Supporting Information

a. Mass balance calculation formulas

The yield of waxy oil (wt.%):

$$m_{quenching\ system(after\ reaction)} - m_{quenching\ system(before\ reaction)} / m_{total\ waste\ PE} \cdot 100(wt.\%)$$

The yield of char (wt.%):

$$m_{feed\ container(after\ reaction)} - m_{feed\ container(before\ reaction)} / m_{total\ waste\ PE} \cdot 100(wt.\%)$$

The yield of Gas (wt.%):

$$100(wt.\%) - (m_{total\ yield\ of\ char}\% + m_{total\ yield\ of\ waxy\ oil}\%)$$

b. Mass balance of pyrolysis products

The mass balance of the products, including gas, waxy oil, and by-product char, was determined after the pyrolysis of waste PE. The yield of pyrolysis products was calculated by subtracting the weight of the total quenching system after the experiment from the weight of the total quenching system before the experiment.

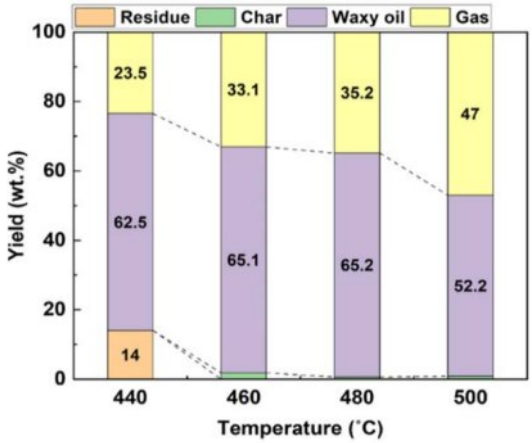

Figure S1. Mass balance of pyrolysis products from waste PE as a function of reaction temperature

Figure S1 presents the yield results of pyrolysis products at reaction temperatures ranging from 440 to 500°C. As the reaction temperature increased, gas production rose due to the intensified cracking reactions, while the yield of waxy oil decreased. It was also due to the effect of reduced residence time of the reactor caused by an increase in reaction temperature. This shorter residence time reduces the time available for the pyrolysis vapors to be captured. At a reaction temperature of 440°C, approximately 14 wt.% of unreacted pyrolysis product was observed. For maximum waxy oil production, the optimal reaction temperature was identified to be between 460 and 480°C, as shown by Runs 2 and 3. Runs 1-4 were injected with the same nitrogen flow rate of 1 L/min.

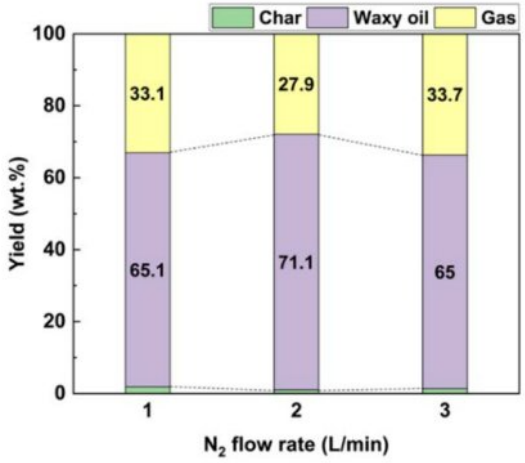

Figure S2. Mass balance of pyrolysis waxy oil by nitrogen flow rate at the reaction temperature 460°C

Figure S2 demonstrates that increasing the rate of N_2 flow from 1 L/min (Run 2) to 2 L/min (Run 5) increased the waxy oil yield from 65.1 to 71.1 wt.%. However, further increasing the N_2 flow rate to 3 L/min decreased the waxy oil yield. The reason why the yield of liquid products among the pyrolysis products was the maximum at 71.1 wt.% when the nitrogen gas flow rate was 2 L/min can be attributed to the following factors. A flow rate of 2 L/min serves as the optimal condition for the pyrolysis reaction, optimizing the interaction of reactants and products and forming the most significant amounts of liquid products. This flow rate contributes to an appropriate dilution of the pyrolysis gases produced within the reactor, allowing them to be recondensed. In addition, it efficiently ensures heat transfer to maintain the reaction rate uniformly, securing sufficient residence time for the liquid products. As the flow rate increases to 3 L/min, the reduced residence time in the reactor leads to insufficient condensation of the liquid product, causing it to be discharged rapidly. Additionally, the higher flow rate enhances the dilution of reactants, which results in a lower yield of waxy oil.

Figure S3 illustrates the mass balance of the waste PE pyrolyzed using zeolite catalysts. The catalyst was introduced at a mass ratio of 10 wt.% for catalyst/waste PE fraction. Polyolefin pyrolysis was performed commercially at a mass ratio of 10 wt.% for catalytic pyrolysis. It was also chosen to make it relatively easy to compare trends in the characteristics of pyrolysis waxy oils. The catalytic pyrolysis experiments were waste catalyst/PE fraction ratio. The yield of waxy oil from pyrolysis products increased in the order of A4 > Y > ZSM-5 > Beta, with yields of 76.5, 45.6, 17.8, and 15.8 wt.%, respectively. A4 zeolite mainly has Bronsted acidity. In the pyrolysis of the waste PE fraction, the direct reaction with A4 zeolite is weak due to the reduced atmospheric conditions. A4 zeolite contains positive ions such as Na^+ and shows catalytic activity in some processes due to its ion exchangeability and high adsorption capacity for water. In addition, it is more advantageous for moisture absorption and hardness control than for reactions with the polymer itself, such as waste PE fraction. It is not generally used as a catalyst of waste PE fraction pyrolysis. Because it is more advantageous in water adsorption and hardness control than polymers such as polyethylene.[1] The Y zeolite has Lewis and Brønsted acidity, including framework and non-framework aluminum. It can promote hydrocarbon cracking in the pyrolysis of PE, producing light hydrocarbons with low molecular weight. The Y zeolite is mainly used in the fluid catalytic cracking (FCC) reaction, and the EFAl (non-framework aluminum) produced after high-temperature steaming acts as an effective catalyst for PE pyrolysis, which is advantageous in producing high value-added compounds.[2] Beta zeolite has both Lewis and Brønsted acidity properties. It can efficiently produce light and gasoline-range hydrocarbons through a complex reaction mechanism during PE pyrolysis. Beta zeolite has high activity in isomerization and oxidation reactions, making it effective in processing the complex hydrocarbon chains of PE to produce selective light hydrocarbons. This is useful for biomass conversion and high-value compound production.[3] ZSM-5 promotes molecular cracking during high-temperature pyrolysis of PE due to its framework-related aluminum and stable Lewis acid sites. In particular, light and low-molecular-weight hydrocarbons are predominantly produced due to their pore structure. ZSM-5 mainly performed reactions that convert methanol to olefins or produce various aromatic compounds. It can also effectively produce gasoline-range hydrocarbons during PE pyrolysis. In this way, each zeolite catalyst contributes to the production of high-value-added compounds through specific hydrocarbon cracking or selective oxidation reactions when reacting with PE, and the types and efficiencies of the products vary depending on the catalytic properties.[4] Additionally, the selective reaction characteristics of these catalysts may lead to the conversion of linear high-density polyethylene (HDPE) into gas at a higher rate.

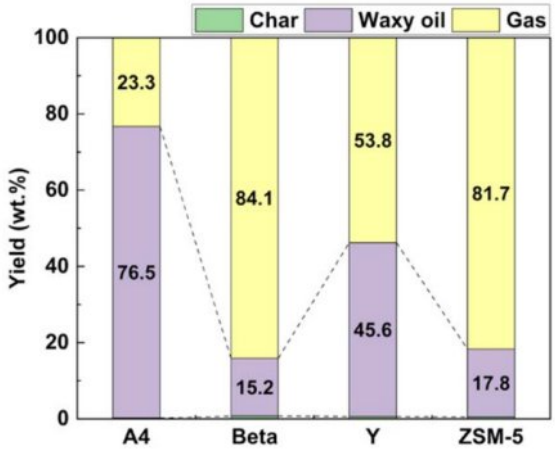

Figure S3. Mass balance of catalytic pyrolysis products from waste PE (Reaction temperature: 460°C, nitrogen gas flow rate: 2 L/min, zeolite/waste PE ratio: 10 wt.%)

Therefore, the rapid reactions facilitated by Beta zeolite and ZSM-5 may require more controlled conditions. Conducting experiments with reduced nitrogen gas flow or lower reaction temperatures would be beneficial. These catalysts are also more suitable for reforming polymers with higher molecular weights than polyethylene.[5] The yield of pyrolysis wax is crucial as it can be utilized in chemical platforms such as base oils or fuel processes. Thus, fractions with lower boiling points and naphtha are generally preferred for further petrochemical processing. Among the catalysts, A4 zeolite demonstrated high-yield results due to its adsorption properties. Additionally, it does not produce char, making the lubricant production process.

c. Effect of A4 zeolite calcination

We investigated the effect of using calcined A4 zeolite on pyrolysis wax. Calcination of the catalyst may serve as a significant experimental variable. To verify this, we conducted experiments using calcined A4 zeolite and compared the results with uncalcined samples. Moreover, there are very few experimental studies or documented cases of using A4 zeolite for upgrading pyrolysis wax or waxy oil. The A4 zeolite was calcined at 550°C for 3 hours in a muffle furnace. Dada et al. examined the thermo-catalytic co-pyrolysis of ironbark sawdust and plastic waste using Y-zeolite with and without calcination. The calcined Y-zeolite exhibited superior catalytic performance due to its enhanced pore structure and modified acidic sites.[6] Araújo et al. focused on the fast pyrolysis of sunflower oil using ZSM-5-based catalysts before and after calcination. Calcination enhanced the structural stability and catalytic activity, improving the hydrocarbon distribution in the bio-oil.[7]

Figure S4 presents the SIMDIS-derived boiling point distribution curves for pyrolysis wax and waxy oil compounds using A4 zeolite with and without calcination. When zeolite was used before calcination, the compounds were primarily composed of low boiling point hydrocarbons. The boiling point distribution of pyrolysis waxy oil obtained from A4 zeolite before calcination showed a recovery rate of 99.5% at an FBP of 591.2°C, with a moisture content of 8.6%. This suggests that the presence of moisture in A4 zeolite contributes to the formation of paraffins with a wide range of carbon numbers, particularly non-normal paraffins. Consequently, the isomerization reaction pathway appears to be relatively favorable. On the other hand, when calcined zeolite was used, the product consisted mainly of high-boiling-point compounds, with only 32.8% recovered even at an FBP of 750°C. This indicates that the reaction products were predominantly concentrated as long-chain high-boiling-point paraffins. Before calcination, A4 zeolite produced hydrocarbons with low boiling points below 370°C. In the case of calcined zeolite, hydrocarbons with a boiling point below 370°C accounted for approximately 10%, whereas in the case of uncalcined zeolite, they accounted for about 57%.

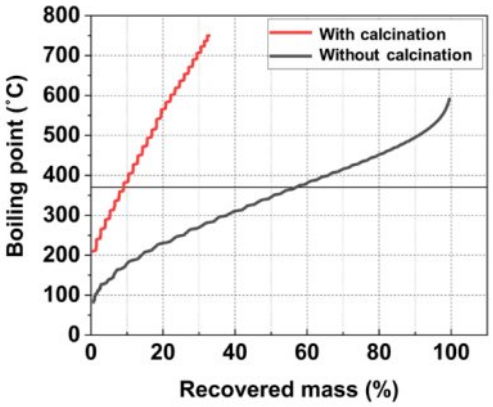

Figure S4. Comparison of SIMDIS analysis results of pyrolysis product with and without calcination of A4 zeolite

Figure S5 shows the paraffin distribution of pyrolysis waxy oil using A4 zeolite without and with calcination. This figure provides a clear visualization of how the paraffin structure and carbon number range change depending on the moisture pretreatment conditions of the catalyst.

First, without calcination, most of the PE pyrolysis products are non-normal paraffins, which account for approximately 92%. This suggests that the acid sites are partially blocked or weakened due to the moisture remaining in the catalyst, and the isomerization reaction is promoted, easily rearranging the carbon skeleton. As a result, non-normal paraffins with various branches become mainstream, forming a wide boiling point distribution. On the other hand, normal paraffins are relatively small at approximately 7.9%, and ultra-long-chain (C_{121} or above) paraffins are virtually non-existent at approximately 0.1%.

On the other hand, the reaction dynamics shift significantly with calcination, as drying the catalyst at high

temperatures removes moisture and modifies the active sites, leading to substantial changes in the reaction pathway. The non-normal paraffin ratio is greatly reduced to about 18.1%, while ultra-long-chain paraffins of C_{121} or more become the dominant product, accounting for 67.1%. This change is considered to occur as the reaction progresses to a higher molecular weight region through calcination. Hydrocarbon chains grow longer, and long-chain formation (oligomerization) or recombination reactions are thought to dominate over isomerization. In addition, the normal paraffin ratio is also slightly increased to about 14.8% compared to before calcination, indicating a tendency toward high-boiling-point paraffins with high structural simplicity overall.

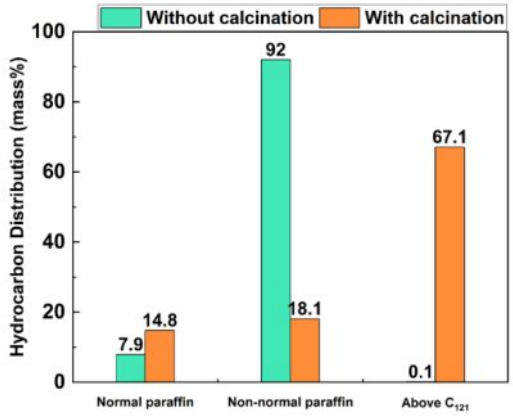

Figure S5. Comparison of paraffin distribution in pyrolysis products with or without calcination of A4 zeolite

Reference of Supporting Information

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