

# Accepted Manuscript

Influence of catalyst bed temperature and properties of zeolite catalysts on pyrolysis-catalysis of a simulated mixed plastics sample for the production of upgraded fuels and chemicals

Jude A. Onwudili, Chika Muhammad, Paul T. Williams



PII: S1743-9671(18)30862-6

DOI: [10.1016/j.joei.2018.10.001](https://doi.org/10.1016/j.joei.2018.10.001)

Reference: JOEI 515

To appear in: *Journal of the Energy Institute*

Received Date: 6 September 2018

Revised Date: 27 September 2018

Accepted Date: 4 October 2018

Please cite this article as: J.A. Onwudili, C. Muhammad, P.T. Williams, Influence of catalyst bed temperature and properties of zeolite catalysts on pyrolysis-catalysis of a simulated mixed plastics sample for the production of upgraded fuels and chemicals, *Journal of the Energy Institute* (2018), doi: <https://doi.org/10.1016/j.joei.2018.10.001>.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

## **Influence of catalyst bed temperature and properties of zeolite catalysts on pyrolysis-catalysis of a simulated mixed plastics sample for the production of upgraded fuels and chemicals**

Jude A. Onwudili <sup>a,\*</sup> Chika Muhammad <sup>b</sup>, Paul T. Williams <sup>b,\*</sup>

<sup>a</sup> School of Engineering and Applied Sciences, Aston University, Birmingham, B4 7ET, U.K.

<sup>b</sup> School of Chemical & Process Engineering, University of Leeds, Leeds LS2 9JT

### Abstract

The pyrolysis-catalysis of a simulated mixture of plastics representing the plastic mixture found in municipal solid waste has been carried out to determine the influence of process conditions on the production of upgraded fuel oils and chemicals and gases. The catalysts used were spent zeolite from a fluid catalytic cracker (FCC), Y-zeolite and ZSM-5 zeolite. The addition of a catalyst to the process produced a marked increase in gas yield, with more gas (mainly C<sub>1</sub> - C<sub>4</sub> hydrocarbons) being produced as the temperature of the catalyst was raised from 500 °C to 600 °C. The Si/Al ratio of the catalysts influenced the composition of other gases with the more basic catalysts producing more CO and the strongly acidic catalyst producing more H<sub>2</sub>. The yield of product oil decreased with the addition of the catalysts, but the oil was of significantly lower molecular weight range, containing a product slate of premium fuel range C<sub>5</sub> – C<sub>15</sub> hydrocarbons. In addition, the content of aromatic compounds in the product oil was increased; for example, benzene and toluene accounted for more than 90% of the aromatic content of the oil from the strongly acidic Y-zeolite catalysts. A reaction scheme is proposed for the production of single-ring aromatic compounds via pyrolysis-catalysis of plastics.

**Key words:** plastic waste, pyrolysis-catalysis, fuel-grade oil, BTX aromatics

\* Corresponding Author.

Jude Onwudili

Tel.: +44 121 204 4703; Fax:

Email address: [j.a.onwudili@aston.ac.uk](mailto:j.a.onwudili@aston.ac.uk)

Paul T. Williams

Tel: +44 113 343 2504; Fax+44 113 246 7310

Email: [p.t.williams@leeds.ac.uk](mailto:p.t.williams@leeds.ac.uk)

## 1.0 Introduction

The use of a cracking catalyst in the pyrolysis of waste plastics is driven by an overriding objective to transform an ever-growing global waste stream into useful and readily useable products. The subject of plastic pyrolysis has been well documented in literature [1-12] with some basic understanding of the pyrolysis process, and in particular the thermochemical reactions involved. Literature has shown that reactions such as C-C bond scission, dehydrogenation, hydrogenation, cyclization, aromatization and condensation are the most prevalent during pyrolysis [4]. The pyrolysis process thus appears to start as a random multi-reaction process leading to the formation of a very wide range of products from simple molecules (e.g. hydrogen) to long-chain hydrocarbons (e.g. up to C<sub>40+</sub> alkanes) and even char [2, 4-5, 12]. The distribution of pyrolysis products as gas, liquid and solid depends largely on the type of feedstock, the process conditions (especially temperature) and vapour residence times. These factors have different influence on the reactions that occur during pyrolysis and therefore determine which of the pyrolysis products are favoured. A readily useful product of plastic pyrolysis is the hydrocarbon-rich liquid, which can be used directly or minimally refined for use as fuel in internal combustion engines or as chemical feedstock. This has been a major research interest in pyrolysis of waste plastics. Fast pyrolysis which is characterized by short vapour residence times favour the production of pyrolysis liquid [13]. However, the avoidance of secondary reactions, which occurs with prolonged residence times, results in a liquid product dominated by less useful long-chain hydrocarbons.

Catalysts can play significant roles in the conversion of plastics to fuel-grade liquid products by promoting reactions which are relevant to their formation, albeit at the appropriate residence times. Several researchers have investigated the catalytic pyrolysis of plastics and literature shows that reactor design, catalyst type and reaction conditions can greatly influence the yields of products from catalytic pyrolysis. Fixed bed reactors offer a simple system for fundamental studies of the pyrolysis process and a number of researchers have used different configurations of fixed bed reactors for catalytic pyrolysis studies. For instance, some fixed-bed reactor studies involved contacting melted plastics with catalysts [8-10]. Others have involved heating a mixture of plastics and catalysts together in a single bed [11-12], while in another configuration, pyrolysis vapours are passed over a heated catalyst bed in a two-stage process [14-15]. Fixed bed reactors can however, suffer from poor heat transfer which can cause operational problems such as blockage, making commercial application difficult. While fluidized-bed reactors can help overcome the operational problems of fixed bed reactors, the former, by design, retains ash present in feedstock in the bed material. The ash content of wastes have been reported to act as catalysts for the pyrolysis process, thereby influencing the composition of the pyrolysis oil [16]. A challenge

is that real-world wastes have highly varied compositions and changes in ash contents would lead to changes in oil compositions making the properties of oil products less predictable. In addition, real-world waste plastics are contaminated with other materials including stones and glass, which can build-up in the fluidized bed material over time to cause severe operational problems such as abrasion, wear and tear of reactor, contamination of catalysts and jamming of moving parts. Fine ash particles can become entrained in the gas/vapour stream leaving the fluidized bed reactor and cause downstream problems, including contamination of condensates. Alternatively, expensive feedstock preparation may be needed in order to make some real-world waste plastics suitable for fluidized bed reactor pyrolysis.

Among the fixed bed configurations, the two-stage process has a better potential for scale-up. In this configuration, the waste plastic is pyrolyzed in a first-stage reactor with pyrolysis vapours swept with an inert gas (e.g. nitrogen) over a heated catalyst bed in a second – stage. This makes it easy to operate the catalyst bed at a different temperature to the pyrolysis reactor and also to recover spent catalysts for regeneration. Shen et al. [11], performed pyrolysis of waste tyres with commercial ultra-stable Y-type (USY) and ZSM-5 zeolite catalysts in a fixed-bed two-stage pyrolysis-catalysis system. The pyrolysis temperature was 500 °C while the catalyst bed was varied from 350 °C to 500 °C. They found that an increase catalyst bed temperature above 450 °C enhanced gas yield at the expense of oil yield, while char yield remained fairly the same. Further, the authors reported that the oil products obtained during the catalytic process was dominated by single-ring aromatic hydrocarbons especially in the presence of USY zeolite. Williams and Brindle [14] also investigated the two-stage pyrolysis-catalysis of tyres and considered the influence of catalyst temperature using zeolite Y and ZSM-5 catalysts. The catalyst was found to reduce the yield of oil with a consequent increase in gas yield and formation of coke on the catalyst [14]. Achilias et al. [12] carried out two-stage pyrolysis of model and waste polymers including high-density polyethylene (HDPE), low-density polyethylene (LDPE) and polypropylene (PP), with the pyrolysis and catalyst bed at temperature of 450 °C. Using acidic zeolite, the authors obtained low gas yield for catalytic pyrolysis of the model plastics (0.5 wt%) but much higher gas yields (8.5 wt%) from waste plastics. The oil products were however dominated by long-chain ( $C_{15+}$ ) alkanes, which was attributed to the low pyrolysis temperature but could also be due to poor catalytic activity of the acidic FCC. In the work of Uemichi et al. [17], HDPE was pyrolyzed in a two-stage system over silica-alumina and ZSM-5 catalysts at 400 °C. The authors reported that pyrolysis over sequential layers of the two catalysts produced oils with improved fuel properties, however, the aromatic contents were low.

Catalytic reactions during pyrolysis are considerably more important for the conversion of degradation products into fuel-range liquid products than for the initial polymer degradation process. In addition, catalytic activities can be influenced by the catalyst bed temperatures

and catalyst types. Therefore, further research is needed to understand the influence of bed temperatures and some properties of different cracking catalysts on pyrolysis reactions in a two-stage process for plastics conversion. The investigation with catalysts was centred on the effect of the silica/alumina ratios and surface areas of the catalysts on the yields and compositions of liquid products. Four different cracking catalysts, including spent FCC catalyst, two zeolite Y catalysts and one ZSM-5 catalyst have been used. The catalysts were selected so that two (FCC and one zeolite Y) have lower Si/Al ratio (more acidic) than the other two (another zeolite Y and ZSM-5). In addition, the catalysts have different surface areas. The application of spent FCC catalyst, which is classified as a problematic hazardous material, in a secondary process such as plastic pyrolysis has environmental and sustainability benefits. Otherwise, it is being discarded due increasing demand for light and high-quality transportation fuels as well as the changes in petroleum feedstock [13, 19]. To improve the relevance of this present study to real-world plastic waste streams, the sample of plastic used was modelled according to the composition of waste plastics in future municipal solid waste (MSW) generation in Europe reported by Delgado et al. [18].

## 2.0 Experimental

### 2.1 Materials

The five plastics samples used to prepared the mixture in this work are as follows; high-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET). These plastics are the main components of household waste plastic mix and their proportions are based on the work reported by Delgado et al. [18]. The proportion of each was as follows; PE 62.0% (HDPE 19.0% and LDPE 43.0%), PP (8.0%), PS (15.0%) and PET (15.0%). The simulated plastic is hereby denoted as SMP waste. Each batch of 2 g feed was directly prepared from the stated proportions of each plastic to ensure uniformity. In addition, commercially available zeolite-based cracking catalysts were obtained from Sigma-Aldrich UK, while the spent FCC was obtained from MOL - a multinational petroleum refinery in Hungary. Table 1 shows some characteristics of the fresh catalysts. The two Y- zeolite catalysts have different silica-alumina ratio and surface area, but ZY-2 has the same silica-alumina ratio (80:1) with the ZSM-5 catalyst.

The pyrolysis-catalysis experiments were carried out in a reactor system consisting of a two-stage fixed bed reactor with oil condensers and gas collection sample bag (Figure 1). The pyrolysis reactor was a stainless steel fixed bed reactor of 480 mm length with an internal diameter of 40 mm and was electrically heated by two separately controlled 1.5 kW tube

furnaces [20]. High purity dichloromethane (DCM), also purchased from Sigma-Aldrich was used to prepare the pyrolysis liquid products for further analysis by gas chromatography.

## 2.2 Methods

For each experiment, the 2 g of plastic was loaded on to the top reactor bed, while the catalysts were loaded on the bottom bed, supported by glass wool. Each 2 g of catalyst was thoroughly mixed with 2 g of pre-cleaned and calcined quartz sand as support. In the absence of catalyst, 4 g of quartz sand was loaded on the catalyst reactor as control (thermal) experiment. The entire reactor system was continuously flushed with nitrogen gas (1 barg,  $\approx 20$  °C) at a flow rate of  $20 \text{ ml min}^{-1}$  to provide an inert environment and serve as carrier for pyrolysis vapours. To begin the process, the catalyst bed was first heated to the desired temperature. Thereafter, the top reactor holding the plastics was heated at  $10 \text{ °C min}^{-1}$  from room temperature to  $500 \text{ °C}$ ; the sample was held at  $500 \text{ °C}$  for 30 min. The evolved pyrolysis volatiles passed directly to the pre-heated catalyst bed held at  $500 \text{ °C}$  or  $600 \text{ °C}$  to investigate the influence of catalyst bed temperatures on pyrolysis yields and composition. The vapour exiting the catalyst bed passed through a condenser system consisting of three dry-ice-cooled condensers. The last condenser was connected to a pre-weighed Tedlar gas sample bag for collection of non-condensable gases. After 30 min of pyrolysis at  $500 \text{ °C}$ , heating of both reactors were turned off but gas collection continued for another 30 min. At the end of the experiment, the condensers were immediately sealed to prevent evaporation of highly volatile products and weighed.

## 2.3. Analysis of products

The Tedlar bag was sealed and re-weighed to determine the total mass of gas collected. Then the gas content of the bag was analysed off-line with a system of Varian CP-330 gas chromatographs [20-21]. Briefly, the gas samples were analysed using three packed column gas chromatographs using standard gas mixtures as external standards. The permanent gases, hydrogen, nitrogen and carbon monoxide were separated on a 2m length by 2 mm diameter 60 – 80 mesh molecular sieve column, feeding into a thermal conductivity detector (TCD) for quantification. Hydrocarbon gases ( $C_1$  to  $C_4$ ) were analysed using a 2 m length by 2 mm diameter Haysep 80 – 100 mesh column and quantified with a flame ionization detector (FID), while carbon dioxide was analysed using a similar Haysep column fitted to a TCD. Details of the chromatographic conditions have been published earlier [21]. Sample injection volumes were adjusted accordingly for analysis within the linear working range of the gas chromatographs. GC results gas volume percentages of the gas components, and assuming ideal gas behaviour, these were equated to mole percentages. The mole percentage of each gas was used to multiply its molecular weight to get a mass value. The mass values were used

to compute mass fractions of the gas components (including the N<sub>2</sub> carrier gas). Finally, the mass fractions were used to multiply the total mass of gas collected in the Tedlar bag to determine the mass of each component. The weight percentage of each product gas was then calculated in relation to the plastic feed using Equation 1 (see section 3.1).

#### 2.4. Oil product analysis

In order to carry out quantitative analysis of the oil, each oil product was recovered from the condensers using DCM solvent. After the oil recovery, the volume of the each sampled oil was made up to 10 mL with more DCM in a glass vial, sealed and quickly stored in a freezer to minimize volatile losses. Using the same volume of oil solution made it easy to compare oil yields via peak area percentages. Each oil sample was analysed on the day of the pyrolysis experiment as a standard procedure to ensure consistency and the integrity of the oils. The first oil produced was qualitatively analysed to identify the major compounds present, using a GC/MS system consisting of a Varian 3800-GC coupled to a Varian Saturn 2200 ion trap MS/MS equipment. The column used was a 30 m x 0.25 mm inner diameter Varian VF-5ms (DB-5 equivalent), while the carrier gas was helium, at a constant flow rate of 1 ml min<sup>-1</sup> [19]. The identified compounds were used as basis for the analytical standards used for quantitation by external standard method on a different GC. Standard mixtures of aromatic, polycyclic aromatic compounds and aliphatic hydrocarbons (C<sub>5</sub> –C<sub>40</sub>) were obtained from Sigma Aldrich, UK. Thereafter, each oil sample was quantitatively analysed by liquid injection into a Varian 430 GC with flame ionization detector (FID), equipped with a split/split less injection port. The analysis was carried out on a ZB-1 capillary column (30 m × 0.53 mm i.d., 0.5 μm), with 100% dimethyl siloxane as liquid stationary phase. Nitrogen was used as carrier gas with a constant flow of 1.0 mL min<sup>-1</sup>. The sample injection volume was 2.0 μL. The column was temperature programmed from 40 to 310 °C at 5 °C min<sup>-1</sup> heating rate.

#### 3.0. Results and Discussions

The results of the pyrolysis-catalysis of the simulated mixed plastic (SMP) waste are presented in this section with relation to catalyst bed temperatures of 500 °C and 600 °C. An initial work with catalyst bed temperature of 400 °C led to deposition of melted plastic on the catalyst bed with no real improvements in the fuel-range compounds in the liquid products. So based on the preliminary work, higher catalyst bed temperatures are reported in this present study.

### 3.1. Product Yields

Figure 1 shows the product yields from the pyrolysis and pyrolysis-catalysis of the simulated mixed plastic at different catalyst bed temperatures of 500 °C and 600 °C, while the pyrolysis temperature was 500 °C.

The product yields were calculated from equations 1 – 3 as follows;

$$\text{Gas yield (wt \%)} = \frac{\sum \text{mass of gas components produced} \times 100}{\text{mass of plastic feed used}} \dots\dots\dots \text{Eq. 1.}$$

$$\text{Oil yield (wt \%)} = \frac{\text{mass of oil produced} \times 100}{\text{mass of plastic feed used}} \dots\dots\dots \text{Eq. 2.}$$

$$\text{Char yield (wt \%)} = \frac{\text{mass of char produced} \times 100}{\text{mass of plastic feed used}} \dots\dots\dots \text{Eq. 3.}$$

The results termed ‘thermal’ refer to when only the quartz sand was the bed material i.e. no added zeolite catalyst. For all the tests, increase in catalyst bed temperature led to increase in gas yields while oil yields decreased as shown in Figure 2. Char yields decreased only slightly from about 3.5 wt% to about 3 wt% for all catalysts, indicating that the main transformations observed were due to the catalytic reactions of the oil fractions. For example, in the experiment with quartz sand alone, gas yield increased 3-fold from 10.3 wt% to 29.8 wt% as the quartz bed temperature was increased from 500 °C to 600 °C. With the spent FCC catalyst, it could be seen that the catalyst led to a 60% increase in gas yield only at 500 °C compared to the quartz sand experiment, but at 600 °C gas yields from both the tests were similar at approximately 30 wt%. This may indicate that for both tests, temperature has the higher influence on gas production than the presence of FCC catalyst. In essence, both the quartz sand and the spent FCC catalyst gave a similar influence on gas yields. With the fresh catalysts, gas yields increased by at least 80% compared to the test with quartz sand alone at 500 °C, with gas yield increasing by 150% with the ZY-1 catalyst.

On increasing the bed temperature to 600 °C, gas yields increased significantly by 1.5 and 1.8 times with the ZY-1 and ZS-1 catalysts, respectively. The gas yield from using ZY-2 catalyst was very similar to those from both the spent FCC catalyst and the quartz sand tests at 600 °C. The increase in gas yield with an increase in catalyst bed temperature has been reported in literature [11, 14] and it is clear the main factor for the observed changes was the bed temperature more than the bed materials. With bed temperature of 500 °C, oil yields were



greater than 70 wt% for all experiments, with the highest oil yield of 79 wt% obtained from the quartz sand test.

However, at 600 °C, oil yields ranged from 45 wt% to nearly 70 wt%. Again, the quartz sand test and catalytic tests with spent FCC and the ZY-2 catalysts gave the highest oil yields with similar values of 68 – 69 wt%. The yields of oil from the quartz sand test and with the ZY-2 catalyst decreased similarly by nearly 13%, while oil yield obtained from the use of spent FCC catalyst only decreased by 3.5 wt% when compared to the corresponding oil yields at 500 °C. The ZY-1 and ZS-1 catalysts led to more dramatic reduction in oil yields by 24% and 37%, respectively compared to yields obtained at 500 °C. Indeed, with the ZY-1 catalyst nearly equal wt% yields of gas and oil products were obtained but in the presence of ZS-1 catalyst, gas yields surpassed oil yield by 8 wt%. These results show that under the same temperature conditions, the catalysts have varied activities towards the reforming of the pyrolysis vapours via catalytic reactions. Detailed analysis of the gas and oils products would help clarify how the catalysts influenced the relevant reactions.

### 3.2 Gas composition

Table 2 shows the volume percentage (nitrogen-free) of components in the gas products from the pyrolysis and pyrolysis-catalysis of SMP using different catalysts at 500 and 600 °C bed temperatures. All the gas products obtained from these tests consisted of hydrogen, light hydrocarbon gases, carbon monoxide and carbon dioxide. Clearly, the formation of carbon dioxide and carbon monoxide must have originated from the pyrolysis of PET in the SMP.

In all cases, the volume percent of carbon dioxide in the gas products decreased with increasing catalyst bed temperatures, which may indicate that decarboxylation of PET occurred much more readily at 500 °C bed temperature than the formation of hydrocarbon gases. Therefore, at 600 °C, when more hydrogen and hydrocarbon gases was favoured, the volume percent of CO<sub>2</sub> decreased in the product gases. In general, the gas products contained higher percentage volumes of alkenes compared to alkanes at both bed temperatures; the only exception being ZY-1 catalyst at 600 °C, where the total volume percent of alkane gases was higher. Although, catalytic cracking of long-chain hydrocarbons are known to result in more alkanes than alkenes, however, with polyolefin-rich feedstock, alkene gases are known to dominate the gas products, with cracking of primary pyrolysis products occurring alongside dehydrogenation [22]. The ZY-1 catalyst, at this temperature also produced the highest volume percent of hydrogen gas compared to other catalysts or reaction conditions, which may indicate the promotion of dehydrogenation. This inference may become clearer when the composition of the oil products are examined in section 3.3.

Thus, the gas yield were further enhanced with the introduction of the catalyst so that at 500 °C bed temperature, the FCC catalyst (Si/Al = 16.4) with strong acidic sites but lowest surface area produced the highest yield of C<sub>2</sub>-C<sub>4</sub> hydrocarbons (89.8 vol.%). The two Y-zeolite catalysts with high surface areas but very different Si/Al ratios produced the lowest yields of C<sub>2</sub>-C<sub>4</sub> (72.4 vol.% and 74.4 vol%, respectively) and the highest hydrogen yields. However, ZS-1 with similar basic strength as ZY-2 produced a higher yield of C<sub>2</sub>-C<sub>4</sub> hydrocarbons and lower H<sub>2</sub> and CH<sub>4</sub> compared to the Y-zeolite catalysts. Lin and Yang [13], reported C<sub>1</sub>-C<sub>4</sub> hydrocarbon distribution from spent FCC catalyzed the conversion of commingled polymer over a temperature range of 340 - 460 °C. The authors observed an increase in C<sub>2</sub>-C<sub>4</sub> hydrocarbon of 18.2% to 28.7%, with the rise in pyrolysis temperature but methane and ethane were detected only at the higher temperatures. Huang et al. [6] also observed a similar change in the hydrocarbon yield with temperature for different catalysts.

Table 2 also shows that the calorific values (in MJ m<sup>-3</sup>) of the gas products increased generally with the introduction of the catalysts at both bed teperature.

The higher heating values (HHV) of the gas products which was calculated by equation 4;

$$HHV \text{ (MJ } m^{-3}) = \sum_{i=1}^n (x_i \cdot HHV_i) \dots\dots\dots \text{Eq. 4.}$$

where;

i ...n = each combustible component in the gas product

x = volume fraction of combustible component in gas product

HHV<sub>i</sub>= calorific value of combustible gas component in MJ m<sup>-3</sup>

However, the increase in calorific values became more dramatic with the catalysts at a bed teperature of 600 °C, with the strongly acidic and high surface area ZY-1 giving a gas with the highest calorific value of 48.8 MJ m<sup>-3</sup>, which is more than twice the calorific values of the gas products from the thermal, spent FCC and ZY-2 experiments at the same teperature. This can be explained from the composition of the gas products, which shows that the ZY-1 produced the highest vol% of hydrogen (a high CV gas). Indeed, ZY-1 produced nearly three times the vol% of hydrogen compared to the other conditions at 600 °C.

Figure 3 shows the wt% yield of the gas components in relation to catalysts and different bed temperatures. The wt.% results in Figure 3 correspond to the vol.% results in Table 3, however they give a clearer picture of the gas yields in relation to the mass of plastic feed. Clearly, the C<sub>3</sub> and C<sub>4</sub> hydrocarbons, along with carbon dioxide (from pyrolysis of PET) were the dominant gases at the catalyst bed temperature of 500 °C, with propene giving the highest yield.

As catalyst bed temperature was increased to 600 °C, there was a corresponding increase in the yields of all gases. The profiles of the carbon oxides show that, in the presence of the fresh zeolite catalysts, more CO was obtained at 600 °C compared to 500 °C; the experiments with quartz and spent FCC however, produced more CO<sub>2</sub> at the higher temperature. The quartz bed and strongly acidic catalysts seemed to favour the production of hydrocarbon gases at this temperature, while the basic catalysts (ZY-2 and ZS-1) favoured increased yields of CO and CO<sub>2</sub> gases. For the basic catalysts, the CO yields increased by a factor of about ten at 600 °C while CO<sub>2</sub> yields reduced slightly at the higher temperature, compared to the results with the same catalysts at 500 °C. This could be explained by the reduction of CO<sub>2</sub> on the catalysts surface via Boudouard reaction. Figure 3 also confirms that ZY-1 produced the highest yield of hydrogen (1.19 wt.%) compared to the other experiments.

### 3.3. Composition of oil products

The oil products were categorized using data from GC/FID analysis into fuel range (C<sub>5</sub> – C<sub>15</sub>) and high molecular weight (C<sub>16+</sub>) compounds. The distribution of the fuel range and high molecular weight compounds for SMP pyrolyzed using different catalysts at 500 °C or 600 °C catalyst bed temperature is shown in Figure 4. The data were evaluated on the basis of percentage peak area of the major components observed from the GC chromatograms. This was possible because the oil products were prepared in the same volume of solvent (dichloromethane) prior to analysis and the same injection volume used each time. The compounds were identified by comparing their retention times to those of compounds in the standards.

Production of fuel range hydrocarbons increased with catalysts introduction from 62.9 to 85.1 % at 500 °C, with the spent FCC giving similar yields as the fresh zeolite catalysts. The more basic ZY-2 catalyst gave the highest fuel range hydrocarbons yield (85.1%) compared ZS-1 with the same Si/Al ratio (80). The difference between the yields from the two basic catalysts may be their different surface areas and pore structures. Thus, comparatively a general trend was observed that showed that fuel range hydrocarbons increased in the presence of the catalysts at 500 °C catalyst bed temperatures. Apart from the spent FCC, fuel range hydrocarbons increased at 600 °C for all the zeolite catalysts and for the thermal run. Although, the overall oil yields decreased at the higher temperature compared to 500 °C, the fuel properties improved with the content of fuel range compounds.

Figure 5 shows the distribution (based on GC analysis) of the hydrocarbons into aliphatic and aromatic compounds in the oil products from the pyrolysis process of SMP at the two catalyst bed temperatures. In general, the aliphatic compounds dominated the oils at 500 °C and much of 600 °C, except for the strongly acidic ZY-1, which produced much higher aromatics

content. The relative contents of the aliphatic and aromatic compounds in the oil product was clearly influenced by both the catalyst type and bed temperature. At 500 °C, the spent FCC with medium acidic property (due to its low silica and alumina ratio), appears to compete favourably with other fresh zeolite catalysts recording higher (36.2%) aromatic yield than ZY-2 (33.7%) with higher Si/Al ratio and low acid catalytic sites. Apart from ZY-1, a change in temperature from 500 °C to 600 °C appeared to be responsible for the change in the distribution of the total aliphatic and hydrocarbon compounds in the oil products. ZY-1 with the strongest acidic catalytic site gave highest aromatic yields at both bed temperatures (47.1% and 61.4%, respectively for 500 °C and 600 °C). For instance, the yield of aromatics from ZY-1 could be linked to the composition of the gas products obtained from the same catalysts. As presented in Table 3, ZY-1 produced the highest yields of hydrogen gas in the gas product at both catalyst bed temperatures, which indicates that the catalyst promoted higher rates of dehydrogenation. Clearly, dehydrogenation would have led to aromatization and therefore the formation of aromatic compounds.

At higher bed temperature 600 °C, spent FCC recorded similar aromatic yield (38.8%) as the zeolite ZY-2 (39.8%) and the ZS-1 (41.1%) but these yields were marginally higher for these catalysts compared to the those at 500 °C. The results showed that temperature was more effective than the catalyst type to alter the composition of the oil products for the other four experiments except for the ZY-1 catalyst. Therefore, irrespective of the large difference in Si/Al ratio between the FCC, ZY-2 and ZS, they gave aromatic yields similar to the quartz bed. It has been suggested that during the pyrolysis of polyolefins, ZSM-5 catalysts lead the reactions through an end-chain scission pathway, yielding light hydrocarbons as primary products, instead of the typical polyolefin random scission pathway that takes place in thermal pyrolysis [22-25].

#### 3.4. Composition of light aromatic compounds in oil products

Due to the higher yields of aromatic compounds observed in these experiments, it became important to present a detailed compositional analysis of the components. Figure 6 shows the chromatograms of the oils products from pyrolysis of the SMP sample with quartz sand alone and in the presence of the strongly acidic ZY-1 catalyst at 500 °C. The chromatograms have been obtained from a GC programme developed for the analysis of aromatic hydrocarbons (hence no aliphatic compounds are labelled but their peaks can be seen). Clearly, the size of the peaks indicate the changes in the yields of, especially the low molecular weight aromatic compound such as benzene, toluene and xylenes (BTX) range of hydrocarbons, in relation to the different catalyst bed materials. BTX aromatic hydrocarbons are important components of gasoline fuel and are high-value chemical feedstock for the manufacture of medicines and

household items. The composition of BTX chemicals in pyrolysis oils from polyolefin plastics have been shown to be promoted by the presence of zeolite catalyst with strong acidic sites [26].

Figure 7 shows the peak area percent of some aromatic hydrocarbons (BTX, styrene and naphthalenes) in the oil products in relation to catalyst type and bed temperature. With quartz alone, styrene was the dominant aromatic compound in the oil products obtained at both bed temperatures. However, its yield appeared to decrease from 21% at 500 °C to 17% for 600 °C catalyst/sand cracking temperature. The presence of styrene is often due to the polystyrene content in the plastic feed. During the non-catalytic pyrolysis of polystyrene, Williams et al. [22] reported a high mass yield for styrene of 53% at 500 °C, which decreased to 34% at a higher upgrading temperature of 700 °C. The authors explained the reduction of styrene as well as styrene dimer and trimer to be via the intermolecular transfer followed by  $\beta$ -scission leading to the production of new radical and alkene.

Literature shows that the pyrolysis of polyolefins can obtain oils with high aromatic concentration; and a large number of researchers have proposed formation mechanism to be based on Diels-Alder reaction of alkenes [22, 26-28]. In addition, other authors suggested that the Diels-Alder reactions are accompanied by dehydrogenation and unimolecular cyclization followed by dehydrogenation [23-25], which is facilitated by the higher alkene content in the catalytic pyrolysis products of polyolefins [27].

In this work, the influence of the various catalysts used can be better evaluated from the yields and composition of aromatic compounds in the oil product. In the test with quartz sand, styrene remained the dominant aromatic compound at both bed temperatures. However, the yields of toluene, benzene, ethylbenzene and naphthalene increased marginally while xylenes almost completely disappeared as the bed temperature was increased from 500 to 600 °C. For the FCC catalyst, ethylbenzene formation was promoted over the other aromatic compounds at 500 °C, including styrene; but at 600 °C, the production of both benzene and toluene increased considerably. Other catalysts also showed modest increases in benzene and toluene yield, however the strongly acidic ZY-1 was the optimum catalyst for the production of low molecular weight aromatic compounds. ZY-1 gave nearly equal yields of benzene and toluene (about 12 peak area %) as the dominant aromatics produced at a temperature of 500 °C. The total yield of these two compounds was more than 90% of all the aromatic compounds at 600 °C with the strongly acidic catalyst. These results for ZY-1, which shows the near complete disappearance of styrene, suggest that a significant percentage of the other aromatic compounds may have originated from styrene.

However, for this ZY-1 catalyst, the yields of aromatic hydrocarbons were consistently higher than those of the other catalysts and the quartz sand. This may indicate that the formation of BTX aromatic compounds was not entirely due to the conversion of styrene via hydrogenation, demethylation and dealkylation. Therefore, the formation of BTX hydrocarbons would have resulted mainly from both the styrene and alkene routes as depicted in Figure 8. This agrees with the work of other authors [21, 26, 28, 29], who suggested formation of aromatic compounds via Diels-Alder reactions of the alkenes produced during the pyrolysis of polyolefins, followed by aromatization via dehydrogenation, promoted by the catalysts (especially ZY-1) and delocalization stability of aromatic rings.

#### 4.0. Conclusions

The influence of catalyst bed temperature and type of zeolite catalysts (based Si/Al ratio and surface area) on pyrolysis of a simulated mixed plastic (SMP) sample have been investigated for the production of valuable liquid fuels and chemical feedstock. Higher catalyst bed temperature led to increased gas production, particularly C<sub>2</sub>-C<sub>4</sub> hydrocarbons, while ZY-1 produced the highest hydrogen gas yield (from dehydrogenation). All the catalysts caused a reduction in oil yields and an increase in gas yields, particularly more so at 600 °C bed temperature. The contents of low molecular weight aromatic compounds in the oil products increased with temperature, an indication of improved gasoline-type fuel quality. ZY-1 produced the highest yields of the aromatic compounds at both pyrolysis temperatures; indeed at 600 °C, the benzene and toluene accounted for more than 90% of the aromatic content of the oil from the experiment involving ZY-1 catalyst. Hence, results showed that ZY-1 could be used to obtain high yields of valuable aromatic chemical feedstocks from polyolefin plastic wastes. The formation of the aromatic compounds involved Diels-Alder reactions but arguably, there was a major contribution from styrene, which appeared to be a primary aromatic compound during the pyrolysis process (mainly from the polystyrene fraction of SMP). Styrene conversion to other aromatics could be via hydrogenation, dealkylation and methylation.

## References

1. Williams, P.T. and Brindle, A. J., Catalytic pyrolysis of tyres: influence of catalyst temperature. *Fuel*, 2002; 81(18): 2425-2434.
2. Bagri, R. and Williams, P. T., Catalytic pyrolysis of polyethylene. *J. Anal. App. Pyrolysis*, 2002; 63(1): 29-41.
3. Pinto, F., Costa, P., Gulyurtlu, I. and Cabrita, I., Pyrolysis of plastic wastes. 1. Effect of plastic waste composition on product yield. *J. Anal. App. Pyrolysis*, 1999; 51(1-2): 39-55.
4. Serrano, D.P., Aguado, J. and Escola, J. M., Developing advanced catalysts for the conversion of polyolefinic waste plastics into fuels and chemicals. *ACS Catalysis*, 2012; 2(9): 1924-1941.
5. Buekens, A. and Huang, H., Catalytic plastics cracking for recovery of gasoline-range hydrocarbons from municipal plastic wastes. *Res. Conservation and Recycling*, 1998. 23(3), 163-181.
6. Huang, W.-C., Huang, M. S., Huang, C. F., Chen, C. C. and Ou, K. L., Thermochemical conversion of polymer wastes into hydrocarbon fuels over various fluidizing cracking catalysts. *Fuel*, 2010; 89(9): 2305-2316.
7. Li, X., Li, J., Zhou, G., Feng, Y., Wang, Y., Yu, G., Deng, S., Huang, J. and Wang, B, enhancing the production of renewable petrochemicals by co-feeding of biomass with plastics in catalytic fast pyrolysis with ZSM-5 zeolites. *Applied Catalysis A: Gen.*, 2014; 481: 173-182.
8. Wu, C., Nahil, M. A, Miskolczi, N., Huang, J. and Williams, P. T., Processing real-world waste plastics by pyrolysis-reforming for hydrogen and high-value carbon nanotubes. *Environ. Science Technol.*, 2013; 48(1): 819-826.
9. Abbas-Abadi, M. S., Hagganeh, H. and McDonald, A.G., Evaluation of pyrolysis process parameters on polypropylene degradation products. *J. Anal. App. Pyrolysis*, 2014; 109: 272-277.
10. Houshmand, D., B. Roozbehani, and A. Badakhshan, Thermal and catalytic degradation of polystyrene with a novel catalyst. *Int. J. Science & Emerging Technol.* 2013; 5(1): 234-238.
11. Shen, B., Chunfei, W., Binbin, G. and Rui, W., Pyrolysis of waste tyres with zeolite USY and ZSM-5 catalysts. *Applied Catalysis B: Environ.*, 2007; 73(1): 150-157
12. Achilias, D. S, Roupakias, C., Megalokonomos, P., Lappas, A. A. and Antonakou, E. V., Chemical recycling of plastic wastes made from polyethylene (LDPE and HDPE) and polypropylene (PP). *J. Hazardous Mater.* 2007; 149(3): 536-542
13. Lin, Y. H. and Yang, M. H., Catalytic conversion of commingled polymer waste into chemicals and fuels over spent FCC commercial catalyst in a fluidised-bed reactor. *Applied Catalysis B: Environ.*, 2007; 69(3): 145-153.

14. Williams, P.T. and Brindle, A.J., Aromatic chemicals from the catalytic pyrolysis of scrap tyres. . *J. Anal. App. Pyrolysis*, 2003; 67(1): 143-164.
15. Aguado, J., Serrano, D. P., San Miguel, G., Castro, M. C. and Madrid, S., Feedstock recycling of polyethylene in a two-step thermo-catalytic reaction system. . *J. Anal. App. Pyrolysis*, 2007; 79(1): 415-423.
16. Atienza-Martínez, M., Fonts, I., Lázaro, L., Ceamanos, J., Gea, G., Fast pyrolysis of torrefied sewage sludge in a fluidized bed reactor, *Chem. Eng. Journal* 2015; 259: 467–480
17. Delgado, C., Barretabena, L., Salas, O. and Wolf, O., Assessment of the Environmental Advantage and Drawbacks of Existing and Emerging Polymers Recovery Processes. Joint Research Centre Scientific and Technical Report, 2007. **jrc37456**, 264.
18. Lee, K.-H., Noh, N. S., Shin, D. H. and Seo, Y., Comparison of plastic types for catalytic degradation of waste plastics into a liquid product with spent FCC catalyst. *Poly. Degrad. Stability*, 2002; 78(3): 539-544
19. Muhammad, C., Onwudili, J. A. and Williams, P. T., Thermal degradation of real-world waste plastics and simulated mixed plastics in a two-stage pyrolysis-catalytic reactor for fuel production. *Energy & Fuels*, 2015; 29(4): 1601-1609.
20. Efika, E. C., Onwudili, J. A., Williams, P.T., Products from the high temperature pyrolysis of RDF at slow and rapid heating rates. *J. Anal. App. Pyrolysis*, 2015; 112: 14–22
21. Williams, P. T., Horne, P. A. and Taylor, D. T., Polycyclic aromatic hydrocarbons in polystyrene derived pyrolysis oil. *J. Anal. App. Pyrolysis*, 1993; 25: 325-334.
22. Escola, J., Aguado, J., Serrano, D. P., Briones, L., Diaz de , T. J. L. Calvo, R. and Fernandez, E., Conversion of polyethylene into transportation fuels by the combination of thermal cracking and catalytic hydro-reforming over Ni-supported hierarchical beta zeolite. *Energy & Fuels*, 2012; 26(6): 3187-3195.
23. Lopez, A., de Marco, I., Cabellero, B. M., Adados, A. and Laresgoiti, M. F., Deactivation and regeneration of ZSM-5 zeolite in the catalytic pyrolysis of plastic wastes. *Waste Management*, 2011; 31(8): 1852-1858.
24. Lopez-Uriónabarrenechea, A., de Marco, I., Caballero, B. M., Laresgpiti, M. F. and Adrados, A., Catalytic stepwise pyrolysis of packaging plastic waste. *J. Anal. App. Pyrolysis*, 2012; 96: 54-62.
25. Serrano, D., Guado, J., Escola, J. M., and Rodriguez, J. M., Influence of nanocrystalline HZSM-5 external surface on the catalytic cracking of polyolefins. . *J. Anal. App. Pyrolysis*, 2005; 74(1): 353-360.
26. Rahimi, N. and Karimzadeh, R., Catalytic cracking of hydrocarbons over modified ZSM-5 zeolites to produce light olefins: A review. *Applied Catalysis A: Gen.*, 2011; 398(1): 1-17.
27. Jing, X., Zhao, Y., Wen, H., and Xu, Z., Interactions between low-density polyethylene (LDPE) and polypropylene (PP) during the mild cracking of polyolefin mixtures in a closed-batch reactor. *Energy & Fuels*, 2013; 27(10): 5841-5851.



28. López, A., de Marco, I., Cabellero, B. M., Laresgoiti, M. F. and Adrados, A., Influence of time and temperature on pyrolysis of plastic wastes in a semi-batch reactor. *Chem. Eng. Journal*, 2011; 173(1): 62-71.

29. Zheng, Y., Tao, L., Yang, X., Huang, Y., Liu, C., Gu, J., and Zheng, Z. (2017). Effect of acidity and manner of addition of HZSM-5 catalyst on the aromatic products during catalytic upgrading of biomass pyrolysis, *BioRes.* 12(4), 8286-8305.

**List of Figures**

Figure 1: Schematic of two-stage fixed bed reactor used in this work

Figure 2. Product yield for pyrolysis of the simulated mixture of plastics (SMP) at (a) 500 °C and (b) 600 °C catalyst bed temperature

Figure 3. Gas component yields from the pyrolysis of the SMP sample at (a) 500 °C and (b) 600 °C catalyst bed temperature

Figure 4: Distribution of fuel range ( $C_5 - C_{15}$ ) and high molecular weight ( $C_{16+}$ ) hydrocarbons from the pyrolysis of the SMP sample at (a) 500 °C and (b) 600 °C catalyst bed temperature

Figure 5: Distribution of aliphatic and aromatic hydrocarbon in oil products from pyrolysis of the SMP sample at; (a) 500 °C and (b) 600 °C catalyst/sand bed temperature

Figure 6: GC outlines of oil products from the pyrolysis of SMP sample at 500 °C; (a) with quartz sand alone; (b) with quartz sand and ZY-1 catalyst

Figure 7: Yield of some selected aromatic compounds from pyrolysis of the SMP at (a) 500 °C and (b) 600 °C catalyst/sand bed temperature

Figure 8: Possible reaction scheme for the formation of BTX hydrocarbons during pyrolysis of simulated plastic sample

Table 1: Some characteristics of catalysts used in this work

Catalyst properties	FCC	ZY-1	ZY-2	ZS-1
<b>Zeolite Structure</b>	FCC-Zeolite	Y-Zeolite	Y-Zeolite	ZSM-5
<b>Surface area (m<sup>2</sup> g<sup>-1</sup>)</b>	148	935	888	467
<b>Si/Al ratio</b>	16.4:1	5.2:1	80:1	80:1
<b>Cation</b>	-	NH <sub>4</sub> <sup>+</sup>	H <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>
<b>Na<sub>2</sub>O (%)</b>	0.14	2.93	0.02	0.00
<b>Micropore volume (cm<sup>3</sup> g<sup>-1</sup>)</b>	0.032	0.340	0.315	0.204
<b>Mesopore volume (cm<sup>3</sup> g<sup>-1</sup>)</b>	-	0.040	0.221	0.117
<b>Pore radius (Å)</b>	-	7.62	7.047	7.50

Table 2. Volume of gas components in gas product from thermal and catalytic pyrolysis of SMP with different catalyst type and at different bed temperatures

Gas (vol %)	Quartz Sand		Quartz Sand + FCC		Quartz Sand + ZY-1		Quartz Sand + ZY-2		Quartz Sand + ZS-1	
	Catalyst bed temperature (°C)									
	500	600	500	600	500	600	500	600	500	600
H <sub>2</sub>	4.55	10.6	5.47	9.91	22.2	31.8	15.7	12.6	14.3	9.46
CH <sub>4</sub>	8.72	15.4	4.72	14.6	9.97	16.7	5.27	10.7	6.38	7.44
C <sub>2</sub> H <sub>4</sub>	12.8	23.1	9.08	17.7	9.96	8.80	9.81	8.98	11.9	21.7
C <sub>2</sub> H <sub>6</sub>	6.14	6.82	2.94	5.88	4.82	6.41	3.06	3.63	3.00	3.40
C <sub>3</sub> H <sub>6</sub>	11.4	11.8	20.3	14.3	17.9	10.7	16.1	18.5	19.3	17.1
C <sub>3</sub> H <sub>8</sub>	5.70	5.91	10.2	7.13	8.93	5.36	8.06	9.26	9.71	8.53
C <sub>4</sub> H <sub>8</sub>	6.21	4.55	13.1	5.72	12.6	5.56	7.35	4.15	9.37	4.64
C <sub>4</sub> H <sub>10</sub>	4.18	3.74	7.09	4.64	4.67	7.65	5.01	2.61	6.73	4.51
CO	14.8	8.92	10.9	7.75	5.82	4.49	7.80	23.6	6.32	19.7
CO <sub>2</sub>	25.5	9.17	16.2	12.5	9.66	2.49	15.2	5.93	12.9	3.55
<b>∑ alkanes</b>	<b>24.7</b>	<b>31.9</b>	<b>24.9</b>	<b>32.3</b>	<b>28.4</b>	<b>36.1</b>	<b>21.4</b>	<b>26.2</b>	<b>25.8</b>	<b>23.9</b>
<b>∑ alkenes</b>	<b>30.4</b>	<b>39.5</b>	<b>42.5</b>	<b>37.7</b>	<b>40.4</b>	<b>25.1</b>	<b>33.3</b>	<b>31.7</b>	<b>40.7</b>	<b>43.4</b>
<b>HHV (MJ m<sup>-3</sup>)</b>	<b>5.18</b>	<b>21.9</b>	<b>10.1</b>	<b>21.8</b>	<b>20.9</b>	<b>48.8</b>	<b>16.5</b>	<b>22.6</b>	<b>13.7</b>	<b>36.7</b>

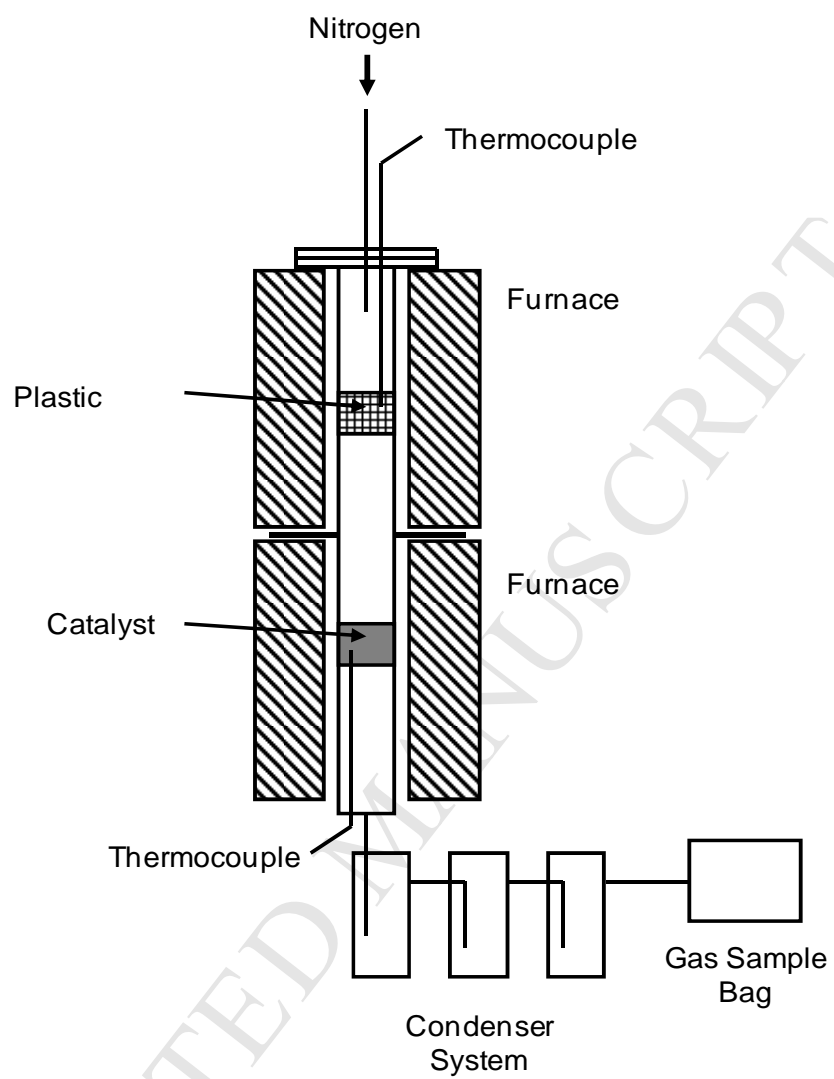


Figure 1

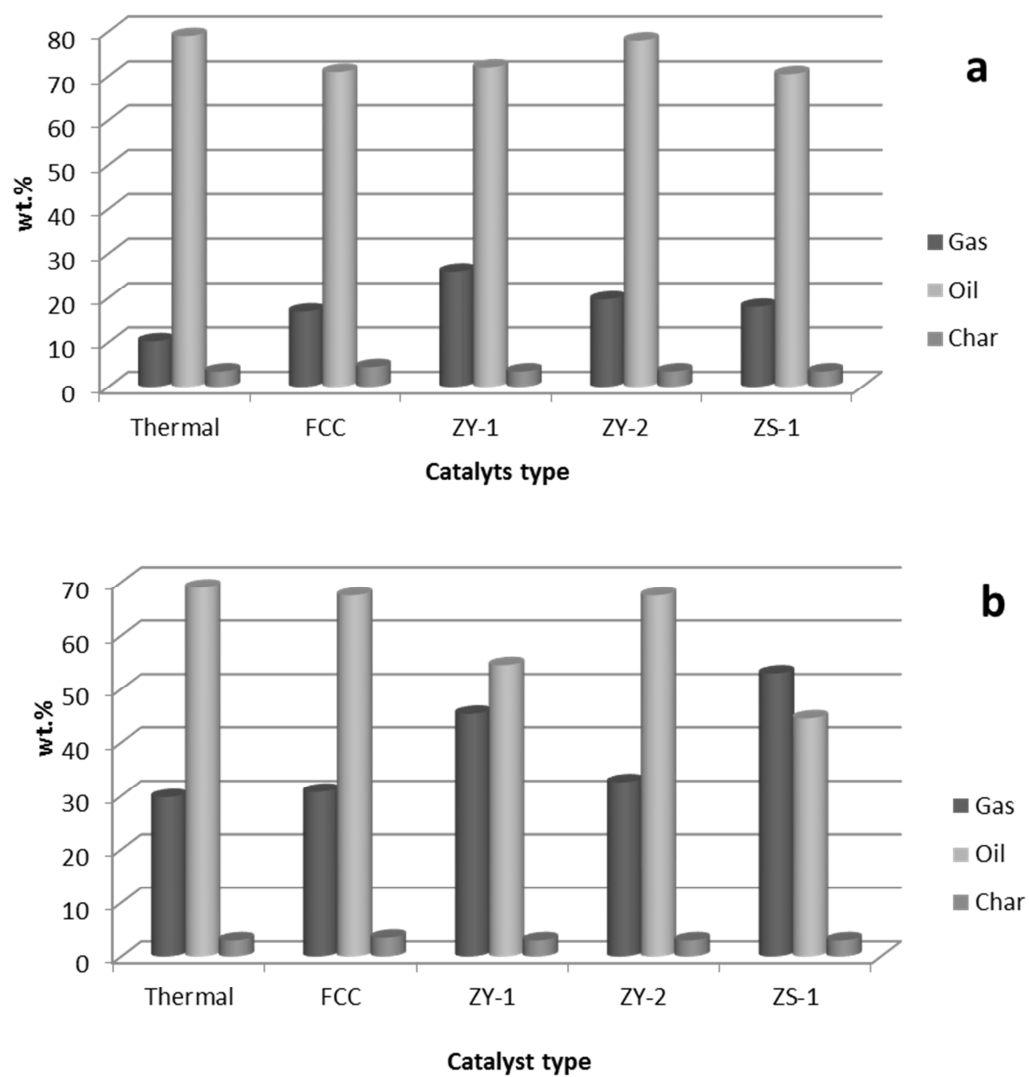


Figure 2

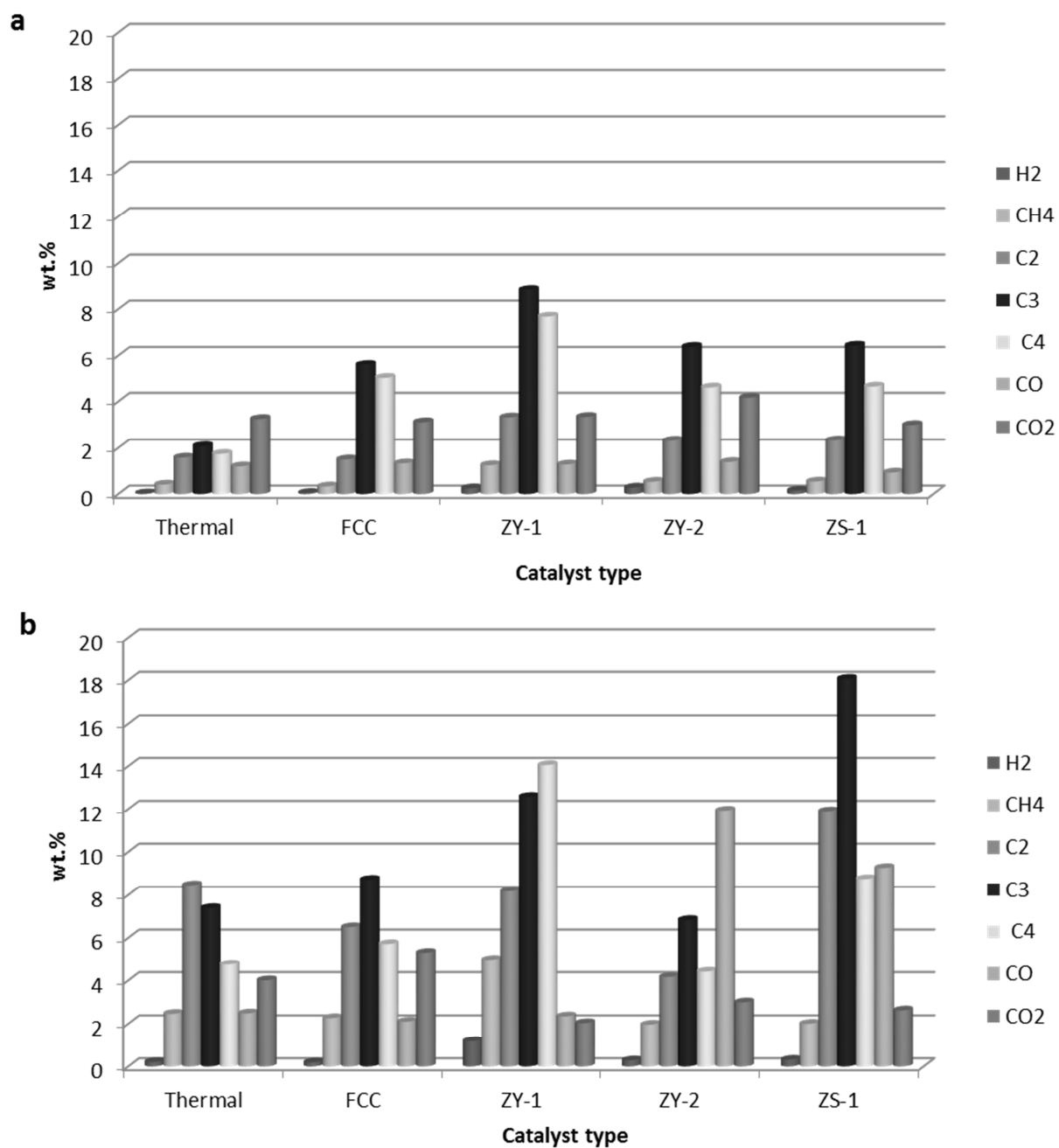


Figure 3

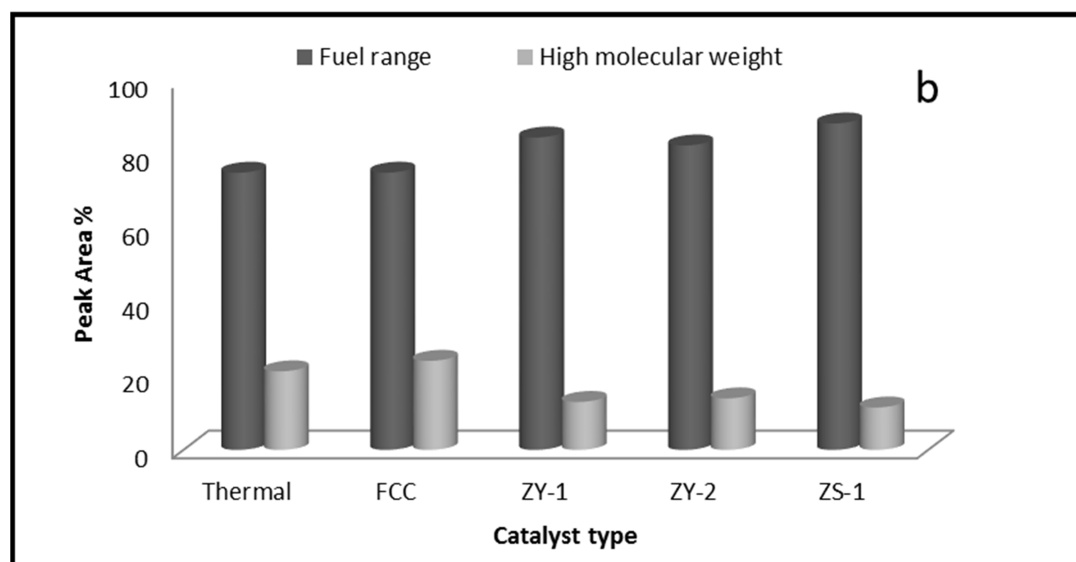
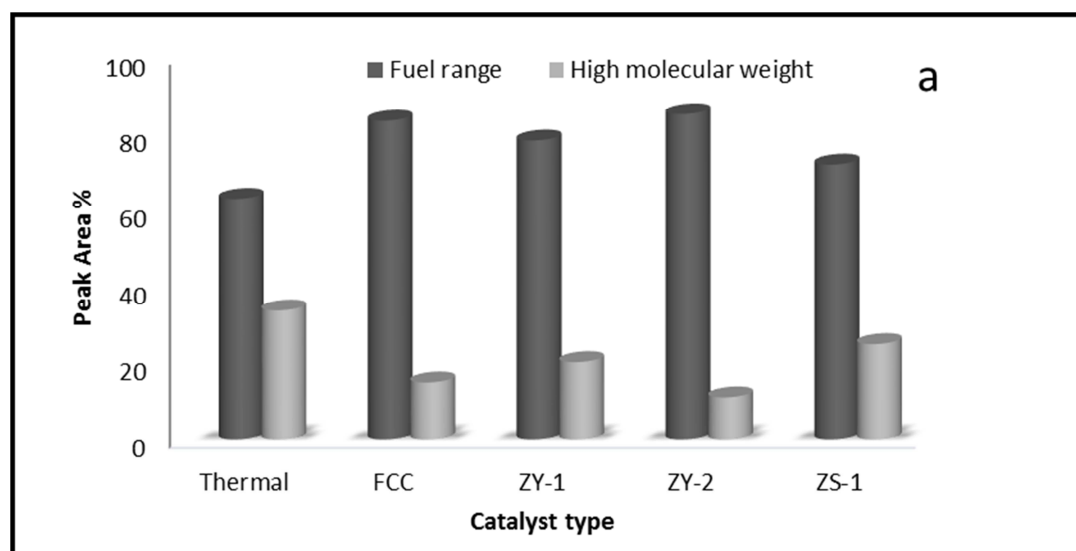


Figure 4



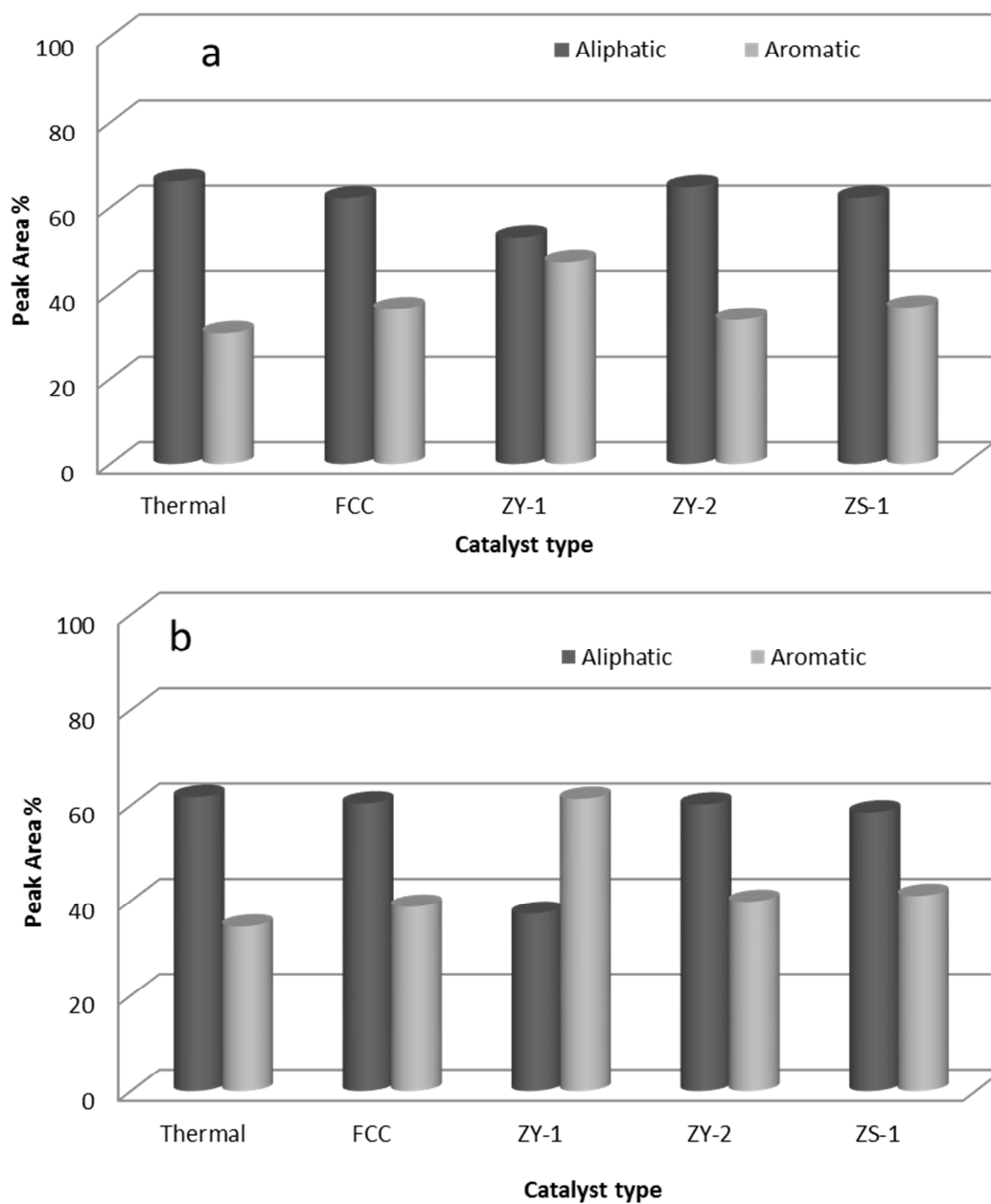


Figure 5

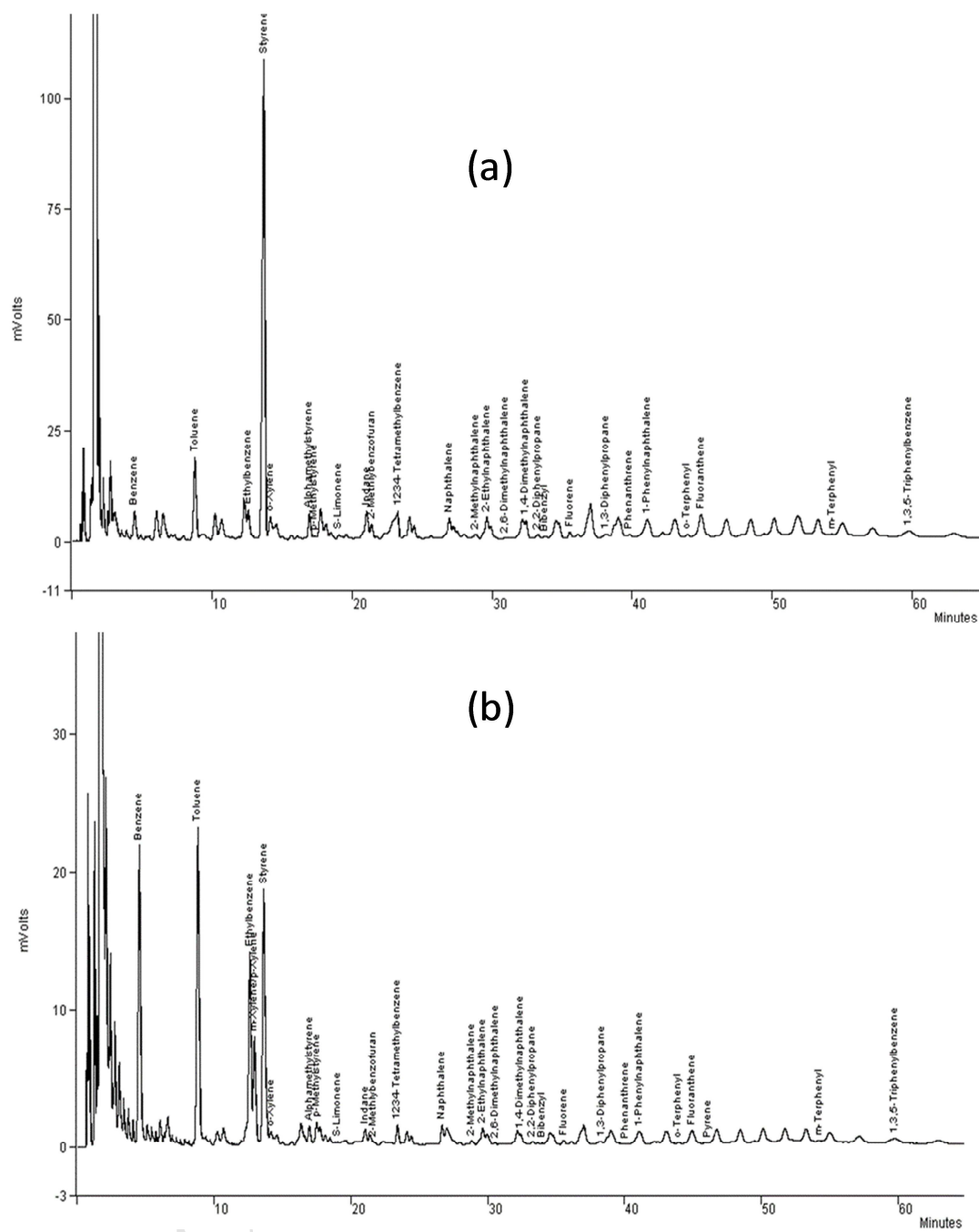


Figure 6

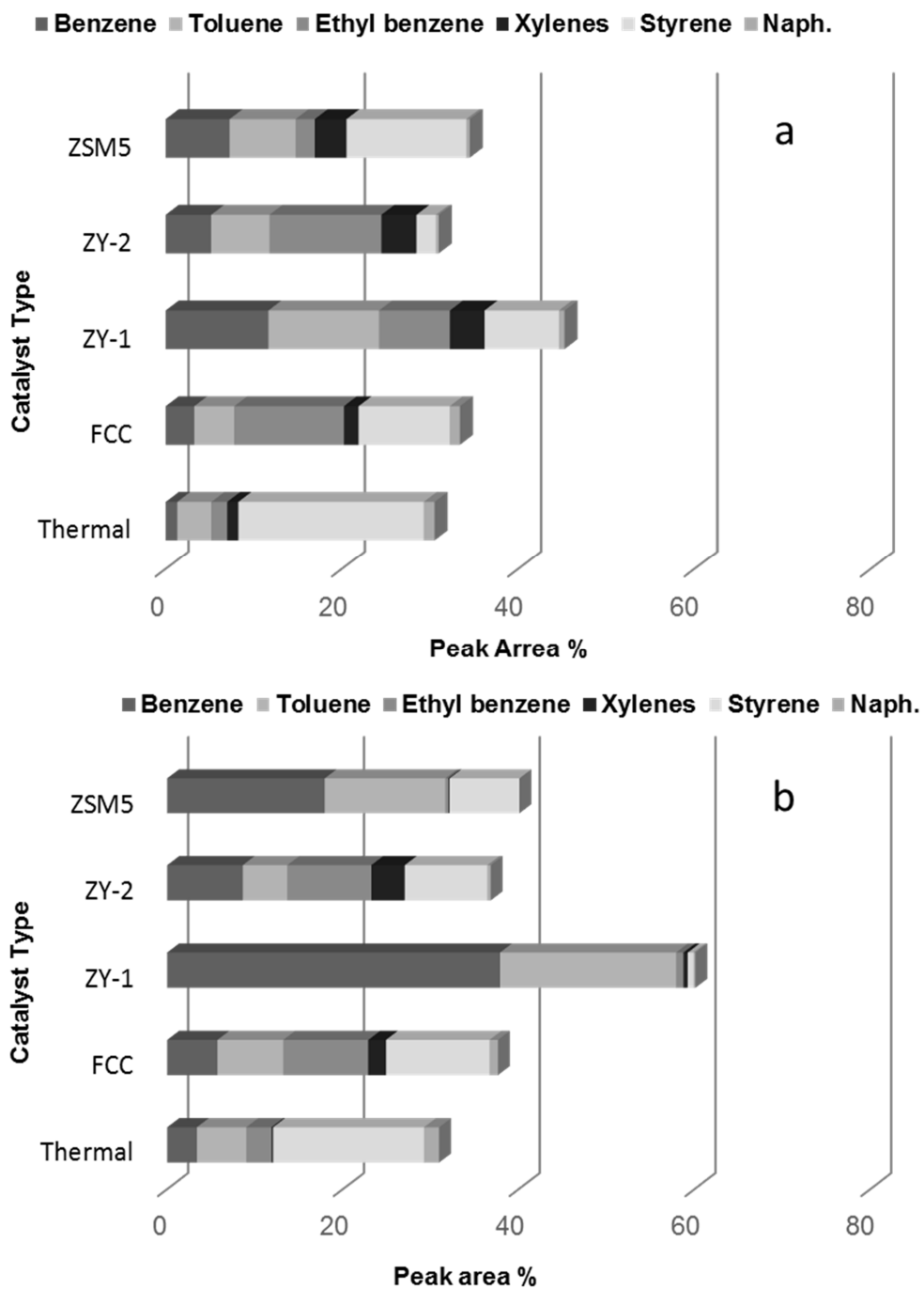


Figure 7

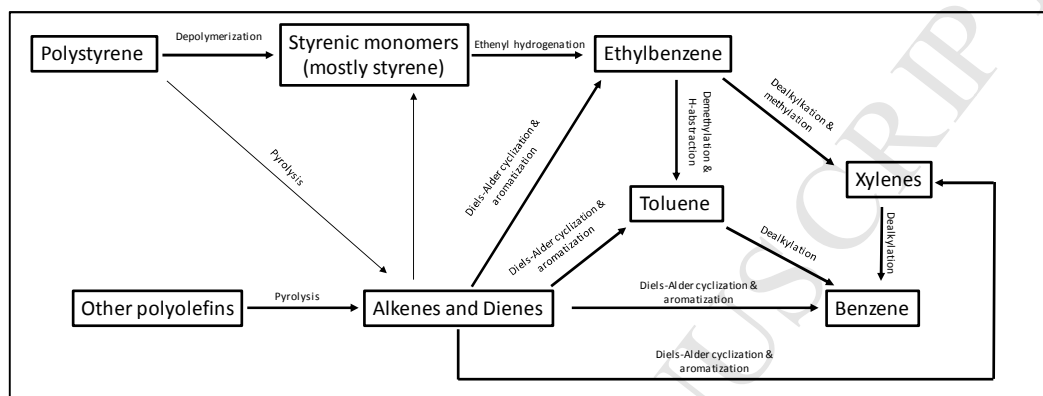


Figure 8

## Highlights

Application of zeolite catalysts increased gas production at the expense of oil product, with dramatic change in oil composition

Aromatic contents of oils increased with presence of catalysts as well as increased bed temperature

Strongly acidic zeolite Y catalyst (Si/Al =5.1) promoted formation of low molecular weight aromatic hydrocarbons

Pyrolysis-catalysis can be tuned to produce fuel-grade liquid product and high-value aromatic chemicals

Possible mechanisms of BTX aromatic formation via styrene and alkene/diene routes