

# AN INTEGRATED APPROACH TO THE RECOVERY OF FUELS AND CHEMICALS FROM MIXED WASTE CARPETS THROUGH THERMOCATALYTIC PROCESSING

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## INTRODUCTION

The recovery of value from the growing volume of mixed polymers in post-consumer waste presents technical and economic challenges when compared to the typical methods of disposal by landfilling and mass burning, which have raised some environmental concerns. Included with typical polymer waste, which currently ends up in landfills, is nearly 3 billion pounds of carpet per year. The high value of the nylon-6, nylon-6/6, and polyester face fiber material is an incentive for their recovery. However, the nature of the carpet construction (face fiber woven into a mixed polymer and inorganic backing material) makes typical recycling methods, such as regrind and remelt, impractical and uneconomical. Integrated, thermocatalytic processing, starting with selective catalytic pyrolysis to recover the high value monomers and followed by gasification of the residual material to generate process energy, is an approach which has shown great promise for recovering the maximum value from this current waste stream.

Selective pyrolysis is a catalytic, thermal technique which optimizes the differences in pyrolysis reaction rates. The pre-sorting requirements for feedstock preparation and the isolation and purification of pyrolysis products are minimized by controlling reaction conditions so that target products can be collected directly in high yields from the waste stream.<sup>1</sup> Figure 1 shows the approach used in this work, which has three major components: (1) identifying target waste streams, (2) developing techniques for the control of conversion processes, and (3) targeting the recovery of high-value chemicals, which are recovered in economically attractive yields. Technoeconomic assessments are used throughout the development process to characterize potential waste streams, identify areas in which improvements can be made, evaluate the overall economic attractiveness of the technology, and compare the technology to competing technologies.

Target wastes include both high-value and high-volume systems. Examples of high-value wastes include the recovery of caprolactam from nylon-6 and bisphenol-A from polycarbonate, both of which currently sell for greater than \$0.70 per pound. High-volume wastes include mixed bottles and residential waste. The high-volume wastes are of great importance, but the economics are not favorable due to the low value, generally less than \$0.15 per pound, of the monomers and chemicals which can be recovered.

In the initial stages of the work, numerous small scale screening experiments are necessary to identify the appropriate catalyst(s) and conditions to optimize the separation and recovery for each of the waste streams. Milligram scale experiments can be studied using pyrolysis molecular beam mass spectrometry (MBMS). The effective quenching of species in their sampled state through free-jet expansion makes MBMS a valuable tool for identifying pyrolysis products.<sup>2,3</sup> Figure 2 shows a schematic of the MBMS used for these experiments. Milligram samples of the plastics are thoroughly mixed with catalyst in a small metal boat. The boat is subsequently inserted into a furnace where hot helium gas is used to sweep the pyrolysis vapors through the reactor. A portion of the vapors are expanded across the stage one orifice on the apex of a cone. The orifice is the entrance to a low-pressure chamber and the pressure difference is sufficient for free-jet expansion, which preserves both light and heavy compounds produced upon pyrolysis. A second expansion collimates a molecular beam, which is introduced into the ion source of the mass spectrometer.

Unlike other pyrolysis-mass spectrometric techniques, large samples can be employed in MBMS studies. The product evolution curves for four of the major packaging plastics are shown in Figure 3. The mixture of pure plastics was pyrolyzed by heating at a rate

of 40°C/min in flowing helium. The rates of product evolution are shown by the key ion current curves that represent major products from each polymer. The times of maximum product evolution for each polymer are different. This suggests that by use of a controlled heating rate, resolution of the individual polymer pyrolysis products may be possible, even for a complex, mixed, plastic waste stream. The PET-derived terephthalic acid (TPA) curve shows two maxima: the first at ~350°C and the second at ~450°C. The first maximum is the result of acid-catalyzed product formation. This demonstrates how a catalyst can be used to selectively influence the rate of product formation and allow the separation of product formation from other components of a mixture.

Once the range of conditions has been sufficiently narrowed, bench-scale experiments can be performed using a stirred-batch or two inch fluidized bed reactor to enable product collection and analysis via conventional analytical techniques. A two inch glass fluidized bed reactor with a heated vacuum shroud enables observation of the melting characteristics of the material as it moves through the fluidizing medium, quickly identifying and heat or mass transfer limitations. After the conditions have been optimized in the two inch reactor, the process is transferred to a continuously fed, engineering scale, four inch fluidized bed reactor. This reactor allows for careful monitoring of temperature and pressure drops. Bed withdrawal enables the reactor to be run in a continuous mode. Validation of the process at this level enables the scale-up to a process development unit (25 kg/hour).

### TECHNOLOGY STATUS

The selective pyrolysis technique has been demonstrated on recovering caprolactam, the monomer of nylon-6, from nylon-6 face fiber carpet, which currently accounts for around 30% of the carpet produced in the United States. A catalyst system allows caprolactam to be recovered at a lower temperature, leaving the polypropylene backing material and the styrene butadiene latex unreacted. Figure 4 shows a ramp and hold experiment, monitored by the MBMS, where nylon-6 and polypropylene are mixed in a steel boat with the catalyst. While the temperature is held around 400°C, caprolactam from the depolymerization of nylon-6 is clearly recovered. Subsequent heating of the sample pyrolyzes the polypropylene and demonstrates that all of the nylon-6 was depolymerized at the lower temperature. Additional catalyst screening identified a catalyst system which improved the depolymerization further, allowing the reaction temperature to be lowered while maintaining a rapid, clean separation of the components.

Continuous tests were performed in a four inch fluidized bed reactor, using shredded whole carpet, and resulted in reproducible caprolactam yields of 85%. Economic analyses performed independently by industry representatives have shown that high purity caprolactam can be recovered from waste nylon-6 carpet for around \$0.50 per pound for a plant which produces 100 million pounds of caprolactam per year. This estimate encompasses the complete process from collection to product purification and assumes that the polypropylene and styrene butadiene used in the carpet backing will be burned for process heat. The major contributor to the production cost is the price for collection and sorting which accounts for around half of the production cost (~\$0.25 per pound of caprolactam produced).

Other applications of the selective pyrolysis technology which have been or are being studied include: recovering dimethyl terephthalate (DMT) from PET containing waste streams, such as polyester carpets, mixed bottles and polyester/cotton fabric blends; bisphenol-A from polycarbonate containing wastes, principally electronics; diisocyanates or diamines from polyurethanes, both methylene and toluene based, from both automotive and appliance applications; phenol, cresol, and xylenol from phenolic resins; and styrene from polystyrene containing residential waste. The PET application is the furthest advanced (after the nylon-6 application). Two inch fluidized reactor results have shown that DMT is recovered from pure PET and mixed PET and polypropylene in yields of greater than 85% when methanol is used as a coreactant in conjunction with the catalytic selective pyrolysis. DMT can also be recovered from waste polyester fabric at comparable yields.

## FUTURE WORK

Current efforts have turned to addressing the problem of the other face fiber materials, nylon-6/6 and PET. The ultimate goal will be to eliminate the need to sort the carpet by face fiber material. It is envisioned that by combining selective pyrolysis with novel purification and separation techniques, all carpets can be pyrolyzed simultaneously while maintaining the ability to separate and recover the valuable. The remaining material, both the backing material and the polyethylene and polypropylene face fiber carpet, will be combusted to fuel the process. An alternative to simply burning the low value material for process energy is to gasify it to produce a clean synthesis gas. This synthesis gas can be used as a feedstock for the production of a wide range of chemicals.

Successful demonstration of the selective pyrolysis approach to handling mixed carpets will be expanded to a complete "Flexible Chemical Processing" technique, wherein any type of plastic waste will be handled at a single processing plant. Minimal on-site sorting will be used to group high-value wastes which can undergo selective pyrolysis to recover the monomers or other high-value chemicals. The remaining waste can be gasified to recover synthesis gas. A portion of the synthesis gas will be used to supply energy for the plant, while the remaining will be converted to chemicals, such as methanol, further lessening the demand for petroleum feedstocks. It is estimated that approximately 10 billion pounds of textile, automotive, and home furnishings waste is available for collection per year. Currently, there are at least 25 major cities in the United States which could support a 200 million pound per year processing plant, resulting not only in an economic way to significantly reduced waste, but also in an energy savings of approximately 7 trillion Btu per year per plant.

## CONCLUSIONS

Selective pyrolysis is a diverse technology which has shown promise for being able to recover high-value products from complex mixed plastic waste streams. The ability to recover caprolactam from waste nylon-6 carpet has been demonstrated to be both feasible and economical at the engineering scale. This technology combined with novel purification technology has the potential to significantly reduce the nearly 3 billion pounds of annual carpet waste. More importantly, high-value products like caprolactam, which sells for around \$0.70 per pounds, are obtained and can be purified to the same grade as virgin material, lessening the demand for petroleum feedstock. Further expansion of this technology will yield the ability to handle even larger plastic waste streams including other textiles, home furnishings, automotive dismantling residue, and residential wastes.

## REFERENCES

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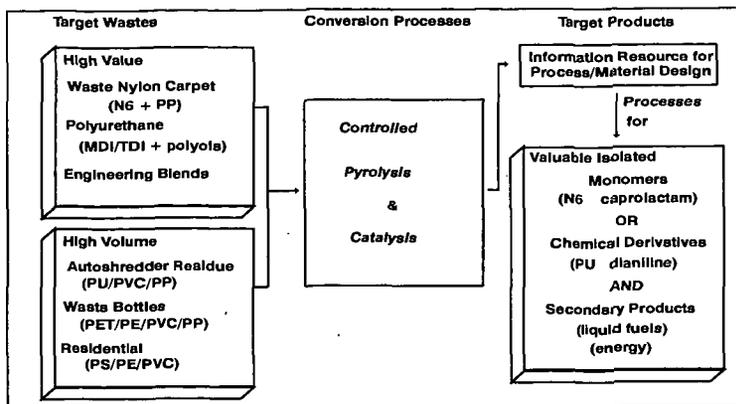


Figure 1. Overview of the NREL approach to the chemical recycling of mixed plastics.

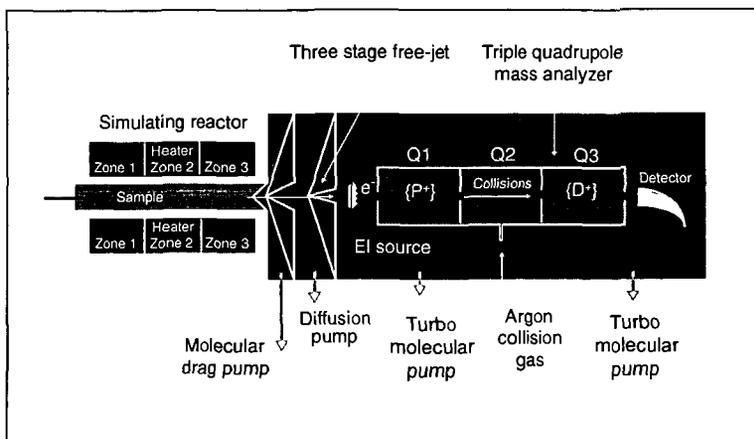


Figure 2. Schematic of Molecular Beam Mass Spectrometric (MBMS) sampling system.

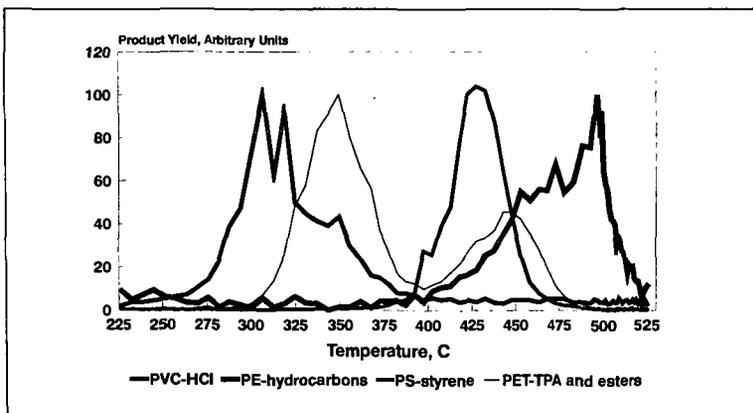
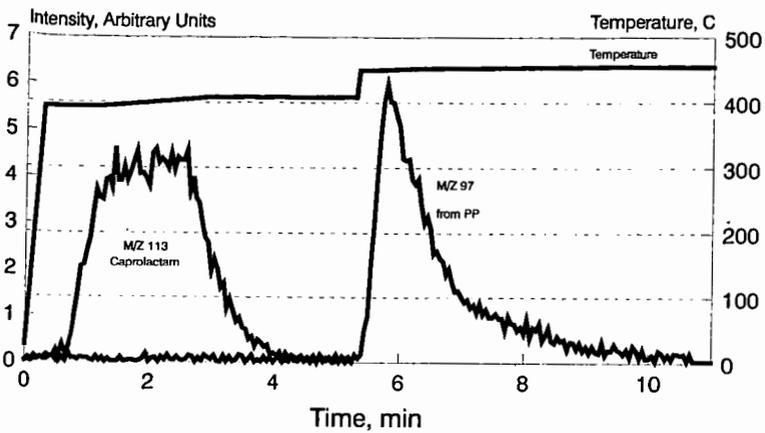


Figure 3. Relative rates of pyrolysis for the four components of a mixture are shown in the time-resolved profile plots of key ion for each polymer: PET -  $m/z$  166, terephthalic acid; polystyrene (PS) -  $m/z$  104, styrene; polyethylene (PE) -  $m/z$  69,  $C_5H_9^+$ , a typical fragment ion of alkenes; and polyvinylchloride (PVC) -  $m/z$  36, HCl.



**Figure 4.** The application of catalytic techniques allows the separation of nylon-6 derived caprolactam from polypropylene derived hydrocarbons.