

Effect of Solid Acid Catalysts on Waste Plastic Liquefaction

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Keywords: plastic, solid acid catalyst, liquefaction.

Introduction

The use of solid acid catalysts for liquefaction of plastic and coprocessing of coal with plastic has proven effective. ⁽¹⁻³⁾ 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, seven different catalysts were tested with two waste plastics: a relatively clean waste plastic provided by the American Plastics Council and a somewhat dirtier plastic provided by the Duales System Deutschland (DSD). Liquefaction experiments were carried out at 435 and 445 °C on the APC plastic and at 445 °C on the DSD plastic.

The results at 435 °C show significant differences in the total conversions and oil yields. However, at 445 °C, the liquefaction yields with different catalysts showed relatively small differences. For the APC plastic, simulated distillation measurements on the oil fraction obtained at 445 °C did show significant differences. The oils from most of the catalytic runs exhibited higher fractions of gasoline (IBP - 200°C) and kerosene (200 - 275 °C) and lower fractions of heavy oils 275 - 550 °C). The HZSM-5 zeolite catalyst was found to be the most effective. The catalysts were less effective for the DSD plastic, possibly because of poisoning.

Experimental Procedure

All liquefaction experiments were performed using 50 ml tubing bomb microreactors. 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
			0 (difference)	0.91	5.49

Approximately 10 g of feedstock was weighed and placed in a tubing bomb. Catalyst was added at a 1 wt. % concentration (0.1g). The bomb was then purged with H₂ gas and charged to a final cold pressure of 200 psig. The apparatus was immersed into a fluidized sand bath at the desired temperature and agitated at 400 rpm. All of the data reported here were obtained from experiments run at 435 °C for 30 minutes or 445 °C for 60 minutes. 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 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 - 275-550 °C.

Seven different catalysts were used in the liquefaction experiments. These included a commercial HZSM-5 zeolite, ⁽¹⁰⁾ a ZrO₂/WO₃ catalyst, ⁽¹¹⁾ 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 with different atomic ratios ([Ti]/[Ti+Si]) = 0.85 and 0.85(+) prepared using the method of Doolin *et al.* ⁽¹⁴⁾

Liquefaction Results

The liquefaction results are shown in Figures 1-3 for the APC plastics. At 435 °C, 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. The simulated distillation results, however, show that the catalysts do have an effect on the quality of the oil product. It is seen that the thermal run gives a gasoline fraction of about 27%, while the HZSD-5 oil product exhibited a gasoline fraction of 42%. The other catalysts gave intermediate gasoline fractions, ranging from 28% for the SiO₂-Al₂O₃ to 38% for the TiO₂-SiO₂ ([Ti]/[Ti+Si]=0.95).

Some results for the DSD waste plastic are shown in Figures 4 and 5. At 445 °C, it is again seen that the addition of a catalyst has 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. Additionally, the preliminary SIMDIST results on these samples indicate that the catalysts also have very little effect on oil quality. The experiments on the DSD plastics will be completed with all catalysts at both temperatures. Chemical analyses on the oil products will be performed to determine the effect of the catalysts on heteroatom content, particularly Cl.

Conclusions

The current results indicate that, at high liquefaction temperatures (445 °C), low concentrations (~1 wt. %) of solid acid catalysts have relatively small effects on either the yield or the quality of products derived from liquefaction of 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⁾

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. Zmierzczak, Xin Xiao, Joseph Shabtai, **1996**, *Fuel Proc. Tech.*, **49**, 31-48.
6. J. Shabtai, X. Xiao, and W. Zmierzczak, **1997**, *Energy & Fuels*, **11**, 76-87.
7. X. Xiao, W. Zmierzczak 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.

Figure 1. Liquefaction yields at 435 C, 200 psig H2 (cold), 60 minutes.

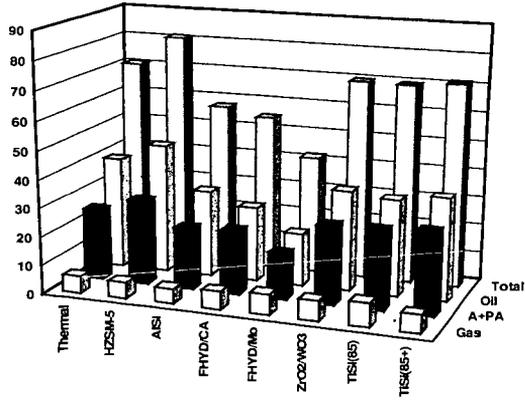


Figure 2. Liquefaction yields at 445 C, 200 psig H2(cold), 60 minutes.

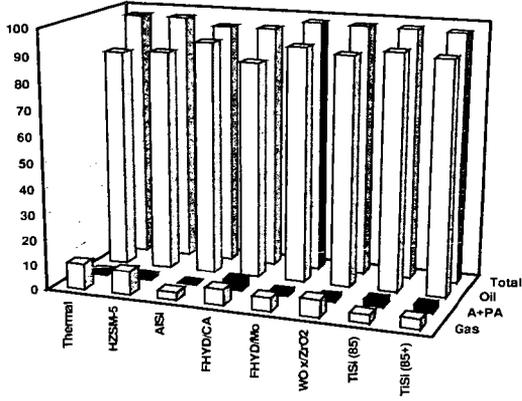


Figure 3. Comparison of slmdist results for thermal and catalytic runs.

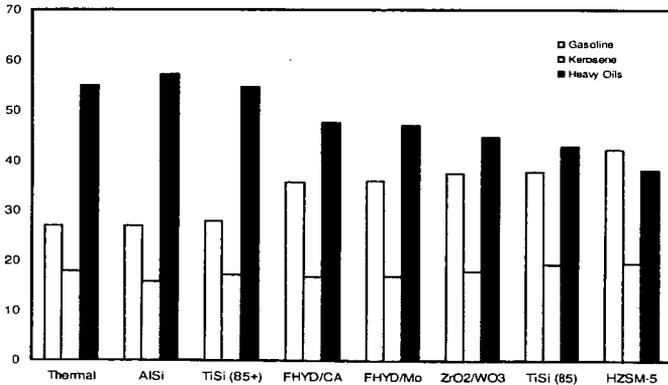


Figure 4. Liquefaction yields for DSD plastic at 445 C.

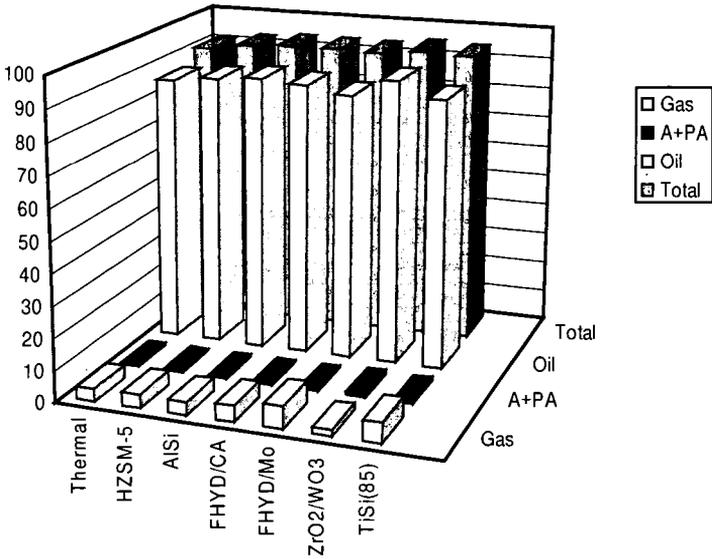


Figure 5. Simdist results for oil from DSD plastic.

