

Bukti KORESPONDENSI JURNAL EUREKA

from journal «EUREKA: Physics and Engineering»_Jimmy roring3
Yahoo/Inbox
Journal Eureka <jr@scijr.info>
To:j_roring@yahoo.com
Mon, Feb 22, 2021 at 8:35 PM
Good afternoon, dear Jimmy roring.

We received an article from you and we will be glad to know you and cooperate with you. Please review our terms and conditions, if you are satisfied, we will continue to work with you.

Journal «EUREKA: Physics and Engineering» (<http://journal.eu-jr.eu/engineering/about/submissions>)

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Please be sure to confirm receipt of the letter so that we know it is not in spam.

If there are any questions, I will be happy to answer them.

With best regards,

Director of the company «Scientific Route»

Helen Klimashevskya

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- roring jimmy <j_roring@yahoo.com>
To:Journal Eureka
Tue, Feb 23, 2021 at 10:22 PM

Dear, Helen Klimashevskaja,
I have sent 2 documents that you requested to fulfill the the journal Eureka submission requirements entitled : "**Biofuel Production Over Fischer-Tropsch Synthesis : Effect Of Fe-Co/Meso-Hzsm-5 Catalyst Weight On Product Composition And Process Conversion**" (1657-Article Text-4639-1-2-20210218)

Thank you.

With best regards,
Dr. Jimmy
Chemical Engineering Dept,
National Institute of Technology Malang
Indonesia

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Wed, Feb 24, 2021 at 7:01 PM
Thank you for your reply, wait for an answer, please.

вт, 23 февр. 2021 г. в 17:22, roring jimmy <j_roring@yahoo.com>:

Masuma Mammadova

Editor-in-Chief

EUREKA: Physics and Engineering

23 February 2021

Dear Dr Mammadova,

Please find enclosed our manuscript entitled “*BIOFUEL PRODUCTION OVER FISCHER-TROPSCH SYNTHESIS : EFFECT OF Fe-Co/meso-HZSM-5 CATALYST WEIGHT ON PRODUCT COMPOSITION AND PROCESS CONVERSION* in EUREKA: Physics and Engineering.

Fischer-Tropsch Synthesis (FTS) using 10Fe-90Co/meso-HZSM-5 catalyst has been investigated. The study emphasized the effect of catalyst weight on product composition and process conversion. The combination of polymerization using metal catalyst (Fe-Co) and cracking (meso-HZSM-5) aimed at producing saturated C₅-C₂₅ hydrocarbons (gasoline, kerosene and diesel oil).

Ammonium ZSM-5 had been converted to HZSM-5 through calcination, desilication, impregnation (10% loading, consisted of 10% Fe and 90% Co by weight), reduced in situ in the reactor with H₂ gas. The catalyst performance was observed in a continuous fixed bed reactor, flow rate of 25 mL/min synthesis gas (30% CO, 60% H₂, 10% N₂) at 250°C, 20 bar, with various catalyst weight (1, 1.2, 1.4, 1.6 gram). The reaction using 1 gram of 10Fe-90Co/meso-HZSM-5 catalyst gave the largest normal selectivity of gasoline (19.15%) and kerosene (55.18%), while the largest normal diesel oil selectivity (24.17%) was obtained from 1.4 gram of catalyst. The CO conversion per gram of catalyst showed similar value (CO conversion of 26-28%) for all catalyst weight.

The data obtained from this study would be applied to develop efficiency of the Fischer-Tropsch reaction condition. FTS had been used to produced alternative energy from coal, natural gas, and some organic compound like carbohydrate or cellulose. Some countries, that limited fossil energy supply would develop this technology for overcoming their high energy demand.

We confirm that this manuscript has not been published elsewhere and is not under consideration by another journal. All authors have approved the manuscript and agree with submission to EUREKA: Physics and Engineering.

The authors have no conflicts of interest to declare.

We would like to recommend the following researchers as potential reviewers for this paper:

1. *[Reviewer 1 name plus contact information]*
2. *[Reviewer 2 name plus contact information]*
3. *[Reviewer 3 name plus contact information]*

We ask that the following researchers are excluded as reviewers because of potential conflict of interest:

1. *[Reviewer 1 name plus contact information]*
2. *[Reviewer 2 name plus contact information]* **[CAN BE DELETED IF NOT RELEVANT]**

Please address all correspondence to:

Chemical Engineering Department, Institut Teknologi Nasional Malang

Jln. Bendungan Sigura-gura No. 2 Malang, East Java, Indonesia 65145

Ph. +62811363906, Fax. +62341553015

Corresponding author : j_roring@yahoo.com

We look forward to hearing from you at your earliest convenience.

Yours sincerely,

Jimmy, Dr.

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on granting a non-exclusive license to using a Work**

Tallinn, Estonia

"12 " June 2021

Jimmy, Achmad Roesyadi, Suprpto, Firman Kurniawansyah

(Full name, Author, Co-authors)

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BIOFUEL PRODUCTION OVER FISCHER-TROPSCH SYNTHESIS : EFFECT OF Fe-Co/meso-HZSM-5 CATALYST WEIGHT ON PRODUCT COMPOSITION AND PROCESS CONVERSION

authored by

Jimmy, Achmad Roesyadi, Suprpto, Firman Kurniawansyah

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10.2. In order to organize operative interaction within the framework of this Agreement, the party "Licensors" must appoint a representative under this Agreement.

This person is Jimmy, contact tel. +62811363906 e-mail account j_roring@yahoo.com.

10.3. Mailing address for sending the Journal: Jln. Bendungan Sigura-gura No. 2 Malang, East Java, Indonesia 65145; the Journal is to be received by: Dr. Jimmy, ST, ST (Full Name).

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Licensor (Licensors), Full name	ID Card	Signature
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2. <u>Achmad Roesyadi</u>	<u>Driving licence : 500415140252</u>	
3. <u>Suprpto</u>	<u>Driving licence : 600615143297</u>	
4. <u>Firman Kurniawansyah</u>	<u>Driving licence : 770515140632</u>	
5. _____	_____	_____
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Sat, Feb 27, 2021 at 12:54 AM

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The article was accepted for consideration of the possibility of publication in the journal «**EUREKA: Physics and Engineering**» for №6. 2021 (release until 30.11.2021).

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Please provide an edited version of the article **by 10.03.2021**.

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We are in touch 24/7.

With best regards,
Director of the company «Scientific Route»
Helen Klimashevskaya
<https://route.ee/en/>

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To:roring jimmy

Wed, Jun 16, 2021 at 3:32 PM

Good afternoon, dear Jimmy roring, thank you for your promptness and work, I accept the license agreement, thank you very much.

We wish you a great day and a good mood!

We are always ready to help you!

With best regards, Helen

вт, 15 июн. 2021 г. в 08:31, roring jimmy <j_roring@yahoo.com>:

• •

roring jimmy <j_roring@yahoo.com>

To:jr@scijr.info

Thu, Jun 17, 2021 at 6:51 AM

Dear Helena

Thank you for accepting the license agreement.

Have a good day.

Best regards,

Jimmy

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from journal «EUREKA: Physics and Engineering» _№6.2021_ Jimmy Jimmy (please acknowledge receipt of the letter)6
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I have sent the revised article strictly according to the reviewer's comments. Please tell me that any further revision about our article.
Thank you.

Best regards,

Jimmy
Chemical Engineering Dept
National Institute of Technology, Malang

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BIOFUEL PRODUCTION OVER FISCHER-TROPSCH SYNTHESIS: EFFECT OF Fe-Co/meso-HZSM-5 CATALYST WEIGHT ON PRODUCT COMPOSITION AND PROCESS CONVERSION

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Abstract

Fischer-Tropsch Synthesis (FTS) using Fe-Co/meso-HZSM-5 catalyst has been investigated. The impregnated iron and cobalt on HZSM-5 could be used as bifunction catalyst which combined polymerizing synthesis gas and long hydrocarbon cracking for making biofuel (saturated C₅-C₂₅ hydrocarbons as gasoline, kerosene and diesel oil). The study emphasized the effect of catalyst weight on product composition and process conversion. The HZSM-5, had been converted from ammonium ZSM-5 through calcination, and then desilicated with NaOH solution. The Co(NO₃)₂.6H₂O and Fe(NO₃)₃.9H₂O were used as precursor for incipient wetness impregnation (IWI) on amorphous meso-HZSM-5. The catalyst consisted of 10 % Fe dan 90 % Co by weight, called 10Fe-90Co/meso-HZSM-5. All catalysts were reduced in situ in the continuous reactor with flowing hydrogen at 25 mL/min, 1 bar, 400°C for 10 hours. The catalyst performance was observed in the same continuous fixed bed reactor at 25 mL/min synthesis gas (30 % CO, 60 % H₂, 10 % N₂), 250°C, 20 bar for 96 hours. Various catalyst weight (1, 1.2, 1.4, 1.6 gram) were applied in FTS. The desilicated HZSM-5 properties (BET analysis) were 6.1-29.9 nm mesoporous diameter, 0.3496 cc/g average mesoporous volume, 526.035 cc/g pore surface area, and the EDX analysis gave 22.1059 Si/Al ratio and 16.11 % loading (by weight) on meso-HZSM-5. The reduced catalyst showed the XRD spectra of Fe (66°), Fe-Co alloy (44.50°) and Co₃O₄ (36.80°). The reaction using 1 gram of 10Fe-90Co/meso-HZSM-5 catalyst produced the largest composition and conversion. The 1 gram catalyst gave the largest normal selectivity of gasoline (19.15 %) and kerosene (55.18 %). While the largest normal diesel oil selectivity (24.17 %) was obtained from 1.4 gram of catalyst. The CO conversion per gram of catalyst showed similar value (CO conversion of 26-28 %) for all catalyst weight.

Keywords: biofuel, HZSM-5, desilication, mesopore, catalyst, iron, cobalt, weight, conversion, Fischer-Tropsch

1. Introduction

Zeolites are used in the process of separation, adsorption, and catalytic (i.e. cracking and other hydrotreating process). Homogeneous micropores, high thermal stability, acidity, and unique ability to stabilize metallic species were several their unique properties [1]. The mesoporous structure provides greater space for metal catalysts to occupy more support pores. The mesopore can be obtained from micropore over desilication treatment. The alkali (NaOH) solution was used as desilication agent. Nitric acid solution was used to transform the mesoporous HZSM-5 into amorphous structure, which could improve the adhesion of the metal catalyst on the mesoporous HZSM-5 support [2–5]. The KOH solution induced greater mesoporous volumes, but it damaged on zeolite crystal structure. The NaOH solutions was able to increased mesopore surface

area and mesopore volume of NaOH-desilicated HZSM-5. The Fe-Co alloys were observed with less oxide of iron (Fe_2O_3) as well cobalt (Co_3O_4) in the produced catalysts [6].

The Fischer-Tropsch synthesis (FTS) is an exothermic and irreversible polymerization reaction that converts a mixture of hydrogen (H_2) and carbon monoxide (CO) into linear hydrocarbons as liquid fuel. FTS always produces various products such as olefins, paraffins and oxygenated compounds (alcohols, aldehydes, acids and ketones). Water was the main product of the FT reaction. Water Gas Shift (WGS) activity occurred significantly in the use of Fe catalyst, but this reaction could be ignored in reactions using Co or Ru catalysts. Iron and cobalt as **polymerization** catalyst were used at FTS. The impregnated iron and cobalt on HZSM-5 could be used as bifunction catalyst which combined **polymerizing** synthesis gas and long chain hydrocarbon cracking for making biofuel [7–11]. The FTS preferred to use cobalt because of some advantages, instead of iron catalyst. Iron catalyst was added in little amount to improve the cobalt catalyst performance (improve olefin selectivity, reduce methane selectivity, reduce temperature and pressure sensitivity to product distribution and reduce the catalyst price) [12, 13].

The combination of the Fischer-Tropsch (FT) reaction and cracking was conducted by combining Fe-Co alloy (Fischer-Tropsch reaction catalyst) and HZSM-5 zeolite (cracking catalyst). The merging of the FTS and cracking was able to produce biofuel product directly [7]. The Fe/HZSM-5 catalyst was able to produce 24.2 % of C_{5-19} hydrocarbon as biofuel fraction [14]. The Co/HZSM-5 catalyst produced 48 % of C_{5-11} [3]. The use of Fe and Co catalysts together (bimetallic) could increase catalytic activity compared to the use single metal catalyst (monometallic). The combination of Fe and Co catalysts (bimetal catalysts) with conventional TiO_2 , Al_2O_3 and SiO_2 supports had been investigated. They could increase the biofuel reaction conversion and fraction compared to the use of Fe and Co catalysts separately [15–17]. The variables that influenced product distribution were temperature, feed gas composition, pressure, catalyst type and promoter. The synthesis gas composition influenced the product selectivity. The lower the CO partial pressure, the lower the surface coverage of CH_2 **species radicals?**, the lower the chain growth chance and the higher the chance of CH_2 **species** desorption. The higher the H_2 partial pressure, increases the chance of **species** termination being paraffin. Increasing H_2/CO ratio would increase the selectivity of short-chain and more saturated hydrocarbons [18–20].

The study emphasized the effect of Fe-Co/mesoHZSM5 catalyst weight on product composition and conversion. The data obtained from this study will be used to develop efficiency of the Fischer-Tropsch reaction condition.

2. Methods

Materials used in this experiment were zeolite ZSM-5 in ammonium form (CBV 8014, Amberlyst International), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Merck), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$

(Merck), NaOH p.a. (Merck), nitric ammonium p.a. (Merck), nitric acid (Merck), Hydrogen gas (PT. Samator Gas Industry, Surabaya, Indonesia), synthesis gas (30 % CO, 60 % H₂, 10 % N₂), glass beads 2 mm (Marienfeld), glass wool, aquadest. The equipment used were the tubular furnace, quartz furnace crucible, hotplate magnetic stirrer, vacuum filter, air compressor, hot air oven, syringe, digital scales and standard glassware for catalyst synthesis. The continuous fixed-bed Fischer-Tropsch reactor (**Fig. 1**), hot trap, cold trap, bubble soap meter, vacutainer (vacuum bottle/container) were used for FTS.

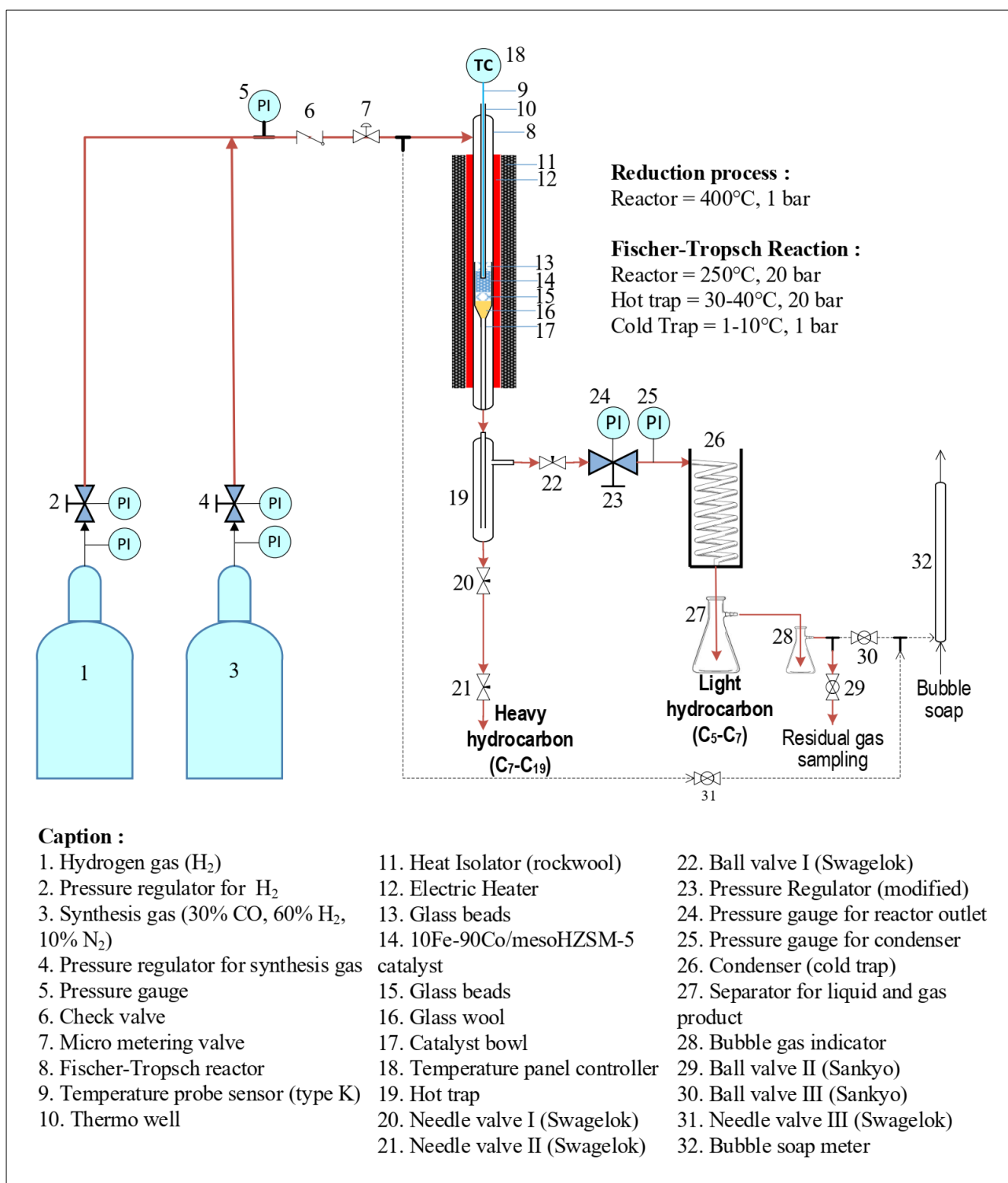


Fig. 1. The reactor unit of continuous Fischer-Tropsch synthesis for 10Fe-90Co/meso-HZSM-5 catalyst using synthesis gas (30 % CO, 60 % H₂, 10 % N₂), 25 mL/min, 250°C, 20 bar, 96 hours on various catalyst weight variation (1; 1.2; 1.4; 1.6 gram)

The 10Fe-90Co/meso-HZSM-5 catalyst was prepared from ammonium salt of ZSM-5 over calcination, desilication, dispersion, acid treatment [6]. The

solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were used as precursor for incipient wetness impregnation (IWI) process on amorphous meso-HZSM-5. Loading metal catalyst was 10 %. The catalyst consisted of 10 % Fe (by weight) dan 90 % Co (by weight). The impregnated HZSM-5 was kept in desiccator at room temperature for 24 hours, dried in oven at 120°C for 12 hours and then calcined at 550°C for 2 hours.

The catalyst performance was observed in a continuous fixed bed reactor (**Fig. 1**) using 10Fe-90Co/meso-HZSM-5 catalyst, 25 mL/min synthesis gas (30 % CO, 60 % H_2 , 10 % N_2) at 250°C , 20 bar. Various catalyst weight (1; 1.2; 1.4; 1.6 gram) were used in the Fischer-Tropsch reaction. The catalyst was mixed with glass beads as much as 6 times of the catalyst weight. The mixture of catalyst and glass beads was inserted into the catalyst bowl which was held with glass wool at the bottom and top of the catalyst to prevent the spilling out of the catalyst during process [21, 22]. All catalysts were reduced in situ in the reactor with H_2 gas flowing at 25 mL/min, 1 bar, 400°C for 10 hours. At the end of the reduction procedure, the reactor was cooled to 250°C and the hydrogen gas flow was stopped, then it was replaced by the synthesis gas flow. The modified pressure regulator was installed after the reactor to maintain 20 bar pressure. The flow rate was calibrated using bubble soap meter at 25 mL/min at the operating pressure and temperature. Some hydrocarbon fractions condensed through hot trap at $30\text{--}40^\circ\text{C}$ and 20 bar. The low boiling point hydrocarbon fraction would be condensed in a cold trap ($1\text{--}10^\circ\text{C}$, 1 bar). The reaction was carried out for 96 hours with gas sampling every 24 hours and liquid sampling at the end of the whole reaction. Gas samples were taken using a 10 mL syringe and injected into 10 mL vacuum bottle (vacutainer).

Brunauer–Emmett–Teller (BET) [23, 24], X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray spectroscopy (EDX) analysis were used for catalyst characterization. Gas Chromatography Mass Spectrum (GCMS) was used to measure hydrocarbon composition in the liquid product. Gas Chromatography with Thermal Conductivity Detector (GC-TCD) was used to measure the releasing gas. Please add the exact type / label /model of equipment that was used.

3. Result and discussion

3. 1. Characterization of Catalyst Fe-Co/meso-HZSM-5

Ammonium ZSM-5 (Si/Al = 40) was converted to microporous HZSM-5 through calcination process in the tube furnace reactor. The formation of mesoporous structures was obtained through the desilication process in which silicon was partly-removed from zeolite framework using NaOH as desilication agent. The desilicated HZSM-5 properties obtained from BET analysis were 6.1–29.9 nm mesoporous diameter, 0.3496 cc/g average mesoporous volume, 526.035 cc/g pore surface area, and from EDX analysis gave 22.1059 Si/Al ratio.

The Fe and Co catalysts loading was 16.11 % weight on mesoporous

HZSM-5. The loading of catalyst was calculated from EDX analyzing. The impregnated mesoporous HZSM-5 was reduced to obtain metal catalyst on the active surface. The XRD analysis was used to observe the reduction results. The diffraction angle position of the metal peaks referred to the spectral Tavasoli's database [25]. The spectra of Fe (66°), Fe-Co alloy (44.50°) and Co_3O_4 (36.80°) were shown in **Fig. 2**.

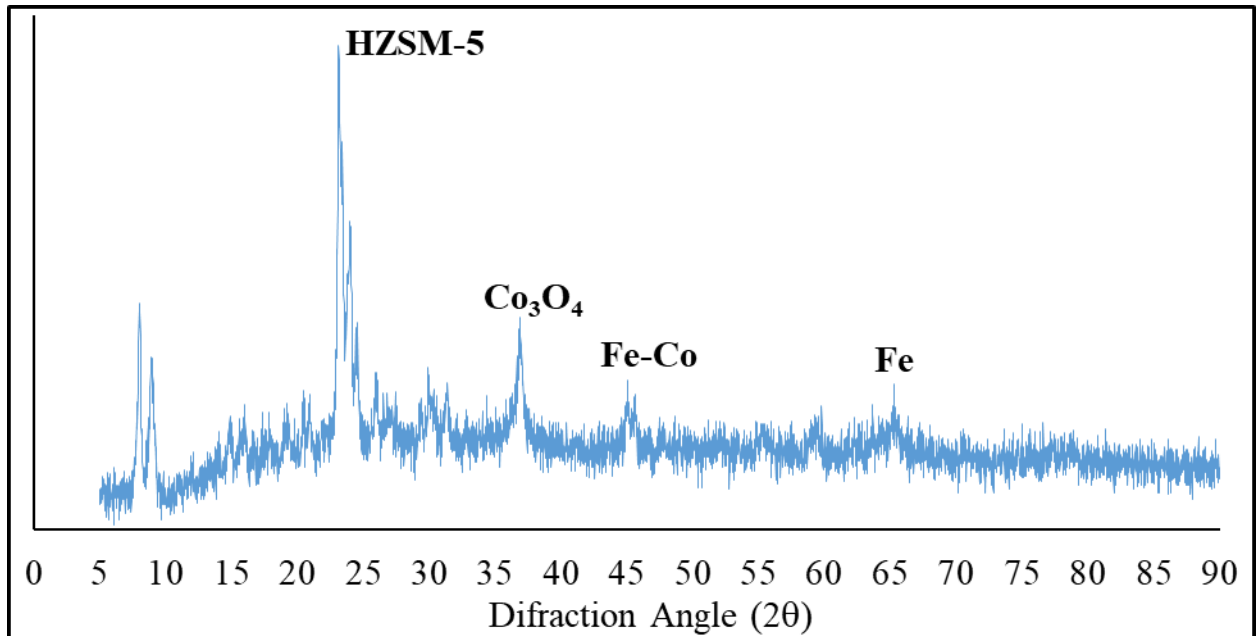


Fig. 2. The XRD Spectra for Fe-Co/HZSM-5 catalyst consisted of 10 %Fe and 90 %Co after reduction (with H_2 gas flowing at 25 mL/min, 1 bar, 400°C for 10 hours)

Please add the description for low-angle double peaks

3. 2. Effect of catalyst weight to product composition

The FTS reaction produced two layers liquid product, each of which has a pungent odor. The two layer liquid product were taken from hot trap chamber ($30\text{--}40^\circ\text{C}$). Both of layers had similar viscosity. The upper layer was clear yellow, while the lower layer was colorless. From GCMS analysis, the upper layer contained alkanes (paraffin) and less alkene (olefin). Carboxylic acids, alcohols, esters and aromatic compounds were found in the lower layer products. The increasing catalyst weight gave the higher alkane selectivity. One gram of catalyst obtained 85.04 % alkanes and 7.56 % alkenes. The alkane composition rose to 96.33 % on 1.2 grams of catalyst and increased again to 99.96 % on 1.4 and 1.6 grams of catalyst. Straight chain hydrocarbon selectivity was quite large (57–72 %). The 1.6 gram catalyst gave the greatest selectivity (72.03 %) when compared to 57.14 % on 1 gram catalyst. The more catalysts used, the greater active surface involved in the reaction so that the catalyst's performance was better. The reactants contained double H_2 than CO (H_2/CO ratio =2). The greater

active surface area increased the concentration of hydrogen free radicals, so the reaction mechanism lead to the formation of paraffins and carboxylic acids.

The combination of polymerization using metal catalyst (Fe-Co) and cracking (meso-HZSM-5) in the FTS intended to produce saturated C₅-C₁₉ hydrocarbons (gasoline, kerosene and diesel oil). The product distribution based on the hydrocarbon chain length in the both layers could be seen in **Fig. 3, 4**. The upper layer was dominated by alkane hydrocarbons with C₇-C₂₅ hydrocarbon chain length (**Fig. 3**). The use of 1 and 1.2 gram catalysts produced C₇-C₁₉ hydrocarbon while the more catalyst weight produced less C₂₀-C₂₅ hydrocarbon (below 1.7 %). The 1 and 1.2 gram catalyst might form C₂₀-C₂₅ in such a small amount, so that GCMS could not detect this traces. Increasing catalyst weight would rise the reaction chance on the catalyst active surface so that the more product was obtained (higher conversion) and the presence of C₂₀-C₂₅ hydrocarbon could be measured using GCMS. The FT reaction using 10Fe-90Co/meso-HZSM-5 catalyst at 250°C and 1 bar produced gasoline, kerosene and diesel oil. Kerosene was the largest product (55.18–61.68 %), was obtained from the catalyst weight of 1–1.6 gram. The largest gasoline fraction (19.15 %) was obtained from 1 gram of catalyst and decreased with increasing catalyst weight. The diesel oil fraction increased with the catalyst weight. The largest solar fraction (19.34 %) was obtained from 1.6 gram of catalyst. The greater the catalyst weight, the greater the diesel fuel produced and the smaller the gasoline produced.

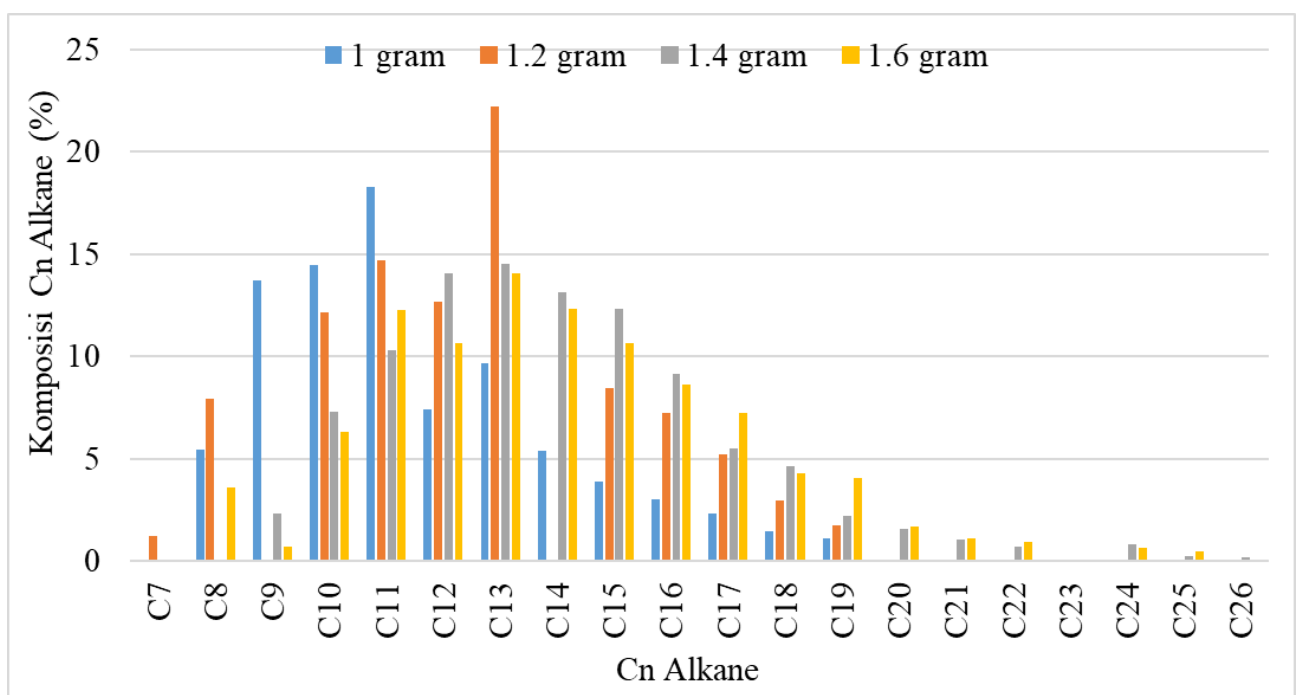


Fig. 3. Distribution of upper layer liquid products from Fischer-Tropsch reaction with catalyst 10Fe-90Co/meso-HZSM-5, loading 10 %, synthesis gas (30 % CO, 60 % H₂, 10 % N₂), 25 mL/min, 250°C, 20 bar, 96 hours at various

catalyst weight variation (1; 1.2; 1.4; 1.6 gram)

The lower layer showed the FTS side reaction, that produced alcohol, carboxylic acid, ester, aromatic and cycloalkane compounds (**Fig. 4**). The carboxylic acid were formed at any weight variation. The alcohol were formed in large amount at 1.2 and 1.4 gram catalyst. This condition could be used to alternative alcohol production from synthesis gas with this catalyst.

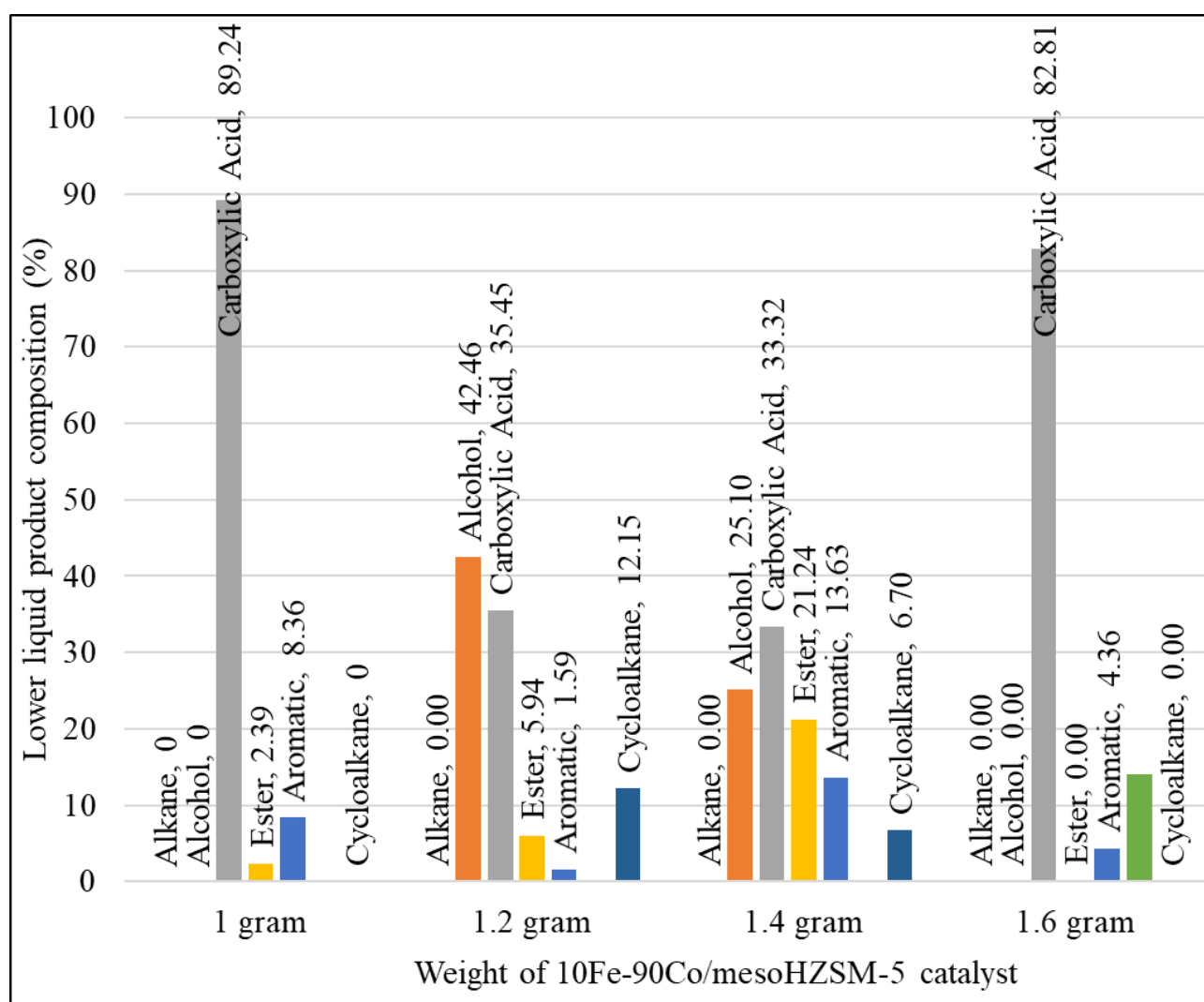


Fig. 4. Distribution of lower layer liquid products from Fischer-Tropsch reaction with catalyst 10Fe-90Co/meso-HZSM-5, loading 10 %, synthesis gas (30 % CO, 60 % H₂, 10 % N₂), 25 mL/min, 250°C, 20 bar , 96 hours at various catalyst weight variation (1; 1.2; 1.4; 1.6 gram)

The more 10Fe-90Co/meso-HZSM-5 catalyst, which used in the FT reaction, would have the greater active surface area. They might increase the reaction chances that increased CO conversion (**Fig. 5**). The larger active surfaces would increase CO dissociation which initiated the polymerization process. The

CO conversion on 1 gram of catalyst was 27.33 % which increased to 42.46 % on the use of 1.6 grams of catalyst.

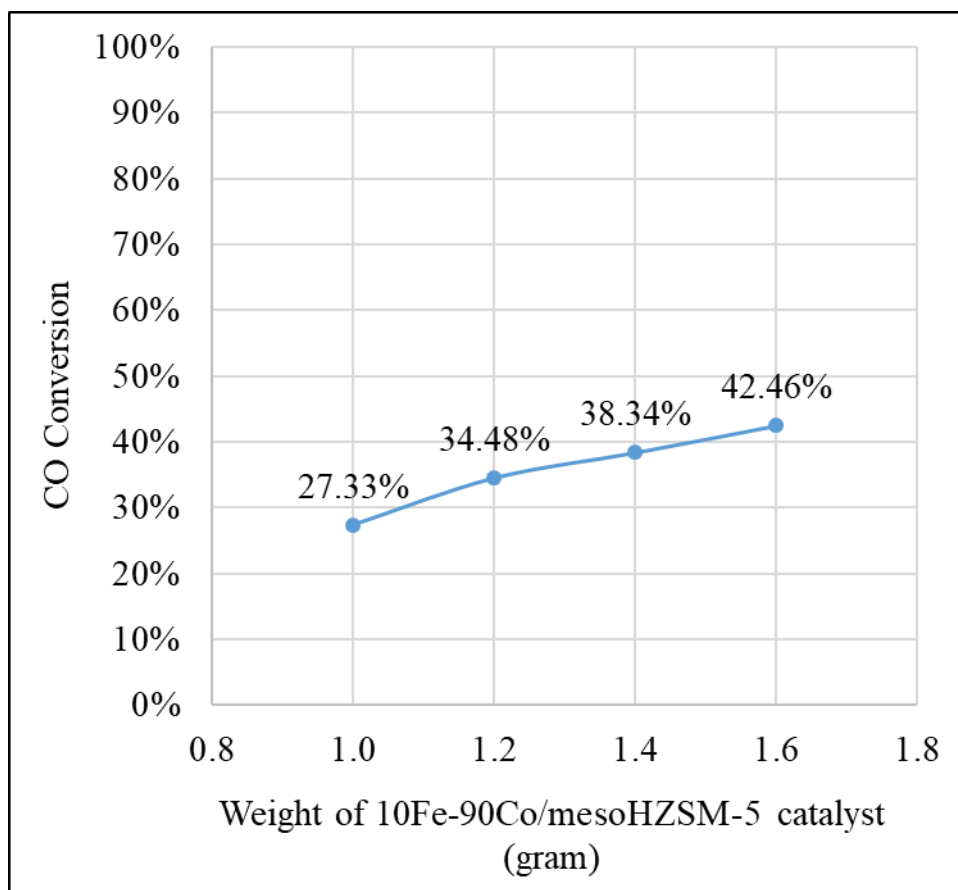


Fig. 5. The CO conversion from the Fischer-Tropsch reaction with catalyst 10Fe-90Co/meso-HZSM-5, loading 10 %, synthesis gas (30 % CO, 60 % H₂, 10 % N₂), 25 mL/min, 250°C, 20 bar, 96 hours on various catalyst weight variation (1; 1.2; 1.4; 1.6 gram). **As far you have less than 4 pairs of X and Y data it is recommended to use a histogram**

The residual gas consisted of CO, H₂, CO₂ and CH₄ were measured by GC-TCD (**Fig. 6**). The decreasing CO fraction in the residual gas showed that CO consumption increased with more catalysts being used. The formation of a relatively small CO₂ indicated that the WGS reaction was not dominant in the condition and catalyst used. The greater Co catalyst (90 %) in the bimetal Fe-Co did not push WGS reaction. But with increasing catalyst weight, the Fe weight was also larger, so that more CO₂ gas formation (1–2 %) was obtained in the use of catalysts 1.2-1.6 gram. However, the larger Co in the Fe-Co would drive the methane formation. The analysis showed that methane was formed in all catalyst weight insignificantly. In the 1 gram of catalyst, only 1 % methane was formed, while the use of more catalysts produced 5-6 % methane. The bimetal combination on supported mesoporous HZSM-5 reduced methane formation

significantly compared to previous studies [3, 17, 26], which produced 7.9–21 % methane

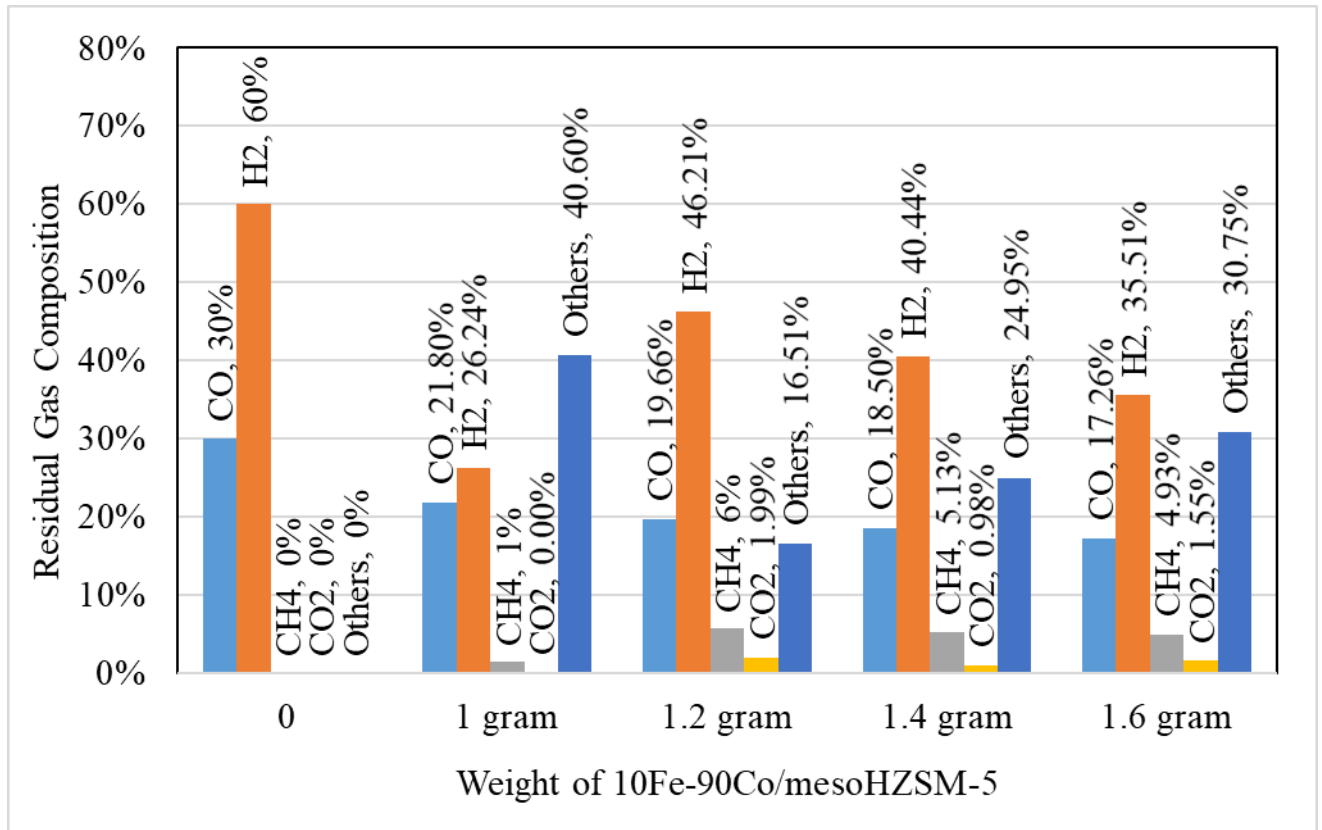


Fig. 6. The residual gas composition from the Fischer-Tropsch reaction with catalyst 10Fe-90Co/meso-HZSM-5, loading 10 %, synthesis gas (30 % CO, 60 % H₂, 10 % N₂), 25 mL/min, 250°C, 20 bar, 96 hours on various catalyst weight variations (1; 1.2; 1.4; 1.6 gram) **Please make subscripts for substances in the figure properly**

3. 3. Normalization of Selectivity and Conversion Conversion

Normalization of liquid products selectivity and reaction conversion to catalyst weight was conducted to determine the efficiency and effectiveness of the catalysts use. The product selectivity and conversion were normalized by the catalyst weight that was varied in this study. This normalization data could be used to take better decision in the catalyst efficiency and effectiveness before commercializing.

Normalization of biofuel selectivity (gasoline, kerosene and diesel) to the 10Fe-90Co/meso-HZSM-5 catalyst weight in the FT reaction of 250°C, 20 bar using synthesis gas (30 % CO, 60 % H₂, 10 % N₂) for 96 hours was shown in **Fig. 7**. The 1 gram catalyst weight gave the largest normal selectivity to gasoline (19.15 %) and kerosene (55.18 %). While the largest normal diesel oil selectivity (24.17 %) was obtained from the use of 1.4 gram of catalyst weight.

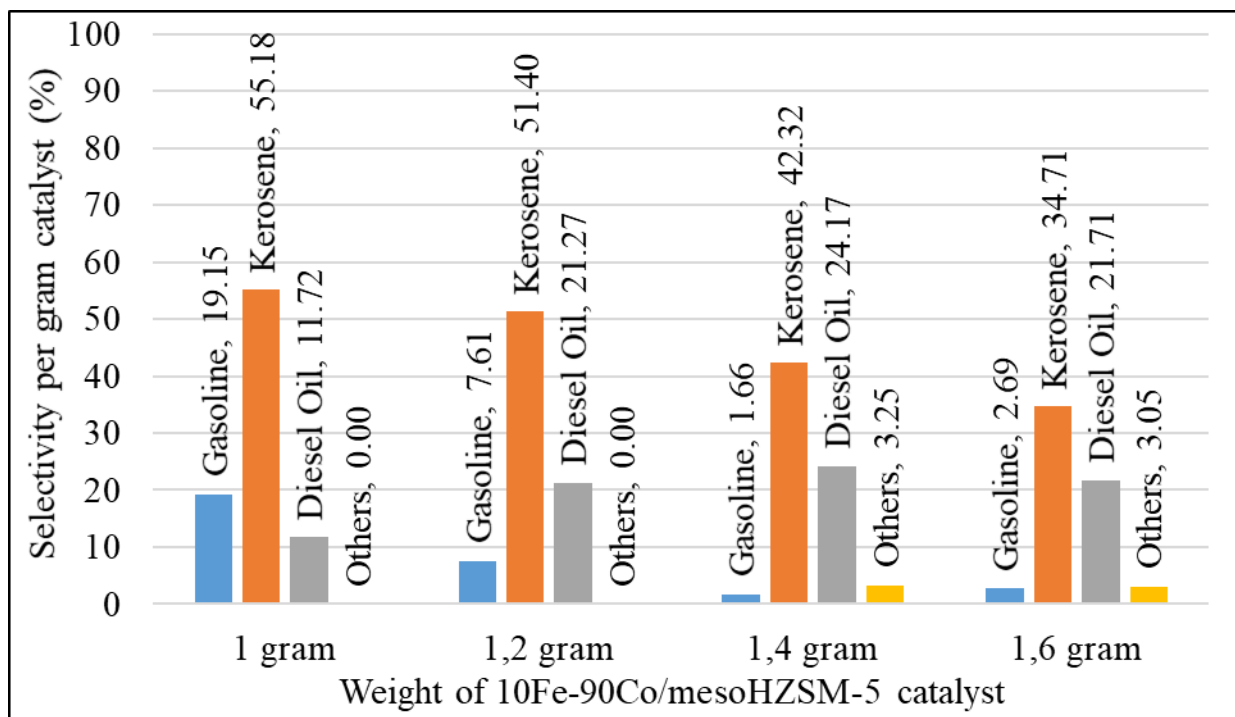


Fig. 7. Normalization of biofuel selectivity (gasoline, kerosene and diesel) to the 10Fe-90Co/meso-HZSM-5 catalyst weight in the 250°C, 20 bar Fischer-Tropsch reaction of using synthesis gas (30 % CO, 60 % H₂, 10 % N₂) for 96 hours

Normalization of CO reaction conversion to the 10Fe-90Co/meso-HZSM-5 catalyst weight in the 250°C, 20 bar FT reaction using synthesis gas (30 % CO, 60 % H₂, 10 % N₂) for 96 hours was shown in **Fig. 8**. The resulting normal conversion showed similar value for all catalyst in the range of 0.26-0.28. All catalyst weight variation showed similar normal conversion over 96 hours, so the use of 1 gram of catalyst was more economically beneficial. These results were in line with the normal selectivity of gasoline and kerosene products that reached the highest value on the use of 1 gram of catalyst.

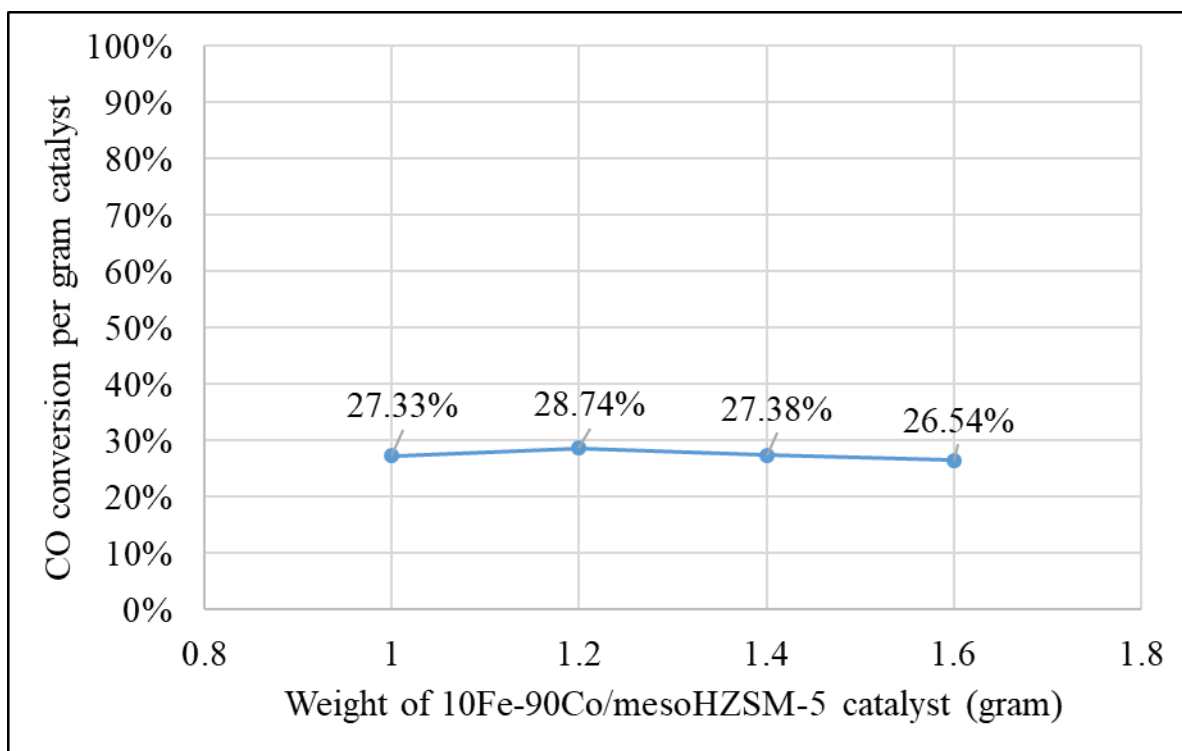


Fig. 8. Normalization of CO conversion to the 10Fe-90Co /meso-HZSM-5 catalyst weight variation in the 250°C, 20 bar Fischer-Tropsch reaction using synthesis gas (30 % CO, 60 % H₂, 10 % N₂) for 96 hours. **As far you have less than 4 pairs of X and Y data it is recommended to use a histogram**

4. Conclusion

The desilicated HZSM-5 properties (BET analysis) were 6.1-29.9 nm mesoporous diameter, 0.3496 cc/g average mesoporous volume, 526.035 cc/g pore surface area, and the EDX analysis gave 22.1059 Si/Al ratio and 16.11 % loading (by weight) on meso-HZSM-5. The reduced catalyst showed the XRD spectra of Fe (66°), Fe-Co alloy (44.50°) and Co₃O₄ (36.80°).

The Fischer-Tropsch reaction using 1 gram of 10Fe-90Co/meso-HZSM-5 catalyst and synthesis gas (30 % CO, 60 % H₂, 10 % N₂) at 250°C, 20 bar, 96 hours in the continuous fixed-bed reactor, showed the largest composition and conversion. The combination of polymerization using metal catalyst (Fe-Co) and cracking (meso-HZSM-5) was intended to produce saturated C₅-C₂₅ hydrocarbons (gasoline, kerosene and diesel oil). The 1 gram catalyst weight gave the largest normal selectivity to gasoline (19.15 %) and kerosene (55.18 %). While the largest normal diesel oil selectivity (24.17 %) was obtained from 1.4 gram of catalyst. The CO conversion per gram of catalyst showed similar value (26–28 %) for all catalyst weight.

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Review

This article contains results that may be of interest to both science and practice. However, one important point should be noted. It refers to the **Discussion** section. It is necessary to add such information:

- what limitations are inherent in this study?
- what direction should the study be developed?

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BIOFUEL PRODUCTION OVER FISCHER-TROPSCH SYNTHESIS: EFFECT OF Fe-Co/meso-HZSM-5 CATALYST WEIGHT ON PRODUCT COMPOSITION AND PROCESS CONVERSION

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Abstract

Fischer-Tropsch Synthesis (FTS) using Fe-Co/meso-HZSM-5 catalyst has been investigated. The impregnated iron and cobalt on HZSM-5 could be used as bifunction catalyst which combined polymerizing synthesis gas and long hydrocarbon cracking for making biofuel (saturated C₅-C₂₅ hydrocarbons as gasoline, kerosene and diesel oil). The study emphasized the effect of catalyst weight on product composition and process conversion. The HZSM-5, had been converted from ammonium ZSM-5 through calcination, and then desilicated with NaOH solution. The Co(NO₃)₂·6H₂O and Fe(NO₃)₃·9H₂O were used as precursor for incipient wetness impregnation (IWI) on amorphous meso-HZSM-5. The catalyst consisted of 10 % Fe and 90 % Co by weight, called 10Fe-90Co/meso-HZSM-5. All catalysts were reduced in situ in the continuous reactor with flowing hydrogen at 25 mL/min, 1 bar, 400°C for 10 hours. The catalyst performance was observed in the same continuous fixed bed reactor at 25 mL/min synthesis gas (30 % CO, 60 % H₂, 10 % N₂), 250°C, 20 bar for 96 hours. Various catalyst weight (1, 1.2, 1.4, 1.6 gram) were applied in FTS. The desilicated HZSM-5 properties (BET analysis) were 6.1-29.9 nm mesoporous diameter, 0.3496 cc/g average mesoporous volume, 526.035 cc/g pore surface area, and the EDX analysis gave 22.1059 Si/Al ratio and 16.11 % loading (by weight) on meso-HZSM-5. The reduced catalyst showed the XRD spectra of Fe (66°), Fe-Co alloy (44.50°) and Co₃O₄ (36.80°). The reaction using 1 gram of 10Fe-90Co/meso-HZSM-5 catalyst produced the largest composition and conversion. The 1 gram catalyst gave the largest normal selectivity of gasoline (19.15 %) and kerosene (55.18 %). While the largest normal diesel oil selectivity (24.17 %) was obtained from 1.4 gram of catalyst. The CO conversion per gram of catalyst showed similar value (CO conversion of 26-28 %) for all catalyst weight.

Keywords: biofuel, HZSM-5, desilication, mesopore, catalyst, iron, cobalt, weight, conversion, Fischer-Tropsch

1. Introduction

Zeolites are used in the process of separation, adsorption, and catalytic (i.e. cracking and other hydrotreating process). Homogeneous micropores, high thermal stability, acidity, and unique ability to stabilize metallic species were several their unique properties [1]. The mesoporous structure provides greater space for metal catalysts to occupy more support pores. The mesopore can be obtained from micropore over desilication treatment. The alkali (NaOH) solution was used as desilication agent. Nitric acid solution was used to transform the mesoporous HZSM-5 into amorphous structure, which could improve the adhesion of the metal catalyst on the mesoporous HZSM-5 support [2–5]. The

KOH solution induced greater mesoporous volumes, but it damaged on zeolite crystal structure. The NaOH solutions was able to increased mesopore surface area and mesopore volume of NaOH-desilicated HZSM-5. The Fe-Co alloys were observed with less oxide of iron (Fe_2O_3) as well cobalt (Co_3O_4) in the produced catalysts [6].

The Fischer-Tropsch synthesis (FTS) is an exothermic and irreversible polymerization reaction that converts a mixture of hydrogen (H_2) and carbon monoxide (CO) into linear hydrocarbons as liquid fuel. FTS always produces various products such as olefins, paraffins and oxygenated compounds (alcohols, aldehydes, acids and ketones). Water was the main product of the FT reaction. Water Gas Shift (WGS) activity occurred significantly in the use of Fe catalyst, but this reaction could be ignored in reactions using Co or Ru catalysts. Iron and cobalt as polymerization catalyst were used at FTS. The impregnated iron and cobalt on HZSM-5 could be used as bifunction catalyst which combined polymerizing synthesis gas and long chain hydrocarbon cracking for making biofuel [7–11]. The FTS preferred preferred to use cobalt because of some advantages, instead of iron catalyst. Iron catalyst was added in little amount to improve the cobalt catalyst performance (improve olefin selectivity, reduce methane selectivity, reduce temperature and pressure sensitivity to product distribution and reduce the catalyst price) [12, 13].

The combination of the Fischer-Tropsch (FT) reaction and cracking was conducted by combining Fe-Co alloy (Fischer-Tropsch reaction catalyst) and HZSM-5 zeolite (cracking catalyst). The merging of the FTS and cracking was able to produce biofuel product directly [7]. The Fe/HZSM-5 catalyst was able to produce 24.2 % of C_{5-19} hydrocarbon as biofuel fraction [14]. The Co/HZSM-5 catalyst produced 48 % of C_{5-11} [3]. The use of Fe and Co catalysts together (bimetallic) could increase catalytic activity compared to the use single metal catalyst (monometallic). The combination of Fe and Co catalysts (bimetal catalysts) with conventional TiO_2 , Al_2O_3 and SiO_2 supports had been investigated. They could increase the biofuel reaction conversion and fraction compared to the use of Fe and Co catalysts separately [15–17]. The variables that influenced product distribution were temperature, feed gas composition, pressure, catalyst type and promoter. The synthesis gas composition influenced the product selectivity. The lower the CO partial pressure, the lower the surface coverage of CH_2 radicals, the lower the chain growth chance and the higher the chance of CH_2 radicals desorption. The higher the H_2 partial pressure, increases the chance of radicals termination being paraffin. Increasing H_2/CO ratio would increase the selectivity of short-chain and more saturated hydrocarbons [18–20].

The study emphasized the effect of Fe-Co/mesoHZSM5 catalyst weight on product composition and conversion. The data obtained from this study will be used to develop efficiency of the Fischer-Tropsch reaction condition.

2. Methods

Materials used in this experiment were zeolite ZSM-5 in ammonium form (CBV 8014, Amberlyst International), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Merck), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Merck), NaOH p.a. (Merck), nitric ammonium p.a. (Merck), nitric acid (Merck), Hydrogen gas (PT. Samator Gas Industry, Surabaya, Indonesia), synthesis gas (30 % CO , 60 % H_2 , 10 % N_2), glass beads 2 mm (Marienfeld), glass wool, aquadest. The equipment used were the tubular furnace, quartz furnace crucible, hotplate magnetic stirrer, vacuum filter, air compressor, hot air oven, syringe, digital scales and standard glassware for catalyst synthesis. The continuous fixed-bed Fischer-Tropsch reactor (**Fig. 1**), hot trap, cold trap, bubble soap meter, vacutainer (vacuum bottle/container) were used for FTS.

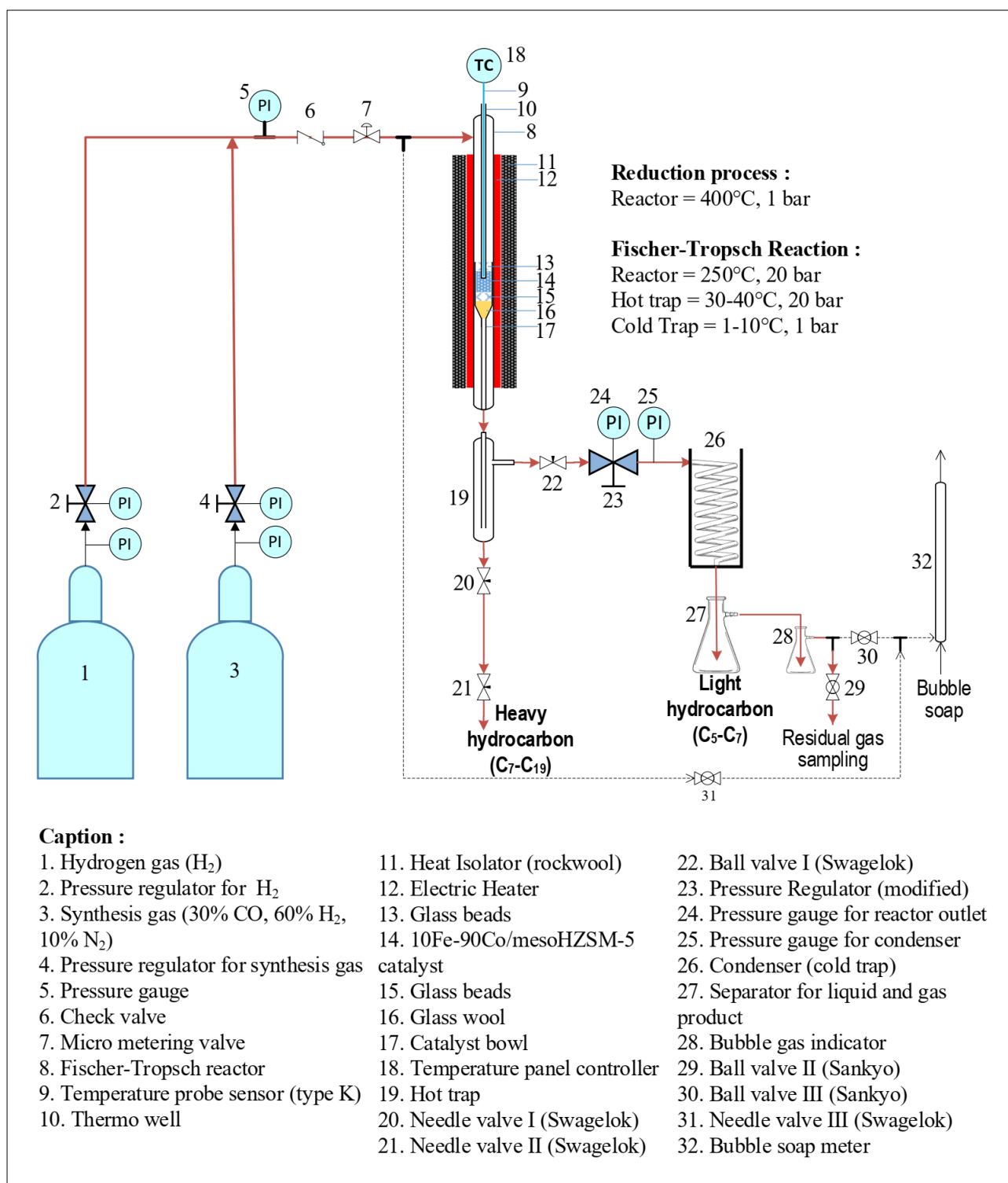


Fig. 1. The reactor unit of continuous Fischer-Tropsch synthesis for 10Fe-90Co/meso-HZSM-5 catalyst using synthesis gas (30 % CO, 60 % H₂, 10 % N₂), 25 mL/min, 250°C, 20 bar, 96 hours on various catalyst weight variation (1; 1.2; 1.4; 1.6 gram)

The 10Fe-90Co/meso-HZSM-5 catalyst was prepared from ammonium salt of ZSM-5 over calcination, desilication, dispersion, acid treatment [6]. The

solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were used as precursor for incipient wetness impregnation (IWI) process on amorphous meso-HZSM-5. Loading metal catalyst was 10 %. The catalyst consisted of 10 % Fe (by weight) and 90 % Co (by weight). The impregnated HZSM-5 was kept in desiccator at room temperature for 24 hours, dried in oven at 120°C for 12 hours and then calcined at 550°C for 2 hours.

The catalyst performance was observed in a continuous fixed bed reactor (**Fig. 1**) using 10Fe-90Co/meso-HZSM-5 catalyst, 25 mL/min synthesis gas (30 % CO, 60 % H_2 , 10 % N_2) at 250°C , 20 bar. Various catalyst weight (1; 1.2; 1.4; 1.6 gram) were used in the Fischer-Tropsch reaction. The catalyst was mixed with glass beads as much as 6 times of the catalyst weight. The mixture of catalyst and glass beads was inserted into the catalyst bowl which was held with glass wool at the bottom and top of the catalyst to prevent the spilling out of the catalyst during process [21, 22]. All catalysts were reduced in situ in the reactor with H_2 gas flowing at 25 mL/min, 1 bar, 400°C for 10 hours. At the end of the reduction procedure, the reactor was cooled to 250°C and the hydrogen gas flow was stopped, then it was replaced by the synthesis gas flow. The modified pressure regulator was installed after the reactor to maintain 20 bar pressure. The flow rate was calibrated using bubble soap meter at 25 mL/min at the operating pressure and temperature. Some hydrocarbon fractions condensed through hot trap at $30\text{--}40^\circ\text{C}$ and 20 bar. The low boiling point hydrocarbon fraction would be condensed in a cold trap ($1\text{--}10^\circ\text{C}$, 1 bar). The reaction was carried out for 96 hours with gas sampling every 24 hours and liquid sampling at the end of the whole reaction. Gas samples were taken using a 10 mL syringe and injected into 10 mL vacuum bottle (vacutainer).

3. Result and discussion

3. 1. Characterization of Catalyst Fe-Co/meso-HZSM-5

Ammonium ZSM-5 (Si/Al = 40) was converted to microporous HZSM-5 through calcination process in the tube furnace reactor. The formation of mesoporous structures was obtained through the desilication process in which silicon was partly-removed from zeolite framework using NaOH as desilication agent. The desilicated HZSM-5 properties obtained from BET analysis were 6.1–29.9 nm mesoporous diameter, 0.3496 cc/g average mesoporous volume, 526.035 cc/g pore surface area, and from EDX analysis gave 22.1059 Si/Al ratio.

The Fe and Co catalysts loading was 16.11 % weight on mesoporous HZSM-5. The loading of catalyst was calculated from EDX analyzing. The impregnated mesoporous HZSM-5 was reduced to obtain metal catalyst on the active surface. The XRD analysis was used to observe the reduction results. The diffraction angle position of the metal peaks referred to the spectral Tavasoli's database [25]. The spectra of Fe (66°), Fe-Co alloy (44.50°) and Co_3O_4 (36.80°) were shown in **Fig. 2**.

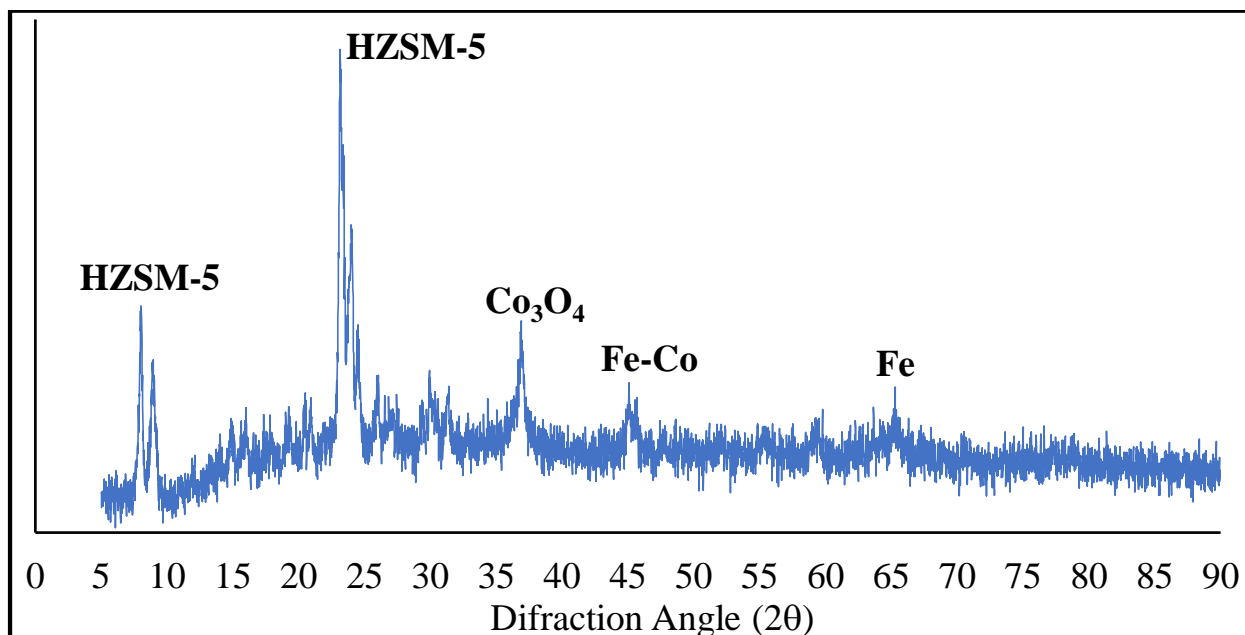


Fig. 2. The XRD Spectra for Fe-Co/HZSM-5 catalyst consisted of 10 %Fe and 90 %Co after reduction (with H₂ gas flowing at 25 mL/min, 1 bar, 400°C for 10 hours)

3. 2. Effect of catalyst weight to product composition

The FTS reaction produced two layers liquid product, each of which has a pungent odor. The two layer liquid product were taken from hot trap chamber (30–40 °C). Both of layers had similar viscosity. The upper layer was clear yellow, while the lower layer was colorless. From GCMS analysis, the upper layer contained alkanes (paraffin) and less alkene (olefin). Carboxylic acids, alcohols, esters and aromatic compounds were found in the lower layer products. The increasing catalyst weight gave the higher alkane selectivity. One gram of catalyst obtained 85.04 % alkanes and 7.56 % alkenes. The alkane composition rose to 96.33 % on 1.2 grams of catalyst and increased again to 99.96 % on 1.4 and 1.6 grams of catalyst. Straight chain hydrocarbon selectivity was quite large (57–72 %). The 1.6 gram catalyst gave the greatest selectivity (72.03 %) when compared to 57.14 % on 1 gram catalyst. The more catalysts used, the greater active surface involved in the reaction so that the catalyst's performance was better. The reactants contained double H₂ than CO (H₂/CO ratio =2). The greater active surface area increased the concentration of hydrogen free radicals, so the reaction mechanism led to the formation of paraffins and carboxylic acids.

The combination of polymerization using metal catalyst (Fe-Co) and cracking (meso-HZSM-5) in the FTS intended to produce saturated C₅-C₁₉ hydrocarbons (gasoline, kerosene and diesel oil). The product distribution based on the hydrocarbon chain length in the both layers could be seen in **Fig. 3, 4**. The upper layer was dominated by alkane hydrocarbons with C₇-C₂₅ hydrocarbon

chain length (**Fig. 3**). The use of 1 and 1.2 gram catalysts produced C_7 - C_{19} hydrocarbon while the more catalyst weight produced less C_{20} - C_{25} hydrocarbon (below 1.7 %). The 1 and 1.2 gram catalyst might form C_{20} - C_{25} in such a small amount, so that GCMS could not detect this traces. Increasing catalyst weight would rise the reaction chance on the catalyst active surface so that the more product was obtained (higher conversion) and the presence of C_{20} - C_{25} hydrocarbon could be measured using GCMS. The FT reaction using 10Fe-90Co/meso-HZSM-5 catalyst at 250°C and 1 bar produced gasoline, kerosene and diesel oil. Kerosene was the largest product (55.18–61.68 %), was obtained from the catalyst weight of 1–1.6 gram. The largest gasoline fraction (19.15 %) was obtained from 1 gram of catalyst and decreased with increasing catalyst weight. The diesel oil fraction increased with the catalyst weight. The largest solar fraction (19.34 %) was obtained from 1.6 gram of catalyst. The greater the catalyst weight, the greater the diesel fuel produced and the smaller the gasoline produced.

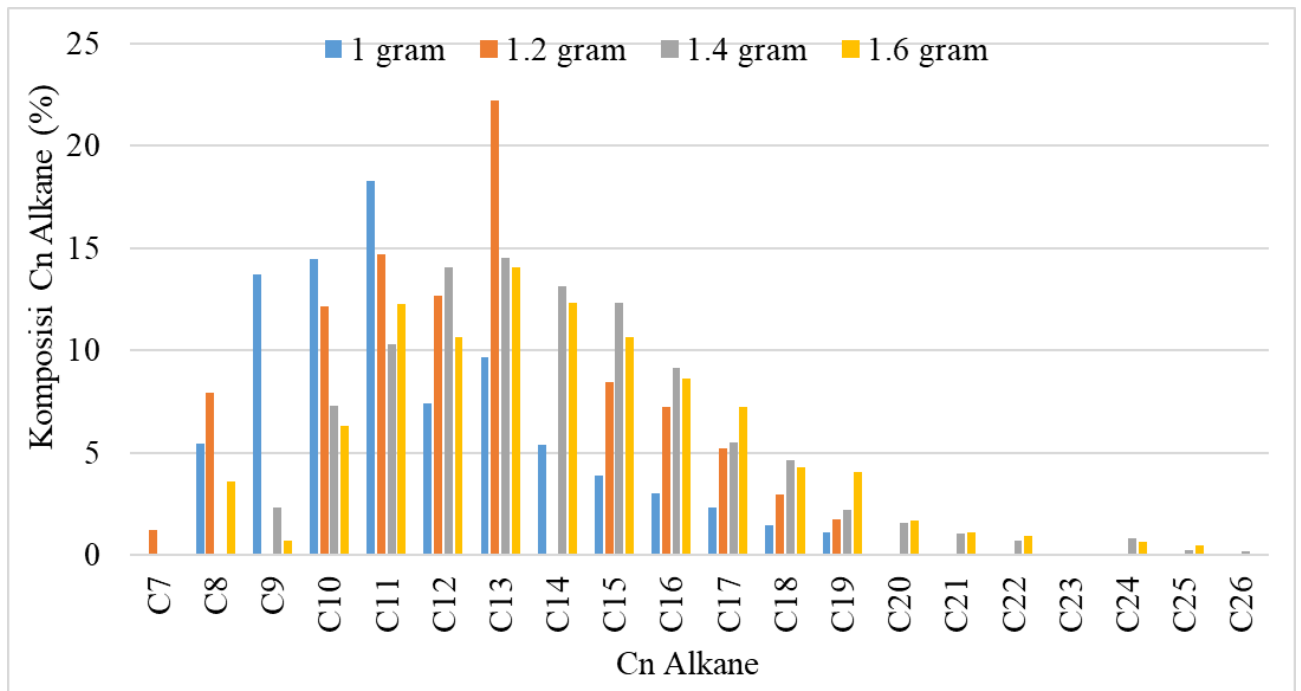


Fig. 3. Distribution of upper layer liquid products from Fischer-Tropsch reaction with catalyst 10Fe-90Co/meso-HZSM-5, loading 10 %, synthesis gas (30 % CO, 60 % H₂, 10 % N₂), 25 mL/min, 250°C, 20 bar , 96 hours at various catalyst weight variation (1; 1.2; 1.4; 1.6 gram)

The lower layer showed the FTS side reaction, that produced alcohol, carboxylic acid, ester, aromatic and cycloalkane compounds (**Fig. 4**). The carboxylic acid were formed at any weight variation. The alcohol were formed in large amount at 1.2 and 1.4 gram catalyst. This condition could be used to alternative alcohol production from synthesis gas with this catalyst.

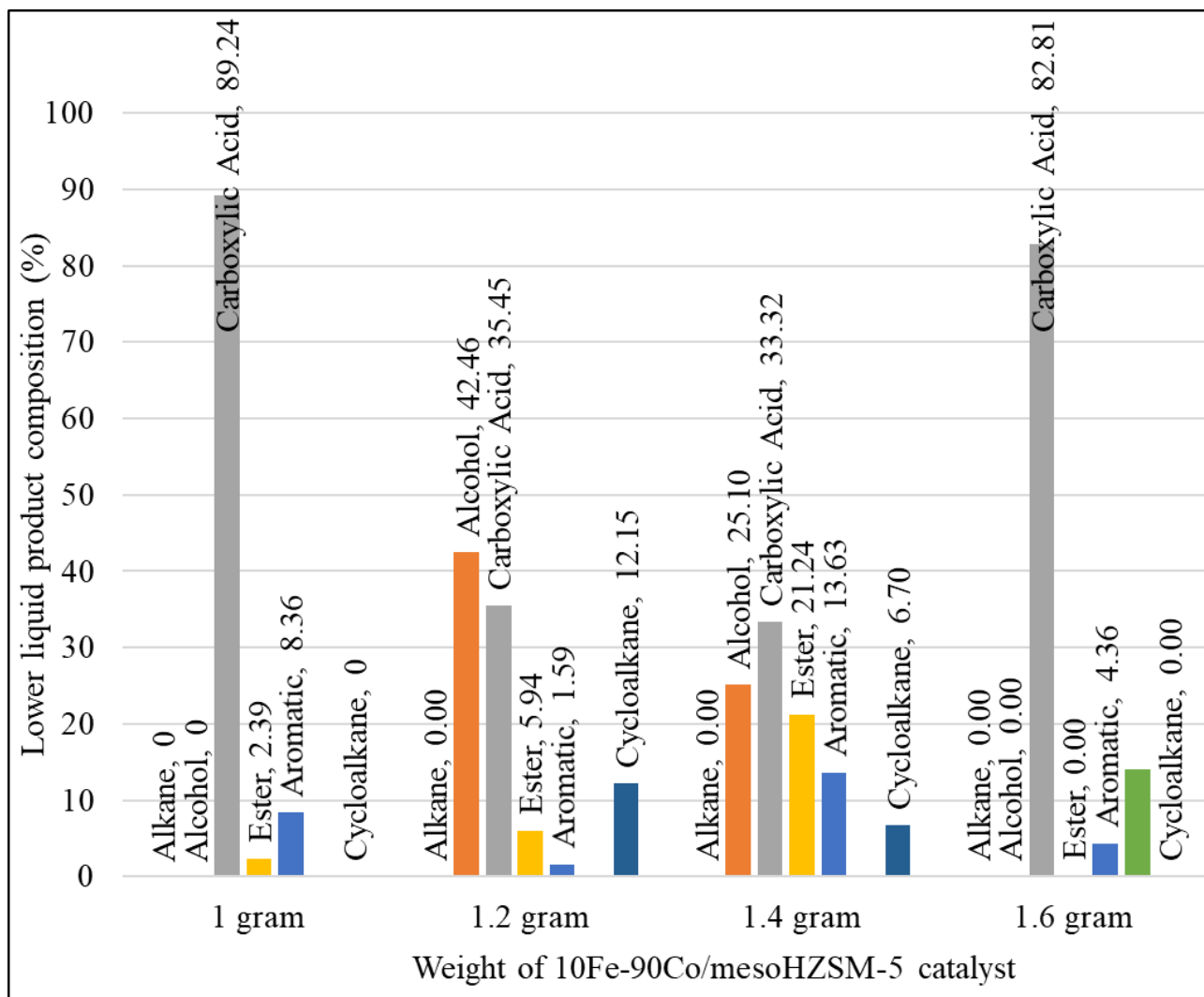


Fig. 4. Distribution of lower layer liquid products from Fischer-Tropsch reaction with catalyst 10Fe-90Co/meso-HZSM-5, loading 10 %, synthesis gas (30 % CO, 60 % H₂, 10 % N₂), 25 mL/min, 250°C, 20 bar , 96 hours at various catalyst weight variation (1; 1.2; 1.4; 1.6 gram)

The more 10Fe-90Co/meso-HZSM-5 catalyst, which used in the FT reaction, would have the greater active surface area. They might increase the reaction chances that increased CO conversion (**Fig. 5**). The larger active surfaces would increase CO dissociation which initiated the polymerization process. The CO conversion on 1 gram of catalyst was 27.33 % which increased to 42.46 % on the use of 1.6 grams of catalyst.

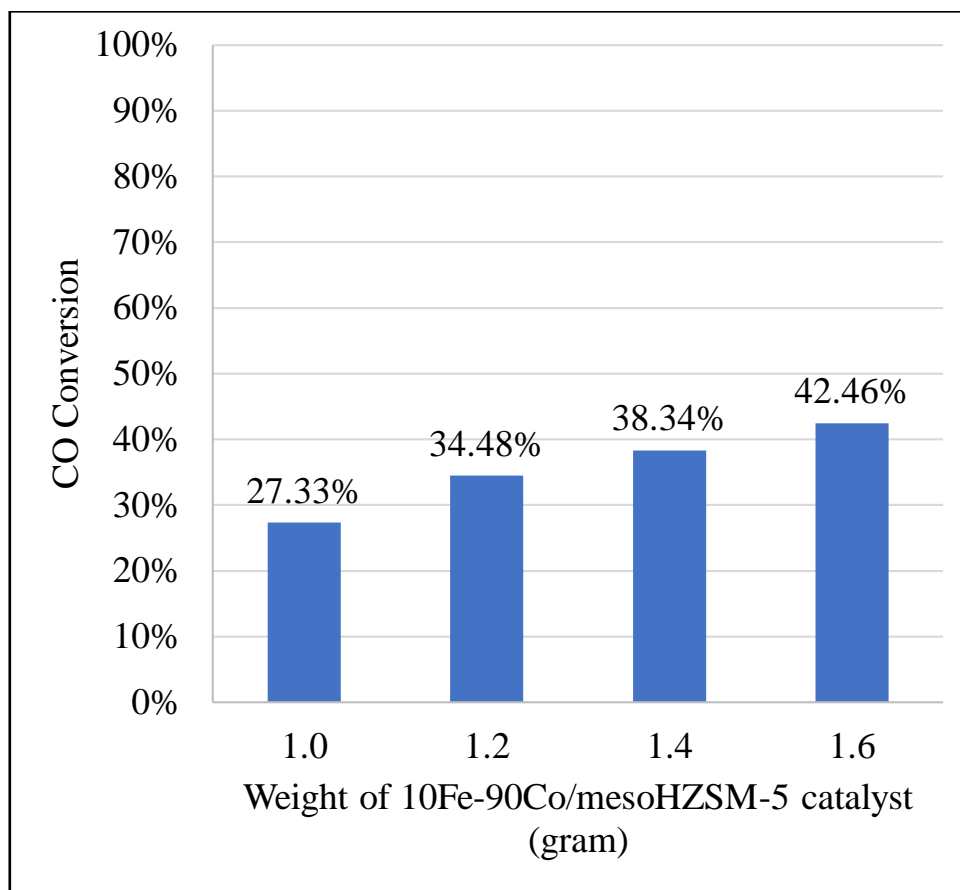


Fig. 5. The CO conversion from the Fischer-Tropsch reaction with catalyst 10Fe-90Co/meso-HZSM-5, loading 10 %, synthesis gas (30 % CO, 60 % H₂, 10 % N₂), 25 mL/min, 250°C, 20 bar, 96 hours on various catalyst weight variation (1; 1.2; 1.4; 1.6 gram)

The residual gas consisted of CO, H₂, CO₂ and CH₄ were measured by GC-TCD (**Fig. 6**). The decreasing CO fraction in the residual gas showed that CO consumption increased with more catalysts being used. The formation of a relatively small CO₂ indicated that the WGS reaction was not dominant in the condition and catalyst used. The greater Co catalyst (90 %) in the bimetal Fe-Co did not push WGS reaction. But with increasing catalyst weight, the Fe weight was also larger, so that more CO₂ gas formation (1–2 %) was obtained in the use of catalysts 1.2-1.6 gram. However, the larger Co in the Fe-Co would drive the methane formation. The analysis showed that methane was formed in all catalyst weight insignificantly. In the 1 gram of catalyst, only 1 % methane was formed, while the use of more catalysts produced 5-6 % methane. The bimetal combination on supported mesoporous HZSM-5 reduced methane formation significantly compared to previous studies [3, 17, 26], which produced 7.9–21 % methane

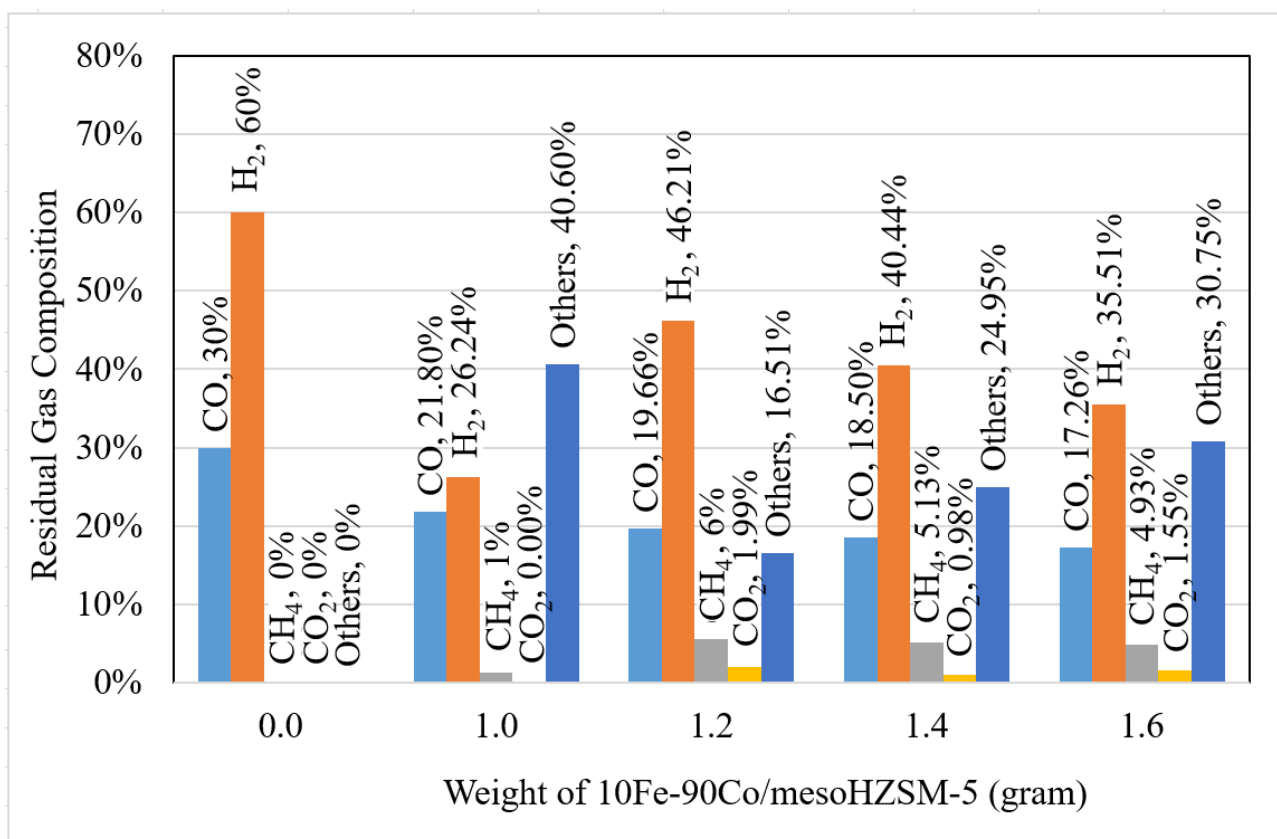


Fig. 6. The residual gas composition from the Fischer-Tropsch reaction with catalyst 10Fe-90Co/meso-HZSM-5, loading 10 %, synthesis gas (30 % CO, 60 % H₂, 10 % N₂), 25 mL/min, 250°C, 20 bar, 96 hours on various catalyst weight variations (1; 1.2; 1.4; 1.6 gram)

3. 3. Normalization of Selectivity and Conversion Conversion

Normalization of liquid products selectivity and reaction conversion to catalyst weight was conducted to determine the efficiency and effectiveness of the catalysts use. The product selectivity and conversion were normalized by the catalyst weight that was varied in this study. This normalization data could be used to take better decision in the catalyst efficiency and effectiveness before commercializing.

Normalization of biofuel selectivity (gasoline, kerosene and diesel) to the 10Fe-90Co/meso-HZSM-5 catalyst weight in the FT reaction of 250°C, 20 bar using synthesis gas (30 % CO, 60 % H₂, 10 % N₂) for 96 hours was shown in **Fig. 7**. The 1 gram catalyst weight gave the largest normal selectivity to gasoline (19.15 %) and kerosene (55.18 %). While the largest normal diesel oil selectivity (24.17 %) was obtained from the use of 1.4 gram of catalyst weight.

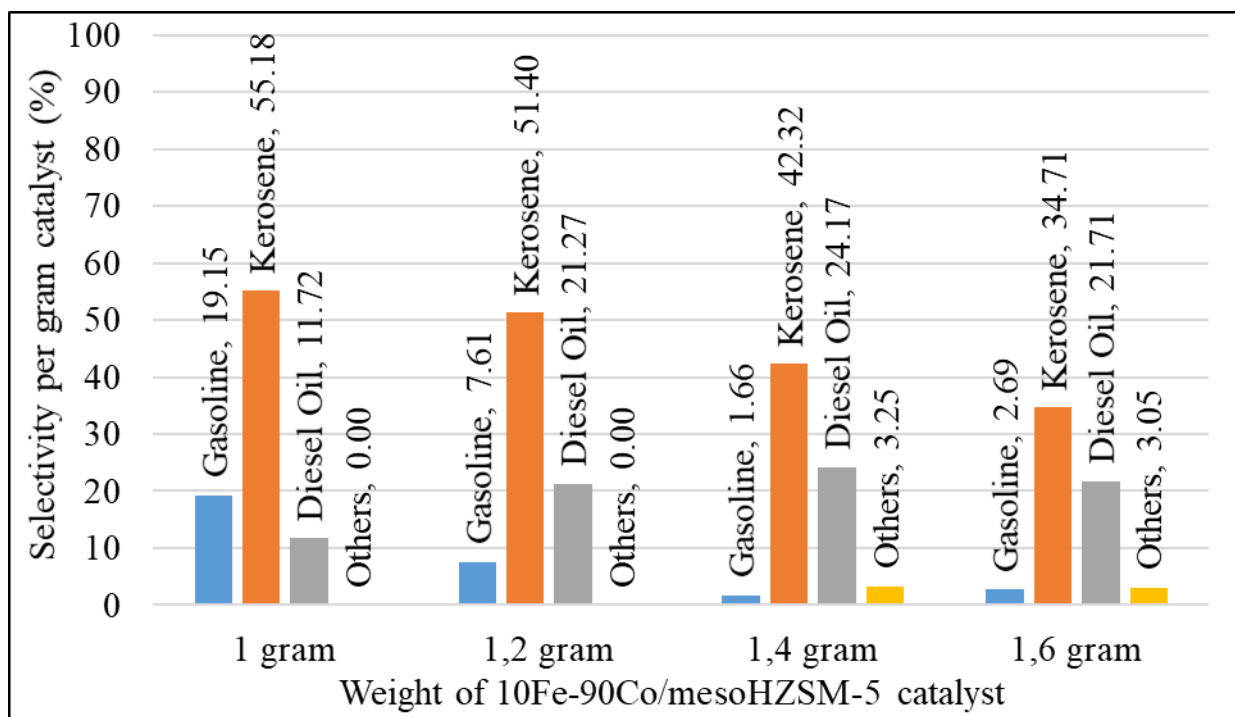


Fig. 7. Normalization of biofuel selectivity (gasoline, kerosene and diesel) to the 10Fe-90Co/meso-HZSM-5 catalyst weight in the 250°C, 20 bar Fischer-Tropsch reaction of using synthesis gas (30 % CO, 60 % H₂, 10 % N₂) for 96 hours

Normalization of CO reaction conversion to the 10Fe-90Co/meso-HZSM-5 catalyst weight in the 250°C, 20 bar FT reaction using synthesis gas (30 % CO, 60 % H₂, 10 % N₂) for 96 hours was shown in **Fig. 8**. The resulting normal conversion showed similar value for all catalyst in the range of 0.26-0.28. All catalyst weight variation showed similar normal conversion over 96 hours, so the use of 1 gram of catalyst was more economically beneficial. These results were in line with the normal selectivity of gasoline and kerosene products that reached the highest value on the use of 1 gram of catalyst.

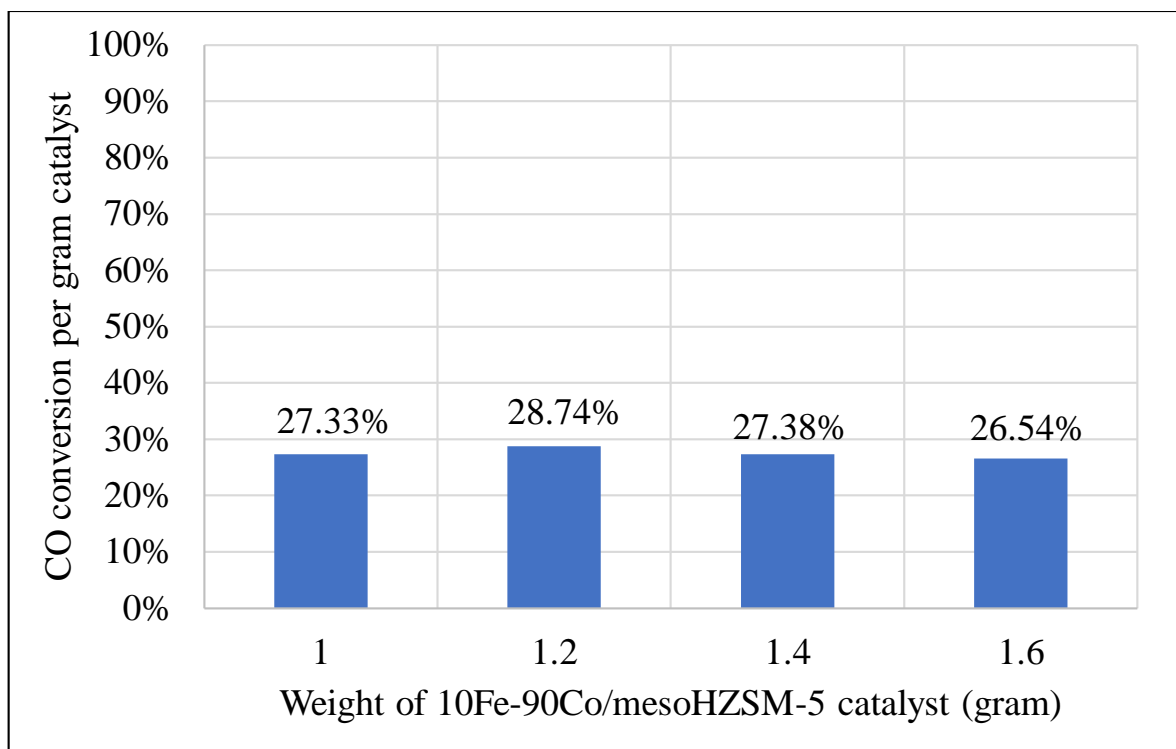


Fig. 8. Normalization of CO conversion to the 10Fe-90Co /meso-HZSM-5 catalyst weight variation in the 250°C, 20 bar Fischer-Tropsch reaction using synthesis gas (30 % CO, 60 % H₂, 10 % N₂) for 96 hours

4. Conclusion

The desilicated HZSM-5 properties (BET analysis) were 6.1-29.9 nm mesoporous diameter, 0.3496 cc/g average mesoporous volume, 526.035 cc/g pore surface area, and the EDX analysis gave 22.1059 Si/Al ratio and 16.11 % loading (by weight) on meso-HZSM-5. The reduced catalyst showed the XRD spectra of Fe (66°), Fe-Co alloy (44.50°) and Co₃O₄ (36.80°).

The Fischer-Tropsch reaction using 1 gram of 10Fe-90Co/meso-HZSM-5 catalyst and synthesis gas (30 % CO, 60 % H₂, 10 % N₂) at 250°C, 20 bar, 96 hours in the continuous fixed-bed reactor, showed the largest composition and conversion. The combination of polymerization using metal catalyst (Fe-Co) and cracking (meso-HZSM-5) was intended to produce saturated C₅-C₂₅ hydrocarbons (gasoline, kerosene and diesel oil). The 1 gram catalyst weight gave the largest normal selectivity to gasoline (19.15 %) and kerosene (55.18 %). While the largest normal diesel oil selectivity (24.17 %) was obtained from 1.4 gram of catalyst. The CO conversion per gram of catalyst showed similar value (26–28 %) for all catalyst weight.

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**BIOFUEL PRODUCTION OVER FISCHER-TROPSCH
SYNTHESIS: EFFECT OF Fe-Co/meso-HZSM-5 CATALYST WEIGHT
ON PRODUCT COMPOSITION AND PROCESS CONVERSION**

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Abstract

Fischer-Tropsch Synthesis (FTS) using Fe-Co/meso-HZSM-5 catalyst has been investigated. The impregnated iron and cobalt on HZSM-5 could be used as bifunction catalyst which combined polymerizing synthesis gas and long hydrocarbon cracking for making biofuel (saturated C₅–C₂₅ hydrocarbons as gasoline, kerosene and diesel oil). The study emphasized the effect of catalyst

weight on product composition and process conversion. The HZSM-5, had been converted from ammonium ZSM-5 through calcination, and then desilicated with NaOH solution. The $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were used as precursor for incipient wetness impregnation (IWI) on amorphous meso-HZSM-5. The catalyst consisted of 10 % Fe and 90 % Co by weight, called 10Fe-90Co/meso-HZSM-5. All catalysts were reduced in situ in the continuous reactor with flowing hydrogen at 25 mL/min, 1 bar, 400 °C for 10 hours. The catalyst performance was observed in the same continuous fixed bed reactor at 25 mL/min synthesis gas (30 % CO, 60 % H_2 , 10 % N_2), 250 °C, 20 bar for 96 hours. Various catalyst weight (1, 1.2, 1.4, 1.6 gram) were applied in FTS. The desilicated HZSM-5 properties (BET analysis) were 6.1–29.9 nm mesoporous diameter, 0.3496 cc/g average mesoporous volume, 526.035 cc/g pore surface area, and the EDX analysis gave 22.1059 Si/Al ratio and 16.11 % loading (by weight) on meso-HZSM-5. The reduced catalyst showed the XRD spectra of Fe (66°), Fe-Co alloy (44.50°) and Co_3O_4 (36.80°). The reaction using 1 gram of 10Fe-90Co/meso-HZSM-5 catalyst produced the largest composition and conversion. The 1 gram catalyst gave the largest normal selectivity of gasoline (19.15 %) and kerosene (55.18 %). While the largest normal diesel oil selectivity (24.17 %) was obtained from 1.4 gram of catalyst. The CO conversion per gram of catalyst showed similar value (CO conversion of 26–28 %) for all catalyst weight.

Keywords: biofuel, HZSM-5, desilication, mesopore, catalyst, iron, cobalt, weight, conversion, Fischer-Tropsch.

1. Introduction

Zeolites are used in the process of separation, adsorption, and catalytic (i.e. cracking and other hydrotreating process). Homogeneous micropores, high thermal stability, acidity, and unique ability to stabilize metallic species were several their unique properties [1]. The mesoporous structure provides greater space for metal catalysts to occupy more support pores. The mesopore can be obtained from micropore over desilication treatment. The alkali (NaOH) solution was used as desilication agent. Nitric acid solution was used to transform the mesoporous HZSM-5 into amorphous structure, which could improve the adhesion of the metal catalyst on the mesoporous HZSM-5 support [2–5]. The KOH solution induced greater mesoporous volumes, but it damaged on zeolite crystal structure. The NaOH solutions were able to increased mesopore surface area and mesopore volume of NaOH-desilicated HZSM-5. The Fe-Co alloys were observed with less oxide of iron (Fe_2O_3) as well cobalt (Co_3O_4) in the produced catalysts [6].

The Fischer-Tropsch synthesis (FTS) is an exothermic and irreversible polymerization reaction that converts a mixture of hydrogen (H_2) and carbon monoxide (CO) into linear hydrocarbons as liquid fuel. FTS always produces various products such as olefins, paraffins and oxygenated compounds (alcohols, aldehydes, acids and ketones). Water was the main product of the FT reaction.

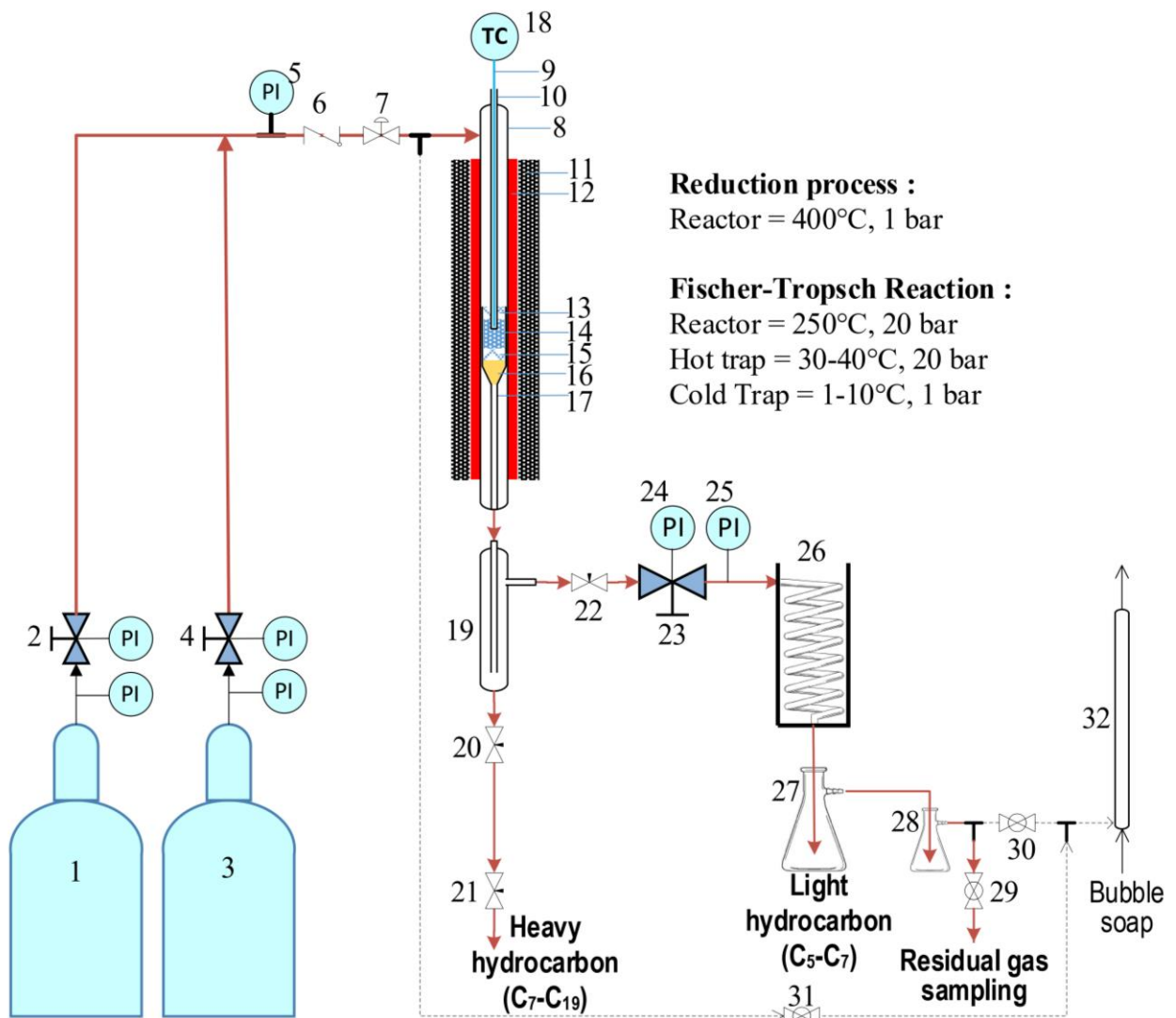
Water Gas Shift (WGS) activity occurred significantly in the use of Fe catalyst, but this reaction could be ignored in reactions using Co or Ru catalysts. Iron and cobalt as polymerization catalyst were used at FTS. The impregnated iron and cobalt on HZSM-5 could be used as bifunction catalyst which combined polymerizing synthesis gas and long chain hydrocarbon cracking for making biofuel [7–11]. The FTS preferred to use cobalt because of some advantages, instead of iron catalyst. Iron catalyst was added in little amount to improve the cobalt catalyst performance (improve olefin selectivity, reduce methane selectivity, reduce temperature and pressure sensitivity to product distribution and reduce the catalyst price) [12, 13].

The combination of the Fischer-Tropsch (FT) reaction and cracking was conducted by combining Fe-Co alloy (Fischer-Tropsch reaction catalyst) and HZSM-5 zeolite (cracking catalyst). The merging of the FTS and cracking was able to produce biofuel product directly [7]. The Fe/HZSM-5 catalyst was able to produce 24.2 % of C_{5–19} hydrocarbon as biofuel fraction [14]. The Co/HZSM-5 catalyst produced 48 % of C_{5–11} [3]. The use of Fe and Co catalysts together (bimetallic) could increase catalytic activity compared to the use single metal catalyst (monometallic). The combination of Fe and Co catalysts (bimetal catalysts) with conventional TiO₂, Al₂O₃ and SiO₂ supports had been investigated. They could increase the biofuel reaction conversion and fraction compared to the use of Fe and Co catalysts separately [15–17]. The variables that influenced product distribution were temperature, feed gas composition, pressure, catalyst type and promoter. The synthesis gas composition influenced the product selectivity. The lower the CO partial pressure, the lower the surface coverage of CH₂ radicals, the lower the chain growth chance and the higher the chance of CH₂ radicals desorption. The higher the H₂ partial pressure, increases the chance of radicals termination being paraffin. Increasing H₂/CO ratio would increase the selectivity of short-chain and more saturated hydrocarbons [18–20].

The study emphasized the effect of Fe-Co/mesoHZSM5 catalyst weight on product composition and conversion. The data obtained from this study will be used to develop efficiency of the Fischer-Tropsch reaction condition.

2. Methods

Materials used in this experiment were zeolite ZSM-5 in ammonium form (CBV 8014, Amberlyst International), Fe(NO₃)₃·9H₂O (Merck), Co(NO₃)₂·6H₂O (Merck), NaOH p.a. (Merck), nitric ammonium p.a. (Merck), nitric acid (Merck), Hydrogen gas (PT. Samator Gas Industry, Surabaya, Indonesia), synthesis gas (30 % CO, 60 % H₂, 10 % N₂), glass beads 2 mm (Marienfeld), glass wool, aquadest. The equipment used were the tubular furnace, quartz furnace crucible, hotplate magnetic stirrer, vacuum filter, air compressor, hot air oven, syringe, digital scales and standard glassware for catalyst synthesis. The continuous fixed-bed Fischer-Tropsch reactor (**Fig. 1**), hot trap, cold trap, bubble soap meter, vacutainer (vacuum bottle/container) were used for FTS.



Reduction process :

Reactor = 400°C, 1 bar

Fischer-Tropsch Reaction :

Reactor = 250°C, 20 bar

Hot trap = 30-40°C, 20 bar

Cold Trap = 1-10°C, 1 bar

Caption :

- | | |
|---|--|
| 1. Hydrogen gas (H ₂) | 17. Catalyst bowl |
| 2. Pressure regulator for H ₂ | 18. Temperature panel controller |
| 3. Synthesis gas (30% CO, 60% H ₂ , 10% N ₂) | 19. Hot trap |
| 4. Pressure regulator for synthesis gas | 20. Needle valve I (Swagelok) |
| 5. Pressure gauge | 21. Needle valve II (Swagelok) |
| 6. Check valve | 22. Ball valve I (Swagelok) |
| 7. Micro metering valve | 23. Pressure Regulator (modified) |
| 8. Fischer-Tropsch reactor | 24. Pressure gauge for reactor outlet |
| 9. Temperature probe sensor (type K) | 25. Pressure gauge for condenser |
| 10. Thermo well | 26. Condenser (cold trap) |
| 11. Heat Isolator (rockwool) | 27. Separator for liquid and gas product |
| 12. Electric Heater | 28. Bubble gas indicator |
| 13. Glass beads | 29. Ball valve II (Sankyo) |
| 14. 10Fe-90Co/mesoHZSM-5 catalyst | 30. Ball valve III (Sankyo) |
| 15. Glass beads | 31. Needle valve III (Swagelok) |
| 16. Glass wool | 32. Bubble soap meter |

Fig. 1. The reactor unit of continuous Fischer-Tropsch synthesis for 10Fe-90Co/ meso-HZSM-5 catalyst using synthesis gas (30% CO, 60% H₂, 10% N₂), 25 mL/min, 250 °C, 20 bar, 96 hours on various catalyst weight variation (1; 1.2; 1.4; 1.6 gram)

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The 10Fe-90Co/meso-HZSM-5 catalyst was prepared from ammonium salt of ZSM-5 over calcination, desilication, dispersion, acid treatment [6]. The solution of Co(NO₃)₂.6H₂O and Fe(NO₃)₃.9H₂O were used as precursor for incipient wetness impregnation (IWI) process on amorphous meso-HZSM-5. Loading metal catalyst was 10 %. The catalyst consisted of 10 % Fe (by weight) and 90 % Co (by weight). The impregnated HZSM-5 was kept in desiccator at room temperature for 24 hours, dried in oven at 120 °C for 12 hours and then calcined at 550 °C for 2 hours.

The catalyst performance was observed in a continuous fixed bed reactor (**Fig. 1**) using 10Fe-90Co/meso-HZSM-5 catalyst, 25 mL/min synthesis gas (30 % CO, 60 % H₂, 10 % N₂) at 250 °C, 20 bar. Various catalyst weight (1; 1.2; 1.4; 1.6 gram) were used in the Fischer-Tropsch reaction. The catalyst was mixed with glass beads as much as 6 times of the catalyst weight. The mixture of catalyst and glass beads was inserted into the catalyst bowl which was held with glass wool at the bottom and top of the catalyst to prevent the spilling out of the catalyst during process [21, 22]. All catalysts were reduced in situ in the reactor with H₂ gas flowing at 25 mL/min, 1 bar, 400 °C for 10 hours. At the end of the reduction procedure, the reactor was cooled to 250 °C and the hydrogen gas flow was stopped, then it was replaced by the synthesis gas flow. The modified pressure regulator was installed after the reactor to maintain 20 bar pressure. The flow rate was calibrated using bubble soap meter at 25 mL/min at the operating pressure and temperature. Some hydrocarbon fractions condensed through hot trap at 30–40 °C and 20 bar. The low boiling point hydrocarbon fraction would be condensed in a cold trap (1–10 °C, 1 bar). The reaction was carried out for 96 hours with gas sampling every 24 hours and liquid sampling at the end of the whole reaction. Gas samples were taken using a 10 mL syringe and injected into

10 mL vacuum bottle (vacutainer).

3. Result and discussion

3. 1. Characterization of Catalyst Fe-Co/meso-HZSM-5

Ammonium ZSM-5 (Si/Al=40) was converted to microporous HZSM-5 through calcination process in the tube furnace reactor. The formation of mesoporous structures was obtained through the desilication process in which silicon was partly-removed from zeolite framework using NaOH as desilication agent. The desilicated HZSM-5 properties obtained from BET analysis were 6.1–29.9 nm mesoporous diameter, 0.3496 cc/g average mesoporous volume, 526.035 cc/g pore surface area, and from EDX analysis gave 22.1059 Si/Al ratio.

The Fe and Co catalysts loading was 16.11 % weight on mesoporous HZSM-5. The loading of catalyst was calculated from EDX analyzing. The impregnated mesoporous HZSM-5 was reduced to obtain metal catalyst on the active surface. The XRD analysis was used to observe the reduction results. The diffraction angle position of the metal peaks referred to the spectral Tavasoli's database [25]. The spectra of Fe (66°), Fe-Co alloy (44.50°) and Co_3O_4 (36.80°) were shown in **Fig. 2**.

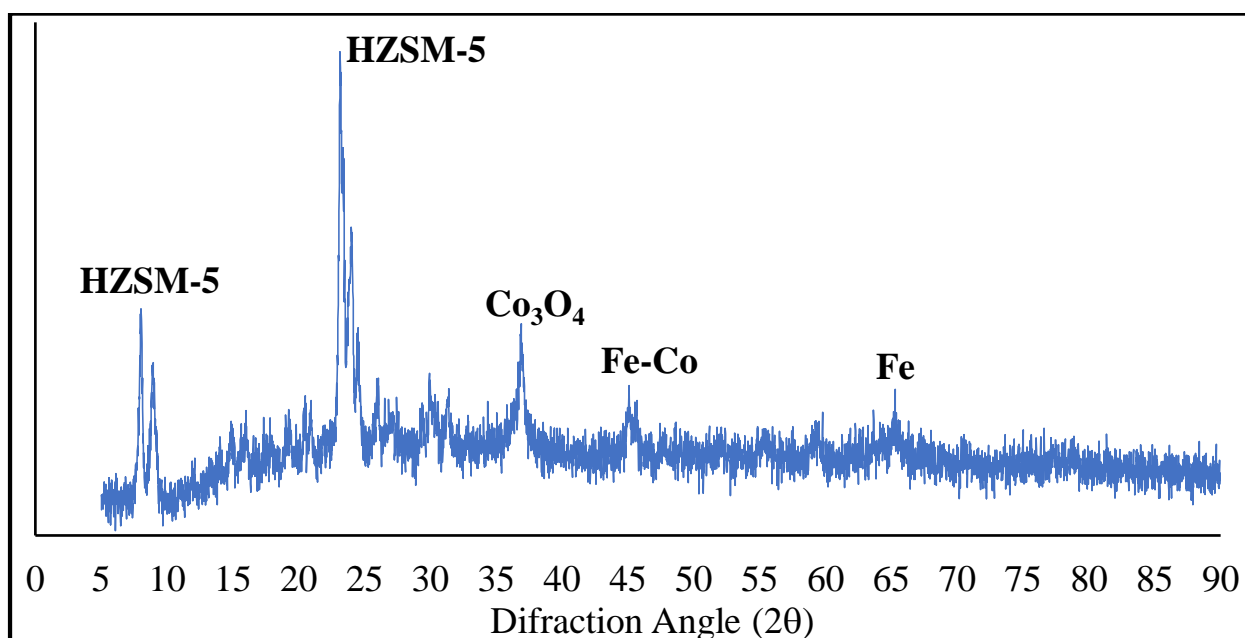


Fig. 2. The XRD Spectra for Fe-Co/HZSM-5 catalyst consisted of 10 %Fe and 90 %Co after reduction (with H_2 gas flowing at 25 mL/min, 1 bar, 400°C for 10 hours)

3. 2. Effect of catalyst weight to product composition

The FTS reaction produced two layers liquid product, each of which has a pungent odor. The two layer liquid products were taken from hot trap chamber ($30\text{--}40^\circ\text{C}$). Both of layers had similar viscosity. The upper layer ass clear yellow,

while the lower layer was colorless. From GCMS analysis, the upper layer contained alkanes (paraffin) and less alkene (olefin). Carboxylic acids, alcohols, esters and aromatic compounds were found in the lower layer products. The increasing catalyst weight gave the higher alkane selectivity. One gram of catalyst obtained 85.04 % alkanes and 7.56 % alkenes. The alkane composition rose to 96.33 % on 1.2 grams of catalyst and increased again to 99.96 % on 1.4 and 1.6 grams of catalyst. Straight chain hydrocarbon selectivity was quite large (57–72 %). The 1.6 gram catalyst gave the greatest selectivity (72.03 %) when compared to 57.14 % on 1 gram catalyst. The more catalysts used, the greater active surface involved in the reaction so that the catalyst's performance was better. The reactants contained double H_2 than CO (H_2/CO ratio=2). The greater active surface area increased the concentration of hydrogen free radicals, so the reaction mechanism lead to the formation of paraffins and carboxylic acids.

The combination of polymerization using metal catalyst (Fe-Co) and cracking (meso-HZSM-5) in the FTS intended to produce saturated C_5 – C_{19} hydrocarbons (gasoline, kerosene and diesel oil). The product distribution based on the hydrocarbon chain length in the both layers could be seen in **Fig. 3, 4**. The upper layer was dominated by alkane hydrocarbons with C_7 – C_{25} hydrocarbon chain length (**Fig. 3**). The use of 1 and 1.2 gram catalysts produced C_7 – C_{19} hydrocarbon while the more catalyst weight produced less C_{20} – C_{25} hydrocarbon (below 1.7 %). The 1 and 1.2 gram catalyst might form C_{20} – C_{25} in such a small amount, so that GCMS could not detect this traces. Increasing catalyst weight would rise the reaction chance on the catalyst active surface so that the more product was obtained (higher conversion) and the presence of C_{20} – C_{25} hydrocarbon could be measured using GCMS. The FT reaction using 10Fe-90Co/meso-HZSM-5 catalyst at 250 °C and 1 bar produced gasoline, kerosene and diesel oil. Kerosene was the largest product (55.18–61.68 %), was obtained from the catalyst weight of 1–1.6 gram. The largest gasoline fraction (19.15 %) was obtained from 1 gram of catalyst and decreased with increasing catalyst weight. The diesel oil fraction increased with the catalyst weight. The largest diesel fraction (19.34 %) was obtained from 1.6 gram of catalyst. The greater the catalyst weight, the greater the diesel fuel produced and the smaller the gasoline produced.

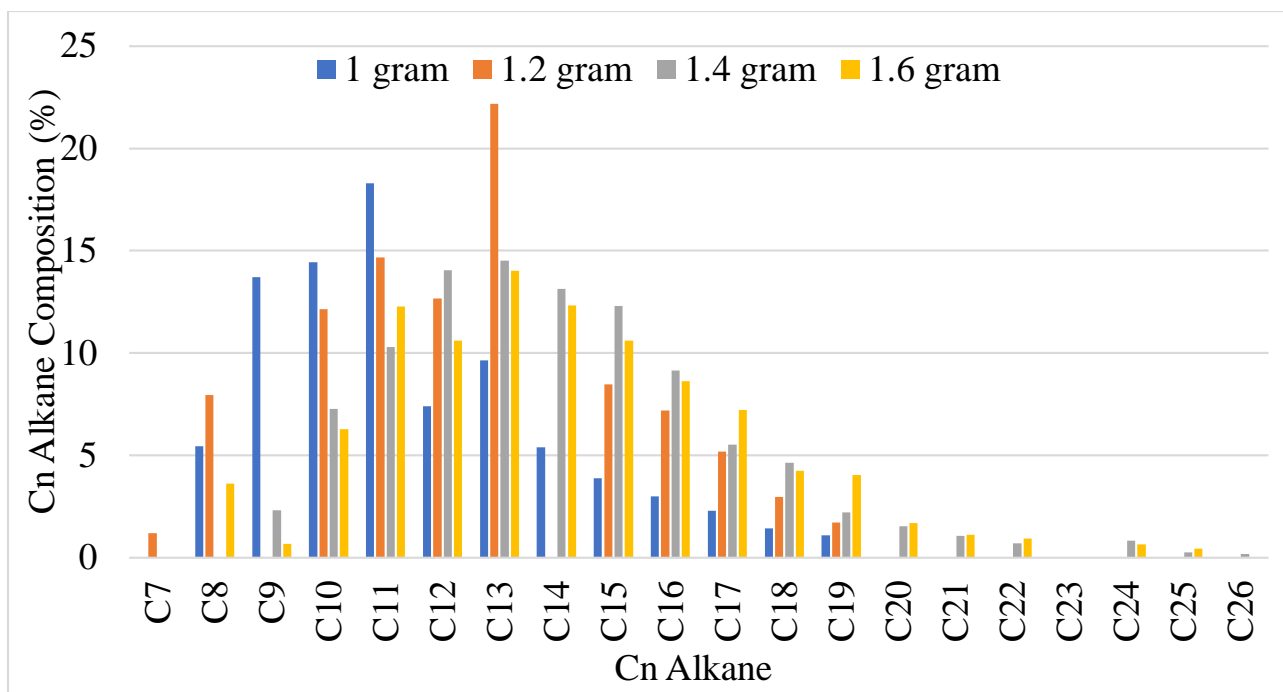


Fig. 3. Distribution of upper layer liquid products from Fischer-Tropsch reaction with catalyst 10Fe-90Co/meso-HZSM-5, loading 10 %, synthesis gas (30 % CO, 60 % H₂, 10 % N₂), 25 mL/min, 250 °C, 20 bar , 96 hours at various catalyst weight variation (1; 1.2; 1.4; 1.6 gram)

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The lower layer showed the FTS side reaction, that produced alcohol, carboxylic acid, ester, aromatic and cycloalkane compounds (**Fig. 4**). The carboxylic acid was formed at any weight variation. The alcohol was formed in large amount at 1.2 and 1.4 gram catalyst. This condition could be used to alternative alcohol production from synthesis gas with this catalyst.

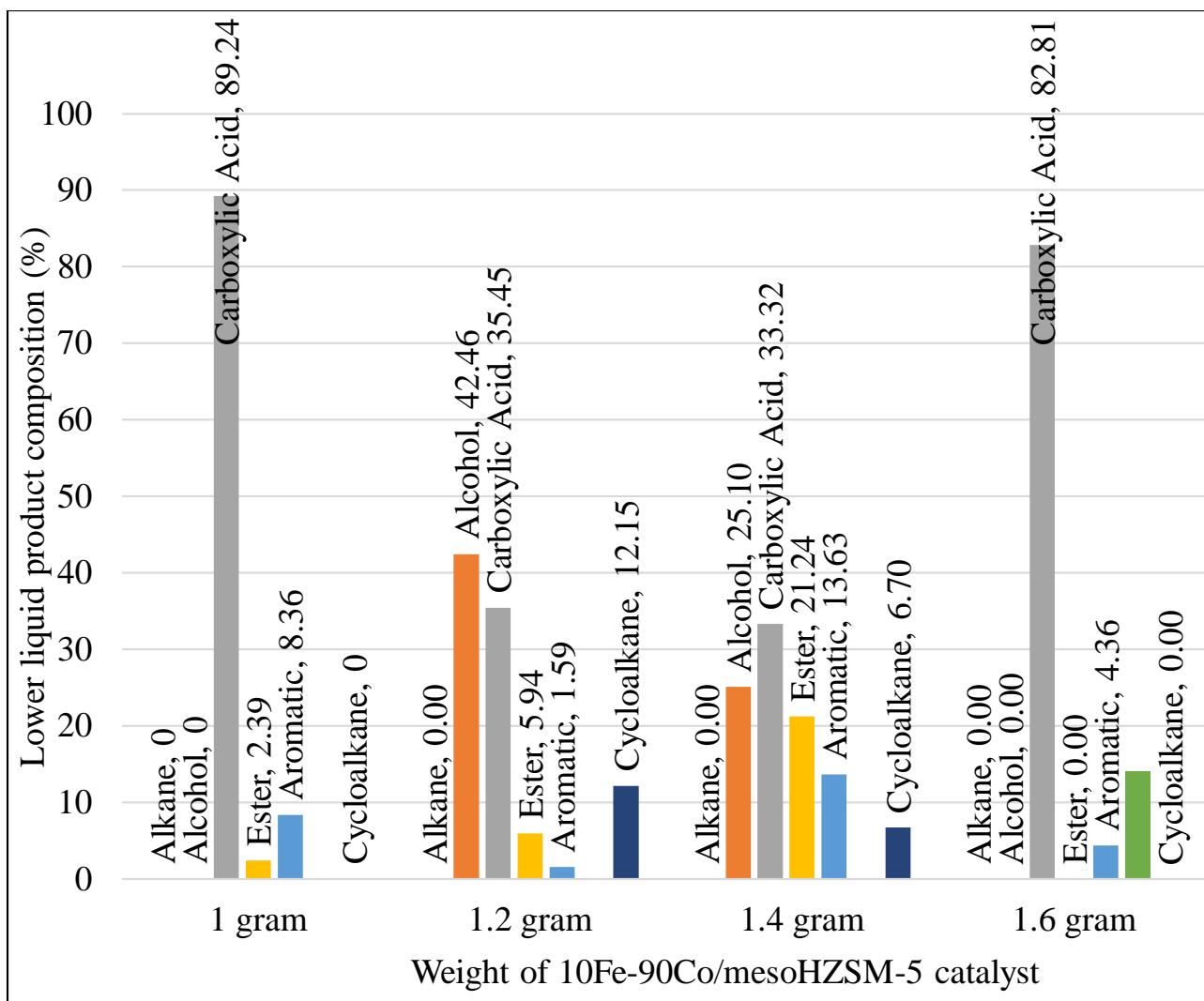


Fig. 4. Distribution of lower layer liquid products from Fischer-Tropsch reaction with catalyst 10Fe-90Co/meso-HZSM-5, loading 10 %, synthesis gas (30 % CO, 60 % H₂, 10 % N₂), 25 mL/min, 250 °C, 20 bar , 96 hours at various catalyst weight variation (1; 1.2; 1.4; 1.6 gram)

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The more 10Fe-90Co/meso-HZSM-5 catalyst, which used in the FT reaction, would have the greater active surface area. They might increase the reaction chances that increased CO conversion (**Fig. 5**). The larger active surfaces would increase CO dissociation which initiated the polymerization process. The CO conversion on 1 gram of catalyst was 27.33 % which increased to 42.46 % on the use of 1.6 grams of catalyst.

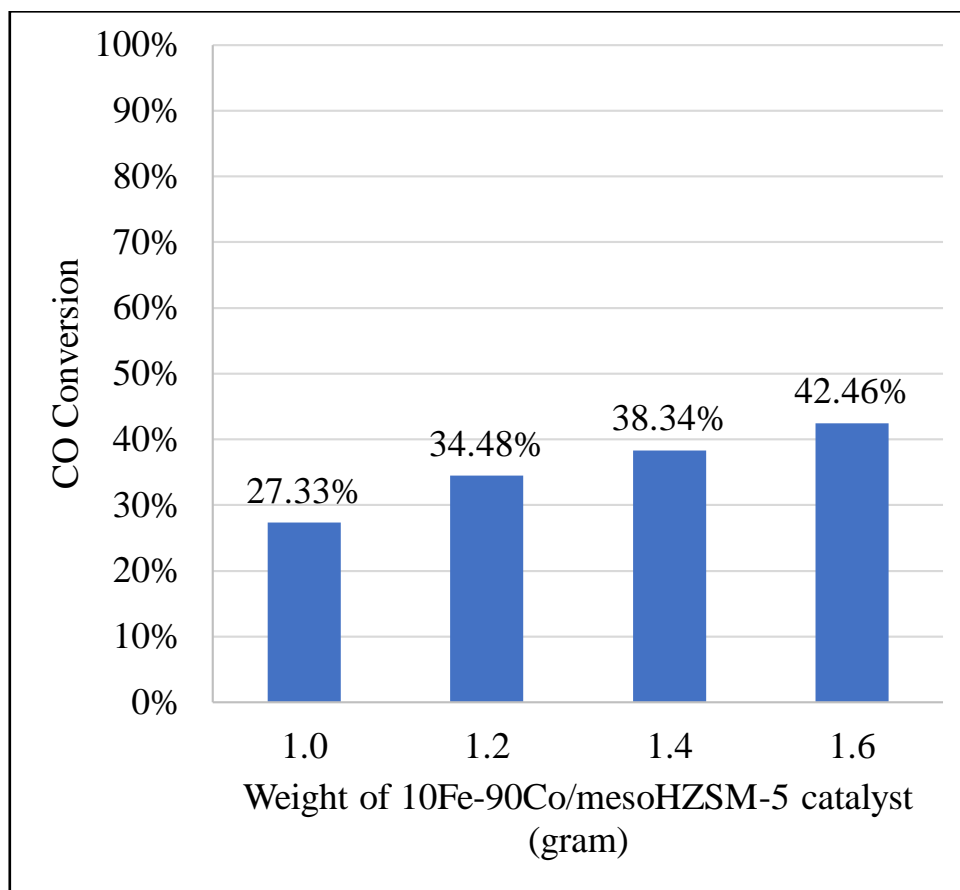


Fig. 5. The CO conversion from the Fischer-Tropsch reaction with catalyst 10Fe-90Co/meso-HZSM-5, loading 10 %, synthesis gas (30 % CO, 60 % H₂, 10 % N₂), 25 mL/min, 250 °C, 20 bar, 96 hours on various catalyst weight variation (1; 1.2; 1.4; 1.6 gram)

The residual gas consisted of CO, H₂, CO₂ and CH₄ were measured by GC-TCD (**Fig. 6**). The decreasing CO fraction in the residual gas showed that CO consumption increased with more catalysts being used. The formation of a relatively small CO₂ indicated that the WGS reaction was not dominant in the condition and catalyst used. The greater Co catalyst (90 %) in the bimetal Fe-Co did not push WGS reaction. But with increasing catalyst weight, the Fe weight was also larger, so that more CO₂ gas formation (1–2 %) was obtained in the use of catalysts 1.2–1.6 gram. However, the larger Co in the Fe-Co would drive the methane formation. The analysis showed that methane was formed in all catalyst weight insignificantly. In the 1 gram of catalyst, only 1 % methane was formed, while the use of more catalysts produced 5–6 % methane. The bimetal combination on supported mesoporous HZSM-5 reduced methane formation significantly compared to previous studies [3, 17, 26], which produced 7.9–21 % methane

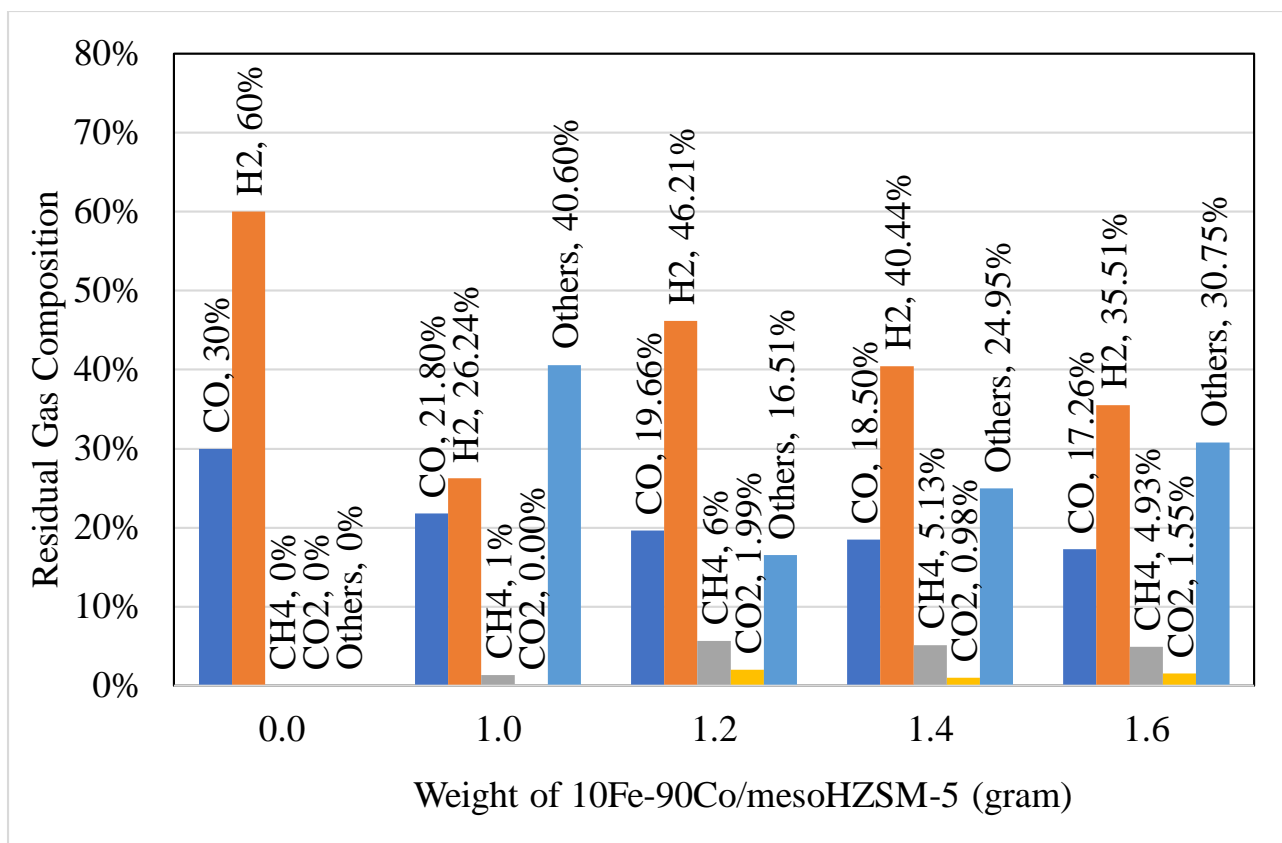


Fig. 6. The residual gas composition from the Fischer-Tropsch reaction with catalyst 10Fe-90Co/meso-HZSM-5, loading 10 %, synthesis gas (30 % CO, 60 % H₂, 10 % N₂), 25 mL/min, 250 °C, 20 bar, 96 hours on various catalyst weight variations (1; 1.2; 1.4; 1.6 gram)

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3. 3. Normalization of Selectivity and Conversion

Normalization of liquid products selectivity and reaction conversion to catalyst weight was conducted to determine the efficiency and effectiveness of the catalysts use. The product selectivity and conversion were normalized by the catalyst weight that was varied in this study. This normalization data could be used to take better decision in the catalyst efficiency and effectiveness before commercializing.

Normalization of biofuel selectivity (gasoline, kerosene and diesel) to the 10Fe-90Co/meso-HZSM-5 catalyst weight in the FT reaction of 250 °C, 20 bar using synthesis gas (30 % CO, 60 % H₂, 10 % N₂) for 96 hours was shown in **Fig. 7**. The 1 gram catalyst weight gave the largest normal selectivity to gasoline (19.15 %) and kerosene (55.18 %). While the largest normal diesel oil selectivity (24.17 %) was obtained from the use of 1.4 gram of catalyst weight.

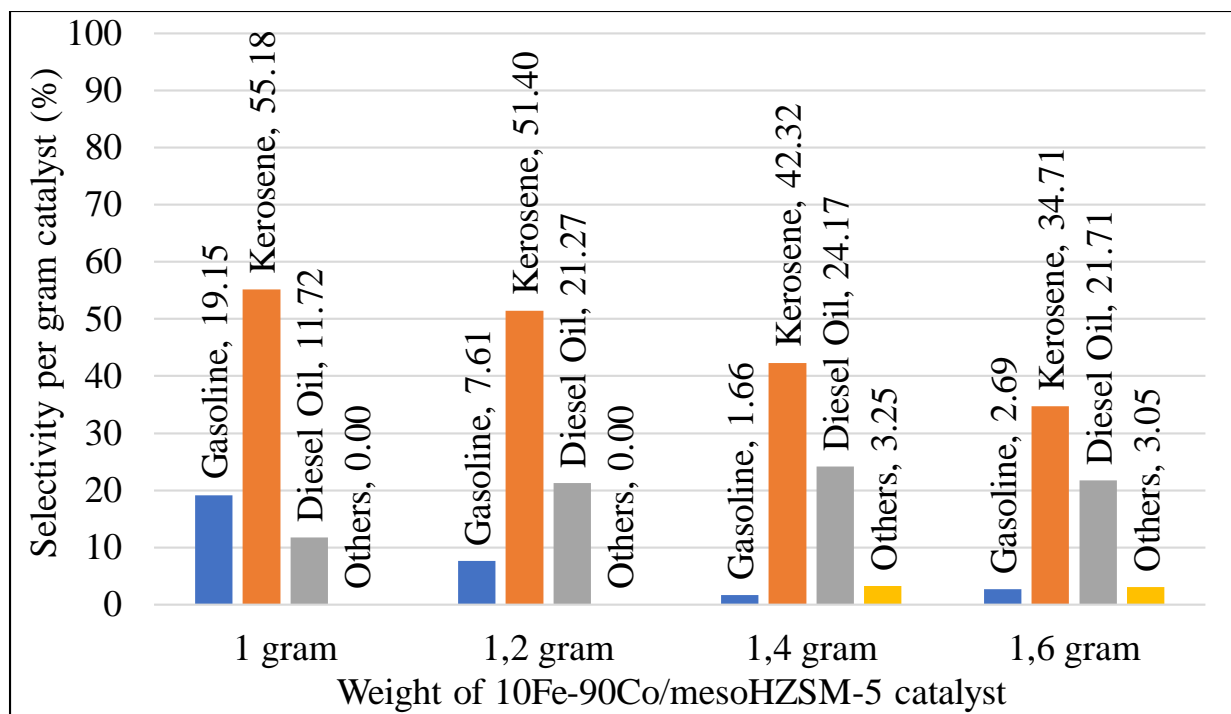


Fig. 7. Normalization of biofuel selectivity (gasoline, kerosene and diesel) to the 10Fe-90Co/meso-HZSM-5 catalyst weight in the 250 °C, 20 bar Fischer-Tropsch reaction of using synthesis gas (30 % CO, 60 % H₂, 10 % N₂) for 96 hours

The Figure is of poor quality.

Normalization of CO reaction conversion to the 10Fe-90Co/meso-HZSM-5 catalyst weight in the 250 °C, 20 bar FT reaction using synthesis gas (30 % CO, 60 % H₂, 10 % N₂) for 96 hours was shown in **Fig. 8**. The resulting normal conversion showed similar value for all catalyst in the range of 0.26–0.28. All catalyst weight variation showed similar normal conversion over 96 hours, so the use of 1 gram of catalyst was more economically beneficial. These results were in line with the normal selectivity of gasoline and kerosene products that reached the highest value on the use of 1 gram of catalyst.

This research has several limitations. A very expensive synthesis gas as raw material make biofuel price can't compete with the fossil fuel. The separated hydrogen, carbonmonoxide and nitrogen with each rate controller could be used to reduce raw material price. Coal or biomass that have the lowest price raw material, could be interesting for the next research. The catalyst development need further research to improve the reaction conversion in simple reactor and mild operation condition (temperature, pressure and time). Continuously data will give better reaction kinetics analysis for gaining best condition. The residual gas analysis as conversion indicator need to be measured continuously with integrated GC-TCD, instead of separately one. Gas sensor with Arduino program

could be used as an alternative to collect large data every second or minute. The carbon monoxide sensor (MQ-7), carbon dioxide sensor (MG-811) and methane sensor (MQ-4) should be developed and integrated with Fischer-Tropsch reactor system.

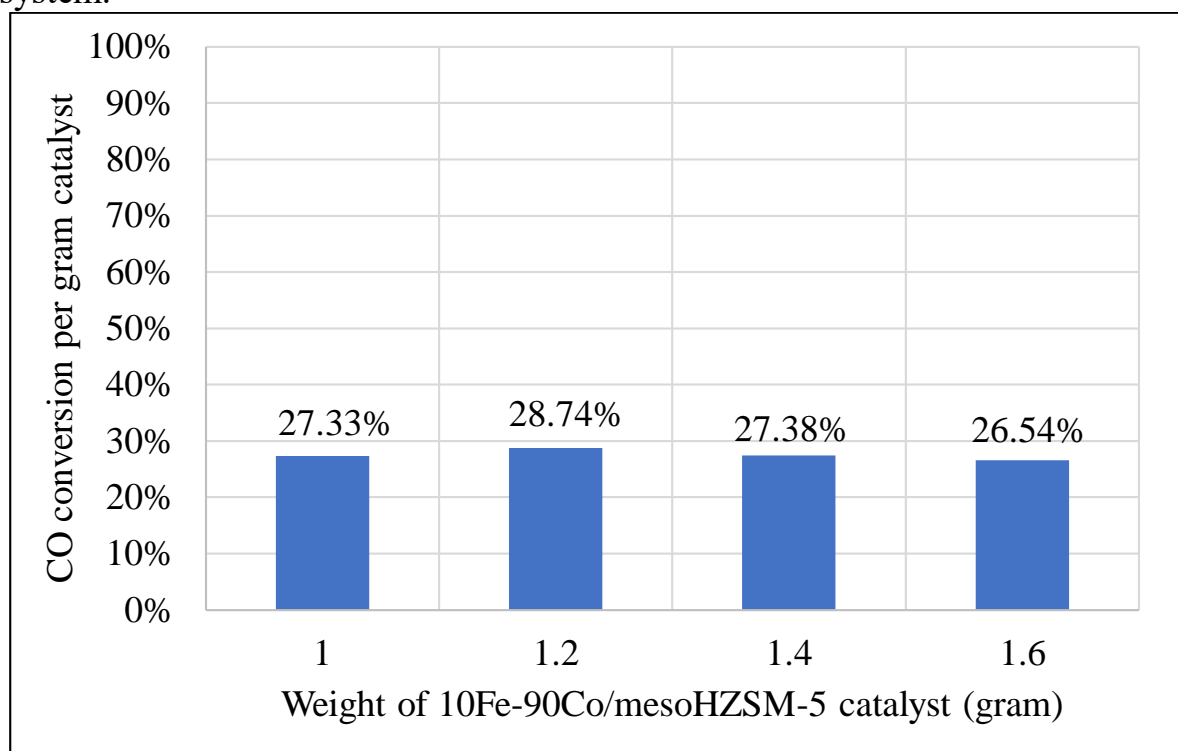


Fig. 8. Normalization of CO conversion to the 10Fe-90Co /meso-HZSM-5 catalyst weight variation in the 250 °C, 20 bar Fischer-Tropsch reaction using synthesis gas (30 % CO, 60 % H₂, 10 % N₂) for 96 hours

4. Conclusion

The desilicated HZSM-5 properties (BET analysis) were 6.1–29.9 nm mesoporous diameter, 0.3496 cc/g average mesoporous volume, 526.035 cc/g pore surface area, and the EDX analysis gave 22.1059 Si/Al ratio and 16.11 % loading (by weight) on meso-HZSM-5. The reduced catalyst showed the XRD spectra of Fe (66°), Fe-Co alloy (44.50°) and Co₃O₄ (36.80°).

The Fischer-Tropsch reaction using 1 gram of 10Fe-90Co/meso-HZSM-5 catalyst and synthesis gas (30 % CO, 60 % H₂, 10 % N₂) at 250 °C, 20 bar, 96 hours in the continuous fixed-bed reactor, showed the largest composition and conversion. The combination of polymerization using metal catalyst (Fe-Co) and cracking (meso-HZSM-5) was intended to produce saturated C₅–C₂₅ hydrocarbons (gasoline, kerosene and diesel oil). The 1 gram catalyst weight gave the largest normal selectivity to gasoline (19.15 %) and kerosene (55.18 %). While the largest normal diesel oil selectivity (24.17 %) was obtained from 1.4 gram of catalyst. The CO conversion per gram of catalyst showed similar value (26–28 %) for all catalyst weight.

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BIOFUEL PRODUCTION OVER FISCHER-TROPSCH SYNTHESIS: EFFECT OF Fe-Co/meso-HZSM-5 CATALYST WEIGHT ON PRODUCT COMPOSITION AND PROCESS CONVERSION

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Abstract

Fischer-Tropsch Synthesis (FTS) using Fe-Co/meso-HZSM-5 catalyst has been investigated. The impregnated iron and cobalt on HZSM-5 could be used as bifunction catalyst which combined polymerizing synthesis gas and long hydrocarbon cracking for making biofuel (saturated C₅-C₂₅ hydrocarbons as gasoline, kerosene and diesel oil). The study emphasized the effect of catalyst weight on product composition and process conversion. The HZSM-5, had been converted from ammonium ZSM-5 through calcination, and then desilicated with NaOH solution. The Co(NO₃)₂·6H₂O and Fe(NO₃)₃·9H₂O were used as precursor for incipient wetness impregnation (IWI) on amorphous meso-HZSM-5. The catalyst consisted of 10 % Fe and 90 % Co by weight, called 10Fe-90Co/meso-HZSM-5. All catalysts were reduced in situ in the continuous reactor with flowing hydrogen at 25 mL/min, 1 bar, 400 °C for 10 hours. The catalyst performance was observed in the same continuous fixed bed reactor at 25 mL/min synthesis gas (30 % CO, 60 % H₂, 10 % N₂), 250 °C, 20 bar for 96 hours. Various catalyst weight (1, 1.2, 1.4, 1.6 gram) were applied in FTS. The desilicated HZSM-5 properties (BET analysis) were 6.1–29.9 nm mesoporous diameter, 0.3496 cc/g average mesoporous volume, 526.035 cc/g pore surface area, and the EDX analysis gave 22.1059 Si/Al ratio and 16.11 % loading (by weight) on meso-HZSM-5. The reduced catalyst showed the XRD spectra of Fe (66°), Fe-Co alloy (44.50°) and Co₃O₄ (36.80°). The reaction using 1 gram of 10Fe-90Co/meso-HZSM-5 catalyst produced the largest composition and conversion. The 1 gram catalyst gave the largest normal selectivity of gasoline (19.15 %) and kerosene (55.18 %). While the largest normal diesel oil selectivity (24.17 %) was obtained from 1.4 gram of catalyst. The CO conversion per gram of catalyst showed similar value (CO conversion of 26–28 %) for all catalyst weight.

Keywords: biofuel, HZSM-5, desilication, mesopore, catalyst, iron, cobalt, weight, conversion, Fischer-Tropsch.

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1. Introduction

Zeolites are used in the process of separation, adsorption, and catalytic (i. e. cracking and other hydrotreating process). Homogeneous micropores, high thermal stability, acidity, and unique ability to stabilize metallic species were several their unique properties [1]. The mesoporous structure provides greater space for metal catalysts to occupy more support pores. The mesopore can be obtained from micropore over desilication treatment. The alkali (NaOH) solution was used as desilication agent. Nitric acid solution was used to transform the mesoporous HZSM-5 into

amorphous structure, which could improve the adhesion of the metal catalyst on the mesoporous HZSM-5 support [2–5]. The KOH solution induced greater mesoporous volumes, but it damaged on zeolite crystal structure. The NaOH solutions were able to increase mesopore surface area and mesopore volume of NaOH-desilicated HZSM-5. The Fe-Co alloys were observed with less oxide of iron (Fe_2O_3) as well cobalt (Co_3O_4) in the produced catalysts [6].

The Fischer-Tropsch synthesis (FTS) is an exothermic and irreversible polymerization reaction that converts a mixture of hydrogen (H_2) and carbon monoxide (CO) into linear hydrocarbons as liquid fuel. FTS always produces various products such as olefins, paraffins and oxygenated compounds (alcohols, aldehydes, acids and ketones). Water was the main product of the FT reaction. Water Gas Shift (WGS) activity occurred significantly in the use of Fe catalyst, but this reaction could be ignored in reactions using Co or Ru catalysts. Iron and cobalt as polymerization catalyst were used at FTS. The impregnated iron and cobalt on HZSM-5 could be used as bifunction catalyst which combined polymerizing synthesis gas and long chain hydrocarbon cracking for making biofuel [3, 7–10]. The FTS preferred to use cobalt because of some advantages, instead of iron catalyst. Iron catalyst was added in little amount to improve the cobalt catalyst performance (improve olefin selectivity, reduce methane selectivity, reduce temperature and pressure sensitivity to product distribution and reduce the catalyst price) [11, 12].

The combination of the Fischer-Tropsch (FT) reaction and cracking was conducted by combining Fe-Co alloy (Fischer-Tropsch reaction catalyst) and HZSM-5 zeolite (cracking catalyst). The merging of the FTS and cracking was able to produce biofuel product directly [7]. The Fe/HZSM-5 catalyst was able to produce 24.2 % of C_{5-19} hydrocarbon as biofuel fraction [8]. The Co/HZSM-5 catalyst produced 48 % of C_{5-11} [3]. The use of Fe and Co catalysts together (bimetallic) could increase catalytic activity compared to the use single metal catalyst (monometallic). The combination of Fe and Co catalysts (bimetal catalysts) with conventional TiO_2 , Al_2O_3 and SiO_2 supports had been investigated. They could increase the biofuel reaction conversion and fraction compared to the use of Fe and Co catalysts separately [13–15]. The variables that influenced product distribution were temperature, feed gas composition, pressure, catalyst type and promoter. The synthesis gas composition influenced the product selectivity. The lower the CO partial pressure, the lower the surface coverage of CH_2 radicals, the lower the chain growth chance and the higher the chance of CH_2 radicals desorption. The higher the H_2 partial pressure, increases the chance of radicals termination being paraffin. Increasing H_2/CO ratio would increase the selectivity of short-chain and more saturated hydrocarbons [16–18].

The study emphasized the effect of Fe-Co/mesoHZSM5 catalyst weight on product composition and conversion. The data obtained from this study will be used to develop efficiency of the Fischer-Tropsch reaction condition.

2. Methods

Materials used in this experiment were zeolite ZSM-5 in ammonium form (CBV 8014, Amberlyst International), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Merck), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Merck), NaOH p.a. (Merck), nitric ammonium p.a. (Merck), nitric acid (Merck), Hydrogen gas (PT. Samator Gas Industry, Surabaya, Indonesia), synthesis gas (30 % CO, 60 % H_2 , 10 % N_2), glass beads 2 mm (Marienfeld), glass wool, aquadest. The equipment used were the tubular furnace, quartz furnace crucible, hotplate magnetic stirrer, vacuum filter, air compressor, hot air oven, syringe, digital scales and standard glassware for catalyst synthesis. The continuous fixed-bed Fischer-Tropsch reactor (Fig. 1), hot trap, cold trap, bubble soap meter, vacutainer (vacuum bottle/container) were used for FTS.

The 10Fe-90Co/meso-HZSM-5 catalyst was prepared from ammonium salt of ZSM-5 over calcination, desilication, dispersion, acid treatment [6]. The solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were used as precursor for incipient wetness impregnation (IWI) process on amorphous meso-HZSM-5. Loading metal catalyst was 10 %. The catalyst consisted of 10 % Fe (by weight) and 90 % Co (by weight). The impregnated HZSM-5 was kept in desiccator at room temperature for 24 hours, dried in oven at 120 °C for 12 hours and then calcined at 550 °C for 2 hours.

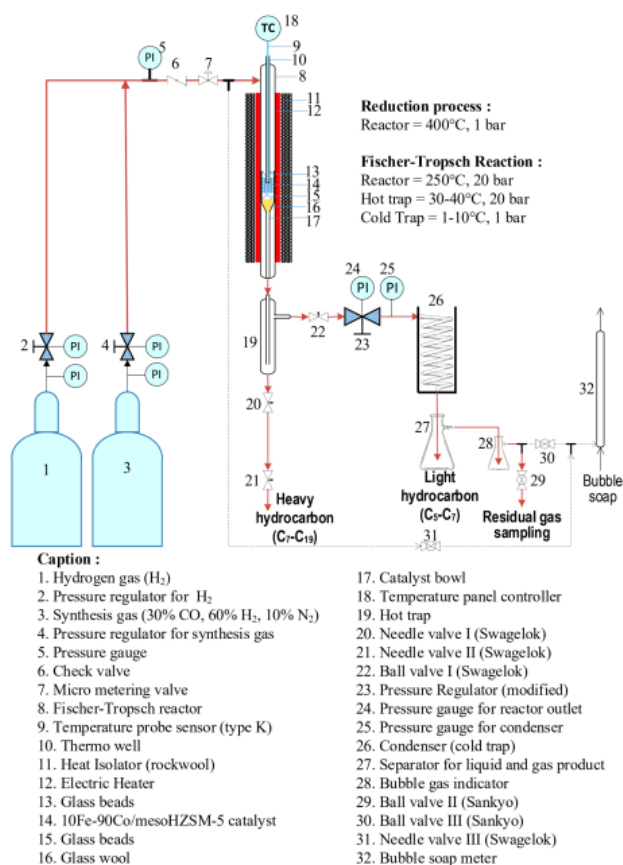


Fig. 1. The reactor unit of continuous Fischer-Tropsch synthesis for 10Fe-90Co/meso-HZSM-5 catalyst using synthesis gas (30 % CO, 60 % H₂, 10 % N₂), 25 mL/min, 250 °C, 20 bar, 96 hours on various catalyst weight variation (1; 1.2; 1.4; 1.6 gram)

The catalyst performance was observed in a continuous fixed bed reactor (**Fig. 1**) using 10Fe-90Co/meso-HZSM-5 catalyst, 25 mL/min synthesis gas (30 % CO, 60 % H₂, 10 % N₂) at 250 °C, 20 bar. Various catalyst weight (1; 1.2; 1.4; 1.6 gram) were used in the Fischer-Tropsch reaction. The catalyst was mixed with glass beads as much as 6 times of the catalyst weight. The mixture of catalyst and glass beads was inserted into the catalyst bowl which was held with glass wool at the bottom and top of the catalyst to prevent the spilling out of the catalyst during process [19–22]. All catalysts were reduced in situ in the reactor with H₂ gas flowing at 25 mL/min, 1 bar, 400 °C for 10 hours. At the end of the reduction procedure, the reactor was cooled to 250 °C and the hydrogen gas flow was stopped, then it was replaced by the synthesis gas flow. The modified pressure regulator was installed after the reactor to maintain 20 bar pressure. The flow rate was calibrated using bubble soap meter at 25 mL/min at the operating pressure and temperature. Some hydrocarbon fractions condensed through hot trap at 30–40 °C and 20 bar. The low boiling point hydrocarbon fraction would be condensed in a cold trap (1–10 °C, 1 bar). The reaction was carried out for 96 hours with gas sampling every 24 hours and liquid sampling at the end of the whole reaction. Gas samples were taken using a 10 mL syringe and injected into 10 mL vacuum bottle (vacutainer).

3. Result and discussion

3. 1. Characterization of Catalyst Fe-Co/meso-HZSM-5

Ammonium ZSM-5 (Si/Al = 40) was converted to microporous HZSM-5 through calcination process in the tube furnace reactor. The formation of mesoporous structures was obtained through the desilication process in which silicon was partly-removed from zeolite framework using NaOH as desilication agent. The desilicated HZSM-5 properties obtained from BET analysis were 6.1–29.9 nm mesoporous diameter, 0.3496 cc/g average mesoporous volume, 526.035 cc/g pore surface area, and from EDX analysis gave 22.1059 Si/Al ratio.

The Fe and Co catalysts loading was 16.11 % weight on mesoporous HZSM-5. The loading of catalyst was calculated from EDX analyzing. The impregnated mesoporous HZSM-5 was reduced to obtain metal catalyst on the active surface. The XRD analysis was used to observe the reduction results. The diffraction angle position of the metal peaks referred to the spectral Tavasoli's database [23]. The spectra of Fe (66°), Fe-Co alloy (44.50°) and Co₃O₄ (36.80°) were shown in Fig. 2.

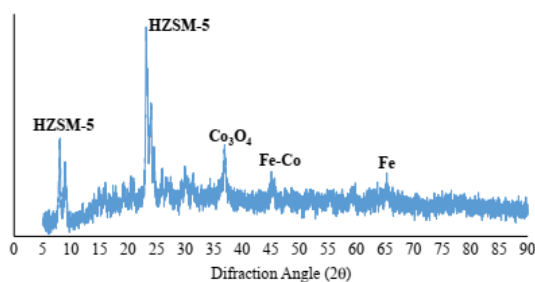


Fig. 2. The XRD Spectra for Fe-Co/HZSM-5 catalyst consisted of 10 % Fe and 90 % Co after reduction (with H₂ gas flowing at 25 mL/min, 1 bar, 400 °C for 10 hours)

3. 2. Effect of catalyst weight to product composition

The FTS reaction produced two layers liquid product, each of which has a pungent odor. The two layer liquid products were taken from hot trap chamber (30–40 °C). Both of layers had similar viscosity. The upper layer ass clear yellow, while the lower layer was colorless. From GCMS analysis, the upper layer contained alkanes (paraffin) and less alkene (olefin). Carboxylic acids, alcohols, esters and aromatic compounds were found in the lower layer products. The increasing catalyst weight gave the higher alkane selectivity. One gram of catalyst obtained 85.04 % alkanes and 7.56 % alkenes. The alkane composition rose to 96.33 % on 1.2 grams of catalyst and increased again to 99.96 % on 1.4 and 1.6 grams of catalyst. Straight chain hydrocarbon selectivity was quite large (57–72 %). The 1.6 gram catalyst gave the greatest selectivity (72.03 %) when compared to 57.14 % on 1 gram catalyst. The more catalysts used, the greater active surface involved in the reaction so that the catalyst's performance was better. The reactants contained double H₂ than CO (H₂/CO ratio = 2). The greater active surface area increased the concentration of hydrogen free radicals, so the reaction mechanism lead to the formation of paraffins and carboxylic acids.

The combination of polymerization using metal catalyst (Fe-Co) and cracking (meso-HZSM-5) in the FTS intended to produce saturated C₅–C₁₉ hydrocarbons (gasoline, kerosene and diesel oil). The product distribution based on the hydrocarbon chain length in the both layers could be seen in Fig. 3, 4. The upper layer was dominated by alkane hydrocarbons with C₇–C₂₅ hydrocarbon chain length (Fig. 3). The use of 1 and 1.2 gram catalysts produced C₇–C₁₉ hydrocarbon while the more catalyst weight produced less C₂₀–C₂₅ hydrocarbon (below 1.7 %). The 1 and 1.2 gram catalyst might form C₂₀–C₂₅ in such a small amount, so that GCMS could not detect this traces. Increasing catalyst weight would rise the reaction chance on the catalyst active surface so that the more product was obtained (higher conversion) and the presence of C₂₀–C₂₅ hydrocarbon could be measured using GCMS. The FT reaction using 10Fe-90Co/meso-HZSM-5 catalyst at 250 °C and 1 bar produced gasoline, kerosene and diesel oil. Kerosene was the largest product (55.18–61.68 %),

was obtained from the catalyst weight of 1–1.6 gram. The largest gasoline fraction (19.15 %) was obtained from 1 gram of catalyst and decreased with increasing catalyst weight. The diesel oil fraction increased with the catalyst weight. The largest solar fraction (19.34 %) was obtained from 1.6 gram of catalyst. The greater the catalyst weight, the greater the diesel fuel produced and the smaller the gasoline produced.

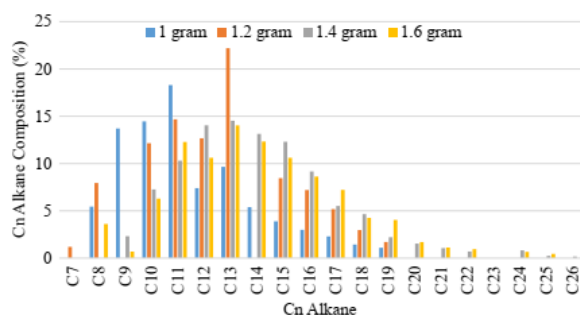


Fig. 3. Distribution of upper layer liquid products from Fischer-Tropsch reaction with catalyst 10Fe-90Co/meso-HZSM-5, loading 10 %, synthesis gas (30 % CO, 60 % H₂, 10 % N₂), 25 mL/min, 250 °C, 20 bar, 96 hours at various catalyst weight variation (1; 1.2; 1.4; 1.6 gram)

The lower layer showed the FTS side reaction, that produced alcohol, carboxylic acid, ester, aromatic and cycloalkane compounds (Fig. 4). The carboxylic acid was formed at any weight variation. The alcohol was formed in large amount at 1.2 and 1.4 gram catalyst. This condition could be used to alternative alcohol production from synthesis gas with this catalyst.

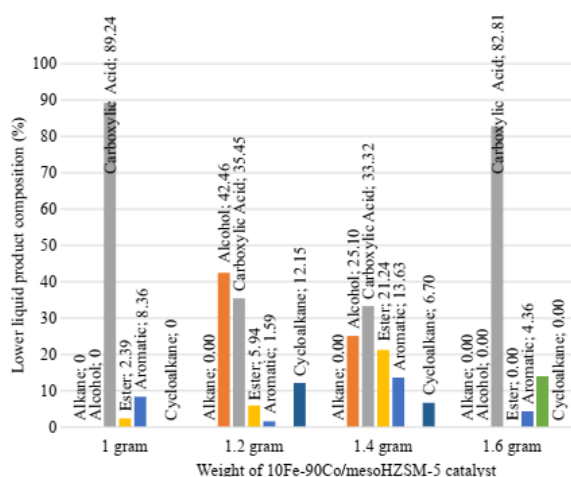


Fig. 4. Distribution of lower layer liquid products from Fischer-Tropsch reaction with catalyst 10Fe-90Co/meso-HZSM-5, loading 10 %, synthesis gas (30 % CO, 60 % H₂, 10 % N₂), 25 mL/min, 250 °C, 20 bar, 96 hours at various catalyst weight variation (1; 1.2; 1.4; 1.6 gram)

The more 10Fe-90Co/meso-HZSM-5 catalyst, which used in the FT reaction, would have the greater active surface area. They might increase the reaction chances that increased CO con-

version (Fig. 5). The larger active surfaces would increase CO dissociation which initiated the polymerization process. The CO conversion on 1 gram of catalyst was 27.33 % which increased to 42.46 % on the use of 1.6 grams of catalyst.

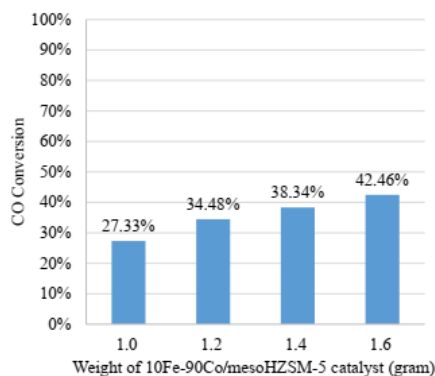


Fig. 5. The CO conversion from the Fischer-Tropsch reaction with catalyst 10Fe-90Co/meso-HZSM-5, loading 10 %, synthesis gas (30 % CO, 60 % H₂, 10 % N₂), 25 mL/min, 250 °C, 20 bar, 96 hours on various catalyst weight variation (1; 1.2; 1.4; 1.6 gram)

The residual gas consisted of CO, H₂, CO₂ and CH₄ were measured by GC-TCD (Fig. 6). The decreasing CO fraction in the residual gas showed that CO consumption increased with more catalysts being used. The formation of a relatively small CO₂ indicated that the WGS reaction was not dominant in the condition and catalyst used. The greater Co catalyst (90 %) in the bimetal Fe-Co did not push WGS reaction. But with increasing catalyst weight, the Fe weight was also larger, so that more CO₂ gas formation (1–2 %) was obtained in the use of catalysts 1.2–1.6 gram. However, the larger Co in the Fe-Co would drive the methane formation. The analysis showed that methane was formed in all catalyst weight insignificantly. In the 1 gram of catalyst, only 1 % methane was formed, while the use of more catalysts produced 5–6 % methane. The bimetal combination on supported mesoporous HZSM-5 reduced methane formation significantly compared to previous studies [3, 15, 24], which produced 7.9–21 % methane.

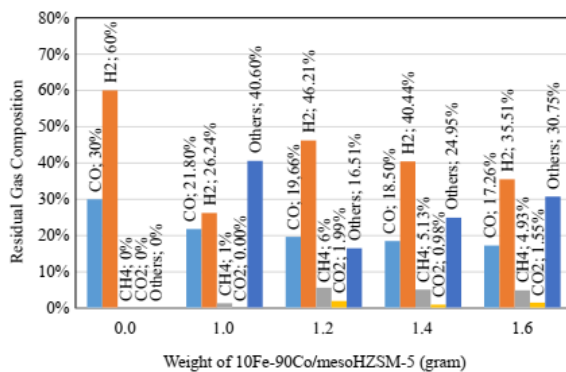


Fig. 6. The residual gas composition from the Fischer-Tropsch reaction with catalyst 10Fe-90Co/meso-HZSM-5, loading 10 %, synthesis gas (30 % CO, 60 % H₂, 10 % N₂), 25 mL/min, 250 °C, 20 bar, 96 hours on various catalyst weight variations (1; 1.2; 1.4; 1.6 gram)

3. 3. Normalization of Selectivity and Conversion

Normalization of liquid products selectivity and reaction conversion to catalyst weight was conducted to determine the efficiency and effectiveness of the catalysts use. The product selectivity and conversion were normalized by the catalyst weight that was varied in this study. This normalization data could be used to take better decision in the catalyst efficiency and effectiveness before commercializing.

Normalization of biofuel selectivity (gasoline, kerosene and diesel) to the 10Fe-90Co/meso-HZSM-5 catalyst weight in the FT reaction of 250 °C, 20 bar using synthesis gas (30 % CO, 60 % H₂, 10 % N₂) for 96 hours was shown in Fig. 7. The 1 gram catalyst weight gave the largest normal selectivity to gasoline (19.15 %) and kerosene (55.18 %). While the largest normal diesel selectivity (24.17 %) was obtained from the use of 1.4 gram of catalyst weight.

Normalization of CO reaction conversion to the 10Fe-90Co/meso-HZSM-5 catalyst weight in the 250 °C, 20 bar FT reaction using synthesis gas (30 % CO, 60 % H₂, 10 % N₂) for 96 hours was shown in Fig. 8. The resulting normal conversion showed similar value for all catalyst in the range of 0.26–0.28. All catalyst weight variation showed similar normal conversion over 96 hours, so the use of 1 gram of catalyst was more economically beneficial. These results were in line with the normal selectivity of gasoline and kerosene products that reached the highest value on the use of 1 gram of catalyst.

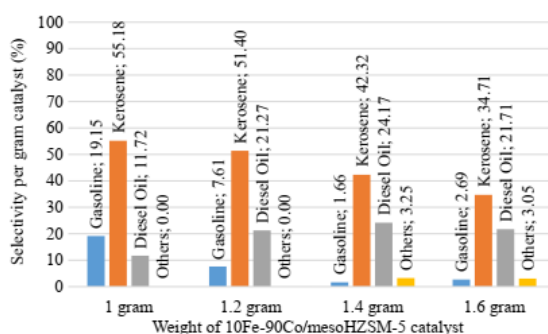


Fig. 7. Normalization of biofuel selectivity (gasoline, kerosene and diesel) to the 10Fe-90Co/meso-HZSM-5 catalyst weight in the 250 °C, 20 bar Fischer-Tropsch reaction of using synthesis gas (30 % CO, 60 % H₂, 10 % N₂) for 96 hours

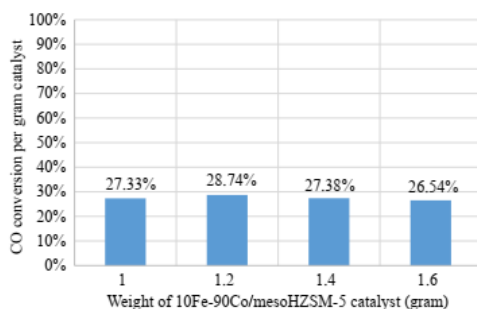


Fig. 8. Normalization of CO conversion to the 10Fe-90Co/meso-HZSM-5 catalyst weight variation in the 250 °C, 20 bar Fischer-Tropsch reaction using synthesis gas (30 % CO, 60 % H₂, 10 % N₂) for 96 hours

This research has several limitations. A very expensive synthesis gas as raw material make biofuel price can't compete with the fossil fuel. The separated hydrogen, carbonmonoxide and

nitrogen with each rate controller could be used to reduce raw material price. Coal or biomass that have the lowest price raw material, could be interesting for the next research. The catalyst development need further research to improve the reaction conversion in simple reactor and mild operation condition (temperature, pressure and time). Continuously data will give better reaction kinetics analysis for gaining best condition. The residual gas analysis as conversion indicator need to be measured continuously with integrated GC-TCD, instead of separately one. Gas sensor with Arduino program could be use as alternative to collect large data every seconds or minutes. The carbon monoxide sensor (MQ-7), carbon dioxide sensor (MG-811) and methane sensor (MQ-4) should be developed and integrated with Fischer-Tropsch reactor system.

4. Conclusion

The desilicated HZSM-5 properties (BET analysis) were 6.1–29.9 nm mesoporous diameter, 0.3496 cc/g average mesoporous volume, 526.035 cc/g pore surface area, and the EDX analysis gave 22.1059 Si/Al ratio and 16.11 % loading (by weight) on meso-HZSM-5. The reduced catalyst showed the XRD spectra of Fe (66°), Fe-Co alloy (44.50°) and Co₃O₄ (36.80°).

The Fischer-Tropsch reaction using 1 gram of 10Fe-90Co/meso-HZSM-5 catalyst and synthesis gas (30 % CO, 60 % H₂, 10 % N₂) at 250 °C, 20 bar, 96 hours in the continuous fixed-bed reactor, showed the largest composition and conversion. The combination of polymerization using metal catalyst (Fe-Co) and cracking (meso-HZSM-5) was intended to produce saturated C₃–C₂₅ hydrocarbons (gasoline, kerosene and diesel oil). The 1 gram catalyst weight gave the largest normal selectivity to gasoline (19.15 %) and kerosene (55.18 %). While the largest normal diesel oil selectivity (24.17 %) was obtained from 1.4 gram of catalyst. The CO conversion per gram of catalyst showed similar value (26–28 %) for all catalyst weight.

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