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TECHNICAL REPORT
1 September 1991 through 30 November 1991

Project Title: A NOVEL TECHNIQUE FOR EVALUATING CLEANED FINE AND ULTRAFINE COAL

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ABSTRACT

As a standard industrial practice all commercially cleaned coals are evaluated by washability analysis to predict their cleaning potential. The results of this analysis are so important that coal washability is a major factor in deciding to purchase and develop coal holdings. However, washability analysis are at present limited to coal particle sizes of greater than -28 mesh (0.6 mm). Coal particles smaller than this limit do separate well in the standard sink-float process used in the washability tests. The increasing demand for cleaner coals requires that coals be crushed to fine (-100 mesh - 0.15 mm) and ultrafine (-325 mesh - 0.045 mm) sizes to liberate more of the fine-grained mineral matter including pyrite. However, such small coal particles can not be analyzed in the standard washability analysis. The purpose of this study is to develop a washability analysis system for fine and ultrafine coal particles using Density Gradient Centrifugation (DGC) and Thermal Gravimetric Analysis (TGA) techniques. The unique advantages of this proposed technique is that it provides a means to obtain usable washability curves on fine and ultrafine coal samples. The DGC technique will produce a large number of density fractions in a single run and, thus, is much faster and more efficient that normal washability analysis. During this quarter all of the samples to be used in this study have been ordered from the Illinois Basin Coal Sample Program and the initial results for one sample have been examined.

This project is funded by the U. S. Department of Energy (PETC) and by the Illinois Department of Energy and Natural Resources as part of their cost-shared program.

EXECUTIVE SUMMARY

As a standard industrial practice all commercially cleaned coals are evaluated by washability analysis to predict their cleaning potential. The results of this analysis are so important that coal washability is a major factor in deciding to purchase and develop coal holdings. However, washability analysis are at present limited to coal particle sizes of greater than -28 mesh (0.6 mm). Coal particles smaller than this limit do separate well in the standard float-sink process used in the washability tests.

The increasing demand for cleaner coals requires that coals be crushed to fine (-100 mesh - 0.15 mm) and ultrafine (-325 mesh - 0.045 mm) sizes to liberate more of the fine-grained mineral matter including pyrite. However, such small coal particles can not be analyzed in the standard washability analysis. The **purpose of this study is to develop a washability analysis system for fine and ultrafine coal particles using Density Gradient Centrifugation (DGC) and Thermal Gravimetric Analysis (TGA) techniques.**

Most of the non-combustible impurities that can be mechanically removed from coal occur as rock fragments and minerals, particulularly pyrite. The specific gravity of the rock fragments is in the specific gravity range of 2.0 to 3.0 and that of pyrite is around 5. Because the specific gravity of coal is around 1.0 - 1.6, separation by heavy-media in which the coal will float and the rock and pyrite will sink is possible. The three types of heavy-media used are: 1.) Organic Liquids, 2.) Salt solutions, 3. Stable suspensions (especially magnetite and water).

The heavy-media separation techniques work best on coal fractions that are greater than 28 mesh (0.6mm) in size. Finer coal size fractions are cleaned by other methods, especially froth-floatation.

The washability properties of coal are the most important parameters available to predict how well a given coal can be cleaned. Evaluation of the washability parameters will reveal how much clean coal of a given quality can be obtained by physical cleaning.

The basic method of analysis is to crush the coal sample to a given top size and then put it through a sequential sink-float separation in heavy liquids of various specific gravities. The ash and sulfur content of the material floating and sinking at the various specific gravities are then determined.

The recent refinement of two experimental techniques, density gradient centrifugation (DGC) and thermogravimetric analysis (TGA), now allows for a better understanding of the distribution of mineral matter within coal samples. Briefly,

the DGC separation technique provides a method of separating coal into individual, very closely spaced density fractions. Thermogravimetric analysis is a proven means of obtaining proximate analysis data, including ash yields, from very small samples. Obtaining the ash yields of each DGC density fraction thus reveals the total distribution of ash within the coal as a function of density. The resulting graph is termed a washability curve. Because individual coal macerals vary considerably in density, these washability curves also help reveal certain ash-maceral associations which may impede coal cleaning.

The unique advantages of this proposed technique is that it provides a means to obtain usable washability curves on fine and ultrafine coal samples. The DGC technique will produce a large number of density fractions in a single run and, thus, is much faster and more efficient that normal washability analysis. The TGA can give accurate ash analyses on very small samples. This technique has already been demonstrated in a few trial runs and promises to be successful in the experiments designed for this proposed project.

The overall objective of this proposal is to develop a washability analysis system for fine and ultrafine coal. The specific objectives are:

1. Use DGC and TGA techniques to generate coal washability data for fine and ultrafine coals.
2. Incorporate this data into an analysis scheme similar to standard washability curves currently used for coarser coals.
3. Use these techniques to test the effects of particle size and chemical additives on the cleaning process.

To accomplish these objectives the following tasks will be undertaken.

<u>TASK I</u>: **Sample Selection and Preparation**
Coal samples from the Illinois Basin Coal Sample Program will be used. Samples 101, 104, 108 represent high ash (104-38.4%), low ash (108-3.8%), and intermediate ash contents (101-10.5%) and high pyrite (104-2.57%), low pyrite (108-0.37%) and intermediate pyrite (101-1.27%). The samples will be ground to -60 mesh (0.25 mm), -200 mesh (0.075 mm), -325 mesh (0.045 mm), and -400 mesh (0.038 mm), and particle size distributions will be made using wet sieving on the -60 mesh size material and on the other samples with a Northrup Microtrack Particle Size Analyzer. The coals will also be characterized by proximate and ultimate, sulfur forms and BTU analyses.

<u>TASK II</u>: **Density Gradient Separation**
In the SIUC Maceral Separation Laboratory all size consists of each sample will be separated into multiple fractions over the density range from 0.0 to 1.70 in 0.05 gm/mL steps using the procedure already described above. Sufficient material at each fraction will be accumulated for both ash and sulfur analysis. Reproducibility checks will be run and checks using commercial fast neutron activation analysis will also be done to confirm the lack of CsCl in the ash. In addition, the effects various surfactants will also be examined.

<u>TASK III</u>: **Analysis of Fractions**
All of the fractions will be analyzed for ash and sulfur. The ash will be determined with the TGA as already described and the sulfur will be determined with a commercial microsulfur analyzer.

<u>TASK IV</u>: **Washability Curves**
The final step will be to construct washability curves for ash and sulfur as shown above. The purpose of the heavy-liquid centrifugation beneficiation process is to remove as much of the pyrite and ash as possible while salvaging as much clean coal as possible. Ideally, in the beneficiation process, all the overflow product would be clean coal which would contain all of the BTU originally in the sample, and all the underflow product would be waste. Although such perfection can never be completely achieved in a physical process, these washability curves should allow the reliable prediction of the cleanability of both fine and ultrafine coal.

During this quarter all of the samples to be used in this study have been ordered from the Illinois Basin Coal Sample Program and the initial results for one sample have been examined. This examination and experience with other samples indicate that instead of a simple increase in ash content with increasing density, there may be significant ash material concentrated in the liptinite macerals, which are the lowest density macerals. These macerals are derived from the resinous and waxy parts of plants and seem to have the ability in some cases to trap mineral matter. For example, it has been well demonstrated that cutinite which is derived mainly from the waxy coatings of fossil plant leaves can trap and hold minerals in its sheet-like structure. Because the liptinite macerals are commonly under 100 micrometers in size they tend to be liberated only at the finer sizes. Therefore it is expected that the ash content of the lowest density maceral fractions will increase. This possibility will be carefully examined. During the next quarter the preparation of all of the samples will be completed and the initial washability curves will be made.

OBJECTIVES

The overall objective of this proposal is to develop a washability analysis system for fine and ultrafine coal. The specific objectives are:

1. Use DGC and TGA techniques to generate coal washability data for fine and ultrafine coals.

2. Incorporate this data into an analysis scheme similar to standard washability curves currently used for coarser coals.

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INTRODUCTION AND BACKGROUND

The presence of inorganic impurities within coal affects its performance during processes of interest, i.e. combustion, gasification, liquefaction, or coking. The inorganic impurities are most commonly found in the form of discrete mineral matter, one of the more common types of which are sulfides. Thus, not only does the presence of mineral matter affect coal performance, but it also is responsible for much of the sulfur emissions.

Removal of unwanted mineral matter from coal would seem to be relatively straight forward due to the large density contrast between the organic constituents of coal, macerals (1.0 to 1.7) gm/mL), and the inorganic impurities, minerals (2.3 to > 5.0 gm/mL). Unfortunately, while many different coal cleaning techniques have been developed, some coal samples have consistently proven to be much more difficult to clean than others. This suggests that the distribution of mineral impurities within coal is not regular and most certainly not the same in all samples. Clearly, a better understanding of the distribution of mineral matter within coal, both before and after cleaning, would aid in more efficient and effective removal techniques.

As a standard industrial practice all commercially cleaned coals are evaluated by washability analysis to predict their cleaning potential. The results of this analysis are so important that coal washability is a major factor in deciding to purchase and develop coal holdings. However, washability analysis are at present limited to coal particle sizes of greater than -28 mesh (0.6 mm). Coal particles smaller than this limit do separate well in the standard float-sink process used in the washability tests.

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The heavy-media separation techniques work best on coal fractions that are greater than 28 mesh (0.6mm) in size. Finer coal size fractions are cleaned by other methods, especially froth-floatation.

Washability tests are run on a number of different types of coal samples. Large samples of 100 tons or more may be tested to help design coal cleaning systems, while much smaller volume drill-core samples are tested to aid in coal property evaluations. In all washability tests, a number of specific gravities will be used on each of a number of size fractions of coal.

The washability properties of coal are the most important parameters available to predict how well a given coal can be cleaned. Evaluation of the washability parameters will reveal how much clean coal of a given quality can be obtained by physical cleaning (1-3).

The basic method of analysis is to crush the coal sample to a given top size and then put it through a sequential sink-float separation in heavy liquids of various specific gravities. The ash and sulfur content of the material floating and sinking at the various gravities are measured. Typical results are given in Table I. From a typical ash-yield curve given in Figure 1, one can determine the ideal specific gravity of separation to use to get a given yield at a given ash content. Much more sophisticated curves can be constructed as the one illustrated in Figure 2.

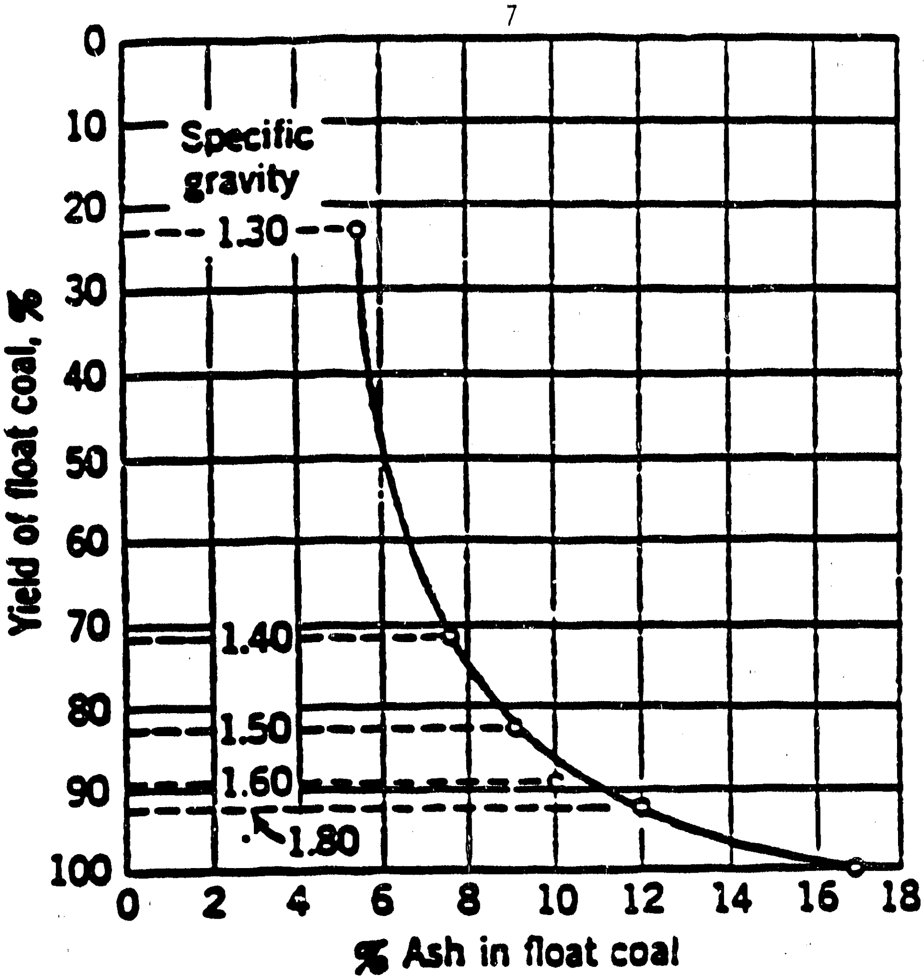

Figure 1. Typical ash yield washability curve (after Mitchell and Charmbury [1]).

Table 1.

Float and Sink Tables

1 Spec Sink	2 Grav Float	3 Wt. % Float	4 Dry % Ash	5 Basis % Sul	6 Cum Recovery (Float) % Wt	7 Cum Recovery (Float) % Ash	8 Cum Recovery (Float) % Sul	9 Cum % Wt	10 Rejec % Ash	11 (Sink) % Sul
	1.30	63.61	1.50	.57	63.61	1.50	.57	100.00	7.61	.57
1.30	1.35	10.56	6.90	.66	74.17	1.68	.58	36.39	18.28	.58
1.35	1.40	6.76	12.98	.60	80.93	3.14	.58	25.83	22.93	.55
1.40	1.45	7.79	18.16	.56	88.72	4.46	.58	19.07	26.57	.53
1.45	1.55	6.98	24.31	.42	95.70	5.91	.57	11.28	32.37	.51
1.55	1.65	2.48	32.02	.49	98.18	6.57	.57	4.30	45.46	.65
1.65	1.80	.64	43.45	.43	98.82	6.80	.57	1.82	63.76	.87
1.80	2.17	.50	59.84	.47	99.32	7.07	.57	1.18	74.48	1.12
2.17		.68	85.77	1.59	100.00	7.61	.57			
			3/8" x 100 M		94.25	7.61	.57			
			100 M x 0		5.75	7.75	.88			
			Total		100.00	7.62	.59			

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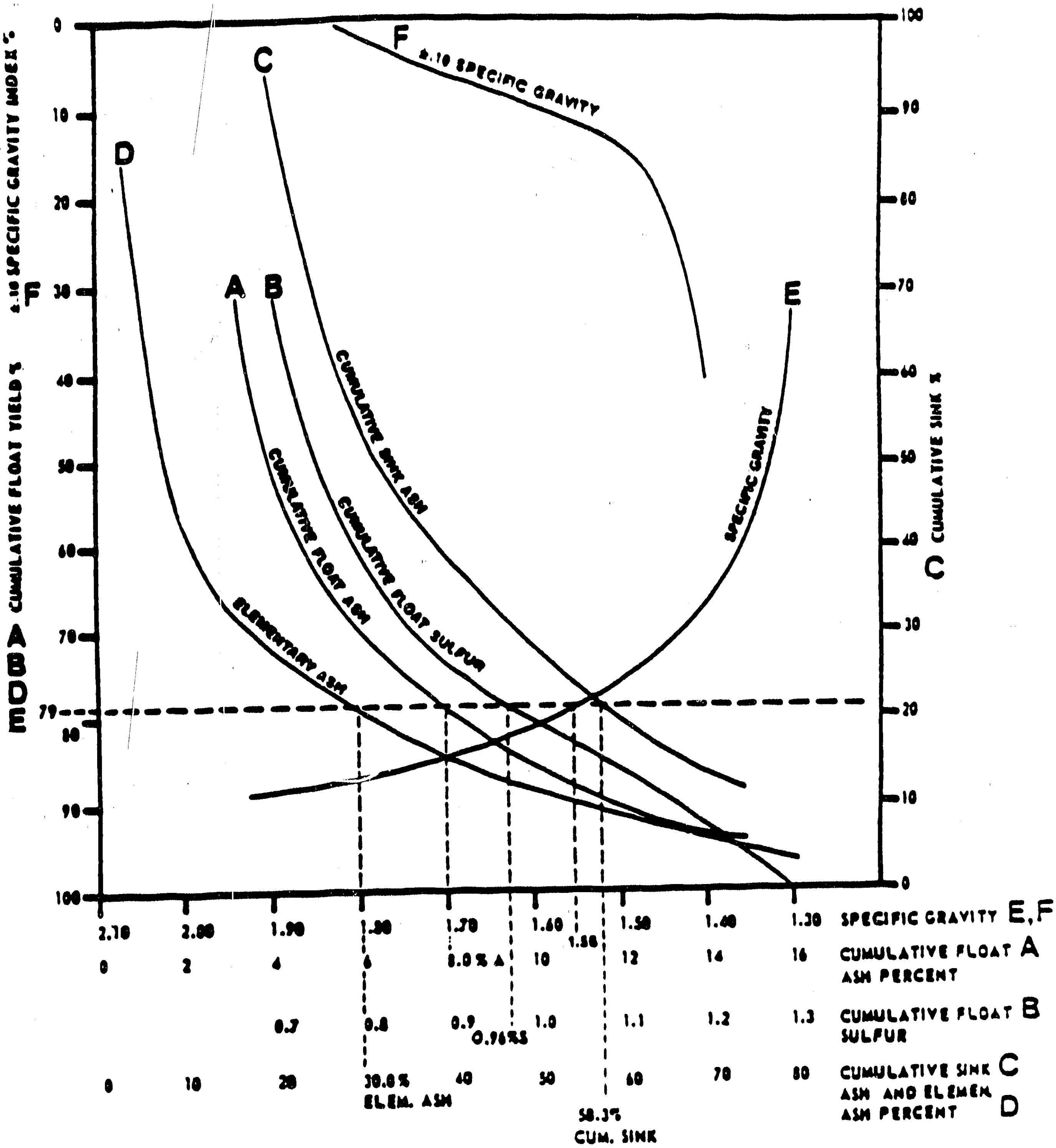

Figure 2. Multiple washability curves (after Austin and Luckie [3]).

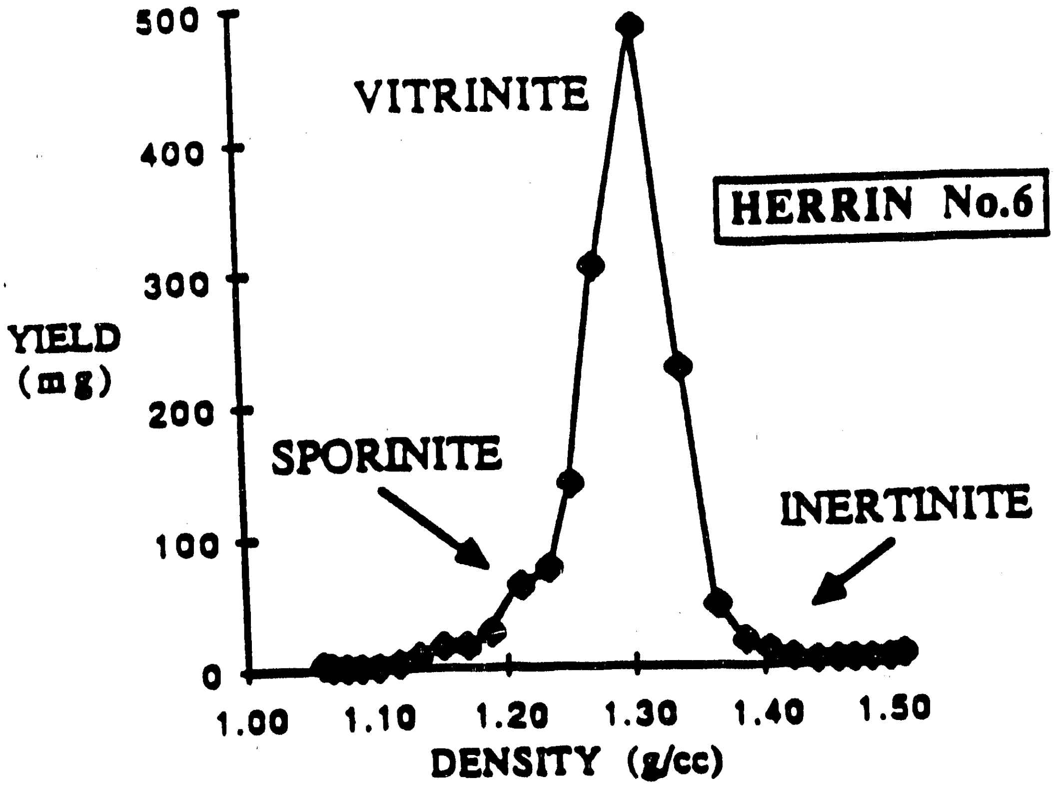

Figure 3. Typical density distribution from DGC analysis.

Thermogravimetric Analysis

Thermogravimetric analysis, the monitoring of sample weight loss as a function of temperature, has been shown to be an effective tool for studying coal combustion behavior (7-11). TGA data has also been found to be useful in routine coal analysis, and is particularly useful when only small samples (5 mg) are available for analysis. Bryers et al.(12) first demonstrated that proximate analysis data (ash, moisture, fixed carbon, and volatile matter)

could be obtained using the TGA. Later, Cumming (10) compared standard proximate analysis data with TGA proximate data for 14 widely varying coal samples. The results were comparable. Moisture and ash yields can be obtained directly from TGA burning profiles in air. Volatile matter is determined from a burning profile generated under an inert atmosphere and correcting for moisture. Fixed carbon is found by difference. TGA proximate data shows little deviation from conventional ASTM proximate analysis methods.

Combustion profiles are obtainable at the SIU-C Coal Technology Laboratory using a Perkin-Elmer TGA7 thermogravimetric analyzer. Perkin-Elmer Delta software version 5.0 is used. Coal samples are evenly distributed in a thin layer in a platinum sample basket which is attached to a microbalance by a platinum hang-down wire. Consistent and reproducible results have been obtained using 4.5 to 5.0 mg samples. A 20% oxygen 80% nitrogen flowing gas atmosphere is used to simulate combustion in air. A constant gas flow rate of 80 cc/min is regulated using flowmeters. The samples are then heated at 15°C/min from ambient temperature until no further weight loss is recorded. The TGA continuously monitors weight loss as a function of temperature, and in addition, the software plots the first derivative of this function. The resulting graph is termed a combustion profile and a typical profile is shown in Figure 4. From these curves, a number of characteristic combustion temperatures and parameters may be obtained. For the purposes of this study

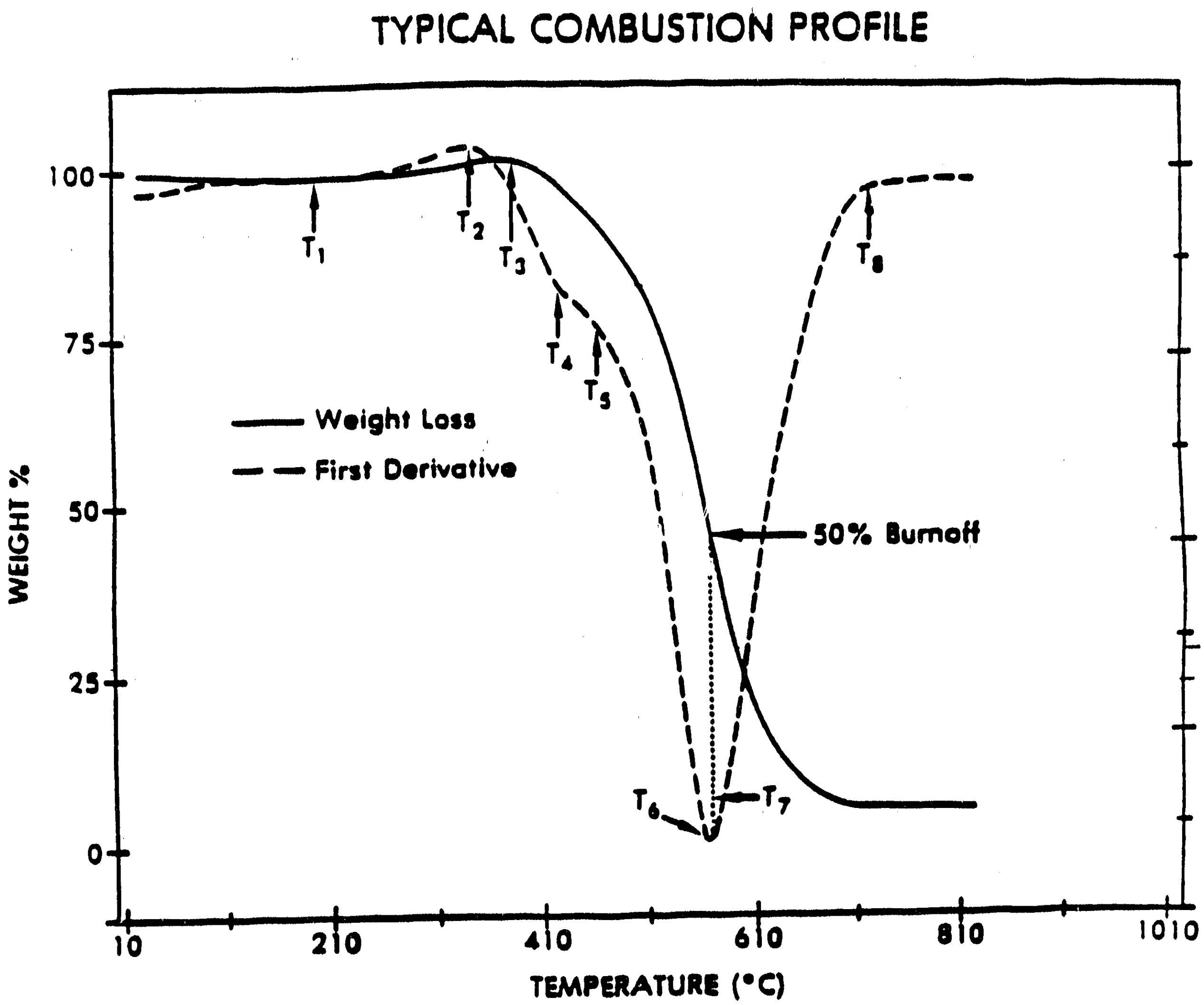

Figure 4. Typical TGA combustion profile.

only moisture content and ash yield are of importance. The moisture content is found by subtracting the weight % at 130°C from the weight % at the starting temperature. The ash yield is the weight % remaining when no further weight loss is recorded. The dry ash content of the sample can then be determined by dividing the ash yield by the moisture content.

PROGRESS DURING THIS QUARTER

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