Investigation of Nickel as a Metal Substitute of Palladium Supported on HBeta Zeolite for Waste Tire Pyrolysis

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Abstract—Pyrolysis of waste tire is one of alternative technique to produce petrochemicals, such as light olefins, mixed C_4 and mono-aromatics. Noble metals supported on acid zeolite catalysts were reported as potential catalysts to produce the high valuable products from waste tire pyrolysis. Especially, Pd supported on HBeta gave a high yield of olefins, mixed C_4 and mono-aromatics. Due to the high prices of noble metals, the objective of this work was to investigate whether or not a non-noble Ni metal can be used as a substitute of a noble metal, Pd, supported on HBeta as a catalyst for waste tire pyrolysis. Ni metal was selected in this work because Ni has high activity in cracking, isomerization, hydrogenation and the ring opening of hydrocarbons. Moreover, Ni is an element in the same group as Pd noble metal, which is VIIIB group, aiming to produce high valuable products similarly obtained from Pd. The amount of Ni was varied as 5, 10, and 20% by weight, for comparison with a fixed 1 wt% Pd, using incipient wetness impregnation. The results showed that as a petrochemical-producing catalyst, 10%Ni/HBeta performed better than 1%Pd/HBeta because it did not only produce the highest yield of olefins and cooking gases, but the yields were also higher than 1%Pd/HBeta. 5%Ni/HBeta can be used as a substitute of 1%Pd/HBeta for similar crude production because its crude contains the similar amounts of naphtha and saturated HCs, although it gave no concentration of light mono-aromatics (C_4) in the oil. Additionally, 10%Ni/HBeta that gave high olefins and cooking gases was found to give a fairly high concentration of the light mono-aromatics in the oil.

Keywords—Catalytic pyrolysis; Waste tire; Pd; Ni; HBeta

I. INTRODUCTION

NOWADAYS, with the increase in the petroleum fuel consumption and the inadequate of conventional fuel, fuels from wastes or alternative fuels are used for substituting petroleum-based fuels. The fuels from wastes can be produced by several sources such as wood, tar sand bitumen, biomass, and especially from waste tires. Because the structure of tire is designed to struggle to degradation, the production of fuels from waste tires becomes interesting. Moreover, a large quantity of waste tires is generated in the world due to the evolution of vehicle technology, which has been causing serious environmental problems. Pyrolysis of waste tires is a suitable option since it does not only produce petroleum-based fuel substitutes, but also solves the environmental crisis.

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Pyrolysis is the thermal degradation process of the tire under the oxygen-free condition.

The pyrolysis products of waste tire can be categorized into three phases at room temperature, i.e., gas product, liquid oil, and solid residue (char or ash) [1]. The tire pyrolysis oil has a high calorific value of around 41-44 MJ kg^-1 [2]. Thus, it can be used as replacements for conventional fuels, and char can be also useful either as a smokeless fuel, carbon black, or activated charcoal [3]. The pyrolysis technique can crack the high molecular weight of rubber and other organic compounds in waste tires. The variety of high value products are obtained such as olefins (ethylene and propylene) cooking gases, mixed C_4, and mono-aromatics (benzene, toluene and xylenes) and etc. Moreover, sulfur elements, which were used for cross-linking the polymer chains of rubber [4], are also cracked in the pyrolysis process. Through pyrolysis, sulfur atoms are present as polar-aromatics in the tire-derived oil. Many researchers reported that the bifunctional catalysts were used for reducing polar–aromatic compounds in the heavy gas oil and gasoline ranges [5]. As well known, the hydrogenation functionality of noble metals makes them the potential catalysts for deep HDS via the hydrogenation (HYD) pathways [6]. In addition, noble metals supported on an acidic support can increase the activity on hydrogenation of aromatic compounds, and improve the deep hydrodesulfurization [7]-[9].

From a previous work, noble metals were used to optimize the high value products from the pyrolysis of waste tires, especially mono-aromatics. The mono-aromatics such as benzene, toluene, and xylenes are very versatile chemical feedstocks used to produce many commercial products. Noble metals supported on acid zeolite catalysts, especially Pd supported on HBeta were reported as potential catalysts to produce the high valuable products as olefins, mixed C_4 and mono-aromatics from waste tire pyrolysis [10]. In case of non-noble metals, Ni is an active catalyst for several industrial processes. Ni catalysts have been used in hydrotreating, and hydroisomerization process [11]. Due to the high prices of noble metal catalysts, the objective of this research was to use non-noble Ni metal as a substitute of Pd metal catalysts. Ni supported on HBeta zeolite catalyst was used in this research because Ni catalysts have high activity in cracking, isomerization, hydrogenation, and the ring opening of hydrocarbons[12]-[13]. Moreover, Ni is elements in the same group as Pd noble metals, which are VIIIB group, aiming to produce high valuable products similar to the noble metals.
II. EXPERIMENTAL

A. Catalyst Preparation

The catalysts prepared based on Beta zeolite supplied by Tosoh Company (Singapore) was calcined at 600°C for 5 hrs with the heating rate of 2°C/min. The Pd and Ni catalysts were prepared by impregnating the zeolites support with a precursor aqueous solution of palladium (II) nitrate-dihydrate (Pd(NO$_3$)$_2$·2H$_2$O) and nickel nitrate hexahydrate (Ni(NO$_3$)$_2$·6H$_2$O), respectively. The amount of Pd loading was fixed to 1%, and that of Ni was varied at 5, 10, and 20% by weight. Then, the samples were dried in an oven at 110°C for 3 hours followed by calcination in a furnace at 500°C for 3 hours with the heating rate of 5°C/min. Before the catalysts were used in the pyrolysis reactor, they were pressed into pellets using a hydraulic pelletizer. Then, the pellets were crushed and sieved into the particle size between 400 and 425 μm using the mesh size between 40 and 60 of sieves. Finally, the catalysts were reduced for 2 hours with H$_2$ in order to convert the metal oxide forms to metal elements.

B. Pyrolysis of Waste Tire

The diagram of experimental setup for waste tire pyrolysis process is shown in Figure 1. The waste passenger car tire (Bridgestone TURUNZA GR-80) was scraped by a grinder, and sieved to obtain a particle size range of 8-18 mesh. First, the scraped waste tire was loaded into the pyrolysis zone (the lower zone), and the prepared catalyst was loaded into the catalytic zone (the upper zone). The reactor was heated by a furnace from room temperature to a final temperature with the heating rate 10°C/min. The catalytic final temperature was 300°C, and the pyrolysis final temperature was 500°C. The evolved product was transported by nitrogen to an ice bath condenser system containing two condensers in order to separate non-condensable gas products from the liquid product. Non-condensable products or gaseous products were passed through the condensers to a gas sampling bag. The non-condensable gas product was analyzed by using a Gas Chromatography. Agilent Technologies 6890 Network GC system, using HP-PLOT Q column: 30 m x 0.32 mm ID and 20 μm film thicknesses. A detector was a FID type using He as the carrier gas.

Oil products were mixed with n-pentane at the ratio of 40:1, and the solution were shaken for 15 min in an ultrasonic bath. It was left overnight to precipitate asphaltenes, after that asphaltene was filtrated by using a 0.45 μm Teflon membrane in a vacuum system. The solution after filtration was evaporated by a rotary vacuum evaporator in 37°C in order to remove n-pentane and obtain maltene solution. Maltene solution was extracted to each functional group as shown in Table 1.

The pyrolysis reactor was heated by a furnace from room temperature to a final temperature with the heating rate 10°C/min. The catalytic final temperature was 300°C, and the pyrolysis final temperature was 500°C. The column was immersed with n-hexane for overnight. The extraction was started with adding a mobile phase as shown in Table 1. The flow rate of the mobile phase was kept constant at 20 cm$^3$/min controlled by an aquarium air pump. Then, the mobile phase was evaporated from each functional group by a rotary vacuum evaporator at about 60°C [14].

All functional groups (saturated hydrocarbons, mono-aromatics, di-aromatics, poly-aromatics, and polar-aromatics) obtained from the liquid chromatography were analyzed for the true boiling point curves using a Varian GC-3800 simulated distillation gas chromatograph (SIMDIST-GC). The liquid samples were injected to the SIMDIST GC after dilution in carbon disulphide (CS$_2$).

III. RESULTS AND DISCUSSION

A. Gas to liquid ratio

The product obtained from waste tire pyrolysis consists of gas, liquid, and solid residue (char). The products obtained from catalytic pyrolysis of waste tire using Pd and Ni supported on HBeta zeolites are compared and discussed qualitatively and quantitatively. The product distributions obtained from waste tire pyrolysis can be explained by plotting the gas to liquid ratio as shown in Fig.2. The results show that, 1%Pd/HBeta as the reference gives a higher the G/L ratio than the non-catalytic case (thermal pyrolysis) and pure HBeta zeolite. Namely, its G/L ratio is 0.6, which is greater than 0.4 (the catalytic case) and 0.55 (pure HBeta case). The increment of G/L ratio suggests that the gas product increases with the decrease in the liquid product, indicating higher cracking activity of a catalyst. This result is attributed to the reason that heavy molecules can be cracked into lighter molecules on the metal and acid sites of Pd/HTBeta.

![Fig. 1 Schematic experimental system of waste tire pyrolysis](image-url)
The presence of all Ni/HBeta catalysts increases the G/L ratio from that of the non-catalytic case, especially 10%Ni/HBeta that gives the highest G/L ratio. The high amounts of Ni (10% and 20%) produce the higher G/L ratios than the non-catalytic and reference cases. The result indicates the high amounts of Ni increase the cracking activity. In addition, 20%Ni/HBeta gives the closest G/L ratio to that of 1%Pd/HBeta.

**B. Petrochemicals**

The non-condensable gases obtained from pyrolysis contain high value petrochemicals such as olefins (ethylene and propylene), cooking gases (hereby presented in terms of propane and mixed C4), and mixed C4. The comparisons on the yields of petrochemicals obtained from Ni-loaded catalysts and 1%Pd/HBeta are shown in Fig. 3-5.

1. **Yield of Olefins**

For the reference, 1%Pd/HBeta gives higher yields of ethylene and propylene than that of pure HBeta zeolite, which are about 1.4% and 2.2% respectively. Fig. 3 shows that when the percentage of Ni loading increases, the yields of ethylene and propylene increase in the same trend. Moreover, the Ni catalysts, except at 5%Ni loading, give a higher yield of light olefins than that of pure HBeta zeolite. In addition, 10%Ni/HBeta exhibits the highest yield of light olefins, which are subsequently slightly decreased when the loading increases to 20%Ni. Nevertheless, 20%Ni/HBeta exhibits the yield of light olefins close to that of 1%Pd/HBeta. From this figure, it can be seen that 10%Ni/HBeta gives the higher yield of light olefins than 1%Pd/HBeta.

2. **Yield of Cooking gases**

The yield of cooking gases (propane and mixed C4) also increases with Ni loading in the similar trend as the yield of olefins, especially propane. As shown in Fig. 4, 1%Pd/HBeta gives 2.2wt% and 6.5wt% yields of propane and mixed C4, respectively, which are higher than that of pure HBeta. It is also exhibited that the yield of propane slightly increases whereas the yield of mixed C4 insignificantly increases with the increased percentage of Ni loading. In case of the propane, the all Ni catalysts show the higher yield of propane than that of pure HBeta zeolite and 20%Ni/HBeta gives the similar yield of propane as 1%Pd/HBeta. Moreover, 10%Ni/HBeta does not only produce the highest yield of light olefins, but also produces the high yields of cooking gases.

3. **Yield of Mixed C4**

One of high economic value gases is mixed C4, which is one of the predominant gas products obtained from the pyrolysis of scrap tire. For the reference, 1%Pd/HBeta produces 6.5% yield of mixed C4. As can be seen in Fig. 5, as the percentage of Ni loading increases, the yield of mixed C4 is constant at about 5% for all Ni-loaded catalysts. It can be concluded that Ni catalyst cannot be used as a suitable catalyst as a substitute of 1%Pd/HBeta for mixed C4 production. As shown in Fig 2-5, the results exhibit that 10%Ni/HBeta seems to be a potential catalyst to produce light olefins and cooking gases. At the higher loading (20%Ni/HBeta), the yields of light olefins and cooking gases slightly decrease. Nonetheless, 20%Ni/HBeta gives the closest yields of light olefins and propane as 1%Pd/HBeta. For a high amount of Ni loading, the agglomeration of Ni can reduce dispersion and active sites. Furthermore, Eswareamoorthi et al. 2003[15] studied the Ni loaded on zeolite-β by incipient wetness impregnation (IWI) for the hydroisomerisation of n-heptane. They reported when the amount of Ni increases, the total acidity of catalyst conti-
nuously falls by reasons of the acid sites covered by Ni species.

C. Maltenes Composition

The chemical compositions of maltenes obtained from using varied loading percentages of Ni/HBeta catalysts as compared to pure HBeta and 1%Pd/HBeta are shown in Fig. 6.

Fig. 6 Chemical compositions in maltenes obtained from using varied Ni/HBeta catalysts in comparison with that from 1%Pd/HBeta

HBeta zeolite produces the highest concentration of saturated hydrocarbons of about 66.2wt%, whereas 1%Pd/HBeta gives the lower concentrations of saturated hydrocarbons of 56.3wt% in the pyrolytic oil. When the percentage of Ni loading increases, the concentration of saturated hydrocarbons slightly decreases. 5%Ni/HBeta and 10%Ni/HBeta give a higher concentration of saturated hydrocarbons than 1%Pd/HBeta. The results show that 1%Pd/HBeta dramatically increases the mono-aromatics concentrations from 10wt% to 27.8wt% when compared to pure HBeta zeolite. On the other hand, the concentration of mono-aromatics is lower with using the Ni-loading catalysts. However, it is still higher than that of pure HBeta, but lower than that of 1%Pd/HBeta. Moreover, the concentrations of poly- and polar-aromatics rapidly increase when all Ni-loaded catalysts are used. It can be suggested that a higher cracking activity catalyst produces a higher concentration of poly-aromatics because the high cracking ability can generate carbocations which are intermediates to form aromatic compounds [6]. 1%Pd/HBeta produces a high quality of oil products with a high concentration of saturated hydrocarbons and low concentrations of poly- and polar-aromatics. The Ni-loaded catalyst at a high Ni loading cannot be used as a substitute of 1%Pd/HBeta for the good quality of oil production because it gives the high concentrations of poly-and polar-aromatics.

D. Petroleum Fractions

Fig. 7 Petroleum fractions in maltenes obtained from using varied %loading of Ni/HBeta catalysts in comparison with that of 1%Pd/HBeta

The maltenes were analyzed by a SIMDIST-GC for the true boiling point curves, and then cut to petroleum fractions, which are naphtha (<200 °C), kerosene (200–250 °C), light gas oil (250–300 °C), heavy gas oil (300–370 °C), and long residue (>370 °C).

Fig. 7 shows the petroleum fractions of maltenes obtained from using varied percentages of Ni loading on HBeta zeolite as compared with 1%Pd/HBeta. It can be clearly seen that pure HBeta give the highest concentration of naphtha and kerosene. The result indicates that pure HBeta produces the lighter oil fraction than that of other catalysts. 1%Pd/HBeta gives the higher concentration of kerosene than that of all Ni/HBeta catalysts. All Ni/HBeta catalysts give the similar concentration of naphtha as that of 1%Pd/HBeta, except 10%Ni/HBeta. The high amount of Ni loaded catalyst produces the higher concentration of light and heavy gas oil. Additionally, the high amount of Ni loading produces the lower concentration of kerosene than that of 1%Pd/HBeta. Moreover, 10%Ni/HBeta produced high poly-aromatics. It can be suggested that 10%Ni/HBeta produces the heaviest oils than the other catalysts. It can be generally concluded that the addition of Ni produces the same amount of naphtha, but the greater in gas oils and long residue in the expense of kerosene reduction. The 5%Ni/HBeta can be used as a substitute of 1%Pd/HBeta for similar crude oil production.

E. Average number of carbon of mono-aromatics.

Fig. 8 Average carbon number of mono-aromatics fractions obtained from using various %Ni/HBeta in comparison with (□) 1%Pd/HBeta

Fig. 8 illustrates the average carbon number of mono-aromatics in obtained from using varied loading percentages of Ni/HBeta catalysts as compared to that of 1%Pd/HBeta.

From this figure, the average carbon number of mono-aromatics slightly decreases with the increased percentage of Ni loading. This result is attributed to the reason that the high Ni loading exhibits hydrogenation and ring-opening activity on Ni metal sites. Moreover, pure HBeta gives the lowest of average carbon number of mono-aromatics. Therefore, it can be concluded that Ni loading helps improving the production of short chain mono-aromatics via the ring-opening of di-aromatics. Additionally, 20%Ni/HBeta gives the similar average carbon number of mono-aromatics as that of 1%Pd/HBeta.

In mono-aromatic portion, 10%Ni/HBeta, however, produces the considerably-high concentration of light mono-aromatics (C\textsubscript{6}-C\textsubscript{11}) as shown in Table II. Additionally, the concentration of light mono-aromatics from 10%Ni/HBeta is as much as a half of those obtained from 1%Pd/HBeta.
5%Ni/HBeta and 20%Ni/HBeta rarely produce light mono-aromatics (C₆-C₁₁). The aromatic compounds can be produced via Diels-Alder reactions of olefins obtained from primary cracking reactions and/or the ring-opening of di-aromatics.

**F. Comparison of catalyst prices**

Since palladium is a noble metal that has a very high price, nickel as an element in the same group (VIII B group) that may be used as a substitute of palladium. Moreover, nickel is a non-noble metal which has a low price. As shown previously, in the case of gaseous products, 10%Ni/HBeta exhibits a good catalyst for light olefins and cooking gases production which produced the yields as high as that of 1%Pd/HBeta. Moreover, 10%Ni/HBeta produces the high valuable mono-aromatics (BTX) as much as a half of that obtained from 1%Pd/HBeta. According to these results, 10%Ni/HBeta catalyst may be used as a substitute of 1%Pd/HBeta to produce highly valuable gas and mono-aromatics products.

Table III shows the comparison of precursor prices. The precursor of Pd (Palladium (II) nitrate dihydrate) is more expensive than that of the non-noble metal (Nickel nitrate hexahydrate). As shown in Table III, if 10%Ni/HBeta is used as a substitute of 1%Pd/HBeta, the cost of catalyst is reduced by 9 times.

**Table III**

**Precursor Prices**

<table>
<thead>
<tr>
<th>Metal</th>
<th>Precursor</th>
<th>Price (Baht)/g</th>
<th>% loaded (% wt)</th>
<th>Price (Baht)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>Palladium (II) nitrate dihydrate (Pd(NO₃)₂·2H₂O)</td>
<td>2,600³</td>
<td>1%</td>
<td>658</td>
</tr>
<tr>
<td>Ni</td>
<td>Nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O)</td>
<td>13.8⁵</td>
<td>10%</td>
<td>75.9</td>
</tr>
</tbody>
</table>

³Sigma-Aldrich in 2011 ⁵Merk in 2011

**IV. Conclusions**

Since palladium is a noble metal that has very high price, nickel was expected to substitute the palladium metal because it is an element in the same group as palladium in the periodical table. Moreover, nickel does not only has low price, but it is also a high potential catalyst. As shown previously, the 10%Ni/HBeta gave the same yield of light olefins and cooking gas and a half of light mono-aromatics yield of that from 1%Pd/HBeta. The 10%Ni/HBeta catalyst can be used as a substitute of 1%Pd/HBeta catalyst for the production of high valuable gases and light mono-aromatics, whereas, 5%Ni/HBeta was found to be a good substitute of 1%Pd/HBeta for the production of similar oil.

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