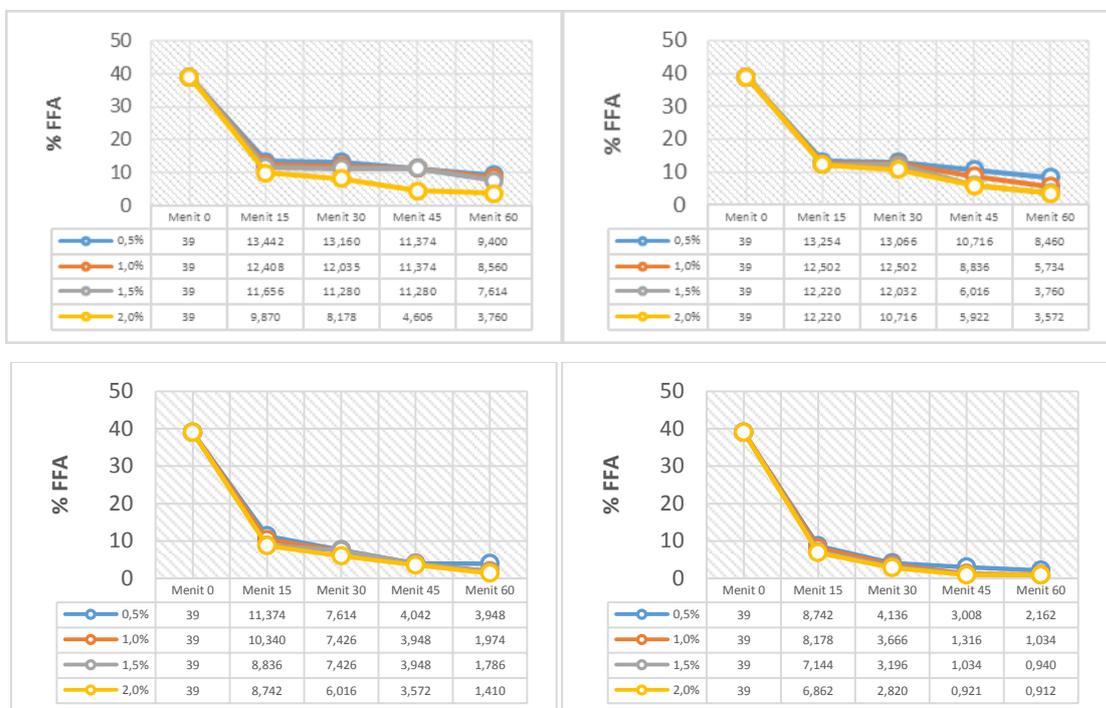


Figure 1. Graph of FFA Esterification Value Temperature at 30°C, 40°C, 50°C and 60°C

Based on the results of varying the Free Fatty Acids so MEFA conversion value appropriate with the results of Free Fatty acid levels. This is appropriate with research of Sues (1999) in susilo (2006) in which the free fatty acid content will determine the conversion yield of biodiesel, if the content Free Fatty Acid decreasing, the yield of biodiesel produced will be even greater. Conversion charts of MEFA with treatment temperature variation and %H₂SO₄ catalyst is shown in Figure 2.

Based on Figures 1 and 2 it can be seen that the Optimum Condition of making biodiesel in the esterification process occurs at a temperature of 60°C using a catalyst process of H₂SO₄ 2% (v/v) with a conversion of 72.43% MEFA. Based on GC-MS Analysis of Chemical Ingredients MEFA largest known that 9,12-octadecenoic acid (Z,Z) Methyl Ester of 30.60% and 9 octadecenoic acid (Z, Z Methyl Ester with 25.41% percentage.

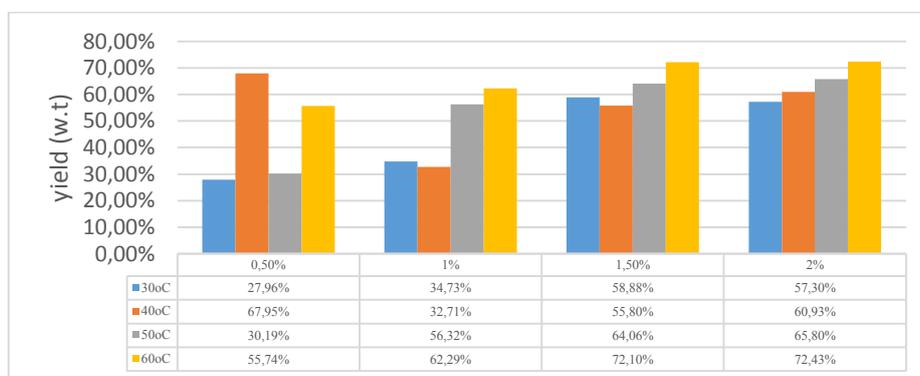


Figure 2. Graph of MEFA Rubber Seed Oil Conversion with treatment% H₂SO₄ catalyst 0.5%, 1%, 1.5% and 2% (v / v) at a temperature of 30°C process, 40°C, 50°C, and 60°C.

ZY Catalyst Characterization and Ni/ZY. Based on the results of infrared spectra ZY catalyst and Ni/ZY shows the frequency shift (wave number spectra IR) that occurs as a result of the asymmetric stretch vibration TO4 group at wave number 1000-1100 cm⁻¹, which is the Y zeolite catalyst that previously had a range of 1049.28 cm⁻¹, after developing of metal on zeolite Y (Ni/ZY) shifted to 1053.15 cm⁻¹ range, this shift is caused by a reduction of Al atoms in the framework be outside the framework Al (non-framework) due to dealumination. This shows the calcinating process and oxidation on Ni/ZY metal was perfect this was confirmed by the results of the analysis of X-ray Diffraction (XRD). Characteristics crystal catalyst Ni / zeolite Y becomes more marked increase with an increase in 2θ (degrees) 6.4315 of intensity 879 turned into 2θ (degrees) 11.8726 with intensity 897, at 2θ (degrees) 15.9528 with 983 intensity increased to 2θ (degrees) 23.6994 with the intensity of 1333 and at 2θ (degrees) 23.9960 with 996 intensity increased to 2θ (degrees) 15.6495 1502. The intensity of the XRD diffractogram can be seen that the solid carrier of zeolite Y, Nickel metal crytalinity increase the intensity seen at the height

of the peak 2θ (degrees) are almost the same but with different intensities, suggesting Ni/ZY perfect cavity filling cavities in zeolite Y.

Analysis of the results of IR spectroscopy and X-ray Diffraction, then ZY catalyst and Ni/ZY analyzed to determine the BET specific surface area, pore volume and mean pore. ZY catalyst surface area obtained from the results of catalyst characterization ZY is $342.651 \text{ m}^2/\text{g}$, while the surface area of Ni/ZY is $539.186 \text{ m}^2/\text{g}$. Surface area is an important character in the catalyst for the catalytic reaction using the catalyst will take place on the surface of the catalyst where the different sites of the catalyst active sites. The larger the surface area of the catalyst, the more the reactant molecules are adsorbed on the surface, and in the end will happen more and more products. ZY total pore volume of the catalyst for $2,362.10^{-1} \text{ cc/g}$ increased to $3.213.10^{-1} \text{ cc/g}$ after the metal impregnation of Ni into the carrier zeolite Y resulting catalyst Ni / ZY. In addition to the total pore volume, the increase also occurred in the mean radial of ZY catalyst wherein the catalyst which has a pore of 13.783 \AA increased to 11.918 \AA the catalyst Ni / ZY. The increase in the total pore volume and average pore indicate that the process of developing of logan Nickel impregnation into the carrier of zeolite Y dispersed evenly and do not experience the clotting process (sintering). The process of developing of metal dispersed on the surface of the catalyst ZY and calcination and oxidation is thought to have led to the formation of new pores.

Optimization of Biogasoline Production. Hydrocracking reaction is a process that occurs split the big molecule into small molecules. In reactions involving hydrocarbons, cracking the termination of the C-C of long chain hydrocarbon compounds which aims to obtain a molecule that has a shorter carbon chain than the original. In the optimization process, the first biogasoline production conducted by Catalyst Activation Test with variations in the ratio of catalyst/feed 1: 2, 1: 4, and 1: 6 with H_2 gas flow rate of 20 mL/minute. Besides done variation of feed/catalyst, hydrocracking process performed by the temperature variation at temperature of 400°C , 450°C and 500°C . From the experimental results gained conversion products as liquid, gas, cocas and residue from the catalytic hydrocracking of rubber seed Oil MEFA which is presented in Figure 3.

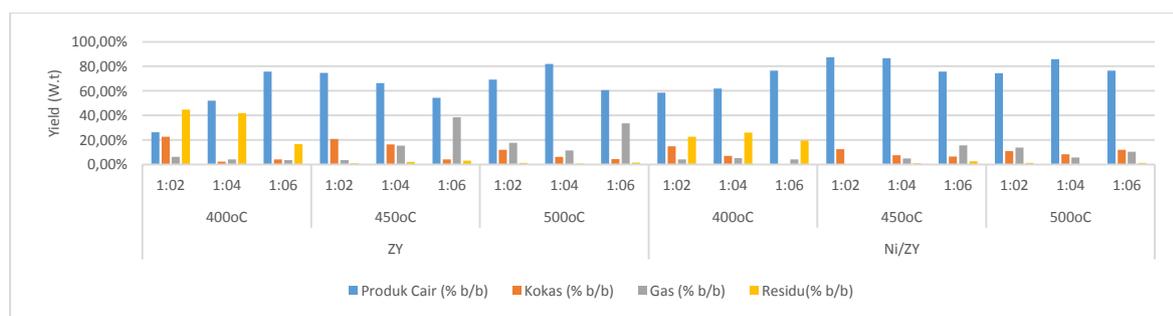


Figure 3. Data of Conversion Results of MEFA Rubber Seed Oil Catalytic Hydrocracking

Then Liquid products were GC analyzed to determine the selectivity of the catalyst so that the gasoline fraction obtained results are presented in Figure 4.

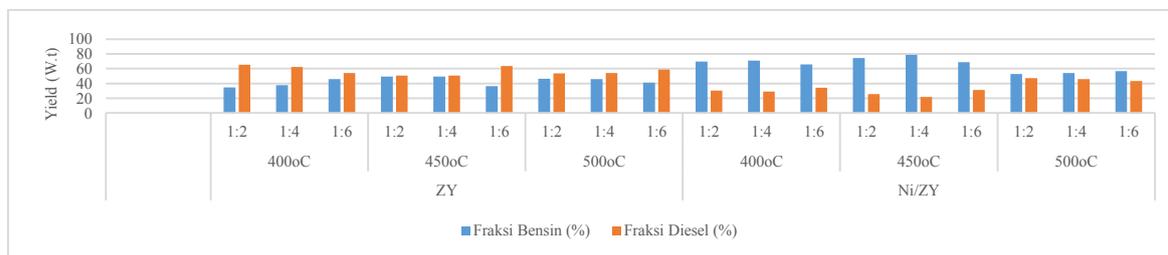


Figure 4. Data Selectivity Catalysts Against Gasoline Fraction

Based on Figure 4 seemed that the general catalyst Ni/ZY selectivity gasoline fraction higher than the catalyst ZY. This is indicated by the magnitude of the percentage fraction of the gasoline produced at the Ni/ZY catalyst based on GC analysis data. As it is known that the Ni/ZY catalyst has a specific surface area and total pore volume of large and small average pore than ZY catalyst. In addition, the presence of Bronsted acid sites and Lewis acid sites on the catalyst surface will be able to sustain short-chain hydrocarbons are formed so that the catalyst Ni/ZY more selective.

Large surface area of the catalyst has a chance of contact with the feed larger pore volume of the catalyst while the greater the carbon chain molecules will be much longer into the catalyst so that the compound will be more susceptible to hydrocrack catalyst and with a mean little spokes will give strong selectivity is only short-chain molecules will pass through the pores.

From Figure 4 it can be seen that the selectivity of the catalyst ZY and Ni/ZY against the gasoline fraction at a temperature and catalyst : feed ratio has a different degree of selectivity, the level of selectivity is influenced by the circumstances in which the catalyst can work with optimum ratio and temperature, for ZY catalyst optimum state occurs according to the temperature and the ratio of the catalyst occurs at a temperature of 400°C catalyst ratio of 1: 6 (w/w), the temperature of 450°C at a ratio of 1: 2 (w/w) and temperature of 500°C at a catalyst ratio of 1: 2 (w/w) while the catalyst Ni/ZY optimum state occurs at a temperature of 400°C premises catalyst ratio of 1: 4 (w/w), at a temperature of 450°C with catalyst ratio of 1: 4 (w/w) and at a temperature of 500°C with a ratio of catalyst 1 : 6 (w/w). Overall the highest selectivity of the catalyst Ni/ZY with temperature process 450°C with a catalyst to feed ratio of 1: 4 (w/w) with selectivity gasoline fractions of 78.49%.

CONCLUSIONS AND RECOMMENDATIONS

It can be concluded that: (a) The development of Nickel Metal on Zeolite Y increases peak intensity of the main bands, Specific surface area, pore volume and mean pore, (b)

Optimization of Biodiesel Production best occur in the esterification process with 60°C temperature process using H₂SO₄ catalyst 2% (v/v) resulted in 0.912% FFA content with Conversion Value 72.43% (w/w), and (c) Optimizing the best biogasoline production occurs in catalyst Ni/ZY with 450°C temperature process with the ratio catalyst: Feed 1: 4 (w/w) with a value of 86.55% conversion with 78.49% selectivity to gasoline fractions.

Undertake research on H₂ gas flow rate at hydrocracking process to determine the selectivity of liquid products

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