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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. Very preliminary microreactor experiments have been performed and the acquisition of some products for analysis has been achieved. Although, these results are preliminary they are also very encouraging.

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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 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 150C /min in a 50ml/min flow of nitrogen. To investigate the pyrolysis behavior of coal blended with waste plastics, RDF, and cellulose, a series of preliminary experiments have been performed using a thermogravimetric analyzer (TGA). In this way pyrolysis temperature ranges required for the larger scale microreactor experiments can be identified and any potential problems identified ahead of time. 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 float-ed, low ash IBC-101 coal.

TGA plots the weight loss of a sample as a function of temperature. In addition, the first derivative of the weight loss curve is plotted. These profiles can be used to identify a number of characteristic parameters that help describe the pyrolysis behavior of the material under investigation. 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. 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 had a char yield of some 63% under the same conditions. In addition, most of the plastics had a very narrow temperature range over which they volatilize, while the coal lost 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 of the weight loss curve. The PVC sample shows two peaks. This is 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.

Coal/waste blends were co-pyrolyzed under the same conditions as the individual materials and the weight loss profile obtained as above. 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. There was a general shift to higher temperatures in the mixtures. It appears that the presence of the coal is retarding the evolution of volatile matter generated by the pyrolyzing polymer. 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.

From the char yield it is possible to estimate the conversion of coal to volatile materials. Increases in the conversion of coal to volatile matter are desirable for the formation of liquid fuels, coal tar pitches 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.

Certain polymers interacted with coal to increase the distillation yield. This is most evident with polypropylene and polyvinyl chloride. Thus when these 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. Further studies of this behavior are necessary before a detailed explanation will be possible.

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. This clearly demonstrates that only small amounts of waste plastic may be needed for coal conversions. Polystyrene on the other hand leads to a lower volatile yield, hence higher char yield.

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.

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. The microreactor system developed consists of a 20ml stainless steel reactor closed at one end but open to a three-way valve at the other. The other connections to the three way valve incorporate a gas sampling device to acquire gas samples, a 2000 psi safety valve, a pressure transducer for continuous pressure monitoring, and a quick-connect assembly for easy gas charging. This microreactor design is currently being 'shaken down.'

Very preliminary microreactor experiments have been performed and the acquisition of some products for analysis has been achieved. At this time the best method for product recovery, contaminant avoidance and reactor quenching are being evaluated. To date a sample of polystyrene heated to 450°C for 1 hour has the appearance and behavior of a pitch sample, a similarly treated polypropylene sample shows clear evidence for the development of aromatic or alkene units in its NMR spectrum and a coal/polyethylene 1:1 mixture heated the same way is completely soluble in THF. Although, these results are preliminary they are also very encouraging.

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 copyrolysis 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 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 terphthalate), 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 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 condi-

tions. 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 the pyrolysis experiments will be 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. The preparation of the IBC 109 coal has been postponed until it is needed. As-received IBC 101 coal was 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 is mixed with 10 liters of cesium chloride solution containing brij. The slurry is then ultrasonicated for 15 minute to disperse the coal particles. It is then pumped to the CEPA Coal Padburg semi-continuous centrifuge at a 100ml/min flow rate. The centrifuge is brought up to speed prior to this and a pure cesium chloride solution is pumped into the rotor to assure that the path way is clear and the rotor is balanced. Particles greater than 1.6g/ml apparent density are pushed to the wall while lighter particles elute at the top of the rotor and are caught in a set of pans and a beaker. At the end of the run the rotor is flushed with pure chase solution of the same density as the separation medium. The rotor is then stopped and the solids are removed. The overflow is filtered and washed with hot water and dilute hydrochloric acid solution to remove and recover cesium. A similar procedure is conducted of the solids retained in the rotor. These samples are 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 each of IBC-101 was ground to -20 and -100 mesh. Characterization of the raw and clean coal will be conducted along with product samples.

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 will be conducted along with reacted products. All coal samples are being stored under nitrogen until needed.

RDF samples received from XL recycling underwent additional screening to remove any metals.

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 is stored in various size fractions between -100 and -400 mesh. Because all the plastic are homogeneous materials there is no need to worry about sampling problems. If polystyrene turns out to be an active component the effect of particle size of the polystyrene will be explored. Characterization of these samples will be conducted along with reacted products. All other plastics, were difficult to grind and were chopped into smaller pieces.

A 500 gram, pure cellulose sample was also obtained from Aldrich. It arrived in powdered form. Characterization of this sample will be conducted along with reaction products.

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 150C /min in a 50ml/min flow of nitrogen.

The microreactor procedure will be discussed in detail in the next report.

RESULTS AND DISCUSSION

TGA pyrolysis and co-pyrolysis

To investigate the pyrolysis behavior of coal blended with waste plastics, RDF, and cellulose, a series of preliminary experiments have been performed using a thermogravimetric analyzer (TGA). In this way pyrolysis temperature ranges required for the larger scale microreactor experiments can be identified and any potential problems identified ahead of time. 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 float-
ed, low ash IBC-101 coal.

a) Pyrolysis of individual materials.

To determine the nature of any interactions between co-pyrolyzing materials it is first necessary to study the pyrolysis behavior of the individual components of the co-pyrolyzing system. A typical pyrolysis profile is shown in Figure 1. This figure plots the weight loss of a sample as a function of temperature. In addition, the first derivative of the weight loss curve is plotted. These profiles can be used to identify a number of characteristic parameters that help describe the pyrolysis behavior of the material under investigation. This includes 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_{py}), and the volatile/char yields. It should be noted that the onset temperature reflects the temperature at the initiation of weight loss and does not necessarily indicate the temperature at onset of pyrolysis. This is because 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_{py}) 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.

From Table 1 it can be seen that with the exception of PVC and PET, all the plastics are completely volatilized, leaving no char yield. The coal sample however has a char yield of some 63% under the same conditions. In addition, most of the plastics have a very narrow temperature range over which they volatilize. This is in sharp contrast to the coal which continues to loose 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 of the weight loss curve. The PVC sample shows two peaks. This is evidence for a two stage degradation involving the initial elimination of HCl followed by the pyrolysis of the remaining carbon backbone. It is interesting that 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. Figures 2-5 show the pyrolysis profiles for coal blended with polypropylene, polyethylene, polystyrene and polyvinyl chloride respectively. In each figure the pyrolysis profiles for the individual components are also shown. Comparison of the pyrolysis profiles for the mixtures (1:1) with those of the corresponding pure components suggests that an interaction between the components takes place during the thermal treatment. One could have expected each component to pyrolyze independently, in which case the pyrolysis profiles of the mixtures would simply be those of the components added together. In this scenario we would still observe the characteristic temperatures (T_{on} , T_{max} , T_{char}) for each component superimposed over each other. The fact that we observe only one T_{on} , T_{max} and T_{char} , at values often widely different from either single component, strongly suggests that the mixture is pyrolyzing as a single substance. If the sample has truly become a single substance during the thermal treatment then 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 Figure 6a and 6b, it can be seen that 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. It is as if the presence of the coal is retarding the evolution of volatile matter generated by the pyrolyzing polymer. However, this can be viewed alternatively with the argument that the plastic is retarding 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.

Of course, the reason for investigating the co-pyrolysis of waste materials with coal is to determine if useful fuels or advanced materials can be made. While the measurement of the characteristic co-pyrolysis temperatures from a pyrolysis profile may go a long way to establishing whether an interaction is taking place, it does not provide detailed information pertaining to the quantity or quality of any products that may be formed.

Although, the quality of the co-pyrolysis products can not be adequately evaluated from a TGA pyrolysis profiles, some indications of the yields of useful materials 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 pitches 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.

The percentage of coal converted to distillable products by the addition of waste materials is shown in Figure 7. It can be seen that certain polymers interact with coal to increase the distillation yield. This is most evident with polypropylene and polyvinyl chloride. Thus when these 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.

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. This clearly demonstrates that only small amounts of waste plastic may be needed for coal conversions. Polystyrene on the other hand leads to a lower volatile yield, hence higher char yield.

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 a 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

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. The microreactor system developed consists of a 20ml stainless steel reactor closed at one end but open to a

three-way valve at the other. The other connection to the three way valve incorporate a gas sampling device to acquire gas samples, a 2000 psi safety valve, a pressure transducer for continuous pressure monitoring, and a quick-connect assembly for easy gas charging. This microreactor design is currently being 'shaken down.'

Very preliminary microreactor experiments have been performed and the acquisition of some products for analysis has been achieved. At this time the best method for product recovery, contaminant avoidance and reactor quenching are being evaluated. To date a sample of polystyrene heated to 450°C for 1 hour has the appearance and behavior of a pitch sample, a similarly treated polypropylene sample shows clear evidence for the development of aromatic or alkene units in its NMR spectrum and a coal/polyethylene 1:1 mixture heated the same way is completely soluble in THF. Although, these results are preliminary they are also very encouraging.

CONCLUSIONS AND RECOMMENDATIONS

Nearly all the preparation is complete and that left to be performed can easily be handled within the context of the project.

TGA analysis has demonstrated that interactions occur during pyrolysis of IBC 101 with some plastics. These result were obtained with a gas sweep and at low pressure. Tests in the microautoclave under isothermal conditions are still needed to determine pressure and temperature effects.

Some of the interactions appear to produce higher volatile yield from the coal at lower temperatures. This information indicate that a small amount of polyalkanes may be beneficial to coal conversion under mild pyrolysis.

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TABLE 1: ONSET, MAXIMUM REACTIVITY, FINAL CHAR, AND PYROLYSIS TEMPERATURES AND CHAR YIELDS FOR VARIOUS COAL/PLASTIC (1:1) MIXTURES.

Sample	T _{on} °C	T _{max} °C	T _{char} °C	T _{py} °C	char Yield wt%
Coal	302	472	879	577	63
Cell	302	375	439	137	3
Paper	297	378	458	161	16
PSB	367	427	430	63	0
PB	395	469	475	80	0
PET	395	456	523	128	16
PMP	402	459	460	58	0
PP	395	481	489	94	0
PE	336	472	480	144	0
PS	367	427	444	77	0
PVC	414	473	575	161	6

FIG. 6a: ONSET TEMPERATURE
COAL/PLASTIC MIXTURES (1:1)

FIG. 6b: TEMPERATURE OF MAX. REACTIVITY
COAL/PLASTIC MIXTURES (1:1)

(A) : COAL, (B) : CELLULOSE, (C) : PAPER, (D) : PSB,
 (E) : PB, (F) : PET, (G) : PMP, (H) : PP,
 (I) : PE, (J) : PS, (K) : PVC

FIG. 7: PERCENTAGE OF
COAL CONVERTED

PROJECT MANAGEMENT REPORT
September 1 through November 30, 1993

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
Department of Mechanical
Engineering and Energy Processes
Southern Illinois University
at Carbondale
Other Investigators: M. E. Blankenship
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Southern Illinois University at
Carbondale
S. R. Palmer
Department of Mechanical
Engineering and Energy Processes
Southern Illinois University
at Carbondale
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	150	6,766
Sept. 1, 1993 to Feb. 28, 1994	Projected	21,304	6,436	2,874	0	0	5,650	3,626	39,890
	Estimated								
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 Liquids**

Cumulative \$
(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.

DATE

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END