Catalytic Thermal Cracking of Postconsumer Waste Plastics to Fuels. 1. Kinetics and Optimization

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ABSTRACT: Thermogravimetric analysis (TGA) was used to investigate thermal and catalytic pyrolysis of waste plastics such as prescription bottles (polypropylene/PP), high density polyethylene, landfill liners (polyethylene/PE), packing materials (polystyrene/PS), and foams (polyurethane/PU) into crude plastic oils. In the first phase of this investigation, a statistical design experiments approach identified reaction temperature and time as the most important factors influencing product oil yield. Kinetic parameters including activation energy determined for both catalytic and noncatalytic processes showed a reduction in activation energy for the catalytic reactions. In the second phase, the interactions of reaction temperature and time with a number of catalysts were investigated to determine the effect on the yield of crude plastic oil. It was found that Y-zeolites increased conversion at reduced temperature for PP and PE while spent fluid catalytic cracking and sulfated zirconia catalysts supported pyrolytic decomposition of PS and PU foams. Response surface methodology (RSM) was utilized to optimize TGA conditions for pyrolytic decomposition of PP. The results were then validated through batch scale experiments, and the resulting crude oils were characterized and distilled into motor gasoline, diesel #1, diesel #2, and vacuum gas oil fractions. Catalysts enhanced cracking at lower temperatures and narrowed the molecular weight (hydrocarbon) distribution in the crude oils. Chemical characterization of the crude oils indicated an increased gasoline-range fraction in oils obtained in the presence of catalyst while the distillate fractions were more evenly distributed among gasoline-range and diesel-range hydrocarbons in the absence of catalyst. The distillates obtained were characterized for fuel properties, elemental composition, boiling point, and molecular weight distribution. The fuel properties of the diesel-range distillate (diesel fraction) were comparable to those of ultralow sulfur diesel (ULSD).

1. INTRODUCTION

Plastics constitute 12.4% of municipal solid waste (MSW) in the US.1 Polyethylene (PE) and polypropylene (PP) plastics comprise more than half of the plastic waste in MSW. The lack of a reliable market for segregated plastics is a barrier to recycling. In Illinois, the Solid Waste Management Act (SWMA), adopted in 1986, establishes the following waste management hierarchy in descending order of preference, as State policy: (1) volume reduction at the source (of generation); (2) recycling and reuse; (3) combustion with energy recovery; (4) combustion for volume reduction; and (5) disposal in landfill facilities.2,3 Thus, wherever reduction, reuse, and recycling efforts are insufficient, conversion of plastic wastes to energy offers a means to divert wastes from landfills while simultaneously producing energy and offsetting the use of other energy sources.

One method for conversion of waste plastics to energy is pyrolysis. Pyrolysis is broadly defined as the irreversible thermochemical decomposition of organic material into smaller units at elevated temperatures (＞300 °C) in the absence of atmospheric oxygen.4,5 Pyrolysis is used to convert low energy density materials into high energy density substances such as liquid and solid fuels along with low energy density syngas. It is an attractive pathway due to its flexibility in processing a variety of feedstocks and producing multiple product streams that have the potential to satisfy multiple market needs. For example, the liquid product from pyrolysis produces value-added products such as BTX (benzene, toluene and xylenes) or a variety of liquid fuels (gasoline, diesel) for transportation and industrial sectors as well as serving as a source of lubricant oil basestock.6−16 The distribution of fuel products is highly dependent on the feedstock as well as the reaction conditions and type of pyrolysis. The distribution of the products obtained from pyrolysis reactions can be controlled using appropriate catalysts.17−19

Catalytic cracking of plastics requires lower energy consumption and the chemical distribution of the product can be narrowed when compared to a thermal process.20 Reported catalysts used in this process are zeolite, alumina, silica—alumina, fluid catalytic cracking (FCC) catalyst, and reforming catalyst, among others.21,22 Catalyst properties such as acidic sites density along with physical properties such as surface area, pore size, pore volume, pore size distribution, pore

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structure, etc. are important factors influencing catalytic performance.20,23,24

Thermogravimetric analysis (TGA) has been widely used to determine the rate of polymer degradation and the influence of major process variables.25–28 Response surface methodology (RSM) was used to predict the influence of experimental conditions on product yield.16,29,30 Reaction temperature and time have been identified to be major factors in previous studies.29,31 Additional factors such as feed size, feed quantity and inert (nitrogen) gas flow rate have also been previously investigated and were included in this study as well.29

The objectives of this investigation were to (1) optimize process parameters, (2) identify suitable catalysts and (3) develop reaction kinetics for catalytic and noncatalytic thermal degradation of waste plastics followed by application of TGA results to batch scale pyrolysis of one plastic type and detailed characterization of plastic crude oil and its distillates. The study was conducted in three phases. First, all process variables were screened in a rapid fashion using a statistical design of experiments (DOE) approach and optimized using TGA. In a second phase, the interaction between catalysts, reaction temperature and time on the yield of oil were studied. Degradation kinetics were developed for reactions involving both catalytic and noncatalytic degradation. Lastly, the results predicted by the models developed using TGA were validated on a bench scale waste plastic to crude oil conversion unit and the obtained crude oils and their corresponding distillates were characterized for chemical and fuel properties.

2. MATERIALS AND METHODS

The plastics used in the study are commonly used plastics that end up in the landfills or incinerators, such as prescription medicine bottles (polypropylene/PP), packing materials (polyethylene/PE), high density polyethylene (HDPE) products collected from a Materials Recovery Facility (MRF), industrial waste materials made of polyurethane foams (PUFs), and land facility (MRF), industrial waste materials made of polyurethane foams (ZSM-5 and Y), MgCO₃, Zr(SO₄)₂, MCM-41, and spent FCC catalyst.

Decomposition of the plastic materials was monitored using a Q50 TGA (TA Instruments, Schaumberg, IL). The temperature of the five waste plastic materials was increased from 40 to 600 °C at 10 °C/min heating rate. A similar experiment was also performed to assess the thermal stability of the catalysts in a temperature region of 100 to 600 °C at a heating rate of 10 °C/min. Initial temperature of the sample was 40 °C. The catalyst was maintained at 100 °C for about 15 min (isothermally) to remove moisture and the weight loss was continuously monitored until the final temperature reached 600 °C at 10 °C/min. Isothermal catalytic experiments were performed by mixing catalysts with the powdered plastic at a 1:10 ratio at various times and temperatures. The levels of the experimental variables were set using a central composite design (CCD). The sample quantity was less than 20 mg to have a representative homogeneous sample and to avoid heat and mass transfer effects. The response variable was the quantity of solid residue. The rate of the depolymerization reaction was calculated from the amount of solid residues present at that time and temperature. Kinetics were also developed using an integral method (Coats-Redfern method), which assumes the degradation mechanism does not change throughout the reaction.32

In order to validate the results from TGA, three batch runs were also conducted on the prescription medicine bottles (MB) using TGA optimized conditions and catalysts in a plastic to oil pyrolysis unit as described earlier.13 About 500 g of plastic were pyrolyzed at two temperatures (390 and 450 °C) in the absence of a catalyst. A third run was conducted in the presence of a catalyst at 390 °C, an optimized condition. Samples were collected every 15 min for the first hour, every 30 min for the second hour, and every hour to determine PCO production with time. Overall reaction conversions and yields were determined for all runs. The crude oils from these runs were distilled in an automated 36–100 spinning band distillation system from BR instrument, Easton, MD into six fractions; <35 °C (lower molecular weight volatile hydrocarbons), motor gasoline (35–185 °C), a transition fraction between motor gasoline and diesel #1 (185–195 °C), diesel #1 (195–290 °C), diesel #2 (290–350 °C), and vacuum gas oil (>350 °C).

2.1. Design of Experiments. RSM was used to design experiments.6,25,30 Four factors (experimental variables) -reaction temperature, reaction time, nitrogen (N₂) flow rate, and feed quantity were investigated at five different levels: These parameters are summarized in Table 1. A circumscribed CCD was selected due to the large design space and the rotatability of the design. The circumscribed CCD composed of 2³ factorial experiments, 2² axial, and m center point experiments, where N is the total number of experiments and is calculated as shown in eq 1. Six center point replicate experiments were conducted (m = 6), for a total of 30 experiments, substantially less than the number of experiments that otherwise would have been required (625) for a 4-variable 5-level factorial design (5⁴).

\[
N = 2^3 + (2.2) + m = 2^4 + (2.4) + 6 = 30
\] (1)

Six factorial experiments were conducted at levels of ±1 from the center point conditions (center point conditions = level 0), and 8 axial experiments at levels of ± α from the center point conditions, as shown in Table 1. The levels were selected based on previous study.29 For a rotatable circumscribed CCD, the α value was calculated according to eq 2.

\[
α = (2n)^{1/4} = (2^4)^{1/4} = 2
\] (2)

RSM develops a quadratic model equation using standard statistical regression techniques that estimate the response surface, Y, which represents percentage conversion in this study. The condensed form of the quadratic model is shown in eq 3.

\[
Y = β_0 + \sum_{i=1}^{n} β_i x_i + \sum_{i=1}^{n} \sum_{j=1}^{n} β_{ij} x_i x_j + \sum_{i=1}^{n} β_i^2
\] (3)

where Y is the value of the estimated response, \( β_i \) is a constant coefficient (intercept), \( β_i \) are the coefficients associated with the four

<table>
<thead>
<tr>
<th>Table 1. List of Experimental Factors and Levels for Experimental Design</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Factor RSM</strong></td>
</tr>
<tr>
<td>---------------------------------------------------------------</td>
</tr>
<tr>
<td>( X_1 )</td>
</tr>
<tr>
<td>( X_2 )</td>
</tr>
<tr>
<td>( X_3 )</td>
</tr>
<tr>
<td>( X_4 )</td>
</tr>
</tbody>
</table>

| Code level and experimental levels | –2 | –1 | 0 | 1 | 2 |
|---------------------------------------------------------------|
| \( X_1 \) | 350 | 400 | 450 | 500 | 550 |
| \( X_2 \) | 0 | 15 | 30 | 45 | 60 |
| \( X_3 \) | 60 | 70 | 80 | 90 | 100 |
| \( X_4 \) | 0 | 8 | 12 | 16 | 20 |
main factors, $\beta_{ij}$ are the coefficients associated with six interaction terms, $\beta_{ii}$ are the coefficients associated with four higher order terms, and $\chi_i$ and $\chi_j$ are the coded factors computed according to eq 4

$$\chi_i = \frac{X_i - X_{i,o}}{\Delta X_i}$$  \hspace{1cm} (4)

where $\chi_i$ is the coded value of the $i^{th}$ factor, $X_i$ is the actual value of the $i^{th}$ factor (Table 1), $X_{i,o}$ is the actual value of the $i^{th}$ center point condition corresponding to $i$, and $\Delta X_i$ is the value change from one coded level to the next.

2.2. Kinetics. Conversion represents the amount of sample that was decomposed and was calculated as

$$\gamma = \frac{w_i - w_t}{w_i - w_f}$$  \hspace{1cm} (5)

where $w_i$, $w_t$, and $w_f$ are the initial mass, pyrolyzed mass of the sample at time $t$ and the final residual mass, respectively.

Assuming that the rate of disappearance of a polymer sample may be expressed by eq 6

$$\frac{dy}{dt} = k(1 - \gamma)^n$$  \hspace{1cm} (6)

Where $\gamma$ is the fraction decomposed at time $t$, $n$ is the order of the reaction and $k$ is the rate constant given by Arrhenius eq 7

$$k = -Ae^{-E/RT}$$  \hspace{1cm} (7)

For a linear and steady heating rates (10 °C/min)

$$\beta = \frac{dT}{dt}$$  \hspace{1cm} (8)

Combining equations

$$\int_0^T \frac{dy}{(1 - \gamma)^n} = \left(\frac{A}{\gamma}\right) \int_0^T e^{-E/RT} dT$$  \hspace{1cm} (9)

Figure 1. Contour plot representing the percentage yield with respect to temperature and nitrogen flow rate: (a) temperature and feed quantity (b) and temperature and time (c).
Expanding the left-hand side of the equation
\[ \gamma + \left( n \frac{\gamma^2}{2} + n(n+1) \left( \frac{\gamma^3}{6} \right) \right) + n(n+1)(n+2) \left( \frac{\gamma^4}{24} \right) + \cdots \]

For low values of \( \gamma, \gamma^2 \) and higher orders can be neglected. Assuming first order reaction, \( n = 1 \).

The right-hand side of the equation is integrated and rearranged as
\[ (\text{ART}^2 / aE)[1 - (2RT/E)]e^{-E/RT} \]

Combining the above two equations and rearranging
\[ \gamma = \frac{\text{ART}^2}{aE} \left[ 1 - \frac{2RT}{E} \right] e^{-E/RT} \]

Logarithmic form of the above equation is
\[ \ln \left( \frac{\gamma}{T^2} \right) = \ln \left( \frac{\text{ART}}{aE} \right) \left[ 1 - \frac{2RT}{E} \right] - \frac{E}{RT} \]

Thus, in the plot of \( \ln(\gamma/T^2) \) against \( 1/T \) the slope is \( (-E/R) \) from which the activation energy can be calculated. Since the intercept is dependent on the order of the reaction and pre exponential factor, the reaction order must be determined. Generally, for the decomposition of polymers the reaction order is assumed to be first order.\(^{13}\)

### 2.3. Characterization

Elemental analysis of crude oils obtained from batch scale runs and the corresponding distillate fractions was conducted in duplicate. Oxygen was calculated by mass balance closure. Heating value was calculated using Dulong’s formula.\(^{13}\) Other characterizations including boiling point distribution, and molecular weight (MW) and poly dispersity index (PDI) which is the ratio of the molecular weight to molecular number) were determined for both the crude oil and its distillates by gas chromatography flame ionization detector (GC-FID) and size exclusion chromatography (SEC) as reported by Vardon et al.\(^{34}\) Chemical functionality information was obtained by analyzing the fractions using Fourier-Transform infrared (FT-IR) and nuclear magnetic resonance (NMR) spectroscopies as reported by Sharma et al.\(^{13}\) Fuel properties including acid value (AV), cold filter plugging point (CFPP), density, flash point (FP), higher heating value (HHV), induction point (IP), kinematic viscosity (KV), lubricity, pour point (PP), specific gravity (SG), and sulfur content were determined following ASTM, AOCS and CEN standard test methods described elsewhere.\(^{13}\)

### 3. RESULTS AND DISCUSSION

#### 3.1. Interaction between Parameters

Isothermal TGA runs were conducted on the plastic samples based on the CCD experimental design (Supplemental Table 1) to determine the interaction between the variables. Conversion was determined for all of the conducted experiments eq 5.

The representative contours for the conversion are shown graphically in Figures 1a, 1b and 1c. Figures 1a and 1b are identical, while Figure 1c is different from the others indicating that 1) conversion is mainly dependent on temperature and time and 2) the carrier gas flow rate and the feed quantity have minimal effect. Results from the present study are in agreement with previous studies that temperature and time are the most significant controlling factors influencing yield.\(^{13}\) TGA runs were conducted on finely powdered and course samples to determine the effect of particle size on conversion. It was observed that nitrogen gas flow rate, feed quantity and particle size had no substantial effect on the yield. Thus, these parameters were not considered for further investigation.

Nonisothermal TGA experiments were conducted on the catalysts and their thermal stability was assessed by continuously recording the weight loss at a ramp rate of 10 \(^{o}\)C/min. All five catalysts showed weight loss around 100 \(^{o}\)C, which indicated moisture loss. The weight loss was more pronounced for magnesium carbonate (Figure 2). MCM-41 was more thermally stable relative to other catalysts. It can be seen from the thermograms that catalytic degradation over the temperature range except for MgCO3 is less pronounced with an average total weight loss of about 30%.

#### 3.2. Kinetics

The degradation of plastics was studied in the absence of catalyst and these results are presented in Figure 3. The degradation of all the investigated plastics occurred at a temperature range between 400 and 450 \(^{o}\)C. As is evident from the Figure 3, the degradation behaviors of HDPE from a MRF facility, landfill liners (PE) and PP are similar, but PUF and PS are different. The differences in the TG curves of different plastic types (PUF, PP, PE and PS) are attributed to the different macromolecular structure and depolymerization mechanism of those macromolecular structures. The difference in the degradation temperature of the three types of polymers (PP, PE and HDPE) is not very large with PP being less resistant to decomposition compared to HDPE. The higher degradation temperature of PE and PP is likely due to the higher activation energy of depolymerization (294 kJ/mol for PE and 182 kJ/mol for PP) (Table 2). These activation energies are in agreement with previous literature data of 280–350 kJ/mol for PE and 190–220 kJ/mol for PP.\(^{35,36}\) The decomposition temperature and activation energies were lower for catalytic reactions (Table 2). In an earlier study, linear chain polymers were observed to decompose with more difficulty than the branched chain polymers and the removal of side chain branches accelerated the overall degradation process.\(^{35}\)

#### 3.3. Catalyst Screening

The five catalysts were screened for all of the polymer types using TGA (Figure 3). The degradation temperature was lowered for all polymer types in the presence of catalysts. No significant correlation between conversion and catalyst type was observed. However, a distinct decrease in degradation temperature is noted (Figure 3), thereby indicating that the catalysts are polymer specific. For instance, Y-zeolites gave better performance for PE and PP, while spent FCC and sulfated zirconia catalysts were more effective for thermal degradation of PS and PUF (Table 2). These results are in agreement with previous studies such as zeolites catalytic cracking of PE and PP as reported by Ali and Qureshi, Angyal.\(^{37,38}\) Zeolites are extensively studied owing to...
Figure 3. Catalysts screening using TGA.

Table 2. Kinetic Parameters Comparison with and without Catalysts

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Medicine bottle</th>
<th>Landfill Liners</th>
<th>Polyurethane waste</th>
<th>Packing material</th>
<th>PE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No catalyst</td>
<td>catalyst</td>
<td>No catalyst</td>
<td>catalyst</td>
<td>No catalyst</td>
</tr>
<tr>
<td>T10 (°C)</td>
<td>390</td>
<td>290</td>
<td>443</td>
<td>384</td>
<td>243</td>
</tr>
<tr>
<td>T50 (°C)</td>
<td>422</td>
<td>352</td>
<td>462</td>
<td>425</td>
<td>343</td>
</tr>
<tr>
<td>T90 (°C)</td>
<td>436</td>
<td>377</td>
<td>476</td>
<td>431</td>
<td>408</td>
</tr>
<tr>
<td>Activation Energy, E (kJ/mol)</td>
<td>182</td>
<td>113</td>
<td>294</td>
<td>169</td>
<td>30</td>
</tr>
<tr>
<td>Significance (R²)</td>
<td>0.90</td>
<td>0.99</td>
<td>0.97</td>
<td>0.87</td>
<td>0.93</td>
</tr>
</tbody>
</table>

*Note: T10, T50, and T100 are the temperatures at which 10%, 50%, and 90% conversion occurred.*
their superior acidic properties. Mixed plastics including PS, PP, PE, PE terephthalate (PET) and polyvinyl chloride (PVC) studied over ZSM-5 was reported to promote gas production, lower MW and higher aromatic containing liquids at low temperatures. Puente et al. (1998), studied the effect of various catalysts including FCC catalyst on PS cracking and indicated that FCC showed a better product distribution in terms of gasoline composition. Spent FCC catalysts have also been studied and compared to that of fresh catalysts for PP cracking. Catalysts are generally selected based on feedstock and desired end product.

All catalysts, except the MCM-41, enhanced the degradation of PP. Zeolite-Y catalyst was found to be most effective in reducing the T_{max} for degradation of PE and PP. The MCM-41 and FCC catalysts had almost no effect on PP degradation although a small change in the temperature profile was noticed for FCC spent catalyst. The number of acid sites on a solid catalyst plays a key role in the catalytic degradation rate of polyolefins. Acid number increases with increasing aluminum incorporation into the zeolite crystal. Another influence on polyolefin degradation using microporous materials is the catalyst pore size. The number of acid sites that are available for polymer cracking increases with the catalyst amount, thereby enhancing the degradation reactions.

The overall conversion for PUF was about 60% in the absence of a catalyst. However, in the presence of catalyst conversion increased by another 10–15%. Sulfated Zirconia provided better conversions at lower temperature likely due to the strong acidic nature of the catalyst. This trend can also be attributed to the acid sites that are available for polymer cracking. Although all five catalysts supported PS thermal degradation, spent FCC catalysts would be the more logical to use from an economical standpoint. The spent FCC catalyst can catalyze the reaction and achieve a similar conversion at a lower temperature relative to the other catalysts.

### 3.4. Optimization of Temperature and Time.

In order to determine the optimum conditions, RSM was developed with reaction temperature and time as controlling factors at five different levels. Fourteen experiments were conducted with six center points. These results are summarized in Table 3 and Figures 4. Finely powdered PP was mixed with Y-zeolites in 10:1 ratio and isothermal TGA runs were conducted as per the experimental design from CCD (Table 3). The conversion increased as a function of both time and temperature. At a temperature of 450 °C, a conversion of about 90% was attained within 0.5 h after the reaction was initiated. At higher temperatures (500 and 550 °C), 99% conversion was obtained within 15 min after the reaction was started. However, at lower temperatures of 400–450 °C and with sufficient residence time over 45 min, a similar conversion was obtained to that of 450 °C and 30 min. RSM plots provided the optimum pyrolysis conditions. Although the other four polymers were not subjected to optimization runs, process variables such as temperature and time can be reasonably estimated from nonsothermal TGA runs for different catalysts.

### 3.5. Validation of TGA via Batch Scale Runs.

The final objective of the current study was to validate the TGA experiments using a batch scale waste plastic to crude oil pyrolysis unit. Two runs were conducted at 390 and 450 °C without catalysts and a third run at 390 °C in the presence of catalyst Y-zeolites (optimized from TGA runs) on MB waste plastic. Gases that evolved from the pyrolysis reactions were condensed, collected, and referred to as liquid fractions, while the solid fraction is the fraction that is left in the reactor and is collected during reactor cleanup, which includes a high boiling fraction and residues. The gaseous (low MW) fraction was calculated from mass balance closure. The liquid condensates were collected at various time intervals from 30 min to 2 h and the conversions were estimated at each time interval. These results are presented in Figure 5. The yield of the total liquid fraction was highest (about 81%) at 450 °C when the reaction was complete. At 390 °C, the yield of the liquid fraction was just 30% in the absence of a catalyst. The results from the two experiments show that 450 °C is slightly too high of a temperature for PP pyrolysis while 390 °C was too low, as only 30% conversion was achieved even after 2 h. However, increasing the reaction time to 5 h increased the conversion to about 80%. In the presence of catalyst at 390 °C, the yield of the liquid fraction increased to 78%. Conversion increased as a function of time and the reaction was complete at the end of 2 h in the presence of Y-zeolites, thus validating the TGA results. This yield is comparable to the yield obtained from the run at 450 °C, which was 60 °C higher than the catalytic run. Catalytic pyrolysis at lower temperature would be advantageous as it enhances cracking at lower temperatures, provides higher collection efficiency and also narrows product selectivity. However, the composition and quality of the obtained oil would vary depending on the catalysts and reaction condition. The crude oils obtained were also characterized for their chemical composition and fuel properties.

### 3.6. Chemical Characterizations.

#### 3.6.1. Elemental Compositions.

Elemental analysis indicated that PP was composed of about 85% carbon (C), 14% hydrogen (H) and 0.5% nitrogen (N). Crude oil and its distillates from both catalytic and noncatalytic pyrolysis had C, H and N values similar to that of the plastic itself (Table 4). The heating value calculated using Dulong’s formula was about 49.5 MJ/kg.

#### 3.6.2. Simulated Distillation.

The boiling point distribution analysis showed an increase in the motor gasoline fraction from catalytic pyrolysis, and higher diesel #1 and #2 fractions from the noncatalytic pyrolysis. The vacuum gas oil fraction was relatively low in the catalytic process likely due to the fact that the catalysts enhanced cracking (Figure 6). Distillation was conducted on the crude oil and the distillate fractional yields were comparable to that obtained from simulated distillations.
The fractions from the distillation were also analyzed for boiling point distributions to ensure purity of the distillate fraction (supplemental Figure 1).

**3.6.3. Size Exclusion Chromatography.** SEC analysis was conducted on the crude oil and on the distillates. The MWs of crude oils from catalytic and non-catalytic high temperature (450 °C) pyrolysis are comparable and were substantially higher than the crude oil obtained from pyrolysis at 390 °C. While this trend is quite contradictory, both the lower MW and PDI might be due to longer residence time (5 h at 390 °C) in the reactor compared to the other runs (3 h). PDI reflects variation in the compounds. The PDI for runs with >2 indicated that hydrocarbon molecules with different structures were formed. The PDIs for the distillate fractions ranged between 1.2 and 1.4, indicating a narrow distribution of MW (Table 4). These results were confirmed by simulated distillations (Supplemental Figure 1). All of the fractions obtained from pyrolysis at 390 °C (with no catalyst) had higher MW compared to that of motor gasoline and diesel #1 from pyrolysis at 450 °C and from the catalytic conversion likely due to the fact that higher temperature and the presence of catalysts enhance cracking.

**3.6.4. NMR and IR Analysis.** ¹H spectra provided information on hydrocarbon type in motor gasoline and diesel #1 fractions. The motor gasoline displayed high aliphatic functionality (¹H NMR 0.5−2.7 ppm), with ~90% of the spectral area located in this region (Table 5, Supplemental Figure 2). The proton percentage increased to >90% in the region between 0.5 ppm-2.7 ppm for crude oil obtained from catalytic pyrolysis. Plastic oil fractions obtained from non-catalytic pyrolysis had a higher percentage of alkenes (olefins) compared to catalytic runs (Supplemental Figure 2). No aromatic or oxygenated species such as carboxylic acids, aldehydes, ketones, ethers, or alcohols were detected.

FT-IR spectral analyses were conducted of the motor gasoline and diesel #1 fractions to support NMR analysis. The FT-IR spectra of the fractions from the catalytic run was dominated by alkane peaks. The peaks at 2,800−3,000 cm⁻¹ represent C−H stretching vibrations of the chemical functional groups −CH₃, −CH₂, and −CH, respectively (Supplemental Figure 2). The presence of C=C stretching vibrations at 1, 640−1,650 cm⁻¹ indicated the presence of alkenes. The peaks

![Figure 4. Optimization of temperature and time using RSM.](image1)

![Figure 5. Yield of different liquid fractions from batch scale runs on MB waste plastic (top); yield of main liquid fraction over time. The zeroth minute is the time when the reactor reached the set temperature.](image2)
at 2,800–3,000 and 1,320–1,480 cm\(^{-1}\) indicated the presence of a higher concentration of alkanes.

### 3.6.5. Fuel Properties of Gasoline and Diesel Fractions.

CP was higher in both the motor gasoline and diesel \#1 fractions obtained from catalytic pyrolysis. The PP was similar in all diesel \#1 fractions and was not detected for motor gasoline obtained from catalytic runs and noncatalytic runs at 390 °C. The derived cetane number (DCN) was slightly below 40, the minimum limitation given by ASTM D975 for diesel.\(^{13}\) The flash point of the diesel samples satisfied the minimum requirement of 52 °C set by ASTM D975. However, diesel \#1 obtained from pyrolysis at 450 °C had a lower flash point, possibly due to the higher content of shorter chain and lower MW constituents promoted by higher temperatures. The CFPPs of all of the motor gasoline and diesel samples were below the detection limit of our instrument (−50 °C).

#### Table 4. Chemical Composition of Plastic, MB Crude Oil, and Its Distillates

<table>
<thead>
<tr>
<th>Samples</th>
<th>Parameters</th>
<th>Elemental Properties</th>
<th>Calorific Value</th>
<th>GPC Molecular Weights</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C%</td>
<td>H%</td>
<td>N%</td>
</tr>
<tr>
<td>Plastic</td>
<td></td>
<td>85.4</td>
<td>14.5</td>
<td>0.1</td>
</tr>
<tr>
<td>Crude Oil</td>
<td>450 °C</td>
<td>85.0</td>
<td>14.5</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>390 °C (no catalyst)</td>
<td>85.3</td>
<td>14.6</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>390 °C (Y-zeolite)</td>
<td>85.0</td>
<td>14.7</td>
<td>0.3</td>
</tr>
<tr>
<td>Distillate Fraction</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Motor Gasoline (35–185 °C)</td>
<td>450 °C</td>
<td>85.7</td>
<td>14.3</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>390 °C (no catalyst)</td>
<td>85.6</td>
<td>14.4</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>390 °C (Y-zeolite)</td>
<td>85.5</td>
<td>14.5</td>
<td>0</td>
</tr>
<tr>
<td>Diesel #1 (185–290 °C)</td>
<td>450 °C</td>
<td>85.6</td>
<td>14.4</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>390 °C (no catalyst)</td>
<td>85.7</td>
<td>14.3</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>390 °C (Y-zeolite)</td>
<td>85.8</td>
<td>14.2</td>
<td>0</td>
</tr>
<tr>
<td>Diesel #2 (290–350 °C)</td>
<td>450 °C</td>
<td>85.6</td>
<td>14.3</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>390 °C (no catalyst)</td>
<td>85.7</td>
<td>14.2</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>390 °C (Y-zeolite)</td>
<td>85.8</td>
<td>14.3</td>
<td>0</td>
</tr>
<tr>
<td>Vacuum gas oil 350 °C +</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### Table 5. Distillate Fuel Properties of the of MB Plastic Crude Oils

<table>
<thead>
<tr>
<th>Methods</th>
<th>Motor gasoline</th>
<th>Diesel</th>
<th>Diesel</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MB450</td>
<td>MB390 (Y-zeolite)</td>
<td>MB450</td>
</tr>
<tr>
<td>Alkanes % NMR</td>
<td>89.8</td>
<td>90.7</td>
<td>94</td>
</tr>
<tr>
<td>Alkenes % NMR</td>
<td>10.2</td>
<td>9.3</td>
<td>6</td>
</tr>
<tr>
<td>Low temperature °C</td>
<td>−63.8</td>
<td>−73</td>
<td>−74</td>
</tr>
<tr>
<td>CP ASTM D5773</td>
<td>−74</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>PP ASTM D5949</td>
<td>−50</td>
<td>−50</td>
<td>−50</td>
</tr>
<tr>
<td>CFPP ASTM D6371</td>
<td>20.8 ± 3.1</td>
<td>6.6 ± 0.1</td>
<td>4.8 ± 0.1</td>
</tr>
<tr>
<td>IP, 110 °C h EN 15751</td>
<td>34.8</td>
<td>36.3</td>
<td>34.1</td>
</tr>
<tr>
<td>KV, 40 °C cSt ASTM D445</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>DCN ASTM D6890</td>
<td>na</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>Flash point °C ASTM D93</td>
<td>19.3</td>
<td>19.0</td>
<td>19.0</td>
</tr>
<tr>
<td>Wear scar, 60 °C μm ASTM D6079</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>SG, 15 °C ASTM D4052</td>
<td>0.391</td>
<td>0.391</td>
<td>0.391</td>
</tr>
<tr>
<td>Density, 15 °C kg/m³ ASTM D6371</td>
<td>0.378</td>
<td>0.378</td>
<td>0.378</td>
</tr>
<tr>
<td>Moisture ppm ASTM D6304</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>AV kg KOH/g ASTM D4809</td>
<td>45.8 ± 0.3</td>
<td>46.0 ± 0.5</td>
<td>46.1 ± 0.4</td>
</tr>
<tr>
<td>HHV MJ/kg ASTM D4809</td>
<td>20.4 ± 0.1</td>
<td>20.3 ± 0.1</td>
<td>20.4 ± 0.1</td>
</tr>
<tr>
<td>Surface tension at 25 °C mN/m</td>
<td>19.1 ± 0.1</td>
<td>19.0 ± 0.2</td>
<td>19.0 ± 0.1</td>
</tr>
</tbody>
</table>
diesel#1 obtained from noncatalytic runs at 450 °C met the minimum oxidative stability specified by EN 590 (induction period (IP), 110 °C) of 20 h. ASTM D975 does not specify limits for oxidative stability. IP was not performed for the motor gasoline samples because they were too volatile. Diesel #1 fractions from catalytic runs and the runs at 390 °C did not meet the minimum IP requirement. The KVs were similar in all catalytic runs. As was the case with petrodiesel, with the exception of the diesel motor gasoline samples because they were too volatile. Diesel period (IP), 110 °C met the minimum oxidative stability specifications. The KVs were similar in all motor gasoline fractions. The KV of the diesel #1 fraction was within the range of 1.9–4.1 cSt, as specified by ASTM D975 for petrodiesel, with the exception of the diesel #1 obtained from catalytic runs. As was the case with flash point, it is anticipated that the lower KV for this sample was due to the presence of shorter-chain, lower MW constituents, which are known to have lower KVs than longer-chain hydrocarbons. A maximum wear scar of 620 μm is specified as the upper limit for lubricity (60 °C) in ASTM D975 (Table 5). The wear scars for the diesel samples were well below the petrodiesel standard. Lubricity was not measured for the gasoline samples because they were too volatile for determination. The AV was negligible in all motor gasoline and diesel#1 samples. The HHV calculated by elemental content differed only up to 3 MJ/kg compared to HHV obtained using the ASTM method (bomb calorimetry). The HHV of the motor gasoline and diesel #1 samples were higher than that of ultralow sulfur diesel (ULSD) (45.15 MJ/kg). Density, specific gravity, and surface tension were similar for the diesel and motor gasoline samples, with diesel samples expectedly providing higher values than the gasoline samples. The one exception was surface tension for diesel obtained via catalytic pyrolysis was lower than the other diesel samples and similar to that of the gasoline samples. Once again, this was attributed to enhanced cracking during catalyzed pyrolysis resulting in a higher percentage of shorter-chain constituents relative to the other diesel samples.

4. CONCLUSIONS

Plastics such as prescription bottles (PP), hard to recycle HDPE from a MRF, landfill liners (PE), packing materials (PS), and waste PUF from an industrial plant were thermally decomposed in the presence and absence of catalysts. A statistical design of experiments (DOE) approach identified reaction temperature and time as the most important factors influencing product yield. Kinetics developed for both catalytic and noncatalytic processes showed a reduction in activation energy for the catalytic reactions. Y-zeolites enhanced PP and PE cracking while spent FCC and the sulfated zirconium catalysts were more suitable for PS and PUF, respectively. Reaction conditions were optimized using RSM developed from CCF using TGA, and validated through batch-scale runs. Pyrolysis of postconsumer medicine bottles (PP) and further characterization of the resulting crude oil and its distillate products demonstrate that catalysts lower the temperature of pyrolysis. Y-zeolite was determined to be an effective catalyst in lowering the pyrolysis temperature of PP by 60 °C (from 450 °C without catalysts to 390 °C). The fuel properties were better in the gasoline and diesel obtained from catalytic pyrolysis than in that obtained from noncatalytic pyrolysis at the same temperature. Catalysts enhanced cracking at lower temperatures and narrowed the MW (hydrocarbon) distribution in the crude oil. Chemical characterization of the crude oils indicated an increased gasoline fraction in oils obtained in the presence of a catalyst compared to ones in the absence of a catalyst. The fuel properties of the diesel-range fraction were comparable to ULSD. Overall, our results show that catalysts lower the pyrolysis temperature, improve the selectivity of motor gasoline, and produce fuel with better quality.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.energyfuels.5b01083.

Table showing the coded and actual experimental conditions of the central composite design, and bar graph of the boiling point distribution of MB distillates from GC-FID (PDF)

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Notes

Disclosure: Mention of trade names or commercial products in this publication is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the U.S. Department of Agriculture. USDA is an equal opportunity provider and employer. The authors declare no competing financial interest.

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REFERENCES


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