

REACTION PATHWAYS IN COPROCESSING

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INTRODUCTION

The coprocessing of coal and petroleum resid has been under active study as a method for the simultaneous utilization of two lower-valued fossil resources. Our research has focused on the coprocessing technology that was developed by Gatsis and coworkers^{1,2} in which optimal reaction conditions (3000 psi total pressure, 420°C, 2:1 resid:coal, and 1 wt percent of a molybdenum-based Universal Oil Products catalyst) enabled the conversion of about 90% of the coal to toluene-soluble products and about 80% of the asphaltenes to heptane-soluble products. We have investigated the chemistry by carrying out the reaction in a dideuterium atmosphere at low and high severity³ and by studying the reactions of representative aliphatic and aromatic hydrocarbons and phenols.⁴

EXPERIMENTAL

Materials. Illinois No. 6 coal was prepared by the Kentucky Center for Applied Energy Research and was used as received (Anal. % C, 68.60; % H, 4.51; % N, 1.39; % S, 3.04; % O, 9.65; % H₂O, 3.15; % ash, 9.65). Lloydminster petroleum resid (Anal. % C, 83.6; % H, 10.3; % S, 4.77; % N, 0.59; % O, 0.54) was obtained from the UOP Research Center. The catalyst was a molybdenum-based UOP proprietary material.

Procedure. Lloydminster petroleum resid (280 g) and Illinois No. 6 coal (165.4 g) and the catalyst (0.2 wt % Mo) were added to an 1800-mL rocking autoclave. The autoclave was sealed and pressurized first with hydrogen sulfide and then with dideuterium to give a 10 vol % hydrogen sulfide and 90 vol % dideuterium at the desired total pressure. The autoclave was heated to the desired temperature in about two hours and then cooled or retained at the temperature as appropriate. The work-up procedure, which has been described previously,³ enabled the isolation of gases and insoluble products as well as the solvent separated oil, resin, and asphaltene.

Analysis. Elemental analyses of the starting coals, resids, and solvent separated products were carried out at Universal Oil Products. Gas analyses for deuterated methanes, ethanes, propanes, butanes, butenes, benzenes, and toluenes were carried out at the Institute of Gas Technology.

Deuterium NMR spectra were obtained on a Varian XL 400-MHz spectrometer, and proton NMR spectra were recorded at 500 MHz. The D/(H + D) ratio was evaluated for the aromatic and the alpha, beta, and gamma aliphatic positions. Detailed procedures that describe the magnetic resonance experiments have been published.^{3,5}

RESULTS

The extent of conversion of the coal and resid into gases, oils, resins, asphaltenes, and solids is displayed in Figure 1. Typical results that illustrate the manner in which deuterium is incorporated into the reaction products are shown in Figure 2. The reaction chemistry of 1-pentyl-2-naphthol, which illustrates the complexity of the catalyzed transformations of even rather simple molecules, is summarized in Figure 3.

DISCUSSION

Molybdenum catalysts have been under study for many years. Indeed, more than 25 contributions were presented at a symposium of the Division of Petroleum Chemistry in Washington in August, 1994. While the detailed molecular mechanisms for these catalysts are not yet fully established, they are effective agents for the reduction of aromatic molecules, especially bi- and trinuclear substances, and for hydrodeoxygenation, hydrodesulfurization, and hydrodenitrogenation. Their hydrodeoxygenation activity is illustrated in Figure 3. In high severity coprocessing, the catalyst removes virtually all the oxygen, 74% of the sulfur, and 42% of the nitrogen from the products of Illinois No. 6 coal and Lloydminster resid. The catalyzed transformations of pure hydrocarbons and heterocycles have been studied by many research teams. For example, Curtis and her coworkers showed that the heteroatom removal and reduction reactions lead to monobenzenoid aromatic compounds, thus benzofuran yields ethylbenzene and 2-naphthol provides tetralin.⁶

The catalyst apparently also accelerates electrophilic reactions, and alkylation occurs during the process. Thus, when low concentrations of phenol are incorporated into the coprocessing reaction system, it undergoes alkylation before it is deoxygenated.⁴ Aromatic deuterium exchange also apparently proceeds in an electrophilic order as suggested by the fact that phenols exchange much more rapidly than benzenes.

Hydrogen-deuterium exchange is facile. The selectivity for the incorporation and exchange of aromatic as well as alpha, beta, and gamma [AromaticCH₂(α)CH₂(β)CH₂(γ)] aliphatic hydrogen was measured for the series of coprocessing reactions. The results at high reaction severity indicate that the hydrogen and deuterium content has almost reached the equilibrium value dictated by the relative abundances than substances in the reaction system. At low severity, the deuterium is selectively incorporated at the aromatic and alpha aliphatic positions. Then, as the reaction proceeds, the amount of deuterium in the beta and gamma aliphatic positions increases, and the quantity of this isotope in the aromatic and alpha positions eventually decreases. Deuterium exchange in thermal reactions shows a much different order. The reactivity at activated benzylic (alpha) positions is clearly dominant under these conditions, with much less chemistry at the aromatic and unactivated aliphatic positions. The molybdenum catalyst and the reagents that were used in this study present a novel pattern of reactivity in which both free radical hydrogen transfer and ionic proton transfer occur rapidly. This dualism of parallel radical and electrophilic chemistry importantly contributes to the success of this coprocessing process.

The outcome is strongly influenced by the high initial hydrogen sulfide concentration, which is augmented by the formation of additional amounts of this acid from the resid and coal. Molybdenum sulfide catalysts contain thiol groups with H/Mo ratios from 0.12 to 0.37.^{7,8} Furthermore, it is known that the exchange of H₂ and D₂ is very rapid.⁹ Thus, the rapid equilibration of H₂S with the D₂ atmosphere in this reaction system is assured.



Hydrogen sulfide is certainly effective as a hydrogen atom transfer agent in thermal coal conversion chemistry.¹⁰ Thus, the myriad of different radicals that are formed in the initial thermal decomposition of the coal macromolecules are rapidly converted to stable molecules by very fast hydrogen atom transfer reactions. The catalyst probably does not participate in these initial reactions, other than by insuring the exceedingly rapid conversion of ineffectual dideuterium into effective hydrogen deuterium sulfide. The thermal coal to asphaltene conversion is not the limiting reaction in coprocessing, Figure 1. One important factor in this successful conversion is the fact that the reaction between the initial coal fragment radicals and other coal constituents can be effectively suppressed by rapid hydrogen transfer. A second factor is that the smaller core molecules are efficiently converted by the catalyst into desirable hydrocarbons free of heteroatoms. These suggestions can be coupled with current ideas of coal structure and coal decomposition to provide a reasonably satisfying picture of coal conversion during coprocessing.

It is well known that the slow conversion reactions of the collections of molecules that constitute the asphaltenes limit the success of this coprocessing reaction.¹² Our new results show that this situation prevails in spite of the fact that the hydrogen atoms of the asphaltenes exchange quite readily, Figure 2. The parameters that govern the reactivity of these molecules have not yet been adequately elaborated.

Acknowledgment. We are indebted to the coal sample program at the Kentucky Center for Applied Energy Research for starting material. We also gratefully acknowledge the special efforts of the analytical group at Universal Oil Products and the Institute of Gas Technology. Irene Fox of the Analytical Chemistry Laboratory at Argonne National Laboratory provided insight concerning the interpretation of the H/D analyses that were obtained by LECO equipment. We are also indebted to the United States Department of Energy for the support of this research via AC22-88PC88811.

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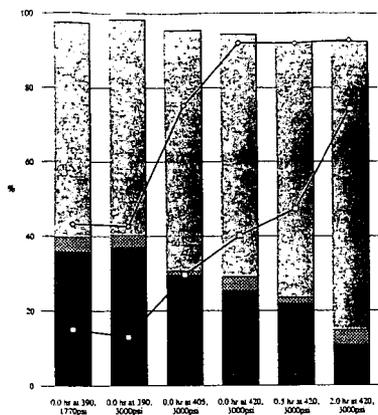


Figure 1. Coal (40 to 90%) and asphaltene (15 to 75%) conversion are portrayed by the lines. The yields of solids, asphaltenes, resins, oils, and gases are displayed from bottom to top in black, gray and white in the bar graph as a function of reaction conditions for the coprocessing reaction of Lloydminster resid and Illinois No. 6 coal.

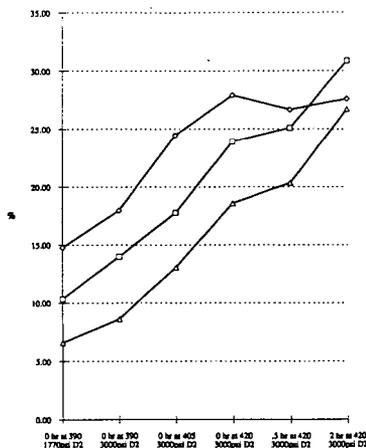


Figure 2. Aromatic % deuterium content, $D/[H + D]$, in the oil (triangle), resin (square), and asphaltene (diamond) fractions as a function of reaction conditions for the coprocessing reaction of Lloydminster resid and Illinois No. 6 coal. Related information is available for alpha, beta, and gamma aliphatic positions.⁵

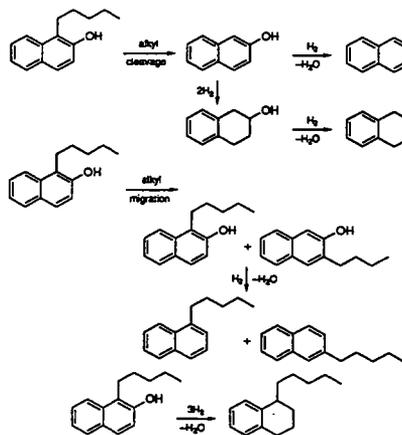


Figure 3. Reaction pathways for 1-pentyl-2-naphthol under the conditions of the catalyzed coprocessing reaction.⁴

DEPOLYMERIZATION-LIQUEFACTION OF PLASTICS AND RUBBERS. 1. POLYETHYLENE, POLYPROPYLENE AND POLYBUTADIENE.

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ABSTRACT

Processing conditions were developed for high-yield depolymerization-liquefaction of isotactic polypropylene (M.W., ~250,000) into a light, gasoline-like product. At 380-420 °C, an initial H₂ pressure of 1200 psig, with 1 wt% of finely dispersed Fe₂O₃/SO₄²⁻ or ZrO₂/SO₄²⁻ as solid superacid catalysts, the polypropylene is converted (yields, 72-83 wt%) into a liquid product consisting predominantly of C₅-C₁₂ branched paraffins. The change in product composition as a function of reaction temperature, time, and catalyst concentration, was examined and optimal conditions for production of gasoline-range branched paraffins determined. Depolymerization-liquefaction of polyethylene with the same catalysts required higher processing temperature (420-450 °C) and longer reaction time. Liquid yields in the range of 78-85 wt% were obtained and the product consisted of a mixture of C₅-C₃₀ (mostly C₅-C₁₂) normal paraffins, accompanied by some branched isomers. Polybutadiene (98 wt% *cis*) was depolymerized-liquefied at 400 °C and 1200 psig initial H₂ pressure in ~85 wt% liquid yield. The product consisted of a mixture of paraffins and cyclic compounds, including alkylcyclohexanes, alkylcyclopentanes, and alkylbenzenes with C₁-C₃ alkyl groups.

Keywords: depolymerization, liquefaction, plastics

INTRODUCTION

The effective disposal of waste industrial polymers is now recognized to be a major environmental problem in North America. Plastics and rubbers are troublesome components for landfilling, inasmuch as they are not presently biodegradable. Their destruction by incineration poses serious air pollution problems due to the release of airborne particles and carbon dioxide into the atmosphere. An alternative would be true recycling, i.e., conversion into monomers that can be reused. However, polyethylene and polypropylene do not depolymerize thermally to ethylene or propylene with sufficient selectivity. On the other hand, waste plastics and rubbers can be regarded as a potentially cheap and abundant source for fuels. Thermodegradation of polyolefins has been investigated extensively since World War II¹⁻⁵, but relatively few studies on the catalytic conversion of the polymers have been carried out, especially for production of liquid fuels. Recently there have been reports on the pyrolysis of polyolefins to aromatic hydrocarbons with activated carbon-supported metal catalysts^{6,7}; cracking of polystyrene and polyethylene on silica-alumna⁸; and reforming of heavy oil from waste plastics using zeolite catalysts⁹. Most of these catalytic studies were conducted under nitrogen at ambient or low pressure. The present paper is concerned with an investigation of the catalytic depolymerization-liquefaction behavior of three representative commercial polymers, i.e., polypropylene, polyethylene and polybutadiene using superacid catalysts¹⁰⁻¹⁶ under high H₂ pressure. The objective was to determine suitable conditions for conversion of such polymers into light liquid fuels, as well as to obtain data needed for predictive modeling of waste polymers coprocessing with coal.

EXPERIMENTAL

Materials. High density polyethylene (d, 0.959 g/cm³; M.W., 125,000) and isotactic polypropylene (d, 0.900 g/cm³; M.W., 250,000) were obtained from Aldrich Chemical Company; and polybutadiene (98% *cis*; d, 0.910 g/cm³; M.W., 197,000) from Scientific Polymers Products, Inc.

Catalysts. Three types of solid superacid catalysts, i.e., Fe₂O₃/SO₄²⁻, ZrO₂/SO₄²⁻ and Al₂O₃/SO₄²⁻ were synthesized. The preparation of the first two was the same as recently described in detail elsewhere¹⁶. Al₂O₃/SO₄²⁻ was prepared by the following procedure: 12.4 g of Al₂(SO₄)₃·(14-18)H₂O was dissolved in 44 ml of distilled water and subjected to hydrolysis at room temperature by slowly adding 28-30% NH₄OH with vigorous mixing, until pH = 8.5 was reached. The precipitate was filtered, washed with distilled water, and then dried at 110 °C for 2 h. The dry solid was pulverized and calcined at 550 °C for 2 h. The resultant Al₂O₃, 2.0 g, was treated with 50 ml of an aqueous solution with concentrations of 1.5M (NH₄)₂SO₄ and 1.0 M H₂SO₄ for 1 h with continuous stirring, then filtered, washed with ~100 ml of water, dried at 110 °C for 2 h, and calcined at 600 °C for 3 h.

Experimental Procedure. A mixture of the polymer, 10.0 g, and catalyst, 0.1 or 0.2 g (without any solvent), was introduced in a 50 ml Microclave reactor (Autoclave Engineers). The latter was closed, purged with nitrogen, and then pressurized with hydrogen to a selected initial pressure. The reactor was heated to the desired temperature in 12-15 min, and stirring (500 rpm) was started after reaching the melting or softening point of the polymer (130-189°C). Initial H₂ pressures from ambient to 2000 psig resulted in reaction pressures between 350-3600 psig in the reaction temperature range of 380-465 °C.

Analytical Methods. At the end of each experiment, the reactor was cooled down and the gas product was passed through a stainless steel trap kept at liquid nitrogen temperature. After weighing, the condensed gas was analyzed by GC. It consisted mostly of C₁-C₄ components, accompanied by some C₅, C₆, and traces of C₇, C₈ compounds. In runs with partial conversion, the liquid and solid products were removed from the reactor and weighed. The liquid was separated by decantation and filtration. The solid was rinsed with a little of n-hexane, dried, and weighed. The solid was then washed with n-hexadecane (~80 °C) and n-hexane (room temperature), dried and weighed in order to determine the weight of recovered catalyst. In this way, the product was separated and the weight of gas, liquid, solid and recovered catalyst was determined. The mass balance of the runs was 90-95% (relative to the weight of the feed). Gas and liquid products were identified mainly by GC, GC/MS and FTIR, and quantitatively analyzed by gas chromatography and simulated distillation (SIMD). Columns used for gas products: 4 m x 0.3 cm o.d. stainless steel packed with Chromosorb 102; for liquid products: 4 m x 0.3 cm o.d. stainless steel packed with 10% OV-17 on Chromosorb W-HP; for SIMD: 0.5 m x 0.3 cm o.d. stainless steel, Supelco PETROCOL™ B column.

RESULTS AND DISCUSSIONS

1. Polypropylene. At 390 - 420 °C and an initial H₂ pressure of 1500 psig, with 1.0 wt% of ZrO₂/SO₄²⁻ as catalyst, and a reaction time of 2.0 hours, the polypropylene was converted in very high yield (over 90 wt%) into a low-boiling liquid product. Branched C₅-C₁₀ paraffins (and some olefins) were predominant components of the product. Results on the change in product composition as a function of reaction temperature are given in Figure 1. As seen, the gasoline range fraction (C₅-C₁₂) reached a maximum (~64.5 wt%) at 400-410 °C, then decreased slowly at higher temperature. The C₁₃₊ components decreased and the C₁-C₄ gas increased with increase in temperature. At 400 °C, about 64 wt% of gasoline range, 29 wt% of higher hydrocarbons and 7 wt% of gas are produced. The depolymerization-liquefaction of polypropylene was investigated also as a function of reaction time. The change in product composition showed the same trends as those indicated above for the temperature effect. This demonstrated the potential of a controllable stepwise depolymerization of polypropylene into light liquid hydrocarbons. The H₂ pressure effect was smaller compared with those of reaction temperature and time. Increase in H₂ pressure from 15 to 500-1500 psig suppressed gas formation, decreased the amount of C₁₃₊ products, and increased gasoline boiling range production. A comparative study of the three different types of solid superacid, i.e., Fe₂O₃/SO₄²⁻, ZrO₂/SO₄²⁻ and Al₂O₃/SO₄²⁻ (see Experimental) was also performed, keeping other processing variables constant (reaction temperature, 410 °C, time 1.0 h, initial H₂ pressure 1500 psig, catalyst amount, 1.0 wt%). For comparison, a run without catalyst was also carried out. The extent of depolymerization of the feed into gasoline range hydrocarbons was significantly higher in the catalytic runs as compared with that in the thermal (non-catalytic) run. Among the catalysts examined, the order of depolymerization activity was Al₂O₃/SO₄²⁻ > ZrO₂/SO₄²⁻ > Fe₂O₃/SO₄²⁻. Based on the change in product composition as a function of reaction temperature and reaction time, a plausible carbonium ion mechanism for depolymerization of polypropylene can be considered (see Figure 4).

2. Polyethylene. Liquid yields in the range of 76-87 wt% were found for polyethylene with ZrO₂/SO₄²⁻ as catalyst at reaction temperatures in the range of 420-450 °C. The product consisted of a mixture of C₅ -C₃₀ (mostly C₅-C₁₂) normal paraffins and smaller amounts of branched isomers. Results on the change in product composition as a function of reaction temperature are given in Figure 2. The gasoline range fraction increased to a maximum of 63 wt% at 450 °C and then decreased at 465 °C. The C₁₃₊ components decreased while C₁-C₄ gas increased with increase in reaction temperature. The change in product composition as a function of reaction time (between 0.5-3.0 h) showed trends similar to those of the temperature effect. This was in good agreement with the above results for polypropylene and again demonstrated the controllable stepwise break-down of the polymer. The effect of H₂ pressure (500-2000 psig) on the product composition was relatively weak. As the H₂ pressure was increased from 500 to 1500 psig, the gasoline boiling range fraction increased while the C₁₃₊ fraction decreased. However, for H₂ pressures higher than 1500 psig, the concentrations of gasoline range and C₁₃₊ fractions remained relatively stable.

3. Polybutadiene. Polybutadiene was smoothly depolymerized-liquefied at 400 °C and 1200 psig initial H₂ pressure, with 1 wt% of Fe₂O₃/SO₄²⁻ as catalyst. The liquid yield was about 85 wt%. Figure 3 shows the GC/MS of the gasoline boiling range product. As seen, the product consists of a mixture of paraffins and cyclic compounds, including alkylcyclohexanes, alkylcyclopentanes, and alkylbenzenes with C₁-C₃ alkyl groups (C₁-C₃ indicating either single or two alkyl substituents). The formation of cyclic hydrocarbons from polybutadiene can be explained as follows. Butadiene obtained by depolymerization of polybutadiene, can undergo fast cyclodimerization to form 4-vinylcyclohexene, which undergoes a sequence of rearrangement and aromatization (or ring hydrogenation) reactions to yield a full range of alkylsubstituted naphthenes and benzenes¹⁷.

CONCLUSIONS

It is found that representative polyolefins, e.g., polypropylene, polyethylene and polybutadiene, undergo high-yield depolymerization-liquefaction in the temperature range of 380-450 °C, under H₂ pressures of 1200-2000 psig, and in the presence of catalytic amounts of finely dispersed solid superacids, i.e., Al₂O₃/SO₄²⁻, ZrO₂/SO₄²⁻ or Fe₂O₃/SO₄²⁻. The depolymerization-liquefaction process is easily controllable for preferential formation of gasoline-range hydrocarbons. Production of the latter can be rationalized in terms of stepwise breakdown of the polymeric chains by a carbonium ion mechanism. The data obtained can be used for predictive modeling of coal coprocessing with waste polymers.

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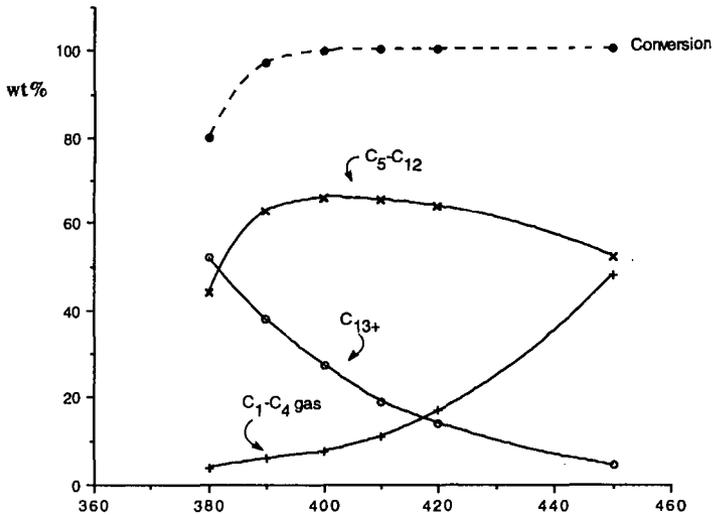


Fig. 1. Change in Product Composition from Depolymerization of Polypropylene as a Function of Reaction Temperature, °C.

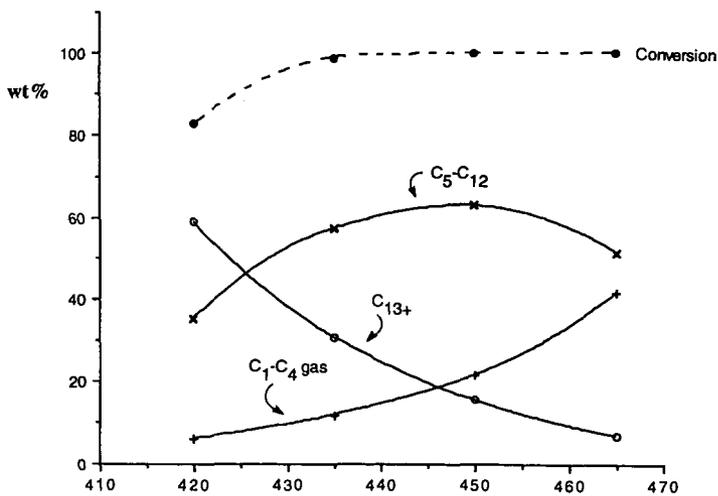


Fig. 2. Change in Product Composition from Depolymerization of Polyethylene as a Function of Reaction Temperature, °C.

CATALYTIC REACTIONS IN WASTE PLASTICS AND COAL STUDIED BY HIGH PRESSURE THERMOGRAVIMETRY WITH ON-LINE GC/MS

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Keywords: on-line TG/GC/MS, waste plastic, coal, catalysis

INTRODUCTION

Waste plastics account for roughly 40% of landfill trash, of which only about 3% is recycled. The disposal of waste plastics is an important environmental problem. Clearly, the dominant components of waste plastics; mainly polyethylene, polystyrene, polypropylene are rich in carbon and hydrogen - the building blocks of petroleum, so that the possibility of converting waste plastic into liquid fuels is a productive alternative for plastic recycling. On the other hand, coal is hydrogen deficient, so co-processing of coal with waste plastics could be another way to recycle waste plastics into useful products.

Pyrolysis is a simple method to break the carbon-carbon bonds into relatively small molecular compounds by heating the polymers, but the major limitation of straight pyrolysis has been the poor selectivity for co-processing of coal and waste plastics. The use of various catalysts is a promising way of improving selectivity and yield. Catalytic liquefaction of coal has been widely studied^{1,2,3}, but little is known about catalytic conversion of waste plastics and co-processing of coal with waste plastics^{4,5}.

Development of efficient processes for converting solid waste materials and coal to useful products is often hindered by the lack of detailed fundamental data on real time thermal and catalytic reactions. A recently developed high pressure thermogravimetry (TG) system with on-line gas chromatography/mass spectrometry (GC/MS) modules provides detailed information on the pathways and mechanisms of the reactions which should benefit the screening of catalysts, help optimize reaction conditions, promote understanding of the function of the catalysts and provide a rapid and cost effective intermediate product analysis.

EXPERIMENTAL

Experiments with commingled waste plastic in the presence of various catalysts and co-processing runs of coal and commingled waste plastic were performed in a high pressure TG/GC/MS system at 900 psi hydrogen or helium pressure. Details of the high pressure TG/GC/MS system have been described previously⁶. The commingled waste plastic analyzed was obtained by washing the colored plastic bottles and containers to remove contaminants and labels before sizing and shaving. Final size reduction was done by grinding in a k-TEC kitchen mill. The coal was Blind Canyon DECS-6 high volatile bituminous coal (-100 mesh) from the Penn State Coal Sample Bank. The characteristics of the commingled waste plastic and coal have been listed elsewhere⁷. The preparation of the superacid catalysts $\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$, $\text{ZrO}_2/\text{SO}_4^{2-}$ was described by Shabtai et al.⁷. The superacid catalysts $\text{Al}_2\text{O}_3/\text{SO}_4^{2-}$, $\text{Al}_2\text{O}_3/\text{SO}_4^{2-}$ (promoted by 0.5% Pt) were also prepared by Shabtai and co-workers, as will be described in this meeting⁸. The 25% SiO_2 -75% Al_2O_3 catalyst was supplied by Gulf Research and Development Company and sized to 100-140 mesh. The catalyst Ni-Mo/ Al_2O_3 , provided by Engelhard Corporation was mixed with $\text{SiO}_2\text{Al}_2\text{O}_3$ in a ratio of 4:1 (20-40 mesh size) and then sulfided.

RESULTS AND DISCUSSION

A characteristic example of the type of analytical results obtainable with the system is shown in Figure 1. Hydrolypyrolysis of Blind Canyon DECS-6 coal was conducted at 900 psig H_2 pressure while heating at 10 C/min up to 700 C. During this process three distinct stages can be distinguished from both the TG weight loss curve (Figure 1a) and the total ion chromatogram (Figure 1b), namely bitumen desorption, hydrolypyrolysis and hydrogasification. Product distributions are shown in Figure 2 by expanding the chromatograms to a single sampling interval. The first process stage (Figure 2a) occurs over the temperature range of 250-350 C with products consisting mainly of substituted two-ring aromatics and long chain alkanes from bitumen desorption due to the evaporation of unattached molecules^{9,10,11}. The second stage spans the temperature range of 370-550 C. The products, primarily thought to be due to hydrolypyrolysis of the coal, include short chain aliphatics, substituted phenols and also long chain n-alkenes and -alkanes (Figure 2b)^{11,12}. The compounds produced in the final hydrogasification stage (at temperatures above 550 C) are mainly non-substituted aromatics including benzene, naphthalene, anthracene/phenanthrene and four-ring aromatics and hydroaromatics (Figure 2c). By selecting a particular ion chromatogram over the entire reaction temperature range, it can be illustrated how the corresponding product is evolved during the reaction. Figure 3 illustrates evolution profiles of propyl phenol, anthracene/phenanthrene, and C5-substituted naphthalene. By looking at the

selective ion chromatograms, it is shown that phenol evolves during the second stage of the process, whereas nonsubstituted aromatics evolve mainly during the third stage, and substituted aromatics evolve during both first and second stages.

Commingled Waste Plastics

Commingled waste plastic (about 35 mg) was subjected to three different temperature programs using a constant heating rate of 20 C/min up to 410 C, 420 C or 430 C separately, isothermal hold for 30 mins and then heating up to 700 C at 20 C/min to observe how decomposition reactions occur at a hydrogen pressure of 900 psig.

Figure 4 illustrates how temperature affects the decomposition reactions as measured by the weight loss as a function of temperature history and reaction time. At the end of the 30 min isothermal period at 410 C, weight loss of the waste plastic is approx. 17%, whereas at 430 C, approx. 84% of the weight is lost. These results illustrate that thermal decomposition reactions of waste plastic (in hydrogen) are strongly dependent on relatively small changes in reaction temperature. As indicated in our previous paper¹³, isothermal runs at relatively low temperatures are found to be effective in bringing out differences between catalytic and thermal processes. By contrast at a linear heating rate of 10 K/min, thermal reactions overwhelm the catalytic effect. An isothermal plateau at 420 C, producing approx. 54% weight loss within 30 min without catalyst, was selected to investigate catalytic effects by comparing the relative decomposition reaction rates, residual char amounts and time-resolved product evolution profiles of thermal and catalytic runs, respectively.

Experiments on the decomposition of commingled waste plastic in two different reactor gas atmospheres (helium and hydrogen) and with several different catalysts were performed at 900 psig using the temperature program mentioned above. Catalysts studied include solid superacids such as $\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$, $\text{Al}_2\text{O}_3/\text{SO}_4^{2-}$, $\text{Al}_2\text{O}_3/\text{SO}_4^{2-}$ promoted by 0.5% Pt, and $\text{ZrO}_2/\text{SO}_4^{2-}$ added at 10% to the feed, as well as conventional cracking catalyst, $\text{SiO}_2/\text{Al}_2\text{O}_3$, hydrocracking catalyst, $\text{NiMo}/\text{Al}_2\text{O}_3$ mixed with $\text{SiO}_2/\text{Al}_2\text{O}_3$ in a 4:1 ratio (added at 50%) and HZSM-5 zeolite (added at 10%). Different shapes of the TG profiles (weight loss vs. reaction time) in Figure 5 indicate catalytic effects on reaction rates and residue formation during waste plastic decomposition reactions.

At 420 C, all catalysts tested increase decomposition reaction rates to a varying degree, as indicated by the slopes of the curves in Figure 5. At these high catalyst addition levels, the $\text{SiO}_2/\text{Al}_2\text{O}_3$ and HZSM-5 catalysts show the highest conversion rates. For the $\text{SiO}_2/\text{Al}_2\text{O}_3$ catalyst, measurable decomposition reactions occur at temperatures lower than 420 C. For the solid superacid catalysts studied, the approximate order of cracking activity is $\text{ZrO}_2/\text{SO}_4^{2-} > \text{Al}_2\text{O}_3/\text{SO}_4^{2-} > \text{Pt}/\text{Al}_2\text{O}_3/\text{SO}_4^{2-} > \text{Fe}_2\text{O}_3/\text{SO}_4^{2-} > \text{no catalyst}$. The weight loss after 30 min at 420°C is presented in Table 1 to illustrate how atmosphere and catalysts increase the yields of volatile products. In a hydrogen atmosphere the conversion yield is slightly increased compared to a helium atmosphere. Although $\text{NiMo}/\text{Al}_2\text{O}_3$ mixed with $\text{SiO}_2/\text{Al}_2\text{O}_3$ catalyst is not as effective as $\text{SiO}_2/\text{Al}_2\text{O}_3$ in cracking ability, it gives less residue formation due to the hydrogenation activity of the sulfided metal component. For catalysts such as $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{NiMo}/\text{Al}_2\text{O}_3$ mixed with $\text{SiO}_2/\text{Al}_2\text{O}_3$ and HZSM-5, the decomposition reactions are completed at 420°C within 30 minutes. Therefore, no further reactions occur upon the increase of temperature.

The catalysts tested clearly improve the conversion rate of the commingled waste plastic, thereby lowering reaction temperature and/or shortening reaction time.

By examining the evolution profiles of volatile products by means of GC/MS changes in volatile product distributions as a function of reaction gas and catalysts can be measured. Several total ion chromatograms representing a single selected sampling period at different conditions are presented in Figure 6. The results show that thermal cracking, either in helium or hydrogen (only shown in hydrogen, Figure 6a) produced more evenly distributed long straight chain aliphatics including alkenes and alkanes (alkenes and alkanes are not separated by the 2 meter short GC column). With the catalysts, such as $\text{Al}_2\text{O}_3/\text{SO}_4^{2-}$, $\text{Pt}/\text{Al}_2\text{O}_3/\text{SO}_4^{2-}$, $\text{ZrO}_2/\text{SO}_4^{2-}$, $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{NiMo}/\text{Al}_2\text{O}_3$ mixed with $\text{SiO}_2/\text{Al}_2\text{O}_3$, more isomers of aliphatic products are produced (only shown with $\text{ZrO}_2/\text{SO}_4^{2-}$; Figure 6c). The stronger the cracking catalysts, the lighter the aliphatics (only shown for $\text{SiO}_2/\text{Al}_2\text{O}_3$; Figure 6b). Strong cracking catalysts such as $\text{SiO}_2/\text{Al}_2\text{O}_3$ and HZSM-5 (zeolite) not only produce light aliphatics but also give high yields of substituted aromatics due to cyclization reactions promoted by acid catalysts as indicated in Figure 6d.

Co-Processing of Coal with Commingled Waste Plastic

Co-processing runs of Blind Canyon DECS-6 coal with commingled waste plastic (in a 1:1 ratio) involved adding several selected catalysts. Samples were subjected to the same temperature history at a hydrogen pressure of 900 psig. Figure 7 illustrates the TG weight loss curves of the coal, the waste plastic as well as the coal plastic mixture under non-catalytic conditions. The dotted line is the predicted weight loss curve of the mixture which is the linear sum of the individual component curves. The mixture of coal with waste plastic shows a slightly

lower reaction rate than the predicted value at 420 C. Subsequently, catalysts found effective in promoting the decomposition reactions of waste plastic including ZrO_2/SO_4^{2-} , SiO_2/Al_2O_3 , $NiMo/Al_2O_3$ mixed with SiO_2/Al_2O_3 and HZSM-5 Zeolite were applied to the mixture of coal with plastic. The TG weight loss curves presented in Figure 8 indicate that catalytic co-processing of coal with plastic is more difficult than catalytic processing of commingled waste plastic alone. The solid superacid catalyst ZrO_2/SO_4^{2-} and the cracking catalyst SiO_2/Al_2O_3 (added at the 10% level) have little influence upon the decomposition reactions of the mixture. A possible explanation could be that the presence of coal-derived nitrogen compounds poisons the active sites of the acid catalysts. By adding relatively large amounts (50%) of the SiO_2/Al_2O_3 catalyst, the decomposition rate is increased, but to a lesser degree than for waste plastic alone. The HZSM-5 catalyst shows a very promising result for co-processing of coal and waste plastic by increasing both reaction rate and volatile product yield. This confirms earlier results by Huffman and co-workers⁴. Apparently, the active sites of the HZSM-5 catalyst are much less readily poisoned by the coal compared to other catalysts. On the other hand, a mixture of $NiMo/Al_2O_3$ with SiO_2/Al_2O_3 reveals better activity than the SiO_2/Al_2O_3 catalyst, whereas the opposite is true for plastic alone.

CONCLUSIONS

High pressure TG/GC/MS is demonstrated to be a viable and useful technique for screening candidate catalysts for processing waste plastic and for co-processing coal with waste plastic.

At the high catalyst levels used the results reveal catalytic waste plastic cracking activity in the following order: $SiO_2/Al_2O_3 > HZSM-5 > NiMo/Al_2O_3$ mixed with $SiO_2/Al_2O_3 >$ solid superacids. Of the solid superacids studied, the ZrO_2/SO_4^{2-} catalyst possesses the highest cracking activity and the approximate order of cracking activity is $ZrO_2/SO_4^{2-} > Al_2O_3/SO_4^{2-} > Pt/Al_2O_3/SO_4^{2-} > Fe_2O_3/SO_4^{2-} >$ no catalysts.

The HZSM-5 zeolite catalyst shows most promising results for co-processing of coal with commingled waste plastic by increasing greatly the rate of the decomposition reactions albeit at the cost of lower MW products (high gas yields) and higher aromatic yields. Hydrocracking catalysts such as $NiMo/Al_2O_3$ mixed with SiO_2/Al_2O_3 show potential promise for co-processing of coal with commingled waste plastic due to their hydrogenation and cracking ability.

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Table 1
Weight Loss Data from High Pressure TG

Items	Weight Loss, %
He	55%
H ₂	59%
Fe ₂ O ₃ /SO ₄ ²⁻ , 10%	75%
Pt/Al ₂ O ₃ /SO ₄ ²⁻ , 10%	79%
Al ₂ O ₃ /SO ₄ ²⁻ , 10%	83%
ZrO ₂ /SO ₄ ²⁻ , 10%	86%
NiMo/Al ₂ O ₃ , mixed with SiO ₂ /Al ₂ O ₃ , 50%	97%
SiO ₂ , Al ₂ O ₃ , 50%	94%
HZSM-5, 10%	97%

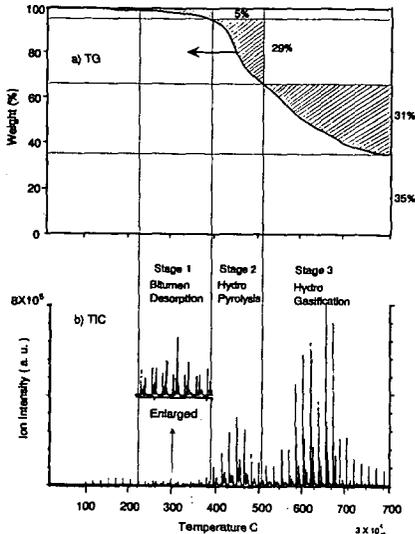
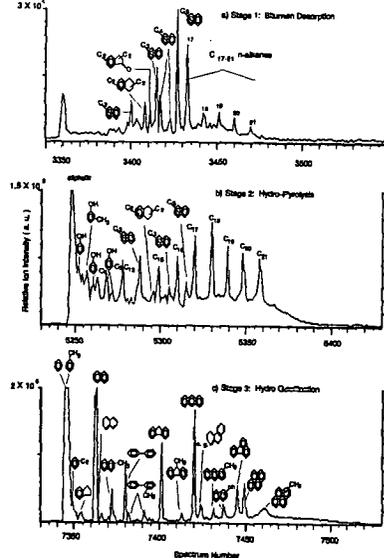


Figure 1. Hydropyrolysis of Blind Canyon DECS-6 coal. a) TG weight loss curve, b) total ion chromatogram.

Figure 2. Product distribution obtained during hydropyrolysis of Blind Canyon DECS-6 coal. a) first stage-bitumen desorption; b) second stage - hydropyrolysis; and c) third stage - hydrogasification.



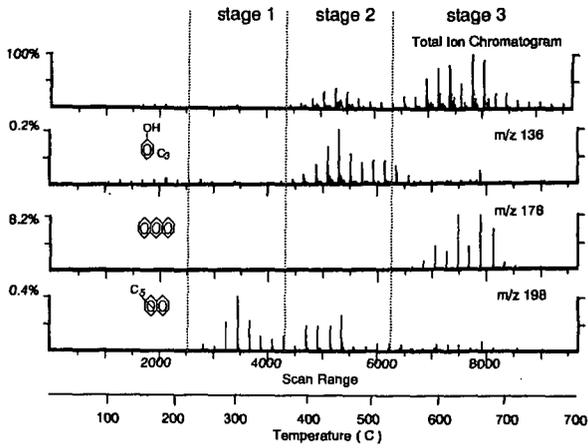


Figure 3. Evolution profiles of several products during hydrolysis of Blind Canyon DECS-6 coal by selective ion chromatograms.

Figure 4. TG curves of the commingled waste plastic at 900 psig (H_2).

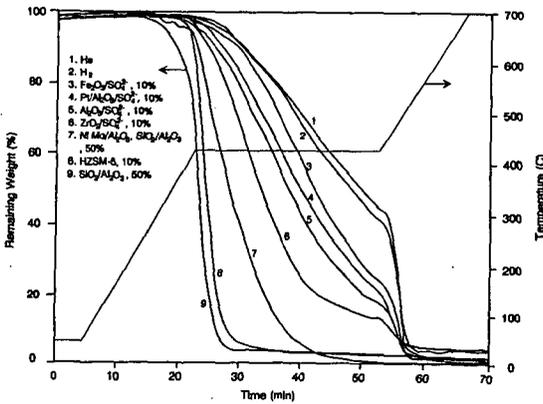
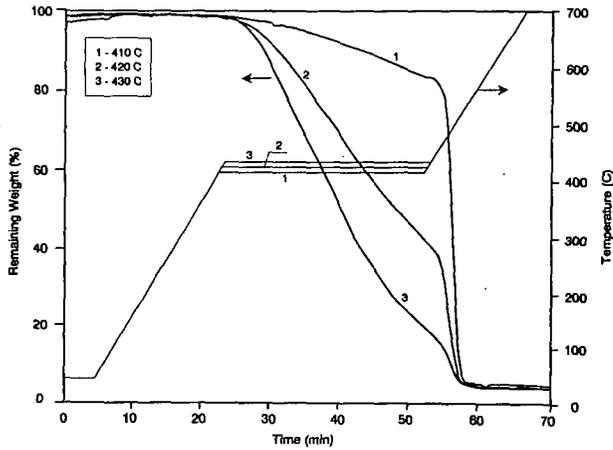


Figure 5. Effects of reactor gas atmospheres and catalysts on decomposition reactions of the commingled waste plastic at 900 psig.

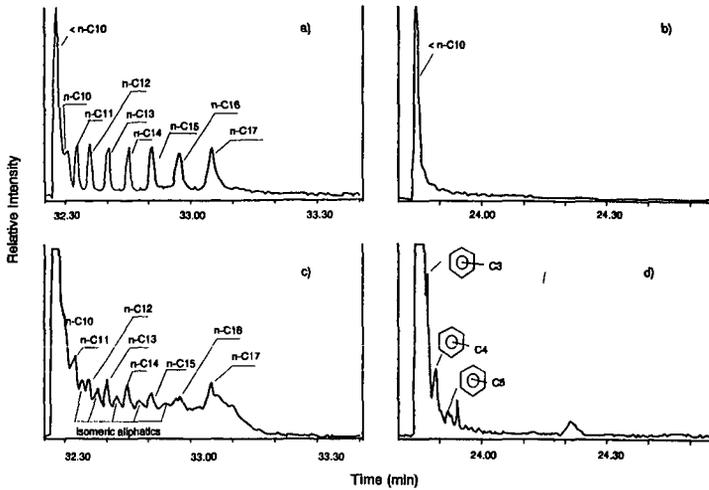


Figure 6. Total ion chromatograms of one sampling period of plastic decomposition products. a) in hydrogen; b) $\text{SiO}_2/\text{Al}_2\text{O}_3$; c) $\text{ZrO}_2/\text{SO}_4^{2-}$; and d) HZSM-5.

Figure 7. TG curves of co-processing of coal with plastic at 900 psig (H_2).

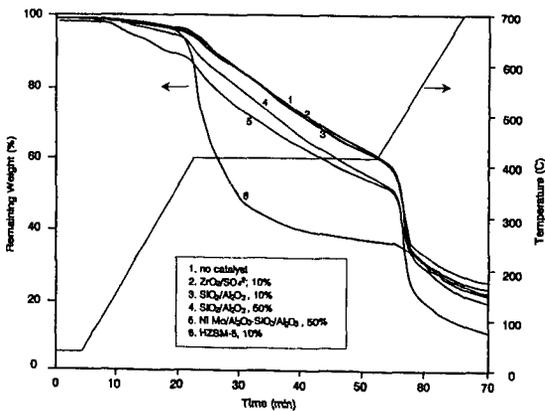
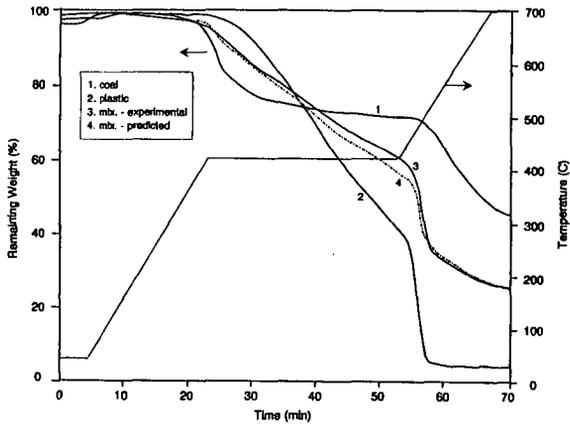


Figure 8. Effects of catalysts on co-processing of coal with plastic at 900 psig (H_2).

EFFECT OF MODIFYING HOST OIL ON COPROCESSING

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Keywords: coprocessing, pretreatment of host oil.

INTRODUCTION

The world's supply of petroleum crudes is becoming heavier in nature so that the amount of vacuum bottoms has been steadily increasing. Coprocessing of coal with these resids (1000°F+) is an attractive way of obtaining useful distillates from these readily available cheap materials. Petroleum resids and coals differ in several ways; coal is more aromatic with a lower H/C ratio, contains more inorganic material than found in heavy resids, is richer in oxygen, and has smaller clusters of organic material. Heavy oils are more aliphatic and less aromatic, have very little oxygen, somewhat smaller amounts of nitrogen, significantly more sulfur, and contain relatively small amounts of vanadium, nickel and iron, some of which are trapped in porphyrin structures.

The objective of this work is to pretreat the host oil in ways that would improve its performance in coprocessing with coal. The following are examples of some ways in which heavy oil could be made into a better host oil: converting aromatic structures to hydroaromatics capable of donating hydrogen to coal, cracking the heavy oil to lower molecular weight material that would be a better solvent, and removing metals, sulfur, and nitrogen.

Other investigators have found that coprocessing performance can be improved by pretreating the host oil. Takeshita and Mochida¹ showed positive results by using a petroleum pitch that had been hydrotreated at high pressure over a Ni/Mo/Al₂O₃ catalyst. A similar approach was taken by Sato and coworkers² who obtained high coal conversion and high distillable oil yields after a tar sand bitumen they were using was hydrotreated with a Ni-Mo catalyst. Curtis and coworkers^{3,4,5} have shown the importance of hydrogen donor compounds in host oil for achieving high coal conversion. Hydroaromatic compounds (hydrogen on a naphthenic carbon at the alpha or beta position from the aromatic ring) are one class of hydrogen donor compounds that are important in coal liquefaction.

EXPERIMENTAL

The work reported here used a Venezuelan oil obtained from the Corpus Christi refinery of Citgo. Its properties are listed in Table I as are those of another heavy oil for comparison; the latter is a vacuum resid from a wide mixture of crudes, obtained from AMOCO. Two coals, Illinois No.6 and Wyodak subbituminous, were coprocessed with host oils; both coals were Argonne premium coal samples. Properties of the coal samples have been previously published⁶.

Four pretreatments of the resid were conducted in a well-stirred 300 ml stainless-steel autoclave batch reactor. Table II lists conditions and yields for the runs. One pretreatment, subsequently referred to as Pretreatment-A, involved cracking the resid at 440°C under H₂, 1000 psig (cold), for 2 hrs; molybdenum naphthenate (MN), supplied by ICN Biomedical Inc, and elemental sulfur, were added at a level of 1000 ppm Mo to suppress coke production to below 3 wt% (in runs made without MN at these conditions, coke production reached levels above 11%). The other three pretreatments involved hydrogenating the resid at milder conditions where cracking is suppressed. In Pretreatment-B the resid was reacted at 375°C under H₂, 1000 psig (cold), for 5 hrs using 1000 ppm of MN. In Pretreatment-C the resid was treated using a finely dispersed Mo/Fe₂O₃/SO₄ catalyst^{7,8} (2 wt%) at the same conditions used in Pretreatment-B. In Pretreatment-D the resid was dissolved in toluene and hydrogenated using a homogeneous catalyst, dicobalt octacarbonyl (Co₂(CO)₈), at 130°C for 2 hrs under 2600 psig of 1:1 synthesis gas. Friedman and coworkers⁹ found this system to be effective for selectively hydrogenating polynuclear aromatic compounds to their hydroaromatic derivatives; e.g., anthracene to 9,10-dihydroanthracene and pyrene to 4,5-dihdropyrene.

Pretreated products were removed from the 300 ml autoclave and separated into three fractions. The workup procedure ensured maximum recovery of products while minimizing losses of lighter material. Light oils (bp < 195°C) produced during pretreatments at 440°C were removed by distillation at atmospheric pressure. Pretreatments made at 375°C and below, generally produced no light oils. In these runs, distillation was not necessary. Products not removed by distillation were recovered by washing the contents of the reactor with THF. After filtration the THF was removed by distillation. Because the boiling point of THF is well below that of the pretreated heavy oils, good separation was possible. For runs made with Co₂(CO)₈, the THF-

washed products were refluxed for three hours to destroy the carbonyl. To further facilitate removal of the cobalt, silica-alumina powder was added to the liquid mixture prior to filtering. All THF-insoluble solids were vacuum dried overnight prior to weighing.

Coprocessing experiments were conducted in a horizontal, stainless-steel microreactor at 425°C for 30 min under 1000 psig (cold) H₂. Three weight ratios of host oil to coal were used; 9:1, 2:1 and 1:1. Most coprocessing runs were made with no added catalyst, but a few were made with either MN (2000 ppm Mo) or 2 wt% Mo/Fe₂O₃/SO₄, plus elemental sulfur. Products from the microreactor were recovered and separated into three fractions; pentane-soluble oils, asphaltenes and THF-insoluble solids. Pentane was removed from the filtered oil by rotovapor under atmospheric pressure to prevent losses of light products. Under these mild separation conditions a small amount of pentane remained with the oil. This was later measured by simulated distillation.

Gases were analyzed using an HP 5880A GC. Pentane-soluble oils (free of ash and asphaltenes) were analyzed using an HP 5890 series II GC/HP 5970 mass selective detector. A boiling curve for pentane-soluble oil samples was determined by simulated distillation¹⁰ using an HP 5890 series II GC. Original and pretreated oil samples were analyzed by ¹H NMR spectroscopy using a Bruker 300 MSL spectrometer; samples were prepared in deuterated chloroform with tetramethylsilane for internal reference.

Catalytic dehydrogenation was used to measure the "available" hydrogen of resids and pretreated oils. Available hydrogen was defined as the amount of hydrogen gas evolved when an oil sample dissolved in phenanthridine was catalytically dehydrogenated for 285 min over a reduced Pd/CaCO₃ catalyst at atmospheric pressure.

Metal contents (Ni, Fe and V) of selected samples were determined by The Pittsburgh Applied Research Corp. using the ICP technique. Elemental analyses were conducted by Galbraith Laboratories Inc. and CONSOL Inc.

RESULTS AND DISCUSSION

Table III lists properties of the pretreated Citgo host oils. The Pretreatment-A oil was lighter, based on wt% of distillate, than the untreated resid as well as the other pretreated host oils. This is a result of the higher pretreatment temperature used. The available hydrogen content of the pretreated oils was higher than that of the untreated resid, which had a value of 9.8 H atoms/100 C atoms. This infers that the pretreated oils contain more donatable hydrogen. The increase in available hydrogen for the oils from Pretreatments B, C and D was slightly below the amount of hydrogen consumed during these runs, indicating significant hydrogen utilization. All pretreated host oils, with exception of the Pretreatment-D oil, had higher H/C atomic ratios than that of the untreated resid; although the increases were not large. The pretreated host oils had lower sulfur concentrations than the untreated resid; nitrogen concentrations remained unchanged.

Figure 1 shows the effect of coal slurry concentration on Illinois No.6 coal conversion to THF-solubles in thermal (no added catalyst) coprocessing runs made with the different host oils. Coal conversion was calculated from the amount of unconverted (THF-insoluble) material recovered from the products after correcting for ash, added catalyst and petroleum-derived coke (this was less than 3 wt% based on repeat runs made without coal). The Figure shows that coal conversions in the oils from Pretreatments B-D were higher than levels achieved in the untreated Citgo resid or the oil from Pretreatment-A. Coal conversions in the Citgo resid and in the oil from Pretreatment-A decreased as the concentration of coal in the feed was increased. This trend has been observed by other investigators^{11,12} demonstrating the limited ability of these host oils to bring about coal dissolution. On the other hand, coal conversions in the oils from Pretreatments B-D appeared to be independent of coal slurry concentration up to 50 wt%. Illinois No.6 coal conversion in these pretreated host oils were slightly higher than conversions obtained when the coal was catalytically coprocessed in the Citgo resid using either MN (2000 ppm) or Mo/Fe₂O₃/SO₄ (2 wt%). These results clearly demonstrate that the host oils from Pretreatments B, C and D are good coprocessing solvents. When these host oils were coprocessed with coal in the absence of hydrogen gas, conversions were significantly less than levels achieved under hydrogen gas.

Figures 2 and 3 show how distillable product yields varied with coal slurry concentrations when Illinois No.6 coal was coprocessed with the untreated resid and the oil from Pretreatment-C, respectively. Distillable product yields are defined as the wt% of ash-free feed converted to gases and pentane-soluble oil that had a simulated distillation boiling point below 565°C. The lower line in the Figures represents the contribution from the host oil assuming no interaction

between coal and host oil. This line was drawn by assuming the distillate yield from the host oil obtained at zero coal concentration did not change. The shaded area above the lower line represents the contribution of distillable product from coal. This value was based on the yield from a thermal coal liquefaction run made with Illinois No.6 and the solvent diphenylmethane. During the run, 84.5% of Illinois No.6 coal was converted to THF-soluble products, of which an estimated 50% was distillable. Rahimi and coworkers¹² also concluded that up to 40-50 wt% of converted coal ends up in the distillate (bp < 525°C).

At coal slurry concentrations below 50 wt%, distillable product yields were generally above the level calculated assuming no interaction between coal and host oil, with exception of runs made with the oil from Pretreatment-A (not shown), which yielded distillate below this level. These results show a possible synergism between coal and host oil, a behavior that has been reported^{11,12,13} by others.

CONCLUSIONS

We have found that mild pretreatment of a Citgo resid (1000°F) using either Mo naphthenate or Mo/Fe₂O₃/SO₄, as well as a pretreatment using the homogenous catalyst Co₂(CO)₈ under synthesis gas can increase the available (donatable) hydrogen content of the resid. When these pretreated oils were thermally (no added catalyst) coprocessed with an Illinois No.6 coal, about 90 wt% of the coal (maf) was converted to soluble products. This high coal conversion was realized even at a high coal loading of 50 wt%. Pretreatments at 440°C, that crack the resid without adding much available hydrogen, showed little promise for improving coal conversion above levels achieved with untreated resid. The products from coprocessing coal and oil were equally split between high boiling material, mostly asphaltenes, and distillate. Distillate yields appeared to be affected by the concentration of coal in the feed, with maximum yields at coal loadings below 50 wt%.

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Table I. Properties of Petroleum Resids (1000°F+)

	Citgo Resid	Amoco Resid
C, wt%	85.4	84.3
H, wt%	10.1	10.2
S, wt%	3.4	4.6
N, wt%	0.8	0.5
O, wt%	0.3	0.4
Atomic H/C	1.42	1.45
V, ppm	555	251
Ni, ppm	110	57
Fe, ppm	12	13
Pentane Insolubles, wt%	27.3	20.1
Aromatic Carbons ^a , fraction	0.33	0.32

a: Based on ¹H NMR by Brown and Ladner's method¹⁴

Table II. Reaction Conditions and Product Yields for Pretreatments of Citgo Resid

	Oil-A	Oil-B	Oil-C	Oil-D
Catalyst, concentration	MN, 1000 ppm	MN, 1000 ppm	Mo/Fe ₂ O ₃ /SO ₄ , 2 wt%	Co ₂ (CO) ₈ , 6.2 wt%
Atmosphere	H ₂	H ₂	H ₂	CO/H ₂ (1:1)
Temperature, °C	440	375	375	135
Pressure (cold), psig	1,000	1,000	1,000	2,000
Time, hrs	2	5	5	2
Gas yield, wt%	10-25	1-12	3	0
Oil yield, wt%	72-87	86-97	95	100
Coke yield, wt%	3	2	2	0

Table III. Properties of Citgo Pretreated Host Oils

	Oil-A	Oil-B	Oil-C	Oil-D
b.p. < 565°C ^a , wt%	62.6	29.7	33.3	17.9
b.p. > 565°C, wt%	37.4	70.3	66.7	82.1
C, wt%	85.1	85.9	85.6	83.7
H, wt%	10.6	10.4	10.8	9.7
S, wt%	2.2	2.7	2.9	2.8
N, wt%	0.9	0.9	0.8	0.8
O, wt%	1.2	0.1	0.0	3.0
Atomic H/C	1.49	1.45	1.51	1.39
V, ppm	392	----	477	----
Available ^b Hydrogen per 100 C atoms	12.4	16.8	14.0	17.5

a: b.p. < 565°C consists of pentane-soluble oil having a simulated distillation b.p. < 565°C (1050°F). b.p. > 565°C consists of pentane-insoluble asphaltenes, and pentane-soluble oil having simulated distillation b.p. > 565°C.

b: Value based on catalytic dehydrogenation, experiment described in text.

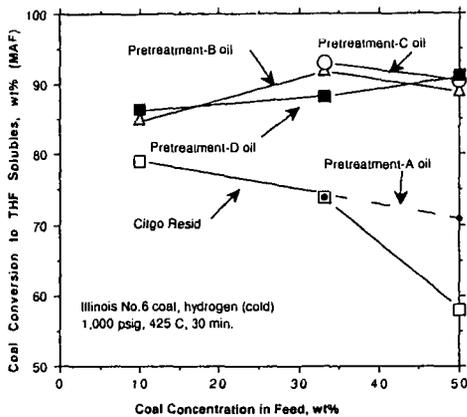


Figure 1. Effect of coal concentration on Illinois No.6 coal conversion to THF solubles in thermal coprocessing with Citgo resid and pretreated host oils (Pretreatment-A: 1000 ppm MN, 440°C, 1000 psig (cold) H₂, 2 hr reaction time; Pretreatment-B: 1000 ppm MN, 375°C, 1000 psig (cold) H₂, 5 hr reaction time; Pretreatment-C: 2% Mo/Fe₂O₃/SO₄, 375°C, 1000 psig (cold) H₂, 5 hr reaction time; Pretreatment-D: 6.2% Co₂(CO)₈, 135°C, 2650 psig CO/H₂ (1:1), 2 hr reaction time).

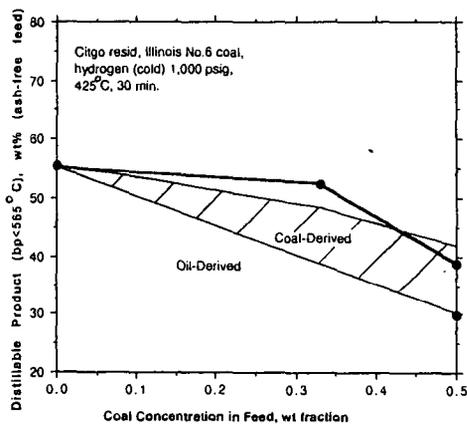


Figure 2. Effect of coal concentration on distillable product yields in coprocessing Illinois No.6 coal with Citgo resid.

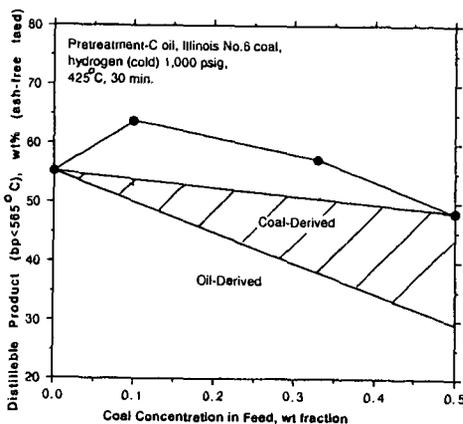


Figure 3. Effect of coal concentration on distillable product yields in coprocessing Illinois No.6 coal with pretreatment-C (2% Mo/Fe₂O₃/SO₄, 375°C, 1000 psig (cold) H₂, 5 hr reaction time) oil.

A TECHNO-ECONOMIC ASSESSMENT OF INTEGRATING A WASTE/COAL COPROCESSING FACILITY WITH AN EXISTING REFINERY

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Keywords: waste/coal coprocessing, plastics, rubber, liquefaction.

INTRODUCTION

About 97 million tons of waste plastics, paper, oils, and tires are generated annually in the United States. The vast majority of this waste is paper, accounting for more than 73 million tons, and the second most abundant waste is plastic, accounting for more than 16 million tons. The number of waste passenger tire equivalents generated in the United States is about 300 million; considerably more than the population. On a rubber basis, this is approximately equal to 1.6 million tons: For waste oils, the average rate of annual generation is about 4.8 million tons, equivalent to about 32 million barrels⁽¹⁾. This rate of waste generation constitutes a major waste management problem with respect to land availability for landfills and public health and pollution concerns. Mandatory recycling of waste paper and plastics is in effect in several states, but the rate of generation of these wastes exceeds existing demand.

Solutions to the problem of excess waste are being put into effect nationwide. Paper can be recycled to a certain extent. Waste oils can be cleaned and re-refined. Plastics that are not recycled can be combusted for thermal value, and tires can either be burned whole in cement kilns, or shredded and used as a supplementary fuel for utility boilers, the so called tire derived fuel or TDF⁽²⁾. Another potential solution to the waste problem is coprocessing of the wastes either with heavy oils or with coal to produce hydrocarbon liquids that can be refined like petroleum to give transportation fuels. This paper addresses the technical and economic feasibility of this coprocessing approach by examining the potential for co-siting a waste/coal coprocessing facility adjacent to an existing oil refinery.

METHODOLOGY

The conceptual waste/coal coprocessing facility is assumed to be sited at a refinery close to the greater Philadelphia metropolitan area. In this area it has been estimated that approximately 3100 tons per day of waste plastics is generated, 250 tons of tire rubber, and about 9000 barrels per day of used oil⁽¹⁾. It is assumed in this analysis that about 25 percent of the waste plastics can be transported and utilized at the site, 15 of the waste oil, and 50 percent of the tires. Four cases were analyzed and these are shown in table 1. In case 1, only plastic and coal is fed to the plant on an equal weight basis. In Case 2, plastics, coal and waste oil are fed to the plant, Case 3 uses plastics, oil, tires and coal. Case 4 is a coal-only case, and is analyzed to provide a comparison by which to measure any potential economic advantages of co-feeding the wastes. In all cases, petroleum coke from the refinery is used as a gasification feed to provide hydrogen both for the refinery and for the coprocessing facility. Figure 1 is a schematic showing the coprocessing facility and how it integrates with the adjacent refinery. These integrations include: letting the refinery process purge gases from the coprocessing plant, sharing of waste water treatment facilities, refining of the raw liquids from the coprocessing plant in the refinery, selling hydrogen and fuel gas to the refinery, and utilizing the petroleum coke from the refinery in the coprocessing facility for hydrogen production.

When this techno-economic analysis was performed there was little data available from continuous units operating in a coprocessing mode with coal and plastics, rubber, and oils. Since then, Hydrocarbon Research Inc. (HRI) has demonstrated the technical feasibility of coprocessing coal with plastic and rubber in their proof-of-concept (POC) facility in New Jersey under the sponsorship of the United States Department of Energy (DOE). For this analysis, it was necessary to make various assumptions as to the performance of coal/ waste coprocessing in the HRI Catalytic Two-Stage Liquefaction (CTSL) process. These assumptions can be summarized as follows: the presence of the coprocessed waste materials do not effect the coal conversion, plastics (excluding PVC) convert to 98 percent to oils and gases, plastics produce four times the gas as coal, waste oil converts to 98 percent oil and gas, tires contain 33 percent carbon black inerts and 98 percent of the remainder converts to oil and gas. It is further assumed that coal is \$25 per ton, and the acquisition costs for the waste materials at the plant gate is zero. The petroleum coke is also free at the plant gate. However, the waste feed stocks must be prepared for coprocessing. It is assumed that it costs \$25 per ton to shred tires, \$20 per ton to shred plastics, and \$5 per ton to prepare the waste oil. The coprocessing plant

can sell hydrogen to the refinery for \$2/Mscf, and fuel gas for \$1/MMBtu. Sulfur and ammonia by-product credit to the coprocessing facility is priced at \$80 and \$150 per ton respectively. For processing the fuel gases the refinery charges the coprocessing facility \$6 million per annum, \$5 million for waste water treatment, and \$3 million to recover sulfur.

To conduct this analysis, conceptual, commercial waste/coal coprocessing plants were developed using the MITRE coal liquefaction cost model methodology based on performance data from the CTSL process. MITRE has developed commercial liquefaction simulation models and these can be used to analyze the impact of process variables on performance and the resulting required selling price of products for any desired set of economic parameters. For this analysis, the performance of the coprocessing plants was based on the known performance of the coal-based process together with the estimated performance of the waste materials from the assumptions noted above. The four cases were analyzed based on the capacity of one liquefaction train of the CTSL process. The size of the overall facility was based on the availability of the waste feedstock and this train size for CTSL is not the optimum size from an economic viewpoint. A larger CTSL train size could be utilized by feeding more coal to the facility but the impact of this was not considered in this analysis.

RESULTS OF THE ANALYSIS

Table 2 summarizes the results of this economic analysis for the three coprocessing facilities and the coal-only plant. The components that make up the capital costs of the coprocessing facility consist of the CTSL train, gasification to produce hydrogen including air separation, and the ROSE-SR deashing process (CSD). In Case 3, the Texaco Tire dissolution process⁽³⁾ is included to dissolve the tires. Total capital for these plants ranges between \$330 and \$350 million (\$1993). Operating costs include feedstock preparation costs for the wastes, coal costs, power, and operating and maintenance costs. Netbacks is the difference between the price paid to the coprocessing facility for hydrogen, fuel gas, sulfur, and ammonia, and the service costs that the coprocessing facility pays to the refinery for sulfur recovery, waste water treatment, and acid gas processing. The required selling price (RSP) of the raw liquid products is calculated from the capital and net operating costs from a DCF analysis based on a fixed set of economic parameters. The liquid product outputs from the four cases are tabulated in Table 1.

This preliminary economic analysis indicates that waste/coal coprocessing has the potential to reduce the RSP of raw liquid products from coal liquefaction by about 30 percent if the assumptions made in this study can be verified experimentally. This conclusion is based on the comparison between the coal-only case (Case 4) where the RSP is \$40 per barrel and Case 2 where coal, plastics, and waste oil are coprocessed together to yield an RSP of only \$28 per barrel. The primary reasons for this significant decrease in the RSP of products from coprocessing lies in the high liquid yields obtained from the plastics and oils, and the lower hydrogen requirement compared to coal liquefaction by itself. Plastics and oils have hydrogen contents of about 14 weight percent compared to coal at only about 5 percent, therefore considerably less hydrogen is required to make liquid hydrocarbons from coprocessing a mixture of plastics and coal. Obviously, the larger the quantity of plastics in the mix the less hydrogen is required and hence the better the resulting economics. The other conclusion from this study is that siting such a coprocessing facility adjacent to an oil refinery offers opportunities for integration and hence can reduce costs. However, since this study is based on little actual continuous performance operations in a coprocessing mode, a comprehensive bench and continuous scale research and development program is needed to verify the assumptions made in this paper and to optimize coprocessing performance.

These above cases were all based on the assumption that the acquisition costs of wastes were zero at the plant gate. This implies that the costs of transporting the wastes to the plant are balanced by the savings in tipping fees. A sensitivity to this assumption has been investigated in this study, and the economic impact on the RSP of products by varying the acquisition costs has been estimated. If tipping fees are increased in the future so that the plant gate acquisition cost is negative \$20 per ton, then the RSP of liquids drops to about \$23 per barrel. If, on the other hand, acquisition costs are greater than zero, for example +\$20 per ton, then the RSP of liquids would rise to about \$32 per barrel.

The overall economic potential for this concept of coprocessing coals and waste materials to make transportation fuels does offer considerable promise. The roles that coal may play in this concept can be summarized as follows: coal allows process flexibility by acting as a feedstock flywheel to stabilize the system during periods of waste feedstock variability; the plant output can be doubled by using up to 60 percent coal and hence benefits of scale can be obtained;

there may be potential chemical synergy with coal by scavenging heavy metals in the coal ash; there may be a catalytic effect of the carbon black in tires; the hydrogen donor recycle solvent from the coal may assist the kinetics of plastics and rubber dissolution; there may be an ability to neutralize chlorine from PVC by coprocessing with low rank coals having alkaline mineral matter; coal allows several different wastes to be utilized simultaneously.

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ACKNOWLEDGMENT

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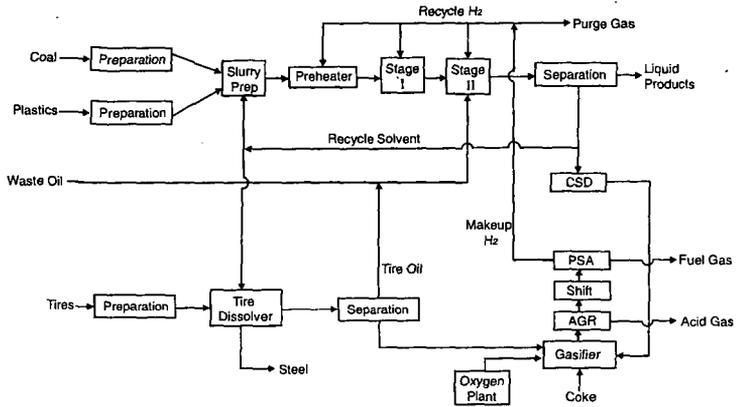
Table 1. Cases Analyzed

Feed (TPD)	Case 1	Case 2	Case 3	Case 4
Plastics	866	866	866	—
Coal (dry)	872	872	872	1,728
Petroleum Coke	1,248	1,248	1,225	1,095
Waste Oil	—	210	210	—
Tires	—	—	135	—
Total C ₃ ⁺ Products (BPSD)	8,830	10,170	10,455	7,360

Table 2. Economic Summary (\$MM)

	Case 1	Case 2	Case 3	Case 4
<u>Capital</u>				
CTSL	110	110	110	110
Hydrogen	97	97	98	97
CSD	10	10	10	11
Other	<u>28</u>	<u>28</u>	<u>28</u>	<u>28</u>
	245	245	246	246
Tire Dissolution	0	0	15	0
Total Capital	332	332	350	338
<u>Operating Costs</u>				
Feedstock	7	7	7	14
Waste Prep	6	6	7	0
Power	17	17	17	17
Other	<u>23</u>	<u>24</u>	<u>26</u>	<u>25</u>
Gross O&M	53	54	57	56
Netbacks	-17	-17	-17	-8
Net Operating	36	37	40	48
RSP \$/Bbl	32	28	29	40

Figure 1. Waste/Coal Coprocessing—Refinery Integration



VIABILITY OF CO-LIQUEFYING COAL AND PLASTIC WASTES

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ABSTRACT

Efforts have been undertaken to assess the technical and economic feasibility of a new process for co-liquefying coal and plastic wastes. This assessment is based on incorporating recent experimental data on plastic/coal liquefaction within a conceptual process framework. A preliminary design was developed to co-liquefy 30,000 kg/hr of plastic waste with an equivalent amount of coal on a weight basis. The plant products include hydrocarbon gases, naphtha, jet fuel and diesel fuel. Material and energy balances along with plant-wide simulation were conducted for the process. Furthermore, the data on plastic-waste availability, disposal, and economics have been compiled. The results from the economic analysis identify profitability criteria for gross profit and return on investment based on variable conversion, yield, and tipping fee for plastic waste processed.

INTRODUCTION

Finding cost-effective energy sources has been a rising concern of our nation for the past twenty years. Coal liquefaction research is at the forefront of potentially feasible options for two reasons. One reason is that coal is the most abundant natural resource readily available in the United States. Furthermore, when coal is liquefied a liquid fraction is produced which can be upgraded to yield transportation fuels (e.g., jet fuel, gasoline, diesel fuel, etc.). At present, the liquefaction of coal alone is not economically feasible. One way of rendering the liquefaction process feasible is to include additional raw materials (e.g. municipal solid waste) that can significantly alter the process economics.

In addition to the energy problem, environmental issues have also been the focus of public attention. The solid-waste problem has escalated to a staggering magnitude. Efficient ways of disposing of/converting solid wastes must be determined. Thus, more focus has been placed on co-processing of coal with waste materials (e.g., tires, plastics, cellulosic material, waste oil, etc.). This alternative is attractive mainly because the waste materials, when co-processed with coal, provide a raw material that increases production capacity and can improve the process economics. This directly offers hope for potential commercialization.

Recent research efforts (Taghiei et al., 1993; Anderson and Tuntawiroon, 1993) have shown that the conversion of coal and plastic waste into liquid fuel is possible on a lab scale. This conversion is achieved by processing coal and waste plastics at a relatively high temperature (400 - 450 °C) and moderate to high hydrogen pressure (800 - 2000 psi). Conversion as high as 100% is achievable for reactions involving plastic waste alone with yields to the oils fraction ranging between 86 - 92% (Taghiei et al., 1993). However, coal/plastic mixtures attain somewhat lower conversions and yields ranging from 53 - 93% and 26 - 83%, respectively. The oil fraction is the portion of the product that can be refined to yield naphtha, light, middle, and heavy distillates. Therefore, it is important to achieve good conversion and to attain high yields to oils.

The objective of this paper is to provide a technical and economic assessment of co-liquefying coal and plastic waste. First, the availability and current technologies for utilizing plastic waste is reviewed. Then, the problem to be addressed in this work is formally stated. A process flowsheet is conceptualized. Then, the material and energy balances for the process along with a plant-wide simulation using the software ASPEN PLUS will be undertaken. Finally, the economic aspects of the process will be analyzed and some profitability criteria will be assessed.

PLASTIC WASTE AVAILABILITY AND CONVERSION

Each year, our nation produces an estimated 58 billion pounds of plastic resin 90% of which are used in the United States (Hegberg et al, 1992). Last year, approximately 32 billion pounds of plastics have entered into the municipal solid waste [MSW] stream as post-consumer plastic waste. The MSW generated annually totals 200 million tons and is composed of yard wastes (17.6%), paper (40%), metals (8.5%), glass (7.0%), plastics (8.0%), food wastes (7.4%), and other material (11.6%). Although plastics make-up only 8% of the MSW by weight, of the estimated 400 million cubic meters of annual MSW, plastic wastes are responsible for 20%. This fact creates a major concern for the dwindling legal landfills that already have limited room. Landfilling as an option of disposal is becoming an expensive, undesirable alternative. The average cost for landfilling today is \$20/ton and can be as expensive as \$150/ton depending on location. Landfills are also becoming unacceptable because of social and public-health reasons (e.g. they provide breeding grounds for mosquitoes). Despite the problems associated with landfilling, the low recycling rates for plastics (<1.5%) suggest that plastics end up in landfills or are perhaps illegally dumped.

PROCESS CONCEPTUALIZATION AND SIMULATION

The first step in designing the process for co-liquefying coal and plastic wastes is to develop a conceptual flow sheet. The conceptualized process flow diagram is schematically illustrated in Figure 1. The waste plastics are sent to a shredder which chips the plastics into processible pieces. Coal is first crushed then distributed to the slurry mixer and to hydrogen generation. The waste plastics and crushed coal are mixed with a recycled solvent to form a slurry. This slurry mixture is fed to a preheater. The preheated slurry is then forwarded to an adiabatically operated reactor which yields vapor, liquid and solid products. The vapor, leaving the reactor at 800 °F and 2200 psi, is first relinquished of hydrogen which is recycled back to the reactor after being mixed with the fresh hydrogen feed. The remainder of the stream is then separated into vapor and liquid products by utilizing a flash column. The gas leaving this flash column is sent to an acid-gas removal system. The remaining gas consists of light petroleum fuel gases. The removed hydrogen sulfide is processed in a Claus unit to yield elemental sulfur. The slurry leaving the reactor is first flashed in the gas oil column. The column yields a vapor product which contains most of the valuable hydrocarbon fractions. The bottom product leaving the column includes heavy hydrocarbons along with the unreacted coal and ash. The vapor stream leaving the gas-oil flash column is hydrotreated and distilled to yield light, middle and heavy distillates. A hydroclone is employed to process the bottoms from the gas oil flash column. The product leaving the top of the hydroclone contains the heavy boiling point fraction (>650 °F). This fraction is recycled to the slurry mixer as a hydrogen-donor solvent. Additional liquid from the fraction is removed using the Wilsonville evolved Residuum Oil Supercritical Extraction-Solid Rejection [ROSE-SR] unit. The recovered liquid is combined with the recycled solvent and this mixture is returned to the slurry mixer. The solid effluent from the ROSE-SR unit, along with some fresh coal, are then used to generate hydrogen needed for processing. A useful fuel gas is also produced in the hydrogen generation process.

Having developed a conceptual flow sheet for the process, one is now in a position to simulate the plant and conduct the necessary calculations for material and energy balances as well as other technical aspects. Material and energy balances for the plant have been conducted. In addition, a plant-wide simulation has also been undertaken using the software ASPEN Plus. Optimization of some units/systems has been carried out to minimize capital and operating costs. In order to yield an environmentally benign plant, the removal and recovery of the sulfur by-product has been achieved via a desulfurization system. Heat integration has also been done for all process streams.

ECONOMIC ANALYSIS

In this section, the economic aspects of this co-processing plant are discussed. Fixed capital investment, total capital investment, total production cost, and annual revenue is evaluated initially. Next, a profitability analysis is accomplished by analyzing the effects of varying conversion, yield and tipping fee on process economics.

Fixed Cost Estimation

Estimation of fixed cost is done by identifying the total purchased equipment cost by relating equipment capacity to cost utilizing available data in literature (e.g., Peters and Timmerhaus, 1991). In particular, the cost of several pieces of equipment was determined by scaling-down based on a recent Bechtel/Amoco study (US DOE-PETC, 1993). This DOE-funded study provides an extensive economic evaluation of direct coal-liquefaction in which Illinois #6 coal is liquefied to yield naphtha, light, middle, and heavy distillates. Design aspects throughout the plant were taken from several pre-existing liquefaction projects (Breckinridge, Wilsonville, HRI, etc.). Based on the capacities of the pieces of equipment needed in this co-liquefaction study, the cost may be calculated using the suggested Bechtel/Amoco scaling exponent of 0.71. For example, at 70% conversion and 90% yield, the total purchased equipment cost is about \$77 million. The liquefaction system (reactor, ebullating pumps, etc.), accounting for \$42 million (approximately 55% of the total purchased equipment cost. This high cost is due to the very specialized design of the ebullated-liquefaction system needed for this type of conversion. From this purchased equipment cost, the fixed and total capital investments were estimated to be \$373 million and \$439 million, respectively.

Total Production Cost

The total production cost has two components; operational and depreciation costs. The main contributors to operational cost are the cost of shredding plastic waste and the cost of raw material and catalyst needed for liquefaction and hydrogen production. The plant utilizes 30,000 kg/hr of waste plastics that must be shredded before being processed. The cost of shredding is about 5 million/yr based on plant operation of 8760 hours per annum and unit cost for shredding of \$0.02/kg. The cost of raw material is an important element in calculation of operational cost. This plant also utilizes and additional 20,000 kg/hr of coal for the production of hydrogen which costs about \$10 million/yr (based unit cost for coal of \$20.5/ton). The amount of catalyst needed for liquefaction and hydrogen generation can be calculated by scaling down based on capacities and cost available in literature (US DOE-PETC, 1993) and assuming that the catalyst cost-capacity functionality behaves linearly. The estimated cost of catalyst for this facility is about \$7 million per annum. Also, waste plastics may have a positive raw material cost if incoming plastics to be processed is paid for, or a negative raw material cost (i.e., generate revenue) if a tipping fee is charged for all incoming plastics to be processed. This issue will be discussed later. The total annual operating cost, excluding depreciation, is approximately 22 million/yr. By using a 10-year straight-line depreciation scheme, one obtains an annual total production cost of \$59million/yr for conversion and yield of 70% and 90%, respectively. Similarly, the total production cost can be evaluated at various conversions and yields.

Annual Sales

Annual revenue which is obtained in this facility is partially attributed to the sale of the liquid and gaseous fuels produced in process. At 90% yield and 70% conversion, \$60,000 kg/hr of oil and gaseous products is produced. The average value of oil was assumed to be \$0.68/gal, which translates into \$79 million per annum. Revenue can also be gained via tipping fees charged for all plastic waste processed at this facility. Annually, 263 million kilograms of plastic waste are processed in this facility. Processed plastic wastes can potentially generate revenue. For example, this facility can function as a non-conventional waste-management facility at which plastic waste material is disposed. In this case, a tipping fee is charged for all waste materials disposed/processed. The tipping fees will increase the

annual revenue generated. In general, plastic wastes can be a source of revenue (via tipping fees) or an expenditure (through vendor charges). For this case study, the tipping fee was varied from free disposal (-\$0.06 to 0.02/kg). The \$ 0.02/kg corresponds to the plant collecting two cents on each kg of plastic waste as tipping fees. On the other hand, -\$0.06/kg corresponds to a post-consumer plastic material which is purchased from a vendor for six cents per kilogram. At a tipping fee of \$0.02/kg, as shown in Figure 2, the annual revenue generated from processing waste material is about \$5 million. This leads to a total annual revenue of \$84 million for the entire plant. At a tipping fee of -\$0.06/kg (the least profitable scenario), 70% conversion, and 90% yield, the annual cost of processing plastic waste material is approximately \$16 million. The total annual revenue for this scenario is about \$63 million.

Profitability

Two important indicators, commonly used in economic assessment, are gross profit and return on investment [ROI]. Gross profit is defined as the difference between the total annual revenue and the total production cost. ROI is determined by dividing this gross profit by the total capital invested. Gross profit and ROI were calculated for several scenarios which include a range of 70 to 90% for yield, 15 to 90% for conversion, and -\$0.06 to 0.02/kg for tipping fee. As conversion increases, profitability also increases. For example, at 70% conversion, 90% yield, and a tipping fee of \$0.02/kg, the gross profit is \$25 million, as shown in Figure 2. By recalling that the total capital investment for degree of conversion and yield is 439 million dollars, the ROI is approximately 5.7%, as shown in Figure 3. The most profitable scenario assessed in this case-study exists at 90% conversion, 90% yield, and a \$0.02/kg tipping fee. For this case, the annual gross profit and ROI have been determined to be approximately 30 million and 7.8%, respectively.

CONCLUSIONS

We have conducted a survey of the current status and availability of plastic wastes. Technical assessment of the proposed conceptual plant, process simulation, and economic analysis have been undertaken. Preliminary screening reveals that it is readily feasible to break-even at reasonable conversion, yield, and tipping fee. In this case, a co-liquefaction facility may be viewed as a waste-management facility for the disposal of plastic waste material and generation of fuel. However, if higher ROI and annual gross profit are required, higher tipping fees must be charged for processing waste plastic material or further research must be conducted to identify ways of attaining higher conversion and yield.

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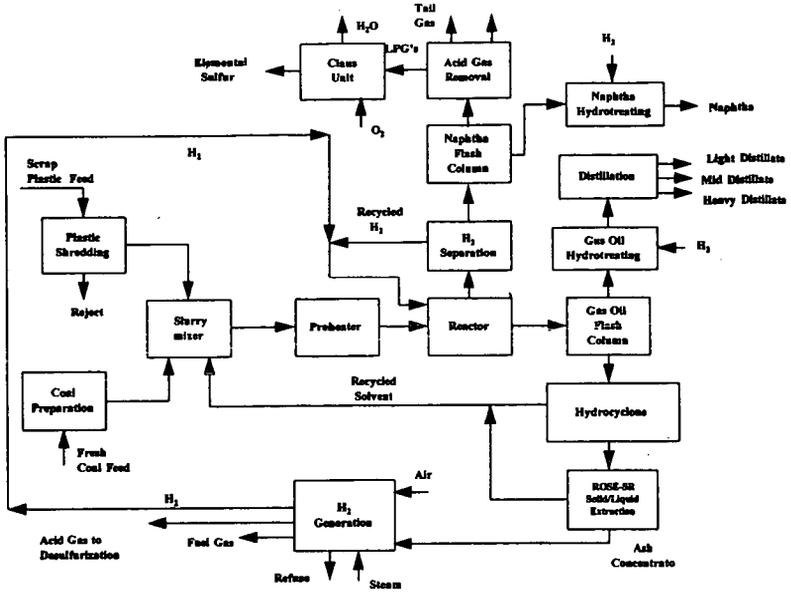


Figure 1: Conceptual Process Flow Diagram for the Co-Liquefaction Plant

Gross Profit,
Million \$/year

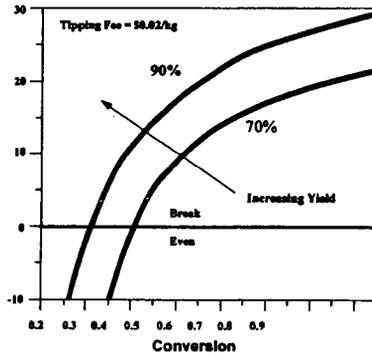


Figure 2: Gross Profit

Return on
Investment %

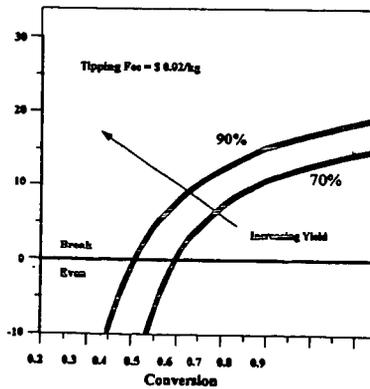


Figure 3: Return on Investment