

Conversion of Waste Plastic to Oil: Direct Liquefaction versus Pyrolysis and Hydroprocessing

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Two approaches for the conversion of waste post consumer plastic (PCP) into oil have been investigated: (1) direct liquefaction and (2) pyrolysis followed by hydroprocessing of the pyrolysis liquids. The PCPs investigated were a washed PCP provided by the American Plastic Council (APC) and a PCP prepared by dry preparation methods provided by the Duales System Deutschland (DSD). The DSD plastic contained significantly more ash, paper, dirt, and chlorine than the APC plastic and is considered to be more representative of true waste PCP. Direct liquefaction of both plastics was investigated using small additions (1–5 wt %) of a number of different solid acid catalysts. At 445 °C, the catalytic effect on oil yields was negligible for both plastics. Several catalysts had a significant effect on the boiling point distribution for the APC plastic, producing lighter products, but had little or no effect for the DSD plastic. An alternative approach of pyrolysis followed by hydroprocessing the pyrolysis liquids was investigated for the DSD plastic. Pyrolysis yields of 75–80% of relatively heavy liquids were achieved at 600 °C. Addition of Na₂CO₃ to the pyrolysis reactor decreased the chlorine content of the pyrolysis liquids to ~50 ppm. The boiling point distribution of the pyrolysis liquid was substantially improved (55–65% gasoline fraction) by either thermal or catalytic hydroprocessing (450 °C, 200 psig initial H₂ pressure). The effect of adding 1–5% of several catalysts was relatively small, increasing the gasoline fraction over that obtained by thermal hydroprocessing by 5–10%. Addition of Na₂CO₃ to the hydroprocessing reactor decreases the chlorine content of the final product to a few ppm. These results indicate that pyrolysis followed by hydroprocessing of the pyrolysis liquids is a good approach for true PCP that contains a significant amount of chlorine, paper and inorganic material.

Introduction

During recent years, there has been extensive research on the liquefaction of waste polymers and the coliquefaction of waste polymers with coal, petroleum resid, and waste oil. Summaries of this research are available in several conference and symposia proceedings volumes^{1–4} and in a recent review on coprocessing of wastes with coal.⁵

A significant amount of research has been conducted on the catalytic liquefaction of plastic. Excellent results have been obtained from liquefaction of individual polymers (polyethylene (PE), polypropylene (PPE), polystyrene (PS), etc.) and relatively clean mixed plastic using solid acid catalysts and metal-promoted solid acid catalysts.^{6–14} For example, Venkatesh et al.¹³ and

Shabtai et al.¹⁴ have obtained high yields of liquids that consist predominantly of isoalkanes in the gasoline boiling range from HDPE, PPE, and PS at relatively low temperatures (300–375 °C) using Pt-promoted ZrO₂/SO₄ or ZrO₂/WO₃ catalysts. However, true post-consumer plastic (PCP) contains heteroatoms (principally chlorine, but also nitrogen and some sulfur), paper, dirt, and inorganic matter that can render such catalysts ineffective.

In the current paper, the effect of small additions (1–5%) of a number of solid acid catalysts on the liquefaction of true PCP is determined. In addition, a two-step approach is investigated in which PCP is first pyrolyzed and the pyrolysis liquid is then hydrotreated. The later approach is found to be preferable for true PCP.

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Table 1. Proximate and Ultimate Analyses of APC and DSD Waste Plastics (wt %)

proximate	APC	DSD	ultimate	APC	DSD
volatile matter	98.8	93.8	C	84.7	79.0
fixed carbon	0.74	1.08	H	13.7	13.5
ash	0.45	4.44	N	0.65	0.67
moisture	0.01	0.16	S	0.01	0.08
			Cl	0.03	1.26
			O (difference)	0.91	5.49

Experimental Procedures and Materials

The feedstocks were a commingled waste plastic obtained from the American Plastic Council (APC) and a post consumer waste plastic provided by the Duales System Deutschland (DSD). The APC plastic has been used in a number of previous experiments.^{7–11} It is a relatively clean waste plastic that has been subjected to a wet washing process to remove labels and inerts. The Duales System Deutschland is the organization that oversees the recycling of most of the waste plastic in Germany. The DSD waste plastic used in this research is the same plastic feedstock used in the German feedstock recycling industry. As discussed elsewhere,^{15,16} this material is subjected to sorting, shredding, automated cleaning by magnetic, eddy current, air and screen separation techniques, and agglomeration to produce a relatively uniform, pelletized PCP feedstock. The proximate and ultimate analyses of these materials are given in Table 1.

The liquefaction procedure has been previously described.^{6,7} The experiments were performed using 50 mL tubing bomb microreactors. Approximately 10 g of feedstock was placed in a tubing bomb. Catalyst was added at concentrations of 1–5 wt %. The bomb was then purged with H₂ gas and charged to a final cold pressure of 200 or 800 psig. The apparatus was immersed in a fluidized sand bath at the desired temperature and agitated at 400 rpm for either 30 or 60 min. Data were obtained at temperatures of 415–455 °C. After liquefaction, the sandbath is lowered and the tubing bomb is air-cooled to room temperature. The gas is collected in a 40 mL gas bomb at liquid nitrogen temperature and weighed. The remaining sample is analyzed by conventional solvent extraction methods. The total liquid conversion is the THF-extractable material, while the oil yield is defined as the pentane-soluble liquid. Asphaltenes + preasphaltenes (A + PA) are defined as the product that is soluble in THF but not in pentane. Mass balances of 90–95% were obtained.

For each reaction condition, two samples were run. A sample of the liquid product was taken directly from the second tubing bomb and subjected to simulated distillation (SIMDIS) analysis using a Perkin-Elmer gas chromatograph with the following operating parameters: column – 18 in. × 1/8 in. packed column; temperature –10 to 360 °C with 10 °C/min ramp; detector, FID at 380 °C; flow rate, 35 mL/min He. SIMDIS software provided by Perkin-Elmer was used to analyze the data. The results are reported as boiling point (BP) ranges as follows: gasoline, IBP–200 °C; kerosene, 200–275 °C; and heavy oil, 275 °C–FBP.

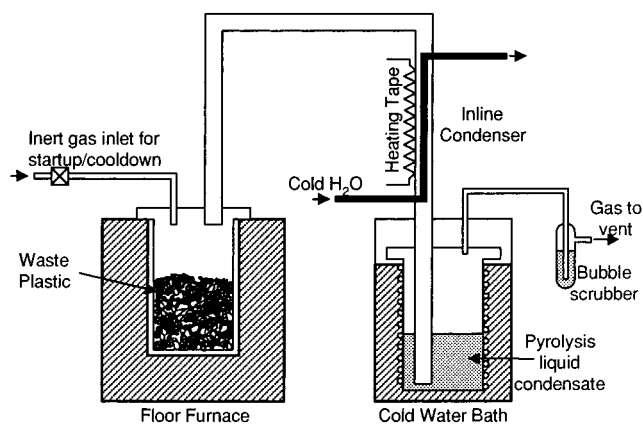
The catalysts used in the liquefaction experiments included commercial HZSM-5 zeolite, a ZrO₂/WO₃ catalyst, nanoscale ferrihydrite treated with citric acid (FHYD/CA),¹⁷ ferrihydrite containing 5% Mo (FHYD/Mo),¹⁸ a SiO₂–Al₂O₃ binary oxide,⁸ and two TiO₂–SiO₂ binary oxides ([Ti]/[Ti + Si]) = 0.85 and 0.85(+) prepared using the method of Doolin et al.¹⁹

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**Figure 1.** Schematic of watch plastic batch pyrolysis process.

Pyrolysis of the PCP was carried out in a batch pyrolysis reactor that contains up to 500 g of material. A diagram of the reactor is shown in Figure 1. During startup, an inert gas (helium) is used to purge the air from the inside of the pyrolysis reactor. As the waste plastic temperature is raised above ~100–150 °C, gaseous products are generated from inherent moisture and nonplastic organic components such as paper and food. The flow of inert gas is turned off shortly after this stage begins and subsequent heating causes the plastic to release additional non-oxidizing gases with sufficient positive pressure to prevent any air from entering the reactor.

As illustrated in Figure 1, the gaseous components then travel to the lower pressure condenser and liquid collection vessel through an unheated transfer tube. The vapors lose heat to the surroundings in this unheated, un-insulated, transfer tube. An inline water condenser further quenches the pyrolysis reaction products to predominantly liquid hydrocarbon products. Since the condensation of solid waxy materials can block the narrow pathway in the condenser section, the temperature of the condenser can be raised by either using an external heating tape or by controlling the flow of the cooling water. The condensate collection vessel is kept at ambient temperature by a cooling water coil outside the vessel and by partially submerging the vessel in a water bath. The inlet to this vessel is at the bottom so that oil vapors have to pass through a pool of cool pyrolysis liquid thereby enhancing the oil yield. Gases then leave the condensate vessel and are vented after bubbling through a water pool. This bubbler scrubs acid gases and prevents the back-flow of air into the vessels. The collected pyrolysis liquids were subjected to simulated distillation analysis and chemical analysis. They were then hydrotreated in the same manner as described above for the liquefaction experiments.

The pyrolysis liquids and residue were weighed to determine yields. Gas yield was determined by difference for most runs. However, for some of the pyrolysis experiments at 600 °C, the gases were collected in a gas bomb kept at liquid nitrogen temperature and weighed. The mass balance for these experiments was >96%.

For many of the pyrolysis and hydroprocessing experiments using the DSD waste plastic or its pyrolysis liquids, a small amount of Na₂CO₃ (2–3%) was added to capture chlorine released as HCl by poly(vinyl chloride) (PVC).

Results and Discussion

Liquefaction Results. As noted earlier, solid acid catalysts have been shown to significantly enhance oil yields from individual polymers and clean mixed plastics. The APC plastic is a PCP that has been subjected

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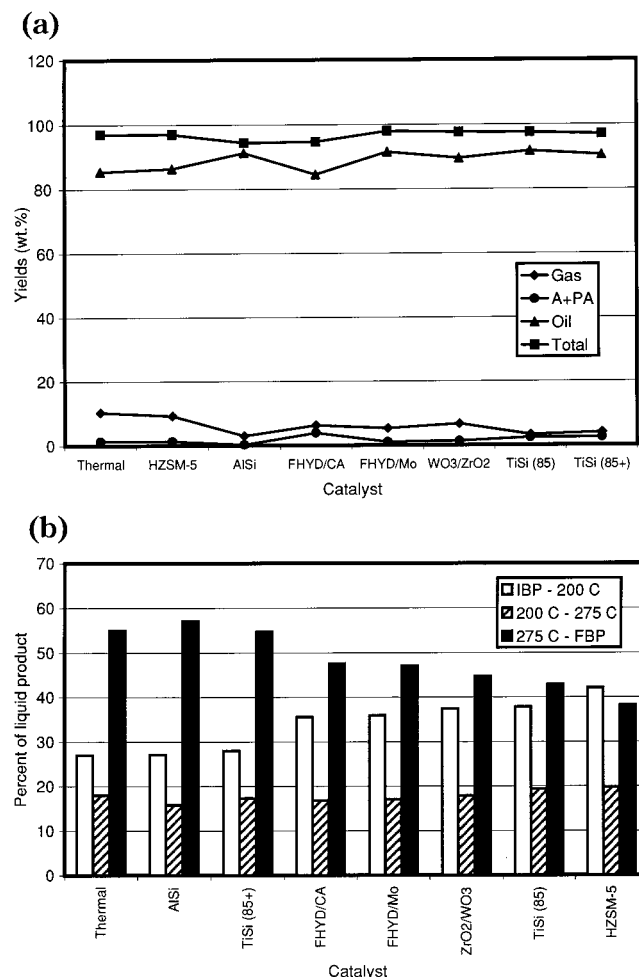


Figure 2. (a) Liquefaction yields for APC plastic at 445 °C, 60 min, 200 psig initial hydrogen pressure. (b) Comparison of SIMDIS results for thermal and catalytic liquefaction of APC plastic at 445 °C.

to a washing process. As seen in Table 1, this process removed most of the PVC and much of the dirt and inorganic matter. It has been observed that solid acid catalysts do have a beneficial effect on total conversion and oil yield from the APC plastic at temperatures below approximately 430 °C.⁸⁻¹¹ At somewhat higher temperatures, however, thermal and catalytic liquefaction yields are quite comparable. This is illustrated in Figure 2a, which shows that the yields obtained from the APC plastic at 445 °C (1 h, 200 psig H₂-cold pressure) thermally and with a 1 wt % addition of a number of different catalysts are generally within a few percent of each other. Nevertheless, there is a catalytic effect on the boiling point distribution of the oil product. As seen in Figure 2b, a 1% addition of HZSM-5 and several of the other catalysts significantly increases the gasoline fraction (IBP-200 °C). Similar experiments by Ding et al.¹⁰ using the APC plastic with higher percentages of HZSM-5 established (by GC-MS) that there was a significantly higher percentage of branched products and aromatics in the catalytically produced oils than in the thermally produced oils.

The dirtier DSD waste plastic is considered to be more realistic in terms of the feedstock that would be available for a large scale operation. As discussed elsewhere,^{15,16} it has been subjected to dry sorting and cleaning processes but still contains a significant amount

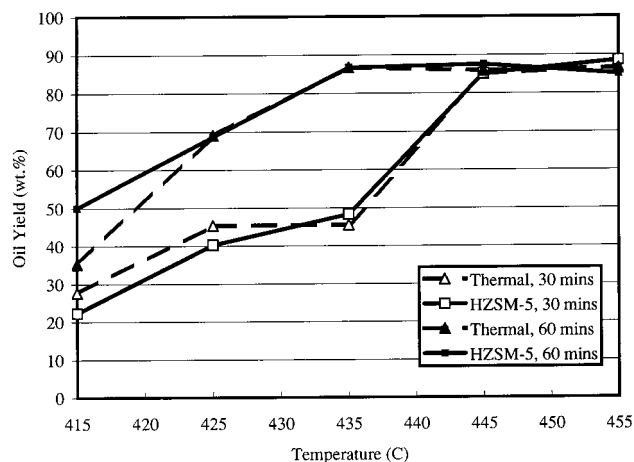


Figure 3. Effect of temperature and time on oil yield obtained from hydrotreatment of DSD plastic (200 psig H₂, cold).

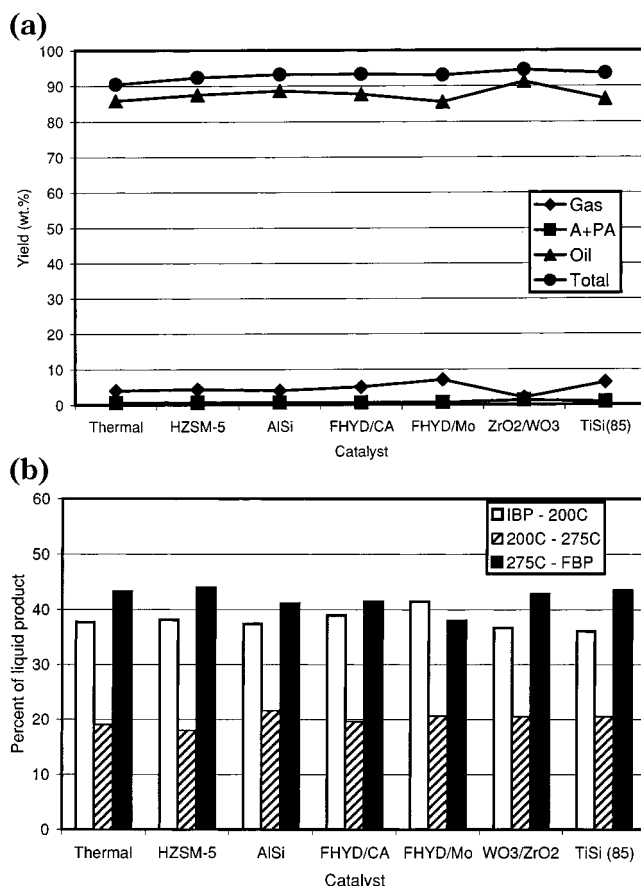


Figure 4. (a) Liquefaction yields for DSD plastic at 445 °C, 60 min, 200 psig initial hydrogen pressure. (b) Simulated distillation results for oils obtained from DSD waste plastic at 445 °C.

of PVC, paper, and dirt (see Table 1). Not surprisingly, the catalytic effects observed for this PCP are significantly less than those observed for the APC plastic, as illustrated by Figures 3 and 4. Figure 3 illustrates the oil yield as a function of temperature for two reaction times under thermal conditions and with a 1 wt % addition of HZSM-5. Only at the lowest temperature and shorter reaction time does there appear to be a catalytic effect that exceeds the error of the measurements ($\pm 5\%$). With a 1 wt % addition of any of the catalysts examined, no effect is observed on either yields or boiling point distributions at 445 °C, as illustrated by Figure 4a,b.

Pyrolysis-Hydroprocessing: A Two-Step Approach. Real post-consumer waste plastic contains a variety of nonplastic materials. These include cellulosic wastes, such as paper, food and other organics, dirt, moisture, aluminum foil, and other inorganic materials. Additionally, post-consumer waste plastic includes polymers such as poly(vinyl chloride) (PVC) and polyurethane, which contain potentially harmful heteroatoms (Cl and N). The results summarized above suggest that a pretreatment is necessary to separate the valuable hydrocarbon component of PCP prior to hydrotreating it. Wet cleaning processes, such as that used for the APC plastic, are one way of achieving this goal. However, such processes are expensive¹⁵ and generate additional waste streams. Thermal processes are therefore preferable. In Germany, a technology has been developed that successfully utilizes the DSD waste plastic as a liquefaction feedstock by employing a low-temperature, long residence time, thermal depolymerization process prior to hydroprocessing.^{15,16,20}

An alternative approach that requires less preprocessing preparation and cleaning of the PCP is pyrolysis. Earlier work on the pyrolysis of plastic has been carried out by Kaminsky and co-workers^{21,22} and by Conrad Industries.^{23,24} Kaminsky et al. have utilized a fluid bed pyrolysis approach while investigators at Conrad Industries have developed an Auger-fed continuous pyrolysis unit. The liquid yields obtained by these investigators when feeding true PCP are generally in the 40–60% range.

In the current study, a longer residence time (1 h) batch pyrolysis system (see Figure 1) was used. Operation of the system was described earlier. The results for the pyrolysis yields and chemical composition of the pyrolysis liquids from the DSD waste plastic as a function of furnace temperature are summarized in Figure 5 and Table 2. It is seen that pyrolysis liquid yields of 75–80% are obtainable with the current system. Maximum liquid yields are obtained at furnace temperatures of 600–650 °C. The simulated distillation results for these liquids (Figure 6) show that they become increasingly heavy with increasing pyrolysis temperature.

Catalytic hydrotreatment of these pyrolysis liquids was carried out at 450 °C (200 psig H₂ pressure (cold), 60 min) both thermally and catalytically (1 wt % HZSM-5). The results are illustrated by Figures 7 and 8. Figure 7 shows the full simdist curves for the pyrolysis liquid obtained at 600 °C before and after both thermal and catalytic hydrotreatment. Figure 8 shows the percentages of liquid product in the gasoline (IBP–200 °C), kerosene (200–275 °C), and heavier oil fractions (275 °C–FBP) for the pyrolysis liquids derived from DSD plastic at several temperatures before and after thermal and catalytic hydrotreatment. These results show that

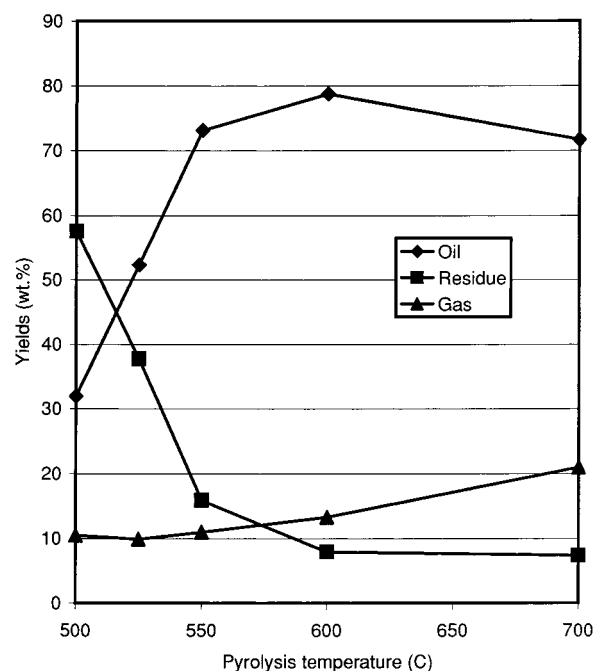


Figure 5. Pyrolysis yields vs temperature for DSD plastic.

Table 2. Pyrolysis Yields from DSD Waste Plastic (columns 2–4); Chemical Analysis for the Liquid Product (columns 5–9)

pyr. temp. °C	liquid wt %	gas wt %	solids wt %	C wt %	H wt %	N wt %	S wt %	Cl* ppm
500	32	11	58	82.7	11.5	0.35	0.08	590
525	52	10	38	82.9	9.4	0.20	0.05	443
550	73	11	16	83.5	11.1	0.05	0.03	330
600	79	13	8	83.8	12.4	0.12	0.04	398
700	72	21	7	84.0	13.2	0.26	0.05	271

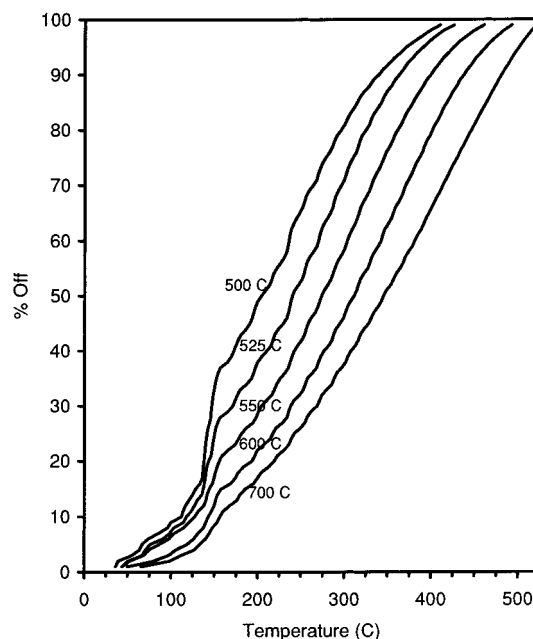


Figure 6. SIMDIS of DSD pyrolysis liquids obtained at different pyrolysis temperatures.

the lighter boiling point fractions are increased significantly by hydrotreatment at 450 °C. The addition of 1 wt % HZSM-5 has a small catalytic effect on the production of lighter fractions.

The effects of a number of different catalysts during hydrotreatment at 425 and 450 °C for 1 h under cold

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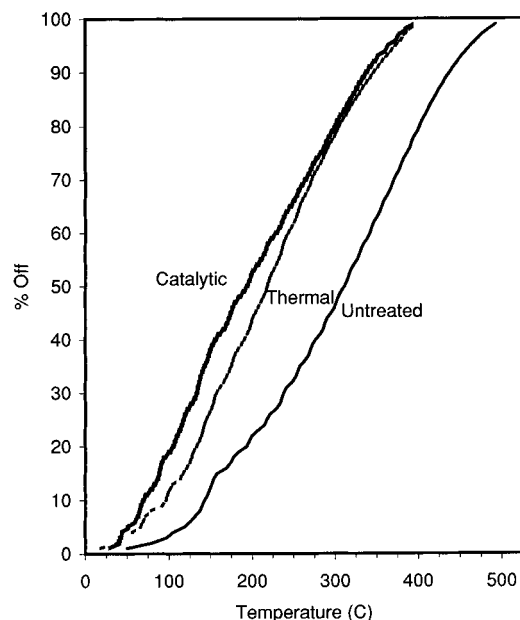


Figure 7. SIMDIS curves for thermally and catalytically (1% HZSM-5) hydrotreated 600 °C pyrolysis liquid from DSD waste plastic.

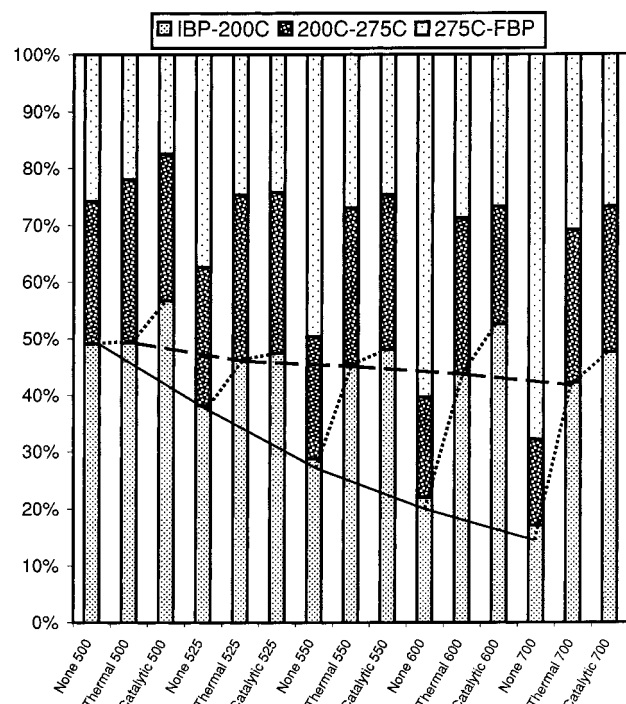


Figure 8. SIMDIS analysis of pyrolysis oil from DSD waste plastic before and after thermal and catalytic hydrotreatment.

hydrogen pressures of either 200 or 800 psig on boiling point distributions were investigated for the pyrolysis liquid obtained from the DSD plastic at 600 °C. Several catalysts were examined at concentrations of 1 and 5 wt %. The resulting boiling point fractions are shown in Figures 9 and 10. Although some catalysts appear to have a modest effect, it is evident that increasing the temperature has the greatest effect on boiling point distributions. The effect of hydrogen pressure also appears to be quite small. The liquids treated at the lower pressure generally appear to be slightly lighter than those treated at the higher pressure.

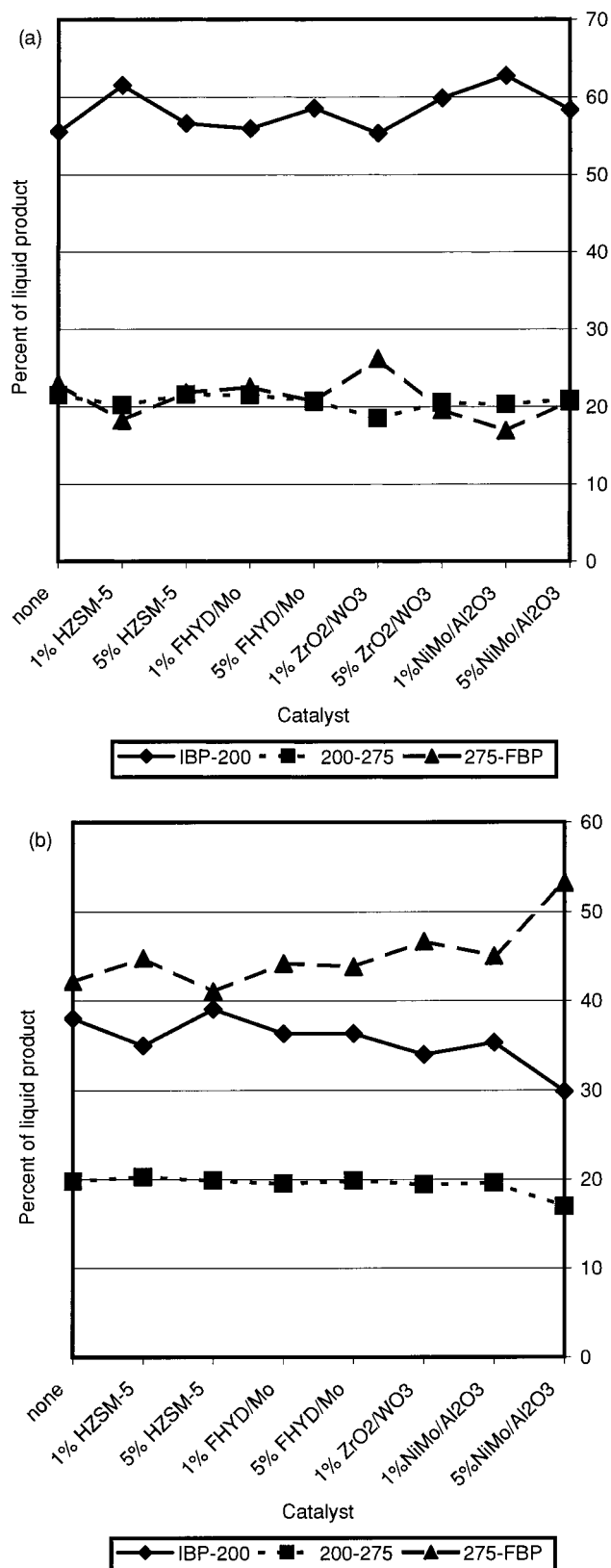


Figure 9. (a) SIMDIS results—600 °C DSD pyrolysis oil hydrotreated at 450 °C, 1 h, 200 psig initial hydrogen pressure. (b) SIMDIS results—600 °C DSD pyrolysis oil hydrotreated at 425 °C, 1 h, 200 psig initial hydrogen pressure.

Chlorine. Chlorine derived from PVC is the impurity of most concern in oil produced from waste plastic. In the current experiments, it was found that chlorine could be reduced to very low levels by the addition of sodium carbonate (Na_2CO_3) to the pyrolysis and hydro-

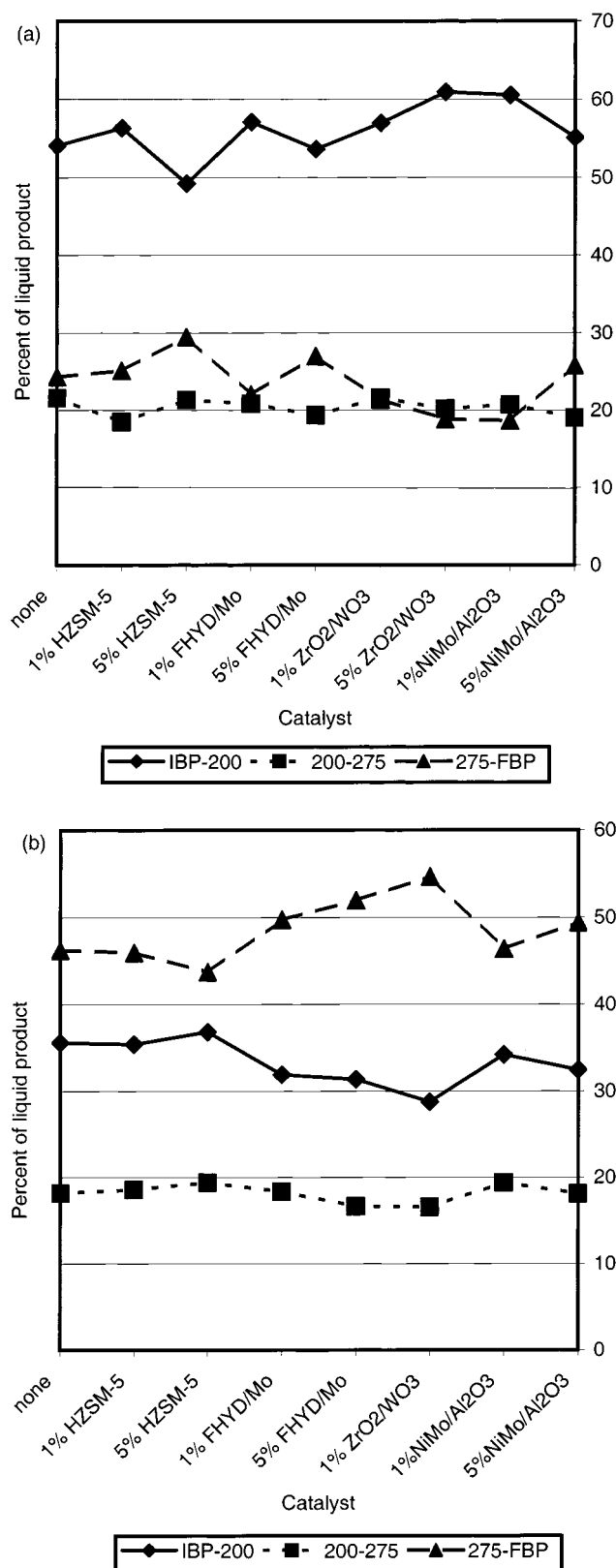


Figure 10. (a) SIMDIS results—600 °C DSD pyrolysis oil hydrotreated at 450 °C, 1 h, 800 psig initial hydrogen pressure. (b) SIMDIS results—600 °C DSD pyrolysis oil hydrotreated at 425 °C, 1 h, 800 psig initial hydrogen pressure.

processing reactors. Similar results have been observed earlier in coal liquefaction.^{25,26} Product yields and boiling point distributions for both types of experiment were essentially unaffected by the addition. Typical results for chlorine contents of the liquid products,

Table 3. Chlorine Concentrations of Pyrolysis Liquid from DSD Waste Plastic (pyrolysis temperature 600 °C)

pyrolysis furnace temperature (°C)	amount of Na ₂ CO ₃ added (wt %)	chlorine content (ppm)
600	0	398
700	0	271
600	3	54
700	3	70

Table 4. Chlorine Content of Oils Obtained by Hydroprocessing a DSD Pyrolysis Liquid with an Initial Chlorine Content of 398 ppm

temperature (°C)	initial H ₂ pressure (psig)	amt. Na ₂ CO ₃ added (wt %)	catalyst	chlorine content (ppm)
400	200	2	5% HZSM-5	7
425	200	2	none	8
425	200	2	5% HZSM-5	6
450	200	2	none	5
450	200	2	1% HZSM-5	4
450	200	2	5% HZSM-5	7
450	800	0	none	19
450	800	0	1% HZSM-5	47
450	800	2	1% FHYD/Mo	<2
450	800	2	1% ZrO ₂ /WO ₃	3
450	800	2	5% ZrO ₂ /WO ₃	3

determined by X-ray fluorescence analysis, are given in Tables 3 and 4. Table 3 shows the effect of adding Na₂CO₃ to the pyrolysis reactor during pyrolysis at 600 and 700 °C. The reduction in chlorine concentration is significant. While the chlorine levels in the pyrolysis liquids produced using Na₂CO₃ are still unacceptable in most oil products, they are low enough that expensive corrosion-resistant alloys would not be required for hydroprocessing reactors.

Table 4 shows the effects of adding Na₂CO₃ to the tubing bombs prior to hydrotreatment for 1 h of the pyrolysis liquid produced from the DSD plastic at 600 °C, which had a chlorine content of 398 ppm. The chlorine levels are reduced to very low levels (2–8 ppm, Table 4), which should be acceptable for most oil products. It is seen that hydrogen pressure and the addition of several different catalysts have little effect on the final chlorine concentration. It should also be noted that much lower amounts of Na₂CO₃ would probably be adequate in the hydroprocessing reactor (~twice the chlorine content of the feedstock).

Summary and Conclusions

Two approaches have been investigated for converting waste post consumer plastic into high quality oil: direct liquefaction and pyrolysis followed by hydroprocessing of the pyrolysis liquids. The two waste PCPs investigated (see Table 1) were a relatively clean PCP provided by the American Plastics Council (APC) that was prepared by a wet washing process and a "dirtier" PCP provided by the Duales System Deutschland (DSD) made by a dry preparation process. At temperatures above 430 °C, oil yields obtained from both plastics by either thermal or catalytic hydroprocessing were simi-

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lar. For the APC plastic, the addition of several solid acid catalysts at a liquefaction temperature of 445 °C had a significant effect on the boiling point distribution of the oil product, increasing the gasoline fraction of the oil product by 30 to 50%. For the DSD plastic, however, the thermal and catalytic BP distributions were approximately the same, within experimental error.

Pyrolysis followed by hydroprocessing of the pyrolysis liquids is an alternative conversion approach that was investigated for the DSD plastic. Using a simple pyrolysis reactor (Figure 1) with a residence time of 1 h, pyrolysis yields and BP distributions were measured as a function of pyrolysis temperature. Maximum liquid yields of 75–80% of relatively heavy liquid products were obtained at 600–650 °C. Pyrolysis liquids obtained at all temperatures were subjected to hydroprocessing at 450 °C, 200 psig initial hydrogen pressure, thermally and with a 1% addition of HZSM-5. The heavier liquid obtained at the pyrolysis temperature of maximum yield (600 °C) was hydroprocessed both thermally and using 1–5% additions of a number of different catalysts at several temperatures using initial hydrogen pressures of both 200 and 800 psig. For the heavier pyrolysis liquids obtained at 600–700 °C, hydroprocessing approximately doubled the gasoline fraction of the oil. However, the increases in the gasoline fractions resulting from the addition of the catalysts over that obtained by thermal hydroprocessing were relatively small (5–10%). Hydrogen pressure had very little effect on BP

distribution. Temperature was the major factor, with oil products obtained by hydroprocessing at 450 °C exhibiting gasoline fractions of 55–60%. To lower the chlorine content of the oil products, small additions of Na₂CO₃ were made to both the pyrolysis and hydroprocessing reactors. The resulting oil products exhibited chlorine contents of 2–8 ppm.

These results, taken together, indicate that a good approach for real waste PCP that contains a significant amount of chlorine, paper, and inorganic material is pyrolysis at temperatures of 600–650 °C, followed by hydroprocessing of the pyrolysis liquid under low hydrogen pressures at 440–450 °C.

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