

SEPARATION AND CHARACTERIZATION OF COAL MACERALS:  
ACCOMPLISHMENTS AND FUTURE POSSIBILITIES

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INTRODUCTION

Macerals are the various organic components that make up coal and control its overall behavior. Macerals were first defined in 1935 by Stopes (1) as the descriptive equivalent of minerals which are the inorganic components of rocks. In 1958 Spackman (2) expanded the maceral concept and made it more useful for applied studies by considering macerals as "organic substances ... possessing distinctive physical and chemical properties...". However, these properties are poorly understood because macerals are usually small, commonly less than a hundred microns in diameter, and well mixed together and, thus, are difficult to separate from the coal matrix. Thus, most of the maceral characterization that has been done has been done in situ with petrographic methods, especially reflectance, fluorescence, infrared, and photoacoustic microscopy.

These petrographic methods have been very successful in identifying and classifying a variety of macerals and in correlating them with the behavior of coal in selected industrial processes. Under the microscope the macerals fall into three major groups: liptinite, vitrinite, and inertinite. The liptinite group is derived from the waxy and resinous parts of plants and mainly consists of sporinite, resinite, and cutinite derived respectively from plant spores, resins, and cuticles. A few coals and most petroleum generating components in source rocks contain alginite which is derived from coalified algae. The vitrinite group is derived from coalified woody tissue and is the dominant group in most north American coals. While a variety of vitrinite macerals can be discerned the two major varieties are normal or matrix vitrinite and pseudovitrinite. The inertinite group is derived from woody tissue that has been altered by fire or biochemical charring. The major inertinite macerals are fusinite and semifusinite derived respectively from coalified charcoal and semicharcoal. The inertinite group is the dominant group in some Canadian and southern hemisphere coals.

The petrographic analysis of the kinds and amounts of macerals present in a given sample characterize the coal composition so successfully that this data can be used in combination with the rank parameters of a coal to predict the process response of coal. The most successful application has been in coking operations in the steel industry where such critical properties as coke strength, coke yield, and peak coking pressure are routinely predicted. The rank of the coal has to be taken into account because coal is a metamorphic rock ranging from peat to anthracite. As the rank changes the properties of the whole coal and the individual macerals also change systematically.

Even though the in situ microscopic techniques have been

successful in characterizing coal, they have yielded only selective data on the properties of the individual macerals. A large body of petrographic data has allowed the detailed classification of macerals, and fluorescence spectral data has expanded this data base on a more quantitative basis (3-8). Time-domain fluorescence analysis has also been used to characterize fluorescent macerals (9). Photoacoustic microscopy has been used to investigate some of the thermodynamic and material properties of some macerals (10-11). In addition, some limited infrared microscopy (12) and thin-section solvent swelling studies have been reported(13). However, none of the *in situ* studies have produced the hard chemical and structural data needed to fully characterize the individual macerals. For this, significant quantities of separated single macerals are needed.

#### MACERAL SEPARATION

Because macerals vary in their chemistry and structure they also vary in their density, and it is this variation that allows them to be separated. However, normal sink-float techniques have had only limited success in separating single macerals. This is mainly because the small particle size (< 10 microns) needed to liberate single macerals and minimize multiple-phase particles are not efficiently separated in the sink-float process. Centrifugation is needed and centrifugation at a large number of densities for a single sample is not practical. A solution to this problem is the use of density gradient centrifugation (DGC) in which a sample is centrifuged through a density continuum and then fractionated.

Notable efforts at using sink-float methods were made by Kroger and van Krevelen and their coworkers (14-15) as well as Fenton and Smith (16). The most successful of these efforts resulted in concentrations enriched in the three main maceral groups. However, these enrichments were not good enough to give definitive characterization data. In a major contribution to coal science the standard medical technique of density gradient centrifugation was first applied to maceral separation by Dyrkacz and others (17-19). In this technique the coal sample is reduced to micron size in a fluid energy mill and then demineralized with HF and HCl. The sample is then put into a vessel that is filled with an aqueous CsCl density gradient commonly ranging from 1 to 1.6 gms/ml. The vessel is then centrifuged and the particles move to the appropriate density level. At this time the largest vessel in use has a two liter capacity which can process a maximum sample size of two grams of coal. After centrifugation the vessel is fractionated by pumping, then filtered, weighed, and dried. The density and weight of each fraction are measured and plotted. The resulting density profile accurately reflects the maceral composition of the sample.

In fact, the density fractions are composed of the material that separated at a particular density and in addition to single-phase maceral particles they may contain mixed-phase particles of two or more macerals or macerals and minerals. Thus, to obtain single maceral fractions the macerals must be liberated from the coal

matrix in the crushing process and the mineral matter must be removed either in the acid demineralizing step or in the centrifugation. Fortunately, in work done to date these conditions have usually been met and some single maceral fractions have been obtained. However, petrographic examination of all of the fractions from a typical two gram DGC run reveals that many fractions are composed of mixed phases although most such fractions have phases from the same maceral group. Therefore, a typical DGC run will do an excellent job of separating the coal into the three main maceral groups - liptinite, vitrinite, and inertinite with liptinite having the lowest density and inertinite having the highest density. Most of the characterization work done to date on DGC fractions has been done on these maceral group separations.

Because most north American coals contain 50% to 90 % vitrinite a typical whole-coal density profile will be dominated by a vitrinite density peak with low density and high density tails to indicate liptinite and inertinite respectively. While petrographic examination shows that fractions taken from the peak are excellent concentrates of the dominant vitrinite there is not enough detail in the rest of the profile to distinguish any other single maceral. To overcome this problem two approaches have been used. One is to use the concentrations already found in nature by selecting whole coal samples that are rich in a target maceral such as a paper coal for cutinite, or coal seam layers (lithotypes) such as fusain for semifusinite and fusinite. Both techniques have been successfully tried by Dyrkacz (19) and Crelling (20), for example. Using lithotypes it has also been possible to separate two vitrinite macerals, matrix vitrinite and pseudovitrinite from each other (20). The other approach is to use the whole coal profile to locate the boundaries or cut points between maceral groups and to then centrifuge the sample at a single gravity to concentrate the target maceral group. When this concentrate is then processed in a two gram DGC run additional maceral peaks may be revealed. Crelling (21) has shown that such processing shows three distinct liptinite maceral peaks and a broad and a narrow inertinite peak in an Indiana paper coal that could be petrographically identified as cutinite, resinite, sporinite, semifusinite, and fusinite. The key to confirming that density fractions are, indeed, concentrations of single maceral groups and particularly single macerals is their petrographic examination. Dyrkacz (18) uses fluorescence microscopy to identify liptinite concentrates and determine their purity, and Crelling (21) used fluorescence spectral analysis microscopy and reflectance analysis to confirm the identity of single maceral separations.

In summary, at this time hundreds of DGC maceral group separations have been made and continue to be made on a daily routine basis. With somewhat greater effort, DGC separations of single coal macerals often from the same maceral group have been demonstrated and are also routinely performed. To date, single maceral separations of varieties of cutinite, resinite, sporinite, vitrinite, pseudovitrinite, semifusinite, and fusinite have been reported.

## CHARACTERIZATION

The availability of maceral group fractions and single maceral fractions has led to a very sudden and broad expansion of our knowledge of maceral properties. The first elemental analyses of high quality DGC maceral group and single vitrinite maceral fractions were reported by Dyrkacz (22-25) and additional analyses were also reported by Karas and others (26), Winans and others (27). Crelling also reported some values for single macerals (20). In general this work has shown that there are distinct chemical differences between the maceral groups and the individual macerals as well as a corresponding change with density. For example, in macerals from the same coal sample the liptinite macerals have the highest hydrogen contents and the inertinite macerals the lowest; both groups have high carbon contents while vitrinite has the lowest carbon; both H and H/C decrease with density. In addition, Tseng and others (28) and Hippo and others (29) found organic sulfur to be two to three times higher in sporinite than in any other maceral.

Separated macerals and maceral groups have been analyzed with a variety of spectroscopic techniques. FTIR results of Dyrkacz and others (24) and Kister and others (30) show systematic differences between macerals (aliphatic H decreases with liptinite > vitrinite > inertinite) and even within a specific maceral group (aliphatic H decreases with increasing vitrinite density). Silbernagel and others (31) have shown that the electron spin resonance "signatures" of various macerals and maceral groups are distinctive and also show variations with rank. Thomann and others (33) also studied the carbon radical spin dynamics of isolated vitrinite coal macerals to show that such data is a sensitive structural probe. Pugmire et al (34), Wilson et al (35), and Botto et al (36) used nuclear magnetic resonance spectroscopy to show that different macerals and maceral groups can be differentiated and that hydrogen aromaticity increases as carbon aromaticity increases with coal rank. A variety of studies using other chemical techniques have also been reported. King and others (25) used tetralin dissolution to show that the reactivity of coal macerals in a donor solvent varied systematically both within and between maceral groups and Choi et al (37) have studied the density separation of alkylated macerals. Winans et al (27) and Nip et al have studied coal macerals with pyrolysis mass-spectrometry and Nip also has shown unique mass spectra signatures for a variety of macerals from the same coal. The combustion reactivity of separated macerals have been shown to be very different for different macerals and to vary inversely with rank (39). Finally, the properties of some single macerals have been studied with a variety of techniques particularly - cutinite (40), sporinite (41), resinite (42), and pseudovitrinite (20). Various types of kerogen have also been separated and chemically characterized (43-44).

In summary, a remarkable amount of work on the characterization of separated coal macerals and maceral groups has been done since the DGC process was introduced in 1981. One common thread throughout all of the representative work reported here is that regardless of

the property investigated or the technique used all of the macerals show significant differences from each other. However, the chemical structure and physical properties of the various macerals are still not very well understood and their behavior in processes of interest can still not be predicted. Much work yet needs to be done.

#### FUTURE POSSIBILITIES

While the author has been requested to briefly discuss the future possibilities of maceral separation and characterization, it is done only with some trepidation. However, if current trends can be considered a reliable guide then in the area of maceral separation it is reasonable to assume that progress will be made in at least two areas. First, techniques of pre-concentration to provide a sample enriched in a target maceral may be developed; electrostatics and other ore dressing technologies are now being looked at. Second, larger volume batch centrifugation and/or continuous centrifugation using commercial scale equipment will have to be developed to take DGC beyond the laboratory scale. In the area of maceral identification, progress is being made in advanced fluorescence spectral analysis of all types of macerals and this should improve the ease and reliability of identifying separated macerals. Finally, in the characterization area it may be that the great variety of physical and chemical analytical techniques now available are sufficient to give the required characterization of macerals. If this is the case, then what is needed is a large coordinated effort to thoroughly characterize a well selected and identified set of macerals of all types and ranks. Once this is accomplished a careful correlation of maceral properties to behavior in processes of interest needs to be done so that useful predictive models can be devised. Finally, after commercial quantities of well characterized macerals can be separated, the refining of coal can be justified and coal will take its place as an organic raw material.

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