Title: Direct liquefaction of plastics and coprocessing of coal with plastics

PI: G.P. Huffman, Zhen Feng, and Vikram Mahajan, CFFLS, 341 Bowman Hall, University of Kentucky, Lexington, KY 40506-0059

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Objectives: To optimize reaction conditions for the direct liquefaction of waste plastics and the coprocessing of coal with waste plastics.

Accomplishments: As summarized below, significant progress has been made in the current contract year in determining the optimum temperature range, in exploring the effect of hydrogen pressure, in evaluating different solvents, and in the development of new catalysts.

Introduction

In previous work,[1] we have investigated the direct liquefaction of medium and high density polyethylene(PE), polypropylene(PPE), poly(ethylene terephthalate)(PET), and a mixed plastic waste, and the coliquefaction of these plastics with coals of three different ranks. The results established that a solid acid catalyst(HZSM-5 zeolite) was highly active for the liquefaction of the plastics alone, typically giving oil yields of 80-95% and total conversions of 90-100% at temperatures of 430-450 °C. In the coliquefaction experiments, 50:50 mixtures of plastic and coal were used with a tetralin solvent(tetralin:solid = 3:2). Using ~1% of the HZSM-5 catalyst and a nanoscale iron catalyst, oil yields of 50-70% and total conversions of 80-90% were typical.

In the current contract year, we have conducted further investigations of the liquefaction of PE, PPE, and a commingled waste plastic obtained from the American Plastics Council(APC), and the coprocessing of PE, PPE and the APC plastic with Black Thunder subbituminous coal.[2,3] Several different catalysts have been used in these studies.

Experimental Procedure

The feedstock materials used in the work reported in this paper included medium and high density polyethylene (PE), polypropylene (PPE), the APC commingled waste plastic, and a subbituminous coal (Black Thunder). Proximate and

ultimate analyses for the coal and APC waste plastic are shown in Table 1. The experiments used several types of catalysts: a commercial HZSM-5 zeolite catalyst[4], an ultrafine ferrihydrite treated with citric acid(FHYD/CA), a ternary Al/Si/ferrihydrite with Al:Si:Fe=1:1:18 ($FHYD_{0.90}/Al_{0.05}Si_{0.05}$), a coprecipitated SiO_2-Al_2O_3, (Si/Al ≈4) and a coprecipitated SiO_2-Al_2O_3 containing 5% ferrihydrite. All catalysts except the zeolite catalyst were synthesized in our laboratory. For all runs, 1 wt.% of catalyst was added. The preparation, structure, and liquefaction activity of the ferrihydrite catalysts has been discussed in detail elsewhere[5-8].

The liquefaction experiments were conducted in tubing bomb reactors with a volume of 50ml which were shaken at 400 rpm in a fluidized sand bath at the desired temperature. The reaction times were 20-60 min. and the atmosphere in the bomb was either hydrogen or nitrogen (cold pressure 100-800 psi). Usually 5 g of plastic or plastic + coal with 7.5 g of solvent(tetralin and/or waste oil) were charged in the tubing bombs. However, a number of experiments were conducted with plastics alone. The reactor was cooled in a second sand bath, and gas products were collected and analyzed by gas chromatography. The other products were removed from the reactor with tetrahydrofuran (THF) and extracted in a Soxhlet apparatus. The THF solubles were subsequently separated into pentane soluble (oils) and pentane insoluble (PA + AS) fractions. Total THF conversion was determined from the amount of insoluble material that remained (residue). Any added catalyst was subtracted from the residue sample weight.

Results and Discussion

Previously, we have shown that a solid acid catalyst(HZSM-5 zeolite) is highly active for the liquefaction of PE, PPE, and mixed waste plastic.[1] Some interesting new results for PE are shown in Figure 1, where it is shown that oil yields are not strongly dependent on hydrogen pressure. Moreover, the oil yield as determined by pentane solubility is as high under nitrogen as it is under hydrogen. The total conversion(THF soluble) was nearly 100% in all cases. Figure 1 also shows the time dependence of the reaction for PE in the presence of HZSM-5.

Our previous paper[1] examined the coliquefaction of a mixed waste plastic with both a bituminous and a

Table 1.

Proximate[a]	Coal	Plastic
% Ash	6.3	0.5
% Volatile	45.4	98.8
% Fixed Carbon	48.3	0.7
Ultimate[b]		
% Carbon	71.6	84.7
% Hydrogen	4.8	13.7
% Nitrogen	1.5	0.7
% Sulfur	0.5	0.01
% Oxygen	15.2	1.0

a = Dry basis, b = Dry ash free basis.

subbituminous coal. Oil yields of 60-70% and total conversions of over 90% were observed in the presence of both the HZSM-5 catalyst and an iron catalyst(430 °C, 800 psi H_2-cold, 60 min., tetralin solvent). We are currently studying the response of individual plastic resins to various catalysts and conditions in more detail. Some typical results are shown in Figure 2, where the coliquefaction results for a 1:1 mixture of polyethylene(PE) and Black Thunder subbituminous coal are compared to those for a 1:1 mixture of polypropylene(PPE) with the same coal. It is evident that PPE undergoes considerably more synergistic reactions with coal than PE.

Several solvents for plastics liquefaction are being explored. An example of this work is shown in Figure 3. The APC commingled plastic was liquefied in mixtures of tetralin and waste automotive oil; the percentage of waste oil in the mixture is indicated. At 445 °C, the effect of using waste oil rather than tetralin is obviously much greater than the effects of the added catalysts. Presumably, the aliphatic structure of the waste oil is more conducive to dissolution of the plastic than the aromatic tetralin solvent.

Currently, an experimental matrix of temperature, catalysts, pressure, solvent, and time is being explored for the APC commingled plastic. This work will be extended to include additional mixed waste plastics as well as individual resins. Some typical results are shown in Figure 4, where the use of a tetralin solvent is compared to liquefaction with no solvent for both thermal and catalytic reactions. It is evident from both Figure 4 and Figure 3 that the aromatic structure of tetralin, which makes it a good solvent for coal liquefaction, is not the best choice for liquefaction of predominantly aliphatic plastics. It is also seen that the coprecipitated silica-alumina catalysts prepared in our laboratory give somewhat better yields than the commercial HZSM-5 zeolite.

Future Plans

A thorough experimental matrix of time, temperature, and pressure will be explored for liquefaction and coprocessing of the APC plastic with coals of different rank. Additional commingled plastics will also be investigated. The reactions of individual resins will be studied in more detail. A primary goal will be to develop a catalyst system that will be simultaneously effective for both coal and plastics.

References:

1. M.M. Taghiei, Z. Feng, F.E. Huggins, and G.P. Huffman, Energy & Fuels, **1994**, *8*, 1228-1332.
2. G.P. Huffman et al., *ACS Division of Fuel Chem. Preprints, 40(1),* 34(1995).
3. G.P. Huffman, Zhen Feng, F.E. Huggins, and V. Mahajan, to be published in the Proceedings, 1995 ICCS Meeting, Oviedo, Spain.
4. United Catalysts Inc., P.O. Box 32370, Louisville, KY 40232.
5. J. Zhao, Z. Feng, F.E. Huggins, and G.P. Huffman, Energy & Fuels, **1994**, *8*, 38-43.

6. J. Zhao, Z. Feng, F.E. Huggins, and G.P. Huffman, Energy & Fuels, **1994**, *8*, 1152-1153.
7. J. Zhao, Z. Feng, F.E. Huggins, K. Rao, and G.P. Huffman, *ACS Division of Fuel Chem. Preprints, **40(2)**,* 351(1995).
8. J. Zhao, Z. Feng, F.E. Huggins, and G.P. Huffman, to be published in the Proceedings, 1995 ICCS Meeting, Oviedo, Spain.

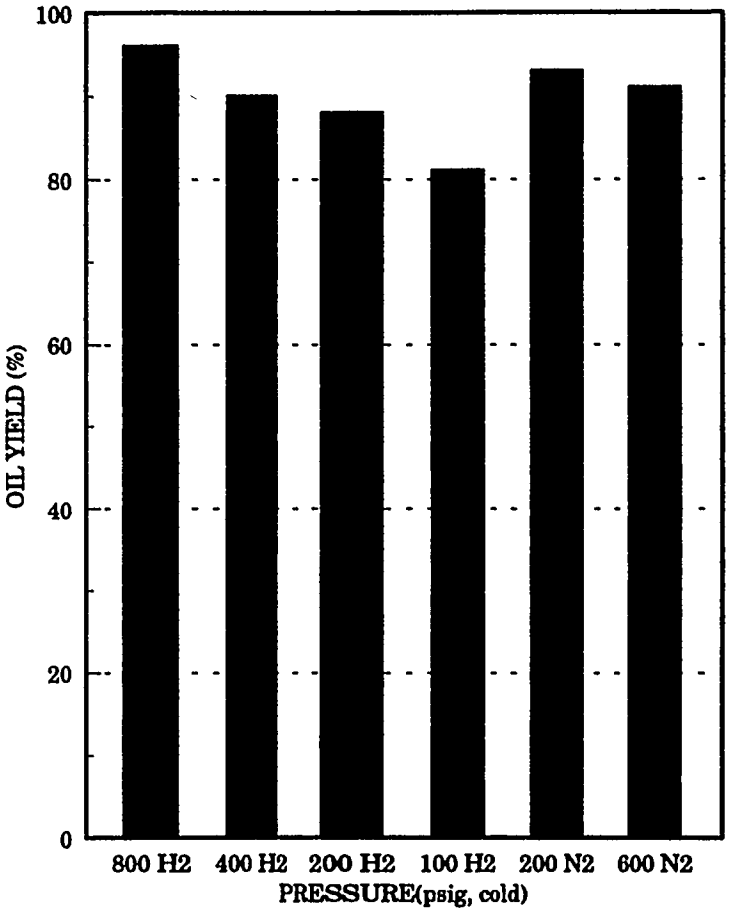

Figure 1. Liquefaction results for MDPE vs. pressure: 430 C, 60 min, 1% HZSM-5, tetralin.

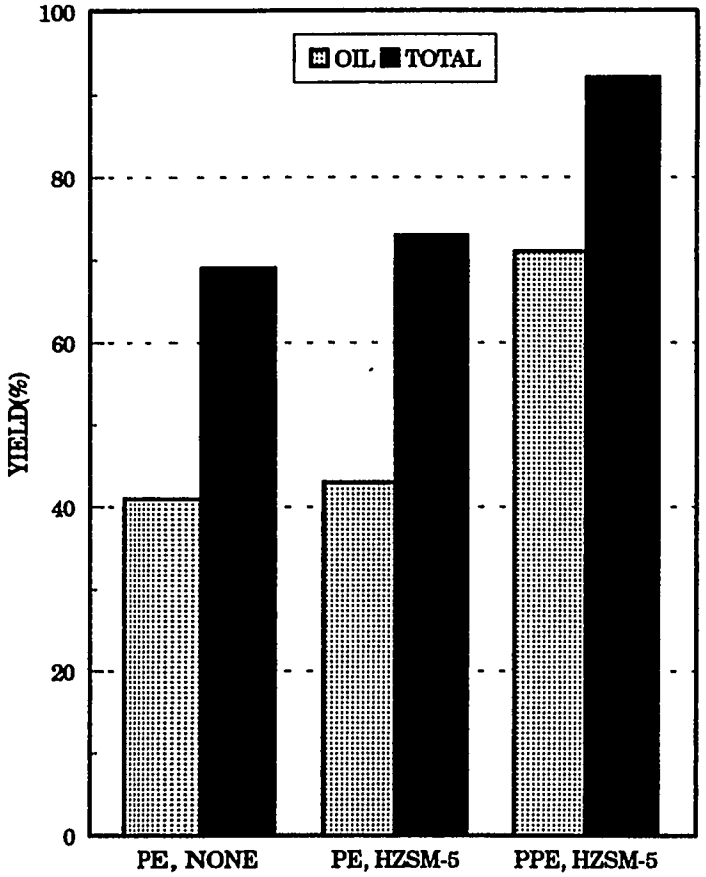

Figure 2. Coliquefaction of coal with PE and PPE: 400 C, 60 min, 800 psig H2(cold), tetralin.

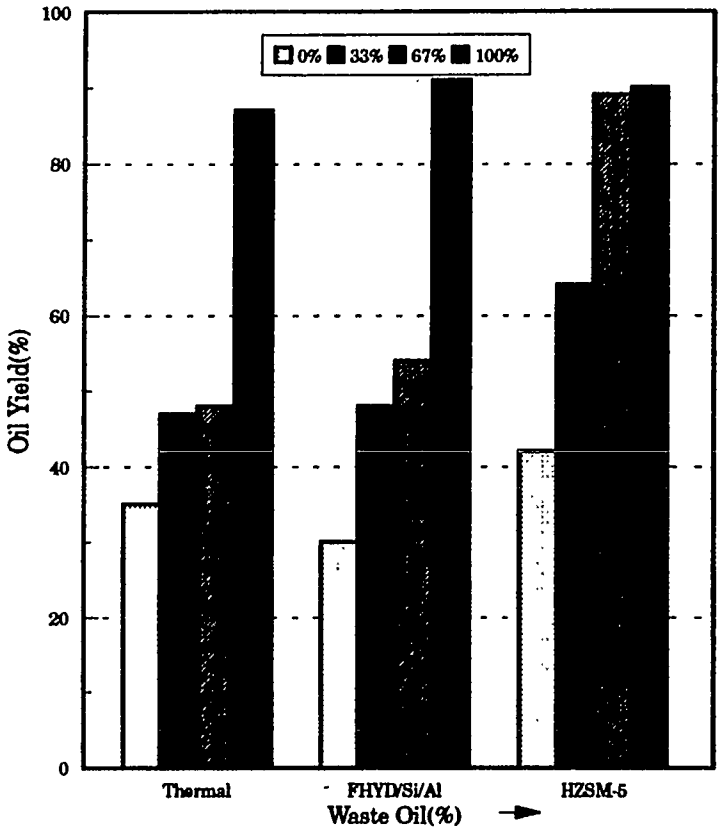

Figure 3. Effect of percentage of waste oil in solvent on oil yields for APC plastic: 445 C, 800 psig H2(cold, 1 wt.% HZSM-5, tetralin.)

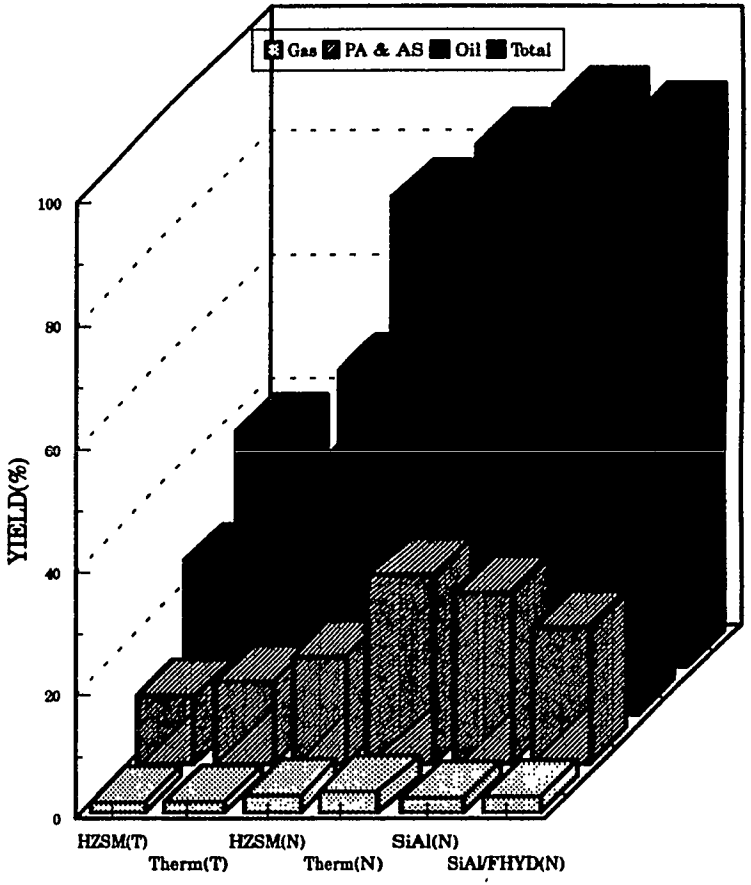

Figure 4. Liquefaction results for commingled plastic: 800 psig H2(cold), 60 min, 430 C: solvent = tetralin(T) or none(N), tetralin.