It is the aim of this study to provide information pertinent to the development of a coal/RDF pyrolysis process capable of economically creating valuable products from high sulfur Illinois coal. A RDF, a cellulose, two coals, and 7 plastic samples were obtained, prepared and characterized. Over 100 TGA, and 341 microreactor tests were conducted. The pyrolysis tests were conducted in 4 environments. Key parameters from the TGA profiles were identified and measured. TGA parameters indicate that the coal and some plastics interact. Coal increases the temperature at which the plastics begin to volatilize and the plastic seems to accelerate volatile loss in the coal. Intimate mixing of plastic and coal is required to obtain any synergisms. The series of screening tests using the microreactors showed that the apparent synergism in nitrogen pyrolysis of coal plastic blends observed in the TGA do not transfer to confined microautoclave tests. Although steam and hydrogen environments retard the volatile evolution in pure plastics, the blends gave conversion similar to those obtained in nitrogen. Conversions in the liquefaction environment are generally greater for all pure substances and blends. There are reaction conditions were synergism in soluble conversions occur. In some cases the conversion to solubles are not as extensive as desired, but in these cases the insoluble residues appear to be contain high quantities of volatile matter.
EXECUTIVE SUMMARY

Of the many environmental issues such as global warming, depletion of the ozone layer, and acid rain, solid waste disposal is one of the most pressing. Addressing the disposal of municipal waste in an environmentally safe and economically feasible manner must be undertaken. The United States is producing about 30 million tons of synthetic polymer material every year. Virtually every plastic product will eventually find its way into a landfill. Utilization of the waste stream plastics and cellulose materials (the major RDF components) with conversion by pyrolysis would significantly reduce the amount of waste reporting to our landfills.

It was the aim of this study to provide information pertinent to the development of a coal/RDF pyrolysis process capable of economically creating valuable products from high sulfur Illinois coal. Reasonable operating parameters consistent with existing pyrolysis processes were utilized. Beside providing fuel, this type of an approach has the potential of producing carbon materials as byproducts. This is the first time high pressure, low temperature coal/RDF pyrolysis has been investigated.

Thus, the primary objective of this project was to investigate the pyrolysis of high volatile Illinois coals with various mixtures of waste plastics and RDF. The specific goals and objectives of this study were to: 1) Select two Illinois Basin coals from the Illinois Basin Coal Sample Program with different mineral, sulfur and chlorine content. 2) Characterize samples of waste plastics and RDF provided by Continental Waste Industries, Three Oaks, MI 49128. 3) Conduct high pressure, low temperature pyrolysis runs of cellulose, RDF, polypropylene, polyvinyl chloride, polystyrene, polyethylene, and one clean Illinois coal to determine a baseline analysis of products generated, their quality, and quantity. 4) To determine any synergistic effects during the co-pyrolysis of coal/waste blends by measuring the quality and quantity of products formed. 5) Investigate the effect of changing blend ratios in the development of the quality and quantity of products as an indication of a change in synergetic action. 6) Conduct a kinetic study at the conditions of highest quality and largest quantity of products; liquid, solid, and gas. 7) Produce a comprehensive mass balance study to verify product output for a given input.

With the immense amount of data generated during the course of this project it is impossible to present all of the results within the page limitation of the report. The following is a summary of general trends with typical data specified.
A RDF, a cellulose, two coals, and 7 plastic samples were obtained, prepared and characterized. Tests using the TGA and microreactors to study pyrolysis behavior of pure components and blended mixtures of components have been developed. Over 100 TGA, and 341 microreactor tests were conducted. The pyrolysis tests were conducted in 4 environments. The product distributions have been obtained. Product quality has been determined for selected samples. Kinetic studies were conducted for some components and some blends. The effect of coal particle size and coal to plastic ratios on total conversion has been evaluated. Mass balances were obtained for some reactions.

A series of preliminary experiments were performed using a thermogravimetric analyzer (TGA). Key parameters from the TGA profiles were identified and measured. Pyrolysis temperature ranges required for the larger scale microreactor experiments were identified. Most of the plastics have a very narrow temperature range over which they volatilize. The coal looses weight over a 580°C temperature range. The temperatures at which the plastics, paper and RDF volatilize occur at approximately the temperature at which the coal softens and becomes plastic. Mixture of coal and plastics had high temperatures of initial weight loss and lower temperature of final weight loss. PE and PP increased volatile yield of the coal in the TGA environment. Studies on heating rate mixing, catalysts, and blend ratios were conducted. The synergisms observed pass through a maximum with increase heating rate. Mixing was important to weight loss. The catalysts employed had little effect on the pyrolysis yield. Even small amounts of plastics resulted in increased coal conversions.

A series of screening tests were conducted using microreactors. Apparent synergism in nitrogen pyrolysis of coal plastic blends observed in the TGA do not transfer to confined microautoclave tests. Although steam and hydrogen retard the volatile evolution in pure plastics, the blends gave conversion similar to those obtained in nitrogen. Conversions in the liquefaction environment are generally greater for all pure substances and blends. There are reaction conditions were synergism in soluble conversions occur. In some cases the conversion to solubles are not as extensive as desired, But in these cases the insoluble residues appear to contain high quantities of volatile matter.

Gas yields tend to increase with increased temperature. The primary gas produced under nitrogen is methane. The presence of steam, hydrogen, and tetralin all inhibit methane formation. Tetralin is the most efficient of these inhibitors.

TGA parameters indicate that the coal and some plastics interact. Coal increases the temperature at which the plas-
tic begin to volatilize. The plastic seems to accelerate volatile loss in the coal. Intimate mixing of plastic and coal is required to obtain any synergisms. Only a small fraction of free radicals from plastic react with the coal and that excess free radicals react amongst each other and do not contribute to the coal volatilization. There is competition between volatile forming reactions and char forming reactions in a nitrogen atmosphere. Radical reactions between the co-pyrolyzing materials are thought to be primarily responsible for the observed behavior. The synergism observed in the TGA must be as a result of the formation of unstable but volatile fragments which form insoluble material in a enclosed space. Steam and hydrogen environments do not produce synergisms in the conversion of blends to soluble material. Under liquefaction environments plastic decomposition is severely inhibited. The inhibition provides a longer period for the coal and plastic to interact. The mechanism for the inhibition of the plastic decomposition is not fully understood, but the results lead to increase coal conversion and to higher quality products. The inhibition of methane gas formation and the decomposition of the plastic are related. Coal particle size is important to nitrogen pyrolysis. The effect of particle size seem to be a result of coal conversion and not coal/plastic interactions. Short reaction times are desired to prevent regressive reactions.

Further studies of the reason for the different behavior of similar plastics in coal blends is required for a detailed understanding of the coal plastic interactions. More detailed study of the inhibition in coal/PS blends would also contribute to a better understanding of coal plastic interactions. Additional work is needed to characterize the quality of products produced from the steam and hydrogen pyrolysis. The lack of identified synergisms in conversion to THF solubles may not be taken as a lack of increased desulfurization. The amount of volatile materials in the extract residues from steam and hydrogen pyrolysis need to be determined. The conditions studied for the conversion of plastic/coal blends should be expanded to include higher temperature at short reaction times and lower temperatures at long reaction times. Liquefaction products need to be characterized in more detail. Particle size effects and blend ratios need to be studied in detail for the liquefaction environment.

Although the value for the total conversion to soluble and volatile products under the liquefaction conditions need to be rechecked. The 95% reported here are quite significant. If these yields can be confirmed, they would indicate that the conversion of coal to liquid transportation fuels need to be revisited. Such conversions are very high considering that no catalysts was used, and the hydrogen partial pressure of 500 psig is low. Upon confirmation of these results
several process options should be considered for economic analysis. Some additional laboratory work is required as discussed above, and catalysis of the systems needs to be checked. Additional bench scale test would need to be conducted to determine gas yield, hydrogen consumption and other key process parameters. On the other hand, if these results are confirmed and the economics look favorable time to commercialization could be very short. That is because all of the equipment needed for large scale application has been developed through the DOE liquefaction program. These results also suggest that long chain aliphatic material in resids may be responsible for the apparent coprocessing synergisms observed in these systems. It may suggest that aliphatic/aromatic solvent mixtures are important in the overall liquefaction mechanism and that appropriately adjusted mixtures might provide a superior liquefaction process.
OBJECTIVES

Overall Goals and Objectives

The primary objective of this project was to investigate the pyrolysis of high volatile Illinois coals with various mixtures of waste plastics and RDF. The specific goals and objectives of this study were to: 1) Select two Illinois Basin coals from the Illinois Basin Coal Sample Program with different mineral, sulfur and chlorine content. 2) Characterize samples of waste plastics and RDF provided by Continental Waste Industries, Three Oaks, MI 49128. 3) Conduct high pressure, low temperature pyrolysis runs of cellulose, RDF, polypropylene, polyvinyl chloride, polystyrene, polyethylene, and one clean Illinois coal to determine a baseline analysis of products generated, their quality, and quantity. 4) To determine any synergistic effects during the co-pyrolysis of coal/waste blends by measuring the quality and quantity of products formed. 5) Investigate the effect of changing blend ratios in the development of the quality and quantity of products as an indication of a change in synergetic action. 6) Conduct a kinetic study at the conditions of highest quality and largest quantity of products; liquid, solid, and gas. 7) Produce a comprehensive mass balance study to verify product output for a given input.

Summary of Task

Task 1  Sample Selection and Preparation

Two coals were selected. Plastic and RDF Samples were obtained. Coals and RDF samples were split, ground, sized, and characterized. Some coal samples were preoxidized and others precleaned in a semi-continuous centrifuge.

Task 2  Screening and Yield

To understand the results and identify synergistic effects of co-processing coal/wastes, baseline data for the individual components were determined. Seven components were tested at various processing conditions. After completion of the baseline runs, a blend of 1:1 IBC-101 and the six other components were tested at the same process conditions.

Task 3  Product Quality

The solid char from promising systems was characterized with 8 analyses. They were TGA combustion profiles, Btu analysis, total sulfur content, total chlorine content, trace element analysis, proximate analysis, ultimate analysis, and selected samples for surface area and pore volume analysis.
The liquid products were characterized with the following analyses: ultimate analysis, Btu analysis, coke yield of any asphaltenes present, distillation analysis, GCMS, GC-FID/FPD, NMR, and FTIR. These tests determine the presence or absence of aromatics, aliphatics, and sulfur compounds.

The gaseous products were characterized by GC-FID/FPD. These tests determined the presence of \( \text{CH}_4 \), \( \text{CO} \), \( \text{CO}_2 \), \( \text{H}_2\text{S} \), \( \text{H}_2 \), \( \text{COS} \), \( \text{CS}_2 \), and higher hydrocarbon molecules.

**Task 4  Optimization**

Upon completion of Task 3, the waste that produced the best blend results for an optimum temperature were blended 1:1 with the various coal samples. These results determined the effects of particle size and coal pretreatments on product desulfurization, dechlorination, and quality. Synergistic effects on desulfurization were evaluated.

The coal sample described in the above tests which exhibited the best quality products at the optimum temperature of that run were blended in various ratios with the six waste components. Runs were conducted using the best identified process conditions. A kinetic study of the best 12 pyrolysis runs was conducted at various time durations.

**INTRODUCTION AND BACKGROUND**

**Solid Waste Disposal**

Of the many environmental issues, such as global warming, depletion of the ozone layer, and acid rain, solid waste disposal is one of the most pressing [2]. Addressing the disposal of municipal waste in an environmentally safe and economically feasible manner must be undertaken. About 180 million tons of municipal solid waste (MSW) is collected annually [2,3]. About 80% is landfilled, 10% incinerated, and only 10% recycled [4]. The economic impact of collection, transportation, landfilling, and regulatory compliance costs is staggering. The U.S. EPA averaged these disposal costs in 1988 to about $12/ton and estimated that the cost will be between $100 to $150/ton by the year 2000 [5]. With the eminent demise of landfilling, incineration or combustion and recycling must be emphasized.

Unprocessed MSW contains about 63% combustibles, 26% free moisture and 10% inert solid material. MSW can be burned directly in most existing boiler facilities either alone or mixed with oil or coal. MSW can be processed further into refuse derived fuel (RDF). RDF has three grades: fluff, medium, and high. Fluff RDF goes through a minimum of
cleaning and shredding that increases the Btu content from 4300 to between 5000 and 5500 Btu/lb. Virtually all MSW is retained at this stage. Only large metal objects, such as water heaters and engine blocks, and hard to shred objects, such as mattresses and parachutes, have been removed prior to shredding and burning. Medium grade RDF undergoes additional shredding and screening to remove inerts and retains approximately 80% of the original MSW. Btu values of this fuel now range from 5500 to 6000 Btu/lb. High grade RDF has a Btu value greater than 6000 Btu/lb. With the additional screening, only about 50% of the original MSW is recovered as fuel. The RDF could be separated further if a market existed for one of its components. The high grade RDF is targeted for this project. This material has virtually all metals removed.

The United States is producing about 30 million tons of synthetic polymer material every year [6]. Production is expected to double by the year 2000 [1]. Virtually every plastic product will eventually find its way into a landfill. Non-biodegradable waste plastics contribute 7 to 9% by weight and over 20% by volume to the waste stream of typical MSW. Currently, only 1.6% of waste plastic is recycled. The breakdown of plastics are polyethylene, high and low density, 63%; polypropylene, 9%; polystyrene, 11%; polyvinyl chloride, 5%; poly(ethylene terephthalate), 7% [7, 8].

Utilization of the waste stream plastics and cellulose materials with conversion by pyrolysis would significantly reduce the amount of waste reporting to our landfills.

**Coal Co-processing**

It was the aim of this study to provide information pertinent to the development of a coal/RDF pyrolysis process capable of economically creating valuable products from high sulfur Illinois coal. Reasonable operating parameters consistent with existing pyrolysis processes were utilized. Beside providing fuel, this type of an approach has the potential of producing carbon materials as byproducts. This is the first time high pressure, low temperature coal/RDF pyrolysis has been investigated. The high sulfur, high chlorine content of many Illinois coals makes them less competitive for direct combustion, and hence any process that would utilize these coals effectively and efficiently would have a pronounced beneficial impact on the marketability of Illinois coals.

Current pyrolysis techniques for coal are well known. The effect of high pressure (up to 2000 psi) is known to produce high molecular weight hydrocarbon compounds. Temperature variations (350° to 550°C) impact the production of alkanes
and alkenes during mild pyrolysis and should minimize any caking problems envisioned. To the authors knowledge, no other work has been conducted to apply this philosophy to coal/RDF pyrolysis. The completion of this project will greatly advance our understanding of co-pyrolysis issues that apply to coal/waste pyrolysis.

EXPERIMENTAL PROCEDURES

Approach

This project was carried out in a systematic manner. First, samples were properly selected, prepared, preserved and characterized. Then coals, various plastics, cellulose, and a high quality RDF were pyrolyzed, steam pyrolyzed, hydro-pyrolyzed, and liquefied at various conditions. Next, blends of coal with various RDF components were reacted under the same conditions. From this work any synergistic effects were identified and process parametric studies were conducted on the appropriate mixtures and single components. Product quality were obtained on some systems. Mass balances were to be determined but the lack of identified synergisms for some systems made this unnecessary. Preliminary pyrolysis work was conducted on a TGA. The majority of the pyrolysis experiments were conducted in microautoclaves.

Procedures

Sample Preparation

Two Illinois Coal Bank coals were selected for this research. The coals selected are IBC-101 and IBC-109. These coals are selected because of their mineral matter content, chlorine content, and sulfur content. IBC-101 coal is a high sulfur, high mineral coal. IBC-109 is a low sulfur, high chlorine, high mineral coal. Most worked centered on IBC-101.

Mr. Frank Volini, Marketing Manager for Continental Waste Industries, Three Oaks, MI 49128 has provided RDF and waste plastics needed for this project. These samples were received in sealed 5 gallon pails. Pure plastics were ordered and received.

The IBC 101 and 109 coals were prepared. The samples were split into 1 kilogram aliquots. About 1.5 kilogram of the IBC-101 was ground to -400 mesh and cleaned by semi-continuous centrifugation in a 1.6 g/ml aqueous cesium chloride solution. In this procedure 0.5 kg of coal was mixed with 10 liters of cesium chloride solution containing brij. The slurry was then ultrasonicated for 15 minute to disperse the coal particles. It was then pumped to the CEPA Coal Padburg
semi-continuous centrifuge at a 100ml/min flow rate. The centrifuge was brought up to speed prior to this and a pure cesium chloride solution was pumped into the rotor to assure that the path way was clear and the rotor balanced. Particles greater than 1.6g/ml apparent density were pushed to the wall while lighter particles eluted at the top of the rotor and were caught in a set of pans and a beaker. At the end of the run the rotor was flushed with pure chase solution of the same density as the separation medium. The rotor was then stopped and the solids removed. The overflow was filtered and washed with hot water and dilute hydrochloric acid solution to remove and recover cesium. A similar procedure was conducted of the solids retained in the rotor. These samples were then characterized. This procedure can process about 3-5 kg/day and can be repeated at different densities. Thus, the procedure can be used to obtain clean coal as in this case or to obtain maceral concentrates on a large scale.

Approximately 500 grams of each coal was ground to -20 and -100 mesh and characterized. About 100 grams of -400 mesh clean IBC-101 was preoxidized with PAA. Details of this procedure are available elsewhere [9]. Characterization of this sample was conducted along with reacted products. All coal samples were stored under nitrogen until needed. RDF samples were ground to -20 mesh. Polypropylene, polyvinyl chloride, polyethylene, and cellulose were received as usable powder. The polystyrene was ground to -100 mesh in a rotary grinder. The material was sieved and stored in various size fractions between -100 and -400 mesh. Because all the plastic are homogeneous materials there was no need to worry about sampling problems. A 500 gram, pure cellulose sample was also obtained in powdered form.

TGA Reaction Tests

A Perkin Elmer TGA-7 Thermogravimetric Analyzer was employed to study pyrolysis. A five to ten milligram sample was placed in a weighing pan and the system was purged with an inert gas and then heated at 150°C/min in a 50ml/min flow of nitrogen. The final char temperature for all pyrolysis profiles was measured at 700°C. Coal and plastics used were loaded in different ways to study the effect of mixing on the volatile yield of the coal. Three different loadings were used, (i) coal-plastic mixed, (ii) coal-plastic unmixed, coal at the bottom, and (iii) coal-plastic unmixed, plastic at the bottom. Various ratios of coal-polyethylene were used to study the effect of excess plastic on volatile yield of coal. Heating rates were varied to study their effect on the volatile yield of the coal. Also, Iron sulfate and Potassium carbonate were tried as catalysts to study any catalytic effects in the coal and coal-plastic pyrolysis.
Microautoclave Reaction Tests

The majority of this work was carried out using a microautoclave system. The apparatus consisted of a 15-ml stainless steel microautoclave. The reactor was linked to one end of a three-way metering valve with high pressure tubing 8" long. A pressure transducer capable of measuring pressure up to 15,000 psi, was connected to the valve with high pressure tubing. A pressure read-out device was connected to the pressure transducer, so that the pressure of the reaction could be monitored. Another segment of high pressure tubing with a quick disconnect fitting attached was connected to the other side of the three-way valve so that any inlet or outlet gas could flow through.

Two fluidized sand baths were employed as heating sources and the temperature controlling device of the reaction system. The air flow rate was controlled by an air control valve so that the sand could be fluidized at a proper level. The temperature of the sand bath was controlled by an Omega on-off temperature controller and a k-type thermocouple. Generally, the temperature fluctuated within a range of 3°C over about a half minute to one minute period depending upon the reaction temperature. A metal cover was placed on the top of the sand bath so that entrained sand would not scatter around the bath. This also provided an insulating barrier for the pressure transducer and reduced the heat load on the bath. There was a small slit between the center and the side of the metal cover that the tubing connecting the microautoclave could pass through.

The reactors were charged with the desired amount of reactants. After pressurization with nitrogen to 600 psi, the valve was closed and leak testing with soap water was performed. If the reactor system passed the leak test, the three-way valve was then opened slowly to reduce the pressure to ambient. Pressurization and depressurization were repeated three times to remove traces of air. If another reactant gas was to be used (hydrogen) the gas was then delivered via a manifold to the reactor. Then the three-way valve was closed. The sand bath was preheated to 25 degrees above the desired reaction temperature before the microautoclave was put into the bath. The reactors were held by a Burell wrist action shaker and the sand baths were raised to the reactor by means of a mechanical jack. During the reaction, the body of the microautoclave along with part of the connecting tube was submerged into the fluidized-bed sand bath.

Following the reaction, the reactors were submerged in a low temperature fluidized sand bath. This cooling was not quite as efficient as a water quench but the reactor tended not to leak during the air cooling. Water quenching resulted in
leak development during cooling and subsequent loss of product. Water quenching also led to reactor deterioration by gauling and embrittlement. These problems are less severe in the air cool approach. A 1 liter gas sampling bag was emptied by application of vacuum, and was connected to the quick disconnect fitting to permit collection of the gas product in the bag by slowly opening the valve. The microautoclave was removed from the valve assembly after the gas products were collected, and the liquid product was then poured from the microautoclave into an extraction thimble. THF was then used to wash the reactor. A drill bit was fabricated to clean out solid material. The reactors were scrubbed with gun cleaning brushes and the contents slurried in THF. All of the product was collected in the extraction thimble. The reactors, valves and tubing were ultrasonically cleaned with acetone after each run to remove any tarry residues.

A soxhlet extraction procedure was then conducted using THF. Prior to placing the reactor contents into the thimble, the dry thimble was weighed. The extraction was conducted overnight (approximately 18 hours). In the morning the thimble containing the extraction residue was placed in a drying oven for 1.5 hours at 110°C. It was then removed and weighed. The THF was rotary evaporated out of the extract. It was then dried and weighed. After weighing, selected samples of the THF extract were slurried in toluene. Care was taken to scrape all of the THF solubles from the extraction flask. For selected samples, a toluene and then a pentane extraction was conducted sequentially.

RESULTS AND DISCUSSION

With the immense amount of data generated during the course of this project it is impossible to present all of the results within the page limitation of the report. The following is a summary of general trends with typical data specified. It is meant to give a general sense of the status of the project. One journal article on TGA pyrolysis has been submitted to Fuel. Several additional articles are planned. Additional detail analysis will be available in these publications.

TGA pyrolysis and co-pyrolysis

A series of preliminary experiments was performed using a thermogravimetric analyzer (TGA). Pyrolysis temperature ranges required for the larger scale microreactor experiments were identified. The materials that have been investigated include, polyethylene (PE), polypropylene (PP), polystyrene (PS), polyisobutylene (PSB), poly(ethylene terephthalate) (PET), polyvinylchloride (PVC), poly(1-butene)
(PB), poly(4-methyl-1-pentene) (PMP), paper, cellulose (CELL), RDF and a floated, low ash IBC-101 coal.

a) Pyrolysis of individual materials.

Figure 1 shows a typical pyrolysis profile where weight loss of a sample is plotted as a function of temperature. In addition, the first derivative of the weight loss curve is plotted. A number of characteristic parameters describing the pyrolysis behavior of the material under investigation are marked and include the weight loss onset temperature ($T_{on}$), the temperature of maximum rate of weight loss ($T_{max}$), the temperature of char formation ($T_{char}$), the temperature range of volatilization ($T_{vol}$), and the volatile/char yields. The onset temperature reflects the temperature at the initiation of weight loss and does not necessarily indicate the temperature at onset of pyrolysis. Pyrolysis may begin at some lower temperature, without immediate weight loss. $T_{max}$ is identified by the peak in the first derivative plot while $T_{char}$ is marked by the return of the first derivative plot to a horizontal straight line. The temperature range of volatilization ($T_{vol}$) is equal to $T_{char} - T_{on}$. These parameters are often characteristic of the materials being examined and changes in them usually indicate that the material has undergone a transformation or an interaction with another material.

With the exception of PVC and PET, all the plastics were completely volatilized, leaving no char yield. The coal sample however has a char yield of some 57% under the same conditions. Most of the plastics have a very narrow temperature range over which they volatilize. The coal loses weight over a 580°C temperature range. All of the materials, with the exception of PVC, show only a single major peak in the first derivative plot. The PVC sample shows two peaks, evidence for a two stage degradation involving the initial elimination of HCl followed by the pyrolysis of the remaining carbon backbone. The temperatures at which the plastics, paper and RDF volatilize occur at approximately the temperature at which the coal softens and becomes plastic. This is fortuitous because it should allow the materials to intimately mix during the co-pyrolysis experiments.

b) Co-pyrolysis of coal/waste mixtures

Coal/waste blends were co-pyrolyzed under the same conditions as the individual materials and the weight loss profile obtained as before. Figure 2 shows the pyrolysis profiles for coal blended with polypropylene and is fairly typical. The pyrolysis profiles for the individual components are also shown. Comparison of the pyrolysis profiles for the mixture (1:1) with those of the corresponding pure components suggests that an interaction between the compo-
ments takes place during the thermal treatment. If each component pyrolyzes independently, the profiles of the mixtures would simply be those of the components added together. The characteristic temperatures ($T_{on}$, $T_{max}$, $T_{char}$) for each component superimposed over each other would be observed in this case. In most cases only one $T_{on}$, $T_{max}$ and $T_{char}$ value is observed in the mixture, and this value is often widely different from either single component. Thus the mixtures are pyrolyzing as a single substance and significant interaction between the components is strongly suggested.

If $T_{on}$ and $T_{max}$ for the mixtures are compared with those of the individual components in Figure 3a and 3b, there is a general shift to higher temperatures in the mixtures. For instance the weight loss onset temperature for pure polyethylene is 336°C but weight loss for the coal/polyethylene mixture does not occur until 409°C. The presence of the coal seems to retard the evolution of volatile matter generated by the pyrolyzing polymer. However, this can be viewed alternatively with the argument that the plastic is retard- ing the coal volatilization. This behavior is not the same for all of the mixtures examined. The onset temperatures for polypropylene, polyisobutylene, poly(1-butene) and PVC mixtures with coal are similar to that of the polyethylene/coal mixture in that they are above the onset temperatures of either component. The other polymer/coal mixtures have onset temperatures in between that of the two pure components.

Although, the quality of the co-pyrolysis products can not be adequately evaluated from a TGA pyrolysis profiles, some indications of the char yield can be obtained. For instance, from the char yield it is possible to estimate the conversion of coal to volatile or distillable materials. Increases in the conversion of coal to volatile matter are desirable for the formation of liquid fuels, coal tar pitch- es and refinery feedstocks. On the other hand, increases in the formation of char from coal are desirable for the direct formation of carbon materials such as activated carbons and cokes. Whether char or distillable matter should be the goal of the co-pyrolysis with waste will largely depend on the potential quality of the materials produced.

Certain polymers interacted with coal to increase the dis- tillation yield. Coal polypropylene mixture had an average char value of 25.6% (51.2% on coal basis), an increase of about 6% in volatile yield of coal. Coal-polyethylene mixture had an average char value of 24.2% (48.4% based on coal), an increase of about 8.8% in the volatile yield of coal. Coal-polystyrene mixture had an average char value of 26.7% (53.4% on coal basis), an increase of about 3.8% in the volatile yield of the coal. Polyvinylchloride showed no
significant interaction with coal. Thus, when these some coal/plastic mixtures are heated not only does the plastic and the original volatile portion of the coal volatilize, but also an additional portion of the coal. This additional volatile portion presumably was formed via an interaction with the plastic. Of the saturated hydrocarbon polymer chains examined, polypropylene gives the highest increases in coal conversions while poly 1-butene gives the smallest. Since the elemental composition of these polymers is the same, the reason for their differing abilities to convert coal must lie in their different structures. It is anticipated that the relationship between the polymer structure and its ability to participate in coal conversion is largely due to the susceptibility of the polymer to form free-radicals and their subsequent reactivity. Further studies of this behavior are necessary before a detailed explanation will be possible.

Unmixed samples (1:1 weight ratio) of coal-polyethylene and coal-polypropylene were also pyrolyzed at 700°C, with a heating rate of 15°C/min. In the first set of the runs, coal was placed at the bottom and plastic at the top. The average char yield obtained for coal-polyethylene was 26.9% (53.8% on coal basis) and for coal-polypropylene was 28.6% (57.2% on coal basis). These experiments suggested that the plastics evaporated faster and that there was little or no interaction between the free radicals produced from plastic and coal. In the second set of experiments, plastics were placed at the bottom and the coal at the top. The char yields obtained for both coal-polyethylene and coal-polypropylene once again showed no significant interaction between coal and plastics. These experiments suggest that thorough mixing of coal and plastics is important for any significant interaction.

Coal-polyethylene mixtures of various weight ratios were pyrolyzed to study the effect of excess plastic on the volatile yield of coal. Coal-polyethylene were mixed in 20/1, 10/1, 5/1, 1/1, 1/2, and 1/4 weight ratios. The TGA pyrolysis profile showed no significant increases in the volatile yields of the coal with excess plastic. Only a small drop in coal conversion occurred in the 20/1 and 10/1 mixtures. This suggests that only a small fraction of free radicals from plastic react with the coal and that excess free radicals react amongst each other and do not contribute to the coal volatilization.

Coal-polyethylene, 1:1 weight ratio, mixtures were pyrolyzed at different heating rates. Heating rates of 5, 10, 12.5, 15, 25, and 50°C/min. were used. A definite shift in the reaction mechanism, from free radical reaction at lower heating rates to coking at higher heating rates, was observed. The switch occurs at the 15°C/min. heating rate and
at this temperature rate the coal-plastic interaction is also maximum. Temperature of maximum reactivity increases almost linearly with the heating rate.

Iron sulfate with seven hydration molecules (FeSO₄·7H₂O) was pyrolyzed in the TGA-7. The pyrolysis profile showed that two molecules of hydration are liberated at 133°C, another four molecules at 265°C and the last molecule of hydration is liberated at 339°C. Sulfur trioxide (SO₃) is liberated between 535-640°C leaving behind ferrous oxide (FeO).

Iron sulfate hepta hydrate was loaded on coal and coal-polyethylene mixtures by incipient moisture technique. Catalyst loading used were 5, 10, 15, and 20 wt.% of iron sulfate on dry basis. There was little or no catalytic effect of iron sulfate on coal-plastic interactions. Five and ten wt.% loadings of potassium carbonate (K₂CO₃) were also studied for catalytic effect on pyrolysis of coal-polyethylene. There was no significant catalytic impact of potassium carbonate on coal-plastic interactions. More catalysts need to be investigated in future.

Another significant change that occurs during the co-pyrolysis of coal with other materials is the temperature range over which coal volatilization occurs. Without the addition of any waste material the coal volatilization covers nearly a 600°C temperature range. When other substances are added to the coal the volatilization of the coal occurs over a 150-300°C range depending on which waste material is used. This significant observation demonstrates that the volatile matter derived from the coal can be distilled from the coal at much lower temperatures through the addition of waste materials. Thus, not only can coal conversions to distillable products be increased by waste plastic addition, the increased yields can be obtained at considerably lower temperatures.

**Explanation of Co-pyrolysis Behavior.**

Although the extent and nature of any interaction between the coal and the waste material is probably dependent on the type of waste material and coal involved, it is generally believed that radical reactions between the co-pyrolyzing materials are primarily responsible for the observed behavior. It is anticipated that as most of the materials are heated they melt together and become intimately mixed. As the temperature is raised further, the cleavage of covalent bonds result in the formation of free radicals. These free radicals can either form in the coal first, the plastic first or in both materials simultaneously. Once these free radicals are formed they can react with the other components in the system. In this way it can be envisioned that hydrogen rich free radicals derived from the degrading plastic
may react with hydrogen deficient molecules in the coal in such a way as to alkylate or hydrogenate the coal. Of course the reaction may involve the abstraction of an alkyl group or hydrogen from the plastic by a coal derived free radical. However, the result is the same. The hydrogen content of the coal derived molecules is increased. Through reactions such as these, it is believed that char forming regressive reactions between coal radicals are reduced. Thus the plastic may provide an alternative substrate for the coal radicals to react with.

The reason why polystyrene increases the char yield from the coal is more uncertain, but it may have something to do with the aromatic groups present in polystyrene. If these benzene rings or styrene units of the polymer can in some way interact with the aromatic clusters in the coal while in a mesophase condition, it is possible that the average aromatic cluster size would increase as a result. Since chars are largely aromatic and primarily derived from the aromatic clusters in coal, it is conceivable that an interaction of this nature may explain the increased char yields via co-pyrolysis with polystyrene. Other polymers with aromatic groups would have to be examined to substantiate this idea.

**Microreactor Studies**

The results from the TGA were used to setup the screening tests. It was obvious from the TGA results that only three candidate plastics (PP, PE, an PS) produced synergisms during pyrolysis. Blends of coal with cellulose and the other tested plastics resulted in TGA curves which were composites of the individual components or demonstrated inhibitory effects. Thus, microreactor studies were limited to these three plastics. Based on the weight loss information, identified interactions occurred between 400 and 500°C. Thus, most of the microautoclave testing was limited to this temperature range. Some interactions may have occurred below this temperature range, but went undetected because of the TGA data dependence on weight loss.

A total of 341 microautoclave runs have been conducted to date. About 100 were conducted this quarter. Of the 341 runs about 40 were shake down runs to work out procedures for sealing, purging, and cleaning the reactors. The remaining tests were conducted under routine procedures and represent screening and optimization tests.

**a) Procedure Development Results**

At first, the reactors consisted of two threaded caps and a high pressure pipe threaded at both ends. Because of the temperature cycling the threads needed to be protected with a high temperature grease. Difficulties arose in removing
products without contaminating them with the high tempera-
ture lubricant. Also the caps were designed in such a way 
that product could get into crevices. This presented materi-
al recovery problems. At first, an aluminum foil plug was 
used to try to prevent the products from getting into the 
crevices. This worked at low temperature, but as soon as 
liquid products formed they were able to get past the alumi-
num plug. Next some ceramic cement was used to seal of the 
crevices. This worked well for one run, but upon cooling, 
the ceramic cracked. This allowed product to leak into the 
crevices and would have allowed coke to form in subsequent 
runs. Thus, a stainless steel plug was designed to fit in 
the cap and the bottom cap was welded to the pipe. Also, a 
drill bit was modified to fit the profile of the plug and to 
fit against the side of the reactor. Riffle bore brushes 
were an ideal tool for cleaning products off the reactor.

Several problems were also experienced in learning to set 
the sand bath temperature at the correct setting so that 
reactor temperature would not undershoot the desired reac-
tion temperature. The bulk of the reactor was sufficient to 
cause a decrease in bath temperature and rewarmed the bath 
at the higher reaction temperatures took an appreciable 
amount of time. So, the sand bath was brought above the 
desired reaction temperature. After the temperature drop 
when the reactors were added, the temperature controller was 
reset to the desired reaction temperature. Thus, the reactor 
temperature increased for 2-3 minutes and then was main-
tained at the reaction temperature without any over- or 
undershoot.

During these runs, it was discovered that liquids were 
vaporizing in the reactor and then condensing in the line to 
the pressure transducer. At the higher reaction temperatures 
the line plugged. Thus, it was decided to forego continuous 
pressure readings. Reaction pressure was only recorded after 
the reactors had cooled. This had improved operations and 
recoveries. Some time dependent pressure information was 
lost, but the new approach saved the transducer from expo-
sure and recalibration was avoided.

These runs were also used to develop the gas sampling proce-
dure. The evacuation of the gas sampling bag was found to be 
necessary. A teed line was connected to the air inlet valve 
of vacuum oven. The other legs of the tee were connected to 
the gas bag and the quick disconnect fitting on the three 
way reactor valve. The bag and line were then evacuated 
through the vacuum oven. The line to the vacuum oven was 
then closed and the three-way valve was opened. The gas in 
the reactor fills the bag and air contamination was avoided. 
Bags containing a separate septum were ideal for GC analy-
sis.
Another problem arose in adjusting the air flow requirements for the fluidized sand baths. As the temperature in the bath was changed the air flow requirements needed to be adjusted to permit proper fluidization.

After dealing with these operation and training procedures, the techniques to transfer material from the reactors to the extraction thimbles were worked out.

b) Screening Runs

A summary of the screening results is described below. In this report, the percent insoluble is defined as the yield of residue from the THF extraction divided by the original weight of the sample times 100. The conversion is defined as 100 minus the percent of the original weight which is THF insoluble. The liquid yield is defined as the weight extracted by THF divided by the original sample weight times 100. The percent gas as reported here is the total conversion minus the % liquid yield. However, this value is a composite of gas and distilled liquids which are trapped in the connection tube. Total conversions are discussed in this section. The other parameters will be discussed in the product quality section.

i) Conversion in Nitrogen

Table 1 reports total conversions of various single materials at various temperatures during one hour standard reaction times in nitrogen. It also contains information on conversions of 1:1 blends of coal and the three plastics studied. In general, an average coal conversion of 25% was obtained with values ranging from 20 to 31%. There was only a small increase in conversion with increase temperature. The plastic conversions were very high at lower temperatures but decreased at higher temperatures due to increase char formation. These trends were expected.

The total conversions can be used to judge any synergisms. If the conversion from the baseline PE and PP runs are averaged with the conversion from the baseline coal runs, the resulting averages do not under predict blend conversion for most cases. This is an indication that apparent synergism observed in the TGA does not transfer to confined microautoclave tests. The PS gave similar results and may indicate slight decrease in overall conversion of the blend as predicted from the base line runs. Additional runs in PS in other atmosphere were not conducted based on these results.

ii) Conversion in Steam

Table 2 reports total conversions of various single materi-
als at various temperatures during 15 minute and one hour standard reaction times in a steam atmosphere. It also contains information on 1:1 blends of coal and the two plastics studied. In general, coal conversion of 25 to 30% was obtained. The coal conversions were similar to those obtained in nitrogen. The plastic conversions were unexpectedly low under 15 minute reaction times and 425°C. Thus, the steam appears to retard plastic depolymerization. If the conversion from the baseline PE and PP runs are averaged with the conversion from the baseline coal runs, the resulting averages do under predict blend conversion for some cases (coal/PE at 425 and 475°C and 15 minutes; and the coal/PP at all temperature and 15 minutes of reaction time). However, most of this synergism appears to result from the retardation of the plastic decomposition under steam. The conversion values for the blends are the same or greater in nitrogen as opposed to steam.

iii) Conversion in Hydrogen

Table 3 reports total conversions of various single materials at various temperatures during 5 minutes and one hour standard reaction times in 500 psig hydrogen. It also contains information on conversions of 1:1 blends of coal and the two plastics studied. In general, coal conversions of 20 to 25% were obtained. The conversion of coal is similar to or even less than that obtained in nitrogen. Smaller conversion may be due to a pressure effect. The plastic conversions are similar to those obtained in nitrogen. If the conversion from the baseline PE and PP runs are averaged with the conversion from the baseline coal runs, the resulting averages do not under predict blend conversion for the PE cases. However, the polypropylene runs show some synergism at 425°C for both 5 and 60 minute reaction times. The results for PE are either lower of the same as those obtained in nitrogen, but the PP appear to yield slightly higher conversions.

iv) Conversion in Hydrogen/Tetralin

Table 4 reports total conversions of various single materials at various temperatures during 15 minutes and one hour standard reaction times in 500 psig hydrogen and a 2:1 tetralin to coal ratio. It also contains information on conversions of 1:1 blends of coal and the two plastics studied. In general, coal conversions of 50 to 55% was obtained. The conversion of coal is greater than that obtained in the other three environments. The plastic conversions are inhibited by the hydrogen tetralin environment. This inhibition is greater than that observed in steam or hydrogen alone. If the conversion from the baseline PE and PP runs are averaged with the conversion from the baseline coal runs, the resulting averages under predict blend con-
version for the PE and PP. Either short time high temperature or long time low temperature give the best results based on solubility alone. However, the insoluble residue in some of the low conversion cases contains larger amount of volatile material. This will be discussed later in the report. The conversion of the blends are higher than those obtained in other environments.

c) Product Quality

Product Distribution

Figure 4 shows a crude breakdown of the product distribution from the pyrolysis of coal/polyethylene blends. The liquid yield containing mostly asphaltenes and pre-asphaltenes decreases with increasing temperature. The gas yields are a combination of gas and unrecovered liquids. In general this yield increases with increasing reaction temperature. At 550°C, the overall conversion increases drastically. More detailed study and better mass balances are needed to determine if this increase in yield is desirable or just the result of increase gas yield due to coking. Similar trends can be seen for the coal/polypropylene blends (Figure 5) and coal/polystyrene blends (Figure 6).

Gas Analysis

GC analysis carried out on the nitrogen pyrolysis runs on raw coal indicated a high nitrogen content > 90% in the product gas. Only a small volume was recovered. Thus, the gas yield was very low and consisted of carbon oxides and a very small amount of methane. The polystyrene produced a very small amount of hydrogen. Both PE and PP produced a moderate amount (200-300 ml) of methane. The percent of methane was typically 80% or more with the remainder being nitrogen, about 8%, and hydrogen, about 2%. Thus about 8% of the plastic is turned into methane. The remaining plastic is converted to light oils and gases. The GC employed was not equipped with a column to separate and detect hydrocarbon gases heavier than methane. The blends produced greater amounts of gases, (300-400 ml) but only a small amount of CO (3%) and hydrogen (9%) were produced. About 86% of the gas is methane which represents 24% of the plastic charged or 12% of the total blend charged.

Similar results were obtained for the raw coal in a steam environment as in nitrogen. The plastic produced 90% methane and 10% CO. The higher CO concentration is probably due to shift reaction with the steam. No hydrogen was produced and is presumed to be consumed in methane production. The amount of gas produced increased with increasing plastic conversion. At high plastic conversions, > 95%, the methane was about 24% of the total charge. At lower conversions,
(about 40%) the methane represented 10% of the charge. The concentration of gases was only slightly influenced by the conversion. The blends gave gas concentrations and amount similar to that obtained in nitrogen. There may be a slight decrease in methane yield and this would be expected since the steam does inhibit plastic conversion as discussed in the screening section.

In hydrogen, a considerably larger amount of methane was formed with the raw coal about 5% by weight of dry coal. The polyethylene produced little methane even when conversions were above 90%. The blend produces 15% methane, which is higher than from either the coal or polyethylene. The pure PP and the coal/PP blend gave a similar result.

The total volumetric gas yields in the liquefaction environment were about the same as in the steam environment. However, most of the gas was hydrogen with less than 10% methane and even smaller amounts of CO₂ and other gases. This shows that the plastic depolymerization to methane was retarded to the largest extent in the liquefaction environment.

Mass Balances

Water produced during the reaction was lost during the work up procedure. We were not able to develop an independent moisture test for the products. The mass balances at the lower temperature were good, particularly for the coal-component blends. At higher temperatures, the liquid refluxes in the line to the three way valve. Some of this was held in the line and was not recovered as part of the cleaning process. The gas yield varied between 0 an 15%. Typically 85-95% of the total feed was recovered or was accounted for with the gas yield. The missing material was estimated to be water lost during workup procedures and tars hanging in the line to the three-way valve.

Proximate Analysis of Extract Residues

TGA pyrolysis tests were conducted on selected extract residues from PE/Coal blends run under nitrogen. They show the presence of at least 10% volatile material remaining after the microreactor pyrolysis. When this is added to the conversion obtained in the microreactors the total conversion was much higher than expected from the coal and plastic alone. This also indicated that the solid product should be somewhat reactive in combustion or gasification conditions. TGA proximate of selected residues in the liquefaction residues gave even higher yields. For example, a coal/PE blend reacted at 400°C gave 60% conversion to THF solubles, but the residue contained 90% volatile yield when heated in the TGA. Several other of the liquefaction residues produce similar results. The higher total conversion for the PE and
PP runs based on volatile yields occurred at 400°C and 15 minutes of reaction time. Both blends yield > 95% conversion. Total conversions to volatiles decreased with increasing temperature and reaction time. These results were obtained at the very end of the project and the results are currently being rechecked. These results also suggest that TGA proximate analysis should be conducted on selected residues from the steam and hydrogen pyrolysis runs.

Ultimate Analysis of Extract Residues

Analysis of the extraction residues from the blends obtained in a nitrogen atmosphere indicate a 50 to 70% reduction in sulfur concentration as opposed to the feed coal. Although this reduction is better than the 25-40% obtained in the coal alone it is not enough to meet reduction requirements. The residues from the PP blend were slightly lower in sulfur than from the PE blends. The sulfur content in the residues range from 0.8 to 1.2%. The sulfur in the original coal was 3%. Reduction in the other atmosphere was presumed to be greater. Samples are currently under analysis.

The residues produced in a nitrogen atmosphere were leaner in hydrogen and slightly lower in nitrogen than the raw coal. Average hydrogen contents were about 3.7%. The H/C dropped from .75 to 0.57 during processing. The drop in hydrogen was worse for the residues derived from coal alone than from the blends. The nitrogen in the raw coal was 1.2% The residue nitrogen contents range from 0.7 to 1.13. The nitrogen content of the residue decreases with increasing temperature and the residues derived from the PP blends was lower than the content from the PE blends. The residues from the other three environments are currently being analyzed.

Due to lack of synergisms observed for the nitrogen pyrolysis runs, trace element analysis and surface area analysis were not carried out this year. Some analysis are planned for the liquefaction residues.

Combustion Profiles

The TGA combustion profile obtained on extracted residues of the blends were similar to the raw coal profile. The same burnout temperature was observed. The derivative curve is broader indicating that the residue will not burn as intensely as the coal. The maximum reaction temperature was also slightly higher. However despite these changes the combustibility was good enough that the residue could be burnt without major problems or major equipment modification.
d) Optimization Tests

Several runs were conducted using -20, -100, and -400 mesh whole coal. Typical data are presented in Table 5 for nitrogen pyrolysis of the raw coal a blend of coal and PE. In both cases increasing coal particle size decreased total conversion. The amount of the decrease is about the same for the coal and the blend. This indicates that the effect is due to the interaction of coal products with themselves and not due to a lack of interaction between the plastic and the coal. This effect need to explored further for the other environments.

The effect of blend ratio on total conversion to THF solubles was studied for both PP and PE blends in a nitrogen environment at 425°C and one hour of reaction time. This condition gave the highest conversion of the 1:1 blend in the screening test. The data are listed in Table 6. If the conversion data are plotted versus percent coal in the blend a straight line is obtained. This line is the same as the one that would be obtained by connecting the pure plastic and pure coal points. Thus, there was no indication of synergism for this case. This was expected since the nitrogen pyrolysis data do not indicate any synergisms in conversion to THF solubles. Since this was also true for conversions in the steam and hydrogen cases, one would expect a similar result. On the other hand, there was some unexpected synergism obtained with the combine tetralin-hydrogen environment. A blend ratio study of some of these conditions should be conducted.

Table 7 contains the conversion to THF solubles for pyrolysis of single components and blends in nitrogen at 425 and 475°C. The conversion of coal was nearly constant versus time. There may be a small maximum in conversion between 15 and 30 minutes. The conversion of PE increases with increasing time until all of the recovered product was soluble. PP conversions was nearly 100% after 5 minutes of pyrolysis and actually decrease at longer times. This indicates a tendency toward char formation. The PE blend conversion reaches a constant at 15 minutes of pyrolysis. However, the PP blend gave the highest conversions at short pyrolysis times and decreased after 15 minutes of pyrolysis. Thus, short pyrolysis times seem to be favored for at least some coal plastic blends. The kinetic data for the other three environments are contained Tables 2-4. They also show similar trends. In these environments the pure plastic conversions were inhibited. However, maximum conversion of the blends tend to occur at long times at the lower temperatures or short times at higher temperatures. This indicates that condensation reactions are competitive with conversion reactions. The matrix of conversion conditions needs to be expanded to cover longer times at low temperatures and short times at
CONCLUSIONS AND RECOMMENDATIONS

Summary

A RDF, a cellulose, two coals, and 7 plastic samples were obtained, prepared and characterized. Tests using the TGA and microreactors to study pyrolysis behavior of pure components and blended mixtures of components have been developed. Over 100 TGA, and 341 microreactor tests were conducted. The pyrolysis tests were conducted in 4 environments. The product distributions have been obtained. Product quality has been determined for selected samples. Kinetic studies were conducted for some components and some blends. The effect of coal particle size and coal to plastic ratios on total conversion has been evaluated. Mass balances were obtained for some reactions.

A series of preliminary experiments were performed using a thermogravimetric analyzer (TGA). Key parameters from the TGA profiles were identified and measured. Pyrolysis temperature ranges required for the larger scale microreactor experiments were identified. Most of the plastics have a very narrow temperature range over which they volatilize. The coal looses weight over a 580°C temperature range. The temperatures at which the plastics, paper and RDF volatilize occur at approximately the temperature at which the coal softens and becomes plastic. Mixtures of coal and plastic had higher temperatures of initial weight loss and lower temperature of final weight loss. PE and PP increased the volatile yield of the coal in the TGA environment. Studies on heating rate mixing, catalysts, and blend ratios were conducted. The synergisms observed pass through a maximum with increase heating rate. Mixing was important to weight loss. The catalysts employed had little effect on the pyrolysis yield. Even small amounts of plastics resulted in increased coal conversions.

A series of screening tests were conducted using microreactors. Apparent synergism in nitrogen pyrolysis of coal plastic blends observed in the TGA did not transfer to confined microautoclave tests. Although steam and hydrogen retarded the volatile evolution in pure plastics, the blends gave conversion similar to those obtained in nitrogen. Conversions in the liquefaction environment are generally greater for all pure substances and blends. There are reaction conditions where synergism was observed in soluble conversions occur. In some cases the conversion to solubles are not as extensive as desired, but in these cases the insoluble residues appear to contain large quantities of volatile matter.
Gas yields tend to increase with increase in temperature. The primary gas produced under nitrogen is methane. The presence of steam, hydrogen, and tetralin all inhibit methane formation. Tetralin is the most efficient of these inhibitors.

Conclusions

TGA parameters indicate that the coal and some plastics interact. Coal will increase the temperature at which the plastic will begin to volatilize. The plastic seems to accelerate volatile loss in the coal. Intimate mixing of plastic and coal is required to obtain any synergisms. Only a small fraction of free radicals from plastic react with the coal and that excess free radicals react amongst each other and do not contribute to the coal volatilization. There is competition between volatile forming reactions and char forming reactions in a nitrogen atmosphere. Radical reactions between the co-pyrolyzing materials are thought to be primarily responsible for the observed behavior. The synergism observed in the TGA must be as a result of the formation of unstable but volatile fragments which form insoluble material in a enclosed space. Steam and hydrogen environments do not produce synergisms in the conversion of blends to soluble material. Under liquefaction environments plastic decomposition is severely inhibited. The inhibition provides a longer period for the coal and plastic to interact. The mechanism for the inhibition of the plastic decomposition is not fully understood, but the results lead to increased coal conversion and to higher quality products. The inhibition of methane gas formation and the decomposition of the plastic are related. Coal particle size is important to nitrogen pyrolysis. The effect of particle size seems to be a result of coal conversion and not coal/plastic interactions. Short reaction times are desired to prevent regressive reactions.

Recommendations

Further studies of the reason for the different behavior of similar plastics in coal blends is required for a detailed understanding of the coal plastic interactions. More detailed study of the inhibition in coal/PS blends would also contribute to a better understanding of coal plastic interactions. Additional work is needed to characterize the quality of products produced from the steam and hydrogen pyrolysis. The lack of identified synergisms in conversion to THF solubles may not be taken as a lack of increased desulfurization. The amount of volatile materials in the extract residues from steam and hydrogen pyrolysis needs to be determined. The conditions studied for the conversion of plastic/coal blends should be expanded to include higher
temperatures at short reaction times and lower temperatures at long reaction times. Liquefaction products need to be characterized in more detail. Particle size effects and blend ratios need to be studied in detail for the liquefaction environment.

Although the value for the total conversion to soluble and volatile products under the liquefaction conditions need to be rechecked. The 95% reported here are quite significant. If these yields can be confirmed, they would indicate that the conversion of coal to liquid transportation fuels needs to be revisited. Such conversions are very high considering that no catalysts were used, and the hydrogen partial pressure of 500 psig is low. Upon confirmation of these results several process options should be considered for economic analysis. Some additional laboratory work is required as discussed above, and catalysis of the systems needs to be checked. Additional bench scale tests would need to be conducted to determine gas yield, hydrogen consumption and other key process parameters. On the other hand, if these results are confirmed and the economics look favorable time to commercialization could be very short. That is because all of the equipment needed for large scale application has been developed through the DOE liquefaction program. These results also suggest that long chain aliphatic material in resids may be responsible for the apparent coprocessing synergisms observed in these systems. It may suggest that aliphatic/aromatic solvent mixtures are important in the overall liquefaction mechanism and that appropriately adjusted mixtures might provide a superior liquefaction process.

REFERENCES


Figure 1. Typical TGA Pyrolysis Profile

Figure 2. TGA Pyrolysis Profiles of Illinois No. 6 Coal and Polyethylene
Figure 3a. Onset Temperature
Coal/Plastic Mixtures (1:1)

Figure 3b. Max. Reactivity Temperature
Coal/Plastic Mixtures (1:1)

(A): Coal, (B): Cellulose, (C): Paper
(E): PB, (F): PET, (G): PMP, (H): PP
(I): PE, (J): PS, (K): PVC
Fig. 4 Coal/PP Conversion in TGA and Microreactor Under Nitrogen

![Graph showing weight % converted vs. temperature (C) for Coal/PP conversion.]

Fig. 5 Coal/PE Conversion in TGA and Microreactor Under Nitrogen

![Graph showing weight % converted vs. temperature (C) for Coal/PE conversion.]

Fig. 6 Coal/PS Conversion in TGA and Microreactor Under Nitrogen

- % Insoluble
- % Liquid
- % Gas
- % Conversion
## TABLE 1
Total Conversion Of Individual Components and 1:1 Blends at 60 Minute Reaction Time

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Coal</th>
<th>*PE</th>
<th>*PP</th>
<th>*PS</th>
<th>Coal/PE</th>
<th>Coal/PP</th>
<th>Coal/PS</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>21</td>
<td>35</td>
<td>97</td>
<td>62</td>
<td>13</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>26</td>
<td>55</td>
<td>97</td>
<td>63</td>
<td>57</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>425</td>
<td>27</td>
<td>100</td>
<td>98</td>
<td>64</td>
<td>60</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>450</td>
<td>26</td>
<td>99</td>
<td>99</td>
<td>64</td>
<td>59</td>
<td>55</td>
<td></td>
</tr>
<tr>
<td>475</td>
<td>23</td>
<td>99</td>
<td>94</td>
<td>100</td>
<td>63</td>
<td>60</td>
<td>57</td>
</tr>
<tr>
<td>500</td>
<td>27</td>
<td>89</td>
<td>91</td>
<td>88</td>
<td>54</td>
<td>56</td>
<td>62</td>
</tr>
<tr>
<td>525</td>
<td>31</td>
<td>85</td>
<td>85</td>
<td>83</td>
<td>55</td>
<td>60</td>
<td>57</td>
</tr>
<tr>
<td>550</td>
<td>23</td>
<td>82</td>
<td>79</td>
<td>84</td>
<td>56</td>
<td>54</td>
<td>52</td>
</tr>
</tbody>
</table>

## TABLE 2
Conversion of Individual Components and 1:1 Blends at 15 and 60 Minute Reaction in a Steam Environment

<table>
<thead>
<tr>
<th></th>
<th>425°C</th>
<th>475°C</th>
<th>525°C</th>
<th>425°C</th>
<th>475°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal</td>
<td>24</td>
<td>32</td>
<td>30</td>
<td>25</td>
<td>26</td>
</tr>
<tr>
<td>PE</td>
<td>32</td>
<td>32</td>
<td>35</td>
<td>98</td>
<td>95</td>
</tr>
<tr>
<td>PP</td>
<td>70</td>
<td>70</td>
<td>82</td>
<td>79</td>
<td>70</td>
</tr>
<tr>
<td>PS</td>
<td></td>
<td></td>
<td>89</td>
<td>94</td>
<td>93</td>
</tr>
<tr>
<td>Coal/PE</td>
<td>35</td>
<td>35</td>
<td>50</td>
<td>57</td>
<td>64</td>
</tr>
<tr>
<td>Coal/PP</td>
<td>54</td>
<td>54</td>
<td>50</td>
<td>57</td>
<td>64</td>
</tr>
<tr>
<td>Coal/PS</td>
<td></td>
<td></td>
<td>54</td>
<td>54</td>
<td>54</td>
</tr>
</tbody>
</table>

## TABLE 3
Total Conversion of Individual Components and 1:1 Blends at 5 and 60 Minute Reaction Times in Hydrogen Environment

<table>
<thead>
<tr>
<th></th>
<th>425°C</th>
<th>475°C</th>
<th>525°C</th>
<th>425°C</th>
<th>475°C</th>
<th>525°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal</td>
<td>23</td>
<td>25</td>
<td>20</td>
<td>20</td>
<td>25</td>
<td>24</td>
</tr>
<tr>
<td>PE</td>
<td>25</td>
<td>95</td>
<td>98</td>
<td>97</td>
<td>96</td>
<td>87</td>
</tr>
<tr>
<td>PP</td>
<td>26</td>
<td>99</td>
<td>95</td>
<td>96</td>
<td>87</td>
<td>89</td>
</tr>
<tr>
<td>Coal/PE</td>
<td>32</td>
<td>55</td>
<td>63</td>
<td>50</td>
<td>58</td>
<td>58</td>
</tr>
<tr>
<td>Coal/PP</td>
<td>66</td>
<td>58</td>
<td>60</td>
<td>63</td>
<td>57</td>
<td>58</td>
</tr>
</tbody>
</table>

*PE is Polyethylene, PP is Polypropylene, PS is Polystyrene

*Water at a 1:1 Ratio of Total Charge
### TABLE 4
Total Conversion of Individual Components and 1:1 Blends at 5 and 60
Minute Reaction Times in ♦ Liquifaction Environment

<table>
<thead>
<tr>
<th></th>
<th>15 Minute</th>
<th></th>
<th></th>
<th>60 Minute</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>400°C</td>
<td>425°C</td>
<td>450°C</td>
<td>400°C</td>
<td>425°C</td>
</tr>
<tr>
<td>Coal</td>
<td>55</td>
<td>51</td>
<td>54</td>
<td>52</td>
<td>50</td>
</tr>
<tr>
<td>PE</td>
<td>45</td>
<td>47</td>
<td>79</td>
<td>42</td>
<td>48</td>
</tr>
<tr>
<td>PP</td>
<td>10</td>
<td>14.3</td>
<td>82</td>
<td>39</td>
<td>53</td>
</tr>
<tr>
<td>Coal/PE</td>
<td>48</td>
<td>60</td>
<td>60</td>
<td>44</td>
<td>62</td>
</tr>
<tr>
<td>Coal/PP</td>
<td>61</td>
<td>62</td>
<td>84</td>
<td>79</td>
<td>71</td>
</tr>
</tbody>
</table>

♦ 500 psig Hydrogen and 1:1 Ratio of Tetralin and Charge

### TABLE 5
Effect of Particle Size on the Conversions in Nitrogen of Coal and
Coal/PE Blends to THF Solubles

<table>
<thead>
<tr>
<th>Sieve Size</th>
<th>Coal</th>
<th>Coal/PE</th>
</tr>
</thead>
<tbody>
<tr>
<td>-20</td>
<td>17</td>
<td>50</td>
</tr>
<tr>
<td>-100</td>
<td>21</td>
<td>55</td>
</tr>
<tr>
<td>-400</td>
<td>24</td>
<td>59</td>
</tr>
</tbody>
</table>

### TABLE 6
Total Conversions to THF Solubles of Coal/Plastic Blends at 425°C
for 1 Hour in Nitrogen

<table>
<thead>
<tr>
<th>% Coal in Blend</th>
<th>Coal/PE</th>
<th>Coal/PP</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>27</td>
<td>27</td>
</tr>
<tr>
<td>95</td>
<td>29</td>
<td>28</td>
</tr>
<tr>
<td>90</td>
<td>38</td>
<td>27</td>
</tr>
<tr>
<td>67</td>
<td>42</td>
<td>37.5</td>
</tr>
<tr>
<td>50</td>
<td>64</td>
<td>60</td>
</tr>
<tr>
<td>10</td>
<td>93</td>
<td>92</td>
</tr>
<tr>
<td>0</td>
<td>100</td>
<td>98</td>
</tr>
</tbody>
</table>
TABLE 7
Kinetic Study of Conversions to THF Solubles as Individual Components and 1:1 Blends at 425°C and 475°C for 1 Hour in Nitrogen

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Time (min)</th>
<th>Coal</th>
<th>PE</th>
<th>PP</th>
<th>Coal/PE</th>
<th>Coal/PS</th>
</tr>
</thead>
<tbody>
<tr>
<td>425</td>
<td>5</td>
<td>21</td>
<td>39</td>
<td>98</td>
<td>50</td>
<td>66</td>
</tr>
<tr>
<td>425</td>
<td>15</td>
<td>24</td>
<td>67</td>
<td>97</td>
<td>59</td>
<td>71</td>
</tr>
<tr>
<td>425</td>
<td>30</td>
<td>26</td>
<td>86</td>
<td>98</td>
<td>58</td>
<td>60</td>
</tr>
<tr>
<td>425</td>
<td>60</td>
<td>27</td>
<td>100</td>
<td>98</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>425</td>
<td>120</td>
<td>18</td>
<td>99</td>
<td>80</td>
<td>58</td>
<td>60</td>
</tr>
<tr>
<td>475</td>
<td>5</td>
<td>21</td>
<td>96</td>
<td>99</td>
<td>64</td>
<td>52</td>
</tr>
<tr>
<td>475</td>
<td>15</td>
<td>27</td>
<td>100</td>
<td>91</td>
<td>63</td>
<td>61</td>
</tr>
<tr>
<td>475</td>
<td>30</td>
<td>28</td>
<td>91</td>
<td>96</td>
<td>64</td>
<td>55</td>
</tr>
<tr>
<td>475</td>
<td>60</td>
<td>23</td>
<td>100</td>
<td>94</td>
<td>62</td>
<td>60</td>
</tr>
<tr>
<td>475</td>
<td>120</td>
<td>27</td>
<td>90</td>
<td>95</td>
<td>57</td>
<td>53</td>
</tr>
</tbody>
</table>