

REFLECTANCE OF LOW-RANK COALS

D. M. Mason

Institute of Gas Technology, Chicago, Illinois 60616

INTRODUCTION

The reflectance of the vitrinite in bituminous coals is very useful as an indicator of their rank and behavior in coking. Determination of reflectance might serve a similar purpose in the characterization of coal for hydrogasification; however, the relation of reflectance to rank of low-rank coal is not so straightforward. Moisture content has been reported to affect the determination of reflectance of Illinois coals, especially those having high surface areas.¹ Furthermore, in the study of the coals tested in our hydrogasification program, we have found that the reflectance does not always fall in line with the rank of the low-rank coals; thus, contrary to expectation, the reflectance of a Colorado subbituminous coal (0.52%) was higher than the reflectance of an Illinois high-volatile C bituminous coal (0.45%). This paper constitutes a progress report on our efforts to elucidate the parameters, including moisture content, that influence the reflectance of low-rank coal.

THEORY

The normal reflectance of the surface of a light-absorbing material such as coal is governed by Beer's relation:

$$R_o = \frac{(n_c - n_o)^2 + k^2}{(n_c + n_o)^2 + k^2}$$

where

- R_o = reflectance in oil
- n_c = refractive index of the material, here a coal constituent
- n_o = refractive index of the immersion medium, here immersion oil
- k = extinction coefficient of the coal constituent

Scattered light from beneath the surface has also been considered as a possible source of difference in reflectance between moist and dry vitrinite. Scattering increases with increasing difference in refractive index between the pore and the matrix, as when water in the pore is replaced with air. However, the extinction coefficients of these vitrinites are high enough that the beam of light can penetrate no more than a few microns, and the pores in question are so small that they are very inefficient scatterers. For these reasons it appears that back-scattering cannot contribute significantly to the reflectance.

McCartney and Ergun have determined refractive indices and extinction coefficients on vitrinites of a series of coals.³ Among low-rank coals the extinction coefficient is low enough that it has only a small effect on the reflectance. Thus, its contribution to the reflectance of a Wyoming subbituminous coal is 0.026% out of 0.54% and to that of a high-volatile A bituminous coal is 0.24% out of 0.88%. Presumably the only significant source of any effect is the change in refractive index with change in the pore content of the submicroscopic pores.

The effect of density and pore content on the refractive index can be handled by the Lorenz-Lorentz relation in the form:

$$\frac{(n_c^2 - 1)}{(n_c^2 + 2) d} = r = w_1 r_1 + w_2 r_2 + \dots w_n r_n$$

where

r = specific refraction

$w_1, w_2,$ and w_n = weight fractions of components in the coal just beneath the surface

$r_1, r_2,$ and r_n = specific refractions of components

d = apparent density with submicroscopic pores (but not larger ones) included in the volume

The relationships between reflectance and refractive index and between reflectance and refraction $[(n^2 - 1)/(n^2 + 2)]$ are shown graphically in Figure 1. These curves were obtained by setting the extinction coefficient in the Beer relation equal to zero, which gives us the well-known Fresnel relation. The actual reflectance of a coal of a given refractive index will be slightly higher than the calculated value from the graph.

To elucidate the effect of moisture and pore filling on reflectance, we need to know the fine porosity properties of the coal. These include true and particle densities, and the extent to which the immersion medium enters the pores.

EXPERIMENTAL

Pore Structure

Samples of high-surface-area Illinois coal were obtained from the Illinois State Geological Survey. Pieces of high vitrinitic content were picked from a sample from No. 2 seam, identified as IGS-IGT No. 1, by observation under a low-power microscope. These were crushed and screened to obtain a 40 to 80-mesh USS sieve fraction. This particle size was chosen to be small enough to make a 5-gram sample representative and large enough to minimize error in the density determination, where the penetration of the interstices between fine particles by mercury is a problem. One portion of the sample was dried over a desiccant; another was treated with boiling water to fill its pores. The latter was then dried in a desiccator over potassium sulfate, the saturated solution of which gives an equilibrium atmosphere of about 96% relative humidity.

After the two samples had come to constant weight, particle density was determined on each sample by mercury displacement with a 6-ml Aminco penetrometer cell. The moist sample was cooled to about 0°C before evacuation to prevent appreciable loss of moisture. Volume readings and densities at 100 and 400 psig pressure were obtained; at 400 psig pores of the dry coal should be filled down to a diameter of 0.35 μ . Moisture was also determined on these two samples; moisture, ash, carbon, hydrogen, and pyrite were determined on a separate sample ground to pass a 60-mesh sieve. True density was also determined on this sample by means of a Beckman air pycnometer with helium. Results are shown in Table 1, together with results of the calculation of densities and pore volumes to a mineral-matter-free basis.

Table 1. PORE VOLUME OF VITRINITE FROM AN ILLINOIS COAL

Sample	Moist 40-80 USS mesh	Dried 40-80 USS mesh	Ground <60 USS mesh
True Density, g/cu cm	--	--	1.291
Particle Density, g/cu cm			
Hg at 100 psig	1.252	1.109	
Hg at 400 psig	1.254	1.113	
Moisture, %	15.12	1.14	2.54
Composition (dry basis), wt %			
C			78.8
H			5.54
FeS ₂			0.93
Ash			1.78
Moisture Content (mmf*), wt %	15.47	1.17	2.61
Particle Density (mmf), g/cu cm	1.236	1.094	--
Moisture (mmf), vol %	19.13	1.28	--
Porosity† (mmf), vol %	19.13	15.55	--
Pore Volume† (mmf), cu cm/g dry coal	0.183	0.144	--
Particle Volume (mmf), cu cm/g dry coal	0.957	0.925	--
True Density (dry and mmf), g/cu cm	--	--	1.280

*Mineral-matter-free.

†Including water volume. Normal density of water assumed.

According to the particle specific volumes (pore space included), it appears that the coal shrinks about 3% in volume when it dries. The "true" specific volume (pore space excluded) calculated from the particle density and moisture content of the moist sample agreed within 1% with the "true" specific volume of the dried sample determined with helium in the Beckman air pycnometer.

Reflectance

Moist and dry samples of the coal described above were prepared for reflectance determination by the method described by Harrison¹. Cargille Type-B immersion oil was used. Other details of our apparatus for the determination are described elsewhere².

The results indicate no difference in reflectance between moist and dry samples. The reason for our failure to obtain Harrison's effect has not been discovered as yet.

DISCUSSION

Harrison¹ found differences in reflectance between moist and dry samples of about 0.1% on high-volatile C bituminous coals having high surface area; the dry samples gave the higher reflectances. With this in mind, it is instructive to calculate the change in reflectance to be expected if water in the pores is replaced with either air or immersion oil. From the measured reflectance of the moist sample we calculate its specific refraction and subtract the contribution of the water, assuming the specific refraction of the moisture in the coal to be equal to the specific refraction of bulk water. From the specific refraction on the coal itself thus obtained, we back-calculate the reflectance of the dry sample if oil does not enter the pores. Similarly, using the density and specific refraction of the oil as determined on a bulk sample, we can calculate the specific refraction and reflectance if the oil does enter the pores. We have done this for the sample on which the pore property and reflectance data above was obtained, with results as follows:

Observed Reflectance of Moist Sample, %	0.45
Calculated Reflectance, %	
Dried Sample, No Oil in Pores	0.22
Dried Sample, Oil in Pores	0.58

Thus, the difference in reflectance between the moist sample and the oil-filled sample is of the right amount and algebraic sign to agree with Harrison's results. However, further work is required to clarify conflicting results on the effect of moisture and to determine to what extent immersion oil enters the pores of low-rank coal.

ACKNOWLEDGMENT

This study was supported by IGT as a part of its in-house basic research program.

REFERENCES CITED

1. Harrison, J. A. and Thomas, J., Jr., "Relation Between Moisture Content, Reflectance Values and Internal Surface Area of Coal," Fuel 45, 501-03 (1966).

2. Mason, D. M. and Schora, F. C., Jr., "Coal and Char Transformation in Hydrogasification," Fuel Gasification; A Symposium, Advan. Chem. Ser. No. 69. Washington, D.C., 1967.
3. McCartney, J. T. and Ergun, S., "Optical Properties of Coals and Graphite," Bur. Mines Bull. No. 641. Washington, D.C.: U. S. Department of the Interior, 1967.

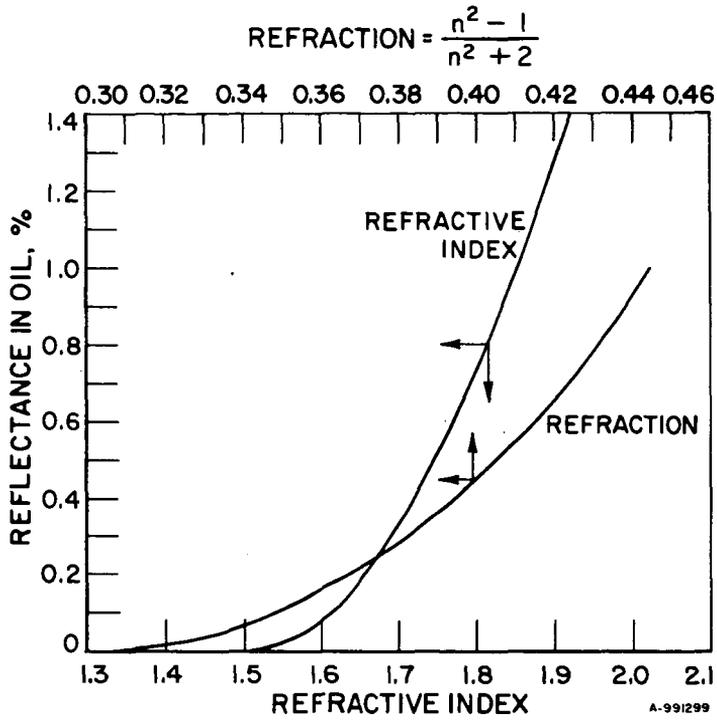


Figure 1. OPTICAL RELATIONSHIPS