Pyrolysis Study of mixed plastics waste

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Abstract. There is limited work reported on the pyrolysis of mixed plastics waste. The objective of this work is to investigate the effect of interaction of various types of plastics on the quality and yields of liquid oil obtained from pyrolysis. The plastics chosen in this work were polyethylene (PE), polypropylene (PP) and polystyrene (PS) since their combination contributes to approximately 80% of the plastics waste in India. In addition, previous studies showed that polyolefins (HDPE, LDPE, PP, and PS) were best suited for chemical recycling through pyrolysis. Experiments were performed in a bench-scale batch reactor with individual components (PE, PP and PS) and binary mixtures of them in various proportions. In this study, the dependent variables were the yields and quality of pyrolysis products. There was non-linearity observed in the liquid and gas yield and product composition with varying mixture constitution. This study on interaction effects is envisaged to help in further development and scale-up of the plastic pyrolysis process.

1. Introduction

Plastics have replaced many of the conventional materials like metals and wood in the modern day owing to their desirable intrinsic properties like durability, versatility, low weight, better resistance to chemicals and water, etc. This is applicable across many products like toys, agricultural equipment, automobiles, mobile handsets, etc. As a result, the use of plastics has been increasing globally and the worldwide plastic production has crossed over 348 million metric tons. The annual demand for plastics has grown at an average rate of about 10%. This is expected to lead to an increase in the plastic waste generation too in the near future.

Owing to mismanagement, a significant part of the plastic waste ends up in open landfill sites, oceans and water bodies, etc. which creates health and environmental hazards. Feed-stock recycling is a recycling method which encompasses different kinds of thermal and chemical processes to recover fuel or raw chemicals from the plastic waste [1]. Plastic pyrolysis is one of these methods to decompose the plastics or polymers into smaller chain length compounds either using heat alone (thermal pyrolysis) or using heat in the presence of a catalyst (catalytic pyrolysis). It occurs in an inert environment in the temperature range of 300-600°C [2]. Pyrolysis of plastics under different operating conditions produces solid (char), liquid (pyrolysis oil) and gases (pyrolysis gas) as the products. The pyrolysis oil obtained from the pyrolysis of plastic waste can be used as fuel oil for heating application in industry. It can also be upgraded further into gasoline or diesel for use as a transportation fuel.

There are several papers on the pyrolysis of plastics [3][4] which discuss the effect of various parameters like heating rate, catalyst loading, temperature, etc. It is necessary to have a technology that can convert a mixture of waste plastics through pyrolysis into fuel oil. In order to develop such a process, it is important to understand the interaction effect between various types of plastics as they
respond to the pyrolysis environment in different ways based on their crystallinity (e.g. HDPE and LDPE), type (e.g. PE and PS), additives used, etc. The novelty of this work lies in trying to develop this understanding about the interaction of mixed plastics, especially using binary mixtures. The main objective in plastic pyrolysis is to maximize the yield of the liquid oil and ensure a good quality for it.

2. Interaction effects of mixed plastics pyrolysis

Despite a large number of studies on plastic pyrolysis, only a few of them consider mixtures of different plastics and their effects [5][6][7]. Pek and Ghosh studied the interaction effect of addition of HDPE in PP – they noticed that addition of HDPE in PP results in a pyrolysis temperature which is lower than both PP and HDPE when fed individually[2]. A maximum liquid oil yield of 48.4% was reported by Maminsky et. al. [8] from their study on a mixture of polyolefins (75% PE and PP, and 25% PS) when the operating temperature was 730°C. Williams et. al. studied the interaction effects of mixed plastics and concluded that the presence of polystyrene is desirable as it enhances the quality of the liquid fuel [5].

This study experimentally investigates the interaction effects during pyrolysis, which are important in deciding the liquid yield and its quality. Since HDPE, LDPE, PP and PS together contribute to 80% of the plastic waste in municipal solid waste (MSW), these were chosen for our study. The influence of feed composition on the product yields and product distribution was evaluated by performing experiments with binary mixtures having various composition ratios of PP, PS, HDPE and LDPE.

3. Experimental Procedure

Pyrolysis of mixed waste PS, PP, and PE plastics was carried out in a glass reactor of 250 mL capacity made of quartz in batch mode of operation. The collected plastics waste was shredded to a size of 3 mm to 5 mm. The binary mixtures of HDPE, LDPE, PP and PS were prepared in the ratios of 30:70, 50:50, 70:30 and 90:10 by weight percent. The weight of the feed used in the experiments varied from 10 to 35 grams, based on the density of the mixture.

![Figure 1. Schematic of the experimental set-up](image)

The reactor was operated at a temperature of 560°C with a heating rate of 10°C/min and residence time of 90 min. The catalyst used was spent FCC catalyst, which is extensively used in the petroleum refineries for cracking of heavy oil into gasoline and lighter fractions. The use of spent FCC catalyst in
plastic pyrolysis has also been reported in literature. The main reasons for choosing spent FCC catalyst are its easy availability (since it is a waste stream for refiners), and sufficient activity retained by the catalyst for the plastic pyrolysis process. It would avoid the cost associated with the development of a new catalyst. The reactor was externally heated using an electrical furnace and a thermocouple was used to monitor and control the temperature at its set point. A condenser with cooling water arrangement is used and the liquid obtained after condensation is collected in a round bottom flask. The non-condensable gases were collected in balloons for further analysis. At the end of each experiment, the pyrolysis liquid and residue (char) were weighed to determine the respective yields, and the gas yield was determined by difference. Fig. 1 shows a schematic of the experimental setup.

4. Method of Analysis
The liquid oil was analysed using Gas Chromatography–Mass Spectrometry Time-of-Flight (GCXGC-TOFMS) technique. One-dimensional GCXGC-TOFMS analysis was performed using Leco Pegasus 4D Time of Flight Mass Spectrometer comprising Agilent 7890-A Gas Chromatograph equipped with Garstel automatic multi-sampler and a secondary oven. The first dimension column used was Rx-5Sil MS (30 mX0.25 mm IDX0.25 µm) and the second dimension column used was Rx-17 Sil MS (2 mX0.25 mm IDX0.25 µm). The injection temperature was set to 290°C and the sample was injected in split-less mode with the injection volume of 1 µL. Helium was used as the carrier gas with a flow rate of 1.5 mL/min. The calorific value of the liquid fuel was analysed using a Parr 6200 calorimeter. Non-condensable gases were analyzed offline using a Gas Chromatograph equipped with a Thermal Conductivity Detector (GC-TCD) and Carbosieve column for separating H2, N2, CH4, CO and CO2. The carrier gas used is Argon and a standard gas mixture with known concentrations of H2, N2, CH4, CO and CO2 in the range of producer gas composition is used as the reference. The retention time range of the gases is shown in table 1.

| Gases | Retention time range (Minute) |
|-------|------------------------------|
| H2    | 0.18-0.22                    |
| N2    | 0.45-0.52                    |
| CO    | 0.57-0.60                    |
| CH4   | 1.24-1.26                    |
| CO2   | 2.88-2.91                    |

The gases found in the samples were hydrogen, hydrocarbons in the range of C1 to C4, and traces of CO and CO2. Hydrogen and methane were found in significant proportion.

5. Results and Discussion
During pyrolysis, the yields of the products depend on various process design and operating parameters like composition of feed, reactor temperature, heating rate, catalyst loading, type of catalyst, impurities present, and residence time. Temperature and heating rate are the most critical parameters that determine the yield and product distribution in plastic pyrolysis [1] apart from the feedstock composition. In this section, the effect of using different feed mixtures on the liquid yield and quality is presented.

5.1. Interaction effect of LDPE-PP mixture
PP was mixed with LDPE in various compositions and its effect on the pyrolytic product yield and the quality of fuel oil was studied. Figure 2 shows the yield distributions of the pyrolytic products from PP-LDPE binary mixture. It was noticed that an increase in the proportion of PP in a binary mixture with LDPE increases the liquid yield and decreases the gas yield. This follows the expected trend since PP pyrolysis gives a higher liquid yield compared to LDPE pyrolysis. Further, oil from LDPE is waxy (high alkane content) in nature as opposed to oil from PP pyrolysis – this is evident from the
shift in major component from alkanes (60%) to aromatics (88%) as we go from 90% LDPE to 90% PP in the mixture as shown in table 2.

![Figure 2. Yield distributions of the pyrolytic products from PP-LDPE binary mixture](image)

Hydrogen to carbon ratio (H/C) is a simple and overall characterization parameter for hydrocarbon fuels. The H/C ratio was obtained using results from the CHNSO analysis. Effective H/C ratio of the fuel oil obtained from the pyrolysis of binary mixture of PP-LDPE in figure 3 shows that the H/C ratio decreases with an increase in the percentage of PP in the mixture. The pyrolytic oil content included alkanes, alkenes, aromatics and cyclic hydrocarbons.

![Figure 3. Effect of addition of PP in a binary mixture with LDPE on the H/C ratio](image)

Table 2 shows the effect on the liquid composition of the oil obtained. It was observed that addition of PP increases the aromatics content in the liquid oil, which also explains the lowering of H/C ratio observed in figure 3.
Table 2. Effect of addition of PP in mixture with HDPE on the composition of liquid fuel

| Binary Mixture     | Alkane | Alkene | Alkynes | Olefins Cyclic | Aromatic |
|--------------------|--------|--------|---------|----------------|----------|
| 10% PP-90% LDPE    | 59.9   | 22.8   | 0.0     | 8.0            | 3.2      |
| 30% PP-70% LDPE    | 15.5   | 20.6   | 4.6     | 5.4            | 53.8     |
| 50%PP-50% LDPE     | 16.0   | 9.8    | 2.9     | 9.3            | 61.8     |
| 70% PP-30% LDPE    | 14.0   | 4.4    | 1.0     | 7.9            | 73.8     |
| 90% PP-10% LDPE    | 2.2    | 1.7    | 1.6     | 4.0            | 88.6     |

5.2. Interaction effect of HDPE-LDPE mixture

Figure 4 shows the distribution of pyrolytic product yields for various compositions of HDPE-LDPE mixtures. It is expected that addition of HDPE would monotonically decrease the liquid yield since it has a higher crystallinity and requires more severe conditions for cracking. However, increase of HDPE in a binary mixture with LDPE did not show a monotonic trend – the liquid yield increased, remained constant and decreased. The opposite trend was observed with the gas yield. However, the solid yield increased almost monotonically with increase in percentage of HDPE - this is possibly due to higher char formation tendency of HDPE.

![Figure 4](image1.png)

Figure 4. Yield distributions of the pyrolytic products from HDPE-LDPE binary mixture

![Figure 5](image2.png)

Figure 5. Effect of addition of HDPE in a binary mixture with LDPE on the H/C ratio
Table 3. Effect of addition of HDPE in mixture with LDPE on the composition of liquid fuel

| Binary Mixture | Alkane (wt%) | Alkene (wt%) | Alkynes (wt%) | Olefins Cyclic (wt%) | Aromatic (wt%) |
|----------------|--------------|--------------|---------------|---------------------|---------------|
| 10% HDPE-90% LDPE | 55.0         | 38.3         | 0.2           | 2.4                 | 2.0           |
| 30% HDPE-70% LDPE | 66.1         | 26.3         | 0.3           | 2.5                 | 3.7           |
| 50% HDPE-50% LDPE | 66.5         | 27.4         | 0.2           | 2.3                 | 2.1           |
| 70% HDPE-30% LDPE | 62.6         | 28.5         | 0.0           | 4.1                 | 3.1           |
| 90% HDPE-10% LDPE | 54.9         | 34.3         | 0.3           | 4.1                 | 2.4           |

Increasing HDPE proportion in the binary mixture with LDPE resulted in an increase in the alkane content in the pyrolytic oil initially and then decreased as shown in table 3. The alkenes follow the opposite trend while no trend was seen in case of aromatics. LDPE has a high degree of branching, and HDPE is highly linear – as the mixture composition varies, it is envisaged that the aromatic content would change appreciably. This did not happen possibly owing to the less than required severity to crack HDPE. Hence, one might have to choose either a higher temperature or higher catalyst loading for this mixture. Except for the initial decrease, the H/C ratio also remains constant (see figure 5).

5.3. Interaction effect of HDPE-PS mixture

From figure 6, it can be inferred that the liquid and gas yields do not show a monotonic trend with increasing addition of HDPE in a mixture with PS and the variation is ~10%. Increasing the amount of HDPE is expected to lower the liquid yield and increase the char yield slightly owing to its higher degree of crystallinity. However, it is interesting to note that the liquid yield is almost the same at 90% PS and 90% HDPE composition. Table 4 shows the effect of addition of PS in a mixture with HDPE on the liquid composition. It was observed that increasing the content of PS increases the aromatics content and decreases the H/C ratio in the liquid oil obtained. Similar observation was reported by Butler et.al. who attributed the aromatic content in the liquid produced to addition of polystyrene during the pyrolysis of a binary mixture of PE and PS [1]. The amount of alkenes is comparable at 50% HDPE and 90% HDPE – 34.3% and 29.6%, respectively. However, the aromatic content (49.5% vs. 41.8%) is higher in case of 50% HDPE while the alkane content (22.4% vs. 11.4%) is higher in case of 90% HDPE. This is possibly due to the increased availability of hydrogen as the HDPE content increases which converts the alkenes to alkanes rather than into aromatics.

![Figure 6. Yield distributions of the pyrolytic products from HDPE-PS binary mixture](image-url)
5.4. Interaction effects of other mixtures
No significant change in the product yields was observed for PP-PS mixtures. Increasing the percentage content of PS in the PP-PS mixtures increased the aromatic content of the oil product and a decrease in the H/C ratio. The product yield and oil composition trends using LDPE-PS mixtures were not monotonic in nature and are under further investigation. In case of HDPE-PP mixtures, it was observed that increase in HDPE content resulted in a decrease in the liquid yield and increase in the gas yield. It also led to an increase in the alkane and decrease in alkene content of the liquid oil.

6. Conclusions
Different binary mixtures of the plastics (HDPE, LDPE, PP and PS) behaved in different ways during catalytic pyrolysis and showed non-linear behaviour with respect to the product yields and distribution. Hence, care should be taken in finding the product yields from mixtures of plastics and a weighted average may not always be accurate which is commonly used in many simulation studies. With increased PP in LDPE, the liquid yield increased as well as the aromatic content as expected monotonically. However, addition of HDPE to LDPE or PS did not show monotonic trends – further investigations to ascertain these differences in behaviour are in progress. Based on the results presented, the following binary mixtures would be preferable as they exhibit maximum liquid yield and have a lower wax content – 90%PP with LDPE, 50% HDPE with LDPE and 90%PS with HDPE.

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Table 4. Effect of addition of PS in mixture with HDPE on the composition of liquid fuel

| Binary Mixture | Alkane | Alkene | Alkynes | Olefins Cyclic | Aromatic |
|----------------|--------|--------|---------|---------------|----------|
| 10% PS-90% HDPE | 22.4   | 29.6   | 0.0     | 2.0           | 41.8     |
| 30% PS-70% HDPE | 15.8   | 25.5   | 0.0     | 3.5           | 52.9     |
| 50% PS-50% HDPE | 11.4   | 34.3   | 0.0     | 2.4           | 49.5     |
| 70% PS-30% HDPE | 2.0    | 13.3   | 0.0     | 1.0           | 81.8     |
| 90% PS-10% HDPE | 0.1    | 7.3    | 0.0     | 0.1           | 92.3     |
| 100% PS-0% HDPE | 0.2    | 0.0    | 0.0     | 0.0           | 98.8     |