

Catalytic Pyrolysis of Fuel Oil Blended Stock to Methane and Hydrogen Gases Products Using Ni/ZSM-5 catalyst

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The complexity of processing fuel oil blended stock (FOBS) has raised environmental and waste management concerns, necessitating the transformation of FOBS into eco-friendly and higher-value products. This study explores the pyrolysis of FOBS, with focus on the production of CH₄ and H₂ using a Ni/ZSM-5 catalyst. The novelty lies in investigating the effects of varying the catalyst-to-feedstock ratio and catalyst weight percentage on gas product yield. Impregnation methods were used to generate 1, 3, and 5 wt. % Ni/ZSM-5, and characterized by XRD, SEM, BET, and FTIR. At a heat rate of 10 - 15 °C/min and 150 °C/min of nitrogen, samples with catalyst-to-feedstock ratios of 1:5, 1:10, and 1:15 were pyrolyzed at 500 °C in 60 min. 1 wt. % Ni/ZSM-5 produced the most H₂ and CH₄ gases at the catalyst to FOBS of 1:15 ratio, with CH₄ and H₂ selectivity 33.11 % and 66.89 %, respectively. This demonstrates that a small amount of Ni loaded into HZSM-5 can efficiently generate a significant quantity of valuable gas products.

1. Introduction

Malaysian electricity is generated from coal, natural gas and fuel oil. The fastest-growing energy source is renewable energy, which will rise by 3 % yearly between 2018 and 2050 (Kar et al., 2018). In response to the escalating global fuel prices driven by a shortage of natural gas and oil, coupled with increasingly stringent regulatory measures, researchers have directed their attention towards the improvement of fuel oil blended stock (FOBS). FOBS refers to the oil and other byproducts that remain after the refining process for crude oil has been completed. These are blended with other similar unfinished oils to produce a refined product that contains a wide range of hydrocarbons. FOBS are ineffective, cause storage and environmental issues (Teo et al., 2022). Therefore, upgrading FOBS into valuable gas products can help in reducing environmental concerns and fulfil the energy demand. Catalytic pyrolysis is considered to upgrade FOBS as the process was known as a catalyst-driven process capable of breaking down long chain hydrocarbon for light olefins production (Meng et al., 2004). The process generates three products which are liquid, solid and gas (Ranizang et al., 2022). Nanoparticles act as catalysts to upgrade heavy and ultra-heavy crude oil and boost methane (CH₄) and hydrogen (H₂) gas products from pyrolysis. Many studies have reported metals loading into supporting materials to modify zeolites to metal-zeolites to increase catalytic activity. Doping Mn, Co, Ni, Ga, Ce, and Pt into zeolite (HZSM-5) can also accurately alter acid site strength and density in zeolites. During pyrolysis, tar and CO₂ emissions can be decreased by using active components like nickel (Ni). As has been widely described in the literature, Ni and NiO encourage the breaking of the C-C and C-H bonds, which results in the creation of CH₄ and H₂ (Yue et al., 2023). Nevertheless, catalytic pyrolysis of FOBS utilising Ni/ZSM-5 as a catalyst to produce valuable gases has not received much attention. In a previous study, it was noted that the use of Ni/ZSM-5 in the catalytic pyrolysis process of pyrolytic oil led to a substantial increase in gas production (Liang et al., 2017). However, the study did not delve deeply into the gas generated from the study even though it is well known that pyrolysis produces mostly CH₄ and H₂ gases. Methane's physicochemical properties can supply the world's expanding electrical demand (Antonopoulou et al., 2008). Reducing atmospheric CH₄ by using it as an energy

source has a quantifiable positive effect on reducing global warming (Bajdor and Biernat, 2011). On the other hand, H₂ has significant potential for use in automobiles and other vehicles since its energy content per unit weight of fuel (142 kJ/g) is roughly three times that of gasoline (Zhang et al., 2015b). Hydrogen demand is predicted to rise by 5 - 10 % annually worldwide, and in countries that prioritise greenhouse gas reduction, demand will rise even higher (Arregi et al., 2018). Therefore, this study focuses on the production of CH₄ and H₂ gases by employing Ni/ZSM-5 catalyst via catalytic pyrolysis of FOBS.

2. Methodology

This section covers important parts of the study, including analysing the feedstock, preparing and characterizing the catalyst as well as outlining the experiments conducted.

2.1 Analysis of Fuel Oil Blended Stock (FOBS)

Gas Chromatography-Mass spectroscopy (GC-MS) analysis was employed as an analytical technique to enable the identification of various chemical species in FOBS. By using Helium (He) as the carrier gas, 0.1 µL of FOBS was injected into a GC-MS instrument with a mass selective detector and HP-5MS capillary column (30 m × 0.25 mm × 0.25 µm). Injector temperature was 250 °C and a 20:1 split ratio was used. The temperature is programmed at a constant 40 °C for 4 min, a 10 °C/min temperature ramp to 200 °C holding for 5 min, and a 50 °C/min ramp to 300 °C holding for 3 min. Chemical compounds corresponding to FOBS chromatogram peaks were identified.

2.2 Catalyst Preparation

Impregnation methods were used to synthesis Ni/ZSM-5 catalyst as the method is commonly used to load metal on HZSM-5 catalyst (Ji et al., 2018). Commercial HZSM-5 (Si/Al = 30) zeolite was purchased from Zeolyst International and nickel (II) nitrate hexahydrate (97 %), Ni (NO₃)₂·6H₂O purchased from Sigma-Aldrich were employed in the synthesis Ni/ZSM-5. Ni/ZSM-5 was synthesized by adding HZSM-5 in 25 mL of deionized water and stirring continuously until the salt dissolved completely. Then, nickel (II) nitrate hexahydrate was also added to the HZSM-5 solution and continuously stirred. Next, the mixture was heated at 80 °C until the water evaporated. The slurry obtained then was dried at 110 °C for overnight and calcined at 550 °C for 5 h. The synthesis of 1Ni/ZSM-5, 3Ni/ZSM-5 and 5Ni/ZSM-5 were different at weight of Ni (NO₃)₂·6H₂O and HZSM-5.

2.3 Characterization of Ni/ZSM-5 catalyst

To study the crystal structure, an X-ray Diffractometer (XRD) was utilized and equipped with Cu Kα radiation (λ=0.15406 nm) with a generator voltage of 40 kW and 30 mA. The diffraction pattern was recorded over the 2θ range of 5 - 35 °C with varying scanning rates of 2 - 6 °/min and step width of 0.02 °. The morphologies and particle sizes of catalysts are determined using Scanning Electron Microscopy (SEM). By scanning the sample's surface with a low-energy electron beam, the test was run at 10 kV and produced an image of the sample with resolutions in the low nanometer range. The Brunauer-Emmet-Teller (BET) is used to determine the surface area based on nitrogen adsorption isotherms. Before N₂ adsorption-desorption measurement, each sample was degassed with a N₂ purge at 77 K for 3 h. The powder density was measured using a pycnometer with xylene as the liquid medium. Fourier-transform Infrared Spectroscopy (FTIR) was used to evaluate the strength of Brønsted acid sites and Lewis's acid sites. The FTIR was used by using the transmitted method to collect spectra and analyses the functional group of the Ni/ZSM-5 catalyst in the range 4,000 - 650 cm⁻¹.

2.4 Catalytic Pyrolysis

In preparation for the catalytic pyrolysis reaction, the FOBS sample and catalyst were combined in an alumina boat, which was subsequently positioned inside a horizontal tubular quartz tube. This tube was then inserted into a furnace and encased within an outer stainless-steel chamber, which had external insulation provided by glass wool. A continuous inert environment was maintained throughout the process using nitrogen flowing at a rate of 150 mL/min through a quartz tube. The furnace's temperature controller monitored the temperature inside the quartz tube. When the temperature reaches 500 °C, the timer will be set for 60 min. Within that time, three sampling bags were employed to collect gas samples: the first bag was used during the initial 10 minutes, the second bag during the average of 30 minutes, and the third bag during the final 10 minutes. The average value of the results obtained from the three gas sampling bags was considered for further analysis using gas chromatography (GC).

3. Results and Discussion

3.1 Composition of FOBS

The analysis of FOBS using GC-MS unveiled its composition, primarily comprising hydrocarbons ranging from C_{10} to C_{21} . Within this composition, nearly 20 different compounds were identified. Among these, the most prominent compounds included naphthalene ($C_{10}H_8$), 2,4-di-tert-butylphenol ($C_{14}H_{22}O$), triethyl 4-phosphonobutanoate ($C_{10}H_{21}O_5P$), 1-octanamine, N-methyl-N-octyl- ($C_{17}H_{37}N$), benzo[h]quinoline, 2,4-dimethyl- ($C_{15}H_{13}N$), pyrene ($C_{16}H_{10}$), and cyclopentylmethylamine, N, N-dioctyl- ($C_{21}H_{42}N$).

3.2 Catalyst Characterization Results

Figure 1 illustrates XRD analysis results, representing Nickel, HZSM-5 and the modified catalyst. Similar diffraction peaks can be seen in all the XRD patterns in Figure 1, showing that the Ni loading does not affect the structure of the ZSM-5 framework. This shows that metal doping modification did not result in a change in the structure of the catalyst. In addition, as can be seen, the intensity was found to be higher at the beginning of the HZSM-5 and the peak intensities at Ni/ZSM-5 have changed, indicating that metals were successfully integrated into the catalyst. When compared to the parents HZSM-5, all the Ni/ZSM-5 catalyst exhibits a decrease in intensities, which may be caused by the modified catalyst's increased absorption coefficient (Kedia and Zaidi, 2014). It is quite likely that the Ni species are well dispersed on the ZSM-5 zeolites which is the reason why there are no detectable diffraction peaks of Ni species in the Ni/ZSM-5 catalysts. Another possibility is that the Ni content is too low to be identified (Zhang et al., 2015a).

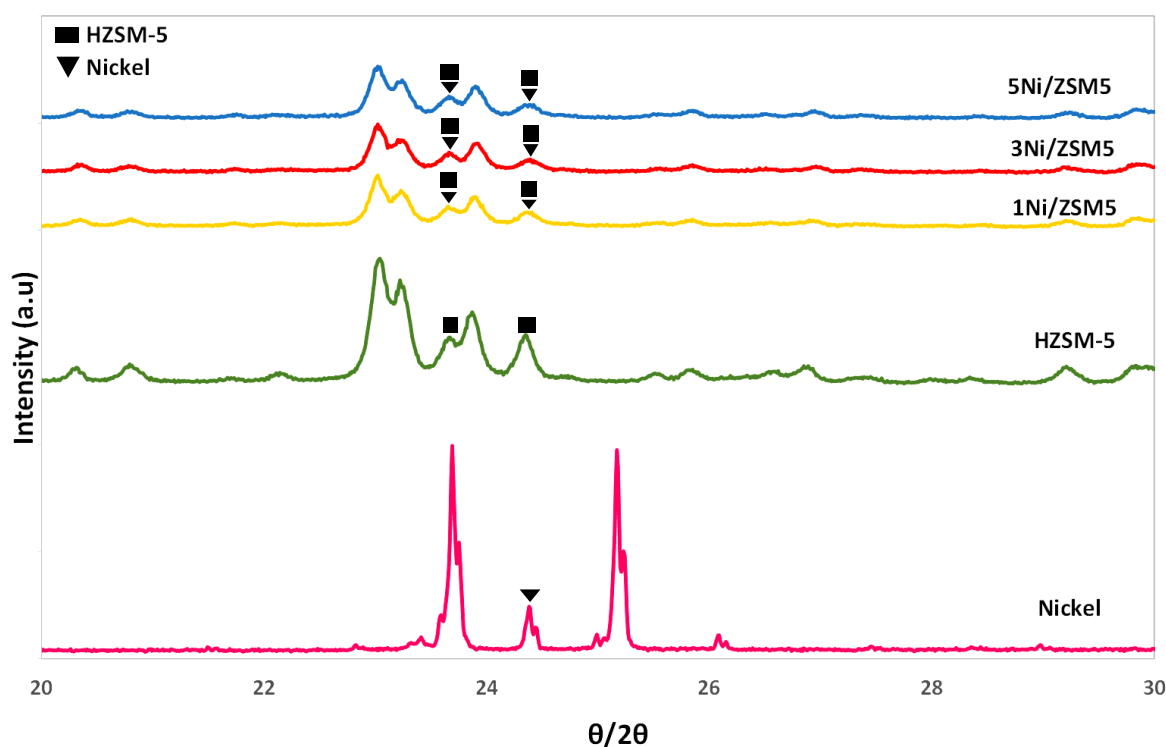


Figure 1: XRD analysis for Ni, HZSM-5 and Ni/ZSM-5 catalysts with different loading of Ni

Subsequently, the catalysts were analyzed using SEM. The images of the catalyst samples for Ni, HZSM5, 1Ni/ZSM5, 3Ni/ZSM5, and 5Ni/ZSM5 are shown in Figure 2. The images of 2a and 2b represent the images of Ni and HZSM-5, while 2c to 2e represent modified catalysts of Ni/ZSM5 with wt. percentage 1, 3 and 5. In the image, HZSM-5 particles are visible at a size of $5\ \mu\text{m}$, while the Ni structure appear much larger at $200\ \mu\text{m}$. The distribution of HZSM-5, with a Si/Al ratio of 30, seems somewhat unclear due to limitations in the instrument's resolution, which can only reveal details down to $5\ \mu\text{m}$. On the other hand, the Ni catalyst displays rod-like crystals at $200\ \mu\text{m}$. However, the catalyst particles seem to be spread out, and resulted to the Ni metals to be observed. This might be because the metal loading is relatively low, and even when the image was magnified to $5\ \mu\text{m}$, the details remain unclear.

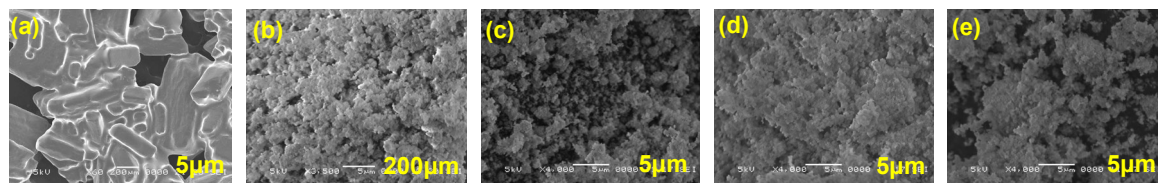


Figure 2: SEM images of (a) Nickel (b) HZSM-5 (c) 1Ni/ZSM-5 (d) 3Ni/ZSM5 (e) 5Ni/ZSM5

Table 1 shows this experiment successfully prepared modified Ni/ZSM-5. Ni species reduced surface areas across all samples by aggregating metal particles and blocking ZSM-5 pores (Jamalzadeh et al., 2013).

Table 1: BET surface area and mesopore volume of all the catalyst samples

Catalyst	Surface area (m ² /g)	Total pore volume (cm ³ /g)	Micropore volume (cm ³ /g)	Mesopore volume (cm ³ /g)
Ni	12.67	0.03420	-0.00278	0.03698
HZSM-5	350.58	0.13370	0.12082	0.01288
1Ni/ZSM5	256.49	0.11971	0.10579	0.01392
3Ni/ZSM5	289.13	0.13242	0.09927	0.03315
5Ni/ZSM5	224.65	0.10987	0.08794	0.02193

The catalysts were subjected further to the vibrational spectroscopy to determine the functional group present in the catalyst. FTIR spectra results ranging between 4,000 to 650 cm⁻¹ are shown in Figure 3. The fact that the structure and location of the IR bands are virtually the same, as seen in the picture that was just presented, provides evidence that the ZSM-5 framework did not undergo any isomorphous substitution (Zakaria et al., 2012). Ni-ZSM5 and HZSM-5 support catalysts exhibited nearly comparable infrared absorbance peaks at 1,215 cm⁻¹, 1,056 cm⁻¹, and 793 cm⁻¹ that could be attributable to the stretching vibration of Si-O-Si (Barros et al., 2008). These spectra are associated with the zeolite lattice's internal connections in SiO₄ or AlO₄. For all catalysts, the asymmetric and symmetric stretching and bending vibrations of OH groups are liable for the bands at 1,625 cm⁻¹ to 1,635 cm⁻¹. These bands relate to the hydroxyl groups, which are Al-OH-Si that are bridged in the framework (Xu et al., 2020). The presence of Ni metals interacts with their OH groups and internal silanol groups, resulting in the production of NiOH⁺ species. There is a possibility that cations will interact with internal silanol groups.

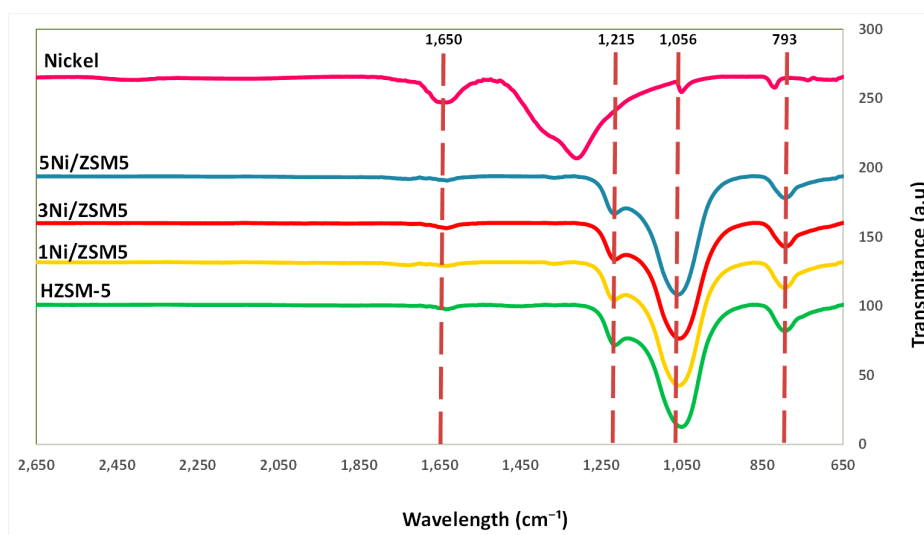


Figure 2: FTIR for various impregnated Ni/ZSM-5 catalysts

3.3 Data Analysis on Pyrolysis Products

Based on the 3-ratio set-up, the basis was fixed to 10 g of FOBS. For ratio 1:5, 2 g catalyst was used, for ratio 1:10, 1 g catalyst was used then for ratio 1:15, 0.67 g catalyst was used. Table 2 tabulates data from the study.

Table 2: Percentage yield of gas, liquid and char obtained from pyrolysis of FOBS (1:5), (1:10) and (1:15)

Catalyst	Yield for ratio (1:5)			Yield for ratio (1:10)			Yield for ratio (1:15)		
	Gas (%)	Liquid (%)	Char (%)	Gas (%)	Liquid (%)	Char (%)	Gas (%)	Liquid (%)	Char (%)
HZSM-5	14.14	60.42	25.44	9.16	79.92	17.93	20.30	68.96	10.74
Ni	57.17	22.83	20.00	37.36	51.04	11.60	32.31	55.14	12.56
1Ni/ZSM5	35.05	39.58	25.37	45.24	35.42	19.35	51.65	32.10	16.25
3Ni/ZSM5	45.63	25.00	29.37	52.84	26.04	21.12	20.51	62.11	17.37
5Ni/ZSM5	45.87	25.00	29.13	28.17	52.08	19.75	25.83	57.23	16.94

From Table 2, for catalyst-to-feedstock ratio of 1:5, the catalyst that produced the highest yield of gas was Ni (57.17 %), followed by 5Ni/ZSM5 (45.67 %), 3Ni/ZSM5 (45.63 %), 1Ni/ZSM5 (35.05 %), and HZSM-5 (14.14 %). Besides, the yields of liquid products were in the range of 23 - 60 %. The yield of liquid product reduces for all catalysts when Ni is loaded into ZSM-5, where 1Ni/ZSM5 is 39 % and both 3Ni/ZSM5 and 5Ni/ZSM5 are 25 %. In a 1:5 catalyst-to-feedstock ratio, Ni catalyst produces the highest yields of gas.

For catalyst-to-feedstock ratio of 1:10, 3Ni/ZSM5 has the highest yield of gas produced while the HZSM-5 has the best yield of liquid produced with 72 %. According to the trend, the catalysts with Ni metal loaded into the ZSM-5 showed an increase in the amount of yield gas production while simultaneously showing a decrease in yield of liquid product. The yield of yield gas has increased from HZSM-5 (9.16 %) to 5Ni/ZSM5 (28.17 %), Ni (37.36 %), 1Ni/ZSM5 (45.24 %), and 3Ni/ZSM-5 (52.84 %). The 3Ni/ZSM5 combination achieved the maximum gas yield in the catalyst and FOBS ratio of 1:10.

As for the 1:15 ratio, 1Ni/ZSM5 produced the highest gas percentage, while HZSM-5 yielded the most liquid product at 68.96 %. The gas yield increased progressively, starting at 20.30 % (HZSM-5) and reaching 51.65 % (1Ni/ZSM5), followed by 20.51 % (3Ni/ZSM5), 25.83 % (5Ni/ZSM5), and 32.31 % (Ni). Introducing metal Ni into ZSM5 reduced the liquid product yield compared to using HZSM-5 alone as the catalyst. This trend suggests that increasing the amount of nickel into ZSM-5 results in higher gas production and lower liquid production. The catalysts that produced the most gas in each ratio were Ni (1:5), 3Ni/ZSM-5 (1:10), and 1Ni/ZSM-5 (1:15). Figure 4 illustrates the gas composition resulting from the process. In Figure 4 (a), at a ratio 1:5 catalyst Ni catalyst was highlighted as the best catalyst for producing a high yield of gas. The gas production primarily consists of two gases (CH₄ and H₂) while the presence of other gases is minimal and can be considered negligible. CH₄ comprise 28.18 % of the gas, while H₂ makes up the remaining 71.82 %. In Figure 4 (b), at a ratio of 1:10, 3Ni/ZSM5 serve as the best catalyst giving a high yield of gas up to 52.84 %. However, instead of CH₄ and H₂, it contains a diverse range of gases, including propane, ethylene, ethane and butene. Among these, H₂ is the dominant gas at 91.75 %, followed by CH₄ (2.94 %), propane (2.20 %), ethylene (1.50 %), ethane (1.11 %) and butene (0.50 %). Figure 4 (c) illustrates the gas composition at a ratio of 1:15 by catalyst 1Ni/ZSM5. At this ratio, only CH₄ and H₂ give a major value, while there is no significant percentage from other gases. CH₄ constitutes 33.11 % of the total gas composition, while H₂ makes up the majority at 66.89 %.

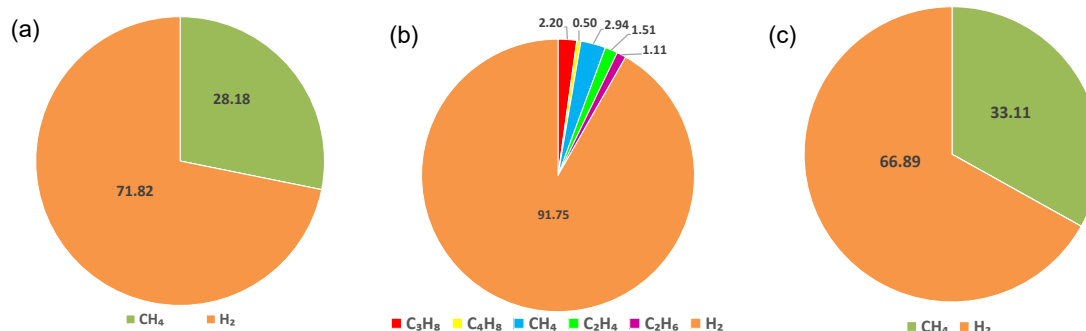


Figure 3: Composition of gas products by using (a) Ni at a ratio of 1:5 (b) 3Ni/ZSM5 at a ratio of 1:10 and (c) 1Ni/ZSM5 at a ratio of 1:15

4. Conclusions

Catalytic pyrolysis of FOBS represents a promising technology for upgrading FOBS into more valuable products, particularly CH₄ and H₂ gases. The incorporation of Ni, into a HZSM-5 catalyst led to modest yet noteworthy improvements in the catalyst's performance regarding gas and liquid product production. Notably, the highest gas yields were achieved with different catalysts in each ratio: Ni catalyst at 1:5, 3Ni/ZSM-5 at 1:10, and

1Ni/ZSM-5 at 1:15. Among these, the 1Ni/ZSM-5 catalyst produced the most CH₄ and H₂ gases, with CH₄ constituting 33.11 % of the total gas composition and H₂ making up 66.89 % at a catalyst-to-FOBS ratio of 1:15.

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