Research Article

Catalytic Copyrolysis of Heavy Oil with Polypropylene

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Cite This: https://doi.org/10.1021/acssuschemeng.2c04768

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ABSTRACT: Catalytic and noncatalytic copyrolysis of plastic and heavy oil was studied using thermogravimetric analysis (TGA), pyrolysis reactor experiments, and GC analysis of the formed liquid. As revealed by the TGA experiments, predegradation as a pretreatment method had further lowered the decomposition temperature of polypropylene− (PP−) bitumen mixtures and reduced the severity of catalyst deactivation by coke. The presence of PP in the copyrolysis had increased the liquid yield and decreased the coke yield. The presence of PP in the copyrolysis had shifted the product distribution from heavier to lighter fractions while copyrolysis using predegradation displayed the highest percentage of C_5-C_9 and C_9-C_{14} fractions. Based on the performance of the catalysts, C_5-C_{14} was produced in the following order, HY > 20% USY > APC > K30, while $C_{14}-C_{20}$ was produced in the reverse order of K30 > 20% USY > APC > HY. In-depth analysis of the percentage product distribution confirmed the availability of synergies during the thermal copyrolysis of PP and Ex-Mwambe heavy oil. Predegradation as pretreatment method has intensified the contact between the two feed constituents, enabling synergistic effects to materialize. The excess percentage of C_5-C_9 and the insignificant amount of C_{20}^+ produced from the thermal copyrolysis affirmed the possibility that the presence of PP facilitates the conversion of waxy hydrocarbons into lighter products. the conversion of waxy hydrocarbons into lighter products. Coke components from predegradation method are more volatile while the coke formed during normal mixing pyrolysis contained a higher percentage of hard coke.

KEYWORDS: Catalytic copyrolysis, Predegradation, Polypropylene, Heavy oil, Liquid boiling point distribution, Coke characterization
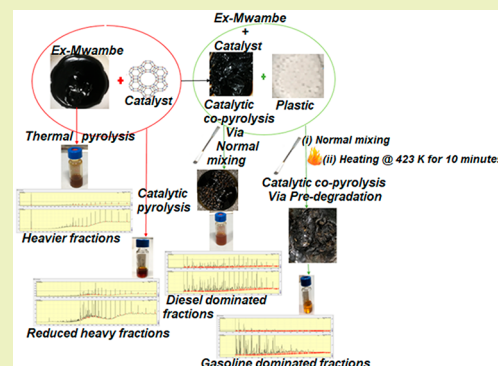
1. INTRODUCTION

The rapid decline in the supply of conventional petroleum reserves necessitated further exploitation and upgrading of heavy oil and bitumen resources.[1−3] Heavy oil is expected to play an increasing role in order to accomplish the world demand for hydrocarbon fuels. The future production of heavy oil is estimated to increase by 200% from 2006 to 2030 while about 53% of the world's total oil reserves are in the form of heavy oil or bitumen.[4] Heavy oils are semisolid materials,[5] black in color,[6] with a low API gravity between 10 and 20° and high viscosities.[5−7] They can serve as an important source of high-value chemicals and transportation fuels after upgrading.[6]

The upgrading of heavy oil and bitumen is relatively expensive due to their low distillate fraction, fast catalyst deactivation, and high asphaltene and heteroatom content.[1−3,8] These raise serious concerns over their production, transportation and processing.[3] Hydrocracking catalysts, shape-selective zeolite-based dewaxing catalysts, and zeolite acidic catalysts are widely used to process heavy oils into clean fuels.[9,10] These catalysts are very versatile with high activity and selectivity for important hydrocarbon transformation reactions.[1] However, catalytic conversion of heavy residues always is accompanied by strong formation of coke as a byproduct.[11,12] The coke deposited on the catalyst blocks the pores, rendering the catalyst less active and nonselective.[2,3,11−13] It also limits the conversion of macromolecules to low boiling point fractions with a subsequent decrease in the liquid yield and increase in the percentage of the wax.[13−15] In most commercial processes, the cost of catalyst deactivation is very high. Hence, facilitating the catalyst stability and optimizing regeneration is an important measure of controlling the activity and selectivity of the catalyst.[16,17] Coke formation can be suppressed by increasing the hydrogen pressure.[1,12,15,17] The addition of hydrogen can offer alternative reaction pathways, by means of inhibiting the dehydrogenation reactions and lowering the amount of coke precursors in the reaction media,[12,15,17] resulting in less coke formation and high liquid yield.[15,16,18] However, the use of hydrogen is very expensive.[15,16,18,19] Alternative technologies with lower processing costs are highly desirable.
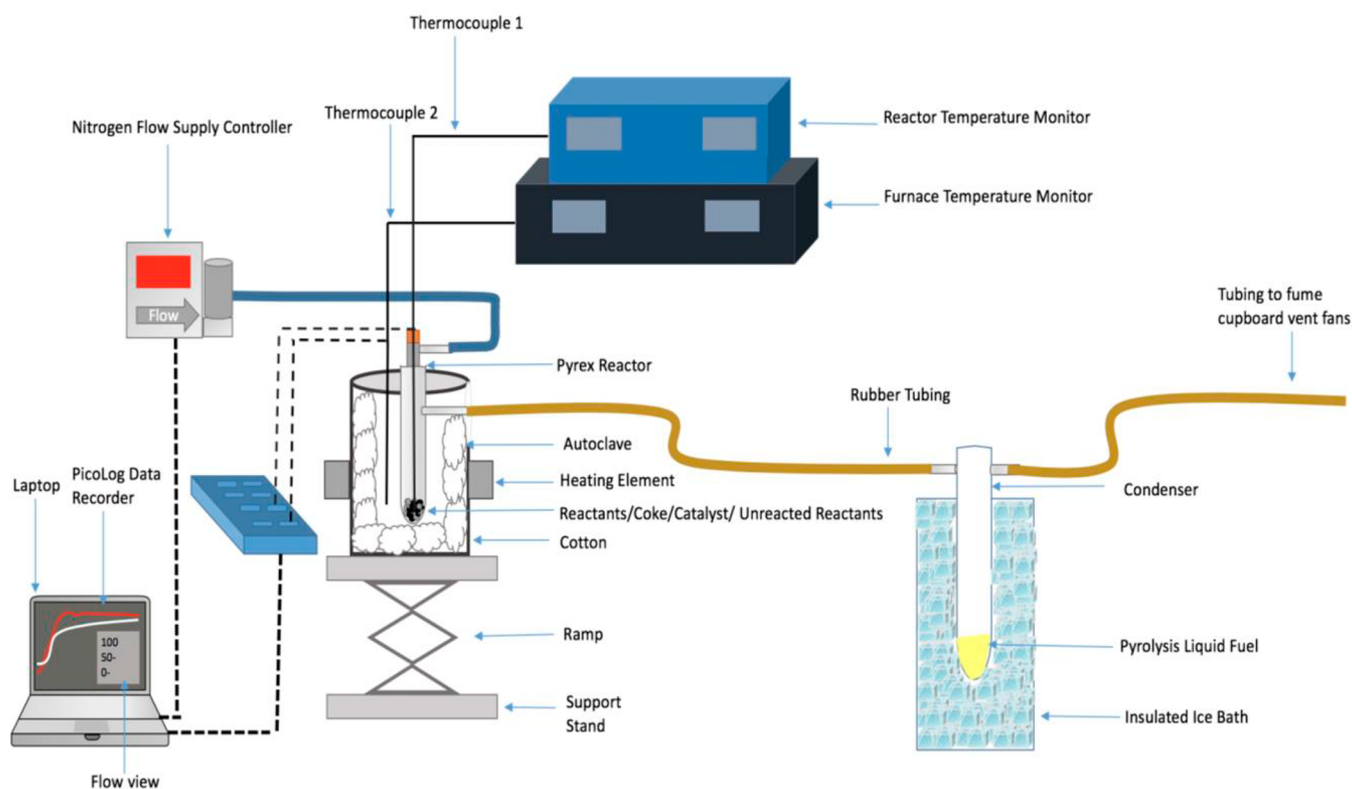
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Figure 1. Schematic diagram of the laboratory semibatch reactor system.

Plastics are cheaper source of hydrogen that can serve as an economically viable source in catalytic upgrading of heavy oil.[13,19] On the other hand, the quantity of waste plastics discarded into the environment is rising every year causing serious detrimental environmental effects.[13,14,20] So, technologies that enable their conversion to useful products are welcome. There is serious commitment for the development of technologies to coprocess waste plastics along with heavy oil and other petroleum residues.[13,20−27] This will create a new possibility with a potential to generate energy resources to meet the rising demand in a cheap sustainable way.[13,21,22,24−27] Previous works related to the copyrolysis of heavy oil and plastic have hinted at positive interactions during the copyrolysis.[13,20−27] This synergistic effect was attributed to the high hydrogen content of plastic.[23,25−27] Ng[13] carried out the copyrolysis of vacuum gas oil and high density polyethylene in a fixed bed reactor at 510 °C. The results showed that higher conversion to lower distillate components including gasoline range fraction was obtained. Similar results with high conversion to lighter valuable products during the copyrolysis of petroleum residues with plastics were also reported by Mahari et al.,[24] Aboulkas et al.,[25] and Mohammad et al.[26] They suggested that the polymer chain might possibly stabilized the radicals from the primary products of heavy oil degradation through hydrogen transfer reactions.[27] They suggest that the polymer might act as a catalyst in the process, initiating the thermal degradation of the organic matter in the heavy oil.[28]

The synergistic effect of the copyrolysis depends on the experimental conditions including the nature of the feed, pyrolysis duration, temperature, catalyst type, and the contact mode between the feed and catalyst.[20,25−31] Thermal cracking of heavy oil and plastic resulted in low conversion[24,32−35] and higher waxy fractions that need further processing.[24,32−35] In contrast, in the presence of a catalyst, the process took place at low temperatures with high conversion and produced hydrocarbons within the gasoline range fraction,[36−38] which eliminates the need for further processing.[24,32,35−40]

Solid acidic catalysts are very effective in hydrocarbon conversion, but their strong acidity produces a higher quantity of gaseous products and coke.[32,34,36,38,39] To address these issues and to optimize the synergies during the copyrolysis of plastic with heavy oil, predegradation method was adopted in this study. Similar procedure was used in our previous studies,[32,35,37,40] whereby the quantity and quality of the liquid and coke yields were improved, respectively. Predegradation improves the contact between catalyst and melted polymer leading to higher activity and making possible for catalytic reactions to occur at lower temperatures.[32,35,37,40] Moreover, this method had increased the synergy in copyrolysis of plastic and biomass, thereby increasing the quantity and quality of the desired liquid product.[35] The application of predegradation can therefore serve to make the process efficient and sustainable. The main objective of this work is to study the synergies during the coprocessing of plastic and heavy oil and the extent to which they can be improved.

To this end, TGA analysis, reactor experiments, and GC characterization were employed. Furthermore, the effects of plastic addition, catalyst type, and content as well as reaction temperature were investigated to assess the best experimental conditions on the quantity and quality of the product yields. Two types of heavy oils were used, bitumen and Ex-Mwambe. Polypropylene, as one of the major plastics found in waste streams, was used as the plastic sample. To understand the effect of catalyst structure and acidity, catalysts including zeolites (HY and USY), cracking catalyst containing 20% USY,
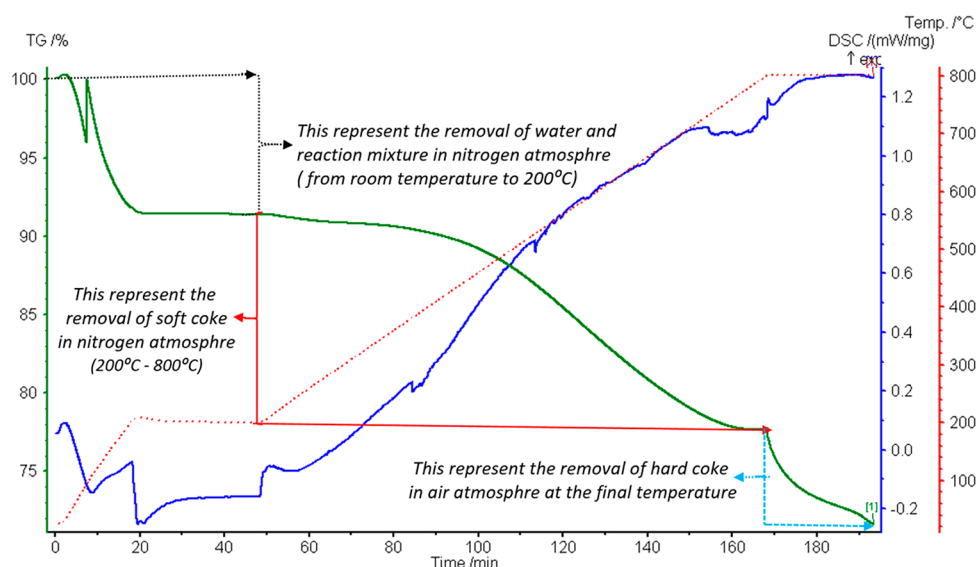
Figure 2. TGA of coked sample containing the description of coke characterization.

acidic clay catalyst (K30), and aluminum pillared clay (APC) were included in this study.

2. EXPERIMENTAL SECTION

2.1. Materials. The plastic used was polypropylene (PP) in pellet forms (particle size 1−2 mm) without additives provided by Vantage Polymers Ltd. The PP density was 0.928 g/cm^3 and its weight-average molar mass was 117 kg/mol.

Bitumen and Ex-Mwambe were used as heavy oil samples. The bitumen sample was kindly provided by the R&D analysis center at Nalco Co. and they are bituminous vacuum residue from the North Sea while Ex-Mwambe heavy oil was supplied by Roemex Oilfield Service Company, U.K.

The catalyst samples used include:

1. Zeolite catalysts, provided by Grace A.G.
    1a. HY. Micropore area (m^2/g): 532.40. Average particle size: 1 μm. BET (m^2/g) = 590.00 ± 23.50. Micropore volume (cm^3/g) = 0.26. External surface area (m^2/g) = 72.58; S$_i$O$_2$/Al$_2$O$_3$ = 2.5.
    1b. USY. Micropore area (m^2/g): 361.02. Average particle size: 1 μm. BET (m^2/g = 433.60 ± 14.08. Micropore volume (cm^3/g) = 0.19. External surface area (m^2/g) = 72.58; S$_i$O$_2$/Al$_2$O$_3$ = 5.7(framework).
2. A commercial cracking catalyst containing 20% USY, provided by AKZO-NOBEL. Micropore area (m^2/g): 60.70. Average particle size: 100 μm. BET (m^2/g) = 172.32 ± 2.84. Micropore volume (cm^3/g) = 0.03. External surface area (m^2/g) = 111.62.
3. Clay-based catalysts purchased from Sigma-Aldrich Co., Ltd. U.K.
    3a. K30. Micropore area (m^2/g): 250.00. Average particle size: 100 μm.
    3b. APC. Micropore area (m^2/g): 330.00. Average particle size: 100 μm.

2.2. Experimental Setup. The pyrolysis reactor experiments were carried out using the rig shown in Figure 1. The rig is made-up of a semibatch pyrex reactor with two semicircle infrared heating elements for fast heating which are connected to a temperature controller, a mass flow controller, and condensers placed in ice for liquid collection. The duration of each experiment was 60 min. The reactor temperature was measured only in the center of the reactor while a radial temperature gradient might have been built up across the reactor. Very fast initial heating rates (40−50 K/min) were observed slowing to reach set point temperature at ca. 15 min. Typical

temperature profiles and the full description of the experimental procedure can be found in the literature.[32]

2.3. Experimental Calculations. The conversion to volatile products was based on the fraction of the initial mass of the feed (polymer+ heavy oil) reacted to form volatile products. The percentage yield of the liquid products and coke was calculated as follows:

$$Y_l = m_l/m_p \times 100 \tag{1}$$

where Y_l= liquid yield.
m_l = mass of the liquid collected.
m_p = mass of the initial (polymer+ heavy oil).

$$Y_c = m_c/m_p \times 100 \tag{2}$$

where Y_c = coke yield.
m_c = mass of the coke produced.
m_p = mass of the initial (polymer + heavy oil).

Coke concentration is the amount of coke deposited on the catalyst divided by the catalyst mass and represents the amount of coke formed per gram of catalyst and is estimated by TGA and converted to the yield based on the catalyst amount in the reactor.

$$C_c = m_c/m_{cat} \tag{3}$$

where C_c = coke concentration.
m_c = mass of the coke deposited on the catalyst.
m_{cat} = mass of the catalyst.
Hence, $C_c = Y_c \times$ (polymer/catalyst mass ratio).

2.4. Liquid Sample Analysis. The liquid products were analyzed on a Shimadzu 2014 gas chromatograph equipped with a flame ionization detector (FID) using a nonpolar Rtx-1 DHA 100 m × 0.25 mm × 0.50 μm capillary column. The hydrogen flow rate was fixed at 30 mL$_N$/min and the injector temperature was set at 270 °C. The temperature program began with a hold at 40 °C for 10 min followed by a ramp of 5 °C/min to 270 °C and a hold for another 30 min while the FID detector temperature was set at 300 °C. A calibration mixture of normal alkanes C$_5$−C$_{20}$ (standard) was run at the beginning of the analysis to assign retention time to each components and their boiling points. The details of the GC procedure, including the above-mentioned correspondence of retention times to boiling points, are available in the literature.[32]

2.5. Thermal Gravimetric Analysis (TGA). *2.5.1. TGA Catalytic Polymer Pyrolysis Runs.* The TGA measurements were carried out with PerkinElmer Pyris TGA instrument available at NICE (Nature Inspired Chemical Engineering) lab facility, University College London and NETZSCH STA 449 C TG-DSC instrument located

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Table 1. Properties of the Heavy Crude Oil Samples

crude oil sample	color	specific gravity (SG)(kg/m3)	API gravity	saturates (wt %)	aromatics (wt %)	resins (wt %)	asphaltenes (wt %)
Ex-Mwambe	black	0.865	32.1	58.18	29.4	10.1	2.32
bitumen	black	0.878	29.9	47.78	23.78	17.79	10.65

at Chemistry Department, University College London. The employed instruments captured the gravimetric analysis and recorded the mass changes and thermal effects that took place with temperature and/or time. In a typical run ca.10 mg of the copyrolysis sample and catalyst was heated to 473 K at a rate of 10 K/min and was maintained there for 30 min under nitrogen flow (30 mL$_N$/min) to remove any adsorbed water. After this period, the temperature was raised to 1073 K at a rate of 5 K/min and kept constant for 30 min. The hard coke deposited on the catalyst was burnt out by switching from nitrogen to air at the final temperature (1073 K) at the same flow rate (30 mLN/min). For the TGA experiments, the sample was held at 873 K for 30 min to complete the degradation and then the temperature was ramped to 1073 K to remove the coke. The amount of soft coke in the catalyst is equal to the difference between the sample mass after drying at 473 K and the sample mass at 1073 K i.e. before switching from nitrogen to air at the final temperature 1073 K. The amount of hard coke is the mass difference of the sample mass before and after the switching from nitrogen to air, when the hard coke was completely burned. For all TGA catalytic experiments, a 2:1 ratio was used and a 1:1 ratio between heavy oil and PP. The full TGA procedure is available in the literature.[32]

2.5.2. Coked Catalyst Characterization and Calculations. As shown in Figure 2, the coked catalyst characterization is based on the volatility of the sample in nitrogen and air atmospheres. This method is very specific and gives information about the character of coke components.

As presented in Figure 2, the first stage consists of removal of water and adsorbed volatile reaction mixture components from room temperature to 473 K in nitrogen atmosphere. The second stage involves removal of the soft coke from 473 to 1073 K (final temperature) through volatilization in inert nitrogen. The last stage is the removal of the hard coke at 1073 K, and it is removed by burning in air i.e. the atmosphere is switched from nitrogen to air at the final temperature.

$$\text{soft coke (\%)} = \frac{\text{mass of soft coke}}{\text{total mass of coke}} \times 100 \qquad (4)$$

$$\text{hard coke (\%)} = \frac{\text{mass of hard coke}}{\text{total mass of coke}} \times 100 \qquad (5)$$

where mass of soft coke is the cumulative weight of the coke components removed in nitrogen atmosphere from 473 to 1073 K and mass of hard coke is the combined weight of the coke components removed in air atmosphere at 1073 K while total mass of coke corresponds to the sum of soft and hard coke.

2.6. Crude Oil Characteristics. *2.6.1. SG and API Gravity.* The API (American Petroleum Institute) gravity is an important characteristic of crude oil that provides insight into its quality.[41] This property was calculated using equation [7] below and its corresponding value depends on the specific gravity of the crude oil given by eq 6.[6,41,42]

$$\text{specific gravity (SG)} = \frac{\rho_{oil}}{\rho_{H_2O}} \qquad (6)$$

$$\text{API gravity} = \frac{141.5}{\text{SG}} - 131.5 \qquad (7)$$

Specific gravity as stated in eq 6 is the ratio of the density of crude oil ρ_{oil} to the density of water ρ_{water} The density of the oil was measured using a pycnometer in reference to the density of water, 1 g/cm^3 or 1000 kg/m^3.[41,42]

Based on API gravity, crude oils are typically classified into light oil (>33° API), medium oil (22.3−33°), heavy oil (10.0−22.3°), and

extra heavy oil (<10°).[42] Light oils are usually associated with lower density due to their higher API gravities values while heavy crude oils are denser.[6,41,42] The characteristics of bitumen and Ex-Mwambe used as heavy oil samples in this study are listed in Table 1.

2.6.2. SARA Analysis. SARA analysis involves separation of crude oil into four distinct fractions namely saturates, aromatics, resins and asphaltenes.[41,42] This analysis represents a reliable compositional characterization of crude oil that is very important for oil source correlations, downstream refining processing, optimization of products performance, fouling propensity, and environmental exposure.[41,43,44] SARA analysis serves as a first step to provide an insight into the quality of crude oil.[41,44] Crude oil with a high percentage of asphaltenes tends to form coke easily,[44,45] which is detrimental to the catalyst performance and the overall process.[44,45] A modified ASTM D2549-02 method (elution chromatography) was used in this work to separate the fractions based on their polarities. The step-by-step procedure is available in the literature.[41]

2.7. Pretreatment Process. To ensure that effective synergy occurs during the copyrolysis of heavy oil and plastic, a predegradation method was introduced into the process. This is expected to improve the degradation behavior and enhance the quality of product yield. Normal mixing without any pretreatment was also used in this study for comparison.

2.7.1. Normal Mixing. Normal mixing involves mixing of the heavy oil, polymer, and catalyst mixtures thoroughly using a spatula. As shown in the graphical abstract, the overall performance of the process can be improved using a predegradation method.

2.7.2. Predegradation Method. Predegradation is a pretreatment process, which involves heating mixtures of heavy oil and plastic with and without catalyst. The predegradation was carried out in an open reactor, in an oven, i.e., before the commencement of the main experiment. After the predegradation, the reactor was sealed for the commencement of the pyrolysis experiment in inert atmosphere. The temperature used depends on the melting point of the polymer. A temperature of 423 K was used for this study. As the reactor used is a glass one in order to be transparent to infrared radiation, it does not have a stirrer that would have facilitated thorough mixing to intensify the contact between melted polymer and solid catalyst particles. As the polymer melts, the mixture is mixed constantly using a spatula for about 1 min to produce intimate contact between the polymer, heavy oil, and catalyst. No volatile products are formed during this process. A pictorial presentation of the process is available in the graphical abstract.

3. RESULTS AND DISCUSSION

3.1. Experimental Results from TGA of PP, Bitumen, and Their Mixtures. TGA analysis of PP, bitumen, and their mixtures in the presence of APC were performed (Figure 3) to evaluate the influence of predegradation in catalytic copyrolysis of PP and bitumen. The thermal degradation of bitumen without catalyst was carried out alongside to further understand the effect of catalyst in improving the degradation of bitumen.

The thermal cracking of bitumen starts around 523 K and occurs over a wide range of temperature up to 773 K. After this temperature, slow pyrolysis continues up to the final temperature with the formation of quite a lot of char. The presence of APC has definitely a catalytic effect as bitumen decomposes faster at quite lower temperatures up to around 723 K, where it slows considerably. It seems that at this stage of 723 K the bitumen has been converted, and the further,
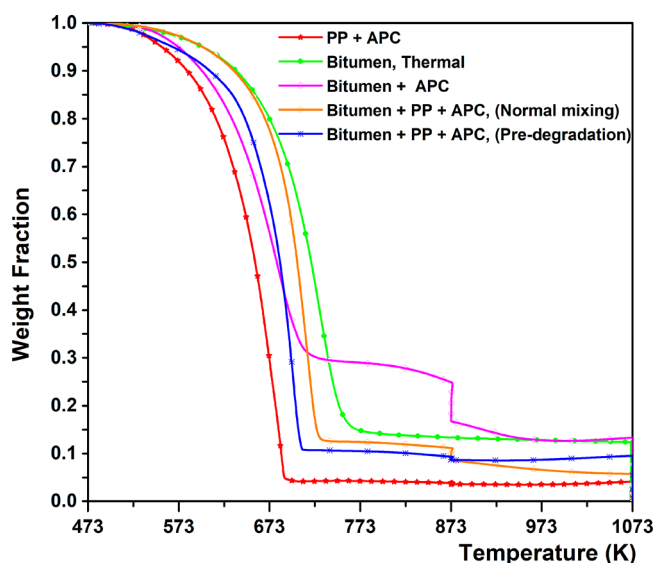
Figure 3. TGA of PP, bitumen, and their mixtures; mass fraction removed against temperature (5 K/min).

much slower stage represents solid phase transformations of the formed soft coke. The total coke formed during catalytic pyrolysis is about 25 wt % of the original bitumen while the amount of hard coke is comparable to the amount of char formed during noncatalytic pyrolysis (12−13 wt %). The amounts of final char/coke (12−13 w%) produced by both thermal and catalytic degradation of bitumen are similar and represent the percentage hard coke removed in air atmosphere at 1073 K (800 °C), i.e., the final temperature.

The catalytic pyrolysis of PP with APC catalyst took place within a narrow temperature range with PP being completely decomposed by 687 K and less than 5% of it converted to coke. For the catalytic copyrolysis of PP and bitumen two different pretreatment methods were used to check the effect of predegradation in improving the pyrolysis pattern. Using normal mixing, the degradation profile of the mixture shifted to higher temperatures compared to the individual catalytic degradation and was much more similar to thermal non-catalytic cracking of bitumen indicating a hindering of contact between APC and the reacting components, PP or bitumen.

Only after 673 K do the two TGA curves, Bitumen/PP/APC normal mixing and Bitumen noncatalytic thermal, deviate, and some catalytic effect is obvious, where the presence of catalyst and/or PP has improved the degradation pattern of bitumen and lowered its decomposition temperature. In order to improve the performance of catalytic copyrolysis of bitumen and PP, a predegradation treatment was introduced. As shown in Figure 3, the pyrolysis temperature was considerably lowered further and the effect of catalyst deactivation by coke deposition was less severe. Both methods, normal mixing and predegradation, reduced significantly the coke amount compared to catalytic pyrolysis of bitumen only, with predegradation affecting a larger coke amount reduction. However, the amount of coke formed is still higher than that during catalytic pyrolysis of PP only. This can be confirmed by the fact that, at 873 K, the TGA was held for 30 min to allow enough time to complete the pyrolysis. At 873 K, the sample with predegradation showed no further conversion while the copyrolysis sample via normal mixing had experienced significant weight loss up to about 973 K. Despite predegradation, however, the bitumen−PP mixture pyrolysis on APC showed worse behavior than the catalytic pyrolysis of bitumen on its own, at least at lower temperatures, below around 700 K. This indicates that the presence of high viscous liquids creates very slow moving interfaces between bitumen and PP and hinders extensively the proper contact of catalyst to each of those phases. Several interplay factors are known to exist and are responsible for the observed changes during the catalytic copyrolysis of bitumen and PP. These factors include fluidity reduction, volatiles stabilization by hydrogen transfer and cross-linking reactions, higher conversion, and reduction in coke deposition.

As shown in Figure 3, there is a delay in the evolution of volatiles when PP is blended with bitumen, causing a shift to higher temperatures. This can be explained by fluidity reduction caused by the addition of PP and the resulted hindering of contact between catalyst and bitumen/PP. Similar results were reported by Espina et al.[46] for the copyrolysis of coal and waste plastics. They observed a delay in the evolution of volatile species, shifting the degradation toward higher temperatures.
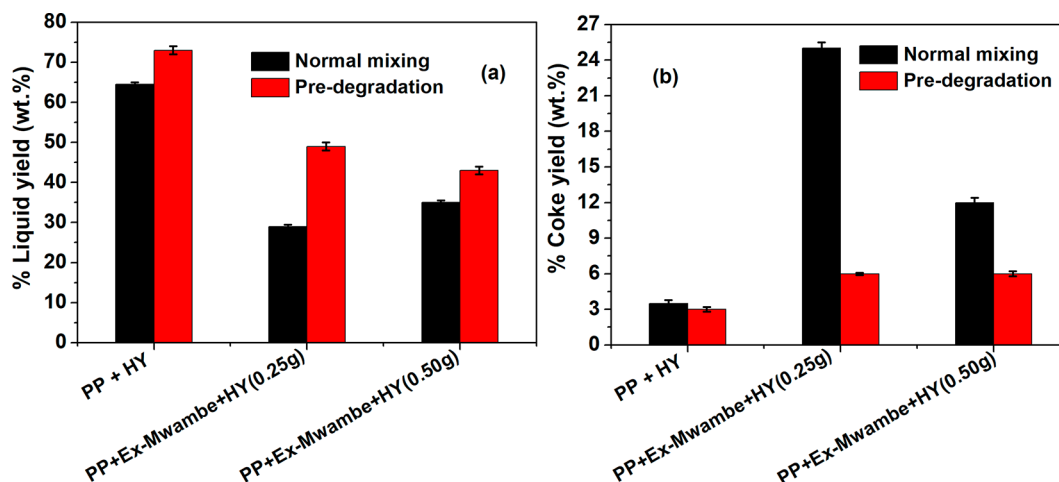

Figure 4. (a) Liquid and (b) coke yields for catalytic copyrolysis of PP and Ex-Mwambe with HY catalyst, showing the effect of using predegradation compared to normal mixing (PP 1.5 g, Ex-Mwambe 0.5 g, reaction temperature 723 K, and N_2 flow rate 10 mL_N/min).
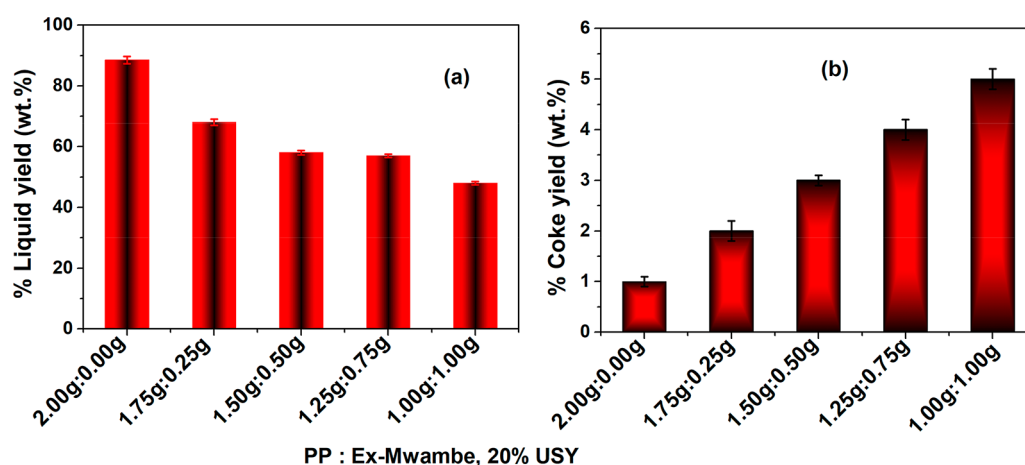
Figure 5. (a) Liquid and (b) coke yields from catalytic copyrolysis of PP and Ex-Mwambe with 20% USY catalyst, showing the effect of varying PP to Ex-Mwambe ratio (catalyst 0.50 g, reaction temperature 723 K, and N_2 flow rate 10 mL$_N$/min).

Stabilization of the primary reaction products was one of the synergy reported during copyrolysis of heavy oil with plastic. The main factor responsible for this process is the hydrogen transfer reaction from a polyolefin chain to heavy oil derived radicals. As shown in Figure 3, there is a postponement in the degradation temperatures of PP and bitumen during copyrolysis; this means that PP and bitumen have stabilized each other, leading to an increased synergy and interactions. Rimez et al.[47] reported stabilization of heavy oil and plastic volatiles components, leading to an increase in the decomposition peak temperatures.

As confirmed in this work, several studies have also reported high conversion and coke deposits in coprocessing of heavy oil and plastics.[27−30] The reason for this synergistic effect is the abundant hydrogen in plastic that enhances degradation reactions of the organic matter in heavy oil.[30]

3.2. Reactor Pyrolysis Experiments. *3.2.1. Effect of Predegradation on the Product Yields.* Among the major objectives of this study was to enhance the quantity and quality of the product yields from catalytic copyrolysis of heavy oil and plastic via a predegradation method. Catalytic copyrolysis experiments of PP and Ex-Mwambe with HY catalyst were conducted using the normal mixing and predegradation methods. The results of the liquid and coke yields are reported in Figure 4. Reproducibility experiments were carried out in triplicate, and based on the calculated experimental error range of these experiments, error bars are added in the figures. The ratio of the initial polymer to heavy oil was kept the same at 3:1 while the initial amount of the feed in all the reactor pyrolysis experiments was maintained at 2.00 g; 1.5 g of PP and 0.5 g of Ex-Mwambe. The feed to catalyst ratio was varied, by varying the amount of catalyst.

As presented in Figure 4, predegradation had produced higher liquid yields and lower coke yields compared with normal mixing. Catalytic pyrolysis of PP with HY using normal mixing produced 64.5% and 3.5% of liquid and coke yields, respectively. With predegradation, the liquid yield increased to 73.0% while the coke yield decreased to 3.0%. When Ex-Mwambe was blended with PP in catalytic copyrolysis experiments, the liquid yield decreased while the coke yield increased compared to catalytic pyrolysis of only PP (2 g PP, 0.5 g HY) irrespective of the mixing method. At lower HY content (0.25 g), the copyrolysis experiment using the normal mixing, had produced 29.0% of liquid yield along with 25.0%

coke yield. Using predegradation on the same sample, the liquid yield has increased to 49.0% while the coke had decreased to 6.0%. Increasing the HY content to 0.50 g resulted in more conversion especially compared to normal mixing where the liquid yield has increased to 35.0% while the coke yield had decreased to 12.0%.

At higher HY content with predegradation, the liquid yield decreased to 43.0% while the coke content remained the same. The lower liquid yield from the predegradation method is attributed to the intimate contact it provided, which increased the availability of the active sites, leading to overcracking of the volatiles into gaseous fraction. Similar results were reported in our previous work of polymer catalytic pyrolysis,[32−40] where the higher catalytic effect of predegradation at lower reaction temperatures leads to higher liquid yield and lower concentration of coke on the catalyst. Based on the good performance of the predegradation method, all the subsequent reactor pyrolysis experiments were carried out using the predegradation method.

3.2.2. Effect of the PP to Ex-Mwambe Ratio on the Product Yields. Reactor pyrolysis experiments were carried out with cracking catalyst (20% USY), in order to check the effect of the amount of PP and Ex-Mwambe on the product yields. The amount of PP was varied from 1.75 to 1.00 g while the content of Ex-Mwambe was varied from 1.00 to 0.25 g. The results of liquid and coke yields are presented in Figure 5.

As shown in Figure 5, the trends are very clear. As the PP to Ex-Mwambe ratio decreases, the liquid yield decreases, much steeper at first and then more gradually, while the coke yield steadily increases with a linear coking contribution from each reactant, much stronger from heavy oil than PP, almost an order of magnitude higher. Furthermore, the linear relationship indicates no synergetic effect between the two reactants, PP and heavy oil. The catalytic pyrolysis of PP without blend produces 88.5% and 1.0% of liquid and coke yields, respectively. When blended with 12.5% Ex-Mwambe the liquid yield decreases to 68.0% while the coke yield increases to 2.0%. Increasing the amount of Ex-Mwambe to 25.0%, 37.5%, and 50.0% decreases the liquid yield to 58.0%, 57.0%, and 48.0% while the coke yield gradually increases to 3.0%, 4.0%, and 5.0% respectively. Several researchers have carried out catalytic copyrolysis of PP and heavy oil (Ahmaruzzaman and Sharma;[21] Kasar et al.;[22] Mohammad et al.;[26] Ballice et al.;[27] Luiz et al.[48]). The results showed that the liquid yield increases

while the solid residue decreases with increasing PP:Ex-Mwambe ratio. These results are in line with the findings from this study; therefore, the copyrolysis of heavy oil with plastic could serve as a feasible process to upgrade the low value heavy oil and waste plastic into high value liquid fuels.

3.2.3. Effect of Catalyst Type on the Product Yields. The activity and selectivity of catalysts vary depending on their structural properties and acidities. This section describes the use of different catalysts in order to explore their influence on the product yields and to recommend the best in enhancing the liquid yield while reducing the coke yield.

The highest and lowest liquid yields of 83.0% and 43.0% were produced by USY and HY catalysts respectively with comparable coke yields, while K30 and the cracking catalyst containing 20% USY got the highest and lowest coke yields of 27.0% and 1.0% respectively. The liquid yields obtained by all catalysts were in the following increasing order USY > APC > 20% USY > K30 > HY while the coke yields followed this decreasing trend 20% USY < APC < HY < USY < K30. These results can be related to the structure and acidity of these catalysts. Zeolites USY and HY have exactly the same structure. As stated in section 2.1, HY has the higher surface area and acid sites concentration, which contributed to its higher initial degradation. However, its apparent poor thermal stability and frequent deactivation[35,38,40,49] resulted in a lower liquid yield. On the other hand, USY, a modified form of HY zeolite, has very strong acidic sites,[49,50] a mesoporous system,[50,51] higher thermal stability,[49,51] and enhanced catalytic activity.[49−51] These properties allowed USY to produce the highest liquid yield compared to most of the catalysts. Aluminum pillared clay catalyst has comparable thermal stability and surface area like zeolites, but it is less prone to coke formation,[52] due to its mild acidity. The result shown by APC in Figure 6 is a reflection of its properties and
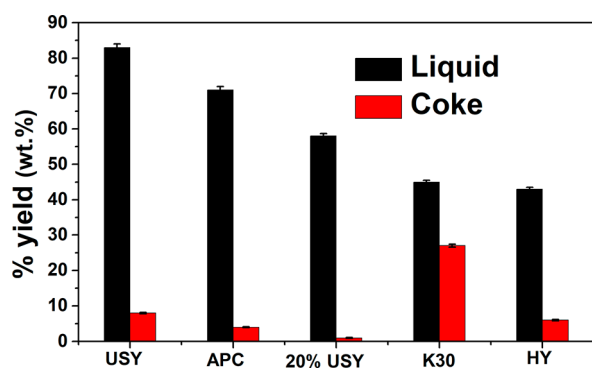

Figure 6. Liquid and coke yields for catalytic copyrolysis of PP and Ex-Mwambe with different catalysts, showing the effect of catalyst types (PP 1.5 g, Ex-Mwambe 0.5 g, catalyst 0.50 g, reaction temperature 723 K, and N_2 flow rate 10 mL_N/min).

implies the advantage of strong acid sites in copyrolysis of polymer and heavy oil. Cracking catalyst containing 20% USY is less acidic, and therefore, it produces a moderate amount of liquid hydrocarbon along with the lowest coke deposit. Even though K30 is an acidic restructured clay catalyst,[53] the low liquid yield and the highest residue/coke produced by this catalyst are challenging for a sustainable process. Jang et al.[54] have shown that for the degradation of polystyrene using montmorillonite clays (K-series) catalysts, as the temperature increases, the amount of liquid product increased at the

expense of the residue.[54] Similar studies by Silva et al.[55] and by Solak and Rutkowski[56] showed that for catalytic copyrolysis of plastic with K-series clay catalyst, the optimum performance was achieved at a higher temperature of 773 K. This implies that the temperature of 723 K used in Figure 6 may not be ideal for K-series catalyst, hence the low conversion produced by K30.

3.3. Liquid Product Characterization. The liquid product analysis results were reported in the form of hydrocarbon atom distribution groups and hydrocarbon fraction groups, according to the methodology described in Section 2.4. In addition to the full detailed boiling point distribution, the boiling point ranges are distributed into three main fractions, light, middle, and heavy fractions, for a better outline of the trends. The light fraction includes the components in the boiling point range from C_5 to C_9 (309.10−424.00 K). The middle fraction comprises the components from C_9 to C_{14} (424.00−526.70 K). Finally, the heavy fraction consists of the components from C_{14} to C_{20} (526.70−617.00 K). Besides these fractions, there are additional two fractions. The first of those, called ($-C_5$), was assigned to hydrocarbons lighter than C_5, i.e. compounds up to the retention time of normal pentane (C_5), and the last group is ($C_{20}-$), for compounds with retention times higher than those for C_{20}, which are predominantly waxy products associated with thermal cracking. In the following figures, the results are presented both ways, detailed with the full boiling point distribution, as well as compressed boiling point distribution.

3.3.1. Effect of Predegradation on the Product Distribution from Catalytic Copyrolysis of PP and Ex-Mwambe with K30 Catalyst. As shown in Figure 7 catalytic pyrolysis of Ex-Mwambe with K30 produces predominantly heavy fraction ($C_{14}-C_{20}$) while PP produced a higher amount of the lighter fraction (C_5-C_{12}). Co-pyrolysis using normal mixing had higher selectivity to middle and heavy fractions (C_8-C_{20}), while predegradation shifted the selectivity to lighter and middle fraction (C_5-C_{15}). Since the boiling point distribution had covered a very wide range of carbon atoms, it would be better to consider their overall performance based on the compressed distribution (Figure 7b).

Catalytic pyrolysis of PP and its copyrolysis with Ex-Mwambe using predegradation showed the highest percentage of C_5-C_9 and C_9-C_{14}, which are predominantly gasoline and kerosene fractions, respectively. Catalytic pyrolysis of Ex-Mwambe and its copyrolysis PP with using the normal mixing produced predominantly diesel fraction ($C_{14}-C_{20}$). As expected, PP had the best product distribution with more gasoline fraction and therefore, predegradation can be used in the copyrolysis to obtain similar product distribution. Muhammad and Manos[40] had reported similar results, where predegradation has maximized the gasoline fraction C_5-C_{12} during catalytic conversion of polyolefins with acidic zeolite catalysts.

3.3.2. Effect of PP to Ex-Mwambe Ratio on the Product Distribution. This section considers the effect of PP to Ex-Mwambe ratio on the product distribution, as the quality of the liquid yield depends on its product distribution. The results as presented in Figure 8, parts a and b, are based on the detailed boiling point distribution and compressed distribution. The trends are very clear, as the PP fraction decreases and Ex-Mwambe fraction increases, the product distribution is shifting from left to right i.e. from lighter to heavier fractions.
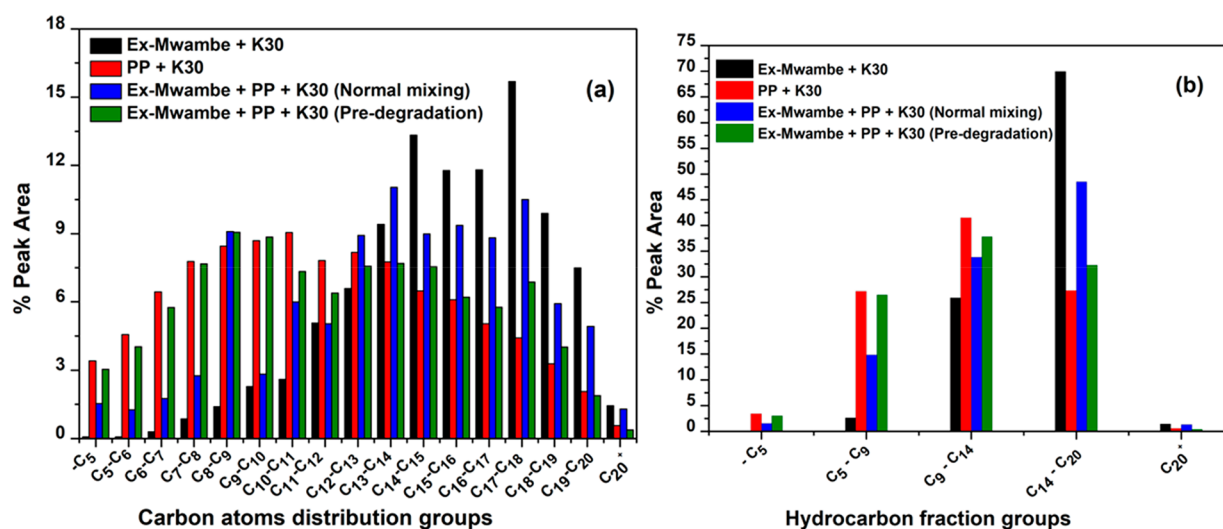
Figure 7. (a) Detailed boiling point fractions and (b) compressed distribution for catalytic copyrolysis of PP and Ex-Mwambe with K30 catalyst, showing the effect of using predegradation compared to normal mixing (PP 1.0 g, Ex-Mwambe 1.0 g, reaction temperature 723 K, and N_2 flow rate 10 mL$_N$/min).
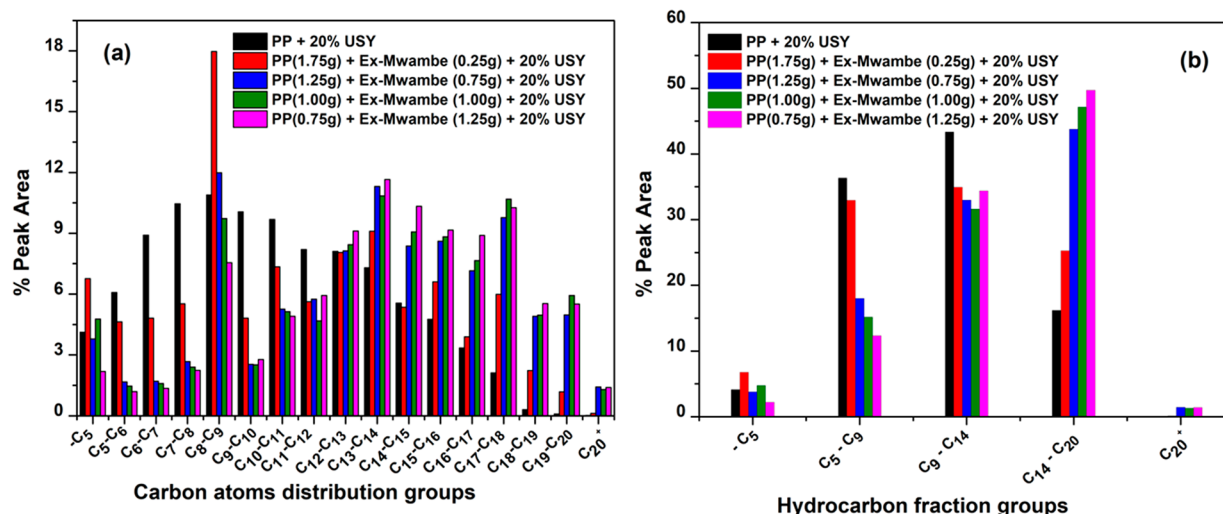

Figure 8. (a) Detailed boiling point fractions and (b) compressed distribution for catalytic copyrolysis of PP and Ex-Mwambe with 20% USY catalyst, showing the effect of varying PP to Ex-Mwambe ratio (catalyst 0.5 g, reaction temperature 723 K, and N_2 flow rate 10 mL$_N$/min).

Based on the detailed boiling point distribution Figure 8(a), the percentage distribution of $C_5–C_6$, $C_6–C_7$, $C_7–C_8$, $C_8–C_9$, $C_9–C_{10}$, and C_{10}-C_{11} decreases with decreasing PP ratio while $C_{12}–C_{13}$, $C_{13}–C_{14}$, $C_{14}–C_{15}$, $C_{15}–C_{16}$, $C_{16}–C_{17}$, $C_{17}–C_{18}$, $C_{18}–C_{19}$, and $C_{19}–C_{20}$ increases with increasing Ex-Mwambe ratio. In other words, the presence of PP enhances the formation of lighter components while the presence of Ex-Mwambe in the mixture increases the amount of the heavy fractions. A better comparison can be made by considering compressed distribution, Figure 8b. Based on these results, the variations in the copyrolysis ratio mainly affected $C_5–C_9$ and $C_{14}–C_{20}$ fractions. The higher the PP ratio, the higher the percentage of $C_5–C_9$ is while increasing the Ex-Mwambe ratio increases the percentage of $C_{14}–C_{20}$. Therefore, PP can be used to optimize the gasoline fraction in the mixture while Ex-Mwambe can be used to enhance the diesel fraction.

3.3.3. Effect of Catalyst Types on the Product Distribution. As seen in Section 3.2.3, the catalyst type affects significantly the liquid products yield. This section examines the catalyst

type effect on the liquid fuel quality in terms of their product distribution.

As shown in parts a and b of Figure 9, acidity has a lot of influence on the product distribution. HY, the most acidic catalyst used, produced the highest percentage of lighter fractions comprising of $C_5–C_6$, $C_6–C_7$, $C_7–C_8$, $C_8–C_9$, and $C_9–C_{10}$. K30, the catalyst with least acidity produced the highest percentage of heavy fractions consisting of $C_{12}–C_{13}$, $C_{13}–C_{14}$, $C_{14}–C_{15}$, $C_{15}–C_{16}$, $C_{16}–C_{17}$, $C_{17}–C_{18}$, $C_{18}–C_{19}$, and $C_{19}–C_{20}$. According to the compressed distribution, all the catalysts had similar amount of middle fraction and they differ in the distributions of lighter and heavier fractions. The performance of the catalysts to produce lighter fraction is of the following order HY > 20%USY > APC > K30. For the heavier fraction, the reversed order was obtained K30 > 20% USY > APC > HY. The first order is the sequence of the highest obtained gasoline fraction while the latter shows their ability to favor the production of diesel fraction. Several studies have reported similar results during catalytic pyrolysis of polyolefins in which HY zeolite favors the liquid production in
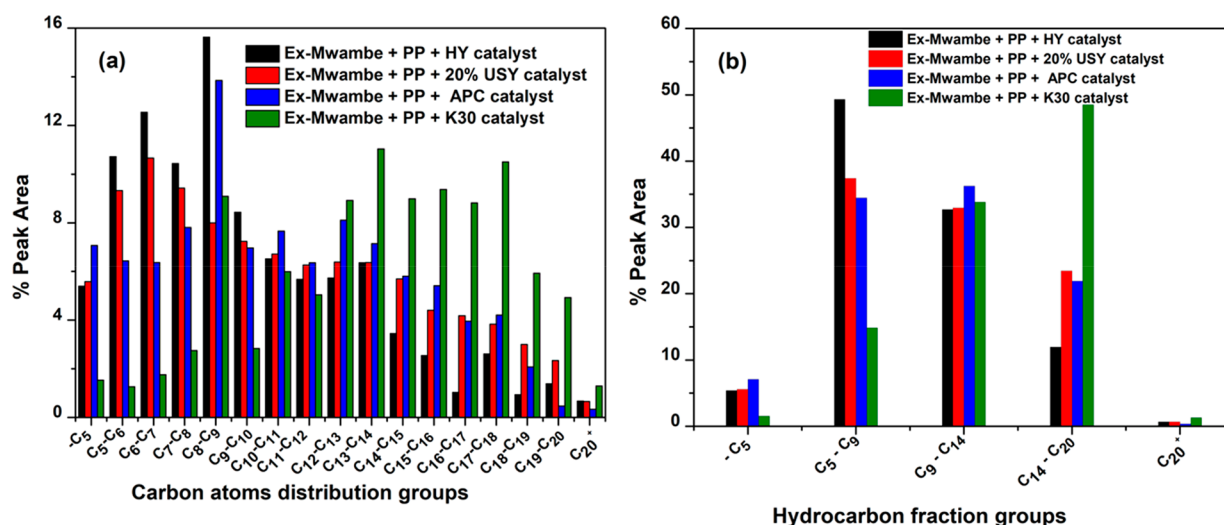
Figure 9. (a) Detailed boiling point fractions and (b) compressed distribution for catalytic copyrolysis of PP and Ex-Mwambe, showing the effect of catalyst types (PP 1.5 g, Ex-Mwambe 0.5 g, reaction temperature 723 K, and N_2 flow rate 10 mL_N/min).
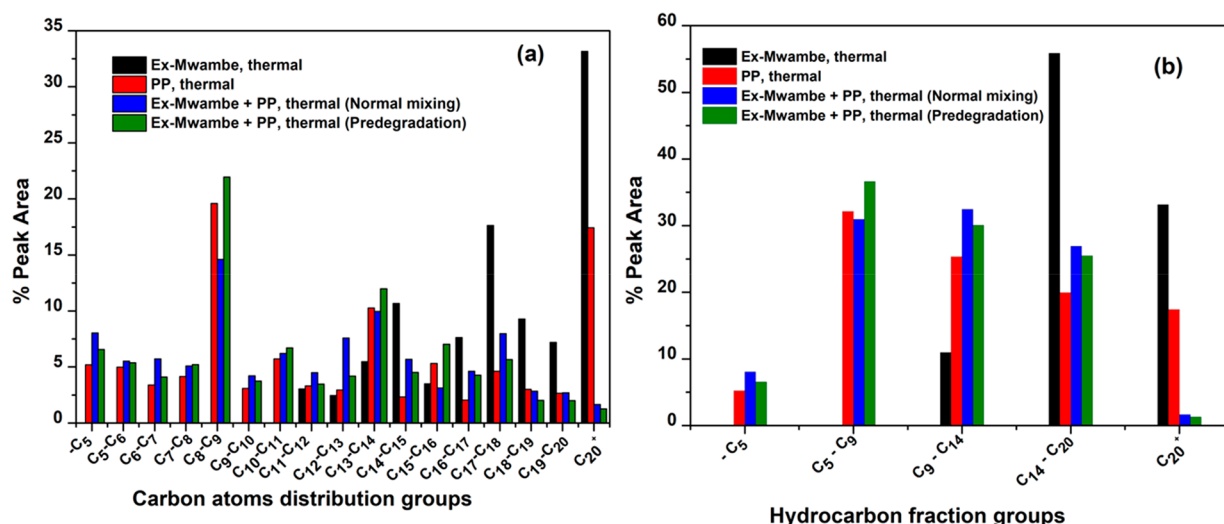

Figure 10. (a) Detailed boiling point fractions and (b) compressed distribution for thermal pyrolysis of PP, Ex-Mwambe, and their mixtures, showing the effect of predegradation compared to the normal mixing (PP 1.0 g, Ex-Mwambe 1.0 g, reaction temperature 723 K, and N_2 flow rate 10 mL_N/min).

gasoline range.[14,32,40] Gobin and Manos,[36] Akpanudoh et al.,[39] and Manos et al.[52] have studied catalytic degradation of plastic over microporous catalysts including clay, pillared clay, and commercial cracking catalysts. The liquid product distribution over clay, pillared clay, and cracking catalysts is characterized by higher content of heavy fractions than the liquid formed over zeolite catalysts. This was attributed to the lower acidity and hence lower cracking activity of clay, pillared clay, and cracking catalysts. Nevertheless, most of these products formed were in the boiling point range of motor engine fuels.

3.3.4. Effect of Predegradation on the Product Distribution of Thermal Pyrolysis of PP, Ex-Mwambe, and Their Mixtures. This section will help in addressing part of the complicated issues related to copyrolysis of heavy oil and plastic. As mentioned in the Introduction, some previous copyrolysis works[24−28,30] argued that plastics act as a catalyst during their copyrolysis with heavy oil. In order to get more insight into the asserted role of plastic, thermal pyrolysis of PP, Ex-Mwambe, and their mixtures were conducted, with normal

mixing as well as predegradation. The results for the liquid products distribution are presented in Figure 10.

As part of the results in Figure 10, predegradation was carried out along with the normal mixing to see if similar effect as with the catalyst can take place. As shown in Figure 10a, thermal pyrolysis of Ex-Mwambe predominantly produced carbon number above C_{20} with no products below the $C_{11}-C_{12}$ fraction. On the other hand, thermal pyrolysis of PP produced wider distribution with the major fractions as C_8-C_9, $C_{13}-C_{14}$ and $-C_{20}{}^+$. The presence of plastic had optimized the product distribution from heavy oil as indicated by the increased percentage of $-C_5$, C_5-C_6, C_6-C_7, C_7-C_8, C_8-C_9, C_9-C_{10}, $C_{10}-C_{11}$, and decreased in the percentage of waxy products $(-C_{20}{}^+)$. Based on the compressed distribution Figure 10b, comparing the percentage fractions corresponding to all samples confirmed the existence of synergies during the copyrolysis. First, the percentages of lighter fractions $(-C_5$ and $C_5-C_9)$ produced by copyrolysis are more than the equivalent produced by PP. Since Ex-Mwambe contained no lighter

fractions, there must to be a synergy responsible for the increased percentage of the lighter fractions in the copyrolysis. Second, both PP and Ex-Mwambe had produced significant amounts of the heavier fraction ($-C_{20}{}^+$), but the copyrolysis samples had an insignificant percentage of $-C_{20}{}^+$. This also confirms the presence of synergies from both samples that facilitated the conversion of waxy hydrocarbons into lighter products. Finally, for C_9-C_{14} and $C_{14}-C_{20}$, the sum of the average percentages from the individual pyrolysis cannot account for the percentages produced by the mixtures. PP-heavy oil mixtures had produced an excess of C_9-C_{14} at the expense of the heavier fraction, affirming a synergy in the copyrolysis that favors gasoline fraction. Finally, the distinction between predegradation and normal mixing is clear as predegradation favors the production of C_5-C_9 while normal mixing increases the percentage of $-C_5$, C_9-C_{14}, and $C_{14}-C_{20}$ (Figure 10b). Muhammad et al.[32] have reported similar results, where predegradation enhances the production of the gasoline range fraction, confirming results from previous studies.[24−28,30] However, the reason for this improvement is the intensification of contact between the two feed constituents, polymer and heavy oil, as we argue below.

As previously confirmed by Muhammad et al.,[32] predegradation has no influential role in the thermal degradation of polymer. It only enhanced the catalytic polymer degradation. In other words, predegradation improves the way the catalyst works. Predegradation does not have a major effect on catalytic pyrolysis either, when the original polymer is in powder form, with fine solid polymer particles.

In a mixture of catalyst and fine polymer particles, when the polymer melts it forms a liquid thin layer around the solid catalyst particles, intensifying their contact and enhancing the catalytic reaction. In a polymer catalyst mixture with relatively large solid polymer particles, as polymer melts and due to the large viscosity of the melt, large pockets of liquid polymer are formed whose redistribution around catalyst particles is extremely slow with the result of the contact between polymer and catalyst to be hindered a lot and consecutively a very reduced catalytic reaction. The predegradation method with polymer melting and rigorous stirring of the melt and catalyst particles intensifies the contact of the two constituents, polymer and catalyst. This is why, in the absence of catalyst, predegradation has no effect on pure thermal polymer pyrolysis. However, predegradation improves thermal copyrolysis of plastic with heavy oil, as it intensifies the contact between the polymer melt and heavy oil allowing synergestic effects to materialize.

3.4. Coked Catalyst Characterization.
Catalyst deactivation is one of the major obstacles in the implementation and scale-up of catalytic cracking of plastic and heavy oil.[57,58] Coke formation is inevitable in catalytic hydrocarbon conversion on acidic catalysts and is predominantly responsible for the catalyst deactivation.[32,35,37,40,59] The nature and rate of coke formation are strongly influenced by the catalyst properties,[14,60,61] nature of the feedstock,[57] reactor medium,[57,61,62] and operating conditions.[57,60] Therefore, an in-depth understanding of the chemical character of coke components is necessary for the development of improved catalysts that are more resistant to catalyst deactivation.[63,64] As described in the Experimental Section, the methodology adopted for the coked catalyst characterization determines how easily the coke components are removed from the catalyst surface in an inert and/or air atmosphere. At each temperature used, the coke components are either volatilized and/or decomposed into smaller fragments and the results are presented below in Table 2.

Table 2. Coked Catalyst Classification

experiment type	% soft coke	% hard coke	total coke concentration (g of coke/g of cat)
PP + Ex-Mwambe + 20% USY (normal mixing)[a]	49.00	51.00	0.15
PP + Ex-Mwambe + 20% USY (predegradation)[a]	60.00	40.00	0.22
PP + Ex-Mwambe + HY (predegradation)[a]	44.00	56.00	0.33
PP + Ex-Mwambe + 20% USY (predegradation)[b]	54.00	46.00	0.14

[a]Reaction temperature = 773 K. [b]Reaction temperature = 873 K.

As shown in Table 2 and parts a and b of Figures 11, comparison of coked catalysts from normal mixing and the predegradation method revealed that coke components from the predegradation method are more volatile while the normal mixing contained a higher percentage of hard coke. This can be explained by the influence of predegradation in lowering the pyrolysis temperature. Coke components formed at lower reaction temperature are more volatile and softer than those formed at higher reaction temperatures.[65,66] On the other hand, the coked catalyst from predegradation contained higher concentrations of coke components due to the emission of large amounts of volatiles during the catalytic pyrolysis of the sample. Similar results were reported by Muhammad and Manos,[35,40] where predegradation produced a higher coke concentration compared to the normal mixing method. Similarly, comparison between different catalysts (Table 2 and Figures 11, parts b and c) shows that HY catalyst produced a higher percentage of hard coke along with a large concentration of coke components. For 20% USY catalyst (cracking catalyst containing 20% USY zeolite) the majority of the coke components are volatiles with a lower concentration of the total coke compared to HY zeolite. The differences in coke content and composition are associated with the catalyst acidity and structure.[38,40,67,68] HY catalyst has reported to promote coke condensation with very fast deactivation due to its high acidity content.[32,69,70] On the other hand, the cracking catalyst containing 20% USY is less acidic than HY catalyst due to its lower zeolite content, and therefore, less severe deactivation and lower coke concentration were observed with 20% USY. This is generally observed with catalysts manufactured using zeolites dispersed on an amorphous silica−alumina matrix.[31,52,71−73] The presence of higher content of strong zeolite acidic catalyst always enhanced coking, since coke formation reactions are catalyzed by strong acid sites.[39,52]

The last two results in Table 2 show the effect of increasing reaction temperature on the coke content from catalytic copyrolysis of PP and Ex-Mwambe. This is also graphically represented by Figure 11, parts b and d, respectively. According to the results, the coke content and components varied at different reaction temperatures. At a reaction temperature of 773 K, most of the coke components are volatiles with 60.0% soft coke while the hard coke is about 40.0%. Upon increasing the temperature to 873 K, further
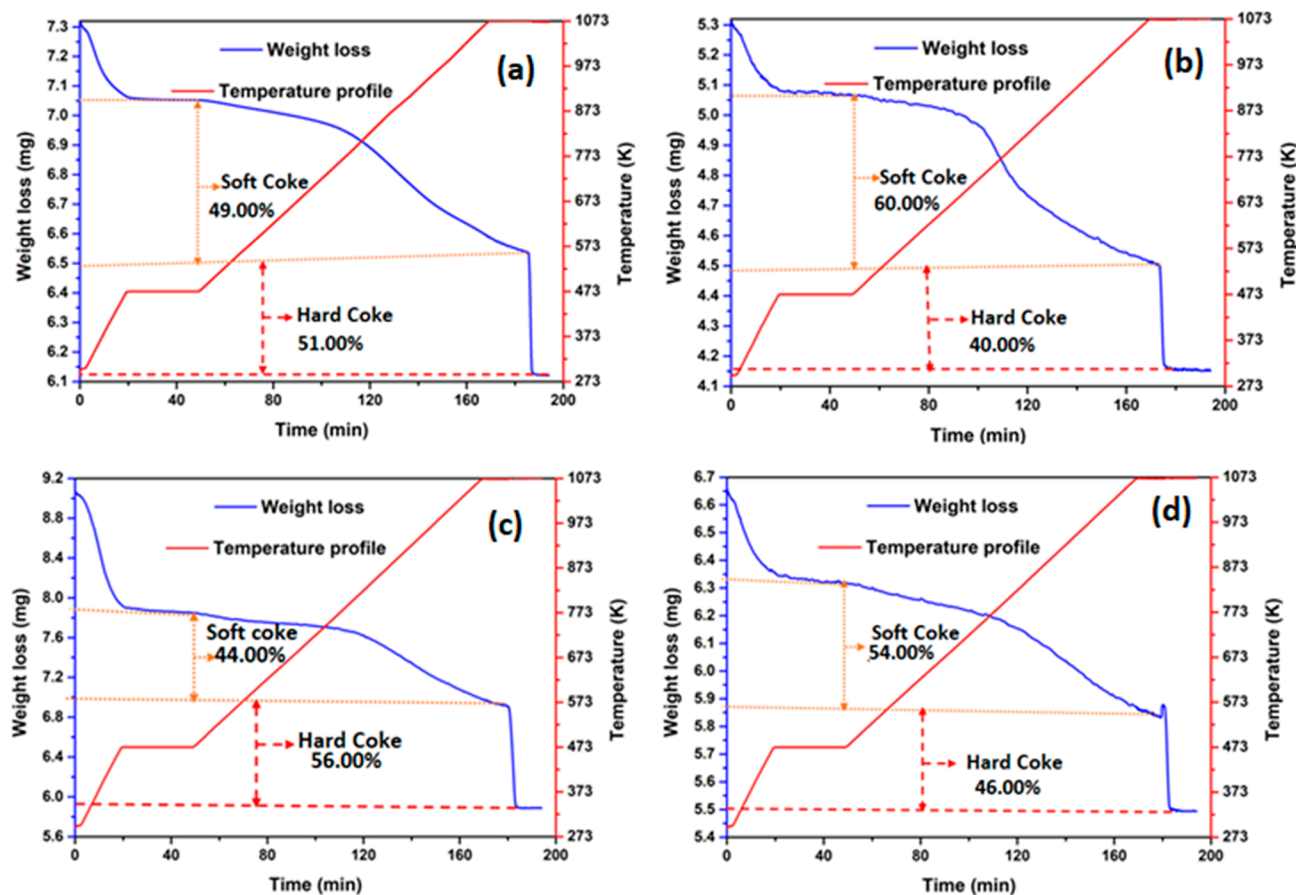
Figure 11. TGA analysis of coked samples showing the characterization of the coke components: (a) PP + Ex-Mwambe + 20% USY (normal mixing) 773 K; (b) PP + Ex-Mwambe + 20% USY (predegradation) 773 K; (c) PP + Ex-Mwambe + HY (predegradation) 773 K; (d) PP + Ex-Mwambe + 20% USY (predegradation) 873 K.

transformation of coke components took place favoring the formation of hard coke components.[66,74]

Part of the soft coke transformed at higher reaction temperatures was converted into the reaction products leading to a decrease in the total coke as expressed by the coke concentration (Table 2). Parts b and d of Figure 11 also revealed that, at low reaction temperature, the rate of coke removal showed different peaks, indicating the existence of diverse varieties of coke precursors, mainly condensed and/or bridged polyromantic components. At higher reaction temperatures, the curve exhibited a single peak with constant rate, signifying the removal of more condensed and identical coke components (Figure 11d). Reaction temperature considerably affects the coke composition.[74–77] Several studies[14,63–65,74–77] have reported the effect of the temperature on the coke composition. At low reaction temperatures dominated by soft coke,[14,63–65] the composition involves nonpolyaromatic deposits formed through condensation and rearrangement reaction steps[64,75,78] which depends on the reactants composition.[64,75] With increasing reaction temperatures, the coke composition is different and independent of the reactants' composition.[74,75] At higher reaction temperatures, coke mainly formed polyaromatic deposits through condensation, rearrangement, and hydrogen transfer reaction steps.[57,69–80] A recent study on the deactivation of a Y-zeolite based catalyst with coke evolution during the catalytic pyrolysis of polyethylene for fuel oil by Chen et al.[14] supports the findings from the present study. The coke composition from their study at

low temperature contained less developed structure, which can be related to a high H/C ratio while the high temperature coke is more condensed with a low H/C ratio.

4. CONCLUSIONS

Catalytic and noncatalytic copyrolysis of plastic and heavy oil was studied. TGA experiments were used to study the effect of predegradation treatment during catalytic copyrolysis of PP and bitumen. Using the normal mixing without any treatment, the degradation profile of the mixture shifted to higher temperatures compared to the individual catalytic degradation. In the presence of predegradation, the degradation temperature was lowered and the effect of catalyst deactivation by coke was less severe. Predegradation had produced a higher liquid yield and a lower coke yield compared to normal mixing. Catalytic pyrolysis of PP and its copyrolysis with Ex-Mwambe heavy oil using predegradation showed highest percentage of C_5-C_9 and C_9-C_{14} which are predominantly gasoline and kerosene fractions respectively. All the catalysts used had similar amount of middle fraction. For the light fraction, their performance was of the following order, HY > 20% USY > APC > K30, and for the heavy fraction, the reversed order was obtained, K30 > 20% USY > APC > HY.

The presence of PP in the thermal copyrolysis of Ex-Mwambe resulted in synergies that increased the gasoline fraction (C_5-C_9) and decreased the heavier fraction ($-C_{20}^+$). This has also confirmed that, PP facilitated the conversion of waxy hydrocarbons into lighter products.

Through coke characterization via TGA, the coke content and components varied at different reaction temperatures. At lower temperatures, soft coke is the predominant coke component, while at higher temperatures, there is more hard coke than soft coke, as part of the soft coke volatilizes into reaction products, leading also to a lower amount of total coke as expressed by the coke concentration. TGA analysis of coked catalysts revealed also the existence of diverse varieties of coke precursors.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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