

Title: Catalytic Liquefaction of Waste Plastic

Authors: G.P. Huffman, J. Rockwell, and N. Shah, CFFLS, 533 S. Limestone St., University of Kentucky, Lexington, KY 40506, cffls@pop.uky.edu

Larry L. Anderson and Weibing Ding, Department of Chemical and Fuel Engineering, University of Utah, Salt Lake City, UT 84112

Introduction

The use of solid acid catalysts for liquefaction of plastic and coprocessing of coal with plastic has proven effective.⁽¹⁻⁸⁾ However, very good results have been obtained under thermal liquefaction conditions and there is some question as to whether the use of a catalyst is justified. In the current study, a number of different catalysts were tested with two waste plastics. The experiments were conducted using a washed plastic from a recycling center provided by the American Plastics Council (APC) and an unwashed, agglomerated plastic feedstock provided by the Duales System Deutschland (DSD). The DSD plastic is the same material used by the German feedstock recycling industry.

The experiments were carried out in tubing bomb microreactors or autoclaves at 420-450 °C under hydrogen at cold pressures ranging from 200 to 1000 psig with 1-5 wt.% catalyst addition. The catalysts tested included HZSM-5, SiO₂-Al₂O₃, TiO₂-SiO₂, ZrO₂/WO₃, TiCl₃, and nanoscale ferrihydrites. At 420-430 °C, the catalysts had a beneficial effect on the oil yield but at temperatures > 440 °C, the catalytic oil yields were similar to the thermal oil yields. For the DSD plastic, which contains more PVC, paper and inorganic material, the oil yields at 445 °C were ~80%, while those for the cleaner APC plastic were ~90%. Several of the catalysts did have a significant effect on the quality of the oil product at 445 °C, as determined by simulated distillation, GC/MS and chemical analysis.

Experimental Procedure

The liquefaction experiments were performed using 27 and 50 ml tubing bomb microreactors and a 150 cm² autoclave. The feedstocks were a commingled waste plastic obtained from the APC and a post consumer waste plastic provided by the DSD. The APC plastic has been used in a number of previous experiments.^(2,3) It is a relatively clean waste plastic that has been subjected to a wet washing process to remove labels and inerts. The DSD sample is the same plastic feedstock used in the German feedstock recycling industry. As discussed elsewhere,⁽⁹⁾ this material is subjected to sorting, automated cleaning by magnetic, eddy current, air and screen separation techniques, shredding, and agglomeration. The proximate and ultimate analyses of these materials are given in Table 1.

Table 1. Proximate and ultimate analyses of the 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

Approximately 10 g of feedstock were 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 200-1000 psig. The apparatus was immersed into a fluidized sand bath at the desired temperature and agitated at 400 rpm for either 30 or 60 minutes. Data were obtained for several catalysts at temperatures of 400-445 °C and for all of the catalysts at 435 °C and 445 °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.

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 – Petrocol B, 20' X 1/8" 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-FBP.

Nine different catalysts were used in the liquefaction experiments. These included commercial HZSM-5 zeolite,⁽¹⁰⁾ a ZrO₂/WO₃ catalyst,⁽¹¹⁾ TiCl₃ and a number of catalysts synthesized in our laboratories. The latter included ferrihydrite treated with citric acid (FHYD/CA),⁽¹²⁾ a ferrihydrite containing with 5 % Mo (FHYD/Mo),⁽¹³⁾ a SiO₂-Al₂O₃ binary oxide,⁽²⁾ and two TiO₂-SiO₂ binary oxides ([Ti]/[Ti+Si]) = 0.85 and 0.85(+) prepared using the method of Doolin *et al.*⁽¹⁴⁾

Liquefaction Results

The liquefaction yields for the APC plastic with 1 wt.% addition of catalyst, 200 psig H₂, are shown in Figure 1. At 435 °C after 30 minutes reaction time, the HZSM-5 catalyst gives the best oil yield and total liquid yield. However, it is not much more effective than the other catalysts tested. Furthermore, the yield results obtained with no catalyst (thermal) are as good as or better than those obtained with all of the catalysts tested except HZSM-5. At 445 °C, there is little or

no difference in the yields obtained from the thermal run and the various catalytic runs.

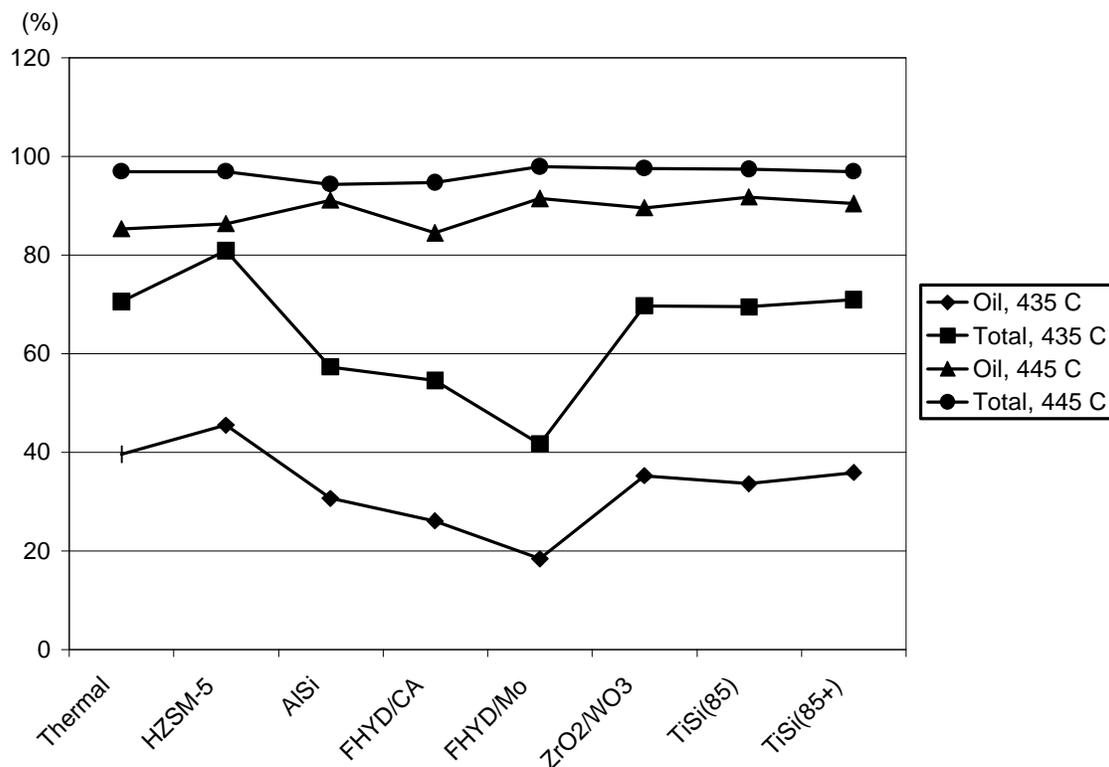


Figure 1. Oil yield and total conversion for APC plastic: 435 °C – 30 min., 445 °C – 60 min.

The effect of adding higher percentages of one catalyst (HZSM-5) and using higher hydrogen pressures (1000 psig, cold) are shown as a function of temperature in Table 2.⁽¹⁵⁾ The results are similar to those shown above and demonstrated earlier⁽²⁾ in that the catalytic effect on oil yield or total conversion is small above ~ 430 °C.

Table 2. Comparison of thermal and catalytic (2% HZSM-5, 435 °C; 4% HZSM-5, 400-430 °C) gas and oil yields.

Temperature, °C	Therm. gas yield	Cat. gas yield	Therm. oil yield	Cat. oil yield
400	3	16	9	22
420	5	19	18	40
430	8	24	52	66
435	8	18	84	76

Although the catalysts tested have little effect on the quantity of oil produced at temperatures >430 °C, they do improve oil quality. This is reflected by the boiling point distributions as measured by simulated distillation. The simdist cutpoints are shown in Figure 2 for the 445 °C runs for 1 wt.% catalyst additions. It is seen that the thermal run gives a gasoline fraction of about 27%, while the HZSM-5 oil product exhibited a gasoline fraction of 42%. The other

catalysts gave intermediate gasoline fractions, ranging from 28% for the $\text{SiO}_2\text{-Al}_2\text{O}_3$ to 38% for the $\text{TiO}_2\text{-SiO}_2$. Similarly, GC/MS data has established that there is a significantly higher percentage of branched products and aromatics in the catalytically produced oils than in the thermally produced oils.⁽¹⁵⁾

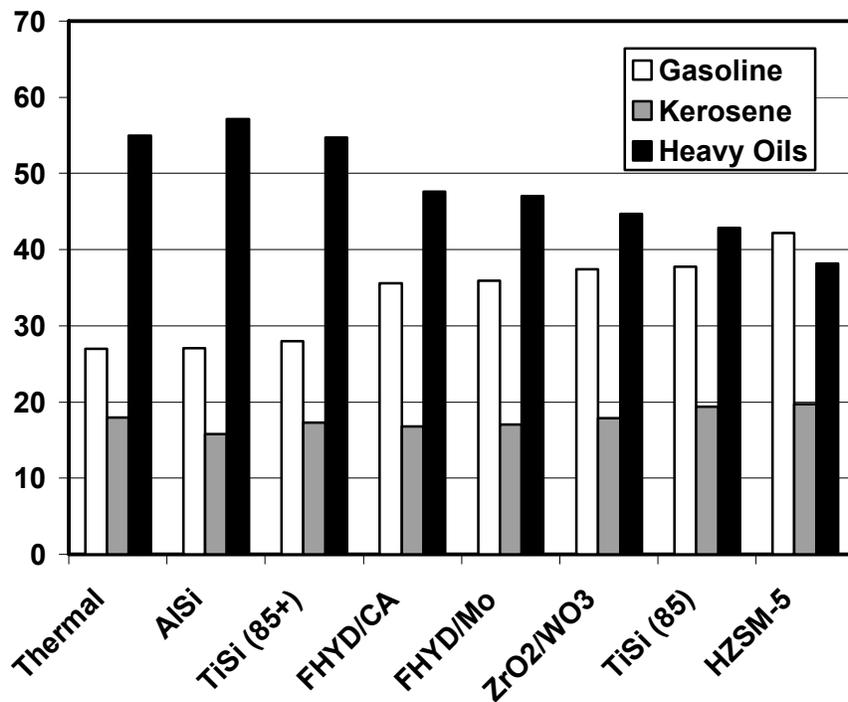


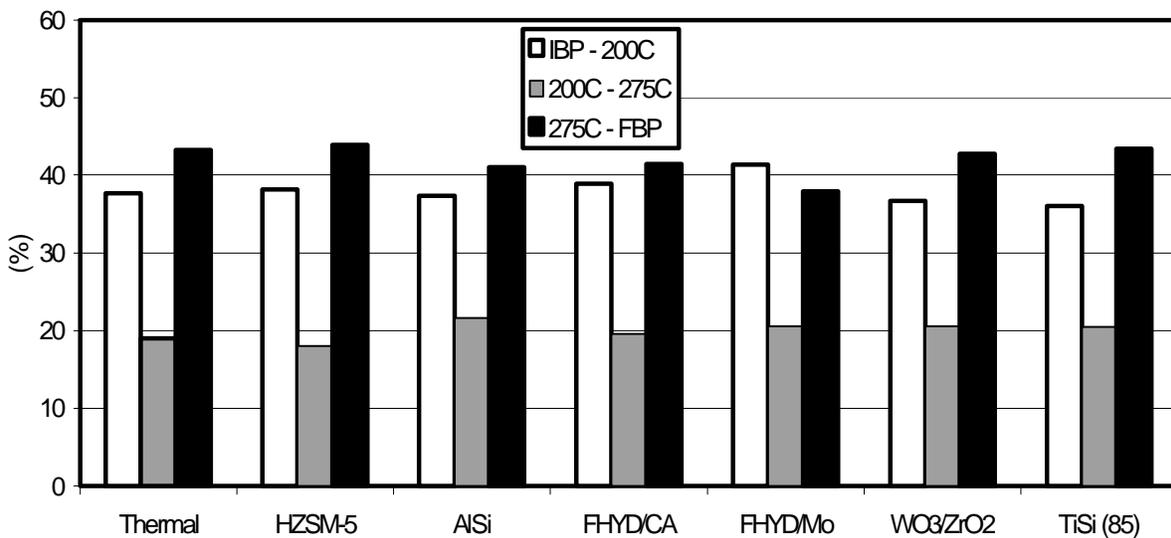
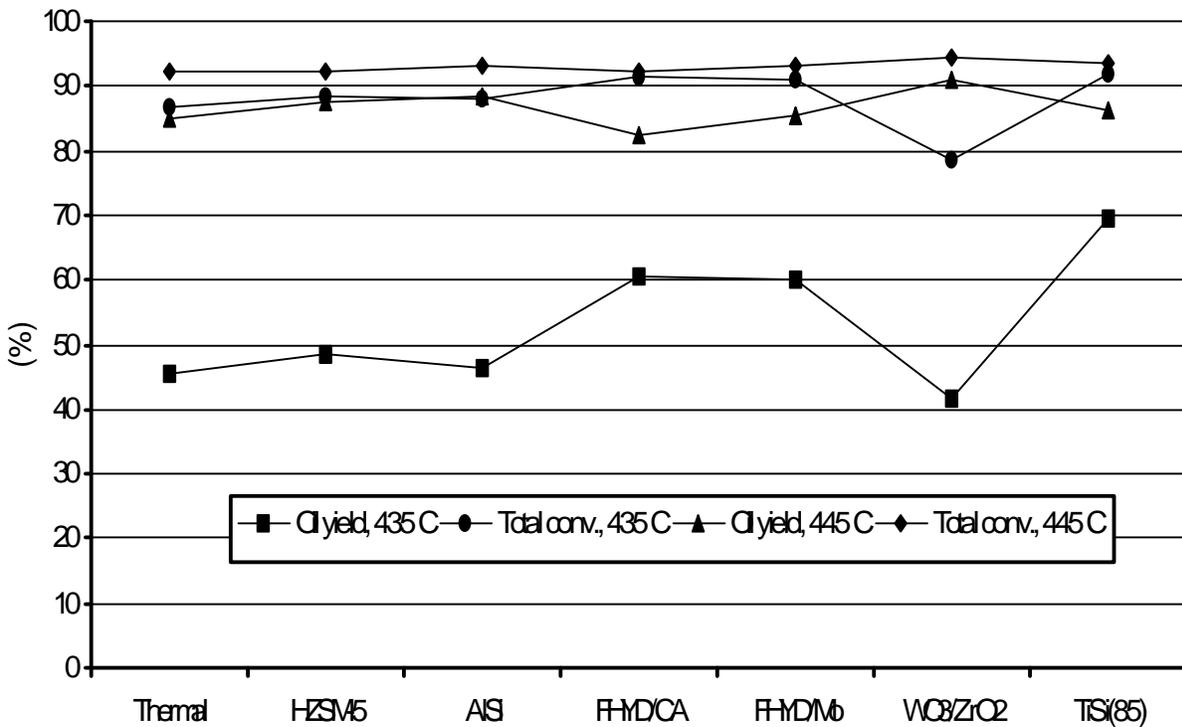
Figure 2. Comparison of simdist results for thermal and catalytic liquefaction of APC plastic.

Similar results for the oil yields and total conversions of the DSD waste plastic are shown in Figure 3. At 445 °C, the catalysts have very little effect. A high oil yield is obtained thermally, and no significant change occurs as a result of adding 1 wt. % of any of the catalysts tested. Unlike the APC plastic, simulated distillation also indicated that the effect of catalysts on the quality of the oil derived from the DSD plastic was small. Additionally, it was observed that addition of 1% HZSM-5 had little effect on oil yields over a wider temperature range, 420-455 °C. Another parameter of great interest is the Cl content of the oil, since the DSD plastics contain ~1% Cl. The results of x-ray fluorescence analysis for a number of oil samples prepared in tubing bombs containing 2% Na_2CO_3 to capture Cl gave Cl contents of 1-10 ppm Cl, both thermally and with 1% HZSM-5, while several thermal and catalytic runs in a one liter autoclave with no additives yielded oils with Cl contents of 9-15 ppm.

Conclusions

The current results indicate that, at high liquefaction temperatures (435-450 °C), additions of ~1-5 wt. % of a variety of solid acid catalysts have relatively small effects on either the yield or the quality of the oil products derived from liquefaction of post-consumer, commingled waste plastic. Although further testing is needed, this suggests that thermal hydroprocessing of waste plastics at 440-450 °C is adequate to produce a good oil product. This would decrease the operating costs of any commercial developments of this technology.⁽⁹⁾

Figure 3. Top – Oil yields and total conversions from DSD plastic at 435 and 445 °C, 200 psig H₂, cold pressure, thermally and with 1% of the indicated catalysts. Bottom – Simulated distillation results for oils obtained from DSD plastic at 445 C.



Acknowledgement: The authors would like to acknowledge the U.S. Department of Energy for supporting this research under DOE contract No. DE-FC22-93-PC93053 as part of the research program of the Consortium for Fossil Fuel Liquefaction Science.

References:

1. M.M. Taghiei, Z. Feng, F.E. Huggins, and G.P. Huffman, **1994**, *Energy & Fuels*, 1228-1232.
2. Z. Feng, J. Zhao, J. Rockwell, D. Bailey and G.P. Huffman, **1996**, *Fuel Proc. Tech.*, **49**, 17-30.
3. W.B. Ding, W. Tuntawiroon, J. Liang, L.L. Anderson, **1996**, *Fuel Proc. Tech.*, **49**, 49-63.
4. M. Luo and C.W. Curtis, **1996a**, *Fuel Proc. Tech.*, **49**, 91-117.
5. W. Zmierczak, Xin Xiao, Joseph Shabtai, **1996**, *Fuel Proc. Tech.*, **49**, 31-48.
6. J. Shabtai, X. Xiao, and W. Zmierczak, **1997**, *Energy & Fuels*, **11**, 76-87.
7. X. Xiao, W. Zmierczak and J. Shabtai, **1995**, *Amer. Chem. Soc., Div. Fuel Chem. Preprints*, **40(1)**, 4-8.
8. K.R. Venkatesh, J. Hu, W. Wang, G.D. Holder, J.W. Tierney and I. Wender, **1996**, *Energy & Fuels*, **10**, 1163-1170.
9. G.P. Huffman, "Feasibility Study for a Demonstration Plant for the Liquefaction and Coprocessing of Waste Polymers and Coal," paper in this volume and DOE report (in preparation).
10. HZSM-5 provided by Dr. Fred Tungate, United Catalysts Corporation.
11. ZrO₂/WO₃ prepared by Dr. Francis Acholla, Rohm & Haas Corporation.
12. J. Zhao, Z. Feng, F.E. Huggins and G.P. Huffman, **1994**, *Energy & Fuels*, **8**, 1152-3.
13. J. Zhao, Z. Feng, F.E. Huggins and G.P. Huffman, **1994**, *Energy & Fuels*, **8**, J. Zhao, Z. Feng, F.E. Huggins and G.P. Huffman, **1994**, *Energy & Fuels*, **8**, 38-43.
14. P.K. Doolin et al., **1994**, *Catalysis Letters*, **38**, 457.
15. W. Ding, J. Liang, and L.L. Anderson, **1997**, *Fuel Proc. Tech.*, **51**, 47-62.