

Formation of Gaseous Fuel via Catalytic Pyrolysis of Fuel Oil Blended Stock (FOBS)

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1 Introduction

Electricity generation in Malaysia relies on diverse sources including coal, natural gas, and fuel oil, with renewable energy emerging as the fastest-growing sector, projected to increase by 3% annually from 2018 to 2050 [1]. Escalating global fuel prices, driven by natural gas and oil shortages, along with stringent regulatory measures, have prompted researchers to focus on enhancing fuel oil blended stock (FOBS), an unwanted byproduct in petrochemical refinery, rarely heard. FOBS, comprising residual oil and byproducts from crude oil refining, poses inefficiency, storage, and environmental challenges [2]. Upgrading FOBS into valuable gas products through catalytic pyrolysis offers a solution to mitigate environmental concerns and meet energy demands. This process, driven by catalysts, breaks down long-chain hydrocarbons to produce light olefins, yielding liquid, solid, and gaseous products [3, 4].

Nanoparticles act as catalysts to improve the conversion of heavy and ultra-heavy crude oil, enhancing the production of methane (CH₄) and hydrogen (H₂) gases during pyrolysis [5]. Research has investigated incorporating metals into supporting materials to modify zeolites, such as HZSM-5, to boost catalytic performance. Adding metals like Mn, Co, Ni, Ga, Ce, and Pt can change the strength and density of acid sites in zeolites, leading to lower tar and CO₂ emissions during pyrolysis. Nickel (Ni) and NiO, in particular, are effective in breaking down carbon-carbon and carbon-hydrogen bonds, thereby increasing CH₄ and H₂ output. [6]. Despite the potential, catalytic pyrolysis of FOBS using Ni/ZSM-5 catalysts remains understudied, with previous research focusing on increased gas production without deep analysis [7]. CH₄'s properties can meet the growing demand for electricity, offering a tangible solution to reduce global warming by mitigating atmospheric CH₄ [8]. Meanwhile, H₂ shows promise as a high-energy fuel for vehicles, with demand expected to rise globally, particularly in regions prioritizing greenhouse gas reduction [9]. Therefore, this study focuses on producing CH₄ and H₂ as gaseous fuels through the catalytic pyrolysis of FOBS, utilizing Ni/ZSM-5 catalysts

2 Methodology

Gas chromatography-mass spectrometry (GC-MS) was used to analyze and identify various chemical components in FOBS. The sample was injected into the GC-MS with a mass selective detector and an HP-5MS column. The temperature started at 40 °C for 4 minutes, increased by 10 °C/min to 200 °C for 5 minutes, then rose by 50 °C/min to 300 °C for 3 minutes. The chemical compounds matching the peaks in the FOBS chromatogram were identified.

As for catalyst preparation, the impregnation method was employed to synthesize the Ni/ZSM-5 catalyst, a common technique for loading metal onto HZSM-5 catalysts [9]. Commercial HZSM-5 zeolite (Si/Al = 30) was obtained from Zeolyst International, and nickel (II) nitrate hexahydrate (97%), Ni(NO₃)₂·6H₂O, was purchased from Sigma-Aldrich. Catalysts were synthesized using the impregnation method with three weight percentage variants and labeled as 1Ni/ZSM5, 3Ni/ZSM5, and 5Ni/ZSM-

X-ray diffraction (XRD) study was conducted to characterize the catalyst. The analysis used Cu K α radiation with a wavelength (λ) of 0.15406 nm, generated by a voltage of 40 kW and a current of 30 mA. The diffraction pattern was captured within a 2 θ range spanning from 5 ° to 35 °. The scanning rates ranged from 2 to 6 degrees per minute, and the step width was set at 0.02 °. Scanning Electron Microscopy (SEM) determined the morphologies and particle sizes of the catalysts, operating at 10 kV to produce high-resolution images in the low nanometer range. Brunauer-Emmett-Teller (BET) analysis assessed surface area via nitrogen adsorption isotherms, following degassing with a N₂ purge at -196 °C for 3 hours. Fourier-transform Infrared Spectroscopy (FTIR) evaluated Brønsted and Lewis acid sites, analyzing functional groups of the Ni/ZSM-5 catalyst spanning from 4,000 - 650 cm⁻¹.

In the catalytic pyrolysis process, the FOBS sample and catalyst were layered and placed in an alumina boat, which was then positioned inside a horizontal quartz tube within a furnace. This setup was encased in a stainless-steel chamber with glass wool insulation. Nitrogen flowed continuously at 150 mL/min to maintain an inert environment. The furnace's temperature was controlled, reaching 500 °C, and then a 60-minute timer was initiated. Gas samples were collected at

intervals using three sampling bags: one at the start, one at the midpoint, and one at the end. The average gas composition from the three samples was analyzed using gas chromatography-thermal conductivity/flame ionization (GC-TCD/FID).

3 Results and Discussion

The GC-MS analysis of FOBS unveiled a composition predominantly comprising hydrocarbons ranging from C_{10} to C_{21} , with identification of nearly 20 distinct compounds. The composition includes aromatic, indene, amine, amide, ketone, and alcohol groups.

Figure 1 illustrated the XRD pattern for nickel (Ni), HZSM-5, and the modified catalyst Ni/ZSM5. The observed diffraction peaks indicated that there were no changes in the structure of the HZSM-5 framework upon loading with Ni metal. Intensity variations suggested the successful integration of metals into the catalyst, as evidenced by the presence of the Ni peak around 23° to 24° . However, the peak intensity was relatively low, potentially indicating either well-dispersed nickel on HZSM-5 or a low Ni content that fell below detection limits [11].

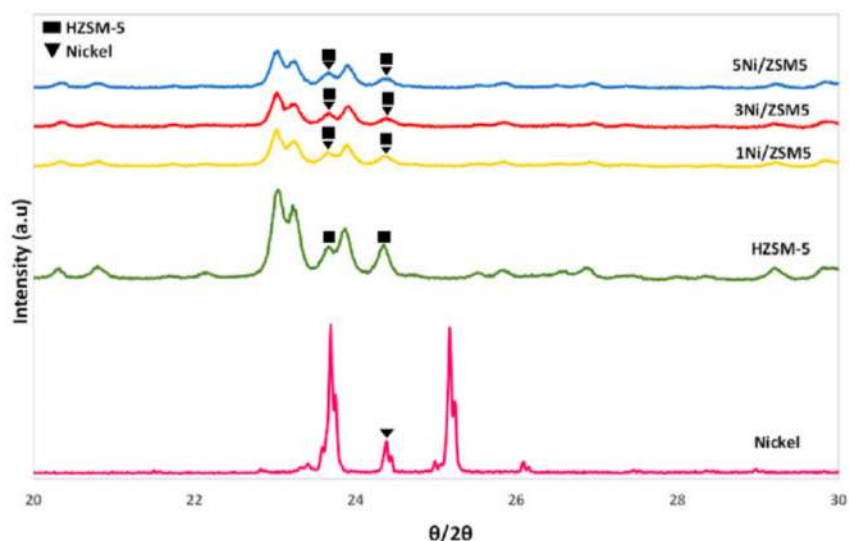


Fig. 1. XRD pattern of Ni, HZSM-5, and Ni/ZSM-5 catalysts with differed Ni loadings.

Next, SEM analysis was conducted on the catalysts. The catalyst samples for Ni, HZSM-5, 1Ni/ZSM5, 3Ni/ZSM5, and 5Ni/ZSM5 were illustrated in Figure 2. Images 2a and 2b depict Ni and HZSM-5, while 2c to 2e illustrate modified catalysts of Ni/ZSM5 with weight percentages of 1, 3, and 5, respectively. HZSM-5 particles are visible at a size of $5\ \mu\text{m}$, whereas the Ni structure appears much larger at $200\ \mu\text{m}$. The distribution of HZSM-5, with a Si/Al ratio of 30, appears somewhat unclear due to resolution limitations, revealing details down to only $5\ \mu\text{m}$. Conversely, the Ni catalyst displays rod-like crystals at $200\ \mu\text{m}$, although the particles seem spread out, making Ni metals observable. This may be attributed to relatively low metal loading, resulting in unclear details even at $5\ \mu\text{m}$ magnification. Table 1 provided surface area and pore volume data for the synthesized catalysts. It was evident that Ni species reduced surface areas across all samples, likely due to the aggregation of metal particles and the blockage of ZSM-5 pores [12].

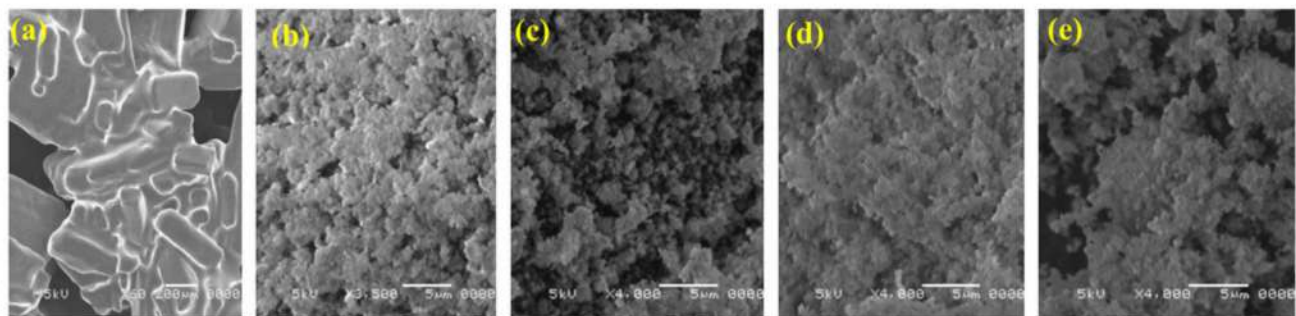


Fig. 2. SEM images of Ni, HZSM-5, and Ni/ZSM-5 catalysts with differed Ni loadings.

The catalysts underwent vibrational spectroscopy for further analysis of the functional groups present. Figure 3 displays the FTIR wavelength spanning from 4,000 to 650 cm^{-1} . The infrared (IR) bands' consistent appearance and positioning in the provided image suggest that the ZSM-5 framework remained unchanged without any substitution. Both the Ni-ZSM5 and HZSM-5 support catalysts showed nearly similar infrared absorption peaks at 1,215 cm^{-1} , 1,056 cm^{-1} , and 793 cm^{-1} , which correspond to the stretching vibration of silanol groups. Silanol groups are crucial in catalytic processes as they serve as active sites during reactions. The presence of silanol groups confirms the successful integration of metal into the catalyst matrix. Additionally, the bands observed at 1,625 cm^{-1} to 1,635 cm^{-1} indicate the stretching and bending vibrations of OH groups, which are associated with bridged hydroxyl groups in the framework [13]. Ni metals interact with these OH groups and internal silanol groups, which could lead to the creation of NiOH^+ species through cation interaction with internal silanol groups.

Table 1. BET data of Ni, HZSM-5, and Ni/ZSM-5 catalysts with differed Ni loadings.

Catalysts	Surface area (m^2/g)	Total pore volume (cm^3/g)	Micropore volume (cm^3/g)	Mesopore volume (cm^3/g)
Ni	12.67	0.0342	-0.0028	0.0369
HZSM-5	350.58	0.1337	0.1208	0.0129
1Ni/ZSM5	256.49	0.1197	0.1058	0.0139
3Ni/ZSM5	289.13	0.1324	0.0993	0.0332
5Ni/ZSM5	224.65	0.1098	0.0879	0.0219

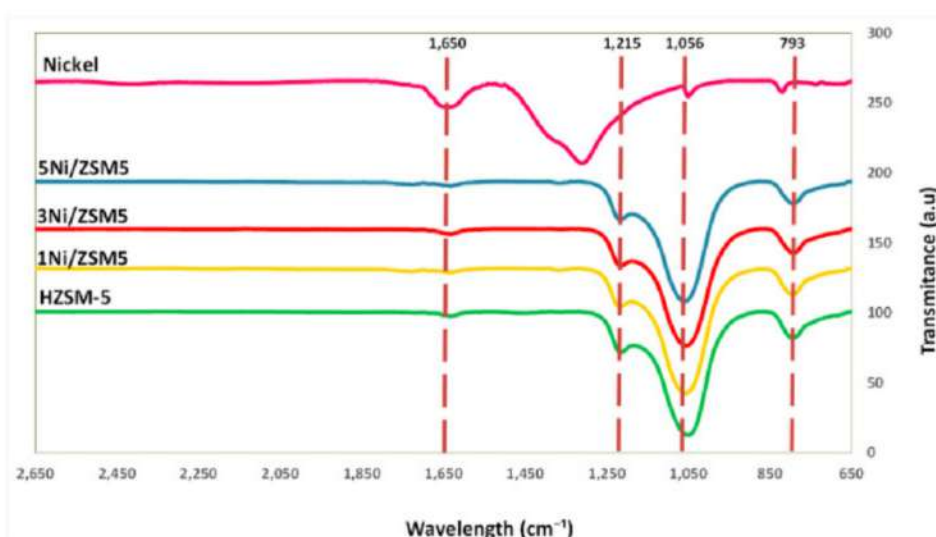


Fig. 3. FTIR spectra of Ni, HZSM-5, and Ni/ZSM-5 catalysts with differed Ni loadings.

Figure 4 depicted the comprehensive outcomes of the catalytic pyrolysis process. The Ni catalyst exhibited the highest gas percentage (57.17%) at a ratio of 1:5, followed by 5Ni/ZSM5 (45.67%), 3Ni/ZSM5 (45.63%), 1Ni/ZSM5 (35.05%), and HZSM-5 (14.14%). Conversely, liquid product yields ranged from 23% to 60%, with a decrease observed when Ni was introduced to ZSM-5. Gas composition primarily consisted of CH_4 and H_2 , with Ni catalyst being optimal at 1:5, 3Ni/ZSM5 at 1:10, and 1Ni/ZSM5 at 1:15, as depicted in Figure 4.

Interestingly, the 3Ni/ZSM-5 catalysts yielded more light hydrocarbon gases (propane, butylene, ethylene, and ethane) at a 1:10 ratio. This indicates that, in addition to their ability to break down the long carbon chains of FOBS into hydrogen and methane, there is great potential to expand the list of valuable gaseous products. However, it is still unknown at this stage how the C_2 to C_4 gases are formed. It could be due to the coupling of methyl free radicals that form ethane and ethylene, and subsequently propane and butylene. If this is the case, several reactions could be involved in the second phase (first phase being the catalytic pyrolysis breaking down of the long hydrocarbon chain), such as a series of dehydrogenation and hydrogenation reactions. More studies are required to confirm this hypothesis, though.

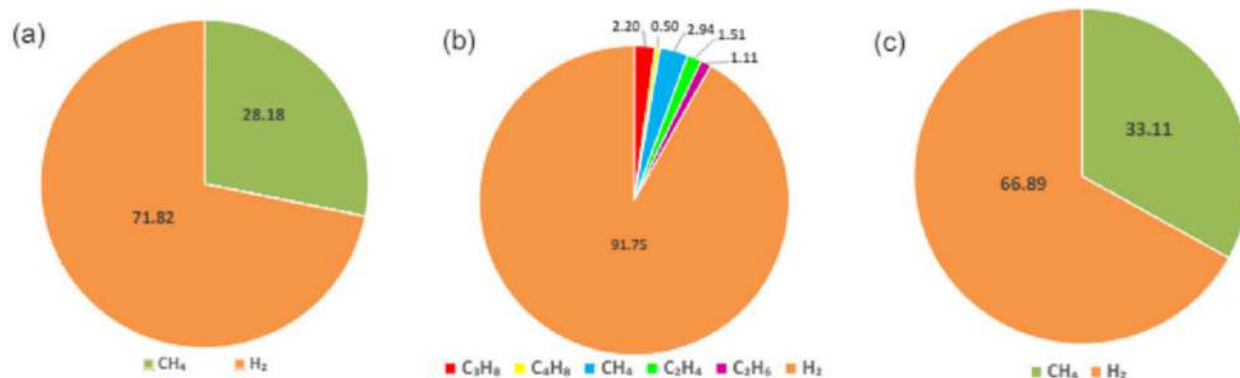


Fig. 4. Gas product composition: (a) Ni at 1:5, (b) 3Ni/ZSM5 at 1:10, and (c) 1Ni/ZSM5 at 1:15.

Conclusion

Catalytic pyrolysis applied to FOBS offers potential for increasing its value through the production of valuable products, notably CH₄ and H₂ gases. Introducing Ni into the HZSM-5 catalyst resulted in significant hydrogen and methane formation. Interestingly, the catalyst's effectiveness varied with different ratios. Particularly noteworthy was the performance of the 1Ni/ZSM-5 catalyst, which yielded the highest amounts of CH₄ and H₂ gases, comprising 33.11% and 66.89% of the total gas composition, respectively, at a catalyst-to-FOBS ratio of 1:15.

Keywords: fuel oil blended stock, catalytic pyrolysis, methane, hydrogen, zeolite catalysts.

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