

INVESTIGATION OF FIRST STAGE LIQUEFACTION OF COAL WITH MODEL PLASTIC WASTE MIXTURES

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INTRODUCTION

As part of the U.S. Department of Energy (USDOE) Fossil Energy program, the Pittsburgh Energy Technology Center (PETC) recently initiated research in coal-waste coprocessing. Coal-waste coprocessing is conversion to liquid feedstocks of a combination of any or all of the following: coal, rubber, plastics, heavy oil, and waste oil. The current effort is on the combined processing of coal, waste oil, and plastics. One reason commonly cited for coprocessing of coal and plastic materials is the higher hydrogen-to-carbon ratio in most plastics as compared to coal, which is hydrogen deficient relative to the petroleum-like liquids desired as products. Furthermore, the free radicals which are present in coal and believed to be produced in the early stages of coal dissolution could aid in the breakdown of plastic polymers.

In this study, screening tests have been conducted in microautoclave reactors, 1-L semi-batch stirred autoclave reactors, and a small-scale continuous unit. All tests employed Black Thunder subbituminous coal with plastic waste streams containing polyethylene (PE), polystyrene (PS), and poly(ethylene terephthalate) (PET) in various combinations and proportions. The materials and conditions were chosen to be compatible with those being investigated by other participants in the USDOE Fossil Energy program [1,2], including the proof-of-concept (POC) scale plant at Hydrocarbon Research, Inc. (HRI) in Princeton, NJ [3]. Due to the rapidly evolving nature of the coal-waste coprocessing initiative, many of the experiments reported here were designed to identify potential problem areas for scheduled runs on larger units rather than to systematically map out the chemistry involved with coliquefaction of coal and plastic materials. However, insights into both chemistry and operability of coal-waste coprocessing can be gained from the data.

EXPERIMENTAL SECTION

Materials. Liquefaction experiments were conducted with -200 mesh Black Thunder mine coal (Wyodak-Anderson seam, Campbell County, WY). High-density polyethylene (PE), melting point 135°C, density 0.96 g/mL, was manufactured by Solvay Polymers. Polystyrene (PS), melting point 95°C, was manufactured by BASF. Poly(ethylene terephthalate) (PET), melting point 215°C, density 1.4 g/mL, was manufactured by Hoechst Celanese as IMPET EKX-105. All plastics were supplied to PETC by HRI as 3.2-mm (1/8-in) extrudates. A mildly hydrogenated (9% hydrogen) fluid catalytic cracking (FCC) decant oil, obtained as the 340-510°C (650-950°F) fraction from run POC-1 on the proof-of-concept coal liquefaction unit at HRI, was used as a vehicle in the coal-waste coprocessing tests. Aged Akzo AO-60 Ni-Mo/Al₂O₃ catalyst was obtained from run POC-1 at HRI. Ni-Mo Hydrous Titanium Oxide (HTO) catalyst on Shell 324 blank was obtained from Sandia National Laboratory [4]. A dispersed sulfated iron catalyst (Fe-S) was prepared at PETC by precipitation of ferric ammonium sulfate in basic solution resulting in Fe₂O₃ doped with 3-4 wt% of SO₄ according to the method of Pradhan [5].

Reactions. Microautoclave reactions were conducted in 43-mL cylindrical, stainless-steel batch reactors constructed at PETC [6]. The base conditions of the tests were 2:1 hydrogenated FCC decant oil vehicle : coal-plastics mixture, one hour at 430°C, 7 MPa (1000 psi) cold hydrogen gas pressure, and 3.3 g aged Akzo AO-60 catalyst, although variations in time, temperature, and catalyst composition were also made. A detailed description of the reaction conditions for each run is listed in Table I. During workup, the reactor contents were sonicated in tetrahydrofuran (THF) for 30 minutes and subsequently filtered through a 0.45-micron filter under 40 psi nitrogen gas pressure. The THF soluble material was stripped of solvent on a rotary evaporator and re-extracted with heptane to produce a heptane soluble fraction. Conversion was calculated from the measured mass of insolubles adjusted for catalyst and coal mineral matter, based on the mass of plastic and MAF coal. The mass of the catalyst was also adjusted for the presence of entrained oil in the material as determined in a separate extraction step. The PE and PET plastics showed no significant solubility in either THF or heptane under the workup conditions used. PS did show appreciable solubility in THF, rendering those conversion calculations meaningless.

Four semi-batch (batch slurry, flow-through gas) tests were performed in a 1-L stirred-tank reactor system [7]. The feed charge consisted of 350 g of slurry that typically consisted of a 2:1 ratio of vehicle:feed with 30 g aged AO-60 catalyst. The feed compositions are listed in Table II. All tests were done at 430°C under 17.5 MPa (2500 psi) hydrogen gas pressure flowing at a rate of 1.9 L/min (4 SCF/h). The products were characterized in terms of gas yield and composition,

solubility in heptane and THF, and 450°C conversion [conversion of all material distilling above 450°C (850°F), including MAF coal, plastics, and 450°C+ oil, to material distilling below 450°C].

A continuous mode catalytic liquefaction experiment was conducted in a computer controlled 1-L bench-scale unit [7]. The unit is a once-through system without recycle. A typical charge consisted of a feed:vehicle mixture of 70:30 at an overall slurry feed rate of 146 g/h. The catalyst, 35 g of aged AO-60, was contained in an annular basket surrounding the stirrer to simulate the action in an ebullated bed. The coprocessing tests were done at a reactor temperature of 430°C under 17.5 MPa (2500 psi) of a 97% H₂ / 3% H₂S gas mixture flowing at a rate of 2.4 L/min (5 SCF/h). The system was run at the conditions listed in Table III. The products were characterized by distillation into three fractions - those boiling below 340°C (650°F), between 340°C-450°C (650°F-850°F), and above 450°C (850°F).

Gas and Pressure Analyses. Microautoclave reactor gas samples were collected at the completion of each run. Product gases were analyzed at PETC by a previously published method [8], and corrected for molar compressibility. Hydrogen consumption was calculated, based on the difference between initial and final (cold) gas pressure as adjusted for product gas composition [9]. Semi-batch unit gas samples were collected once slowly during the run (tail gas), and at its completion (flash gas). Hydrogen consumption was calculated, based on the assumption that the tail gas sample was representative of the gas make throughout the run.

Viscosity Measurements. Viscosity measurements were made to obtain data on feed mixtures in support of a continuous unit run. These measurements were conducted on a CANNON Model MV 8000 rotational viscometer equipped with an optional heating jacket and spindle capable of measuring viscosities as high as 500,000 cP at temperatures up to 260°C. The sample holder was loaded with 10.5 mL of material and tests were conducted over the temperature range corresponding to actual operating conditions. Viscosities were also measured over a series of shear rates, again corresponding to unit operating conditions. Regressions indicated that the oil-coal-plastics mixtures are well represented as power law fluids.

RESULTS AND DISCUSSION

Microautoclave Tests. The THF conversion, heptane conversion, and hydrogen consumption results for the microautoclave reactions are found in Table I. The Black Thunder coal yields 83% THF solubles and 51% heptane solubles with the hydrogenated FCC decant oil vehicle at 430°C for 60 minutes with AO-60 catalyst. Under these conditions, PE does not convert. Whether the THF insoluble plastic product has undergone any degradation or molecular weight reduction as a result of processing cannot be determined from the data available. The negative conversion given in Table I is attributed to the fact that the PE probably melted over the catalyst surface, trapping some of the entrained oil in the catalyst, thus inflating the mass of the insoluble extraction residue. In these and the semi-batch experiments, sheetlike deposits of plastic were observed in the residual material, indicating unconverted PE was present and had re-solidified upon cooling. At a temperature of 465°C for 30 minutes, the PE does convert, yielding a light, grease-like mixture of wax and oil vehicle in the heptane solubles. However, about half of the PE ends up in the form of C₁ to C₄ gases with production of approximately 10 - 15 mmol each of methane, ethane, propane, and butanes. PE is expected to show random degradation along the polymer chain, as all the carbon-carbon bonds are equal [10]. Under the base conditions, PS converts quantitatively to heptane solubles. PS is expected to depolymerize to styrene monomer [10], which would subsequently hydrogenate to ethylbenzene (EtBz) in the reducing environment. EtBz has been observed in GC/MS and LVHRMS analysis of products from other PS-containing feeds, such as the HRI POC-2 run. In fact, PS converts to heptane solubles in the absence of catalyst. Under the base conditions, PET shows nearly quantitative conversion to heptane solubles. PET is expected to undergo scission at the C-O linkages, because they have a lower bond strength than the C-C bond [10]. Under hydrogenation conditions, this would yield two moles of carbon dioxide, one mole of ethane, and one mole of benzene, all requiring two moles of H₂ per mole of monomer. Substantial quantities of both carbon dioxide and ethane were observed, providing qualitative support to the postulated breakdown.

Several binary and multicomponent systems were studied. In Table I, the THF and heptane conversions are compared with those predicted from the assumption of a noninteracting system. A predicted conversion is calculated based on the assumptions that coal conversion is as given by run I; PE conversion to both THF and heptane solubles is zero; and PS and PET conversion to both THF and heptane solubles is 100. This simple assumption is able to predict the THF conversions of the five two-component and multicomponent runs of similar time, temperature, and catalyst composition (VIII, XI, XII, XVI, and XVII) surprisingly well, with average absolute deviations of about two percent. The heptane conversions are not predicted nearly as well by this method, with average absolute deviations of about five percent. It is noteworthy that all the heptane conversion numbers are better than would be predicted from the assumption of a noninteracting system, with the greatest deviations occurring in the three runs which contained coal (VIII, XVI, and XVII). These preliminary results indicate that there may be some beneficial effect on the coconversion of coal with plastics, an effect also reported by other workers [1]. The coal plus plastics system also seems to be quite sensitive to the reaction conditions of time,

temperature, and catalyst composition, although varying the vehicle-to-feed ratio between 2:1 and 1:1 does not appear to have a significant effect on the results. In the remaining five runs where time, temperature, or catalyst differed from the base conditions (IX, X, XIII, XIV, XV), the THF and heptane conversions varied widely, particularly in runs XIV and XV, made at both longer time (120 min) and higher temperatures (445°C). A more systematic approach will be required to determine the influence of reaction conditions on conversion.

Semi-Batch Tests. The tests at semi-batch scale were performed very early in the program. As evidenced by the results in Table II, the conversion and hydrogen consumption results were highly inconsistent, and no conclusions could be made from these data. The semi-batch unit has provided consistent results in the past with coal-only systems, and the erratic behavior was unexpected. This unpredictability is likely due to issues in reactor configuration, which may be appropriate for coal-only slurries, but not for mixtures containing plastics. More needs to be learned about the influence of reactor design when processing coal-plastics mixtures.

Viscosity Measurements. Successful operation of a continuous unit introduces another important requirement, that of pumping the feed slurry. To determine the feasibility of pumping these composite feedstocks, viscosity measurements as a function of temperature were made on several oil-coal-plastics mixtures. Figure 1 shows viscosity as a function of temperature for three mixtures of 70% vehicle and 30% plastic. The plastics content varies from all PS, to all PE, with an intermediate commingled mixture of PE, PS, and PET in the ratio 50:35:15. Although the viscosity of all mixtures is quite high, the PE appears to be most responsible for the increase in viscosity with plastics content.

Figure 2 shows viscosity measurements as a function of temperature for four model feed mixtures. All of the mixtures contained 70% vehicle and 30% coal-plastics material, with commingled plastics in the ratio 50:35:15 / PE:PS:PET. The coal:plastics ratios ranged from 75:25 to 50:50. The data show an increase in viscosity with increasing plastics content (decreasing coal content) at all temperatures. All samples also show a decrease in viscosity with increasing temperature, although the decrease was greatest for those samples with the highest plastics content. The 75:25 and 50:50 mixtures were subsequently fed to a continuous liquefaction unit.

Continuous Unit Test. The continuous unit was operated for 116 hours without plugging or stoppage, including over 80 hours of coprocessing coal with plastics. The run conditions and distillation results are given in Table III. Successful operation of the continuous unit required control of the feed slurry viscosity by means of the temperature. When viscosity was too high, the mixture could not be pumped. When viscosity was too low, the coal would settle out, causing plugging. In the continuous tests, the 75:25 coal:plastics mixture could be pumped at a temperature of 120°C. However, the 50:50 coal:plastics mixture became extremely viscous at 150°C, the upper limit for the heated lines on the continuous unit. Because of the high pressure drop associated with pumping such a viscous mixture, it was decided to terminate the run after eight hours at this condition. As a result of these observations, it has been decided to modify the lines on the continuous unit to allow for pumping at higher temperatures.

SUMMARY AND CONCLUSIONS

Individually, plastics degrade as reported in the literature, and products rapidly hydrogenate to saturation. PE generally requires more severe conditions for conversion to solubles than either PS or PET. The traditional solvent extraction methods for evaluating coal conversion are not particularly appropriate for plastics. For PS and PET, degradation is rather straightforward, but better characterization of PE products, especially of the "insoluble" fraction, is needed.

To realize an advantage from the higher hydrogen content of plastics, degradation rates must be carefully controlled. Under traditional liquefaction conditions, each C-C bond scission still consumes one molecule of H₂, because any olefinic products formed as a result of depolymerization rapidly hydrogenate to saturates. This is particularly true with PE, which tends to degrade randomly along the polymer chain. If gas production can be minimized, less hydrogen will be required to produce saturated products from plastics, since the average waste plastic stream is less aromatic than coal.

In the two-component and multicomponent microautoclave tests, THF solubles could be reasonably well predicted from the behavior of the individual components under similar conditions. However, the heptane solubles were greater than that predicted by the assumption of individual behavior. This may be indicative of some type of synergistic behavior in coliquefaction of coal with plastics. Further work in this area is warranted.

The results on two-component and multicomponent mixtures were highly sensitive to reaction conditions, especially those of time and temperature. This is of special concern for PE-containing mixtures, where degradation to gases would be undesirable. Information concerning the rate of thermal degradation vs. gas formation in coal-plastics mixtures would be valuable. The optimum conditions for coal-waste coprocessing may not be the same as for liquefaction of coal alone.

The erratic results from the semi-batch unit indicate that more needs to be learned about the effects of reactor design.

The viscosity of coal-plastics mixtures increases significantly as the plastics concentration increases. PE seems to have the greatest influence on viscosity. Higher temperatures were required to pump the mixture when the composition was raised from 25% to 50% plastics. Control of viscosity by control of temperature was the key to successful operation of continuous mode coprocessing.

DISCLAIMER

Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

REFERENCES

1. Taghiej, M. M.; Feng, Z.; Huggins, F. E.; Huffman, G. P. Energy and Fuels, **1994**, *8*, 1228-1232.
2. Anderson, L. L.; Tuntawiroon, W. Am. Chem. Soc., Fuel Chem. Div., Prepr. Pap. **1993**, *38*(3), 816-822.
3. Comolli, A. G. Proc., Coal-Waste Coprocessing Workshop, September 9, 1994, Pittsburgh, PA. To be published.
4. Lott, S.; Dosch, R. Proc., 10th Ann. Int'l Pittsburgh Coal Conf., Chiang, S. H., Ed., p. 229-234, September 20-24, 1993.
5. Pradhan, V. R. Ph.D. Thesis, University of Pittsburgh, 1993.
6. Rothenberger, K. S., Cugini, A. V.; Schroeder, K. T.; Veloski, G. A.; Ciocco, M. V. Am. Chem. Soc., Fuel Chem. Div., Prepr. Pap. **1994**, *39*(3), 688-694.
7. Cugini, A. V.; Krastman, D.; Lett R. G.; Balsone, V. D. Catalysis Today, **1994**, *19*(3) 395-408.
8. Hackett, J.P.; Gibbon, G.A. In Automated Stream Analysis for Process Control, Manka, D.P., Ed., Academic Press, 1982; pp 95-117.
9. M. V. Ciocco, A. V. Cugini, K. S. Rothenberger G. A. Veloski, and K. T. Schroeder. Proc., 11th Ann. Int'l Pittsburgh Coal Conf., 1, 500-505, September 12-16, 1994.
10. Madorsky, S. L. Thermal Degradation of Organic Polymers; John Wiley and Sons: New York, 1964.

TABLE I: SUMMARY OF MICROAUTOCLAVE REACTION CONDITIONS AND RESULTS

Run	Feed Mixture (%)			Vh:F ¹	Catal.	Time min.	Temp. (°C)	Conv. %		H ₂ cons (mmol)	Pred. Conv. % ²	
	Coal	PE	PS/PET					THF	Hept		THF	Hept
Single-Component Reactions												
I	100	0	0	2:1	AO-60	60	430	83	51	50		
II	0	100	0	1:1	AO-60	60	430	-19	20	28		
III	0	100	0	2:1	AO-60	30	465	79	76	75		
IV	0	0	100	0	none	60	430	94	77	N/A		
V	0	0	100	0	2:1	AO-60	60	430	98	98	N/A	
VI	0	0	100	0	2:1	AO-60	60	430	97	96	54	
VII	0	0	100	0	2:1	AO-60	60	430	93	86	N/A	
Two-Component Reactions												
VIII	33	67	0	1:1	AO-60	60	430	28	26	38	28	17
IX	50	50	0	6.5:1	H ₂ O	60	430	36	27	41		
X	50	50	0	6.5:1	H ₂ O	60	430	34	24	39		
XI	0	67	33	1:1	AO-60	60	430	36	36	N/A	33	33
XII	0	67	0	1:1	AO-60	60	430	35	35	46	33	33
Multicomponent Reactions												
XIII	70	15	10	5	2:1	AO-60	60	445	71	37	73	
XIV	70	15	10	5	2:1	AO-60	120	445	48	13	N/A	
XV	70	15	10	5	2:1	Fe-S	120	445	67	26	N/A	
XVI	50	25	16	9	2:1	AO-60	60	430	65	57	54	67
XVII	50	25	16	9	2:1	AO-60	60	430	63	56	49	67

TABLE II: SUMMARY OF SEMI-BATCH CONDITIONS AND RESULTS

Run	Feed Mixture (%)			Vh:F ¹	Catal.	Time min.	Temp. (°C)	Conversion %		H ₂ cons. (mmol)	
	Coal	PE	PS/PET					THF	Hept		Tot /g MAF feed
I	50	25	17	8	AO-60	60	430	47	49	36	760
II	50	25	17	8	AO-60	60	430	58	56	47	1100
III	50	25	17	8	AO-60	60	430	32	28	-12	660
IV	50	25	17	8	AO-60 ³	60	430	57	56	51	311

TABLE III: SUMMARY OF CONTINUOUS UNIT TEST CONDITIONS AND RESULTS

Cond	Feed Mixture (%)			Vh:F ¹	Catal.	Duration (hr)	Temp. (°C)	Average Conv. % (°C)	
	Coal	PE	PS/PET					0-340	340-450
I	100	0	0	70:30	AO-60	36	430	66±10 ⁴	25±6 ⁴
II	75	12	9	4	AO-60	72	430	47±6 ⁵	34±4 ⁵
III	50	25	17	8	AO-60	8	430	N/A	N/A

¹ 2:1 Vehicle:Feed (Vh:F) represents 6.6g vehicle : 3.3g feed; 1:1 Vh:F = 3.3g vehicle : 3.3g feed; 6.5:1 Vh:F = 6.6g vehicle : 1g feed
² Prediction conversion calculated assuming Coal(THF)=83%, Coal(Hept)=51%, PE(THF)=PE(Hept)=0%, PS(THF)=PS(Hept)=PET(THF)=PET(Hept)=100%
³ Silica, 2 g, was added to semi-batch run IV.
⁴ Average of 5 determinations
⁵ Average of 25 determinations

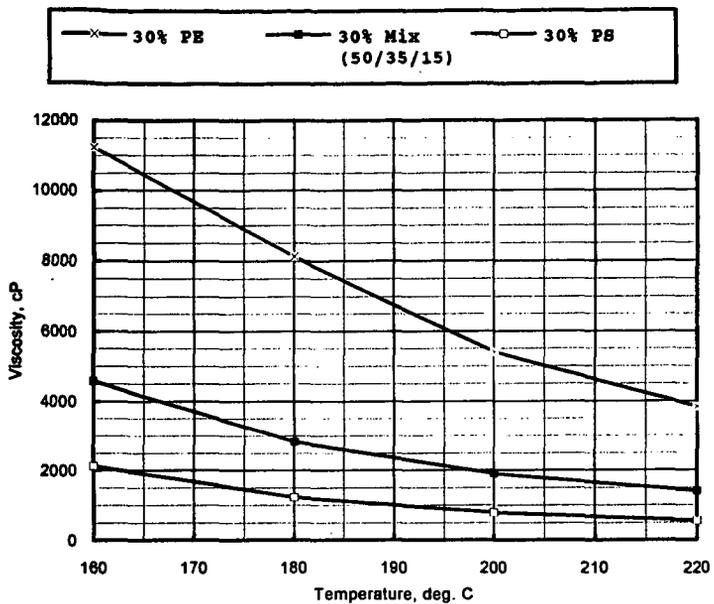


Figure 1. Effect of Plastics Composition on Viscosity

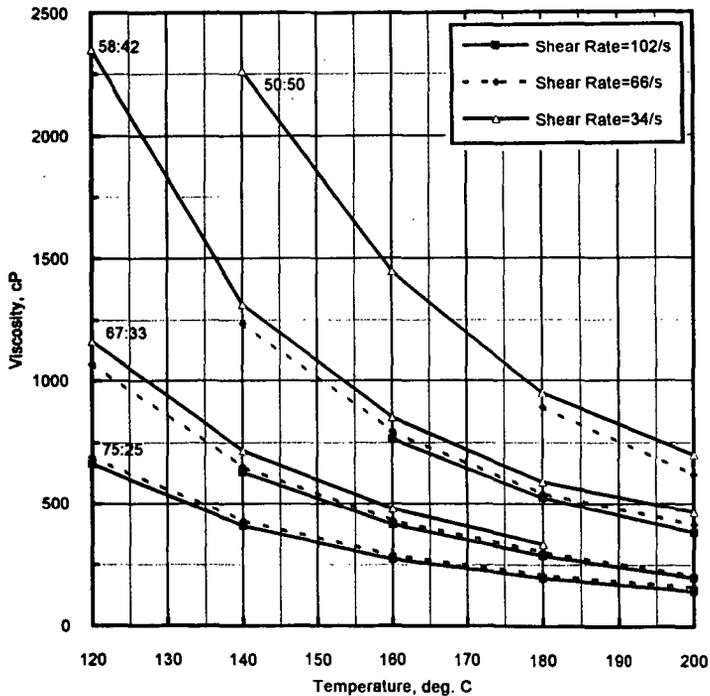


Figure 2. Viscosities of Coal:Plastics Mixtures