

CO-CONVERSION OF COAL/WASTE PLASTIC MIXTURES UNDER VARIOUS PYROLYSIS AND LIQUEFACTION CONDITIONS

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INTRODUCTION

For strategic and economic reasons the conversion of coal to liquid fuels has been a constant goal of the coal science community (1). Although the economics of coal liquefaction are primarily governed by the price of crude oil, other factors such as the need for large quantities of hydrogen gas, play an important role. If methods could be found that reduce the amount of hydrogen gas required for liquefaction, considerable benefits would be realized. To explore this possibility the use of waste plastics as materials capable of upgrading coal into liquid fuel products has been investigated.

The use of waste plastics for this purpose could become possible because over 30 million tons of synthetic polymer material is produced in the United States every year (2). Some projections estimate that this production will double by the year 2000 (3). The vast majority of this material ends up in the waste stream and is simply landfilled. It is estimated that of the 160 millions tons of municipal solid waste that needs disposal every year in the United States, waste plastics contribute 7-9% by weight and over 20% by volume (4,5). 70% of the discarded plastic is derived from packaging materials of which polyethylene (PE) represents 63%, polypropylene (PP) 9%, polystyrene (PS) 11%, polyvinyl chloride (PVC) 5% and poly(ethylene terephthalate) (PET) 7%.

The concept of using waste plastic to aid the liquefaction of coal is based on the premise that the hydrogen present in many waste plastics can be used to hydrogenate coal. It is believed that this would be possible because waste plastics usually have very high hydrogen contents (14.3 % for PE and PP) compared to most raw coals (5-6%). It is anticipated that coal/waste plastic co-pyrolysis procedures could allow for hydrogen migration from the plastic to the coal via radical abstraction and radical combination reactions. This would increase the hydrogen content of the coal so that either, liquid fuels could be formed directly, or less hydrogen gas would be required during subsequent liquefaction and upgrading.

This concept has been investigated by several research groups. Most studies have involved co-pyrolysis in a hydrogen atmosphere with added catalysts (6-11). It has been found that higher conversions to oil are obtained using a hydrogen versus an inert atmosphere (7) and that molybdenum based catalysts can also improve liquid yields. In many instances it has been determined that although conversions for individual materials are high, when they are mixed together liquid yields are somewhat diminished (8). Rubber tires have been found to enhance coal liquefaction, presumably via hydrogen donation, while PS and PE are reported to enhance the hydrocracking of coal (9).

In this study co-conversion experiments were performed on single plastics, an Illinois No.6 coal and coal/plastic blends. After initial screening studies using a thermogravimetric analyzer (TGA), several pyrolysis/liquefaction environments were examined using stainless steel microreactors. Pyrolysis was conducted in nitrogen, steam and hydrogen environments, while liquefaction reactions used tetralin/H₂ conditions. Various reaction times and temperatures were investigated. No added catalysts were used in these experiments.

EXPERIMENTAL

Materials

Samples of PE, PS and PP were obtained from Aldrich Chemical Company. The coal sample (Illinois No. 6) was obtained from the Coal Research Center at Southern Illinois University at Carbondale. The coal was physically cleaned to remove mineral matter

via a combination of micronization and centrifugation in a solution of cesium chloride of 1.6 specific gravity. Ultimate analysis of the cleaned coal sample gave: 76.2% C, 5.02% H, 1.07% N, 2.79% S, 3.89% ash and 7.32% moisture. (All reported on a dry basis except moisture.)

Thermogravimetric Analysis

Initial screening experiments were performed on a Perkin-Elmer TGA7 using a sample weight of about 10mg. An inert gas flow of nitrogen was maintained throughout the heating period which was ramped from room temperature to 1000°C at 15°C per minute. Weight loss was measured continuously at a frequency of 0.2Hz. Pyrolysis profiles were presented as a function of weight loss versus temperature and also as a first derivative of weight loss versus temperature.

Microreactor Experiments

The microreactor apparatus used consisted of a 15 mL stainless steel tube type reactor sealed at one end but open to a three-way valve at the other. The other connections to the three-way valve incorporated a gas sampling device to acquire gas samples, a 2000 psi safety valve, a pressure transducer, and a quick-connect/disconnect assembly for easy gas charging. Typical co-conversion experiments used a 2g charge of coal, plastic or coal/plastic mixture. After the sample was loaded, air was eliminated from the system by repeatedly pressurizing then depressurizing with the desired gas (nitrogen or hydrogen). The microreactor was then immersed in a fluidized sand bath maintained at the desired reaction temperature. After completion of the reaction period the microreactor was cooled in a cold fluidized sand bath. (A cold water bath was found to cause the development of leaks in the microreactor set-up.) The microreactor was continuously shaken throughout the reaction period. When steam and tetralin were used, 2 mL of distilled water or tetralin were added to the microreactor respectively. A cold pressure of 500psig of hydrogen was used for the hydrolysis and liquefaction experiments. Conversions were measured via extraction of the products with tetrahydrofuran (THF) using soxhlet apparatus. The percentage conversion is given by the difference in weight between the original charge and the THF insoluble material, divided by the original charge weight.

RESULTS

Thermogravimetric Analysis of Co-pyrolysis

Initial examination of the behavior of a co-pyrolyzing system using the TGA suggested that there was significant interaction between the components of the system. This data has been examined in some detail and has been submitted for publication and therefore will receive only brief mention here. Generally it was found that characteristic pyrolysis parameters such as the temperature of weight loss onset, the temperature of maximum rate of weight loss, the temperature of final char formation and the temperature range of volatilization are all dramatically altered by the presence of another component in the system. For example, the presence of coal appears to retard the volatilization of both PP and PE such that the observed weight loss onset temperatures for the coal/plastic mixtures are higher than either the coal or the plastic. Also, the addition of PP and PE to coal appears to aid the conversion of the coal. Lower normalized chars yields are obtained when these plastics are co-pyrolyzed with the coal. In addition, these increased coal conversion are obtained at much lower temperatures than when the plastic is absent. These results point to an interaction between the coal and plastic as they both pyrolyze. Such interactions are necessary if our goal of liquefying coal using waste plastics is to be realized.

Microreactor studies

i) Conversion in Nitrogen:- Table 1 reports the conversions of single materials and their 1:1 blends obtained at various temperatures during a one hour standard reaction time. In general, conversions increase up to a temperature of 425°C where they remain constant until about 475°C after which they tend to decline. This can be attributed to the initial decomposition of the plastics into soluble materials at the lower temperatures, but then to the formation of char at higher temperatures. In general, the conversion data for the 1:1 blends in a nitrogen pyrolysis atmosphere is very close to that predicted by simply averaging the conversions of the individual components. This is an indication that the apparent synergisms observed in the TGA experiments do not transfer to confined microreactor tests.

In another two series of experiments the pyrolysis temperature was held constant at 425°C and 475°C respectively, but the reaction time varied from 5 minutes to 2 hours. It was found that in most cases maximum conversions were obtained after only 15 minutes. In general, longer reactions times did not improve the conversions and in some cases actually led to diminished conversions. This indicates a tendency towards char formation at longer reaction times. Small synergistic conversions for some coal/plastic blends were observed at the shorter reaction times. At longer reaction times this apparent synergism was lost.

ii) Conversion in Steam:- Table 2 reports conversions obtained at various temperatures in a steam atmosphere. Both 5 minute and one hour reaction times were investigated. In general, coal conversion of 25 to 30% was obtained which is similar to that obtained in nitrogen. The plastic conversions in a steam environment were somewhat lower than they were under nitrogen. Thus, the steam appears to retard plastic depolymerization. Some apparent synergistic conversion of the coal/plastic blends is observed especially for the coal/PP mixture. However, most of this synergism appears to result from the retardation of the plastic decomposition under steam. In general, the conversion values obtained for the blends in the steam atmosphere are similar to those obtained in nitrogen.

iii) Conversion in Hydrogen:- The conversions obtained using various temperatures with a 5 minutes and one hour reaction time in 500 psig (cold pressure) hydrogen are reported in Table 3. Somewhat surprisingly the conversions obtained for both the individual materials and the blends were similar to those obtained in nitrogen. Thus, the presence of hydrogen does not appear to enhance the conversion of these materials to soluble products.

iv) Conversion in Hydrogen/Tetralin:- Table 4 reports conversions obtained using 500 psig hydrogen and a 1:1 tetralin to charge ratio. Not surprisingly coal conversions are significantly higher in the liquefaction environment. However, the conversion of the individual plastics appears to be dramatically inhibited by these liquefaction conditions. Indeed, PP conversions as low as 14% were observed after 15 minutes at 425°C in the presence of tetralin and hydrogen gas. Under similar conditions in a nitrogen environment a PP conversion around 95-100% is observed. In some case the total conversions of the coal/plastic blends do not show that much improvement over those obtained in the other pyrolysis environments. However, other coal/plastic mixtures, especially those involving PP, do show higher conversions in the liquefaction environment compared to the other pyrolysis environments. Due to the low conversions of the individual plastics, the conversions of the coal/plastic blends often indicate significant synergistic conversion. Either short time high temperature or long time low temperature conditions appear to give the best results.

v) Product analysis:- Ultimate analysis was performed on some of the insoluble residues obtained from the microreactor experiments. Although the data is preliminary at this time it is clear that many of the insoluble residues from the co-pyrolysis and co-liquefaction experiments have very high volatile matter contents. For instance, a coal/PE blend reacted at 400°C in the liquefaction environment gave a conversion of 60% based on THF solubility. However, the residue was found to contain a 90% volatile yield when heated in the TGA. If we assume all the material soluble in THF is volatile, then distillation of this product would give a distillate yield of 95%. Comparison of elemental compositions showed that the residues derived from coal/plastic blends were depleted in sulfur but enhanced in hydrogen compared to the residues derived from the coal alone. This suggests that hydrogen was transferred from the plastic to the coal and helps to explain the high volatile matter contents of many of the insoluble residues.

SUMMARY AND CONCLUSIONS

Initial investigation of the co-pyrolysis behavior of coal with plastics using a TGA indicated that there were significant interactions between the coal and plastic as both degraded simultaneously. These interaction led to increased coals conversion at lower temperatures. Attempts to repeat these results using microreactors were only partially successful with much of the synergism that was observed during the TGA experiments apparently being lost when the larger scale and higher pressure microreactors were used. This discrepancy between the TGA and microreactor conversion data should not be that surprising since the TGA conversions are based on distillate yield whereas

microreactor conversions are based on solubility in THF. Indeed, many of the THF insoluble residues from the microreactors contain significant volatile matter contents which would have been reported as converted material in a TGA analysis.

In general, it was found that the conversion of pure plastics to liquid or gaseous products was almost complete during pyrolysis experiments but was significantly retarded in a liquefaction environment. On the other hand the highest conversions of coal and coal/plastic blends, especially coal/PP blends, were achieved under these liquefaction conditions. The majority of the conversion values obtained in a reactive pyrolysis environment such as steam or hydrogen, were very similar to those obtained in an inert nitrogen atmosphere. In some instances the presence of the steam or hydrogen gas appeared to hinder the formation of THF soluble material. Throughout the series of co-conversion systems examined in this study there was a general trend towards lower conversions with increasing process temperature and increased reaction time. This is attributed to char formation under these conditions. Although the results gathered so far are preliminary in nature, it can be appreciated that the use of waste plastics in coal liquefaction processes has great potential.

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TABLE 1.

Conversions obtained after 1 hour in a nitrogen atmosphere.

Temperature	Coal	PE	PP	PS	Coal/PE	Coal/PP	Coal/PS
350	21		35	97	62	13	
400	26	55	97	98	63	57	50
425	27	100	98	99	64	60	60
450	26	99	99	99	64	59	55
475	23	99	94	100	63	60	57
500	27	89	91		54	56	
525	31	85	85	83	55	60	57
550	23	82	79	84	56	54	52

Table 2.

Conversions obtained in a steam pyrolysis atmosphere

	5 minutes			60 minutes	
	425°C	475°C	525°C	425°C	475°C
Coal	24	30	25	26	18
PE	32	35	98	95	60
PP	70	82	79		70
PS				94	93
Coal/PE	35	50	57	64	60
Coal/PP	54	50	57	51	
Coal/PS				64	62

Table 3.

Conversions obtained in a hydrogen pyrolysis atmosphere

	5 minutes			60 minutes		
	425°C	475°C	525°C	425°C	475°C	525°C
Coal	27	25	20	20	25	24
PE	23	95		97	96	93
PP	26	99	95	96	87	87
Coal/PE	32	55	63	50	58	58
Coal/PP	66	58	60	63	57	58

Table 4.

Conversions obtained in a liquefaction environment.

	15 minutes			60 minutes		
	400°C	425°C	450°C	400°C	425°C	450°C
Coal	55	51	54	52	62	52
PE	45	47	79	42	48	70
PP	10	14	82	39	53	96
Coal/PE	60	40	60	44	62	
Coal/PP	61	62	84	79	71	73

DIRECT LIQUEFACTION OF PLASTICS AND COLIQUEFACTION OF COAL-PLASTIC MIXTURES

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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. Our earlier work on the coliquefaction of paper(newsprint) with coal⁽²⁾ also established that high total conversions were obtained; however, the gas yields were high, while the oil yields were moderate.

In the current work, we have conducted further investigations of the liquefaction reactions of PE and the coliquefaction reactions of PE, PPE and Black Thunder subbituminous coal. We have also investigated the coliquefaction reactions of PE, PPE, and newsprint. Several different catalysts have been used in these studies. Initial work has been completed on the direct liquefaction of a commingled waste plastic obtained from the American Plastics Council.

Experimental Procedure

The feedstock materials used in the work reported in this paper included medium density polyethylene (PE), polypropylene (PPE), a commingled waste plastic obtained from the American Plastics Council(APC), 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 3 types of catalysts: a commercial HZSM-5 zeolite catalyst⁽²⁾, an ultrafine ferrihydrite treated with citric acid(FHYD/CA), and a ternary Al/Si/ferrihydrite with Al:Si:Fe=1:1:18 (FHYD_{0.90}/Al_{0.05}Si_{0.05}). The ultrafine ferrihydrite catalysts are synthesized in our laboratory. For all runs, 1 wt.% of catalyst was added. Dimethyl disulfide (DMDS) was sometimes added to convert the ultrafine ferrihydrite to pyrrhotite during the reaction. The preparation, structure, and liquefaction activity of the ferrihydrite catalysts has been discussed in detail elsewhere^(3,4).

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 100-300 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. The reactor was cooled in a second sand bath, and gas products were collected and analyzed by gas chromatography⁽⁵⁾. 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.

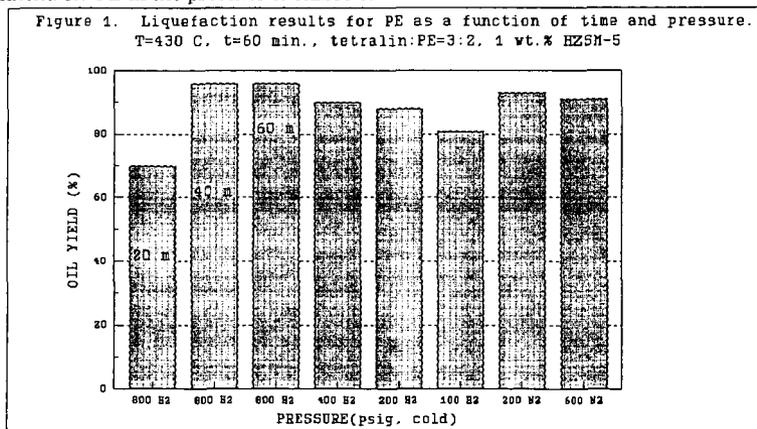
Table 1. Proximate and ultimate analyses of Black Thunder coal and APC commingled waste plastic used in this research.

Proximate ^a	Black Thunder Coal	APC Waste Plastic
% Ash	6.33	0.45
% Volatile	45.40	98.8
% Fixed Carbon	48.27	0.74
Ultimate ^b		
% Carbon	71.59	84.65
% Hydrogen	4.83	13.71
% Nitrogen	1.51	0.65
% Sulfur	0.49	0.01
% Oxygen	15.24	0.98

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

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. 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 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 H₂-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 Table 2. PE and PPE both respond strongly to the HZSM-5 catalyst. PPE also responds very well to the citric acid-treated ferrihyrite although PE does not. It is also seen that the mixtures of PE and coal do not liquefy as well as PPE-coal mixtures or as well as we observed previously for a mixed plastic⁽¹⁾. Neither the HZSM-5 or the FHYD/CA catalyst has a strong effect on the liquefaction of PE-coal mixtures.

Table 2. Liquefaction results(yields in wt.%) for medium density polyethylene(PE), polypropylene(PPE), and 50:50 mixtures of PE and PPE with Black Thunder coal.

FEED	CATALYST	T (°C)	OIL	GAS	PA+A	TOT.
PE	NONE	430	26	1	39	65
PE	FHYD/CA	430	33	1	34	68
PE	HZSM-5	430	96	1	2	99
PE/COAL	NONE	430	41	3	26	69
PE/COAL	FHYD/CA	430	42	4	22	68
PE/COAL	HZSM-5	430	41	4	28	72
PPE	NONE	420	83	<1	4	88
PPE	FHYD/CA	425	98	2	0	100
PPE	HZSM-5	425	100	<1	0	100
PPE/COAL	HZSM-5	430	71	4	18	93

Some interesting results for a commingled waste plastic provided by the American Plastics Council are shown in Table 3. Here, we have examined the effect of varying both the catalyst and the solvent. It is seen that at 445 °C the nature of the solvent has a larger effect on the oil yield and total conversion than the catalyst. Both catalysts are moderately effective at this temperature; however, the solvent has a much larger effect, with the oil yields increasing from 30-40% to ~90% as tetralin is replaced with a waste motor oil.

Paper and other lignocellulosic wastes constitute a major fraction of the organic portion of municipal wastes. Previous work has focused on the coliquefaction of coal with lignocellulosic materials by two approaches: Route A used H₂, a molybdenum catalyst and tetralin, while Route B used CO and water in the presence of alkali.⁽²⁾ Both approaches gave good results, although an improvement in product quality was achieved via Route B.

Table 3. Liquefaction results(yields in wt.%) for APC waste plastic with different solvents and catalysts. Experiments conducted at 445 °C, 800 psig H₂(cold) in a tubing bomb, with 7.5 g of solvent and 5 g of plastic.

FEED	CAT.	SOLV.	OIL+ GAS	OIL	GAS	PA+AS	TOTAL
W.PL	HZSM-5	OIL-7.5	89.3			5.1	94.4
W.PL	HZSM-5	TET.-2.5 OIL-5.0	88.4			5.7	94.1
W.PL	HZSM-5	TET.-5.0 OIL-2.5	66.8	63.7	3.1	17.8	84.6
W.PL	HZSM-5	TET.-7.5	42.9			12.3	55.2
W.PL	NONE	OIL-7.5	87.1			7.9	95.0
W.PL	NONE	TET.-2.5 OIL-5.0	48.6			27.1	75.7
W.PL	NONE	TET.-5.0 OIL-2.5	51.0	48.3	2.7	15.2	66.2
W.PL	NONE	TET.-7.5	35.8			23.2	58.9
W.PL	FHYD AISI	OIL-7.5	90.9			4.8	95.7
W.PL	FHYD AISI	TET.-2.5 OIL-5.0	61.8	58.4	3.4	21.2	83.0
W.PL	PHYD AISI	TET.-5.0 OIL-2.5	51.2	48.6	2.6	22.2	73.4
W.PL	FHYD AISI	TET.-7.5	30.2			16.5	46.7

In more recent work, a high conversion of plastics such as polypropylene, polystyrene and polyethylene terephthalate was achieved at 400 °C using Route B. With Route A, however, the conversion of polypropylene did not exceed 20% at 400 °C. Coliquefaction of coal and polypropylene in Route B showed an increase in the overall oil product and a decrease in the asphaltene fraction from coal. A similar effect was observed in the liquefaction of polypropylene and newsprint using Route B. Oxygen contents of liquid fuels from biomass are usually high, especially using the Route A process. However, the oxygen content of the oil product from Route B was less than 9% because of decarboxylation. The oxygen content of the oil from the coprocessing of polypropylene and newsprint was 3.5%.

Summary

New results for plastics liquefaction and coal-plastic coliquefaction suggest that the nature of the plastic, the solvent, and the reaction atmosphere can all have a significant on product yields. A thorough experimental matrix is needed to explore this parameter space. Further catalyst development aimed at producing cheaper, more robust catalysts for coal-waste plastic coliquefaction is required.

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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.

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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	33	1:1	AO-60	60	430	35	35	46	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	PE-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

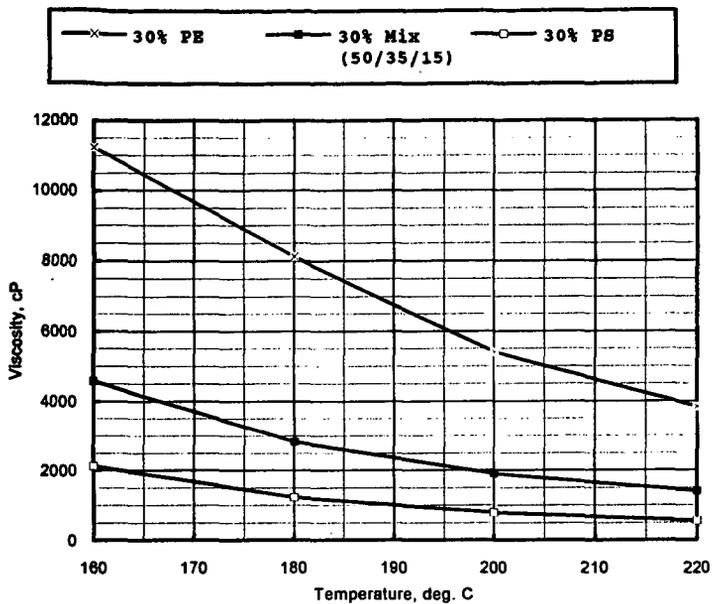


Figure 1. Effect of Plastics Composition on Viscosity

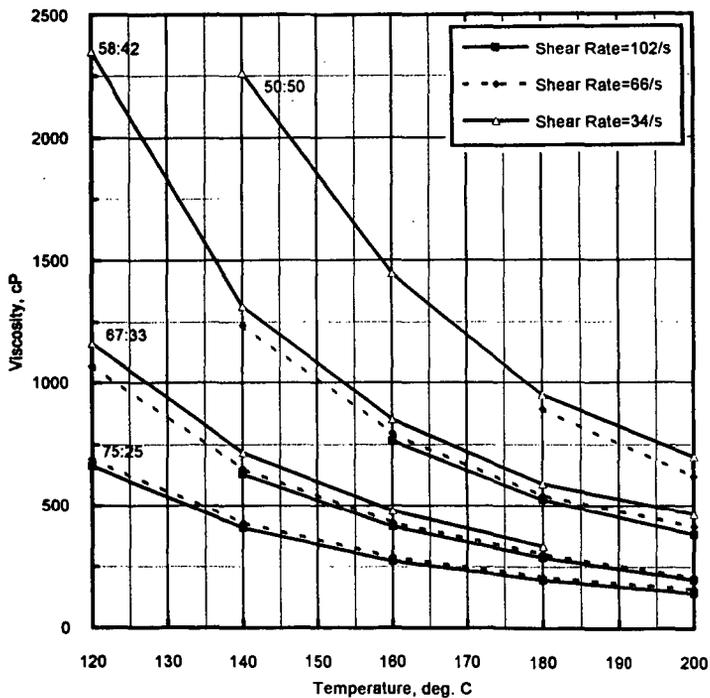


Figure 2. Viscosities of Coal:Plastics Mixtures

THERMAL AND CATALYTIC COPROCESSING OF COAL AND WASTE MATERIALS

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KEYWORDS: Coal liquefaction, Waste Rubber Tires, Waste Plastics

Introduction

Coprocessing of coal with waste materials to produce liquid fuels with emphasis on finding reasonable reaction pathways and catalysts for such processing is presently the subject of intensive investigation. Polymer wastes such as polyethylene, polystyrene, polypropylene and used rubber tires are not naturally degraded over time. More than 22 million tons of plastic waste are annually discarded in landfills and over 75 percent of used rubber tires are similarly treated.¹ In order to obtain distillate liquids or petroleum compatible refined products from coal, addition of hydrogen is necessary. A possible method for hydrogen addition is coprocessing of coal with polymeric waste materials since these latter materials contain hydrogen at levels much higher than are found in coal. The breakdown of waste rubber tires is interesting because the liquids derived may prove to be important as a coal dissolution and/or hydrogen donor solvent.² Recently, Badger and coworkers³ reported that hydrogenated tire oils (hydrogenated in the presence of CoMo catalyst) were effective for the dissolution of coal. Studies on the coprocessing of coal and waste materials have only recently been done intensively. Limited data are available on reaction conditions and catalytic effects for processing coal mixed with post-consumer wastes. The purpose of the present study was to determine the effects of reaction temperature, pressure, catalysts, and mixture ratio on the coprocessing of coal and waste materials.

Experimental

Blind Canyon (Utah) coal (DECS-6, -60 mesh) was obtained from the Penn State Coal Sample Bank and stored under nitrogen. Ground waste rubber tire material (-20 mesh, 0.4 % moisture, 68.7 % volatile carbon, 7.6 % ash, and 23.3 % fixed carbon) was obtained from the University of Utah Center for Microanalysis. Ground waste rubber tire was stored under air at ambient conditions. The commingled plastic mixture (mostly high density polyethylene) used in this experiment was obtained in two batches. The first batch was obtained from a recycling center in Utah (Recycling Corporation of America) in the form of detergent or soft-drink bottles. Samples were washed to remove the labels and contaminants before size reduction by cutting and shaving. Final size reduction was done by grinding in a kitchen flour mill (stainless steel) to -8 +25 mesh before analyses and use in coprocessing experiments.

The second waste plastic was obtained through the American Plastic Council (APC) from a recycling center in Oregon. Polyethylene and polystyrene were purchased from Aldrich Chemical Co. Melting and softening temperatures of some plastic polymers are given below:

<i>Plastic</i>	<i>Temperature</i>
Low Density Polyethylene	T.M. : 115 ° C
Mid Density Polyethylene	T.M. : 120 ° C
High Density Polyethylene	T.M. : 130 ° C
Polypropylene	T.M. : 189 ° C
Polystyrene	T.S. : 60-93 ° C

T.M. = Melting Temperature, *T.S.* = Softening Temperature

Reaction feed samples were composed of various amounts of waste plastic and rubber tire combined with Blind Canyon DECS-6 coal. When catalysts were used they were added to the mixture and their content given as a weight per cent of the solid feed material. Before reaction the feed solids were vacuum dried for two hours at 100°C. Samples were placed in glass tubes stoppered with glass wool. The glass tubes were placed in 27 cm³ tubing bomb reactors, purged with nitrogen, and pressurized to 1000 psig H₂ (cold). Reactors were heated by a fluidized sandbath held at various reaction temperatures. The tubing reactors were shaken vertically at 160 rpm for various lengths of time, removed, and allowed to cool overnight under pressure.

Rubber tire/coal reaction products were removed and extracted with tetrahydrofuran (THF). The THF solubles were filtered to remove carbon black. The THF was removed with a rotary evaporator, and the THF soluble portion was dried under vacuum for two hours. The

sample was then extracted with cyclohexane. The cyclohexane was removed using a rotary evaporator leaving rubber tire/coal oil. The cyclohexane insoluble residue will be referred to as preasphaltenes and asphaltenes. The THF-insoluble portion is referred to as char. All product yields are calculated on a dry, ash-free, and carbon black-free basis.

Plastic/coal reaction products were removed and extracted with cyclohexane. The cyclohexane was removed with a rotary evaporator and the residue (preasphaltenes and asphaltenes) was dried under vacuum for two hours. Cyclohexane-insolubles were subsequently extracted with THF. The THF-insoluble portion is referred to as char. This char also contains any inorganic material present in the coal or waste polymer feed. Products soluble in THF were obtained using a rotary evaporator, and dried for two hours under vacuum at 100°C. All product yields are calculated on a dry, ash-free basis.

Results

Waste Rubber Tire Material

Figure 1 shows the breakdown of products including the total conversion, oil + gas yields, and preasphaltene/asphaltene yields for various mixtures of tire rubber and Blind Canyon DECS-6 coal coprocessed under hydrogen for one hour at 350°C with a molybdenum catalyst (ammonium tetrathiomolybdate). Total conversion values reported here are reproducible within $\pm 2\%$. Figure 1 suggests that as the rubber tire content of the mixture increased, so also did the oil and gas yields. Accordingly, as the tire rubber percentage decreases and coal becomes the dominant reactant, the yield of asphaltenes increases, and oil + gas yields decrease. Since tire rubber breaks down into THF soluble components quite readily, the increase of the gas and oil products and the decrease in preasphaltenes/asphaltenes with increasing tire rubber content is not surprising. The straight diagonal line is drawn on Fig. 1 to indicate the conversion expected for a tire and coal sample mixture calculated from samples consisting only of tire/catalyst and only of coal/catalyst assuming no interaction of the two reactants takes place that would inhibit or enhance total conversion. The total conversion points above the solid line show that there is some synergism for sample compositions between 10% tire rubber and 30% tire rubber by weight. It appears from the preasphaltene/asphaltene curve in Fig. 1 that this may be related to an increase in production of preasphaltenes/asphaltenes. Figure 2 presents results of further work with various mixes of tire rubber and coal with the same molybdenum catalyst but at 430°C. Again the solid line indicates a theoretical value for the total conversion based on samples consisting of only coal/catalyst liquefied at 430°C and only tire/catalyst at 430°C. It is interesting to note that the synergism which takes place at 350°C does not seem to occur at the same tire/coal composition at which synergism is observed for samples processed at 430°C. Instead, at 430°C the synergism is noted for almost all samples coprocessed. The observed synergism at 430°C also is due to an increase in yields of preasphaltenes/asphaltenes.

Coprocessing for one hour periods at 430°C is found to be more beneficial than at 350°C for enhancement of product yields (Figure 3). Table 1 shows the amount of zinc found in the oil products from coal/tire coprocessing. Samples obtained by reaction at 430°C were found to contain less zinc than samples obtained at 350°C. Higher temperatures may enhance zinc deposition in the ash or zinc scavenged by the coal, thus diminishing the amount of zinc found in the products. Such scavenging could be beneficial in eliminating the need for a secondary process to remove zinc from the coprocessing-derived oils. While processing samples at different temperatures, we have noted a difference in the amount of carbon black found in the product oils. The carbon black is thought to be unsuited to hydrotreatment. During the extraction procedure using THF, some carbon black passes through the cellulose filters into the extraction mixture. The carbon black tends to stick to the solvent extraction apparatus. We have further noted that samples coprocessed at 430°C tend to dirty the glassware less. In order to calculate conversion to products accurately the carbon black is filtered out. We then observed for some of these samples coprocessed at higher temperatures and made up of more than 50% tire rubber that less carbon black was being filtered out. Figure 4 compares the amount of carbon black that was filtered out for samples coprocessed at 350°C and 430°C. The percentage of carbon black filtered out of the THF solubles is plotted versus the composition of the tire/coal mixture. At the lower temperatures and at higher tire rubber percentages larger amounts of the carbon black passed through the cellulose filter. This result may only be related to conditions of coprocessing with a tubing reactor and the manner in which we extracted our samples, but the result may be of some use in decreasing the amount of carbon black that becomes mixed into the oil products in a commercial operation.

Plastic Wastes

We have studied extensively the liquefaction of Blind Canyon coal, which has a low pyrite content. Hydroliquefaction of this and other coals of similar rank gives high yields of liquid products at temperatures around 350–430°C. As shown in Fig. 5, liquefaction of coal at higher temperatures results in decreased liquid yields and higher quantities of gases being produced. Maximum oil production was obtained at 430°C.

Commingled plastic wastes used in these experiments contained some polystyrene, and other plastics, but the most abundant polymer in this waste was high density polyethylene (HDPE). HDPE has the highest decomposition temperature of the plastic materials we tested (400–430°C) which made the optimum reaction temperature for processing commingled plastic higher than for coal.

From Fig. 6 (processing of commingled plastic for one hour), the maximum total conversion was reached (96%) at 430°C and higher temperatures. Oil production increased as the reaction temperature increased. Maximum oil production occurred at 430°C. Once the temperature was above 430°C the oil yield dramatically decreased as the gas production increased. Coprocessing plastic and coal together showed optimum conditions for total conversion and oil production at 430°C and a reaction time of one hour (Fig. 7).

As shown in Fig. 8, mixing plastic with coal did not result in any improvement of total conversion. Synergism was observed only for oil production for coal/plastic coprocessing. The observed synergism appears to be due to a decrease in the yield of asphaltenes.

Summary

Coprocessing at 430°C was found to give the highest total conversion yields for coal/rubber tire material coprocessing for one hour under a hydrogen atmosphere with a molybdenum catalyst. The zinc and carbon black contamination in the derived liquids was diminished when samples were coprocessed at 430°C. Coprocessing of coal with commingled plastic showed a synergistic effect on oil production but not on the total conversion

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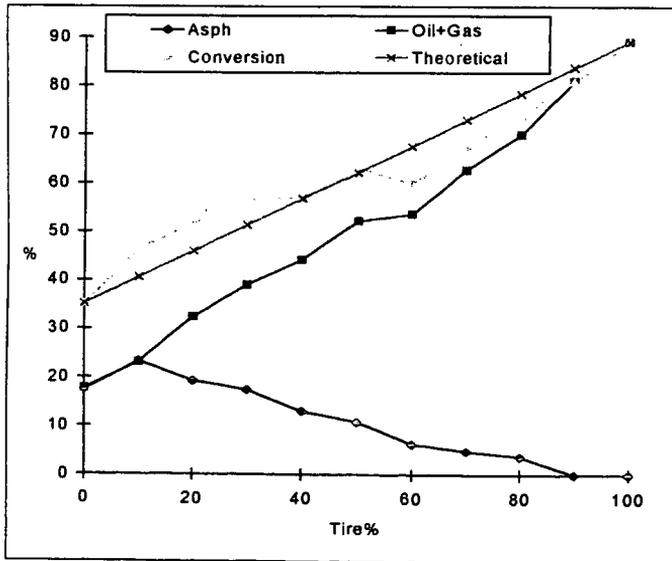


Fig. 1. Tire/coal products from coprocessing at 350 Celsius for 1 hour in tubing bomb reactors under 1000 psig (cold) hydrogen with a molybdenum catalyst.

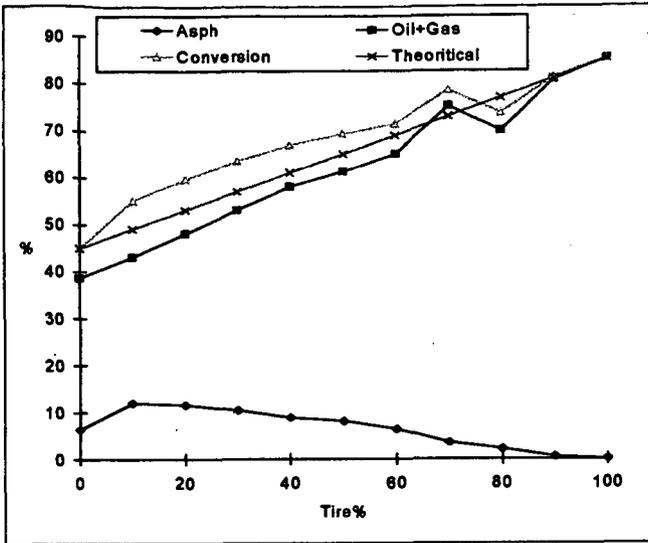


Fig. 2. Tire/coals products from coprocessing at 430 Celsius for 1 hour in tubing bomb reactors under 1000 psig (cold) hydrogen with a molybdenum catalyst.

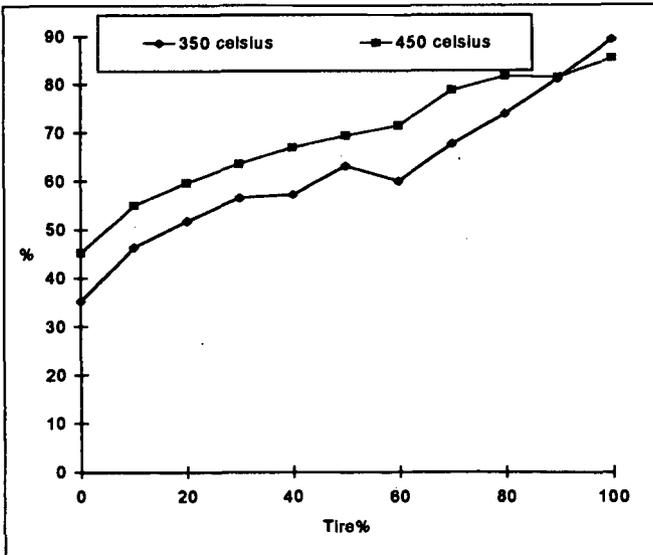


Fig. 3. Tire/coals total conversion comparison for samples coprocessed at 430 Celsius and 350 Celsius for 1 hour in tubing bomb reactors under 1000 psig (cold) hydrogen with a molybdenum catalyst.

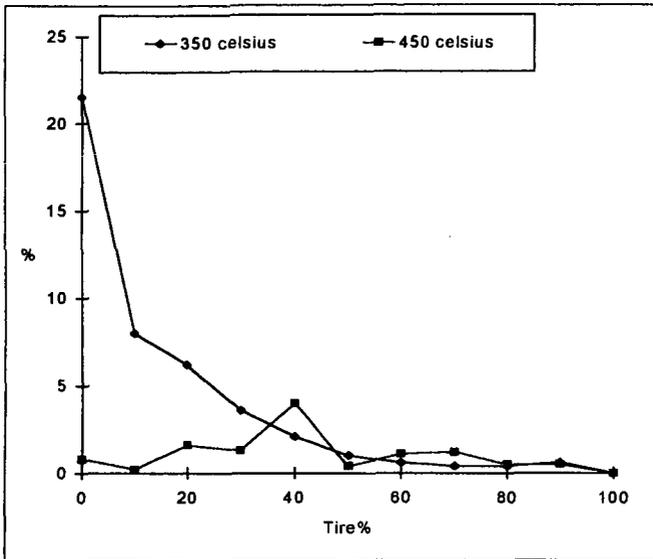


Fig. 4. Percentage of carbon black filtered out of THF soluble liquids for coal/tires samples coprocessed at 350 Celsius and 430 Celsius for 1 hour in tubing bomb reactors under 1000 psig (cold) hydrogen with a molybdenum catalyst

Table 1. Percentage of zinc (by weight) in cyclohexane soluble oils obtained from coal/tire rubber samples coprocessed in tubing bomb reactors with reaction times of 1 hour under at 1000 psig (cold) hydrogen with a molybdenum catalyst.

Coal %	Tire %	350° Celsius	430° Celsius
0	100	0.017 %	0.007 %
30	70	0.016 %	0.008 %

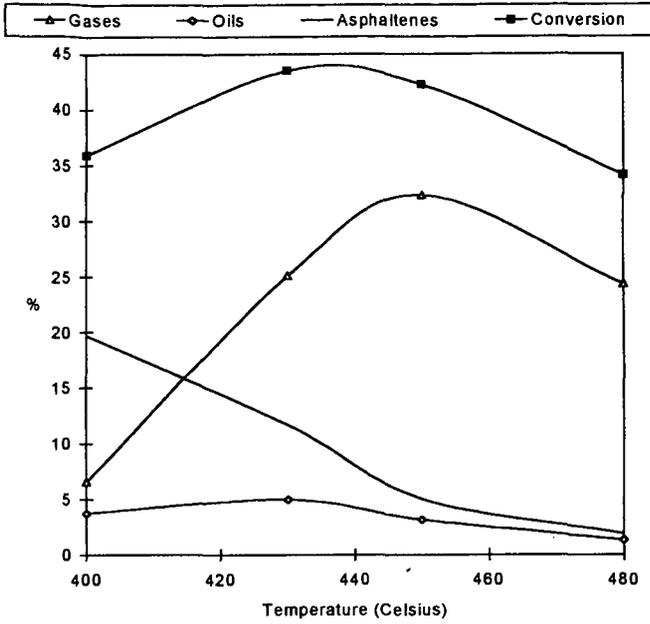


Fig. 5. Liquefaction results for DECS-6 coal hydrotreated for 1 hour in tubing bomb reactors under 1000 psig (cold) hydrogen

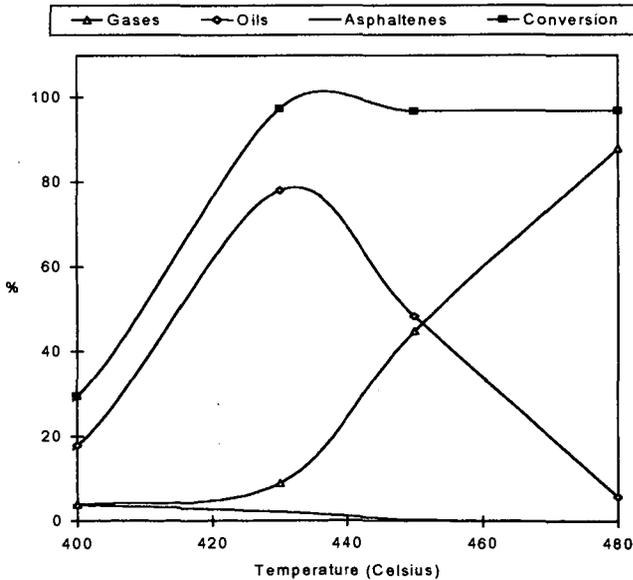


Fig. 6. Liquefaction results for commingled plastic #2 [APC] hydrotreated for 1 hour in tubing bomb reactors under 1000 psig (cold) hydrogen.

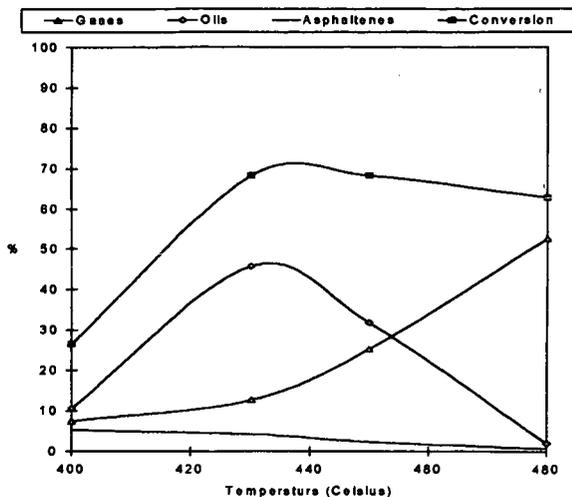


Fig. 7. Results for coprocessing of commingled plastic #2 [APC] and DECS-6 coal for 1 hour in tubing bomb reactors under 1000 psig (cold) hydrogen.

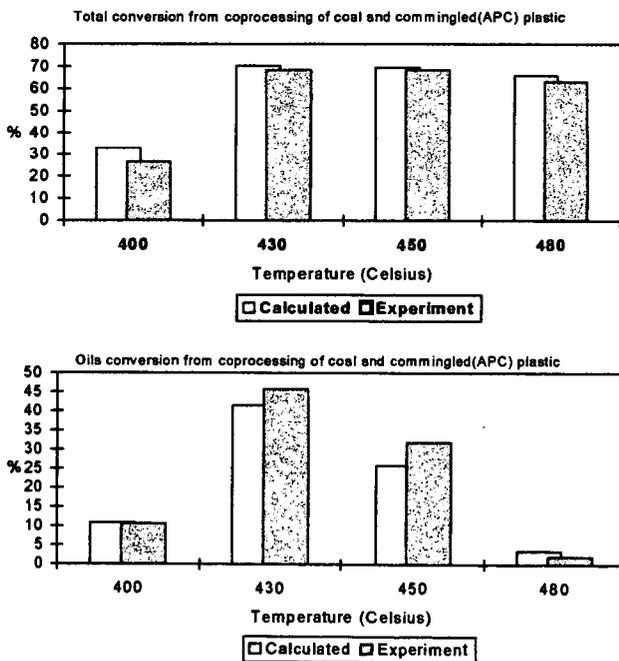


Fig. 8. Experimental and calculated results for coprocessing of commingled plastic #2 [APC] and DECS-6 coal for 1 hour in tubing bomb reactors under 1000 psig (cold) hydrogen.

COPROCESSING OF WASTE HYDROCARBON FEEDSTOCKS USING COUNTERFLOW REACTOR TECHNOLOGY

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Keywords: Co-Liquefaction, waste plastics, rubber tires

INTRODUCTION

Like many jurisdictions in North America, the Province of Alberta is in the early stages of introducing measures to collect and recycle hydrocarbon wastes. In 1992 a levy of \$4 was added to the purchase price of each automotive tire. This levy was accumulated in a fund to promote the use and recycle of waste rubber tires.¹ The fund has supported several diverse uses of the waste tires, including incineration in cement kilns and rubber crumb generation for marketable products. To date these projects have only utilized 1.8 million of the 2.5 million tires which are discarded annually and have not started to reduce the backlog of over 4 million tires which was accumulated prior to 1992.

Recently several European plastics manufacturers have joined together to invest in a pilot project to convert waste plastic containers into oil.² In this process the produced naphtha will be converted into hydrocarbon monomers which can then be fed to polymerization units for complete recycle to fresh plastics. Similar efforts are underway in North America to recycle hydrocarbon wastes to oil or gaseous products. Much of this work is directed at co-liquefaction of polymers and coal, and has been reviewed by Huffman.³ Indications are that waste plastics and rubber tires can be converted into liquids using technologies which have been developed for the liquefaction of coal. Both Taghiei⁴ and Anderson⁵ have reported that there is a synergistic effect when coal and plastics are co-liquefied. Similarly enhanced coal liquefaction performance has been observed when co-liquefying waste tires and coal.^{6,7}

Alberta Research Council together with Canadian Energy Developments have developed technologies for the direct liquefaction of coal⁸ and coprocessing of coal and heavy oil/bitumen.⁹ It was a small step to envision the application of these technologies to the processing of other hydrocarbons such as waste plastics and rubber tires. This paper reports on a preliminary experimental program that was conducted to investigate the coprocessing of waste hydrocarbons with coal and heavy oil.

CO-LIQUEFACTION CONCEPT

The generic waste processing scheme is depicted in Figure 1. Initially there is a simple preparation step in which the waste hydrocarbon (and catalyst) is blended into a slurry with a recycle solvent or a refinery derived stream. Depending upon the feed characteristics the preparation step may be a digester to partially melt or solubilize the feed. The feed slurry is then introduced close to the top of the counterflow reactor (CFR) which is the heart of the process. This unit, operating at or near coal liquefaction temperatures and pressures, converts the hydrocarbon waste into liquid or gaseous products. The lighter boiling components are swept from the top of the reactors by the carrier gas. The carrier gas is most likely hydrogen but could be carbon monoxide or natural gas depending on the nature of the waste or solvent.

Light products are separated by conventional refinery processes. Liquid components from the bottoms slurry could be separated by a variety of procedures geared to the particular feed, including centrifugation, filtration or flashing. With plastic wastes the bottoms stream would be small and solids virtually absent. The withdrawal rate would then be dependant on the need for the slurry solvent. Tires produce a solid residue which if treated successfully could give regenerated carbon black and other byproducts.

EXPERIMENTAL

Alberta Research Council has traditionally employed 1 litre batch autoclaves as a screening tool to test new concepts or process operating conditions for the CFR. The procedures have been described elsewhere⁸. Feedstock properties are listed in Table 1. The solvent LO-6282 (boiling range 250-550°C) was obtained from the HRI facility

in Princeton, New Jersey. It was generated from a liquefaction run using Illinois #6 coal. Cold Lake heavy oil was taken from the Alberta Research Council Sample bank.

In a typical test, 75g of feed (polyethylene, coal, rubber crumbs or mixtures of each), was slurried with 150g of the solvent or heavy oil, and if required catalyst was added. The autoclave was charged to 1250 psi (cold) with hydrogen. This gave an operating pressure of 2000-2500psi depending on the process temperature or feed/solvent composition.

At the completion of the run the gas was discharged and the autoclave was flushed with hydrogen. The combined gas sample was analyzed by gas chromatography. The liquid slurry was recovered from the autoclave and a portion was subjected to extraction, either with tetrahydrofuran (THF) or sequentially with toluene, then THF.

Hydrocarbon conversion is reported as:

$$\frac{\text{Feedstock(DAF)}_{\text{In}} - \text{THF Insolubles}_{\text{Out}}}{\text{Feedstock(DAF)}_{\text{In}}} \times 100 \text{ weight\%}$$

where feedstock is polyethylene or rubber crumb or mixtures of either with coal.

In a limited number of runs a liquid sample was prepared by filtration to allow more detailed characterization.

RESULTS AND DISCUSSION

Co-Liquefaction of Polyethylene

The influence of temperature, catalyst and coal concentration, as well as a soak step were investigated for the co-liquefaction of polyethylene. By itself polyethylene proved intractable. At 425°C for 60 minutes, where coal conversion exceeded 90%, polyethylene conversion was barely 20% (Table 2). After correction for solvent decomposition, less than 1% of hydrocarbon gas was produced. Introduction of coal into the system improved feedstock conversion with Fe₂O₃ catalyst. Assuming that coal conversion at this temperature was 90% then the predicted feedstock conversion was calculated to be 28.3% with a coal to polyethylene ratio of 1:9, and 41.3% at a ratio of 1:1. Thus the experimental results suggest that there was a synergistic effect in this system. Product quality was visually poor; the almost clear polyethylene pellets had been transformed into a greyish rubbery solid. The hydrogen: carbon ratio of the solid residue from Run W-1 was 1.93, less than in the polyethylene 2.0. Further tests are in progress to determine if the polymer degradation products had incorporated chemically bonded solvent.

Increasing the process severity to 440°C for 30 minutes, and replacing the catalyst with the potentially more active molybdenum naphthenate (~600 ppm Mo on feed), improved feedstock conversion, but not to those levels which might be acceptable in a commercial process (nominally set at >90%). Polyethylene itself gave 65% conversion and almost the entire conversion product slate was a liquid (THF soluble). Coal addition did little to enhance the polyethylene conversion. Using an assumed value of 90% for coal conversion, the predicted values for feedstock conversion for Runs W-5 and W-6 matched the experimental.

The maximum potential for conversion and liquid yields had not been reached at 440°C/60minutes (Run W-7). Feedstock conversion had risen to 83% with the majority of the additional product being oils. Again assuming 90% coal conversion only 78% of the polyethylene had been solubilized or converted to gases. Therefore there was an opportunity to produce more liquid products from this feedstock combination by maximizing the process severity. This scenario was dependant on the stability of the solvent which at 440°C/60 minutes generated 2.3g of gas/100g solvent.

Finally the benefit of a soaking period prior to the hydroprocessing step was investigated (W-8). Polyethylene melts at ~125°C and a soaking or digestion step might help liquefy or solubilize the material and in a continuous operation improve flow and transfer characteristics of the feedstock slurry or solution. Dimethyl disulphide was also added to the charge as a sulphiding agent for the molybdenum. A small increase in feedstock conversion was recorded but it was

within the reproducibility of $\pm 2\%$ found in 1L batch autoclave tests. Hydrocarbon gas yield rose by about the amount attributable to the methane produced by the decomposition of the dimethyl disulphide.

Co-Liquefaction of Rubber Crumb

Following the preliminary program with polyethylene the conditions selected initially for rubber crumb were the relatively high severity $440^\circ\text{C}/60$ minutes using the molybdenum naphthenate catalyst. At these process conditions, Run W-9, the residual solids (THF insoluble), $34.7\text{g}/100\text{g}$ feed, corresponded almost exactly to the sum of the fixed carbon plus ash in the rubber crumb, $34.6\text{g}/100\text{g}$ (Table 3). Gas production was moderate at $3.9\text{g}/100\text{g}$ feed much of which can be attributed to decomposition of the solvent, i.e. $2.3\text{g}/100\text{g}$ solvent at similar process operating conditions. Product recovery and mass balances both for this Run and W-10, were well below the norm of 98-98%, which suggested that large quantities light hydrocarbons were produced and lost during the workup procedure. Characterization of the liquid product by simulated distillation indicated that the bulk of this material was within the naphtha boiling point range ($<183^\circ\text{C}$).

Introduction of coal into the feed, Run W-10, resulted in essentially complete conversion of both coal and rubber crumb. Using the previous value for rubber crumb conversion (Run W-9), the coal conversion was estimated to be greater than 95%. Gas production increased but was largely due to carbon oxides derived from the coal.

The above conditions were selected in most part to ensure coal liquefaction. Since the rubber crumb was at its maximum conversion, less severe condition might be effective. Lower temperature (375°C), in the absence of catalyst or hydrogen were taken as the opposite end of the spectrum of processing severity (Run W-13). Even so the liquefaction of the rubber crumb was then close to its maximum, 62.5% versus 65% for the high severity run. Gas production was minimal and product recovery was 99% indicating that fewer light hydrocarbon had been produced from the rubber or solvent. A simulated distillation of the filtered liquid product showed that the rubber crumb derived components were heavier than for the high severity run and were largely concentrated in the middle distillate fraction ($183\text{-}343^\circ\text{C}$).

Performance, in terms of rubber crumb conversion and production distribution, was unchanged when using the catalyst and hydrogen atmosphere at 375°C . Liquid product quantities increased due to the large uptake of hydrogen during the run (W-14). This contrasted with the nitrogen run where hydrogen was actually produced. Characterization of the liquid products by gas chromatography with a mass spectroscopy detector displayed a concentration of monocyclic hydrocarbons with isopropyl and methyl group attached to the ring. In the presence of hydrogen the cyclics were mostly cyclohexane or cyclohexene with lesser quantities of the corresponding aromatic analogues. In the nitrogen atmosphere the situation was reversed with the aromatics dominating. Still the presence of partially and fully hydrogenated rings pointed to the transfer of hydrogen from the solvent. This leads to the question of what type of solvent is the preferred medium. In coal liquefaction hydrogen donor and transfer properties are valued. With rubber crumb hydrogen donation may prove disadvantageous since the products formed by hydrogen addition may not be the best choice either for gasoline blending or as a petrochemical feedstock.

The proposed waste processing scheme would have to accept a variety of feedstocks and solvents. Alberta heavy oilsand bitumens are proven solvents for subbituminous coals.⁹ The effectiveness of Cold Lake heavy oil for solubilizing both coal and rubber crumb was demonstrated in Run W-12. Feedstock conversion was comparable with the LO-6282 solvent. The high severity led to low product recovery and very high hydrogen consumption. This was deceptive since consumption was reported on $\text{g}/100\text{g}$ feedstock basis (coal + rubber crumb) but much of the hydrogen would have been used during the upgrading of the bitumen. The same reasoning applies to gas yield which incorporates bitumen derived gases including hydrogen sulphide which had not been observed from the coal or rubber crumb.

CONCLUSIONS

Batch autoclave tests indicated that counterflow reactor technology was a promising procedure for co-liquefaction of waste plastics and rubber tires. The versatility of the process has been demonstrated by coprocessing coal, wastes and reactive solvent (heavy oil). It was successful at producing an all liquid slate of products from all the potentially convertible hydrocarbon in the rubber crumb.

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Figure 1
GENERIC WASTE PROCESSING SCHEME
USING COUNTERFLOW REACTOR TECHNOLOGY

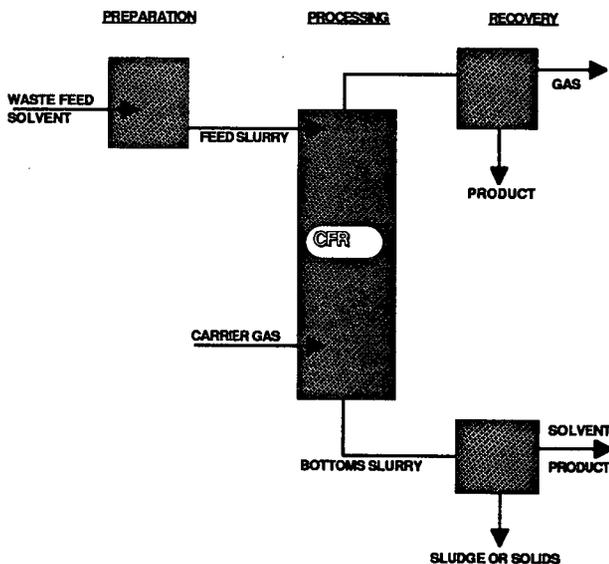


Table 1 Feedstock and Solvent Properties

	Rubber Crumb	Coal	Solvent LO-6282	Heavy Oil
Source	Alberta Environmental Rubber Products	Black Thunder	HF	Cold Lake
Nature	1 to 5mm	sub-bituminous	250-525°C	Full range
Characterization, Weight %				47% +525 resid
Carbon	83.1	71.0	88.5	82.8
Hydrogen	7.4	5.2	10.5	10.4
Sulphur	2.4	0.97	0.07	4.6
Ash	5.8	6.2		
Fixed Carbon	29.1	51.4	1.9*	12.6*

* Conradson Carbon Number

Table 2 Co-Liquefaction of Polyethylene

Run #	W-1	W-2	W-3	W-4	W-5	W-6	W-7	W-8
Feedstock								
PolyE	100	90	50	100	50	90	50	50
Coal		10	50		50	10	50	50
Catalyst		Fe2O3/DMDS			Mo naph		Mo naph	
Solvent		LO-6282			LO-6282		LO-6282	
Process Conditions								
Temperature, °C		425			440		440	
Pressure, psi(cold)		1250			1250		1250	
Time, min		60			30		60	
Process Performance								
Recovery, %	99	99	98	99	97	99	100	96
Conversion, weight %	19	35	61	64	72	62	82	84
Predicted@90%		28	43		75	66		
Yields, g/100gMAF feed								
Gas	3.2	4.1	7.3	2.0	6.8	2.9	8.8	9.4
Oils	16.9	33.0	36.2	63.2	66.2	59.6	74.1	77.1
Solids	81.1	64.6	38.9	35.7	27.9	38.2	18.4	15.7
Hydrogen consumption	1.21	1.67	2.39	0.89	0.98	0.66	2.32	2.14

Table 3 Co-Liquefaction of Rubber Crumb

Run #	W-9	W-10	W-13	W-14	W-12
Feedstock					
Rubber Crumb	100	50	100	100	50
Coal		50			50
Catalyst		Mo naph		None	
Solvent		LO-6282		Cold Lake	
Process Conditions					
Temperature, °C		440		375	440
Pressure, psi(cold)		1250		0(N2)	1250
Time, min		60		80	60
Process Performance					
Recovery, %		94		99	89
Conversion, weight %		65		62	64
Predicted@90%cc		77			77
Yields, g/100gMAF feed					
Gas		3.9		5.4	13.4
Oils		63.7		74.3	69.0
Solids		34.7		20.0	67.0
Hydrogen consumption		2.39		2.71	3.62
				-0.49	3.85
					8.71

COAL-TIRE CO-LIQUEFACTION

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Keywords: Tire liquefaction, coal liquefaction, iron catalyst.

ABSTRACT

Co-liquefaction of ground coal and tire rubber was studied at 400°C both with and without catalyst. Two different tire samples were used. In the non-catalytic runs, the conversion of coal increased with the addition of tire and the increase was dependent on tire/coal ratio and hydrogen pressure. Using a ferric sulfide-based catalyst, the coal conversion increased with an increase in the catalyst loading. However, the increase was more pronounced at loadings of around 0.5 wt%. The addition of tire to coal in the catalytic runs was not particularly beneficial, especially, when the tire/coal ratio was above 1.

INTRODUCTION

Disposal of used tires is a major environmental problem. Recently, the liquefaction of such tires in conjunction with coal was suggested as an alternative for their disposal [1,2]. Liu et al. [1] studied the co-liquefaction of tire and DECS-6 coal. The tire sample was prepared from an used Goodyear Invicta tire. When the tire and coal were co-liquified at 400°C it was observed that the conversion of coal increased in the same way as with the addition of tetralin (a good hydrogen donor solvent) to coal. Similar results were obtained by Farcasiu and Smith [2] for the liquefaction of tire and Illinois No. 6 coal at 425°C. In both these studies a complete conversion of tire was obtained.

In this work, the effect of H₂ pressure and tire/coal ratio on the co-liquefaction of tire and coal was studied at 400°C. Two different tire samples were used. Runs were made with tire and coal separately as well as using tire-coal mixtures with tire/coal ratios of 0.4. The hydrogen pressure was varied between 0-1500 psi (cold). Experiments were also done using a ferric sulfide-based catalyst at loadings of up to 1.67 wt% based on coal.

EXPERIMENTAL

The coal used was DECS-6 which is a high-volatile-A bituminous coal from the Blind Canyon seam in Utah. Two different tire samples were used. The first sample was prepared from a Goodyear Invicta tire, recycled in-house at WVU (Tire-1). The other sample was obtained from the University of Utah Tire Bank and represented mixed recycled tires ground to -30 mesh. The proximate and ultimate analyses showed that the Tire-1 contained 67 wt% volatile matter (on a dry, ash-free basis) and 33 wt% fixed carbon while Tire-2 contained 71 wt% volatile matter and 29 wt% fixed carbon. The fixed carbon essentially represents the content of carbon black in the tires. The amounts of volatile matter and fixed carbon in coal were 49 wt% and 51 wt%, respectively.

The experimental equipment, run procedures and analytical techniques have been described earlier [1] and are given briefly. A stainless steel tubing bomb reactor with a volume of 27 ml was used for the liquefaction. The reactor was loaded with the feed and, purged and pressurized with H₂ or helium to the desired pressure. The feed consisted of tire or coal or a mixture of the two in different ratios. In the catalytic runs, the catalyst was impregnated in-situ on the coal. The gaseous products were collected and analyzed by gas chromatography. The solid and liquid products in the reactor were washed and extracted with tetrahydrofuran (THF) for 24h. The THF-insoluble material (TI) was separated by filtration. The conversion is calculated from the amount of THF-insoluble material.

After the removal of THF by rotary evaporation, the THF-solubles were extracted with hexane for 2h. The extract was separated into hexane-insoluble (HI) and hexane-soluble (HS) fractions by filtration. The HS fraction was used to recover the 'oil fraction'. The THF-soluble/hexane-insoluble fraction, i.e. the HI fraction, represents asphaltenes. The conversion (X) and the yield of asphaltenes (A) were calculated as follows:

$$X = (F_m - TI) / F_{daf} \quad (1)$$

$$A = HI / F_{daf} \quad (2)$$

where F_m and F_{daf} represent the amount of feed on moisture-free and dry, ash-free (daf) basis, respectively. The gas yield (G) was determined independently from the gas analysis. The oil yield (O) was obtained by difference:

$$O = X - A - G \quad (3)$$

In many cases, the combined oil + gas yield was calculated by difference. Most runs were made in duplicate and the experimental error was $\pm 2.5\%$.

In the co-liquefaction runs, the overall conversion and the yields of asphaltenes and oil + gas fractions were calculated as above. However, in order to get a better insight, the results were also analyzed in terms of incremental conversion and yields, based on coal, which were calculated as follows;

$$X_{cm} = (X_{ov} - w_t x_t) / w_c \quad (4)$$

where X_{ov} is the total conversion and w_t and w_c are the weight fractions of tire and coal in the feed, respectively. In equation (4), x_{cm} is the estimated conversion of coal in the mixture and x_t is the conversion of tire which was assumed to be the same as in tire-alone runs. The yield of oil + gas from coal was estimated similarly. The asphaltenic yield from coal was calculated by difference. It should be recognized that the conversion of tire in the co-liquefaction runs may be different from that in tire-alone runs. However, the above assumptions were made simply to 'lump' the entire incremental effect into a single component, i.e., coal.

RESULTS AND DISCUSSION

Effect of Hydrogen Pressure

The effect of hydrogen pressure on the product slate from coal-alone and tire-alone (Tire-2) was studied at 400°C. The runs at zero hydrogen pressure were made using 1000 psi (cold) helium. The effect of hydrogen pressure on the tire conversion was found to be minimal. Also, the hydrogen pressure affected the coal results only slightly. The conversion of coal increased with increase in hydrogen pressure, resulting in an increase in the yields of both asphaltenes and oil+gas fractions. At all the pressures, the yield of asphaltenes was lower than that of oil plus gas. Thus it appears that the gaseous hydrogen is necessary to stabilize the coal radicals. This is consistent with the observations of Malhotra and McMillen [3] and Whitehurst et al. [4] that the retrogressive reactions in coal liquefaction become more pronounced under hydrogen-deficient conditions. The results indicated that the relative contribution of hydrogen to the stabilization of asphaltenic radicals is somewhat greater than to the radicals in the oil range.

Figures 1 and 2 show the effect of hydrogen pressure in the co-liquefaction runs using Tire-1 and Tire-2, respectively. The tire/coal ratio was unity. The conversion and oil + gas yield from tire were assumed to be the same as those for the liquefaction of tire alone and the results are reported on coal-alone basis. It is seen that, with Tire-1 (Figure 1), both the conversion and oil+gas from coal increase with an increase of H_2 pressure, up to around 500 psi (cold). At higher H_2 pressures, the results are relatively insensitive to the pressure. However, when Tire-2 was used, the conversion of coal increased monotonically with the H_2 pressure (Figure 2). This led to increase in the yields of both asphaltenes and oil+gas. When these results were compared to those for the coal alone, it was found that the effect of hydrogen pressure on the product slate is greater in the co-liquefaction runs than in the coal-alone runs. The synergistic effect of Tire-2 also appears to depend on H_2 pressure, i.e. there is an increased synergism at high hydrogen pressures. The yields of asphaltenes in the co-liquefaction runs (Figure 2) are almost double those which were observed in the coal-alone runs. On the other hand, the yields of oil+gas are lower compared to those in coal-alone runs, especially at low hydrogen pressures. This indicates that both the gaseous hydrogen and the tire radicals are used in the stabilization of coal radicals that are in the asphaltenic range. Further, the contribution of tire to the radical stabilization and bond scission is considerably higher compared to that of hydrogen. In contrast, the coal radicals in oil range are probably stabilized mainly by the hydrogen and the addition of tire seems to have little effect especially at low hydrogen pressures.

Effect of Tire/Coal Ratio

The effect of tire/coal ratio on conversion and product yields using Tire-1 is shown in Figure 3. As before, the results are based on coal, i.e. the contribution of tire has been subtracted out. The conversion of coal increases from around 35 wt% in the absence of tire to over 65 wt% when the tire/coal ratio was 4. The yield of oil+gas appears to be independent of tire/coal ratio. Similar results were obtained with Tire-2 where the effect of tire addition was found to be more significant at low tire/coal ratios (Figure 4). The conversion of coal increases from 38 wt% (coal-alone runs) to 49 wt% at tire/coal ratio of 1. At higher ratios, the addition of tire has only a small effect on coal conversion. There seems to be a slight maximum in the conversion at tire/coal ratio of 3 where the conversion was 54 wt%. The oil yield for the co-liquefaction may be maximum at a tire/coal ratio of 2.

Effect of Using Ferric Sulfide-based Catalyst

The catalytic runs were made using catalyst based on iron sulfide, Fe_2S_3 . The catalyst was impregnated *in-situ* on the coal. The coal was first mixed with a dilute aqueous solution of Na_2S and agitated vigorously before adding $FeCl_3$ solution. The suspension containing coal and catalyst was filtered, washed and dried in N_2 under vacuum.

Figure 5 shows the effect of catalyst loading on the conversion and product yield. In these runs, Tire-1 was used and the tire/coal ratio was 1. Again, the results are based on coal. The conversion of coal increases from around 45 wt% in the absence of catalyst to over 80 wt% when the catalyst loading was 1.67 wt%. The yield of oil+gas increased from 10 wt% to 20 wt%. This indicates that the increased loading is beneficial to the activity and selectivity of the catalyst. However, the incremental effect of catalyst loading is more pronounced at loadings of around 0.5 wt%.

The effect of tire/coal ratio on the conversion and product yields in the catalytic runs is presented in Figure 6. These runs were made with Tire-2 and the catalyst loading was 1.67 wt%. The addition of tire appears to have only a small effect on the conversion and product yields below a tire/coal ratio of 1. At higher ratios, both the conversion and yields decrease indicating that the addition of excess tire is detrimental to the activity of the catalyst. This may be due to the poisoning of the catalyst by the polymeric compounds present in the tire rubber.

CONCLUSIONS

1. The co-liquefaction of tire rubbers with coal has a considerable synergistic effect on the conversion and product yields from coal.
2. The synergism due to the addition of tire increases with an increase in hydrogen pressure and tire/coal ratio.
3. The conversion and product yields from coal increase using ferric sulfide-based catalyst. However, the synergistic effect of tire in the catalytic runs is small, especially, at high tire/coal ratios where the conversion and yields actually decrease.

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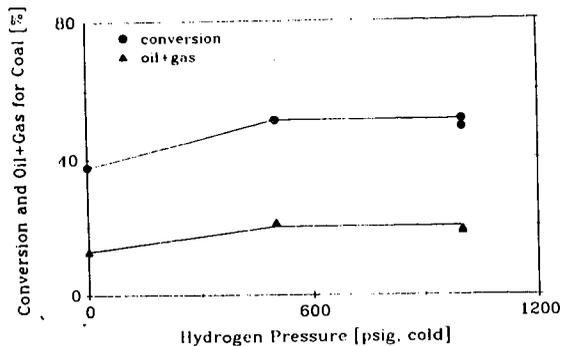


Figure 1. Effect of H_2 pressure on conversion and yields of coal in a coal/tire mixture. Conditions: $400^\circ C$, 30 min, tire/coal =1. Tire-1 and DECS-6 coal were used.

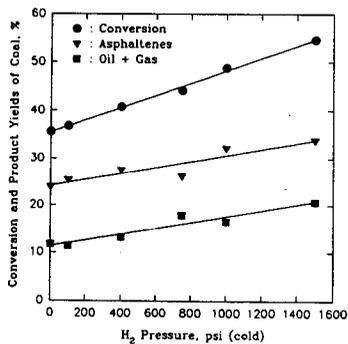


Figure 2. Effect of H_2 pressure on conversion and yields of coal in a coal/tire mixture. Conditions: same as in Figure 1. Tire-2 and DECS-6 coal were used.

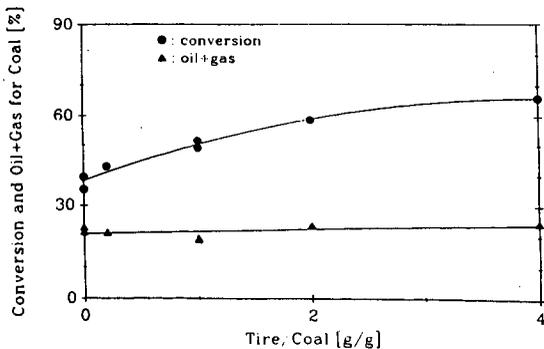


Figure 3. Effect of tire/coal ratio on conversion and yield of coal in a coal/tire mixture. Conditions: $400^\circ C$, 30 min, H_2 pressure = 1000 psi (cold). Tire-1 and DECS-6 coal were used.

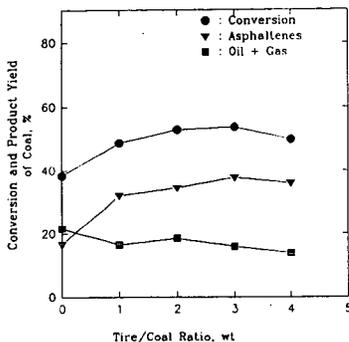


Figure 4. Effect of tire/coal ratio on conversion and yield of coal in a coal/tire mixture. Conditions: Same as Figure 3. Tire-2 and DECS-6 coal were used.

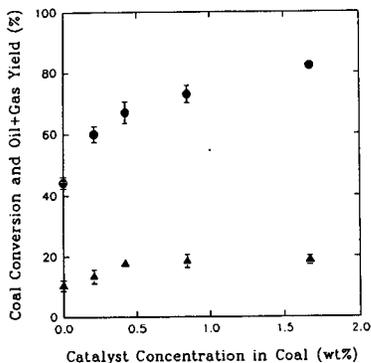


Figure 5. Effect of catalyst loading on conversion and yield of coal in a tire/coal mixture. Conditions: same as in Figure 3. Tire-1 and DECS-6 coal were used.

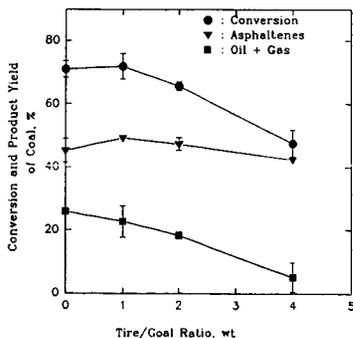


Figure 6. Effect of tire/coal ratio on conversion and product yields of coal. Conditions: 400°C, 30 min, 1000 psi (cold), 1.67% catalyst loading. Tire-2 and DECS-6 coal were used.