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TECHNICAL REPORT
March 1, 1994 through May 31, 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 been completed. A Perkin Elmer TGA-7 was employed to study pyrolysis. Significant interactions have been observed. About 200 microreactor experiments have been performed and the acquisition of products for analysis has been achieved. Interactions occur between 400-450°C. Synergism occurs at short reaction times. High temperature and long reaction times result in higher residue yields and a loss of synergisms. Reactive species may be required to stabilize intermediate products.

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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 terphthalate), 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 behavior of coal blended with waste plastics, RDF, and cellulose. TGA profiles can be used to identify a number of characteristic parameters. This includes the weight loss onset temperature, the temperature of maximum rate of weight loss, the temperature of char formation, the temperature range of volatilization, and the volatile/char yields. The temperatures at which the plastics, paper and RDF volatilize occur at approximately the temperature at which the coal softens.

Coal/waste blends were co-pyrolyzed. Characteristic temperatures of the mixtures varied widely and were often different from those of either single components. This strongly suggests that significant interaction between the components occurred. Certain polymers interacted with coal to increase the distillation yield. This is most evident with polypropylene. In addition, it was found that coal/polypropylene ratios of 10:1 gave almost the same amount of coal conversion as a coal/polypropylene ratio of 1:2. Thus, only small amounts of waste plastic are needed for coal conversions. When other substances are added to the coal the volatilization of the coal occurs over a smaller temperature range. 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. Unmixed samples (1:1 weight ratio) of coal-polyethylene and coal-polypropylene were also pyrolyzed. Coal was placed at the bottom and plastic at the top. There was no interaction between plastic and coal. Plastics were placed at the bottom and the coal at the top. This also showed no significant interaction between coal and plastics. Thorough mixing of

coal and plastics is important for any significant interaction. Heating rates of 5, 10, 12.5, 15, 25, and 50°C/min. were used. At the 15°C/min. heating rate the coal-plastic interaction is also maximum. Temperature of maximum reactivity increases almost linearly with the heating rate.

To provide sufficient sample to allow the determination of product quality it was necessary to design a microreactor system so that gram quantities of each sample could be handled. A total of 200 microautoclave runs have been conducted to date. Of the 200 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 tests.

A summary of the screening results to date is described below. The percent insoluble is 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 is the total conversion minus the % liquid yield. However, this value is a composite of gas and distilled liquids which are being trapped in the connection tube.

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 is estimated to be about 15 % of the charge at the higher temperatures. 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 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.

Total conversions of various single materials at various temperatures follow expected trends. A constant coal yield was obtained at all temperatures. The plastic yields are very high at lower temperatures but decrease at higher temperatures. Coal conversion is also independent of time except at high temperature where conversion decreases.

Total conversions of 1/1 coal-plastic blends at 425 and 475°C decreases with increasing time. The shortest time run give the largest yields. Also the tests at 425°C give slightly higher yields than the tests conducted at 475°C. The conversions with polypropylene show this effect more dramatically than the conversions with polyethylene. Shorter reaction times are required to avoid the recombining of light products with the solid residue. The conversion at 425°C for 5 minute reaction times are similar to those obtained in the TGA. This leads to the conclusion that the plastics lead to the formation of reactive coal derived intermediates. In the presence of light product these intermediates can convert to less soluble products. However, if a reactive, light material such as methanol or hydrogen were present, the decrease in conversion with time might be overcome.

Results of some steam pyrolysis tests are reported Figure 8. Increased conversions in steam over the equivalent pyrolysis condition are only seen for a few blends. The increased yields are only 5% at best. For most of the coal and pure plastic runs steam is a detriment to total conversion. The increase yields may not justify the increase in operating pressure required by the steam. The data does indicate that the steam may be somewhat effective in stabilizing intermediates.

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. 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 were explored and were found to be beneficial. There is evidence of reactive intermediates which can coke or be stabilized by steam. Lower temperatures and shorter reaction time lead to larger conversions and increase heavy liquid yields. Gas and light liquid yield are favored at higher temperatures. Synergistic interactions obtained in the TGA can be repeated at short reaction times in the microreactors. The small increases in conversion of blends obtained with steam may not justified the increase pressure requirements.

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 were 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 was 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 were simpler than for the coal samples because they were 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. 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 can 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 can 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 (i.e. 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 galling 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 scrubbed 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 are 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

Microreactor studies

A total of 200 microautoclave runs have been conducted to date. About 100 were conducted this quarter. Of the 200 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 tests.

A summary of the screening results to date is described below. The percent insoluble is 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 being trapped in the connection tube.

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 estimated 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 from 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.

Figure 1 reports total conversions of various single materials at various temperatures during a one hour standard

reaction time. In general, a constant coal yield of about 25% was obtained at all temperatures. The plastic yields are very high at lower temperatures but decrease at higher temperatures due to increase char formation. These trends are expected. The total conversions will be used to judge synergisms.

Figure 2 reports total conversions of single materials at 425°C during various times. Coal yields increase with time through 1 hour but decrease drastically after 2 hours of pyrolysis. Polyethylene and polypropylene show an odd behavior with the conversion dropping between 5 and 15 minutes of reaction and then yield increasing up to 1 hour. Polyethylene gave a smaller conversion after 2 hours of reaction which is probably due to char formation. The low yield from the 15 minute tests appears to be the result of some preliminary crosslinking which is reversible. The trend appears to be real as it occurs in the coal plastic blend tests (Figure 4).

Figure 3 reports total conversions of single materials at 475°C during various times. At this temperature total conversion appears to be independent of time except for the initial coal pyrolysis. Figure 4 reports total conversions of 1/1 coal-plastic blends at 425 and 475°C during various times. Besides the large dip at 15 minutes, the total conversion decreases with increasing time. The shortest time run give the largest yields. Also the tests at 425°C give slightly higher yields than the tests conducted at 475°C. The conversions with polypropylene show this effect more dramatically than the conversions with polyethylene. These data indicate that the phenomena observed with the pure plastics remains or is amplified in the presence of coal derived intermediates. Also, shorter reaction times are required to avoid the recombining of light products with the solid residue. The conversion at 425°C for 5 minute reaction times are similar to those obtained in the TGA. Combining the TGA results from the first quarter with the microautoclave results leads to the conclusion that the plastic lead to the formation of reactive coal derived intermediates. In the presence of light product these intermediates can convert to less soluble products. However, if a reactive, light material such as methanol or hydrogen were present the decrease conversion with time might be overcome. If the phenomena is a result of competitive depolymerization and condensation reactions yields high than those seen in the TGA might be possible. At the very least low temperature short time runs will produce synergistic conversion levels.

Figure 5 shows a crude breakdown of the product distribution from the pyrolysis of coal/polyethylene blends. The liquid yield containing mostly of the asphaltenes and pre-asphaltenes decreases with increasing temperature. The gas yields is 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 6) and coal/polystyrene blends (Figure 7).

Results of some steam pyrolysis tests are reported Figure 8. Increase conversions in steam over the equivalent pyrolysis condition are only seen for a few blends. The increase yields are only 5% at best. For most of the coal and pure plastic runs steam is a detriment to total conversion. Although this is an interesting phenomena, the small increase in conversion of the blend would not justify the increase in operating pressure required by the steam. The data does indicate that the steam may be somewhat effective in stabilizing intermediates. Some 5 minute tests at 3 temperatures will be conducted for the blends to determine the effect of the steam at short time. Also higher temperatures may be required to see the effect of the steam. Thus, some tests will also be conducted at 550°C.

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 reactive intermediates which can coke or be stabilized by steam. Lower temperatures and shorter reaction time lead to larger conversions and increase heavy liquid yields. Gas and light liquid yield are favored at higher temperatures. Second, synergistic interactions obtained in the TGA can be repeated at short reaction times in the microreactors. The small increases in conversion of blends obtained with steam may not justify the increase pressure requirements.

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FIG 1 Total Conversions for Single Materials at Variable Temperatures for 1 Hour Pyrolysis

FIG 2 Total Conversions for Single Materials for Variable Times at 425°C

FIG 3 Total Conversion of Single Materials for Variable Times at Constant Temperature of 475°C

FIG 4 Total Conversions for 1:1 Coal/Plastic Blends for Variable Times at 425 and 475°C

FIG 5 Product Distributions for Coal/Polyethylene Blends (1:1)
Reacted at Various Temperatures for 1 Hour

FIG 6 Product Distributions for Coal/Polypropylene Blends (1:1)
Reacted at Various Temperatures for 1 Hour

FIG 7 Product Distributions for Coal/Polystyrene Blends (1:1) Reacted at Various Temperatures for 1 Hour

FIG 8 Comparison of Total Conversions of Various Single and Blend Materials Under Variable Reaction Conditions

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PROJECT MANAGEMENT REPORT**March 1, 1994 through May 31, 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	30,688	6,299	2,706	0	0	5,053	4,475	49,221
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 Liquids**

Cumulative \$
(thousands)

Months and Quarters

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.

**DATE
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