E. Post-Shred Materials Recovery Technology Development

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Changing World Technologies is cost-sharing on the evaluation of its thermal depolymerization process.
The Polyurethanes Recycle and Recovery Council (PURCC) is also participating and cost-sharing on the evaluation of the Troy Polymers, Inc., polyurethane glycolysis process.

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Objective

- Develop technology for the cost-effective recovery of materials from post-shred residues.

Approach

- Characterize shredder residue from a number of sources to determine composition variability.
- Conduct bench-scale and large-scale process/technology tests to benchmark technology.
- Build and operate a pilot-plant for the separation of shredder residue to produce recovered materials for market evaluation and to provide "control" samples of materials for testing of alternative technologies, as appropriate.
- Conduct cost and performance analysis of alternative technologies to establish the business case for the technologies and to identify technology gaps.

Accomplishments

Mechanical Separation of Shredder Residue

- Processed over 160,000 lbs of shredder residue in Argonne's mechanical separation pilot-plant. Over 50,000 lbs of plastics concentrate were produced. Construction of the plant was completed in the first quarter of FY 2004, and shakedown of the facility occurred during the second and third quarters.
- Increased, through process improvements, yield of polymer concentrate from as low as 40% to 95%.
- Performed mass balance on the process and characterized the shredder residue and the polymer concentrate. Ten shredder residues, including two European and eight United States, were characterized.

Froth Flotation Process for Recovering Plastics

- Completed construction and shakedown of a six-stage froth-flotation plastics separation plant in the first quarter of FY 2005 and started froth-flotation separation trials.
- Recovered over 3,500 lbs of polyolefins (polypropylene [PP] and polyethylene [PE]) product.
- Completed a series of tests to define density distributions and settling velocities of polymers and other materials present in the polymer concentrate.
- Upgraded process to isolate unexpected high content of wood and rubber in the plastics concentrate.

Thermal/Chemical Conversion Processes

- Completed bench-scale and pilot-scale batch testing of Changing World Technologies' (CWT's) thermal depolymerization process for converting shredder residue to fuels.
- Conducted testing in a five-gallon reactor of Troy Polymer, Inc.'s (TPI's) glycolysis process for conversion of urethane foam to polyol initiators. Over 1,200 lbs of foam were used, and over 100 gallons of polyol initiators were produced.

Other Accomplishments

- Completed large-scale tests of Salyp's "thermoplastics sorting" technology by using residue from two European locations and one U.S. location as feed materials.
- Developed an Excel-based process cost model that incorporates two primary modules for the recovery of automotive plastics: the first module includes the unit operations required for recovering a plastics concentrate from shredder residues, and the second module includes the unit operations required to recover selected plastics from the mixed plastics concentrates.

Future Direction

- Continue Argonne froth-flotation campaigns and evaluate process performance and economics; define path forward.
- Complete CWT thermal depolymerization process evaluation; define path forward.
- Complete Polyventure/TPI glycolysis process evaluation; define path forward.
- Test and evaluate the Volkswagon/Sicon (VW/Sicon) technology for separating plastics from shredder residue.
- Update process cost analysis model.
- Review/critique technology developments with representatives of the automotive shredding industry..

Summary

The objective of this project is to develop technology for the cost-effective recovery of materials from post-shred residues. Research will provide data essential to establishing a business case for sustainable recycling of automotive materials from post-shred residue. A wide range of materials recovery technologies is at various stages of development worldwide. Technologies specific to the recovery of materials from post-shred material streams are being evaluated and demonstrated to determine their commercial viability. The performance (e.g., yield, purity, efficiency, and cost) of these emerging technologies will be determined to enable the development of an integrated process for recovering materials from shredder residue.

Research has been completed on the Salyp physical separation/thermosorting process and on Argonne's physical separation process. Research is ongoing on the Argonne froth-flotation process, the Changing World Technologies (CWT) thermal depolymerization process, and the Polyventure/Troy Polymers process for glycolysis of urethane foam.

Characterization of Shredder Residue

To facilitate the development of technology for the recovery of materials and resources from shredder residue, MBA Polymers characterized five shredder residues (two European and three American) by using 2-kg samples. The analysis showed significant variations in these samples. For example, the fines in these fractions ranged between 5% and 38%, and foam in the samples ranged between 21% and 37%, which is about four to seven times what is expected for polyurethane foam. These differences are due to a large extent to the small size of the samples used and demonstrate the difficulty in sampling the heterogeneous shredder residue. After processing over 80 tons of shredder residues from five different U.S. shredders in Argonne's mechanical separation plant, which is described in the next section, we observed (Figure 1):

- Large variations in non-plastic materials (e.g., fines, residual metals, rubber and wood) and
- Less-significant variation in the composition of the polymer fraction.

In addition, the polymer concentrate separated from different shredder residues showed, for the most part, little variation (Figure 2), and the weight percent (wt%) of the polymer concentrate recovered from a given source over a six-month period was reasonably consistent (Table 1).

Argonne Pilot-Plant

Argonne's pilot plant consists of two major facilities. The first is a mechanical (physical) separation facility; the second is a wet-density/froth-flotation separation facility. The pilot-plant was used to:

1. Recover materials from shredder residue,
2. Conduct process improvement/integration studies,
3. Provide a capability to produce large samples of recovered materials for market evaluation,
4. Define the effectiveness of alternative separation technologies and systems, and
5. Serve as a user/demonstration facility to conduct separation tests for residue from specific sources.

The mechanical separation facility is shown in Figure 3. The mechanical separation facility processes the raw shredder residue to yield a polymer concentrate and other fractions, as shown in Figure 1.

The wet density/froth-flotation facility is shown in Figure 4. It includes six continuous stages for the separation and recovery of targeted materials from the polymer concentrate derived from shredder residue. Its design capacity is 1,000 lb of mixed plastics per hour.

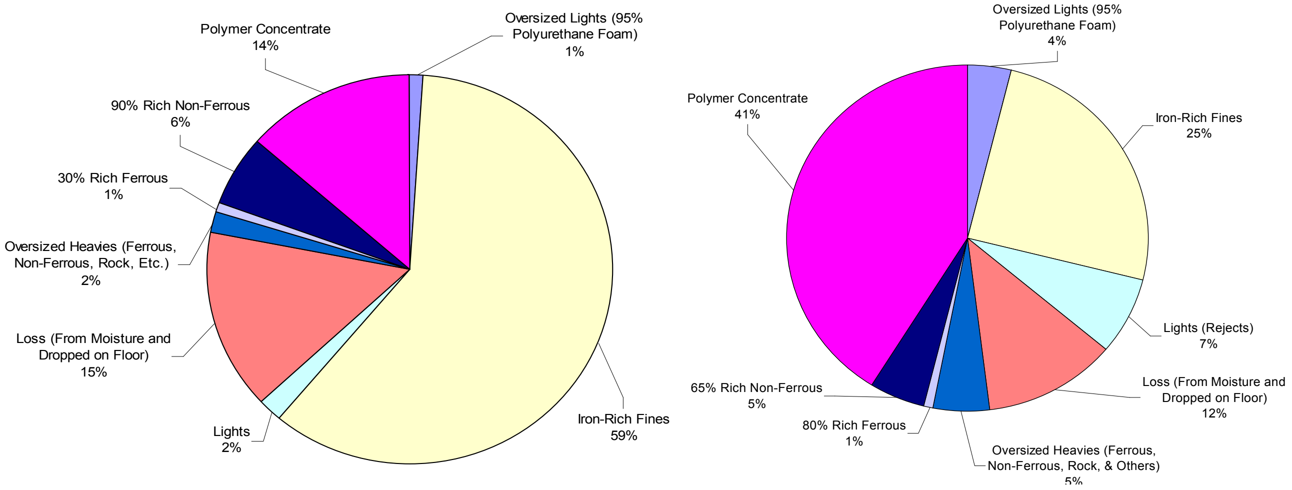

Figure 1. Comparison of shredder residue composition from two shredders.

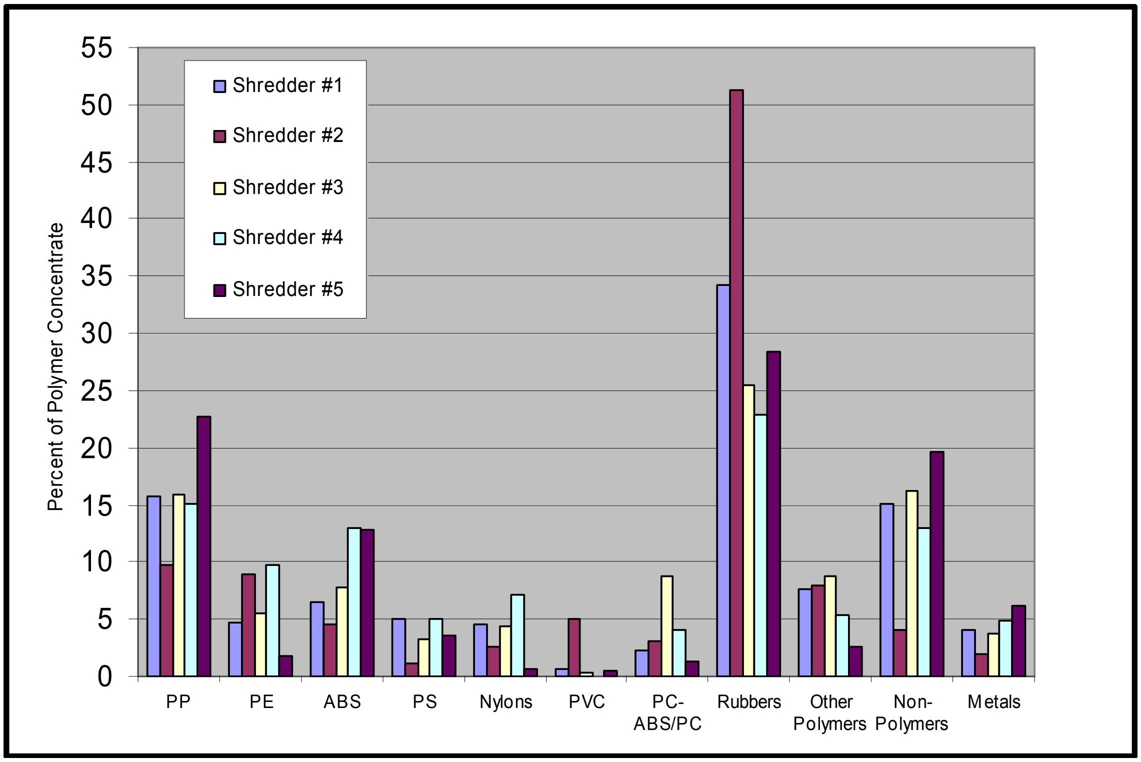

Figure 2. Similarity in composition of polymer concentrate from different shredders.

Table 1. Variability of yield of polymer concentrate from a given source over a six-month period

Run #	Polymer Concentrate (wt%)	Run #	Polymer Concentrate (wt%)
2	41	6	45
3	26	7	37
4	36	8	43
5	39	9	45
		Average	40

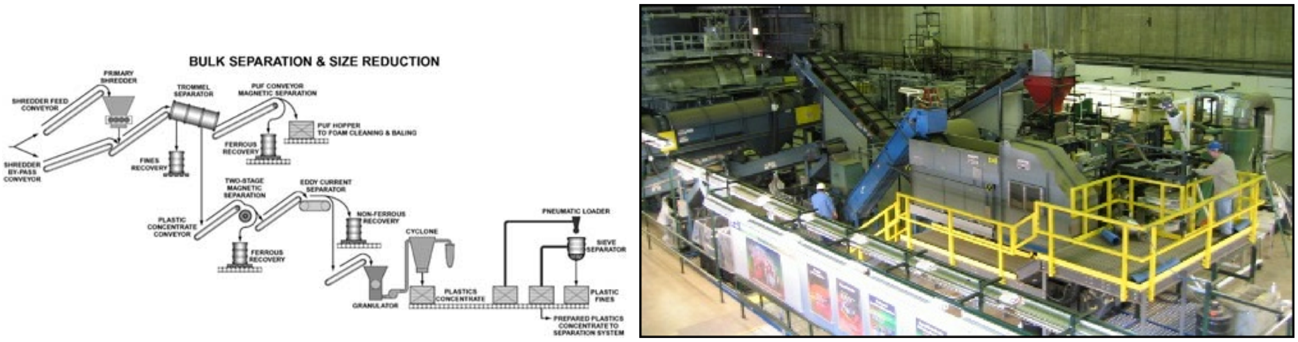

Figure 3. Argonne pilot mechanical separation system for processing raw shredder residue.

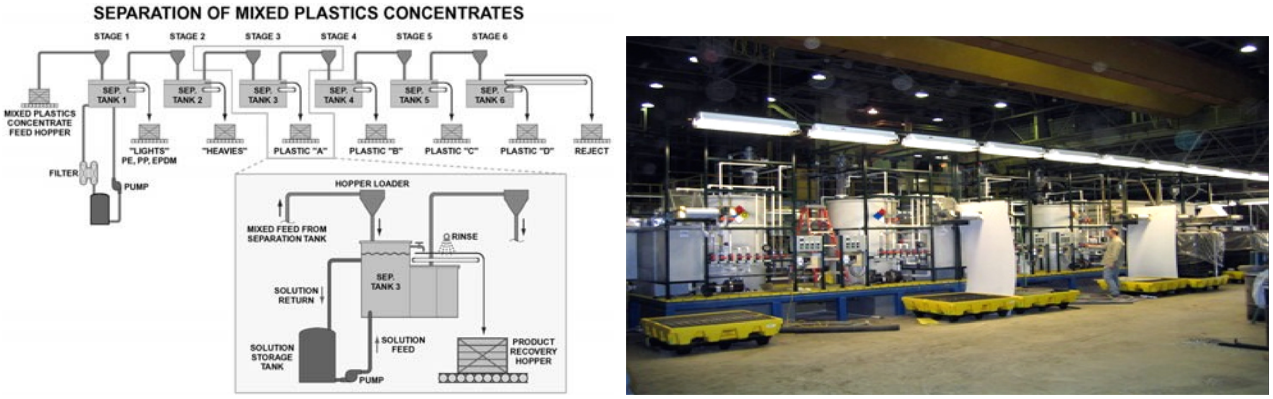

Figure 4. Argonne pilot wet separation system for recovery of plastics from shredder residue.

Mechanical Separation Pilot-Plant

Initially, six campaigns totaling 60,000 lbs of shredder residue were undertaken to debug and shake down the mechanical separation pilot-plant. The average yield of polymer concentrate recovered from these campaigns was only about 17% of the total weight of the shredder residue. This yield was significantly lower than anticipated. Analysis of the various separated streams showed that the recovery of the polymers from shredder residue in the polymer concentrate fraction was also low (40–70%) for the different source materials. As a result, a loss analysis was undertaken. The analysis included sampling and quantification of residual polymers in each of the fractions that are generated in the bulk processing of shredder residue to recover the polymer concentrate. On the basis of this loss analysis, minor process modifications were made, and some of the fractions were reprocessed. As a result, the yield of plastics concentrate more than doubled.

Loss analyses were also conducted on the various non-polymer concentrate fractions after the modifications were made. These analyses indicated that the recovery of polymers targeted for recovery in the polymer concentrate was about 95% of those polymers available in the shredder residue. Although the yield of the polymers targeted for recovery in the polymer concentrate was about 95%, the polymer concentrate also included an unexpectedly high and varying concentration of wood and rubber (Figure 2). The wood content was about 1–4% by weight. In Figure 2, the wood is included in the “non-polymers.”

Trials were conducted by using commercially-available air aspirators, classifiers, air-gravity tables, and mineral jigs to remove wood and rubber from the polymer concentrate. Using this equipment did not yield satisfactory results.

Froth-Flotation Pilot-Plant

A shakedown of the wet density/froth-flotation facility was conducted during the second quarter of FY 2005 by using about 4,000 lbs of post-consumer electronics and appliance mixed plastics. These materials were used because their composition is much less variable than the composition of plastics concentrate from shredder residue. The shakedown tests were conducted to target the recovery of acrylo-nitrile-butadiene-styrene (ABS) and polystyrene (PS). Trials were also conducted by using colored plastics supplied through the American Plastics Council. These trials confirmed the effectiveness of the basic system.

The initial trials of the froth-flotation system on shredder residue plastics were complicated by the unexpected high rubber and wood content of the polymer concentrate. Bench-scale tests were conducted to define the specific gravity and settling velocities of the wood and rubber relative to other species in the polymer concentrate. Several plastics, wood, and rubber species were found in every specific gravity range. Several plastics, wood, and rubber species were also found to have overlapping settling velocities. The data indicated that neither specific gravity nor settling velocity differences were large enough to effect the separation of wood and rubber from the plastics.

Trials using various process solution conditions were also conducted. These trials ultimately yielded a set of conditions to remove almost 100% of the wood and to concentrate the rubber into two separate fractions with a nominal loss (less than 5%) of the polymers (such as the polypropylene [PP] and polyethylene [PE]) that are being targeted for recovery. The resultant process conditions have been incorporated into the Argonne froth-flotation process. More than 3,500 lb of a PP/PE fraction that is over 95% PP/PE have been consistently produced. Its wood content is less than 0.2%. The recovered PP/PE has properties similar to those of some commercially-available PP materials. The recovered PP/PE product constituted about 5%–6% of the starting shredder residue weight.

An 80% rubber concentrate was also recovered. A 50-lb sample of the rubber concentrate was submitted for testing by using the "TireCycle" process used for recycling rubber materials. It was determined that the presence of the plastics in the rubber concentrate is likely to improve the properties of the recycled rubber when used to make construction products (such as roofing shingles).

A 75% ABS concentrate has been recovered. The ABS concentrate contained incompatible materials, including filled PP. Trials are ongoing to improve the composition of the ABS concentrate and to recover other polymers from the polymer concentrate.

Changing World Technologies

Changing World Technologies, Inc. (CWT), has developed a thermal conversion process that converts organic material into high hydrocarbon oil. The process was tested for processing shredder residue. The process was able to convert the shredder residue samples into three product fractions: an oil, a gas, and a carbon char. A pilot-scale test apparatus was designed and built by CWT to simulate commercial-scale handling and depolymerization/dissolving of a mixed automotive waste stream (90% shredder residue/10% post-consumer tires). Tests were conducted to confirm the technical and economic feasibility of this process.

In the process, a 1/16-in. mesh vibrating screen was used to separate the fines (mostly inorganic matter), which constituted about 36% of the total shredder-residue sample weight. The shredder residue was supplied by Argonne. About 700 lb of the remaining fines-free material was processed along with 80 lb of shredded tires and 1,700 lb of used motor oil. Samples of the various products were sent out for analysis to determine the fate of the inert solids and contaminants (i.e., heavy metals, polychlorinated biphenyls [PCBs], and chlorine).

Thermal cracking tests of this CWT hydrocarbon fuel were performed in bench-scale Parr reactors to simulate the production of transportation fuels. The products generated were hydrocarbon oil, a fuel-gas, and a solid carbon product. The distribution of oils/gas/carbon fractions was determined to be 84%, 10%, and 6%, respectively. A fractional distillation of the oil was also performed. This process generated gasoline, diesel, and heavy hydrocarbon oils (Figure 5). The distribution was gasoline (12%), middle-distillate (38%), diesel (32%), heavy-oil (15%), and gas (3%).

Figure 5. Left to right: gasoline, middle distillate, diesel, and heavy fuel oil reduced by the CWT process.

Troy Polymers Process for Glycolysis of PUFs

Troy Polymers, Inc. (TPI), has developed a patented process for the conversion of mixed polyurethane foams (PUF), such as that present in shredder residue, into polyol initiators (Figure 6), which can then be utilized to produce urethane products. PUFs first undergo glycolosis, followed by filtration and removal of PCBs and other substances of concern from the liquid glycolyzed product. In a second stage, the glycolyzed products are propoxylated by using propylene oxide to produce polyols.

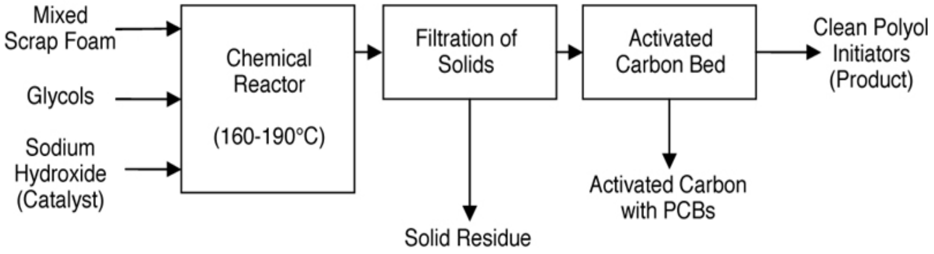

Figure 6. TPI's glycolysis process conceptual process flow sheet.

In FY 2004, bench-scale testing was undertaken to establish proof-of-concept. The results demonstrated the technical feasibility of the process for converting mixed, clean PUF from shredder residue to polyol initiators at a yield of about 88%. The yield for dirty foam was about 72%. The product from dirty foam required extensive filtration to remove the solid residue. The results also indicated that commercially available activated carbons were able to reduce the concentration of PCBs to below 1 ppm.

In FY2005, the process was scaled up in a 5-gal reactor. Scale-up included testing of the filtration of solid impurities and removal of PCBs and other substances of concern from the polyol initiator. Over 1,200 lb of foam separated from shredder residue have been processed, and over 100 gal of polyol initiator have been produced. The effects of temperature, glyocol-to-foam ratio, and catalyst types on the reaction yields have been evaluated. Results indicate that diethylene glycol (DEG) gives a higher yield and allows reaction at lower temperature than dipropylene glycol (DPG). Potassium hydroxide (KOH) was preferred over sodium hydroxide (NaOH) as a catalyst. By using optimized reaction conditions with DEG and KOH catalyst, >90% reaction yields were consistently achieved.

Various filtration methods were also evaluated for the removal of unreacted solids from the polyol initiator. A nylon bag filter was installed in a recirculation loop with the 5-gal reactor to remove solids larger than 200 μm. Although bag filtration worked well on a 5-gal scale, for a production-scale process, continuous filtration systems will most likely be required.

Treatment with activated carbon was also capable of removing PCBs from the polyol initiator to nondetectable levels (<2 ppm). The PCBs are removed more readily from the polyol initiators produced from DEG than DPG. The removal of PCBs via activated carbons from polyol initiator was demonstrated by using Aquasorb 1500 activated carbon. Twenty gallons of the polyol initiator, which had an equivalent weight of 163, was also submitted for propoxylation to Pelron Corporation in Illinois, where two lots were produced. In one lot, the equivalent weight of polyol was 354, and in the other lot, it was 173. That two different equivalent weights were produced proves that polyols with different equivalent weights can be produced from the recycled polyol initiators.

The recycled polyols produced from shredder-residue foam were also tested in preparing rigid PUFs. The recycled polyols exhibited several advantages over the virgin commercial polyols. They were more reactive than the virgin polyols in that they required fewer or no catalysts. Furthermore, the foams based on the recycled polyols had much better flame resistance than the foams based on the virgin polyol.

Initial economic analysis of the process to produce polyol initiator and polyols via propoxylation indicated that the glycolysis process is economical.

Publications

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