



Catalytic pyrolysis of high-density polyethylene over nickel-waste chicken eggshell/HZSM-5

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ABSTRACT

The main objective of the current work is to investigate the effect of nickel-waste chicken eggshell modified Hydrogen exchanged Zeolite Socony Mobil-5 (Ni-WCE/HZSM-5) on pyrolysis of high-density polyethylene (HDPE). Ni-WCE/HZSM-5 was synthesized via the impregnation incipient wetness (IWI) method with Ni and WCE mass loading of 4 and 12 wt% respectively. HZSM-5, CaO, WCE, WCE/HZSM-5, and Ni/HZSM-5 were prepared for comparison purposes with Ni-WCE/HZSM-5. All the synthesized catalysts were characterized for phase analysis, metal loading, surface morphology, and textural properties. The impregnation of nickel and WCE had significantly affected the original framework of HZSM-5, where the crystallinity percentage and average crystal size of HZSM-5 dropped to 44.97% and increased to 47.90 nm respectively. The surface morphology of HZSM-5 has drastically changed from a cubic-like shape into a spider web-like surface after the impregnation of WCE. The BET surface area of HZSM-5 has been lowered due to the impregnation of nickel and WCE, but the total pore volume has increased greatly from 0.2291 cm³/g to 0.2621 cm³/g. The catalyst performance was investigated in the pyrolysis of HDPE via a fixed bed reactor and the pyrolysis oil was further analysed to evaluate the distribution of C₆ to C₉> hydrocarbons. Among the tested catalytic samples, the highest pyrolysis oil yield was achieved by WCE (80%) followed by CaO (78%), WCE/HZSM-5 (63%), HZSM-5 (61%), Ni/HZSM-5 (44%) and Ni-WCE/HZSM-5 (50%). For hydrocarbon distribution in pyrolysis oil, the Ni/HZSM-5 produced the highest of total C₆ and C₇ hydrocarbons at 12% and 27% respectively followed by WCE/HZSM-5 (4% and 20%), non-catalytic (5% and 13%), Ni-WCE/HZSM-5 (0% and 15%), WCE (0% and 10%), HZSM-5 (0% and 6%) and CaO (0% and 0%).

1. Introduction

Hydrogen exchanged Zeolite Socony Mobil-5 (HZSM-5) is a man-made zeolite which commonly used as a supported catalyst to enhance catalytic cracking in petroleum refineries for hydrocarbon productions (Al-asadi and Miskolczi, 2021). This is because, the HZSM-5 catalyst is deemed to such a high reputation than other acid catalysts due to higher catalytic cracking properties on heavy hydrocarbons (Dwivedi et al., 2021). The popularity of HZSM-5 is its solid-state properties, which have high porosity and good thermal stability during the cracking process (Ali et al., 2021). Consequently, the drawbacks of HZSM5 are its short product cycle where coke formation easily occurs which leads to low yield organic liquid and selectivity (Wang et al., 2021).

Interestingly, calcium oxide (CaO) is a base catalyst and was reported to be a reliable catalyst in the transesterification process (Rahman et al., 2019). Xing et al. (2018) reported that generally CaO was obtained from limestone quarry and also an alternative, environmentally friendly, and cheaper resource can be extracted from waste chicken eggshell (WCE). Coincidentally, based on the previously reported work we found that the applications of WCE in pyrolysis have not been well investigated. The CaO can act as both active metal and promoter catalyst to stabilize the acidic properties of HZSM5 and improve the synergy of hydrocarbon fuel properties (Awogbemi et al., 2021). Laca et al. (2017) found that CaO has a small surface area that limits the exposure of active basic sites which impacted the long reaction time needed for the completion of catalytic cracking of heavy compounds into light compounds. Hence, the

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usage of WCE as a catalyst over CaO commercially produce, can reduce the environmental impact and alter the HZSM-5 framework to have a longer product cycle. However, the alkaline metal impregnated with HZSM-5 alone is not enough to increase catalytic cracking performance, a varied selection from transition metal series can further help the catalytic activity.

Commonly nickel shows beneficial results compared to other metal loadings in the catalytic cracking process in pyrolysis (Xing et al., 2018). The impregnated nickel on HZSM-5 can enhance the catalytic cracking process to break down the long polymer chain HDPE (Sulaiman et al., 2021). Since WCE has its unique surface morphology of fibre rod porous structure, it can further increase the surface area of the catalyst for the active site to optimize successful cracking attempts when the hydrocarbon is in contact with the active metal nickel embedded in WCE over HZSM-5.

High-density polyethylene (HDPE) is a common plastics wastes found in household items. From detergent bottles to plastic containers, stationaries, and plastic furniture are made from HDPE. Miandad et al. (2016) highlighted that improper plastic waste management had led to a global crisis and its presence everywhere in the globe. Interestingly, plastics are polymers derived from non-renewable petroleum (Liew et al., 2021). The monomers obtained from these natural resources are polymerized to produce long-chain polymers made up of hydrogen and carbon only (Al-Salem et al., 2017). Therefore, an attempt to convert plastic wastes into affordable hydrocarbon fuels using pyrolysis technology is considered a solution to handle the plastics waste crisis (Putra et al., 2022). Sogancioglu et al. (2017) investigated the pyrolysis of HDPE and they found that three types of products are produced such as 79.8% of pyrolysis oil, 17% of gas, and 3.2% of solid wax from HDPE. The pyrolysis oil generated from the pyrolysis of plastic waste is similar to those of conventional petroleum. This aligns with United Nations Sustainable Development Goals efforts, mainly on affordable and clean energy (SDG 7) and responsible consumption and production (SDG 12).

For this reason, in this paper, HDPE was used as feedstock in catalytic pyrolysis to test out and investigate the catalytic performance of Ni-WCE/HZSM-5 to produce hydrocarbons fuel and compared with individual pyrolysis of HDPE over HZSM-5, CaO, WCE, WCE/HZSM-5, and Ni/HZSM-5 catalysts. To the best of our knowledge, the catalytic performance of WCE, WCE/HZSM-5, and Ni-WCE/HZSM-5 on the pyrolysis of HDPE has not yet been evaluated as a function of hydrocarbon contents (%) in pyrolysis oil. The Ni-WCE/HZSM-5 catalyst was synthesized using the incipient wetness impregnation method (IWI) and characterized for phase analysis via X-ray diffraction (XRD), metal loading was validated via X-ray fluorescence (XRF), surface morphology via field emission scanning microscopy (FESEM), and textural properties via Brunauer Emmett Teller (BET). The influence of catalysts in the pyrolysis of HDPE on hydrocarbon production in pyrolysis oil was discussed.

2. Methodology

2.1. Feedstock preparation

High-density polyethylene (HDPE) type plastic waste was used as pyrolysis feedstock. HDPE in pellet form was supplied by a local recycling company in Malaysia.

2.2. Catalyst preparation

The preparation of HZSM-5, CaO (commercial), waste chicken eggshell (WCE), and WCE/HZSM-5 catalysts was reported in our previous work (Ali et al., 2021). In this work, Ni-WCE/HZSM-5 was prepared to investigate the effect of nickel loading into WCE/HZSM-5. Additionally, Ni/HZSM-5 was also prepared for comparison with loaded WCE. Nickel (II) nitrate hexahydrate (99% purity) was purchased from Acros Organics. Ni-WCE/HZSM-5 was synthesized via the incipient wetness impregnation (IWI) method with mass loading of Ni at 4 wt%

and WCE at 12 wt%. All three chemicals were added into a beaker with 80 mL of deionized water and continuously stirred for a homogenous solution using a hot plate magnetic stirrer at 80 °C for 4 h. Next, the formed paste was filtered and washed with deionized water before proceeding to dry in a laboratory oven at 100 ± 2 °C for 12 h. Lastly, the dried paste was calcined at 600 °C for 4 h (5 °C/min). The synthesis was repeated for Ni/HZSM-5 with mass loading of Ni at 4 wt%

2.3. Catalyst characterization

Physicochemical properties such as phase analysis via X-ray diffraction (XRD), metal loading was validated via X-ray fluorescence (XRF), surface morphology via field emission scanning microscopy (FESEM), and textural properties via Brunauer Emmett Teller (BET) for HZSM-5, CaO (commercial), WCE, and WCE/HZSM-5 catalysts were reported in our previous work (Ali et al., 2021). Meanwhile, the physicochemical properties for Ni/HZSM-5 and Ni-WCE/HZSM-5 were reported in this study and compared with HZSM-5, CaO (commercial), WCE, and WCE/HZSM-5 from our previous work (Ali et al., 2021).

2.4. Catalytic pyrolysis of HDPE

The effect of non-catalytic, HZSM-5, CaO, WCE, WCE/HZSM-5, Ni/HZSM-5, and Ni-WCE/HZSM-5 catalysts on pyrolysis of HDPE was investigated via a lab-scale fixed bed reactor. The setup consists of a fixed bed reactor, tubular furnace, condenser system, gas sample bag, and nitrogen (N₂) gas flow. All the experiments were performed in batch runs at a fixed temperature of 500 °C. For each run, the HDPE and catalyst were fixed at equal mass loading of 2g. The standard operating procedures for pyrolysis experiments and analysis of organic compositions in pyrolysis oil via gas chromatography-mass spectrometer (GC-MS) were reported in our previous work (Balasundram et al., 2018).

3. Results and discussion

3.1. Physicochemical properties of catalysts

3.1.1. Phase analysis, crystallinity, and crystal size

The phase analysis of HZSM-5, CaO, WCE, WCE/HZSM-5, Ni/HZSM-5, and Ni-WCE/HZSM-5 catalysts was characterized by XRD as shown in Fig. 1. Meanwhile, the crystallinity and crystal size of catalysts were tabulated in Table 1. The XRD scanning range is from 5° to 60° for all types of catalysts. The main peaks for HZSM-5 were present at 7.91°, 8.85°, 23.10°, 23.96°, and 24.01° as reported in our previous work (Ali et al., 2021). As shown in Fig. 1, CaO and WCE exhibit similar peaks at 32.35°, 37.43°, and 53.91°. Hence, it can be concluded that WCE is pure and has the same crystal properties as CaO. For Ni-WCE/HZSM-5, the presence of Ni and WCE over HZSM-5 could not be seen significantly due

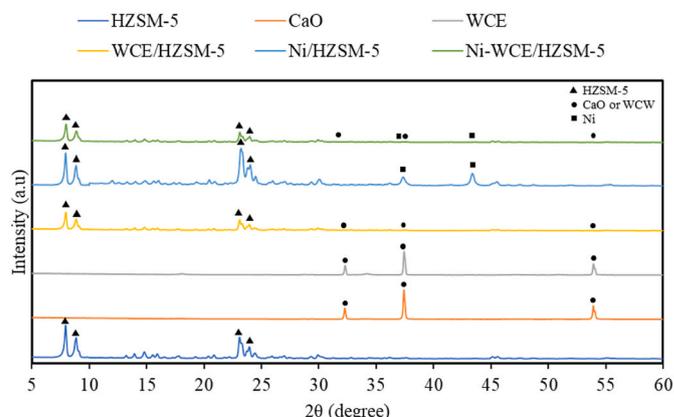


Fig. 1. XRD patterns of respective catalysts.

Table 1
Crystallinity and average crystal size of synthesized catalysts.

| Catalysts | Crystallinity (%) | Average crystal size (nm) |
|---------------|-------------------|---------------------------|
| HZSM-5 | 99.90 | 42.90 |
| CaO | 40.22 | 53.97 |
| WCE | 40.42 | 45.13 |
| WCE/HZSM-5 | 44.97 | 45.00 |
| Ni/HZSM-5 | 43.51 | 46.21 |
| Ni-WCE/HZSM-5 | 45.01 | 47.82 |

to the higher weight percent of WCE (12 wt%) and lower weight percent of Ni (4 wt%). However, it can be observed that the presence of new two peaks for Ni/HZSM-5 at 37.47° and 43.25° which resembles the presence of nickel in HZSM-5 (refer Fig. 1). Thus, it can be concluded that the addition of WCE into Ni/HZSM-5 has a significant effect on covering the presence of nickel. All of the main peaks for each catalyst are present, however, the presence of some noise in the peaks may indicate some impurities or transition from amorphous to the crystalline phase. The average crystal size of all catalysts was calculated using Debye Sherrer equations. The catalyst crystal size increases at the scale of 42.90–47.82 nm except for CaO at 53.97 nm as shown in Table 1. This could be due to the vibration mode of the crystal lattice from the heat transfer in the muffle furnace environment to the crystal lattice by van der Waals interaction. Hence, the migration and displacement of the atoms create a shear, convergence, or divergence space with Ni and Ca atoms in the free space HZSM-5 similar to results reported by Loza et al. (2020).

3.1.2. Metal loading

Each catalyst metal loading was validated via XRF as shown in Table 2. It was observed that the HZSM-5 consists of 1.952% of alumina (Al₂O₃) and 96.757% of silica (SiO₂). Meanwhile, CaO (98.894%) and WCE (98.559%) have around the same purity of element loading. The WCE/HZSM-5 consists of a slightly higher trace of WCE (14.213%) than the theoretical loading of 12 wt%. However, it can also be seen traces of Al₂O₃ (1.859%) and SiO₂ (82.848%) are lower than the HZSM-5. A possible reason could be during the impregnation, drying, and calcination there are traces of other elements that contaminated the samples. A similar explanation can be made for Ni/HZSM-5 and Ni-WCE/HZSM-5, where the Al₂O₃ (2.215% and 1.520%) and SiO₂ (75.444 and 81.303%) also have lowered element loading traces of HZSM-5. The amount of Ni traces in Ni/HZSM-5 is slightly lower at 3.951% than the theoretical Ni loading at 4 wt%. CaO content from WCE in Ni-WCE/HZSM-5 is aligned with the theoretical loading during the impregnation, and it was verified that Ni is present in the sample with 3.554% loaded. The results in Table 2 justified the unseen presence in Fig. 1 of XRD where traces of WCE in WCE/HZSM-5 and Ni-WCE/HZSM-5 while Ni in Ni/HZSM-5 and Ni-WCE/HZSM-5 is unclear.

3.1.3. Surface morphology

The surface morphology of all synthesized catalysts was shown in Fig. 2. HZSM-5 grains can be seen as an irregular grains pattern and also porous slits surface. On the contrary, for CaO and WCE, the differences are in the porous structure of CaO which has an irregular porous mesh agglomerate structure and WCE has a porous fibre rod-like structure.

Table 2
XRF results of element loading.

| Catalysts | Element Loading (%) | | | |
|---------------|--------------------------------|------------------|--------|-------|
| | Al ₂ O ₃ | SiO ₂ | CaO | Ni |
| HZSM-5 | 1.952 | 96.757 | 0 | 0 |
| CaO | 0.54 | 0.143 | 98.894 | 0 |
| WCE | 0.482 | 0.032 | 98.559 | 0 |
| WCE/HZSM-5 | 1.859 | 82.848 | 14.213 | 0 |
| Ni/HZSM-5 | 2.215 | 75.444 | 0 | 3.951 |
| Ni-WCE/HZSM-5 | 1.520 | 81.303 | 12.689 | 3.554 |

The reason between this two is one is extracted from earth's natural resources like quarries where CaO formation derives from limestone minerals. The growth and formation of limestone minerals that contain Ca(CO₃) are by the formation of sedimentary rock in form of calcite or aragonite and was studied by Hou et al. (2018). Meanwhile, the WCE is from bio-mineralization in which proteins are responsible to create the fibre rod membrane structure of the chicken eggshell as reported by Gautron et al. (2021). WCE/HZSM-5 and Ni-WCE/HZSM-5 catalysts have similar spider web-like surfaces; due to the reactions caused by strong acid and strong alkali in contact. A similar encounter can be found by Kumagai et al. (2017) on CaO in contact with acid sites but Ni/HZSM-5 are differed due to both materials being acid where its surface is similar to HZSM-5. In this study, the CaO deteriorates over HZSM-5 during calcination at 600 °C processes to synthesize WCE/HZSM-5 and Ni-WCE/HZSM-5. HZSM-5 has a giant crystal structure compared to the face cent cubic of Ni and Ca, therefore the presence of crystallinity is much clearer for HZSM-5 than Ni or Ca.

3.1.4. Surface area and pore analysis

The surface area and pore analysis for all the synthesized catalysts were shown in Table 3. As expected, the HZSM-5 has a higher BET surface area at 365.81 m²/g, while WCE/HZSM-5, Ni/HZSM-5, and Ni-WCE/HZSM-5 have almost similar BET surface areas at 292.10 m²/g, 288.44 m²/g, and 292.14 m²/g respectively (refer to Table 3). This could be potentially due to Ni impregnated in the pores of both WCE and HZSM-5 creating more active metal sites, thus increasing its surface area. Interestingly, all the catalysts have almost similar pore diameters at 3.7 ± 0.1 nm except CaO at 3.58 nm. The impregnation of WCE, Ni, and Ni-WCE into HZSM-5 shows almost similar results of total pore volume at 0.2663 cm³/g, 0.2687 cm³/g, and 0.2621 cm³/g respectively. This could be due to the repeated calcination process for Ni to be impregnated into WCE/HZSM-5, where an increase in the temperature environment expanded the pores sizes to be larger and also creates new openings. The addition of Ni into WCE/HZSM-5 does not significantly affect the total pore volume of WCE/HZSM-5. This could be due to the small Ni mass loading at 4 wt% into WCE/HZSM-5 which only shows very few changes in surface area, total pore volume, and pore diameter. Hence, it can be concluded that a higher surface area of the catalyst, allows easier conversion via catalytic activity, to break down the carbon chain of HDPE into hydrocarbon.

3.2. Pyrolysis of HDPE

3.2.1. Pyrolysis product yield

The pyrolysis product yields were shown in Fig. 3. The non-catalytic consist of 90% of pyrolysis oil. The CaO (78%) and WCE (80%) catalysts produced a higher pyrolysis oil yield at 78% and 80% respectively compared to HZSM-5 at 61%. This is due to the nature of the CaO-based catalyst (base) which has lower acid sites to break down heavy compounds into non-condensable gas during pyrolysis of HDPE. Finally, the heavy compounds in vapours will be gradually condensed into a higher yield of pyrolysis oil. This can be observed in the lower yield of pyrolysis gas from CaO and WCE compared to HZSM-5. The HZSM-5 is an acidic catalyst; thus, it enhances the cracking process of heavy compounds in vapour, turning them into lighter compounds that end up as a non-condensable gas. The pyrolysis product results of HZSM-5 can be reflected by its surface morphology and pores characteristics from FESEM and BET results. The HZSM-5 consists of a high density of porous channels which enables a large surface area with acidic active sites for breaking down the heavy compound into lighter compounds in large quantities.

However, for the WCE/HZSM-5 catalyst, the pyrolysis oil is the highest at 63%, compared to Ni/HZSM-5 (44%) and Ni-WCE/HZSM-5 (50%). This proves that WCE with HZSM-5 which may be related due to stabilising conditions in catalytic cracking as mentioned by Awogbemi et al. (2021). For Ni/HZSM-5, the Ni metal can be seen in Fig. 3

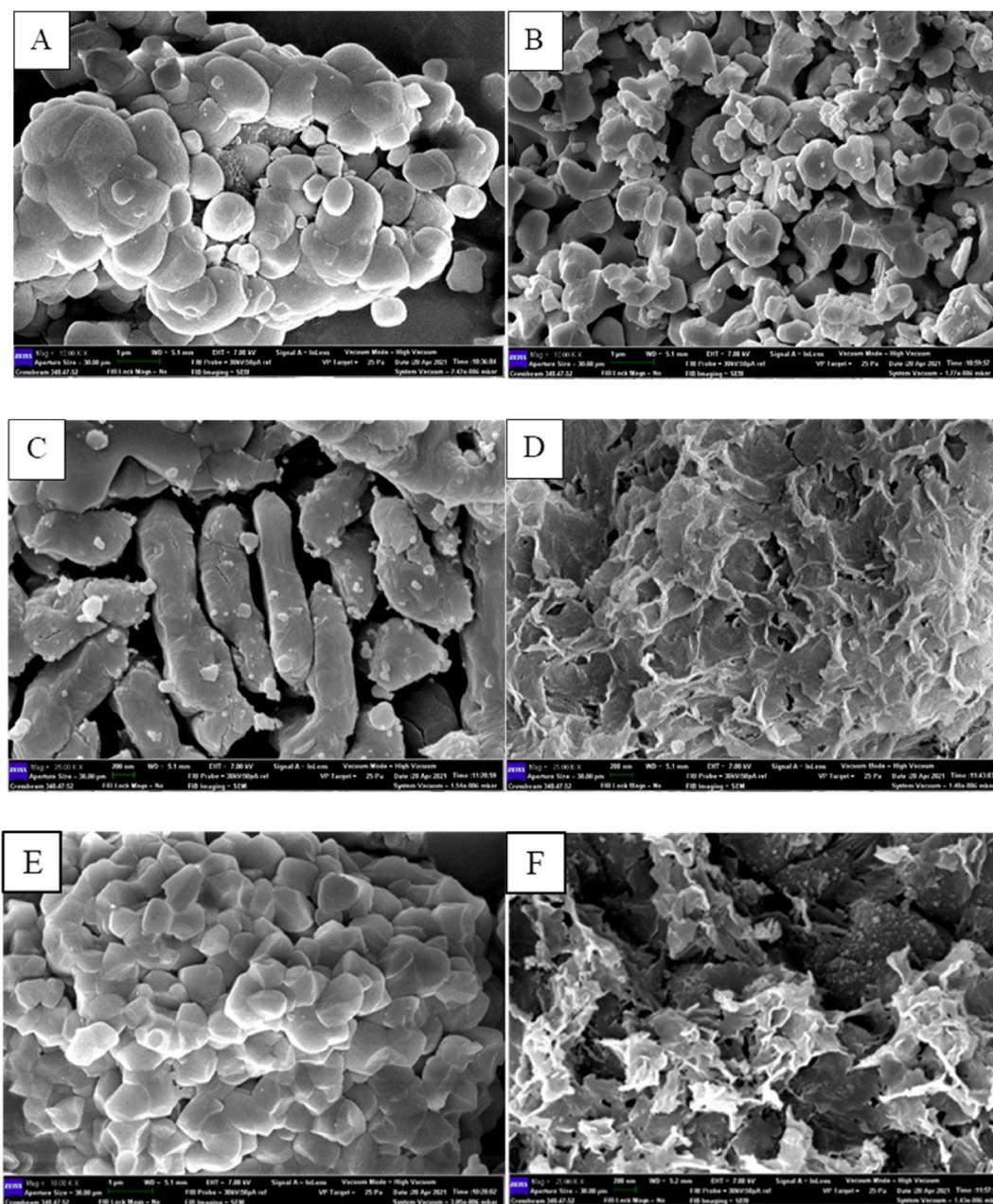


Fig. 2. Surface morphology for A) HZSM-5, B) CaO, C) WCE, D) WCE/HZSM-5, E) Ni/HZSM-5 and F) Ni-WCE/HZSM-5.

Table 3
Textural properties of synthesized catalysts.

| Catalysts | ^a S _{BET} (m ² /g) | ^b V _{total} (cm ³ /g) | ^c D (nm) |
|---------------|---|--|---------------------|
| HZSM-5 | 365.81 | 0.2291 | 3.87 |
| CaO | 3.80 | 0.0063 | 3.58 |
| WCE | 8.72 | 0.0156 | 3.87 |
| WCE/HZSM-5 | 292.14 | 0.2663 | 3.88 |
| Ni/HZSM-5 | 288.44 | 0.2687 | 3.83 |
| Ni-WCE/HZSM-5 | 292.10 | 0.2621 | 3.86 |

^a S_{BET} (BET surface area) was obtained by the BET method.

^b V_{total} (total pore volume) was obtained from the adsorbed amount at P/P₀ = 0.99.

^c D (pore diameter) was obtained from the adsorption branches of the iso-therms by the BJH method.

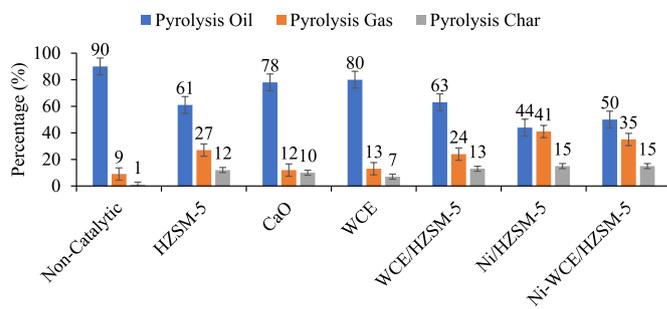


Fig. 3. Pyrolysis product yield of HDPE in form of pyrolysis, pyrolysis gas, and pyrolysis char.

which might promote cracking and gasification, while WCE provides much greater control of the cracking activity. The combination of both catalysts as Ni-WCE/HZSM-5 did not meet the expectations initially made, which we assume can further produce higher pyrolysis oil than other catalytic samples. This shows the challenge of synthesizing an impactful multifunctional catalyst in the pyrolysis of plastic wastes. As can be seen in Fig. 3, all the catalysts produce a low yield of pyrolysis char with the highest by Ni/HZSM-5 (15%) and Ni-WCE/HZSM-5 (15%) followed by WCE/HZSM-5 (13%), HZSM-5 (12%), CaO (10%), and WCE (7%). The highest pyrolysis char was produced by Ni/HZSM-5 and Ni-WCE/HZSM-5 indicates the unconverted plastic waste. This could be due to the rapid and repeated cracking by nickel that has led to the formation of carbonaceous material and finally covered the active acid sites. Overall, it can be concluded that in this study the addition of WCE and Ni on HZSM-5 as Ni-WCE/HZSM-5 catalyst does not show beneficial results in terms of pyrolysis oil yield from pyrolysis of HDPE.

3.2.2. Composition of C₆–C₉> hydrocarbons in pyrolysis oil

The C₆ to C₉> hydrocarbon range was selected, as C₆ to C₈ is widely used and applicable in gasoline while C₉> is outside the range of gasoline hydrocarbon (Hees et al., 2019). Gasoline is predominantly a mixture of paraffin, naphthene, aromatics, olefins, benzene, aliphatic, alicyclic, alkanes, isoalkanes, and cycloalkenes (Jia et al., 2021). From Fig. 4, it can be observed that the non-catalytic consist of 5% of C₆, 13% of C₇, 16% of C₈, and 66% of C₉> hydrocarbons. The C₆–C₈ hydrocarbons for the non-catalytic sample mostly consist of 1-octene, toluene, and benzene, 1,3-dimethyl-o-xylene. The hydrocarbon distributions for CaO (C₆:0%, C₇:0%, C₈:2%, C₉>:98%) and WCE (C₆:0%, C₇:10%, C₈:10%, C₉>:80%) are slightly different because of the porosity differences (refer Table S1). However, the hydrocarbon content in CaO is mainly 1-octene, while for WCE is 1-octene, octane, and 1-heptane. CaO and WCE have the lowest percentage of C₆–C₈ hydrocarbons compared to HZSM-5 (C₆:0%, C₇:6%, C₈:19:75%) and vice versa for C₉>. This might be due to the acidic properties of HZSM-5 to crack heavy hydrocarbons into light hydrocarbons effectively compared to CaO and WCE which are the base catalyst. The HZSM-5 and WCE are both porous materials that help create many interworking channels for cracking framework flexibility, mass transfer, regeneration, and adsorption of HDPE into hydrocarbon as reported by Zhang et al. (2021). Meanwhile, the hydrocarbon content in HZSM-5 is mainly cis-1-butyl-2-methyl cyclopropane. For Ni-WCE/HZSM-5 catalytic sample, it has generated hydrocarbons as follows: C₆ at 0%, C₇ at 15%, C₈ at 15%, and C₉> at 70%, which has resulted in the lower distribution of C₆–C₈ hydrocarbons compared to WCE/HZSM-5 (C₆:4%, C₇:20%, C₈:17%) and Ni/HZSM-5 (C₆:12%, C₇:27%, C₈:25%). A possible reason is due to the acidity and alkalinity of the Ni-WCE/HZSM-5 when in contact with pyrolyze of HDPE. The Ni-WCE/HZSM-5 and WCE/HZSM-5 have a similar large content of 1-octene, 1-heptane, and toluene, while Ni/HZSM-5, largely contains phenol, p-cresol, and 4-ethyl-phenol. In addition, even the non-catalytic sample has a higher percentage of C₆ to C₈ hydrocarbons than from Ni-WCE/HZSM-5. This could be due to the higher weight percent of WCE (12 wt%) that had significantly covered the large area of acid sites for cracking the C₉> into C₆ to C₈ hydrocarbons. Hence, it can be concluded that the weight percent of nickel and WCE in HZSM-5 should be further investigated in the future. Overall, it can be concluded that in this study the addition of a higher weight percent of WCE than Ni does not show beneficial results in terms of total C₆ to C₈ hydrocarbons.

4. Conclusions

The catalytic pyrolysis of HDPE over Ni-WCE/HZSM-5 was successfully achieved and compared with the non-catalytic and catalytic pyrolysis over HZSM-5, CaO, WCE, WCE/HZSM-5, and Ni/HZSM-5. The WCE/HZSM-5 shows 63% pyrolysis oil compared to Ni/HZSM-5 (44%) and Ni-WCE/HZSM-5 (50%), which consists of valuable C₆ and

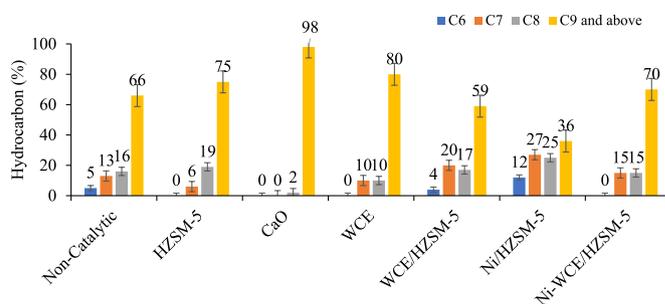


Fig. 4. Hydrocarbons percentage of C₆–C₉> in pyrolysis oil.

C₇ hydrocarbons at 4% and 20% respectively. The formation of higher percentage of C₆ and C₇ than C₈ and C₉> are mostly from WCE/HZSM-5 (C₆:4%, C₇:20%, C₈:17%, C₉>:59%) and Ni/HZSM-5 (C₆:12%, C₇:27%, C₈:25%, C₉>:36%). However, the combination of nickel and WCE into HZSM-5 as Ni-WCE/HZSM-5 has produced lower C₆ to C₈ hydrocarbons and higher C₉> hydrocarbons as follows C₆:0%, C₇:15%, C₈:15%, and C₉>:70%. Before the investigation, we hypothesize that the addition of alkali metal (CaO) from WCE could fine-tune the physicochemical properties of HZSM-5 and be favourable in cracking C₉> into C₆ to C₈ hydrocarbons. However, this paper proves the challenge of synthesizing Ni-WCE/HZSM-5 as a multifunctional catalyst to enhance the production of C₆ to C₈ hydrocarbons from the pyrolysis of HDPE. This paper also shows how WCE can rival other synthesized catalysts in terms of pyrolysis oil yield. WCE alone is insufficient in cracking heavy hydrocarbons (C₉>) into desirable light hydrocarbons (C₆ to C₈). Hence, the addition of acidic properties from HZSM-5 or metals (nickel) is highly recommended to enhance the cracking. Unfortunately, the application of WCE/HZSM-5 cannot be considered a green catalyst, but it shows some promising results in terms of physicochemical properties and yield of C₆ to C₈ hydrocarbons. This work is an attempt in screening the possibility of WCE as a catalyst in the pyrolysis of plastic waste. In the future, this type of catalyst can be explored in the pyrolysis of biomass or other processes. Thus, the application of WCE/HZSM-5 as a catalyst can be considered a promising catalyst to be used as an alternative to Ni in the catalytic pyrolysis of plastic wastes.

Declaration of competing interest

The authors declare that they have no known competing interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jenvman.2022.116392>.

References

- Al-asadi, M., Miskolczi, N., 2021. Hydrogen rich products from waste HDPE/LDPE/PP/PET over Me/Ni-ZSM-5 catalysts combined with dolomite. *J. Energy Inst.* 96, 251–259.
- Al-Salem, S.M., Antelava, A., Constantinou, A., Manos, G., Dutta, A., 2017. A review on thermal and catalytic pyrolysis of plastic solid waste (PSW). *J. Environ. Manag.* 197, 177–198.
- Ali, N.S.M., Balasundram, V., Shamel, K., Ibrahim, N., Isha, R., Manan, Z.A., 2021. The effect of calcium oxide from waste chicken eggshell on HZSM-5. *Chem. Eng. Transact.* 89, 181–186.
- Awogbemi, O., Kallon, D.V.V., Aigbodion, V.S., 2021. Trends in the development and utilization of agricultural wastes as heterogeneous catalyst for biodiesel production. *J. Energy Inst.* 98, 244–258.
- Balasundram, V., Zaman, K.K., Ibrahim, N., Kasmani, R.M., Isha, R., Hamid, M.K.A., Hasbullah, H., 2018. Catalytic upgrading of pyrolysis vapours over metal modified HZSM-5 via in-situ pyrolysis of sugarcane bagasse: effect of nickel to cerium ratio on HZSM-5. *J. Anal. Appl. Pyrol.* 134, 309–325.
- Dwivedi, U., Pant, K.K., Naik, S.N., 2021. Controlling liquid hydrocarbon composition in valorization of plastic waste via tuning zeolite framework and SiO₂/Al₂O₃ ratio. *J. Environ. Manag.* 297, 113288.
- Hou, B., Zhang, R., Tan, P., Song, Y., Fu, W., Chang, Z., Kao, J., Muhadasi, Y., Chen, M., 2018. Characteristics of fracture propagation in compact limestone formation by hydraulic fracturing in central Sichuan, China. *J. Nat. Gas Sci. Eng.* 57, 122–134.
- Gautron, Stapane, Le Roy, 2021. Avian eggshell biomineralization: an update on its structure, mineralogy and protein tool kit. *BMC Molecular and Cell Biology* 22 (11), 1–17.
- Hees, T., Zhong, F., Stürzel, M., Mülhaupt, R., 2019. Tailoring hydrocarbon polymers and all-hydrocarbon composites for circular economy. *Macromol. Rapid Commun.* 40, 1800608.
- Jia, C., Xie, S., Zhang, W., Intan, N.N., Sampath, J., Pfaendtner, J., Lin, H., 2021. Deconstruction of high-density polyethylene into liquid hydrocarbon fuels and lubricants by hydrogenolysis over Ru catalyst. *Chem Catalysis* 1, 437–455.
- Kumagai, S., Yamasaki, R., Kameda, T., Saito, Y., Watanabe, A., Watanabe, C.I., Teramae, N., Yoshioka, T., 2017. Aromatic hydrocarbon selectivity as a function of CaO basicity and aging during CaO-catalyzed PET pyrolysis using tandem μ -reactor-GC/MS. *Chem. Eng. J.* 332, 169–173.
- Laca, A., Laca, A., Diaz, M., 2017. Eggshell waste as catalyst: a review. *J. Environ. Manag.* 197, 351–359.
- Liew, J.X., Loy, A.C.M., Chin, B.L.F., Alnoss, A., Shahbaz, M., Al-Ansari, T., Govindan, R., Chai, Y.H., 2021. Synergistic effects of catalytic co-pyrolysis of corn cob and HDPE waste mixtures using weight average global process model. *Renew. Energy* 170, 948–963.
- Loza, K., Heggen, M., Epple, M., 2020. Synthesis, structure, properties, and applications of bimetallic nanoparticles of noble metals. *Adv. Funct. Mater.* 30.
- Miandad, R., Barakat, M.A., Aburizaiza, A.S., Rehan, M., Nizami, A.S., 2016. Catalytic pyrolysis of plastic waste: a review. *Process Saf. Environ. Protect.* 102, 822–838.
- Putra, P.H.M., Rozali, S., Patah, M.F.A., Idris, A., 2022. A review of microwave pyrolysis as a sustainable plastic waste management technique. *J. Environ. Manag.* 303, 114240.
- Rahman, W.U., Fatima, A., Anwer, A.H., Athar, M., Khan, M.Z., Khan, N.A., Halder, G., 2019. Biodiesel synthesis from eucalyptus oil by utilizing waste egg shell derived calcium based metal oxide catalyst. *Process Saf. Environ. Protect.* 122, 313–319.
- Sogancioglu, M., Yel, E., Ahmetli, G., 2017. Pyrolysis of waste high density polyethylene (HDPE) and low density polyethylene (LDPE) plastics and production of epoxy composites with their pyrolysis chars. *J. Clean. Prod.* 165, 369–381.
- Sulaiman, N.F., Ramly, N.I., Abd Mubin, M.H., Lee, S.L., 2021. Transition metal oxide (NiO, CuO, ZnO)-doped calcium oxide catalysts derived from eggshells for the transesterification of refined waste cooking oil. *RSC Adv.* 11, 21781–21795.
- Wang, S., Li, Z., Yi, W., Fu, P., Zhang, A., Bai, X., 2021. Renewable aromatic hydrocarbons production from catalytic pyrolysis of lignin with Al-SBA-15 and HZSM-5: synergistic effect and coke behaviour. *Renew. Energy* 163, 1673–1681.
- Xing, S., Lv, P., Zhao, C., Li, M., Yang, L., Wang, Z., Chen, Y., Liu, S., 2018. Solvent-free catalytic deoxygenation of oleic acid via nano-Ni/HZSM-5: effect of reaction medium and coke characterization. *Fuel Process. Technol.* 179, 324–333.
- Zhang, Z., Peh, S.B., Kang, C., Chai, K., Zhao, D., 2021. Metal-organic frameworks for C₆–C₈ hydrocarbon separations. *Energy* 3.