HYDRODEOXYGENATION OF CASTOR OIL AS AN ALTERNATIVE SOURCE OF BIOHYDROCARBON USING NICKEL CATALYST LOADED ON HZSM-5 ZEOLITE

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Abstract: The need for energy continues to increase along with rapid population growth. Fuel is one of the most critical energy sectors. However, the limited availability of fossil fuels and the issue of air pollution have prompted various studies to find alternative fuels that are renewable and environmentally friendly. In this study, the conversion of castor oil into biohydrocarbons through the hydrodeoxygenation (HDO) process using the HZSM-5 catalyst loaded with Ni (Ni/HZSM-5) aims to produce biohydrocarbon products as a component of liquid fuel. This research has been carried out in 3 main stages, including: 1) Catalyst preparation; 2) Catalyst characterization; and 3) Activity and selectivity test of HZSM-5 catalyst and Ni/HZSM-5 in the hydrodeoxygenation process of castor oil at reaction temperatures of 350 ^oC, 375 ^oC, and 400 ^oC. The conversion results of castor oil using HZSM-5 and Ni/HZSM-5 catalysts were 3.23%, 25.65%, 43.72%, and 13.78%, 35.03%, 71.01%, respectively. From the GC-MS analysis data on the product at 400 ^oC, the selectivity of HZSM-5 and Ni/HZSM-5 was 20.02% and 23.71% for the kerosene fraction, as well as 15.79% and 11.01% for the gasoil fraction, respectively.

Keywords: Biohydrocarbon; Hydrodeoxygenation; Castor Oil

Abstrak: Kebutuhan energi terus meningkat seiring dengan pertumbuhan jumlah penduduk yang sangat pesat. Salah satu sektor energi yang paling dibutuhkan adalah bahan bakar minyak. Namun kesediaan bahan bakar fosil yang terbatas dan isu pencemaran polusi udara, mendorong berbagai penelitian untuk menemukan alternatif bahan bakar yang terbarukan dan ramah lingkungan. Dalam penelitian ini, konversi minyak jarak menjadi biohidrokarbon melalui proses hidrodeoksigenasi (HDO) menggunakan katalis HZSM-5 teremban logam Ni (Ni/HZSM-5) bertujuan untuk menghasilkan produk biohidrokarbon sebagai komponen bahan bakar cair. Penelitian ini telah dilakukan dengan 3 tahapan utama yaitu 1) Preparasi katalis, 2) Karakterisasi katalis, 3) Uji aktivitas dan selektifitas katalis HZSM-5 serta Ni/HZSM-5 dalam proses hidrodeoksigenasi minyak biji jarak dengan temperatur proses 350 ^oC, 375 ^oC, dan 400 ^oC. Hasil konversi minyak biji jarak dengan menggunakan katalis HZSM-5 dan katalis Ni/HZSM-5 berturut-turut sebesar 3.23%, 25.65%, 43.72% dan 13.78%, 35.03%, 71.01%. Dari data analisis GC-MS produk di suhu 400 ^oC diperoleh selektivitas katalis HZSM-5 dan katalis Ni/HZSM-5 berturut-turut adalah 20.02% dan 23.71% untuk fraksi kerosene, serta 15.79% dan 11.01% untuk fraksi gasoil.

Kata kunci: Biohidrokarbon; Hidrodeoksigenasi; Minyak biji jarak

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Introduction

Energy needs are increasing along with the rapid population growth. Most of the energy needs are still supplied from non-renewable natural resources such as coal, natural gas, and petroleum whose availability is increasingly limited. The sector with the highest consumption of fossil fuel energy is the transportation sector. CO_2 gas emissions resulting from the burning of fossil fuels are the main source of CO_2 gas emissions in the world reaching 9.67 billion tons of carbon, equivalent to 35.4 billion tons of CO_2. The emission of CO_2 from fossil fuel burning increases the global temperature. Removal of this CO_2 from the atmosphere requires tremendous expenses, and currently, there is no proven technology to carry out this action. Therefore, clean, efficient and renewable energy is needed to reduce harmful gas emissions from fossil fuels (Gea et al., 2022).

To overcome this problem, biomass conversion is carried out to obtain biohydrocarbons as an alternative to renewable energy. Biohydrocarbon is a renewable energy that is clean and environmentally friendly because it produces far less pollutant gas emissions when compared to fossil energy sources so the impact on CO_2 emissions is negative so that the application of unconventional fuels such as biohydrocarbons is needed to reduce the concentration of CO_2 in the atmosphere (Zahed et al., 2021). Vegetable oil is a promising alternative source in the production of biofuels. One type of vegetable oil that can be used for biohydrocarbon synthesis is castor oil. Castor oil can be converted into biohydrocarbons such as liquid alkanes as a source of transportation fuel. The presence of fatty acid chains similar to n-paraffin hydrocarbon chains, therefore by carrying out modification processes such as hydrogenation (double bond saturation), hydrogenolysis (breakdown of fatty acid triglyceride molecules), and deoxygenation (oxygen removal) n-paraffin compounds can be obtained from biofuels (Nur Azreena et al., 2022).

The method that can be used for biohydrocarbon synthesis is generally through a transesterification reaction by reacting triglycerides in vegetable oils with short-chain alcohols such as methanol or ethanol to produce biodiesel and glycerol (Al-Muttaqii et al., 2020). In addition, there are various other routes to produce biohydrocarbon, one of them is hydrotreating, which is the hydrodeoxygenation process with hydrogen treatment involving the main reaction, and the side reaction in the form of decarboxylation. If vegetable oil contains unsaturated fatty acids, then before the hydrotreating reaction occurs, the double groups will be saturated (Nur Azreena et al., 2022).

HZSM-5 is a type of zeolite that has strong acidic sites, as a result at high temperatures it is superacid and is able to protonate paraffin. The pore structure of the zeolite greatly affects the rate of coke accumulation and HZSM-5 is resistant to coke formation due to steric constraints in the transition phase (Zhao et al., 2017). Zeolite HZSM-5 is the most effective catalyst for the hydrodeoxygenation process because of its shape selectivity, containing active sites, high surface area, and suitable pore diameter. This is important to improve the hydrocracking process conditions to obtain high hydrocarbon yields (Al-Muttaqii et al., 2020).

Based on the above explanation, research was conducted on the performance of Ni metal catalyst with HZSM-5 zeolite carrier in the hydrodeoxygenation reaction of castor oil to produce bio-hydrocarbons which are expected to become raw materials for environmentally friendly renewable energy sources in the future.

Materials and Methods

Materials

The materials used in this study were synthetic zeolite type HZSM-5, deionized water, $Ni(NO_3)_2{\cdot}6H_2O$ p.a (E.Merck), Hydrogen gas (H_2), and Nitrogen (H_2) obtained from PT. Samator Gas Medan, Indonesia and castor oil are commercially available in Medan, Indonesia.

Methods

HZSM-5 catalyst preparation

A total of 5 g of HZSM-5 was weighed, then dried for 24 h at a temperature of 120 °C or calcined at a temperature of 550 °C for 5 h to reduce the compounds adsorbed on the surface (Zhu et al., 2017).

Ni/HZSM-5 catalyst preparation

Zeolite HZSM-5 was impregnated with a solution containing the active metal, $Ni(NO_3)_2{\bullet}6H_2O$. This process was carried out by slowly adding a metal solution to the HZSM-5 zeolite at room temperature. The steps are as follows: (1) Weighing 5 g of HZSM-5. (2) Impregnation of 2 mL $Ni(NO_3)_2{\bullet}6H_2O$ 1% solution added little by little (sprayed) onto the surface of the zeolite and kept the zeolite dry. (3) The catalyst was stored for 24 h in a desiccator. (4) The catalyst was dried at 120 °C for 12 h. (5) The powder catalyst was calcined at 550 °C in the air for 3 h and the catalyst was reduced with hydrogen gas at 550 °C for 2 h (J. Gao et al., 2022).

Catalyst characterization

The catalyst was analyzed by X-Ray Diffractometer (XRD Shimadzu 6100) to determine the crystallinity of the catalyst. Analysis of surface morphology and amount of metal impregnated on HZSM-5 catalyst using Scanning Electron

Microscope with Energy-Dispersive X-Ray Spectroscopy series model (SEM-EDS Type Zeiss EPOMH 10Zss). The N_2 gas sorption analysis was performed with Gas Sorption Analyzer (NOVA 1200e) Quantachrome instrument at 77 K. The surface area was obtained through the Brunauer-Emmett-Teller (BET) method, while pore characteristics were estimated with an adsorption branch based on the Barrett-Joyner-Halenda (BJH) model.

Activity test and catalyst selectivity in the hydrodeoxygenation process of castor oil

The HDO process was carried out in a fixed bed reactor filled with 1 g of catalyst and the reactor is coated with a heating element. Then 100 mL of castor oil was put into the fixed bed reactor. Heat the reactor from room temperature to the desired operating temperature and the temperature is kept constant throughout the reaction for 2 h. Setting the temperature so that it shows the desired temperature variable (e.g T1 = 400 °C) (Al-Muttaqii et al., 2020). After the hydrotreating process was carried out, the liquid product was analyzed by Gas Chromatography-Mass Spectrometry (GC-MS type QP2010 Plus) to determine the hydrocarbons formed in the liquid product of the reaction.

Results and Discussion

Catalyst Crystallinity

XRD analysis is used to identify the crystalline phase in the material. A comparison of the diffractograms of HZSM-5, nickel metal, and Ni/HZSM-5 catalysts are shown in Figure 1.

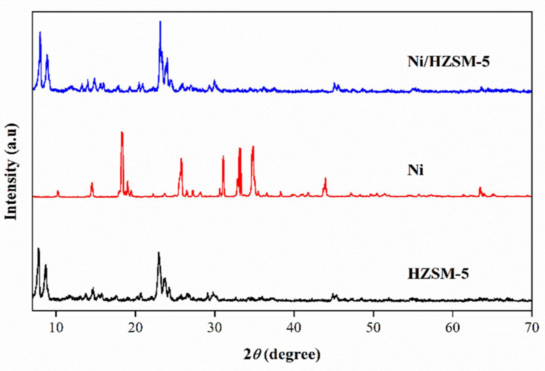

Figure 1. Diffractogram comparison of HZSM-5, Nickel, and Ni/HZSM-5 catalysts.

Table 1. Some main peaks of HZSM-5 and Ni/HZSM-5 catalysts

Catalyst	2θ (°)	Intensity	Crystallinity
HZSM-5	7.74	181	86.48%
	8.65	124	
	22.97	174	
Ni/HZSM-5	7.95	194	96.70%
	8.86	129	
	23.19	224	

From the analysis that has been carried out, the commercial HZSM-5 XRD pattern has characteristic diffraction peaks at 2θ = 7.74°, 8.65°, 22.27°, 23.64° and 24.22° in the 2θ region between 7° and 24°. The main peak was observed at 2θ = 7.74° with an intensity of 181. The peak position in the range of 2θ = 7-8° and 2θ = 22-24°, is a typical and specific peak of HZSM-5. Meanwhile, the XRD Ni/HZSM-5 pattern has a diffraction peak characteristic of 2θ = 7.95°, 8.86°, 23.19° and 23.87° in the 2θ region between 7° and 23°. The main peak was observed at 2θ = 23.19° with an intensity of 224. The peak position was in the range of 2θ = 7-8° and 2θ = 23°. An angle of 2θ = 44.60° indicates Ni metal and an angle of 2θ = 52.2° indicates NiO metal (C. Gao et al., 2021). Metal in the pores of HZSM-5 and thermal treatment which includes oxidation and reduction on the catalyst resulted in a shift in the diffraction pattern in the HZSM-5 zeolite structure. This result shows that the addition of metal and oxidation and reduction treatment on the Ni/HZSM-5 catalyst affects the zeolite structure and increases the intensity. This increase in intensity affects the degree of crystallinity of the catalyst from HZSM-5 86.48% to 96.70% on the Ni/HZSM-5 catalyst (Sihombing et al., 2020).

Morphology and composition of the catalyst

SEM data obtained surface topology information, while EDS data obtained chemical composition on the surface of the sample. Figure 2 (a) and (c) are the surface topology of Ni/HZSM-5 and HZSM-5 with 1000 times magnification. The results of the observations of the two catalysts showed the uniformity and regularity of the crystal morphology. The uniformity and regularity of the crystal morphology will provide good accessibility to the active center site and can provide high mobility of the product (Moon et al., 2019). From the two catalysts, there are still visible lumps so the granules are less homogeneous (Sihombing et al., 2020). Meanwhile, Figure 2 (b) and (d) show a graph of the chemical composition of Ni/HZSM-5 and HZSM-5. From these data, the Ni/HZSM-5 catalyst contains 0.6 wt% nickel metal composition. The concentration of metal on the surface of the catalyst may be due to some nickel metal entering the pores of the catalyst (Jimmy et al., 2018).

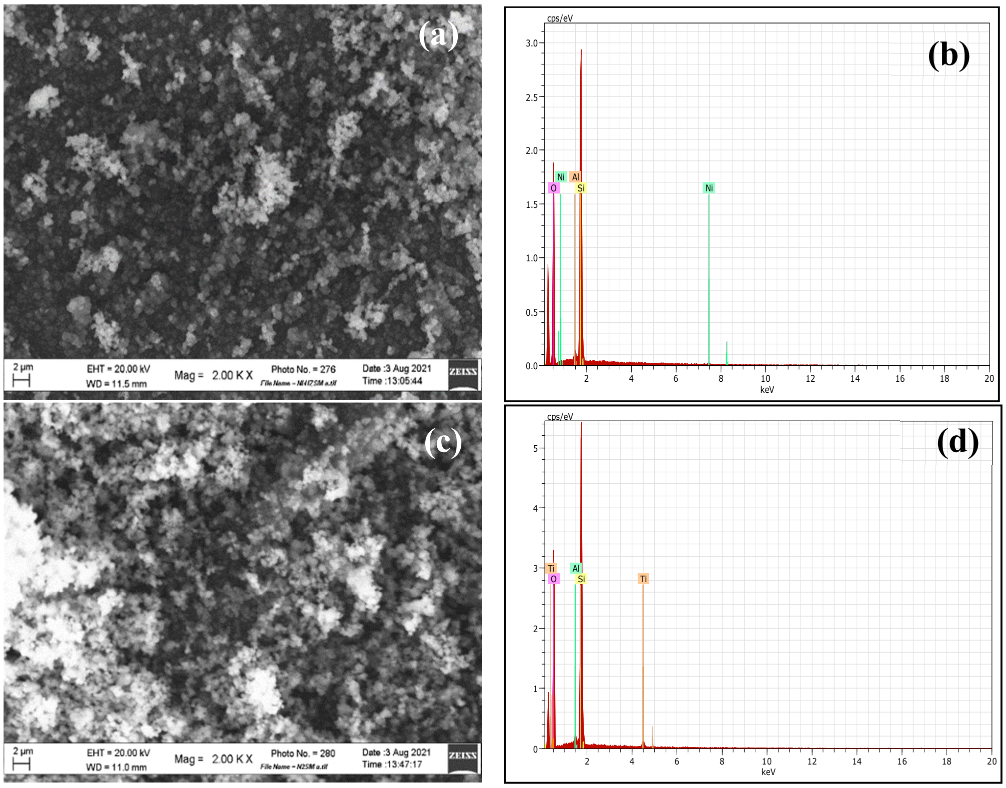

Figure 2. Morphology and composition of catalysts; (a) SEM Ni/HZSM-5, (b) EDS Ni/HZSM-5, (c) SEM HZSM-5, (d) EDS HZSM-5.

Surface Area and pore analysis

Table 2 shows that the HZSM-5 catalyst has a larger surface area than the Ni/HZSM-5 catalyst. The metal surface area of HZSM-5 decreased after the addition of nickel. This is in accordance with the research of (C. Gao et al., 2021), which states that NiO particles are located on the outside of the catalyst surface so that they inhibit HZSM-5 micropores and cause inaccessibility of N_2 molecules on the catalyst. The catalysts HZSM-5 and Ni/HZSM-5 had average pore radius of 1.5596 and 1.5577 and total pore volumes of 0.047 cc/g and 0.048 cc/g. However, based on the image of the adsorption-desorption isotherm below, the diagram of the desorption adsorption pattern of HZSM-5 and Ni/HZSM-5 belongs to Type II where the absorption of the interaction between the adsorbate and adsorbent is strong and the graph increase is high in P/P_0 (Gea et al., 2020).

Table 2. Surface areas, pore volumes and average pore radius of HZSM-5 and Ni/HZSM-5

Samples	Surface area (m^2/g)	Total pore Volumes (cc/g)	Average pore radius (nm)
HZSM-5	380.342	0.047	1.5596
Ni/HZSM-5	316.898	0.048	1.5577

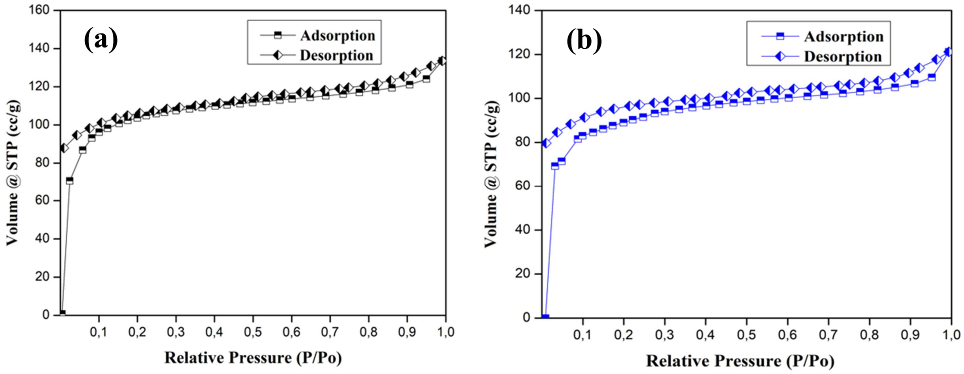

Figure 3. N_2 adsorption-desorption isotherm comparisons of (a) HZSM-5 and (b) Ni/HZSM-5

In Figure 3, the adsorption volume of HZSM-5 is larger than that of Ni/HZSM-5. These data correlate with previous data, that HZSM-5 has a larger surface area and pore diameter than Ni/HZSM-5. The following is a graph of the pore size distribution on a scale of 0-900 Å and 20-100 Å.

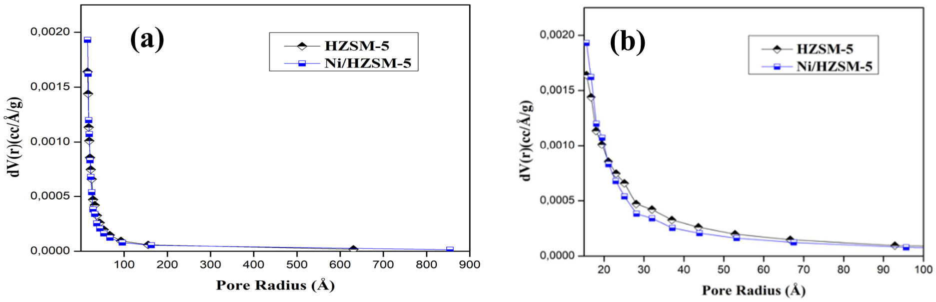

Figure 4. Pore size distribution using the BJH method of HZSM-5 and Ni/HZSM-5 catalysts with the range of (a) 0-900 Å and (b) 20–100 Å

The comparison of the pore size distribution of each catalyst is shown in Figure 4. The value of dV(r) (differential volume radius) represents the pore distribution of the catalyst. The greater the value of dV(r) at each pore diameter, the more pores are distributed to the catalyst. Figure 4 shows that the Ni/HZSM-5 catalyst experienced a decrease in dV(r) value compared to HZSM-5 due to nickel metal impregnation in the catalyst pores. This is in accordance with the research of Sihombing et al., (2020), which stated that the metal impregnation treatment, either monometal or bimetal combination in the catalyst pores, could reduce the dV(r) value. Furthermore, Figure 4 shows that the pore size distribution of each catalyst is dominated in the same region between 20-100 Å.

Catalytic Performance on Distribution of Biohydrocarbon Products

The activity test of each catalyst HZSM-5 and Ni/HZSM-5 was carried out in the hydrocracking process of castor oil. The process conditions in this study were carried out with variations in temperature of 350 °C, 375 °C and 400 °C, for 2 h. The volume of oil used in one run is 100 mL. The distribution of castor oil HDO products is shown in Figure 5. The parameters observed were the conversion value of liquid, gas and coke products.

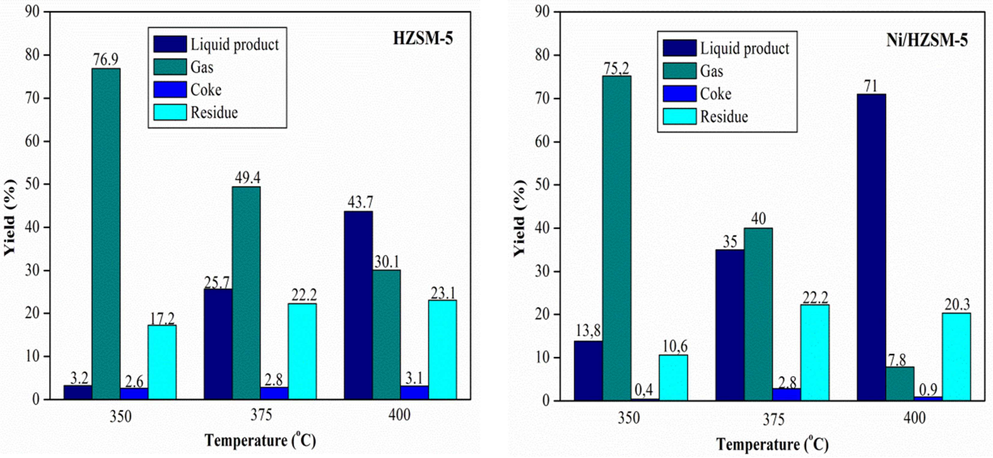

Figure 5. The yield of HDO using HZSM-5 and Ni/HZSM-5 catalysts.

Based on the graph in Figure 5, the optimum conditions obtained were using a Ni/HZSM-5 catalyst at a temperature of 400 °C with a liquid product of 71.01%, gas of 7.79%, coke 0.90% and residue of 20.30%. While the results obtained for the HZSM-5 catalyst, the optimum conditions were at a temperature of 400 °C with a percentage of liquid product 43.72%, gas 30.08%, coke 3.06% and residue 23.14%. The catalytic activity of Ni/HZSM-5 catalyst which is better than HZSM-5 is possible because the inclusion of Ni metal in the carrier pores provides more active sites to play a role in the reaction process, therefore the possibility of a reaction occurring at the active site is greater. The presence of Brønsted acid sites and metal active sites causes the Ni/HZSM-5 catalyst to have more active catalytic properties (Sihombing et al., 2020).

Product analysis

This GC-MS analysis was conducted to determine the selectivity of the reaction products and the fractions contained in the sample. The main components of the castor oil samples before the hydrodeoxygenation process are summarized in Table 3.

Table 3. The fatty acid component of castor oil

Fatty Acid	Formula	RT	% Area
Palmitic acid	$C_{17}H_{34}O_2$	19.581	4.48
Linoleic acid	$C_{19}H_{34}O_2$	24.010	9.77
Oleic acid	$C_{19}H_{36}O_2$	24.241	9.73
Stearic acid	$C_{19}H_{38}O_2$	24.957	2.54
Ricinoleic acid	$C_{19}H_{36}O_3$	28.399	72.93

The mechanism of the hydrocracking process of castor oil using HZSM-5 and Ni-HZSM-5 catalysts is presented in

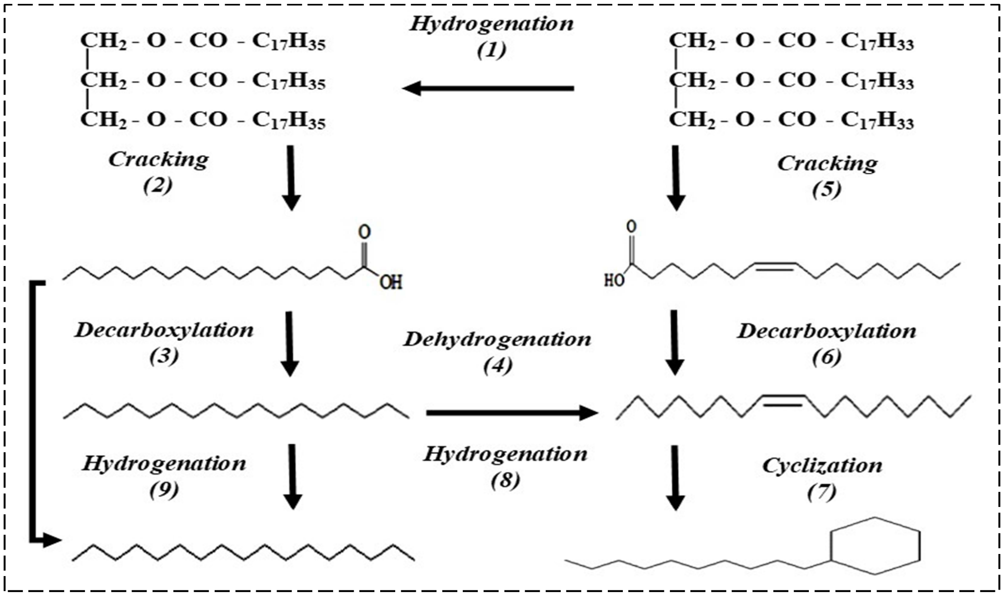

Figure 6. HDO reaction pathways of castor oil with HZSM-5 and Ni/HZSM-5 catalysts (Oleic Acid path = $C_{17}H_{33}COOH$ and Stearic Acid path = $C_{17}H_{35}COOH$ based on GC-MS product

Based on the reaction pathways in Figure 6, the formation of pentadecane ($C_{15}H_{32}$) is dominantly seen through the 1-2-3 route through the formation of palmitic acid intermediate ($C_{15}H_{31}COOH$). The formation of heptadecana ($C_{17}H_{36}$) was seen in routes 5-6-9 through the formation of oleic acid and heptadecene intermediates. Once paraffin compounds are formed (C15 and C17) as the main abundant products of the overall hydrocracking reaction, small amounts of paraffins (C15) are thermally dehydrogenated to form olefin compounds (route 4) which will eventually become the corresponding cyclic compounds. (n-nonylcyclohexane/$C_{15}H_{30}$) via cyclization (route 7) (Marlinda et al., 2017).

These compounds were successfully obtained in the hydrodeoxygenation process of castor oil at a temperature of 400 °C using a Ni/HZSM-5 catalyst. After the HDO process is carried out, then the HDO products are analyzed for the components contained therein. The analysis of HDO products was carried out only at the optimal temperature, namely the product at a temperature of 400 ^{o}C. The results of the Spectra analysis of GC-MS are presented in Figure 5.

Based on the results of the analysis using GC-MS, there are biohydrocarbon products formed. Several types of biohydrocarbon compounds formed can be seen in Figure 7.

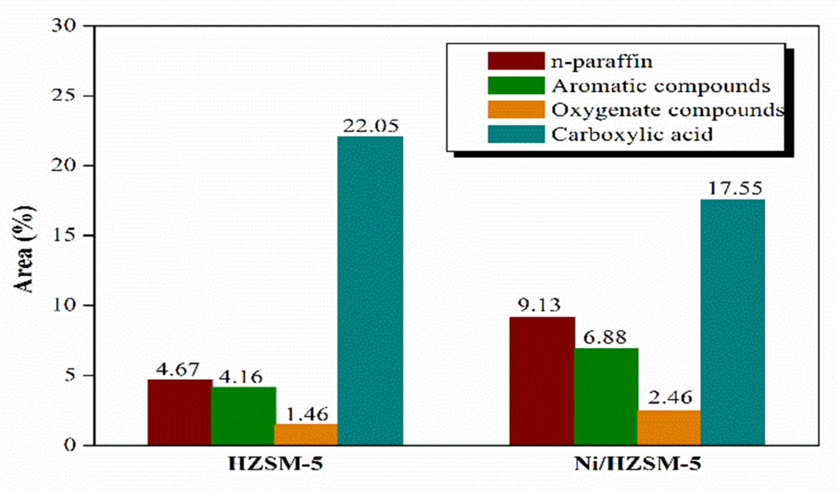

Figure 7. Composition of hydrocarbon using HZSM-5 and Ni/HZSM-5 catalysts at 400^{o}C

Figure 7. shows that at a temperature of 400 ^{o}C, the HZSM-5 and Ni/HZSM-5 catalyst contains several compositions of liquid hydrocarbon compounds produced, which are n-paraffin, aromatic, carboxylic acid and oxygenate compounds. When compared between HZSM-5 and Ni/HZSM-5 catalysts in the percentage area of the biohydrocarbon component produced, it can be seen that n-paraffin, aromatic and oxygenate compounds experienced an increase in area percentage and the content of carboxylic compounds decreased. It can be indicated that the catalytic activity of the Ni/HZSM-5 catalyst is better in the HDO reaction in castor oil when compared to the HZSM-5 catalyst without metal. This is because the Ni/HZSM-5 catalyst has a large surface area and pore diameter, making it easier for triglycerides to enter the HZSM-5 channel support and also as the reaction temperature increases, the conversion of products into hydrocarbons also increases (Liu et al., 2022).

Table 4. Catalysts selectivity on gasoline, kerosene, and gasoil fraction

Fraction	Catalyst selectivity (%)	
	HZSM-5	Ni/HZSM-5
Gasoline (C_5-C_8)	-	-
Kerosene (C_9-C_{13})	24.41	28.91
Gasoil (C_{14}-C_{22})	19.25	13.42

Based on data in Table 4, Jatropha seed oil products with the highest percentage selectivity ranged from C9-C13 (kerosene) of 23.71% for the Ni/HZSM-5 catalyst and 20.02% for the HZSM-5 catalyst. Meanwhile, the highest product selectivity of C14-C22 (gasoil) was obtained using the HZSM-5 catalyst, which was 15.79%, while the Ni/HZSM-5 catalyst was 11.01%. According to (Qi & Fan, 2019), the gasoline fraction (C5-C8) which is produced is very little or even non-existent using high temperatures because it cracks into the gas phase or the cracking process is more stable towards the shorter carbon chain.

Conclusions

Dry impregnation has been successfully carried out as shown by the results of the analysis of the characteristics of the catalyst, namely XRD (improvement of metal Ni on HZSM-5 zeolite can increase the crystallinity of the catalyst from 86.48% to 96.70%), BET (concentration of Ni metal reduces the surface area of catalyst 380.342 m^2/g to 316.898 m^2/g) and SEM-EDX (Ni metal has been distributed over the entire surface of the HZSM-5 catalyst with a percentage of 0.6 wt%)**.** The Ni/HZSM-5 catalyst has the highest selectivity for the Kerosene (C9-C13) fraction, which is 28.91%, while the highest selectivity for the gasoil fraction is owned by the HZSM-5 catalyst, which is 19.25%. Utilization of bifunctional catalysts such as Ni/HZSM-5 in the HDO process of castor oil proved to have better activity than non-metallic catalysts such as HZSM-5.

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