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TECHNICAL REPORT

December 1, 1993 through February 28, 1994

Project Title: **ILLINOIS COAL/RDF COPROCESSING TO PRODUCE
HIGH QUALITY SOLIDS AND LIQUIDS**

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ABSTRACT

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. This project will be carried out in a systematic manner. First, samples will be properly selected prepared, preserved and characterized. Then coals, various plastics, cellulose, and a high quality RDF will be pyrolyzed, steam pyrolyzed, hydro-pyrolyzed, and liquefied at various conditions. Next, blends of coal with various RDF components will be reacted under the same conditions. From this work synergistic effects will be identified and process parametric studies will be conducted on the appropriate mixtures and single components. Product quality and mass balances will be obtained on systems showing promise. Preliminary pyrolysis work will be conducted on a TGA. The majority of reactions will be conducted in microautoclaves. If this research is successful, a new market for high sulfur, high mineral Illinois coal would emerge.

Samples needed for this project have been obtained and sample preparation have nearly been completed. A Perkin Elmer TGA-7 Thermogravimetric Analyzer was employed to study pyrolysis. Significant interactions have been observed. Over 100 microreactor experiments have been performed and the acquisition of products for analysis has been achieved. Interactions occur between 400-450°C. The use of higher temperatures should be avoided if liquids are the desired product. Although, these results are preliminary they are also very encouraging.

"U.S. DOE Patent Clearance is NOT required prior to the publication of this document."

MASTER

EXECUTIVE SUMMARY

The primary objective of this project is 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 are 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 XL Recycling, Crestwood, IL 60445. 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.

This project will be carried out in a systematic manner. First, samples will be properly selected prepared, preserved and characterized. Then coals, various plastics, cellulose, and a high quality RDF will be pyrolyzed, steam pyrolyzed, hydro-pyrolyzed, and liquefied at various conditions. Next, blends of coal with various RDF components will be reacted under the same conditions. From this work synergistic effects will be identified and process parametric studies will be conducted on the appropriate mixtures and single components. Product quality and mass balances will be obtained on systems showing promise. Preliminary pyrolysis work will be conducted on a TGA. The majority of reactions will be conducted in microautoclaves.

The United States is producing about 30 million tons of synthetic polymer material every year. 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. Up to 70% of discarded plastic is packaging material. The breakdown of plastics are polyethylene, high and low density, 63%; polypropylene, 9%; polystyrene, 11%; polyvinyl chloride, 5%; poly(ethylene terephthalate), 7%. Utilization of the waste stream plastics and cellulose materials with conversion would significantly reduce the amount of waste reporting to our landfills.

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. If this research is successful, a new market for high sulfur, high mineral Illinois coal would emerge.

This research is significant because it represents the initial step into a virtually unexplored area. 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.

Work Performed

Samples needed for this project have been obtained and sample preparation have nearly been completed.

A Perkin Elmer TGA-7 Thermogravimetric Analyzer was employed to study pyrolysis. A five to ten milligram sample is placed in a weighing pan and the system purged with an inert gas and then heated at 15°C/min in a 50ml/min flow of nitrogen. The char yield was measured at 700°C and at a heating rate of 15°C/min. The char yield obtained from these experiments was $57.2 \pm 0.2\%$. The coal sample was also combusted in an air atmosphere and the combustion profile from TGA-7 reported an average ash value of 2.63%.

Pyrolysis profiles for various coal-plastic (mixed) samples (1:1 weight ratio) were also obtained. 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. All the char yields were measured at 700°C and at a heating rate of 15°C/min.

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 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. 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 hepta hydrated 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 (K_2CO_3) were also studied for catalytic effect on pyrolysis of coal-polyethylene. There was no significant catalytic impact of Potassium carbonate on coal-plastic interactions.

A total of 108 microautoclave runs were conducted this quarter. Of these, about 40 were shakedown runs to work out procedures for sealing, purging, and cleaning the reactors. The remaining tests were conducted to begin the screening tests. After dealing with these operation and training procedures, the techniques to transfer material from the reactors to the extraction thimbles were worked out. The last 60-70 runs have been uneventful and reliable results have been obtained.

The mass balances at the lower temperatures are good, particularly for the coal-component blends. At higher temperatures, the liquid refluxes in the line to the three way valve. Some of this is held in the line and is not recovered as part of the cleaning process. The gas yield varies and has not yet been calculate for the runs. It is estimate to be up to 15% of the charge at the higher temper-

ature and calculated weights will be reported next time. GC analysis carried out thus far show that the plastic is decomposing to methane and more is produced at the higher temperatures. Only a small amount of CO and hydrogen are produced in a nitrogen atmosphere. No gas data is available for the other reaction environments. Water produced during the reaction is lost during the work up procedure. We are currently evaluating how to measure this yield. If the yields from the baseline PE and PP runs are averaged with the yields from the baseline coal run, the resulting averages under predict blend conversion for temperatures below 450°C. At higher temperatures this apparent synergism is not seen. One TGA pyrolysis test was conducted on an extract residue from a PE/Coal blend run conducted at 550°C. It showed the presence of 11% volatile yield remaining after the microreactor pyrolysis. When this is added to the conversion obtained in the microreactors the total conversion is much higher than expected from the coal and plastic alone. This also indicates that the solid product should be somewhat reactive in combustion or gasification conditions. Further evaluations are underway.

Due to the preliminary nature of the results a full data analysis is not available at this time. However, a few points can be made. First, there is evidence of coking at higher temperatures. This is clear for the pure polyethylene and polypropylene runs. Second, Hydrogen runs at low temperature gave a consistent increase in total yield. Third there are some discernible synergisms at lower temperature but this effect is lost at higher temperatures. Large amounts of liquids are being formed at reaction temperatures between 400 and 450°C. Because of the evidence of regressive reactions, shorter reaction times should be studied. We plan to continue the screening studies and start the optimization test next quarter.

OBJECTIVES

Overall Objectives

The primary objective of this project is to investigate the pyrolysis of high volatile Illinois coals with various mixtures of waste plastics and RDF. This is a one year project.

Specific Goals and Objectives

The specific goals and objectives of this study are 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 XL Recycling, Crestwood, IL 60445.
- 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 Tasks

Task 1 Sample Selection and Preparation

Two coals are to be selected. Plastic and RDF Samples are to be obtained. Coals and RDF samples are to be split, ground, sized, and characterized. Some coal sample is to be preoxidized and others precleaned in a semi-continuous centrifuge. Completion of Task 1 will meet the specific objectives described as number 1 and 2.

Task 2 Screening and Yield

To understand the results and identify synergistic effects of co-processing coal/wastes, baseline data for the individual components are to be determined. The seven components will be tested at various processing conditions. After completion of the baseline runs, a blend of 1:1 IBC-101 and the six other components will be tested at the same process conditions. Completion of Task 2 will fulfill specific objectives 3 and 4.

Task 3 Product Quality

The solid char will be characterized with 8 analyses. They are 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 will be 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 will determine the presence or absence of aromatics, aliphatics, and sulfur compounds.

The gaseous products will be characterized by GC-FID/FPD. These tests will determine the presence of CH_4 , CO , CO_2 , H_2S , H_2 , COS , 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 will be blended 1:1 with the various coal samples. These results will determine the effects of particle size and coal pretreatments on product desulfurization, dechlorination, and quality. Synergistic effects on desulfurization will be evaluated.

The coal sample described in the above tests which exhibits the best quality products at the optimum temperature of that run will be blended in a 1:2 and a 2:1 ratio with the six waste components described in Task 2. Runs will be conducted using the best identified process conditions. A kinetic study of the best 12 pyrolysis runs will be conducted at various time durations.

Upon completion of Tasks 3 and 4, specific objective 5, 6, and 7 will have been met.

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 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. Reasonable operating parameters consistent with existing pyrolysis processes will be utilized.

If this research is successful, a new market for high sulfur, high mineral Illinois coal would emerge; market vast enough to encompass a portion of a \$3.7 billion/year market now held by petroleum and binding cokes for activated carbons, nuclear graphites, friction materials, etc. This market share would be determined by the quality of the product. In addition, a substantial market is available not only for the chemical products that are currently being produced from petroleum and natural gas, but also for the low sulfur char as PFB combustion material.

This research is significant because it represents the initial step into a virtually unexplored area. 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 is being 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 are being pyrolyzed, steam pyrolyzed, hydro-pyrolyzed, and liquefied at various conditions. Next,

blends of coal with various RDF components are reacted under the same conditions. From this work synergistic effects will be identified and process parametric studies will be conducted on the appropriate mixtures and single components. Product quality and mass balances will be obtained on systems showing promise. Preliminary pyrolysis work was conducted on a TGA. The majority of the pyrolysis experiments are being conducted in microautoclaves.

Procedures

Sample Preparation

Two Illinois Coal Bank coals have been 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. The coal needed has been obtained.

Mr. Frank Volini, Marketing Manager for XL Recycling, 13701 South Kostner, Crestwood, IL 60445, has provided RDF and waste plastics needed for this project. These samples were received in sealed 5 gallon pails. Pure plastics have been ordered and received.

The IBC 101 coal has been prepared. Samples have been prepared at three particle sizes (-20, -100, and -400 mesh). A portion of -400 mesh coal was cleaned by semi-continuous centrifugation in a 1.6 g/ml cesium chloride solution. About 100 grams of -400 mesh clean IBC-101 was preoxidized with PAA. The preparation of the IBC 109 coal will be completed in the third quarter. RDF samples received from XL recycling have been screened to remove any metals. All plastic and Cellulose samples needed for the project have been received. Only the polystyrene needed to be ground. Sampling of these materials are simpler than for the coal samples because they are pure materials. Characterization of the raw and clean coal has begun and will continue to the end of the project.

TGA Reaction Tests

A Perkin Elmer TGA-7 Thermogravimetric Analyzer was employed to study pyrolysis. A five to ten milligram sample is placed in a weighing pan and the system is purged with an inert gas and then heated at 15°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 ratio 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 a catalyst to study any catalytic effects in the coal and coal-plastic pyrolysis.

Microautoclave Reaction Tests

The majority of this work will be carried out using a microautoclave system, shown schematically in Figure 4.1. The apparatus consisted of a 15-ml stainless steel microautoclave 13 cm long, 2.5 cm O.D. and 1.1 cm I.D. with working pressure up to 15,000 psi. The reactor is linked to one end of a three-way metering valve with working pressure up to 60,000 psi (HIP 30--15HF4) by high pressure tubing (Tu 3) 8" long, 1/16" O.D. and 1/4" I.D. with working pressure up to 60,000 psi (HIP 60-9H4-304). A pressure transducer (PX3--K, from Omega Engineering Inc.), capable of measuring pressure up to 15,000 psi, is connected to the valve by high pressure tubing (Tu 1) 4" long (HIP 60-9H4-304). A pressure read-out device (DP64, from Omega Engineering Inc.) is connected to the pressure transducer, so that the pressure of the reaction could be monitored. Another segment of high pressure tubing (Tu 2) 10" long (HIP 60-9H4-304) with a quick disconnect fitting attached is placed to the other connection of the three-way valve so that any inlet or outlet gas could flow through.

A fluidized-bed sand bath (Tecam Fluidized Bath SBL--2, from Techne Inc.) is employed as the heating source and the temperature controlling device of the reaction system. The heating coil located at the bottom of the sand bath provides the heat. The sand in the sand bath is fluidized by air flow through the air flow pipe to the bottom of the sand bed. The air flow rate is controlled by an air control valve (V1) so that the sand can be fluidized at a proper level. The temperature of the sand bath is controlled by an Omega on-off temperature controller (Model 149) through detection by a k-type thermocouple (Omega Engineering Inc.). Generally, the temperature fluctuates within a range of 3°C over about a half minute to one minute period depending upon the reaction temperature. A metal cover is placed on the top of the sand bath so that entrained sand would not scatter around the bath. This also provides an insulating barrier for the pressure transducer and reduced the heat load on the bath. There is a small slit between the center and the side of the metal cover that the tubing connecting the microautoclave could pass through.

Before the reaction, the microautoclave is first flushed with nitrogen by alternate pressurization/depressurization to remove any oxygen present. The reactor is then charged with the desired amount of reactants. After pressurization with nitrogen to 600 psi, the valve is closed and leak

testing with soap water is performed. If the reactor system passes the leak test, the three-way valve is then opened slowly to reduced the pressure to ambient.] If another reactant gas is to be used (hydrogen) the gas is then delivered via a manifold to the reactor. Then the three-way valve is closed. The sand bath is preheated to 25 degrees above the desired reaction temperature before the microautoclave is put into the bath. The reactors are held by a Burrell wrist action shaker and the sand baths are raised to the reactor by means of a mechanical jack.

During the reaction, the whole body of the microautoclave along with part of the connecting tube is submerged into the fluidized-bed sand bath.

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

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

RESULTS AND DISCUSSION

TGA pyrolysis and co-pyrolysis

Micronized DGC floated IBC 101 coal was pyrolyzed in nitrogen atmosphere in a Perkin Elmer TGA-7. The char yield was measured at 700°C and at a heating rate of 15°C/min. The char yield obtained from these experiments was $57.2 \pm 0.2\%$. The coal sample was also combusted in an air atmosphere and the combustion profile from TGA-7 reported an average ash value of 2.63%.

Pyrolysis profiles for various coal-plastic (mixed) samples (1:1 weight ratio) were also obtained. 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. All the char yields were measured at 700°C and at a heating rate of 15°C/min.

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 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. 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 ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) 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 (SO_3) is liberated between 535-640°C leaving behind Ferrous oxide (FeO).

Iron sulfate hepta hydrated 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 (K_2CO_3) 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.

Microreactor studies

A total of 108 microautoclave runs were conducted this quarter. Of these about 40 were shake down runs to work out procedures for sealing, purging, and cleaning the reactors. The remaining tests were conducted to begin the screening tests.

In the beginning, 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 temperature lubricant. Also the caps were designed in such a way the product could get into crevices. This presented material 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 Aluminum plug. Next some ceramic cement was used to seal off 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 bottom 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 reaction temperature. The bulk of the reactor is sufficient to cause a decrease in bath temperature and rewarming the bath at the higher reaction temperature can take an appreciable amount of time. So, the sand bath is brought above the desired reaction temperature. After the temperature drop when the reactor is added, the temperature controller is reset to the desired reaction temperature. Thus, the reactor temperature increases for 2-3 minutes and then is maintained 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. Now reaction pressure is only recorded after the reactors have cooled. This has improved operations and recoveries. Some time dependent pressure information is lost, but the new approach saves the transducer from exposure and recalibration is avoided.

These runs were also used to develop the gas sampling procedure. The evacuation of the gas sampling bag was found to be necessary. A tee line is connected to the air inlet valve of vacuum oven. The other legs of the tee are connected to the gas bag and the quick disconnect fitting on the three way reactor valve. The bag and line are then evacuated through the vacuum oven. The line to the vacuum oven is then closed and the three-way valve is opened. The gas in the reactor fills the bag and air contamination is avoided. It was found that bags containing a separate septum were ideal for GC analysis which is now being performed on a majority of the runs.

Another problem arose in adjusting the air flow requirements. As the temperature in the bath is changed the air flow requirements must be adjusted to permit proper fluidization. Several of the operators did not appreciate this fact and several components in the electrical systems and the elements overheated. These were replaced. Another set of elements broke when one of the reactors leaked as a result of the threads backing off during heat-up. The reactor contents coked sand onto the element and the element fused with the coke and sand causing a break. Some leaks also developed in the three-way valve when the heat shield was not properly employed. This resulted in the valves needing to be repacked.

After dealing with these operation and training procedures, the techniques to transfer material from the reactors to the extraction thimbles were worked out. The last 60-70 runs

have been uneventful and reliable results have been obtained.

A summary of the screening results to date is contained in Tables 1-3. The Yield is defined as the sum of extract and residue weight 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 % THF soluble is defined as weight of the THF extract divided by the original sample weight times 100. The fraction THF, toluene, and pentane sums to the THF solubles. The column labeled gas and light hydrocarbons is the % conversion minus the % THF soluble. Not all of the extraction procedures are complete. Thus, the tables contain many blanks, but contain all the information on what runs are completed up to the analysis step. Table 1 contains data for RDF and its components. Table 2 contains data for mixtures of coal and RDF components. Table 3 contains data for baseline coal runs. The run description is coded. RDF and PVC are self explanatory. PS is polystyrene, PP is polypropylene, PE is polyethylene, and cell is cellulose. The second code stands for the reaction gas environment, and the third code is the reaction temperature. All runs were 2 gram charges. The blends are one part coal and one part RDF components.

The mass balances at the lower temperature are good, particularly for the coal-component blends. At higher temperatures, the liquid refluxes in the line to the three way valve. Some of this is held in the line and is not recovered as part of the cleaning process. The gas yield varies and has not yet been calculated. It is estimate to be up to 15 % of the charge at the higher temperatures and calculated weights will be reported next time. GC analysis carried out thus far show that the plastic is decomposing to methane and more is produced at the higher temperatures. Only a small amount of CO and hydrogen are produced in a nitrogen atmosphere. No gas data is available for the other reaction environments. Water produced during the reaction is lost during the work up procedure. We are currently evaluating how to measure this yield. If the yields from the baseline PE and PP runs are averaged with the yields from the baseline coal run, the resulting averages under predict blend conversion for temperatures below 450°C. At higher temperatures this apparent synergism is not seen. One TGA pyrolysis test was conducted on an extract residue form PE/Coal blend runs at 550°C reaction temperature. It showed the presence of 11% volatile yield remaining after the microreactor pyrolysis. When this is added to the conversion obtained in the microreactors the total conversion is much higher than expected from the coal and plastic alone. This also indicates that the solid product should be somewhat reactive in combustion or gasification conditions. Further evaluations are underway.

Conversions in the TGA at various temperatures are listed in Table 4 for coal, PE, PP, coal/PE mixture and coal/PP mixture. These data are plotted with the microreactor data in Figures 2-6. The plots are of % conversion versus temperature. The TGA data is a kinetic yield while the microreactor data represents a long time conversion. Yet, the coal conversion in the microreactor appears to be retarded. Conversion of the plastic gives a more expected trend. The microreactor conversion are higher at the lower temperatures. However some evidence of regressive reaction is obvious at the higher temperatures. A similar pattern is noted with the blends. The PE blend gave slightly higher yield than the PP blend. Evidence of regressive reaction is seen at temperature as low as 425°C for the PP blend. The above results indicate that shorter reaction times should be explored. The more reactive steam and hydrogen atmosphere are expected to give significantly higher conversions.

CONCLUSIONS AND RECOMMENDATIONS

Due to the preliminary nature of the results a full data analysis is not available at this time. However, a few points can be made. First, there is evidence of coking at higher temperatures. This is clear for the pure polyethylene and polypropylene runs. Second, Hydrogen runs at low temperature gave a consistent increase in total yield. Third there are some discernible synergisms at lower temperature but this effect is lost at higher temperatures. Large amounts of liquids are being formed at reaction temperatures between 400 and 450°C. Because of the evidence of regressive reactions, shorter reaction times should be studied. We plan to continue the screening studies and start the optimization test next quarter.

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TABLE 1. BASELINE RUNS FOR PLASTICS CELLULOSE AND RDF RUNS TO DATE

Run	TEMPERATUR	YIELD	COVERSIO	% THF	THF	TOLUENE	PENTANE	GAS AND
Description		%	%	SOLUBLE	FRACTIO	FRACTIO	FRACTIO	LIGHT HC
RDF/N2/355	355	55.53	68.5	43.2	27.0	10.5	5.7	25.3
RDF/H2/350	350	54.50	69.5	44.0	32.8	7.3	3.6	25.5
RDF/H2/350	350	60.50	65.5	43.0	25.6	13.8	3.6	22.5
PVC/H2O/350	350							
PS/N2/525	525							
PS/N2/500	500							
PS/N2/450	450							
PS/N2/450	450							
PS/N2/350	350							
PS/N2/350	350	36.02	97.7	93.5	0.3	61.3	31.8	4.2
PS/H2/350	350	116.50	94.2	95.0	9.4	78.1	6.9	-0.8
PP/N2/525	525							
PP/N2/500	500		90.3					
PP/N2/475	475							
PP/N2/450	450							
PP/N2/450	450		99.0					
PP/N2/425	425		98.7					
PP/N2/400	400		97.7					
PP/N2/400	400							
PP/H2/350	350	139.78	-11.3	20.4	7.9	7.4	5.1	-31.7
PP/H2O/350	350	83.40	30.1	16.2				13.9
PP/H2O/350	350							
PE/tetralin/H2/35	350	114.70	17.8	28.3	10.9	12.5	4.9	-10.5
PE/N2/520	520		84.4					
PE/N2/500	500							
PE/N2/475	475							
PE/N2/475	475	14.16	99.0	92.8				5.2
PE/N2/450	450							
PE/N2/450	450	23.98	98.4	93.2	22.1	28.6	42.5	5.2
PE/N2/450	450	46.00	99.1	98.0	1.1	19.1	78.6	1.1
PE/N2/450	450							
PE/N2/425	425		99.6					99.6
PE/N2/400	400	107.52	54.5	57.7				-3.2
PE/N2/350	350							
PE/N2/350	350							
PE/H2/350	350	112.82	20.7	29.7	20.4	3.0	6.3	-9.0
PE/H2O/350	350							0.0
cell/N2/450	450	51.92	63.1	28.9				34.2
cell/N2/350	350	35.50	66.9	6.9	0.9	2.2	3.8	60.0

TABLE 2. RUNS FOR BLENDS OF COAL AND WASTE FEEDSTOCK COMPONENTS

Run	TEMPERATUR	YIELD	COVERSIO	% THF	THF	TOLUENE	PENTANE	GAS AND
Description		%	%	SOLUBLE	FRACTIO	FRACTIO	FRACTIO	LIGHT HC
coal/RDF/N2/450	450	82.50	33.8	19.7				14.1
coal/RDF/N2/350	350	98.50	19.0	17.8				1.2
coal/PS/N2/525	525		56.8					56.8
coal/PS/N2/500	500							
coal/PS/N2/475	475							
coal/PS/H2O/350	350	80.43	38.6	23.6	15.5			15.0
coal/PP/N2/550	550	53.82	53.9	14.3				39.6
coal/PP/N2/550	550	52.53	50.4	5.6				44.8
coal/PP/N2/525	525	41.04	62.6	9.0				53.7
coal/PP/N2/525	525	44.99	60.1	11.3				48.8
coal/PP/N2/500	500	55.82	52.5	14.9				37.6
coal/PP/N2/500	500	45.17	57.9	6.9				51.1
coal/PP/N2/475	475	57.38	47.6	8.7				38.9
coal/PP/N2/450	450	53.96	55.3	17.2				38.1
coal/PP/N2/425	425	61.75	59.2	33.9	10.8	11.1	12.0	25.3
coal/PP/N2/400	400	73.80	60.4	46.4				14.0
coal/PP/N2/350	350	95.94	13.1	9.4	1.5	5.9	2.0	3.7
coal/PP/N2/350	350	78.00	30.3	10.7	3.6	2.2	4.9	19.6
coal/PE//N2/350	350	45.00	62.2	15.9	7.9	3.5	4.5	46.3
coal/PE/N2/533	533	56.25	54.3	18.8	12.9	2.2	3.7	35.5
coal/PE/N2/525	525	69.73	54.8	35.1	10.0	22.1	3.0	19.6
coal/PE/N2/500	500	61.32	54.2	25.3	14.9	2.3	8.1	28.9
coal/PE/N2/500	500	61.20	65.5	43.7	34.5	5.4	3.8	21.8
coal/PE/N2/475	475	71.32	61.5	46.0	35.5	5.4	5.0	15.5
coal/PE/N2/455	455	67.04	58.4	38.0	13.7	4.3	20.0	20.4
coal/PE/N2/450	450	74.67	62.0	49.1	15.9	7.5	25.8	12.9
coal/PE/N2/435	435	97.52	51.4	50.2	13.5	3.8	32.9	1.2
coal/PE/N2/425	425	86.38	63.9	58.2	23.9	6.5	27.9	5.7
coal/PE/N2/425	425	70.20	59.8	42.7	13.5	4.1	25.1	17.1
coal/PE/N2/406	425	67.54	44.0	17.0	7.4	0.0	11.6	26.9
coal/PE/H2O/350	350	82.04	58.5	49.4	1.8	36.4	11.2	9.1

TABLE 3. BASELINE RUNS FOR IBC 101 COAL

Run	TEMPERATUR	YIELD	COVERSIO	% THF	THF	TOLUENE	PENTANE	GAS AND
Description		%	%	SOLUBLE	FRACTIO	FRACTIO	FRACTIO	LIGHT HC
coal/N2/525	525	71.46	30.5	2.7				27.8
coal/N2/500	500	87.48	26.8	16.3				10.5
coal/N2/475	475	81.06	22.3	4.2				18.1
coal/N2/450	450	87.18	25.6	14.7				10.9
coal/N2/425	425	85.60	26.4	14.0				12.4
coal/N2/400	400	112.11	9.0	18.8				-9.8
coal/H2/350	350	118.09	-2.6	13.1	4.7	6.4	2.1	-15.7
coal/H2O/500	500							
coal/H2O/450	450	73.14	27.4	0.7				26.7
coal/H2O/350	350	102.00	23.5	25.0	16.1	6.3	2.1	-0.5

TABLE 4. CONVERSION IN TGA UNDER NITROGEN
(COAL:PLASTIC 1:1)

Sample	Coal	PE	PP	Coal/PE	Coal/PP
Temperature					
300	10.6	1.4	0.6	2.4	1.6
325	11.3	2.2	0.7	3.1	1.9
350	12.1	3.7	1.0	4.0	2.5
375	13.5	6.6	1.6	5.3	3.4
400	16.0	12.5	3.0	6.9	5.0
425	20.2	24.8	6.9	9.9	9.1
450	26.2	49.5	21.7	16.2	18.5
475	32.5	94.8	71.6	36.0	50.9
500	36.9	100.0	100.0	68.1	66.5
525	39.5	100.0	100.0	70.0	67.8
550	41.3	100.0	100.0	70.9	68.6

PE : Polyethylene

PP : Polypropylene

SB, sand bath; TC, on-off temperature controller;
 PR, pressure read-out; PT, pressure transducer;
 V, three-way valve; V1, air control valve;
 R, micro-reactor; T, thermocouple; H, heating source wire;
 A, air flow pipe; Cover, metal cover of the sand bath;
 Tu 1, tubing connecting V and PT; Tu 2, exhaust tube;
 Tu 3, tubing connecting V and R.

FIG. 1 SCHEMATIC DIAGRAM OF MICROREACTOR SYSTEM USED IN THE COAL/PLASTIC PYROLYSIS.

FIG. 2 COAL CONVERSION IN TGA AND AUTOCLAVE UNDER NITROGEN

FIG. 3 POLYETHYLENE CONVERSION
IN TGA AND AUTOCLAVE UNDER N₂

FIG. 4 POLYPROPYLENE CONVERSION
IN TGA AND AUTOCLAVE UNDER N₂

FIG. 5 COAL/PE CONVERSION
IN TGA AND AUTOCLAVE UNDER N₂

FIG. 6 COAL/PP CONVERSION
IN TGA AND AUTOCLAVE UNDER N₂

PROJECT MANAGEMENT REPORT

December 1, 1993 through February 28, 1994

Project Title: ILLINOIS COAL/RDF CO-PROCESSING TO PRODUCE
HIGH QUALITY SOLIDS AND LIQUIDS

DOE Grant Number: DE-FC22-92PC92521 (Year 2)
ICCI Project Number: 93-1/1.1B-2M
Principal Investigator: E. J. Hippo
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Project Manager: Dan Banerjee, Illinois Clean Coal
Institute

COMMENTS

Projected and Estimated Expenditures by Quarter

Quarter*	Types of Cost	Direct Labor	Fringe Benefits	Materials & Supplies	Travel	Major Equipment	Other Direct Costs	Indirect Costs	Total
Sept. 1, 1993 to Nov. 30, 1993	Projected	10,652	3,218	1,437	0	0	2,825	1,813	19,945
	Estimated	3,800	567	737	0	0	1,512	661	7,277
Sept. 1, 1993 to Feb. 28, 1994	Projected	21,304	6,436	2,874	0	0	5,650	3,626	39,890
	Estimated	14,607	1,986	1,575	0	0	2,470	2,064	22,702
Sept. 1, 1993 to May 31, 1994	Projected	31,955	9,654	4,312	0	0	8,475	5,440	59,836
	Estimated								
Sept. 1, 1993 to Aug. 31, 1994	Projected	49,113	14,096	5,750	1,000	0	11,300	8,126	89,385
	Estimated								

*Cumulative by Quarter

COSTS BY QUARTER

Illinois Coal/RDF Co-Processing to Produce High
Quality Solids and LiquidsCumulative \$
(thousands)

O = Projected Expenditures -----

 Δ = Estimated Actual Expenditures _____

Total Illinois Clean Coal Institute Award \$89,385

SCHEDULE OF PROJECT MILESTONES

Milestones:

- A. Sample preparation (Task 1).
- B. Screening and yields (Task 2).
- C. Product quality (Task 3).
- D. Optimization (Task 4).
- E. Reporting.

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**DATE
FILMED**

6 / 29 / 94

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