

## USEFUL LIQUID PRODUCTS FROM THE PYROLYSIS OF MIXED PLASTICS

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### Introduction

Waste plastics pose a very serious environmental challenge because of their huge quantity and disposal problem all over the world. Plastics have now become indispensable materials in the modern world and its applications in the industrial field are continually increasing. The pyrolysis of mixed plastics has been considered as an effective way to convert waste plastics into useful hydrocarbon liquid products. Understanding the interaction of the most widely used plastic types in the plastic mixtures will be a significant step towards predicting the composition of the products from different plastic mixtures.

Pyrolysis of waste plastic affords high rates of conversion into liquid fuels that can be used as feedstock in refinery. There has been a lot of research work on the pyrolysis of individual and mixed plastics into liquid fuels [1-4]. Pyrolysis is a very important and most widely used tertiary recycling process, where plastics are heated in the absence of oxygen. Covalent bonds are broken in a more random fashion, producing a mixture of organic molecules. Polyethylene produces olefins of varying chain length and aromatic polymers produces aromatic compounds such as benzene, toluene and styrene. Pyrolysis can tolerate mixtures of different plastic resins as well as high levels of organic contamination, which is also pyrolyzed [5-7]. The advantage of pyrolysis is that the waste plastics do not have to be separated ahead of time, thereby, eliminating the labor-intensive step as required in the hydrolysis and mechanical recycling methods. Pyrolytic process is therefore ideal for converting waste plastics into liquid fuels is a productive alternative for plastic recycling.

Saudi Arabia is one of the major producers of plastic in the world with total production capacity of around six million metric tons per year. The amount of plastic wastes in Saudi Arabia is about 15wt% in the composition of domestic municipality waste. Saudi Arabia is also one of the largest oil producing country in the world. The present study is concerned with the investigation to develop a processing methodology suitable for the direct liquefaction of actual post consumer waste plastics into useful petrochemical liquid products. The work extends the tertiary recycling investigations further to include thermal and catalytic degradation of mixed plastic waste and the effect of polymer mixture and pyrolysis conditions on the composition of products.

### Experimental

Pyrolytic reactions were carried out in a 25cm<sup>3</sup> stainless steel tubular micro autoclave reactor under different

conditions of weight and type of catalysts, time duration, pressure and temperature with a programmable temperature controller obtained from the Parr Scientific, USA. The operating conditions were evaluated for maximizing the desired liquid products. First, a series of thermal cracking of all plastics, HDPE, LDPE, PP, PS, PVC and PET individually were carried out in a micro autoclave reactor under nitrogen atmosphere in order to establish their thermal behavior and reactivity [2]. Then, in second step of the binary thermal reactions of individual HDPE, LDPE, PP and PET with PS was conducted. Third, the binary catalytic reactions of individual HDPE, LDPE, PP and PET were carried out with PS and catalyst to evaluate the reactivity and interactive effects among the reactants. The reactor was gradually heated at the rate of 5°C/min and temperature was kept at around 430°C for one-hour under the nitrogen. The micro reactor was agitated by a built-in mechanical stirrer and heated with a temperature controlled built-in heater. The gas pressure throughout the experiments remained between 450-650 psi at ambient temperature with nitrogen and evolved gases. After one hour, the reactor was cooled to room temperature keeping under nitrogen and the gases evolved during the pyrolysis were vented out.

**Separation and calculation of liquid products.** After the reaction, the liquid and solid products were separated and analyzed by the solvent fractionation methods. The liquid product was dissolved in three different solvents successively hexane, toluene and THF. The fractions obtained were hexane-soluble materials (HXs); toluene-soluble and hexane-insoluble material (TOLs); THF-soluble and toluene-insoluble material (THFs); and THF-insoluble material called as insoluble organic material (IOM). The masses of HXs, TOLs, and THFs fractions were determined after the fractioning solvent was removed by rotary evaporation and the fractions were air-dried.

Percent conversion of plastics and residue was calculated from the following expression:

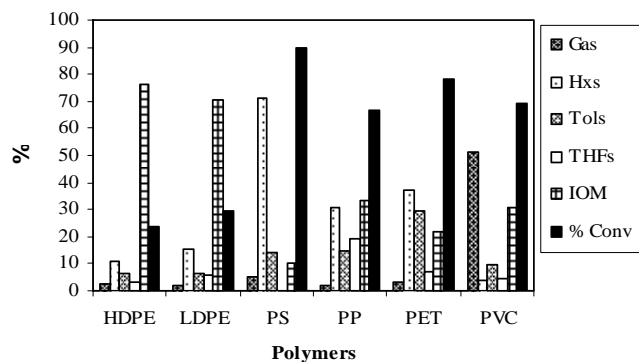
$$\% \text{ Conversion} = \left[ 1 - \frac{\text{g of IOM}}{\text{g of total charge}} \right] \times 100$$

### Results and Discussion

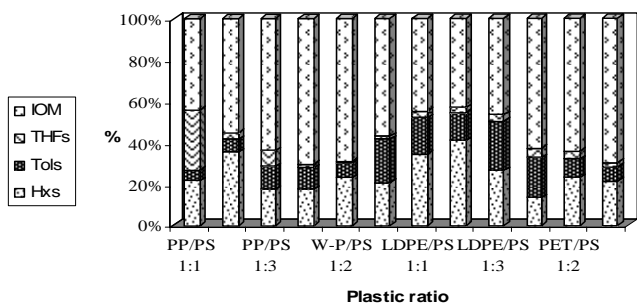
Each component used in this study was reacted individually at optimal reaction conditions. The product distributions from single component thermal pyrolysis are shown in **Figure 1**. The conversion for the single component reactions show that under similar conditions of temperature and nitrogen pressure PS undergo nearly complete conversion whereas LDPE and HDPE yielded lower conversions and PP, PET and PVC remained in the moderate to high conversion. PS was almost completely liquefied so it was selected to investigate the effects of its chemistry on the depolymerization reactions of other waste plastics.

Therefore, thermal and catalytic reactions containing binary combinations of the PS and LDPE, HDPE, PP, PET plastics were studied. The product distributions from the

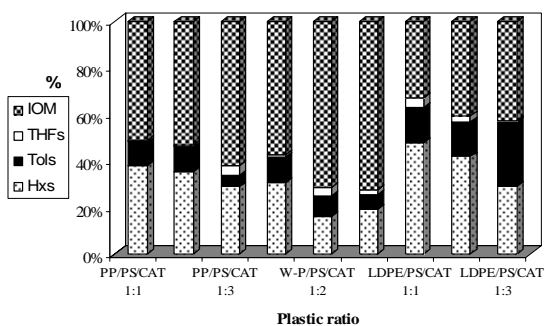
thermal coprocessing of these plastics and PS are shown in **Figure 2**. Three reactions of each plastic with PS were conducted in the ratio of 1:1, 1:2 and 1:3. The amount of PS was varied to understand its reactivity. The result indicated that ratio 1:1 afforded best results in the form of conversion. The conversion includes conversion of total charge (plastics + PS) into gases and liquids products that is called pyrolysis oils. Increasing the amount of PS decreased the conversion percent. It shows that reactivity of PS is not open ended rather depends on the amount of feed. Since PS contains small aliphatic, non-polar, and large aromatic, polar, groups that might be hindering the conversion of other alkyl plastics into liquids. This concept needs to be investigated in depth.



**Figure 1.** Product distributions from the thermal pyrolysis of individual plastics



**Figure 2.** Product distributions from the thermal pyrolysis of mixed plastics.



**Figure 3.** Product distributions from the catalytic pyrolysis of mixed plastics.

The product distributions from the catalytic coprocessing of these plastics and PS are shown in **Figure 3**. In all catalytic coprocessing of mixed plastics, ratio 1:1 afforded the best yields in the form pyrolytic oils. On increasing the ratio to 1:2 and 1:3, the amount of IOM increased appreciably at cost of Hxs. However, in some cases, the amount of Tols is also increased.

## Conclusions

The thermal and catalytic coprocessing of waste plastics with PS is seems to be a feasible process by which waste plastics and waste PS can be converted into liquid fuels or chemical feed stocks. The ratio of PS with other plastics strongly affected the conversion process and the production of hexane soluble material. The coprocessing reaction depends on the nature and compatibility of plastics with PS. Further studies required to investigate the chemical composition of Hxs, Tols and THFs.

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## References

- 1 Scheirs, J. and Kaminsky, W. (Editors), *Feedstock Recycling and Pyrolysis of Waste Plastics*, John Wiley & Sons, March 2006
- 2 Ali, M. F.; Siddiqui, M. N. and Redhwi, S. H. H., *Journal of Material Cycles and Waste Management*, 6 (2004) 27.
- 3 Williams, P. T. and Williams, E. A. *J. Anal. Appl. Pyrolysis* 51 (1999) 107
- 4 Bhaskar, T.; Tanabe, M.; Muto, A.; Sakata, Y.; Liu, C.; Chen, M. and Chao, C. *Polymer Degradation and Stability* (2005), 89, 38-42.
- 5 De Marco, Isabel; Caballero, Blanca; Torres, Amelia; Laresgoiti, Ma Felisa; Chomon, Ma Jesus; Cabrero, M. Angel "Recycling Polymeric Wastes by Means of Pyrolysis", *Journal of Chemical Technology & Biotechnology*, Vol. 77, No. 7, p. 817-824, 2002
- 6 Feedstock Recycling of Plastics Wastes by J. Aguado and D. Serrano, RSC Clean Technology Monographs, Series Editor, James H. Clark, 1999
- 7 Czernik, Stefan; French, Richard J., Production of Hydrogen from Plastics by Pyrolysis & Catalytic Steam Reform, *Energy & Fuels* (2006), 20(2), 754-758