Tertiary recycling of commingled polymer waste over commercial FCC equilibrium catalysts for producing hydrocarbons

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ABSTRACT

A mixture of post-consumer polymer waste (PE/PP/PS) was pyrolysed over cracking catalysts using a fluidising reaction system similar to the FCC process operating isothermally at ambient pressure. Greater product selectivity was observed with a commercial FCC equilibrium catalyst (FCC-E1) with about 53 wt% olefin products in the C3–C6 range. Experiments carried out with various catalysts gave good yields of valuable hydrocarbons with differing selectivity in the final products dependent on reaction conditions. A kinetic model based on a lumping reaction scheme for the observed products and catalyst coking behaviours has been investigated. The model gave a good representation of experiment results. This model provides the benefits of lumping product selectivity, in each reaction step, in relation to the performance of the catalyst used and particle size selected as well as the effect of operation conditions, such as rate of fluidising gas and reaction temperature. It is demonstrated that under appropriate reaction temperatures and suitable catalysts can have the ability to control both the product yield and product distribution from polymer degradation, and can potentially lead to a cheaper process with more valuable products.

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1. Introduction

The recycling of polymer waste is important in the conservation of resources and the environment [1]. The destruction of wastes by incineration is prevalent, but is expensive and often generates problems with unacceptable emissions. It is also undesirable to dispose of waste plastics by landfill due to high costs and poor biodegradability. If one accepts that landfill storage is not the most rational solution and can only be considered as provisional, then one is left with the most desired primary and secondary waste recycling processes. However, these are limited to present technical limitations for the treatment of mixed polymer wastes, together with the limited size of the market for recycled products, difficulties in maintaining product quality, and fluctuations in the price. Owing to these limitations, tertiary, chemical or feedstock recycling is growing in importance [2]. Therefore, tertiary recycling, i.e., thermal and/or catalytic conversion of waste polymers into fuels or chemicals, has been recognised as an ideal approach and could significantly reduce the net cost of disposal [3].

Two main chemical recycling routes are the thermal and catalytic degradation of waste polymers. Thermal cracking or pyrolysis is a well-known technique and is often used in petrochemical processing. The pyrolysis of waste polymers is the thermal decomposition in the absence of oxygen and is carried out in vessels, shaft kilns, autoclaves, rotary kilns, screw conveyors or fluidised beds [4–6]. However, the thermal degradation of polymers to low molecular weight materials has a major drawback in that a very broad product range is obtained. In addition, these processes require high temperatures typically more than 500 °C and even up to 900 °C. These facts strongly limit their applicability and especially increase the higher cost of feedstock recycling for waste plastic treatment. Catalytic pyrolysis is being investigated as a means to address these problems [7–9]. Catalysts can promote the degradation reaction to occur at lower temperatures, which implies lower energy consumptions. Moreover, the shape selectivity exhibited by certain catalysts allows the formation of a narrower distribution of products, which can be directed towards fuels, chemicals and valuable hydrocarbons with higher market values. The catalytic degradation of polymeric materials has been reported for a range of model catalysts centred around the active components in a range of different catalysts, including zeolite based such as ZSM-5, BEA, USY, MOR, and modified nanocrystalline of Y, and ZSM-5 [10–17], amorphous silica–aluminas (ASA) [18–20], and the family of mesoporous MCM materials [21–23]. However, these catalysts have been used that even if performing well, they can be uneconomic from the point of view of practical use due to the cost of manufacturing and the high sensitivity of the process to the cost of the catalyst. An economical improvement of processing the
recycling via catalytic cracking would operate in mixing the polymer waste with fluid catalytic cracking (FCC) commercial catalysts. To date, the catalyst used in the FCC process comprises 5–40% zeolite dispersed in a matrix of synthetic silica–alumina, semi-synthetic clay-derived gel, or natural clay. These catalysts increase significantly the commercial potential of a recycling process based on catalytic degradation, as cracking catalysts could cope with the conversion of polymer waste co-fed into a refinery FCC unit. It is certainly possible to develop commercial processes based on these approaches [24,25].

Studies of the effects of catalysts on the catalytic degradation of polymer have been performed by contacting melted polymer with catalyst in fixed bed reactors [11–14], passing the products of polymer pyrolysis through fixed bed reactors containing cracking catalysts [15–18] and heating mixtures of polymer and catalyst powders in reaction vessels [19–22]. However, the configuration of the pyrolysis–refining reactors poses serious engineering and economic constraints. For the study of these pyrolysis-refining reactions, it is difficult to measure the exact mass-flow rate of the reactant from the pyrolysis to catalytic zones, and consequently it is virtually impossible to identify and quantify the reactant and to control its quality. It is difficult to develop a kinetic model of the reaction which is an integral requirement in the design and scale-up of the catalytic reactor. Also, the use of fixed beds or adiabatic batch where polymer and catalyst are contacted directly leads to problems of blockage and difficulty in obtaining intimate contact over the whole reactor. Without good contact the formation of large amounts of residue is likely, and scale-up to industrial scale is not feasible. Additionally, most of the studies have been employed for catalytic recycling of typically pure polymer such as linear low-density polyethylene (LLDPE), low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP), and polyethylene (PS), over various cracking catalysts [10–26]. It seems that in the process of polymer pyrolysis, a particular kind of catalyst is effective for a particular kind of polymer. Unfortunately it can only be applied to pure polymers and mixed polymer wastes are not recommended. A more difficult task is tertiary recycling of commingled post-consumer polymer waste since it consists of not only hydrocarbons but also nitrogen- and sulfur-containing mixed polymers as well as some modified materials. Potential concepts have been investigated in our group using a laboratory catalytic fluidised-bed reactor to study the product distribution and selectivity of catalytic degradation of several different textiles of post-consumer polymer mixtures [27,28]. However, papers concerning kinetic modeling of catalytic process for polymer degradation have great limitations, which are shared with the study of other complex reaction schemes such as catalytic cracking and reforming. An interesting approach is that of adding mixture of polymer waste into the FCC process, under suitable process conditions with the use of FCC commercial catalysts, a large number of waste polymers can be economically converted into valuable hydrocarbons. Therefore, the objective of this work is to explore the capabilities of a catalytic fluidising pyrolysis system similar to the FCC process with the use of an FCC equilibrium catalyst (FCC-E1) for the study of product distribution and selectivity on the catalytic degradation of mixture of post-consumer polymer waste, and specifically for identification of suitable reaction conditions for enhancing the potential benefits of catalytic polymer recycling.

2. Experimental

2.1. Materials and experimental procedures

The commingled polymer waste used in this study was obtained from post-consumer plastic waste stream in South Taiwan with the component of polyethylene (~54 wt% PE = ~39 wt% HDPE + ~25 wt% LDPE), polypropylene (~34 wt% PP) and with about 2 wt% polystyrene (PS) mixtures. Typically, the content of waste plastic sample tested by elemental analysis was about 86.54% C, 12.95% H, 0.16% O, 0.22% N, and 0.13% S. The catalysts employed and their textural properties are given in Table 1. Surface area, pore volume and pore size distribution were measured from the adsorption–desorption isotherms of nitrogen at 77 K on a Micromeritics ASAP 2020 apparatus. Total surface area of the catalysts was estimated by application of the BET equation and total pore volumes from the nitrogen adsorbed at p/p0 = 0.99. Pore size distribution was obtained following the BJH model, whereas the micropore specific surface area and the micropore volume were calculated by the t-plot method. The external specific area (i.e. macropore and mesopore surface areas) used in this work was determined by the difference between the total area and the micropore area. All the catalysts were crushed, pelleted and sieved to give particle sizes ranging from 75 to 180 μm. The catalyst (~0.25 g) was then dried by heating in flowing nitrogen (50 ml min−1) to 120 °C at 60 °C h−1. After 2 h the temperature was increased to 520 °C at a rate of 120 °C h−1 to activate the catalyst for 5 h. In contrast with the micrometer size of the crystals in conventional zeolites, ZSM-5 and USY used in this work synthesised with smaller crystallite sizes present a high proportion of external surface, which accounts for approximately 10–20% of the total zeolite surface area. High-purity nitrogen was used as the fluidising gas and the flow was controlled by a needle valve and pre-heated in the bottom section of the reactor tube. Before catalytic pyrolysis experiments were started, several fluidisation runs were performed at ambient temperature and pressure to select (i) suitable particle sizes (both catalyst and polymer waste) and (ii) optimise the fluidising gas flow rates to be used in the reaction. The particle size of both catalyst (75–180 μm) and polymer (75–250 μm) was chosen to be large enough to avoid entrainment but

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Si/Al</th>
<th>Pore size (nm)</th>
<th>Surface area (m² g⁻¹)</th>
<th>Pore volume (m³ g⁻¹)</th>
<th>Commercial name</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Total</td>
<td>Micropore</td>
<td>External</td>
</tr>
<tr>
<td>ZSM-5</td>
<td>17.5</td>
<td>0.55 ± 0.51</td>
<td>426</td>
<td>263</td>
<td>128</td>
</tr>
<tr>
<td>USY</td>
<td>13.6</td>
<td>0.74</td>
<td>547</td>
<td>429</td>
<td>118</td>
</tr>
<tr>
<td>FCC-E1</td>
<td>2.1</td>
<td>3.28</td>
<td>386</td>
<td>295</td>
<td>91</td>
</tr>
<tr>
<td>MCM-41</td>
<td>14.3</td>
<td>4.2–5.2d</td>
<td>775</td>
<td>0</td>
<td>775</td>
</tr>
<tr>
<td>ASA</td>
<td>6.6</td>
<td>3.38–4.6</td>
<td>268</td>
<td>21</td>
<td>247</td>
</tr>
</tbody>
</table>

a Total surface area (BET).
b Chinese Petroleum Corp., CPC, Taiwan, ROC.
c The FCC-E1 catalyst used in this study is a fresh equilibrium catalyst obtained from a commercial FCC unit with different levels of rare earth oxide (1.3 wt% REO), a mixture of Y zeolite, a silica–alumina matrix (32.5 wt% Al₂O₃) and binder.
d Single-point BET determined.
e Synthesised by procedure outlined by Beck et al. [29].
f Crosfield Chemicals, Warrington, UK.
not too large as to be inadequately fluidised. High flow rates of fluidising stream improve catalyst–polymer mixing and external heat transfer between the hot bed and the cold catalyst. On the other hand, an excessive flow rate could cause imperfect fluidisation and considerable entrainment of fines. Hence, velocities in the range 1.5–4 times the value of the minimum fluidation velocity of catalyst ($U_{mf}$) were used in the course of this work.

2.2. Experimental procedures and product analysis

A process flow diagram of the experimental system is given elsewhere [9,10] and shown schematically in Fig. 1. A three-zone heating furnace with digital controllers was used and the temperatures of the furnace in its upper, middle and bottom zones were measured using three thermocouples. By these means the temperature of the pre-heated nitrogen below the distributor and catalyst particles in the reaction volume could be effectively controlled to within ±1 °C. The polymer feed system was designed to avoid plugging the inlet tube with melted polymer and to eliminate air in the feeder. The feed system was connected to a nitrogen supply to evacuate polymer into the fluidised catalyst bed. Thus, commingled polymer particles were purged under nitrogen into the top of the reactor and allowed to drop freely into the fluidised bed at $t = 0$ min. At sufficient polymer–catalyst ratios (more closer resembling FCC conditions) the outside of the catalyst particles is not wet with polymer, so the catalyst particles move freely.

Volatil e products leaving the reactor were passed through a glass-fiber filter to capture catalyst fines, followed by an ice-acetone condenser to collect any condensable liquid product. A three-way valve was used after the condenser to route product either into a sample gas bag or to an automated sample valve system with 16 loops. The Tedlar bags, 15 L capacity, were used to collect time-averaged gaseous samples. The bags were replaced at intervals of 10 min throughout the course of reaction. The multiport sampling valve allowed frequent, rapid sampling of the product stream when required. Spot samples were collected and analyzed at various reaction times ($t = 1, 2, 3, 5, 8, 12, 15, 20$ min). The rate ($R_{gp}$, wt% min$^{-1}$) of hydrocarbon production of gaseous products collected by automated sample system in each run was defined by the relationship:

$$R_{gp} = \text{hydrocarbon production rate of gaseous products in each spot run (g min$^{-1}$)} \times 100/\text{total hydrocarbon production of gaseous products over the whole spot runs (g)}$$

Gaseous hydrocarbon products were analyzed using a gas chromatograph equipped with a thermal conductivity detector (TCD) fitted with a 1.5 m × 0.2 mm i.d. Molecular Sieve 13X packed column and a flame ionization detector (FID) fitted with a 50 m × 0.32 mm i.d. PLOT Al$_2$O$_3$/KCl capillary column. A calibration cylinder containing 1% C$_1$–C$_5$ hydrocarbons was used to help identify and quantify the gaseous products. The solid remaining deposited on the catalyst after the catalytic degradation of the polymer was deemed “residues” and contained involatile products and coke. The amount and nature of the residues was determined by thermogravimetric analysis (TGA). A number of runs were repeated in order to check their reproducibility. It was found that the experimental error was within ±5%.

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2.3. Kinetic modeling

A four-lump model was proposed which separately takes into account the unconverted feedstock, gasoline, light gases and coke lumps and is considered to represent the product distributions. On the basis of the proposed reaction pathway shown in Fig. 2, this model can be adopted for simulation of the fluidised-bed reactions. The individual rate constants are conveniently grouped as follows:

\[ k_0 = k_1 + k_3 \]  
\[ k_1 = k_{11} + k_{12} \]  
\[ k_2 = k_{21} + k_{22} \]

where \( k_0 \) is the overall cracking rate constant, \( k_1 \) and \( k_2 \) are the individual disappearance rate constants from the four-lump scheme. The kinetic expression of the four-lump reaction may be written as

\[ r_i (i = A, B, C, D) = k_i \times W_i^\eta_i \times \eta_i \]  

where \( r_i \) is the rate of consumption of the \( i \)th lump, \( k_i \) is the rate constant of the \( i \)th lump, \( W_i \) is the weight fraction of the \( i \)th lump, \( \eta_i \) is the catalyst activity decay of the \( i \)th lump, \( n_i \) is the reaction order and suffixes A–D refer to unconverted polymer, gasoline, light gases and coke. An exponential decay function with activity decaying as a function of coke on catalyst was employed [30].

\[ \eta = \exp[-aC(c)] \]

where \( C(c) \) is coke content deposited on the catalyst. It is assumed that all sites leading to the generation of unconverted polymer, gasoline, light gases, or coke are deactivated at the same rate.

\[ \eta = \eta_A = \eta_B = \eta_C = \eta_D \]  

Eqs. (7)–(10) were obtained with a first-order reaction and catalyst deactivation involving four simultaneous equations describing the evolution of unconverted polymer lump (A), the gasoline lump (B), the light gases lump (C), and the coke lump (D).

\[ -dW_A/dt = \eta k_0 W_A = \eta (k_1 + k_3) W_A \]  
\[ dW_B/dt = \eta (k_{11} W_A - k_{21} W_B) = \eta (k_{11} W_A - k_{21} W_B - k_{22} W_B) \]  
\[ dW_C/dt = \eta (k_{12} W_A + k_{21} W_B) \]  
\[ dW_D/dt = \eta (k_3 W_A + k_{22} W_B) \]

The mass balance can be written as follows:

\[ -dW_A/dt = dW_B/dt + dW_C/dt + dW_D/dt \]

Eqs. (7)–(11) were numerically integrated by a fourth-order Runge-Kutta algorithm for the four lumps linked with the calculation programme to minimise the sum of the square deviations between the calculated and the experimental results. This gave values for the apparent rate constants.

3. Results and discussion

3.1. Degradation of commingled polymer waste (PE/PP/PS) over various catalysts

Catalytic pyrolysis products (P) are grouped together as hydrocarbon gaseous (<C5), liquids (gasoline (C5–C9), condensate in condenser and captured in filter and BTX) and residues (coke and products, involatile at reaction temperature, deposited on catalyst) to enable the overall pyrolysis processes to be described more easily. The term "yield" as used in this paper is defined by the relationship

\[ \text{yield (wt\%)} = (P(g) \times 100)/\text{polymer fed (g)} \]

Both the carbon number distribution of the products of polymer waste cracking at 390 °C over various catalysts and the nature of the product distribution were found to vary with the catalyst used. As shown in Table 2, the yield of volatile hydrocarbons for zeolitic microporous catalysts (ZSM-5 = USY) gave higher yield than zeolite-based equilibrium FCC catalyst (FCC-E1) and non-zeolitic mesoporous catalysts (MCM-41 = ASA), and the highest was obtained for ZSM-5 (nearly 90 wt%). Some similarities were observed between ZSM-5 and FCC-E1 with C1–C4 and C5–C9 yields, which were approximately 50–53 wt% and 37–39 wt% respectively. However, with MCM-41 and ASA the C1–C4 and C5–C9 yields were approximately 24–28 wt% and 55–57 wt%, respectively.

The bulk of the products observed with these acidic cracking catalysts was in the gaseous and liquid phase with less than 17 wt% solid residues of involatile residue and coke collected. Greater product selectivity was observed with FCC-E1 with about 53 wt% olefin products in the C3–C6 range. USY produced more paraffinic product selectivity was observed with FCC-E1 with about 53 wt% olefin products in the C3–C6 range. USY produced more paraffinic products, involatile at reaction temperature, deposited on catalyst.

3.2. Product selectivity variation with reaction conditions

The influence of operation conditions including reaction temperatures, flow rates of fluidising gas (300–900 ml min⁻¹) and
catalysts (catalyst to polymer ratio 20 wt% and catalyst particle size 125–180 μm). The whole reaction with the polymer being degraded over 20 min. The rate of hydrocarbon production was significantly lower throughout higher temperatures. At 450°C compared in Fig. 4 and as expected, faster rates were observed at low flow rates (high contact times for primary products), secondary products are observed with increased amounts of coke precursors (BTX) although the overall degradation rate is slower as shown by increasing amounts of partially depolymerised residual products (Table 3).

Equilibrium ratios of i-butane/n-butane and i-butene/n-butane were predicted using Gibbs free energy minimisation on the PRO/II flowsheets package for the temperatures used experimentally and are presented alongside the corresponding experimental results in Table 4. The i-butene/n-butene ratio is very close to the predicted equilibrium values and thus the reactions involved in the production and interconversion of butenes are very fast over FCC-E1 catalyst, and their ratio is primarily equilibrium controlled. The i-butane/n-butane ratio reflects the involvement of tertiary C4 carbenium ions in bimolecular hydrogen-transfer reactions and since tertiary carbenium ions are more stable than primary ions, a higher ratio of i-butene is expected. As shown in Table 4, the observed i-butane/n-butane ratios are well above calculated equilibrium values and the high ratio is consistent with the cracking of waste degradation good mixing is required, with a dramatic drop-off in the rate of degradation observed only at the lowest fluidising flow used (300 ml min⁻¹). Furthermore, changing the fluidising flow rate influences the product distribution. As more flow rate was increased, lower C1–C4 hydrocarbon gases’ yields but higher liquid yields and involatile products were observed. On the other hand, at low flow rates (high contact times for primary products), secondary products are observed with increased amounts of coke precursors (BTX) although the overall degradation rate is slower as shown by increasing amounts of partially depolymerised residual products (Table 3).

Table 2
Summary of the main products of post-consumer polymer mixture (PE/PP/PS) degradation at reaction temperature of 390°C over various catalysts (fluidising N₂ rate 570 ml min⁻¹, catalyst to polymer ratio 20 wt% and catalyst particle size 125–180 μm).

<table>
<thead>
<tr>
<th>Degradation results</th>
<th>Catalyst type</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ZSM-5</td>
</tr>
<tr>
<td>Yield (wt% feed)</td>
<td></td>
</tr>
<tr>
<td>Gaseous (C₁–C₄)</td>
<td>53.3</td>
</tr>
<tr>
<td>Liquid</td>
<td>36.6</td>
</tr>
<tr>
<td>Gasoline (C₅–C₉)</td>
<td>31.9</td>
</tr>
<tr>
<td>Condensate liquid</td>
<td>3.7</td>
</tr>
<tr>
<td>BTX</td>
<td>0.9</td>
</tr>
<tr>
<td>Styrene</td>
<td>0.8</td>
</tr>
<tr>
<td>Residue</td>
<td>10.1</td>
</tr>
<tr>
<td>Involatile residue</td>
<td>8.5</td>
</tr>
<tr>
<td>Coke</td>
<td>1.6</td>
</tr>
</tbody>
</table>

Distribution of C₁–C₉ hydrocarbon products (wt% feed) |
<table>
<thead>
<tr>
<th>C₁</th>
<th>C₂</th>
<th>C₃</th>
<th>C₄</th>
<th>C₅</th>
<th>C₆</th>
<th>C₇</th>
<th>C₈</th>
<th>C₉</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>0.8</td>
<td>3.2</td>
<td>15.6</td>
<td>7.6</td>
<td>21.6</td>
<td>3.4</td>
<td>8.7</td>
<td>5.3</td>
</tr>
<tr>
<td>0.1</td>
<td>0.4</td>
<td>1.3</td>
<td>6.6</td>
<td>12.3</td>
<td>20.5</td>
<td>5.5</td>
<td>9.3</td>
<td>5.3</td>
</tr>
<tr>
<td>0.1</td>
<td>0.7</td>
<td>2.9</td>
<td>16.4</td>
<td>8.2</td>
<td>25.5</td>
<td>5.5</td>
<td>9.5</td>
<td>5.3</td>
</tr>
<tr>
<td>0.7</td>
<td>0.8</td>
<td>2.3</td>
<td>6.3</td>
<td>12.3</td>
<td>15.5</td>
<td>3.7</td>
<td>9.5</td>
<td>4.6</td>
</tr>
<tr>
<td>0.2</td>
<td>0.8</td>
<td>1.7</td>
<td>6.3</td>
<td>12.3</td>
<td>15.5</td>
<td>3.7</td>
<td>9.5</td>
<td>4.6</td>
</tr>
<tr>
<td>0.1</td>
<td>0.2</td>
<td>0.1</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
</tr>
</tbody>
</table>

- Condensate liquid: condensate in condenser and captured in filter.
- BTX: benzene, toluene and xylene.
- Residue: coke and involatile products.
- Less than 0.01 (wt%); n.d.: not detectable.

Fig. 4. Comparison of hydrocarbon yields as a function of time at different reaction temperatures for the catalytic degradation of post-consumer polymer mixture (PE/PP/PS) over FCC commercial catalyst (FCC-E1) (rate of fluidisation gas = 600 ml min⁻¹, catalyst to polymer ratio = 20 wt% and catalyst particle size = 125–180 μm).

Fig. 5. Comparison of hydrocarbon yields as a function of time at different fluidisation temperatures for the catalytic degradation of post-consumer polymer mixture (PE/PP/PS) over FCC commercial catalyst (FCC-E1) (rate of fluidisation gas = 600 ml min⁻¹, catalyst to polymer ratio = 20 wt% and catalyst particle size = 125–180 μm).
increased bimolecular hydrogen transfer in the order: of the zeolite-based FCC-E1 catalyst and zeolite catalysts resulted in limited within its structure. By comparison, the stronger acid sites which lead to the production of saturated compounds are sterically olefins with zeolites were expected since bimolecular reactions broadest carbon range of hydrocarbons. The observed yields of (ASA (o/p $= 4.16$) and gave rise to the production of saturated compounds are sterically limited within its structure. By comparison, the stronger acid sites of the zeolite-based FCC-E1 catalyst and zeolite catalysts resulted in increased bimolecular hydrogen transfer in the order:

\[
\text{FCC-E1 (} \frac{\sum \text{olefin}}{\sum \text{paraffin}}: o/p = 3.17) \quad < \quad \text{ZSM-5 (} o/p = 2.69) \quad < \quad \text{USY (} o/p = 0.73)
\]

The observed $i$-butane/$n$-butane ($i$-$C_4$/-$n$-$C_4$) ratios at $390 \, ^\circ C$ are consistent with the steric constraints of their structures following the order:

\[
\text{ZSM-5 (} i$-$C_4/n$-$C_4 = 3.25)/\text{FCC-E1 (} i$-$C_4/n$-$C_4 = 4.14) \quad < \quad \text{USY (} i$-$C_4/n$-$C_4 = 6.52)
\]

The selectivity could be varied by changes in different operating conditions used in this study. In Table 4, at fast flow rates, primary cracking products are favoured as evidenced by the increasing ratios of $i$-butene/$\sum$butenes ($i$-$C_4$/-$\sum$-$C_4 = 0.45$ in $300 \, \text{ml min}^{-1} \, N_2$ fluidising rate versus $i$-$C_4$/-$\sum$-$C_4 = 0.57$ in $900 \, \text{ml min}^{-1} \, N_2$ fluidising rate) and $\sum$olefin/$\sum$paraffin ($o/p = 2.61$ in $300 \, \text{ml min}^{-1} \, N_2$ fluidising rate versus $o/p = 3.79$ in $900 \, \text{ml min}^{-1} \, N_2$ fluidising rate).

Additionally, further evidence of the increase in the reaction of bimolecular hydrogen transfer, in the experimental range, was seen in the lowering of the $\frac{\sum \text{olefin}}{\sum \text{paraffin}} (o/p = 3.52$ at $330 \, ^\circ C$ versus $o/p = 2.86$ at $450 \, ^\circ C)$ and $i$-butane/$n$-butane ($i$-$C_4/n$-$C_4 = 5.62$ at $330 \, ^\circ C$ versus $i$-$C_4/n$-$C_4 = 3.23$ at $450 \, ^\circ C$) ratios as temperature increases.

3.3. Kinetic results and discussion

The four-lump model was used to predict product distributions for the degradation of polymers over FCC-E1 under the operating conditions of the fluidised-bed reaction. As shown in Figs. 6 and 7, it shows that the calculated values using various catalysts are in good agreement with the experimental data. Additionally, in Tables 5 and 6 the model gives a good prediction for the correlation coefficient calculated between theoretical and experimental results from the degradation of commingled polymer waste over fluidised cracking catalysts. While $k_2 = k_{21} + k_{22}$ reflects gasoline overcracking, those two constants have in practice very different magnitudes, $k_{21} > k_{22}$, and consequently, $k_{21}$ was the only overcracking constant considered further in the analysis. The effect of different catalysts on the kinetic parameters obtained from the lumping scheme is summarised in Table 5. The lumping rate constants for each reaction step is found to be affected by the microstructure of catalysts with the larger pore size material resulting in smaller rate constants, under the same reaction conditions. The $k_{11}$ value for the catalysts used in this study was higher for zeolites (ZSM-5 and FCC-E1) than for ASA, while the $k_{12}$ value for FCC-E1 was higher than for ASA, but much lower than for ZSM-5. This suggests that the value of both $k_{11}$ and $k_{12}$ for the catalysts used in this study for the given reaction stream was dependent on the nature of the acid sites, which are much stronger in both ZSM-5 and FCC-E1 than in ASA. Table 5 also shows that the selectivity to gasoline ($k_{11}/k_{0}$) was similar for ASA (62.4%) and FCC-E1 (56.3%), but much higher than for ZSM-5 (38.9%). ASA with large mesopes and low acidity (very small value of $k_{21}$ with less gasoline overcracking) gave rise to the broadest carbon range ($C_5$-$C_9$). A much higher selectivity to light gases ($k_{12}/k_{0}$) for ZSM-5 (60.5%) compared with FCC-E1 and ASA (40.4% and 35.4%) was obtained, which reflects, presumably, increased cracking of pre-gasoline products to light gases with ZSM-5 as compared to the other catalysts. The difference in the value of $k_{21}$ for different catalysts is in the order ZSM-5 $>$ FCC-E1 $>$ ASA. This order presumably reflects the differences in the activity of the catalyst for the cracking of molecules in the gasoline fraction. The smaller pores in ZSM-5 generate a higher concentration of smaller gasoline molecules, e.g. $C_6$-$C_8$, which also enhances production of light gases. The relatively low values of the $k_{21}$ constant point towards only a moderate contribution to light gases.

Table 3

Product distributions shown from FCC-E1 catalysed degradation of post-consumer polymer mixture (PE/PP/PS) at different fluidising $N_2$ rates (reaction temperature $= 390 \, ^\circ C$, catalyst to polymer ratio $= 20 \, \text{wt} \%$; catalyst particle size $= 125–180 \, \mu m$ and total time of collection $= 30 \, \text{min}$).

<table>
<thead>
<tr>
<th>Degradation results</th>
<th>Fluidising $N_2$ rates (ml min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>900</td>
</tr>
<tr>
<td>Yield (wt% feed)</td>
<td></td>
</tr>
<tr>
<td>Gaseous ($\sum C_1$-$C_4$)</td>
<td>46.5</td>
</tr>
<tr>
<td>Liquid</td>
<td>43.0</td>
</tr>
<tr>
<td>Gasoline ($\sum C_5$-$C_9$)</td>
<td>37.4</td>
</tr>
<tr>
<td>Condensate liquid$^a$</td>
<td>3.7</td>
</tr>
<tr>
<td>BTX$^b$</td>
<td>0.3</td>
</tr>
<tr>
<td>Styrene</td>
<td>1.6</td>
</tr>
<tr>
<td>Residue$^c$</td>
<td>10.5</td>
</tr>
<tr>
<td>Involatile residue</td>
<td>7.3</td>
</tr>
<tr>
<td>Coke</td>
<td>3.2</td>
</tr>
</tbody>
</table>

$^a$ Condensate liquid: condensate in condenser and captured in filter.  
$^b$ BTX: benzene, toluene and xylene.  
$^c$ Residue: coke and involatile products.

Table 4

Influence of reaction conditions on product selectivity for the catalysed degradation of post-consumer polymer mixture (PE/PP/PS) over various cracking catalysts (catalyst particle size $= 125–180 \, \mu m$): experimental and predicted equilibrium results.

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Reaction conditions$^a$</th>
<th>Catalyst type$^b$</th>
<th>Temperature$^c$ (°C)</th>
<th>$N_2$ rate$^d$ (ml min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$i$-Butene/$\sum$butenes</td>
<td>ZSM-5 USY FCC-E1 MCM-41 ASA</td>
<td>330 390 450 300 600 900</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$i$-Butene/$\sum$butenes$^a$</td>
<td>0.49 0.54 0.51 0.64 0.57 0.55 0.51 0.43 0.45 0.51 0.57</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$i$-Butane/$n$-butane$^a$</td>
<td>2.69 0.73 3.17 4.16 3.92 3.52 3.17 2.86 2.61 3.17 3.79</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Represents a series of runs where reaction temperature $= 190 \, ^\circ C$, catalyst to polymer ratio $= 20 \, \text{wt} \%$ and fluidising $N_2$ rate $= 600 \, \text{ml min}^{-1} \, N_2$ fluidising rate.  
$^b$ Catalyst to polymer waste ratio $= 20 \, \text{wt} \%$ and fluidising $N_2$ rate $= 600 \, \text{ml min}^{-1} \, N_2$ fluidising rate.  
$^c$ FCC-E1 catalyst to polymer waste ratio $= 20 \, \text{wt} \%$ and fluidising $N_2$ rate $= 600 \, \text{ml min}^{-1} \, N_2$ fluidising rate.  
$^d$ FCC-E1 catalyst to polymer waste ratio $= 20 \, \text{wt} \%$ and reaction temperature $= 390 \, ^\circ C$.  
$^e$ Denotes the ratio of the sum of all olefinic to paraffinic products.
Polymer cracking is known to proceed over acidic catalysts by carbocation mechanisms, where the initially formed ions undergo chain reactions via processes, such as scission or β-scission and isomerisation and hydrogen-transfer alkylation and oligomerisation, to yield typically smaller cracked products. In Table 5, the results of this kinetic model indicate that catalyst deactivation can be produced by active-site coverage, and consequently decrease the activity of the catalyst, giving the reason of decreasing of reaction rate with reaction time over the course of the reaction. Both acidity and diffusion constraints within individual surface areas of each catalyst may play significant roles in the apparent rate constant and product selectivity. Moreover, the value of the $k_{c1}/k_0$ (coke selectivity) in FCC-E1 (3.3%) than with ASA catalyst (2.2%) may indicate possible constraints on the diffusion of liquid polymer into the pores, although the differences in the nature of the sites may also be relevant. However, ZSM-5 with narrower pore openings (0.55 × 0.51 nm) and no supercages, the bulky feed molecules have restricted access to the internal active catalytic sites and special restrictions within the pore system tend to inhibit the bimolecular processes leading to coke production (0.6%).

The rate constants for the catalytic degradation of commingled polymer waste over FCC-E1 with particle sizes of 125–180 μm and 75–120 μm at five different temperatures (330–450 °C) are listed in Table 6. The selectivity towards the gasoline fraction ($k_{11}/k_0$) as a function of reaction temperature shows that the amount of gasoline formation decreased with increasing reaction temperature from 330 to 430 °C and then increased at 450 °C. On the other hand, the results show that the highest amount of light gases ($k_{12}/k_0$) occurred at 430 °C rather than at the higher temperature of 450 °C. It could be the case that selectivity products of light gases increased with increasing reaction temperature and gasoline decreased with an increase in temperature below 430 °C. But at higher temperature (450 °C), the degradation of commingled polymer waste to volatile products may proceed both by catalytic and thermal reactions leading to the variation of product distributions. In Fig. 7 and
selectivity products of light gases increased with increasing reaction temperature and gasoline decreased with an increase in temperature. This product deviation could be ascribed to the nature of scission degradation in the presence of each catalyst and the differences in product selectivity from transient change in volatile fragment diffusion to the effect of different level of reaction temperature. The external surface of the catalysts is an important factor controlling activity and selectivity. From values of $k_{11}/k_0$ and $k_3/k_0$, the smaller particle FCC-E1-S catalyst (75–120 μm) shows a higher selectivity for gasoline (56.5–66.2% vs. 54.1–63.5%) and a lower selectivity for coke (2.3–3.0% vs. 2.7–3.4%) than the larger particle FCC-E1-L catalyst (125–180 μm). The FCC-E1 catalyst containing cracking activity with bimodal pore structures, which is composed of both the micropore of zeolite and the mesopore of...
silica–alumina used in the FCC catalyst matrix, can provide the cracking ability when they are enough accessible to the reactant and may allow bulky reactions to occur, ultimately leading to the generation of hydrocarbon products with some coke content deposited on the catalyst. The result appears that the feed can be cracked at or close to the external surface of the catalysts and therefore, the controlling catalytic parameters will be not only the total number of acid sites but also the number of accessible ones related to the particle size selected.

4. Conclusions

A catalytic fluidising reaction system has been used to obtain a range of volatile hydrocarbons by catalytic degradation of polymer waste in the temperature range 330–450 °C. The catalytic degradation of polymer waste over a commercial FCC equilibrium catalyst (FCC-E1) using fluidising cracking reactions was shown to be a useful method for the production of potentially valuable hydrocarbons. Greater product selectivity was observed with FCC-E1 with about 53 wt% olefin products in the C3–C6 range. Observed differences in product yields and product distributions can be influenced by the change in reaction conditions.

A kinetic model with four lumps, representing unconverted polymer, light gases, gasoline, and coke, was used to determine the kinetics of catalytic degradation of the post-consumer polymer waste. A good fit between calculated and experimental results was obtained. This model provides the benefits of lumping product selectivity, in each reaction step, in relation to the performance of various acidic catalysts. The model allows for the prediction of the effects of reaction conditions on the product distribution and the selectivity of the reaction products.

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References