

ADVENTURES IN MACERAL SEPARATION

ANLCHM CP--81225

Gary R. Dyrkacz
Chemistry Division
Argonne National Laboratory
9700 S. Cass Ave.
Argonne, Illinois 60439

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

The submitted manuscript has been authored by a contractor of the U. S. Government under contract No. W-31-109-ENG-38. Accordingly, the U. S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U. S. Government purposes.

MASTER

875
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

*This work was performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy, under contract number W-31-109-ENG-38.

Gary R. Dyrkacz
Chemistry Division,
Argonne National Laboratory
9700 S. Cass Ave
Argonne, Illinois 60439

Introduction

Understanding coal structure tasks the best researchers with the latest equipment. The problems start with the raw materials to produce coal - the profusion of plant tissues and minerals of the peat swamps. The problems are further compounded by environmental processing of this raw material through a host of biochemical, chemical and thermal transformations.¹ The resulting coal is then physically and chemically heterogeneous, both in terms of the organic material and the mineral components. Just how heterogeneous is not even clear. Indeed, from the organic chemistry perspective, it is not even known whether any regular structure can even be assigned to coal.

Physically we divide coal into macroscopic or microscopic components called macerals as one measure of the physical heterogeneity. Some macerals are relatively easily associated with certain living tissues such as spores or algae. More often the identity of the original material is uncertain. Partly this is due to the accepted methods of preparing samples for microscopic observation, but often the original peat is so extensively degraded that any remnants of the original physical structure are gone.²

Because macerals are the first level of heterogeneity that can be readily observed, separating them to obtain more pure species would appear to be worthwhile. This is true even for a single maceral type, such as vitrinite, which can still be heterogeneous. However, it is notable that maceral separations are not routinely done, even when fundamental structure studies are anticipated. This is contrary to many other fields (e.g. plant science or bioscience areas) where physical and chemical separations of complex organic materials is a mandatory first stage in unraveling structures. One reason may have been a lack of maceral separation science. One of our goals has been to put maceral and, lately, submaceral separations on a more scientific basis.

The methodology of maceral separations can be broken down into several processes which are listed in Table I. Each of these processes, when viewed in depth, is intertwined with complex and often little understood issues of coal's physical and chemical structure. As a result viable separation procedures are achieved mostly by guessing, faith and a lot of work. For efficient maceral separations to be realized, all these subprocesses must interlock in concert. We have been able to either thread our way through or skirt a number of the problems. However, there is still a largely unexplored vein of information within each area that is specifically important to maceral separations, and probably generally to coal science. A complete idea of where work is needed to improve separations cannot be fully addressed here. Only a brief overview and flavor of where work stands can be given.

Discussion

Liberation

Coal constituents must be liberated from each other for optimal separation even to be possible. Without sufficient liberation some macerals may not be liberated at all. At best, they can only be enriched. Incomplete liberation also affects other constituents by limiting the pure materials that can be separated. This can potentially bias the type of material that is recovered as monomaceral particles. For example, liptinites are usually difficult to liberate cleanly from vitrinites. In density separations, these bimaceral particles will usually be found mixed in with low density monomaceral vitrinite particles. This vitrinite is different from any of the other vitrinite material.³ Eliminating this portion of material to obtain pure vitrinite can lead to differences in vitrinite properties that do not reflect the original coal.

Mechanical grinding has been the primary method for liberation. The small size of many maceral species means that the coal must be ground very fine - on the order of 10 microns. Fluid energy

mills appear to be particularly effective at producing coal particles in this range. They also appear to cause the least amount of reaccretion or rehomogenization of the coal.⁴

What is the appropriate stage to stop grinding? This question is not only important from the aspect of maceral separation, but can extend to how we perceive the chemical heterogeneity of coal. Ideally, grinding needs to be continued until all particles are completely monomaceral. This goal is opposed by the problem of identification of the ground material. Simple optical identification based on reflectance differences between the macerals is not possible below about 2 microns. In addition, another limiting factor is reached in the submicron range (<0.5 microns). Particles in this range can strongly interact with separation media giving quite different densities than larger particles with the same density.⁵

The preceding demands of maceral liberation critically depend on the maceral concept and maceral identification. But what is the nature of chemical heterogeneity within even a single monomaceral particle? If coal is ground to submicron sizes will new distinct particulate species appear? This would suggest that macerals themselves consist of chemical domains of regular structure? Often vitrinite will exhibit detailed substructures, when coal samples are polished and etched.^{1,2} Alternatively, what if no further resolution occurs? This would be true if coal is so heterogeneous that its structure varies on a nanometer scale, or if monomaceral particles are chemically homogeneous. These questions are not easy to answer, but point to a level of physical separation that has received only a small amount of attention.⁴

Demineralization

The common minerals found in coal have densities from ~1.5 to 4 times that of the organic coal material. Thus, a small amount of included mineral can have a large influence on maceral particle density. Optimum separation of macerals demands that the coal be as mineral free as possible. Mechanical demineralization by density methods is not sufficient to remove the inorganic materials.⁵ Chemical demineralization using strong acids is the alternative, but the effect of this procedure on the chemical structure of coal is still uncertain. Fortunately, pyrite, which has a density of ~4.5 g cm⁻³ and is particularly difficult to remove chemically, is nearly completely liberated from the coal particles during fluid energy mill grinding.

Wetting and Dispersion

Most maceral separations are based on differences in maceral densities in liquid suspensions. If coal particles extensively aggregate in a medium, then separation will be inefficient. There are two related components to the problem: 1. The coal particles must be completely wetted by the media. 2. The particles must remain isolated from one another or undergo nearly elastic collisions over the separation time. Wetting is a necessary condition for dispersion. Just what governs the effectiveness of a particular media for maceral particle dispersion is not clear. The result is that the dispersion remains in the realm of "shake-the-shelf" chemistry. An example of the importance of dispersion can be seen in Figure 1. This data is taken from a study of centrifugal sink/float separations for coal in a variety of commonly used suspension media.⁶ SI is a separation index, which is a measure of the efficiency of separation. An SI value of 0 represents no separation relative to the original coal while 1 represents a complete disengagement of the float and sink material. A negative value is due to aggregation effects. RI is the recovery index and represents the fraction of float or sink phase found after separation, relative to the maximum fraction of material expected from a perfect separation. Thus, a value of 0 represents no desired phase found, while 1 represents all the phase isolated. Of the five media systems investigated, only two stood out: aqueous CsCl/Brij-35 and Ca(NO₃)₂/Brij-35. (Brij-35 is the nonionic surfactant polyoxyethylene-23-lauryl ether.) Other commonly used media, such as ZnCl₂ or organic systems based on CCl₄, were not as effective. Contrary to expectations, recycling material in aggregating media showed no further separation. Although Brij-35 seems to be a magic material that fixes all dispersion problems, it is not. Separations in aqueous ZnCl₂/Brij-35 solutions were only moderately better than ZnCl₂ solutions. Thus, the effect of the media can be subtle. Much more work is needed to understand what drives the interactions.

Separation

The heart of maceral enrichment is the separation step. Sedimentation methods are the most commonly used, particularly centrifugal sink/float. A relative newcomer on the maceral separation scene is density gradient centrifugation(DGC). This technique is superior to any type of sink/float separation. It has the highest density resolving ability of any maceral separation method, and

functions both as a separation and characterization method. DGC methods are definitely the method of choice for optimum enrichment of macerals. However, DGC methods do have limitations on the amount of material than can be obtained in any single separation cycle. This can be overcome by first using sink/float methods to isolate desired density regions.

In some studies high density resolution of macerals may not be necessary. Thus, sink/float techniques will remain an alternate separation method or at least an adjunct to DGC separations. With this in mind, we have recently examined the process of centrifugal sink/float (S/F) separations to understand its limitations and provide guidance in its use.^{5,7} In addition, we have explored in detail a continuous flow centrifugation (CFC) technique that allows much larger amounts of material to be separated in a shorter time than by simple centrifugal sink/float.^{8,10} Both studies could not have been done without the resolving power and speed of analytical density gradient centrifugation (ADGC) methods. Each study required over two hundred separate ADGC analyses of float or sink phases.

Several general observations emerged from the sink/float studies. The effect of media has already been discussed. Figure 2 displays the ADGC results of a complete separation sequence on a single high volatile bituminous coal using CsCl/Brij-35. The vertical bars represent the nominal solution densities used for each fractionation. This particular separation sequence was from low density to high density. Note that several fractions are not very pure. This is a consequence of two effects. First, even though a density separation may have a constant separation efficiency (i.e., the fraction of mass that will report to the proper phase), the amount of contamination depends on the efficiency factor and the density distribution. Hence, separations made near large bands will be more contaminated than separations further from the main band. We were able to predict the purity of fractions based on the former effect with only moderate success. The second general observation is that float phases invariably contaminates the sink phase due to solution instabilities during the centrifugation process. Much more work is needed to optimize and predict the dynamics of such separations. In the course of this work, we also realized that the density interval of a fraction can also dramatically effect the purity. The narrower the density interval between successive separations, the more contaminated will be the resulting fractions. This is due to the fact that the separation inefficiency is constant, but the mass of a fraction will be smaller as the density interval between separations decreases. DGC is not as affected by this phenomena; this is one reason for its high resolving power. Generally, the S/F separations produced fractions with purities >60%. Many fractions were routinely better than 80% pure.

Continuous flow centrifugation separations, another version of sink/float separations, had very similar constraints to the simple centrifugal sink/float. Even the overall fraction purities were about the same. CFC separations are carried out in a special centrifuge that allows the continuous removal of liquid from the rotor. Float material is entrained with the expelled liquid, while sink material is retained in the rotor (or in more sophisticated centrifuges, separately ejected). Very dilute solutions can be used so that particle aggregation can be minimized. Single density separations with up to 300g of coal can be accomplished within a day. This is far more than can be conveniently handled by simple centrifugal sink/float methods for finely ground coal. We believe that the efficiency of CFC separations can be substantially improved. For one the rotor dynamics appeared to be more complicated than generally believed. We suspect that there are regions within the separation section of the rotor where the particles are not subjected to the expected flow and centrifugal dynamics. Detailed studies of this device are needed to corroborate this. Modifications to the rotor may be necessary to increase the efficiency.

Isolation

Isolation is included in Table 1 mainly because of its impact on time for a complete separation cycle. The largest fraction of time in the separation of ultrafine coal is spent filtering and washing the separated samples. It is often wise to use membrane filters to avoid selective loss of fine coal, which further slows the filtration process.

Summary

Progress has been made in recent years in the science of maceral separation. However, there are many areas that can be improved, and new areas to be investigated. The power of DGC to physically resolve macerals and submacerals species coupled with other instrumental techniques is particularly attractive for defining the limits of coal heterogeneity as well as investigating the ability of other separation methods.

Acknowledgement

This work was performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U. S. Department of Energy, under contract number W-31-109-ENG-38.

References

1. Stach, E., Mackowsky, M.-Th., Teichmüller, M., Taylor, G. H., Chandra, D., Teichmüller, R., Murchinson, D.G., and Zienke, F., 'Stach's Textbook of Coal Petrology', 2nd Edn., Gebrüder Borntraeger, Berlin, 1975.
2. Kroger, C., *Erdöl und Kohle Erdgas Petrochem.*, 1964, 17, 802-812.
3. Dyrkacz, G. R., Bloomquist, C. A. A., and Ruscic, L. R., *Fuel*, 1984, 63, 1166-1173.
4. Dyrkacz, G. R., Bloomquist, C. A. A., in preparation.
5. Dyrkacz, G. R., and Horwitz, E. P., *Fuel*, 1982, 61, 3-12.
6. Dyrkacz, G. R., Ruscic, L.R., and Fredericks, J., *Energy and Fuels*, 1992, 6, 720-742.
7. Dyrkacz, G. R., Ruscic, L.R., *ibid.*, 1992, 6, 743-752..
8. Dyrkacz, G. R., Bloomquist, C. A. A., *ibid.*, 1992, 6, 357-374.
9. Dyrkacz, G. R., Bloomquist, C. A. A., *ibid.*, 1992, 6, 375-386.
10. Dyrkacz, G. R., Bloomquist, C. A. A., Ruscic, L.R., *ibid.*, 1992, 7, 655-660.

Table 1. Coal Maceral Separation Subprocesses.

Liberation of constituents
Demineralization
Wetting and dispersion of maceral particles
Separation
Isolation

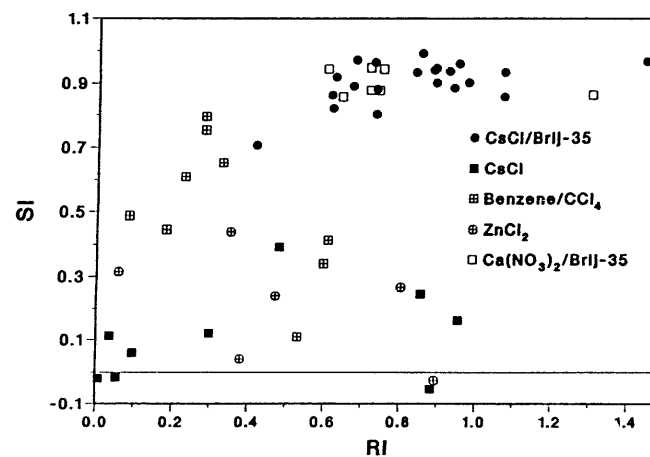


Figure 1. S/F Separation and recovery indices for float fractions from three high volatile bituminous coal.

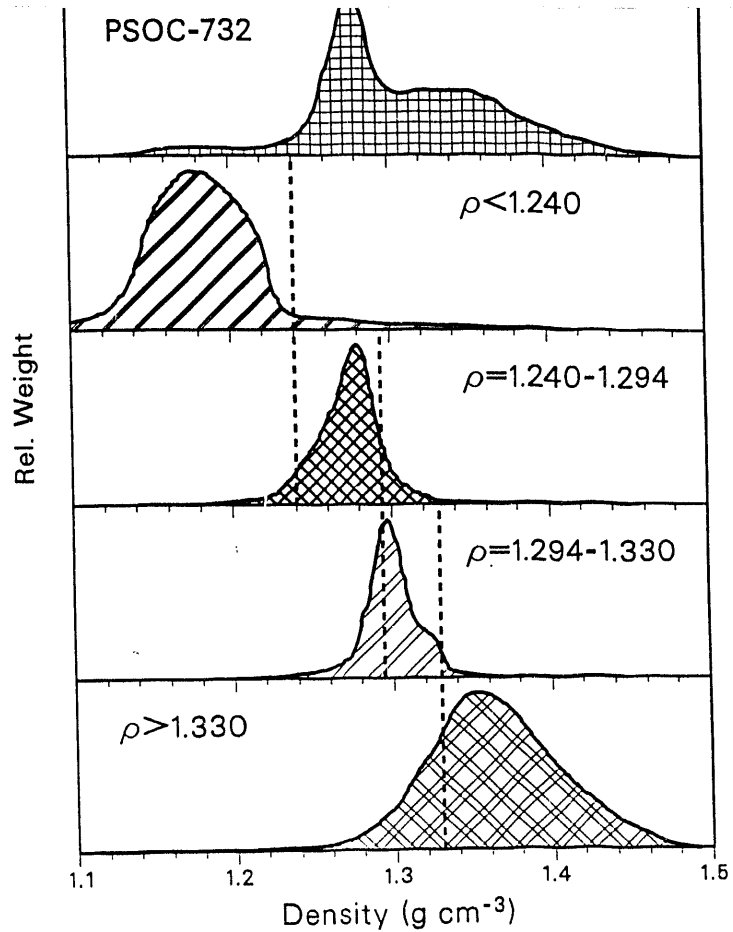


Figure 2. Sequential S/F Separation of a high volatile bituminous coal distributions are normalized to peak values.

END

**DATE
FILMED**

3 / 18 / 1944

