

PAPER • OPEN ACCESS

Fischer-Tropsch process from synthesis gas over fe-co/HZSM-5 catalyst to produce biofuel

To cite this article: A Roesyadi *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **673** 012010

View the [article online](#) for updates and enhancements.

Fischer-Tropsch process from synthesis gas over Fe-Co/HZSM-5 catalyst to produce biofuel

A Roesyadi*, Jimmy, D H Ihsanti and A Nuraini

Chemical Reaction Engineering Laboratory, Department of Chemical Engineering,
Faculty of Industrial Technology, Sepuluh Nopember Institute of Technology,
Surabaya, 60111, Indonesia

*Email: aroesyadi@yahoo.com

Abstract. Fischer-Tropsch synthesis is the process of converting hydrogen into liquid fuel through several stages, namely: polymerization of CO and H₂ gases into long chain hydrocarbons. From the FT process that requires many of these steps, this research was carried out in order to be able to simplify the Fischer-Tropsch process through limited polymerization to obtain liquid fuels. By combining Co and Fe metal catalysts, it is expected to show better performance than the use of individual metals. Using a Fe-Co/HZSM-5 metal catalyst combination in a fixed bed reactor at a reaction temperature of 225°C. Fe-Co / HZSM-5 catalyst was made by wet impregnation, then Fe-Co/HZSM-5 catalyst was characterized using XRD, BET, and SEM-EDX. From the XRD results, the addition of Fe and Co did not change the crystal structure of the HZSM-5 catalyst. The surface area of the HZSM-5 was 526.03 m²/g and decreased after the addition of metal (Fe and Co) to the HZSM-5. This change indicates that Fe and Co particles were successfully dispersed on the surface of the HZSM-5 and inserted into the HZSM-5 pore. Hydrocarbon biofuel products are analyzed using GC-MS. The results of GC-MS hydrocarbon products showed the highest compounds for hydrocarbons C₁₃ and C₁₄ chains were 5.78% and 6.68% at 225 °C.

1. Introduction

High population growth has become a central issue of energy lately. In addition, the increasing industrial demand for raw materials derived from petroleum derivative products has also become a separate issue for the industrial sector. These two things cannot be balanced by the production and availability of petroleum reserves in the bowels of the earth. This makes scientists and researchers look for alternatives to find synthetic liquid fuels that can be used generally and commercially as a substitute for fossil fuels so that the reduction of petroleum can be achieved. Several fuel synthesis technologies based on XTL (X to Liquid) conversion technology have begun to be developed, one of which is the Fischer Tropsch process.

The raw material for this technology is synthesis gas (a mixture of CO and H₂ gases) which can be obtained from coal, natural gas or biomass. There are two main stages in the conversion of synthesis gas to liquid fuel, namely the polymerization (Fischer-Tropsch) reaction and cracking. CO gas is polymerized to form long-chain hydrocarbons which are then cut selectively in the cracking process to produce short-chain hydrocarbons (C₅-C₁₂) which is the desired liquid fuel. Metal catalysts, such as Co and Fe, are widely used in Fischer-Tropsch reactions, while zeolite HZSM-5 is widely used in the



hydrocracking process. The use of these two stages of the process is quite expensive, so this technology is less commercially viable and does not develop much when world oil prices are low. So that an alternative is needed to simplify these two stages. Incorporation of metal/zeolite catalyst [1] [2] [3] and limited polymerization using metal/carbon [4], [5] to short-chain hydrocarbons can simplify the process into one stage [6]. The concept of limited polymerization is a new concept that will be studied in this study.

The most special characteristic of zeolite is the presence of empty space that forms a channel in it. When zeolite is used in the catalysis process there will be diffusion of molecules into the free space between crystals and chemical reactions also occur at the channel surface [7].

Based on research conducted by [8]. The main advantage of using zeolite in combination with the FTS function is one of several zeolites that are produced and applied industrially for hydrocarbon conversion reactions catalyzed by acids, have relatively stable catalytic performance, especially in conditions of the LTFT process, and in addition to cracks catalyzed by acids zeolite has the same isomerization and oligomerization activity at low temperatures. The latter oligomerization starts the hydrocracking reaction through a bimolecular mechanism because olefins are the main FTS product.

The results of this study are expected to provide alternative energy fuel products that are identical to fossil fuels so that they can add to the diversification of the synthesis of new and renewable energy sources. In this experiment, iron-cobalt/HZSM-5 catalyst was designed as a bifunctional catalyst. The purpose of inserting metal into the HZSM-5 framework is to improve the catalytic activity of both active metal sites and zeolite acid sites. The purpose of this study was to study the effect of iron-cobalt/HZSM-5 catalysts to produce hydrocarbon biofuels with the Fischer Tropsch process in fixed bed reactors. Determine the effect of reaction temperature on hydrocarbon biofuel products. The chemical composition of biofuel was analyzed using Gas Chromatography-Mass Spectrometry (GC-MS). The main objective is to produce gasoline and kerosene compounds through the Fischer Tropsch process.

2. Materials and methods

2.1. Materials

Synthesis gas (mix CO, H₂ and N₂) was purchased from PT. Samator Gas Industry, Surabaya. The Ammonium ZSM-5 (NH₄-ZSM-5) zeolite powders were purchased from Zeolyst International, USA (CBV 8014) Si/Al mole ratio: 40). Co(NO₃)₂.6H₂O (Merck), Fe(NO₃)₃.9H₂O (Merck), NaOH p.a (Merck), nitric acid p.a (Merck), aquadest.

2.2. Preparation of catalyst

ZSM-5 ammonium salt was calcined at 550°C for 5 hours to obtain micropore HZSM-5 zeolite in the calcination reactor. Desilication of HZSM-5 powder was carried out by adding 1 M NaOH solution and stirring at 70°C for 1 hour. The residue is separated from zeolite crystallites through continued dispersion in deionized water and filtered by vacuum filtration. Then the sample is washed to neutral pH. The sample was allowed to stand for 24 hours at 50°C and dried at 120°C for 12 hours, then calcined at 550°C for 5 hours. After heat treatment, the mesoporous fraction HZSM-5 was processed using 1 M HNO₃ solution at 70°C for 2 hours and stirred to form an amorphous phase. Subsequently, the sample was washed with deionized water, dried and calcined by the same procedure after the above desilication process. Next is the process Impregnation of Iron and Cobalt Metal Catalysts, iron metals and cobalt, in the form of Co(NO₃)₂.6H₂O solution and / or Fe(NO₃)₃.9H₂O solution, are impregnated using incipient wetness impregnation (IWI) in amorphous HZSM-5 mesos. The impregnated sample was left in the desiccator at room temperature for 24 hours, dried in an oven at 120°C for 12 hours and subsequently calcined at 550°C for 2 hours. Then end with reduction using a continuous flow of H₂ gas with a temperature of 450°C for 5 hours.

2.3. Preparation of catalytic reaction (Fischer-Tropsch process)

Catalytic reaction (Fischer-Tropsch process) used to make hydrocarbon biofuels from gas synthesis. The Fischer-Tropsch process is carried out in a fixed bed reactor type with a length of 37 cm and 3.5 cm in diameter. This reactor is equipped with heating. As much as 1 g of catalyst and 5 g glassbeads are placed in the reactor. The temperature of the experimental reaction was carried out at 225, 250 and 275°C for 120 hours and a pressure of 20 bar. Every 24 hours gas sampling is carried out, after reaching 120 hours of liquid products produced and collected into sample bottles

2.4. Catalyst analysis

Some character tests that will be carried out are: PANalytical X'Pert PRO X-Ray Diffractometer series to determine the crystal structure of the catalyst and the shape of the impregnated metal catalyst. The surface morphology and the amount of metal impregnated on the HZSM-5 catalyst were analyzed using Scanning Electron Microscope with the Energy-Dispersive X-ray (SEM-EDX) series: EVO MA10. To determine surface area, pore diameter and volume catalyst pore of the catalyst were characterized by the Brunauer Emmett-Teller (BET) series Quantachrome NovaWinVersion 11.03.

3. Results and discussion

3.1. The effect of desilication

XRD characterization was carried out to analyze the crystal structure of a material. XRD in this study was used to analyze the crystallinity of zeolite before and after treatment and zeolite impregnated with iron and cobalt metals with a ratio of 3: 7 ratio. This can help identify damage to the zeolite structure after desilication of 1M NaOH is carried out. The results obtained from the test in Figure 2 XRD test results from the HZSM-5 zeolite which is the result of the calcination of ammonia ZSM-5 at the bottom and XRD test results from mesoporous HZSM-5 zeolite with alkaline NaOH at the top, and the uppermost image zeolite analysis results that have been impregnated with metal. Sharp peaks indicate that mesopore HZSM-5 zeolite synthesis is quite high. Diffractogram of zeolite HZSM-5 showed a similar pattern with a standard HZSM-5 diffractogram after calcination. The mesoporous HZSM-5 pattern is formed at an angle of 2θ at 7.89° , 8.08° , 23° , 23.27° , 23.91° . The peaks in this area show similarities to the standard HZSM-5 diffractogram, namely in areas 2θ from 7° - 8° and at 23° and 23.91° which are typical peaks of the HZSM-5. These data indicate that the mesoporous HZSM5 crystal structure is still maintained and no other crystalline phases in the mesoporous ZSM-5 zeolite are synthesized.

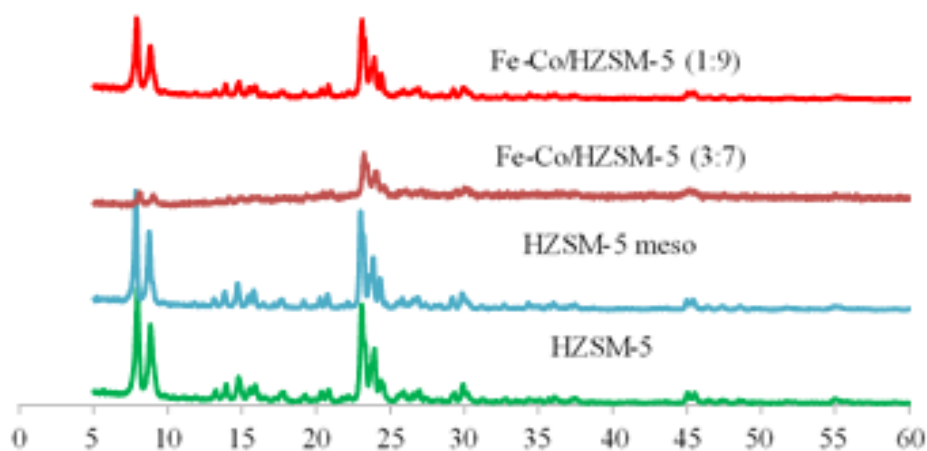


Figure 1. Diffractogram of zeolite HZSM-5, zeolite meso-HZSM-5, zeolite HZSM-5 impregnated Fe : Co (3:7) and zeolite HZSM-5 impregnated Fe : Co (1:9)

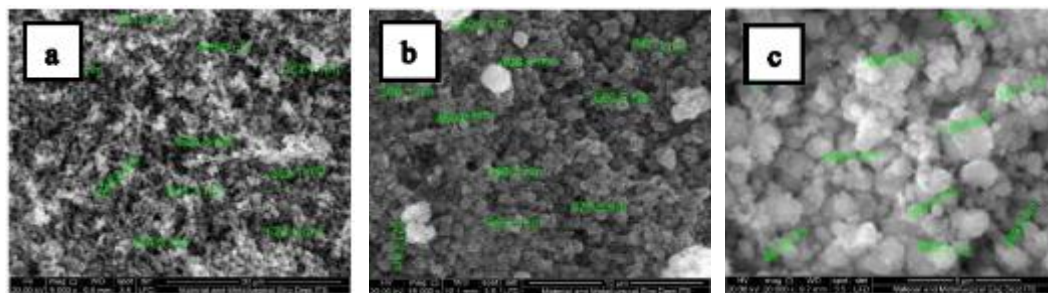


Figure 2. (a) Results of SEM HZSM-5 test after calcination, (b) SEM-HZSM-5 SEM test results (c) Results of Fe-Co / HZSM-5 SEM test (1: 9)

SEM testing for this study was carried out on HZSM-5 zeolite after calcination, zeolite after desilication namely meso-HZSM-5, and meso-HZSM-5 after impregnation with 10% iron metal and 90% metal cobalt the result was as follows. Based on Figure 2, there are small fragments which are zeolites. The SEM image for meso-HZSM-5 (NaOH) zeolite is shown in Figure 2. Based on the image there are small pieces of zeolite and large white flakes. The SEM result image for 10% meso-HZSM-5 zeolite is shown in Figure 3. Based on the image there are small fragments which are zeolites. Can also be seen there are dark, ash, and white. This shows that metal has been mixed on the zeolite surface even though it has not been evenly distributed as a whole.

Table 1. BET data analysis of meso-HZSM-5 and impregnated Fe-Co/HZSM-5 in ratio 1:9 and 3:7.

	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)
HZSM-5	266.28	0.140	2.104
HZSM-5/meso	526.03	0.486	3.029
Impregnation (1:9)	284.90	0.699	4.906
Impregnation (3:7)	296.92	0.499	3.360

Table 1. Shows the result of BET analysis of HZSM-5 and meso HZSM-5, this increase in surface area from 266.28 m²/g to 526.03 m²/g, indicates that the formation of a larger pore size. If the zeolite structure collapses, there will be a drastic decrease in surface area due to the absence of zeolite pores. The total volume of mesoporous zeolites also increased from zeolites after calcination to mesoporous NaOH zeolites. The formation of larger pores can also enlarge the total volume of zeolites before desilication. This increase is assumed due to the formation of micropore-sized pores into mesoporous-sized pores after the desilication process. Zeolite HZSM-5 after calcination which is the starting material for desilication from mesoporous synthesis also has a meso-sized pore at first, but its distribution is small. The formation of meso-sized pores in HZSM-5 zeolites is probably caused by the formation of imperfect pores in zeolites, so there are several pores that combine to form larger pores and are detected as mesoporous-sized pores. However, the increase in mesoporous pore size in mesoporous HZSM-5 zeolites is not very significant. Thus it can be said that the synthesis of mesoporous zeolites by this method produces relatively small mesoporous pores. Furthermore, BET analysis data after the impregnation process showed a decrease in surface area from 526.03 to 284.90 and 296.92. This indicates that the impregnation process using iron metals and cobalt salts has spread on the surface of the catalyst, causing the surface area of the HZSM-5 catalyst to decrease. As previously done by the researchers, that the addition of metals causes a reduction in the surface area and pore volume of the two metals to block the micropore and block the mesoporous [9] [10] [11] [12].

3.2. The effect of catalyst iron-cobalt/HZSM-5 to catalytic reaction (Fischer-Tropsch process)

It can be seen in Figure 3 and Figure 4, where 2 catalysts are used in the ratio (1: 9) and (3: 7). From the results of the catalytic reaction (Fischer Tropsch Process), the performance of the catalyst is still less selective on C₅-C₁₂ hydrocarbon as targeted. The performance of this catalyst is more directed at long-chain hydrocarbon products. This can be caused by Co catalysts that are less stable in high-temperature reactions because Co catalysts are expected to be capable of cracking so as to produce C₅-C₁₂ chain hydrocarbons as targeted. A deeper study is needed and from this research can be used as a basis so that in the future this research can produce products with selectivity in the direction of C₅-C₁₂.

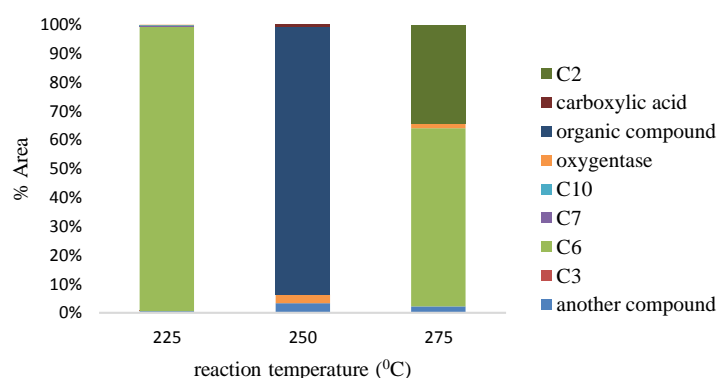


Figure 3. Product composition at reaction temperature using F-Co (1:9)/ HZSM-5 catalyst

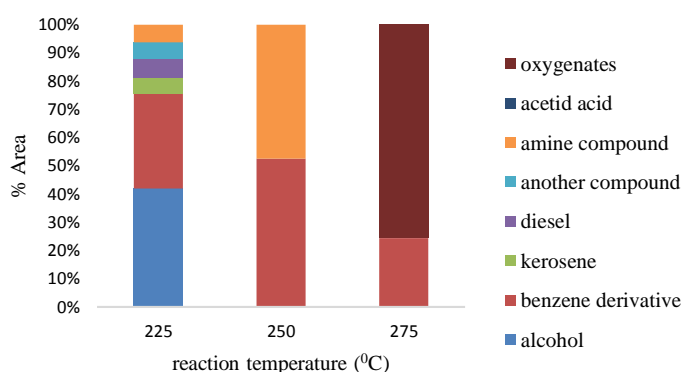


Figure 4. Product composition at reaction temperature using Fe-Co (3:7)/ HZSM-5 catalyst

4. Conclusion

XRD test results on HZSM-5 and meso-HZSM-5 (NaOH) in the angle range 2 θ of 7-80 and 23-23,910 prove that the crystal structure is still maintained at meso-HZSM-5. BET HZSM-5 results showed an increase in pore diameter before and after desilication from 2.104 nm to 3.029 nm, increasing surface area from 266.28 m²/g to 526.03 m²/g. based on the catalyst characterization, it has qualified as a catalyst for the Fischer Tropsch process, but after catalytic testing, it has not been able to produce the C₅-C₁₂ chain hydrocarbons as targeted. The ability of the catalyst has not been able to crack from the long-chain into the short-chain because diesel and kerosene are still produced.

Acknowledgments

This work is supported by the Program Master Thesis Directorate of Research and Community Service Sepuluh Nopember Institute of Technology in 2019. This research is partly done with self-designed equipment.

References

- [1] Bessell S 1995 Investigation of bifunctional zeolite supported cobalt Fischer-Tropsch catalysts *Applied Catalyst A General* **126** 235–244
- [2] Pour A N, Zare M, Shahri S M K, Zamani Y, and Alaei M R 2009 Catalytic Behaviors of Bifunctional Fe-HZSM-5 Catalyst in Fischer Tropsch Synthesis, *Journal Natural Gas Science Engineering* **1** 183–189
- [3] Valero-Romero M J, Sartipi S, Sun X, Rodríguez-Mirasol J, Cordero T, Kapteijn F and Gascon J 2016 Carbon/H-ZSM-5 composites as supports for bifunctional Fischer-Tropsch synthesis catalysts *Catal Sci Technol* **6** 2633-2646
- [4] Fu T, Jiang Y, Lv J, Li Z 2013 Effect of Carbon Support on Fischer-Tropsch Synthesis Activity and Product Distribution over Co-based Catalysts *Fuel Processing Technology* **110** 141-149
- [5] Xiong H, Moyo M, Motchelaho M A, Jewell L L, and Coville N J 2010 Applied Catalysis A General Fischer – Tropsch Synthesis over Model Iron Catalysts Supported on Carbon Spheres The effect of Iron Precursor Support Pretreatment, Catalyst Preparation Method and Promoters *Applied Catal A General* **388** 168– 178
- [6] Sineva L V, Asaliev A Y, Mordkovich V J 2015 The role of zeolite in the Fischer–Tropsch synthesis over cobalt–zeolite catalysts. *Russian Chemical Reviews* **84** 1176-1189
- [7] Sartipi S, Parashar K, Valero-Romero M J, Santos V P, Van der Linden B, Makkee M, Kapteijn F, and Gascon J 2013 Hierarchical HZSM-5-supported cobalt for the direct synthesis of gasoline-range hydrocarbons from syngas Advantages limitations and mechanistic insight *J Catal* **305** 179-19
- [8] Hao K, Shen B, Wang Y, Ren J 2012 Influence of combined alkaline treatment and Fe-Ti-loading modification on ZSM-5 zeolite and its catalytic performance in light olefin production *Journal of Industrial and Engineering Chemistry* **18** 1736-1740
- [9] Wang S, Yin Q, Guo J, Ru B, Zhu L 2013 Improved Fischer-Tropsch synthesis for gasoline over Ru, Ni promoted Co/HZSM-5 catalyst *Fuel* **108** 597-603
- [10] Vitale G, Molero H, Hernandez E, Aquino S, Birss, V, Pereira-Almao, P 2013 One-pot preparation and characterization of bifunctional Ni-containing ZSM-5 catalyst *Applied Catalyst A General* **452** 75-87
- [11] Niu X, Gao J, Dong M Q, Dong, M, Wang G, Fan, W, Qin Z, Wang, J 2014 Influence of preparation method on the performance of Zn-containing HZSM-5 catalysts in methanol-to-aromatics *Microporous and Mesoporous Materials* **197** 252–261
- [12] Gayubo A G, Alonso A, Valle B, Aguayo A T, Olazar M, Bilbao J 2010 Hydrothermal stability of HZSM-5 catalysts modified with Ni for the transformation of bioethanol into hydrocarbons, *Fuel* **89** 3365–3372