A Chemist Looks at Coal Petrology

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Petrology is in general defined as the study of rocks, and is considered a branch of geology. In the study of inorganic rocks the petrologist relies heavily for identification of mineral species on such optical properties as refractive index and birefringence, and on characteristic crystal form or morphology. The coal petrologist also relies on optical properties to distinguish "macerals" in the organic rock, coal, but has to use reflectance or color in transmitted light rather than refractive index, and cannot derive help from crystal form. Instead he has to study the palaeobotany of the sample and make what use he can of differences in botanical structure or of types of association of differently shaped bodies in a sample; it is this difference from inorganic petrography that gives the study of coal its peculiar difficulty.

The nomenclature and classification of the entities discerned in coals by petrologists is a complicated matter which has been productive of much controversy, and there is still no universally accepted system. Consequently it is not easy for other workers in coal science to grasp the nature and significance of the petrologist's work, and they may be tempted to dismiss the work as still too ill-defined and controversial to be worth basing their own researches on, or even to be worth finding out about.

Such a dismissal would be a grave mistake. It is true that there is still lack of agreement about the significance of some of the entities claimed to be present in coal samples, and about their classification and origin. Nevertheless, there is a body of solidly established fact which should be taken account of by any chemist or physicist studying coal, and which is of demonstrable importance even in practical operations for the use of coal. It is regrettable that papers are still being published in which often excellent experimental work is marred by inadequate choice and description of samples. Furthermore, it is often forgotten that describing a coal solely in terms of one of the various national technological classification systems, such as the A.S.T.M., has little <u>scientific</u> value even to a worker familiar with the system, and none at all to workers elsewhere. The systems were devised to define whole coals for technological purposes.

It is the purpose of this paper to review briefly how "macerals" come to be present in coals, and to discuss the relation between those aspects of contemporary classification systems that seem of most importance to the chemist and physicist. It is hoped that this will facilitate the use of petrological concepts by non-petrologists.

Most major coal measures were laid down in elongated depressions in the earth's surface known as geosynclines. For substantial deposition of any kind of sediment in a geosyncline, it is necessary that the rate of accumulation of sediment is approximately balanced by the rate of subsidence of the floor of the depression due to the increasing load on it. Vegetation can only thrive and its products of decay be preserved while the physical conditions, particularly the level of the water table, remain within fairly narrow limits. Since the two rates referred to above do not remain in balance indefinitely, a core of the material accumulated in a geosyncline

reveals a fairly regular variation in type of sediment with depth. Thus the coal seams are separated by a regular and repeating sequence of inorganic sediments, with fossils indicating the varying depth of the water in which the sediment was transported from neighboring high land and then deposited.

Even during the formation of one coal seam, conditions vary. Varying water level and movement changes the degree of aeration and hence the activity of aerobic bacteria in bringing about decay. The different types of chemical substance present in plants - cellulose, lignin, resins, waxes, tannins, etc. - are present in different relative proportions in living woody tissue, in dead cortical tissue, in seed and leaf coatings, and so on; and also these substances show differing degrees of resistance to decay. It can therefore be seen that as conditions fluctuate during the accumulation of plant debris, the botanical nature and chemical composition of the material surviving complete breakdown will fluctuate also. This fluctuation is the origin of the familiar banded structure of coal seams, which is visible to the naked eye, and it provides a prima facie case for supposing that the banded constituents will differ chemically and physically.

There is another deduction to be made from the mode of origin of the banded constituents. The average nitrogen content of coals is appreciably more than that of plants, and it is commonly supposed that the extra nitrogen originates from the protein content of the bacteria that brought about decay in the peat swamp, the bacterial remains having been included in the coal structure. Varying nitrogen contents in coals therefore reflect varying amounts of metamorphosed protein mixed in with the plant debris.

The character of the biochemical system and of the physical conditions was never such as to preserve only one kind of plant debris to the exclusion of others. Consequently the banded constituents are merely concentrates of some more fundamental components. The European classification of these components into material derived from woody tissue (vitrinite), from spores, seed coatings, cuticles, etc. (exinite), from woody tissue carbonized or changed in some other way to "natural charcoal" (fusinite), and from an unknown source, possibly humic mud (micrinite), is too well known to need discussion here (see, for example, Van Krevelen[1], Brown[2]). The significance of this basic classification has been confirmed by chemical, carbonization, and other studies (see Given[3] and references therein).

European and other petrologists have believed for some time that the four main categories are themselves not fundamental, and research on proper sub-division and classification continues actively. No doubt in time purified samples of the sub-components will become available for further study by other techniques. So far no attempt has been made to substantiate physically and chemically the petrological distinction between tellinite and collinite (forms of vitrinite with and without cellular structure respectively). Of the various members of the exinite group, only sporinite (from megaspores) has received any extensive chemical study.

In the chemical and physical study of coals it is customary to correlate, for a series of samples, the property being measured with some other property presumed to measure rank. Even with pure vitrinites there is appreciable scatter in any plot; there is much scatter with spore-rich exinites; while with fusinites the concept of rank seems to break down altogether since no rank parameter gives any correlation. The scatter may be due to the incorrect choice of rank parameter (on this, see below) or to the random operation of nature in the metamorphic process. However, the scatter may also be taken to indicate that the materials are still heterogeneous, and that the petrologists are correct in insisting on further sub-division of the classification referred to.

The European maceral concept has been criticized by American petrologists on the grounds that it takes no account of rank. In the author's view this criticism

is based on a misconception. Clearly the fundamental point is that to define a pure sample completely, at least two statements are necessary: one showing the maceral group to which the specimen must be assigned, and the other locating the point in the sequence of changes from plant material to graphite (or graphitic carbon) reached by metamorphosia. This point can be indicated in a number of ways, of which the commonest are the use of carbon content, yield in the standard volatile matter test, and maximum reflectance under oil immersion.

European workers (and chemists elsewhere) most commonly define rank by means of the carbon content (d.a.f. or d.m.m.f.) of the sample or in the case of fusinite by the carbon content of the associated vitrinite. Since metamorphosis is essentially a chemical process, and its trend is towards pure carbon, the carbon content appears to the author to be the best available and most nearly direct measure of rank. However, it must be admitted that if reflectance is used as a measure of rank, the same set of microscopic observations can be used both to identify the maceral group and assign a specimen to its place in the group; use of the carbon content requires a separate observation.

In recent years, a number of new ideas have been introduced into coal petrology by American workers, which involve a considerable amount of re-definition of concepts. Groups of workers at Pennsylvania State University, the U. S. Steel Corporation, the Illinois Geological Survey and other centres have been active in formulating these ideas, which however have not yet been made widely available to chemists.

Spackman, Berry and their co-workers[4] have made extensive microscopic studies of coals by transmission of light through thin sections. They observed that the material derived from woody tissue (vitrinite) commonly contained fairly well-defined regions of different color, some of which showed remains of cellular structure and some did not. In a suite of samples covering a wide range of rank they observed regions of color ranging from bright yellow through orange, red and deep red to an almost opaque red-brown. In any one sample there were not more than two or three predominating colors, and in general the color shifted across the spectrum towards red as the rank of the sample increased. They felt that in a series of samples nine different shades of color could be reproducibly distinguished, and termed the components of different color vitrinoids. The vitrinite from a low-rank bituminous coal might therefore be composed on their hypothesis predominantly of vitrinoids 2 and 3, a medium-rank of vitrinoids 4 and 5, and so on. Two vitrinitic coals of similar rank might differ chiefly in the relative proportions of the same vitrinoids. By specifying the vitrinoid analysis of a sample, therefore, they were defining both the maceral group and the rank from the same set of observations. However, there is one reservation: in certain cases it is difficult to distinguish a high-rank vitrinoid from a semi-fusinite; this point is discussed below.

Some confirmation that the vitrinoids differ in some significant manner was obtained from color cinematography of samples mounted on the hot-stage of a microscope; in this way differing behavior - melting, swelling, change of color, etc. - of the various components could be observed directly. Further evidence of the significance of this vitrinoid concept was obtained as a result of the preparation of pure vitrinoids by careful micro-manipulative techniques applied to selected samples. In a series of experiments, the pure vitrinoids were carbonized in mixture with various proportions of inert filler (fused alumina), and the hardness of the coke was then measured. It was found that the curve obtained by plotting coke hardness against proportion of inert had a characteristic shape for each vitrinoid, the shape of the curve being reproducible with samples of the same vitrinoid separated from different coals.

The hypothesis of Spackman and Berry and their supporting evidence at least establish a case for the heterogeneity of vitrinites which is worthy of further investigation. The hypothesis is easily comprehended in chemical terms, and it should not be difficult to devise experiments for testing it provided sufficiently

sensitive physical and chemical methods are available. On the other hand, it is not easy to see how any probable combination of biochemical and geological conditions could have produced such a strictly limited number of fundamental constituents of which all vitrinitic coals are to be presumed to be composed. Moreover, since the absorption of light by coals in unselective, that is, not in well-defined bands, division into materials of color shade distinguishable by eye has an element of arbitrariness.

Because of the necessary lack of objectivity in separating materials according to their color in transmitted light, current petrological research is placing more emphasis on the use of reflectance measurements. A detailed system of classification of coal components based on reflectance has now won general acceptance among petrologists in this country (see Schapiro and Gray[5]). In this system, the observed range of reflectance values of vitrinitic materials in oil is divided up arbitrarily into smaller ranges or steps of 0.1% reflectance, experimental values being significant to about 0.01%. A component of vitrinite having a reflectance of 0.83%, for example, is designated vitrinoid no. 8 or V8, and one of reflectance 1.37% is V13. (Note that the same word vitrinoid is used as in Berry's system, though the significance is different; note also that the numbering in the two systems does not correspond at all.) Other macerals are designated similarly. Thus the system includes both maceral type and an indication of rank. The reflectance of the technically important medium to low volatile vitrinites is a good index of rank, and varies rapidly with carbon content. The reflectance of low to medium rank vitrinites, however, is low and varies only slowly with carbon content. The system has practical advantages in specifying coking blends and predicting carbonization behavior, but no fundamental significance is claimed for the reflectance ranges used to define the maceral type number.

No correlation has yet been established between the two "vitrinoid concepts". According to the Fresnel equation, the reflectance of a substance is a function of the refractive index and the absorption index. In the case of medium to low rank coals, the absorption index makes a relatively small contribution to the reflectance of visible light, and the latter property is therefore determined mainly by the refractive index, which in turn is related to the density and electron polarizability of the substance. (With high rank coals absorption becomes more important.) Hence reflectance and absorption measurements often relate to different fundamental properties. However, if the vitrinoids distinguished by color by Spackman and Berry have fundamental significance one might expect the reflectance values of a large number of points on the polished surface of a single block of vitrinite to fall into a bi- or tri-modal distribution curve. In fact a range of reflectance values are found for a series of points on a vitrinite surface, but they are distributed fairly evenly over the range, no sign of two or more peaks being observed as a rule. Reflectance measurements, in that a range of values is found for one sample, do therefore support to some extent the idea that vitrinites are still heterogeneous, but not that they are heterogeneous in the sense suggested by Spackman and Berry. Some histograms illustrating the spread of reflectance values found in vitrinites are shown in Fig. 1.

There is one major difficulty common to all systems of detailed classification; this arises from the fact that there appears to be a completely continuous gradation in both color in thin section and in reflectance from high-rank vitrinites through semi-fusinites to fusinites. Thus Berry and Spackman frequently observed regions of very dark-colored material in predominantly light-colored (low-rank) vitrinite; one can either suppose this material to result in the peat swamp from the same kind of biochemical process that led to the formation of vitrinites but more severe, or that it is a product of the same process that produced fusinite, again at the peat stage. At any rate the differentiation of this material from the rest must have occurred at an early stage of coalification and not during geological metamorphism. Similar observations to the above are made in reflectance studies at all levels of rank. Carbonization data are of no help in making distinctions, since vitrinitic materials

of very dark color or of reflectance in oil above about 2.5% are inert, in the sense that they do not swell or fuse on heating; in this respect they have the same behavior as semi-fusinites and fusinites. Matters are made more difficult by the fact that the nature of the fusinization process is not known.

It is clear therefore that in any attempt to identify and group correctly pure components in coals there is at present an ambiguity about some small part of the whole sample; it could be either chemically akin to the rest of the vitrinite family but highly altered, or it could be the remains of woody tissue that has undergone some fusinization, whatever that may be, and belong chemically with the fusinite group. In any case the distinction becomes both harder to make and less important in high rank coals.

Summary and Conclusions

Vitrains may contain about 60-95% vitrinite, the balance usually being made up mostly of fusinite, spore exinite and resin inclusions. The relative proportions of the minor constituents vary from coal to coal. It is already established that such chemical properties as the proportion of phenolic hydroxyl and the distribution of hydrogen in different forms of combination differ widely between the various maceral groups.[6] In some cases, where the purity is high or the effects of impurities tend to cancel one another out, an average property of a vitrain may differ little from that of the pure vitrinite. In other cases there will be significant differences; for example, Wyss and Given[7] found the hydroxyl content of a series of vitrains from British coals to run consistently lower (10-20% of the total content) than the values for a similar series of pure vitrinites.[6] Moreover the trend of values with rank was different, and only the pure vitrinite set of results was in reasonable agreement with the values found by Blom et al.[8] for a series of vitrinites from continental European seams.

It is therefore submitted that in any scientific investigation the purest and most homogeneous materials available should always be used. At present these materials will be vitrinites or members of one of the other three main maceral groups. It is not difficult to obtain vitrinites at least in good purity, and the purification has the further advantage of eliminating most of the mineral matter, which greatly complicates chemical analysis if present in large amounts. If pure macerals, in the sense just defined, cannot be used, then at least a petrographic analysis should be reported.

It is not yet certain whether or how far the further sub-division of maceral groups is justified on chemical and physical grounds, and intensified research to settle this is demonstrably worthwhile and highly desirable. In the meantime, it is suggested, chemists and physicists should be aware of current thinking on the subject.

In conclusion, the author would like, with respect, to suggest to coal petrologists two urgent needs in the immediate future:

1. greater attention to the physical separation of pure components for further study.

2. research on the nature of fusinization and on the vitrinite-semi-fusinite gradation; in this, full cooperation between all disciplines will be needed.

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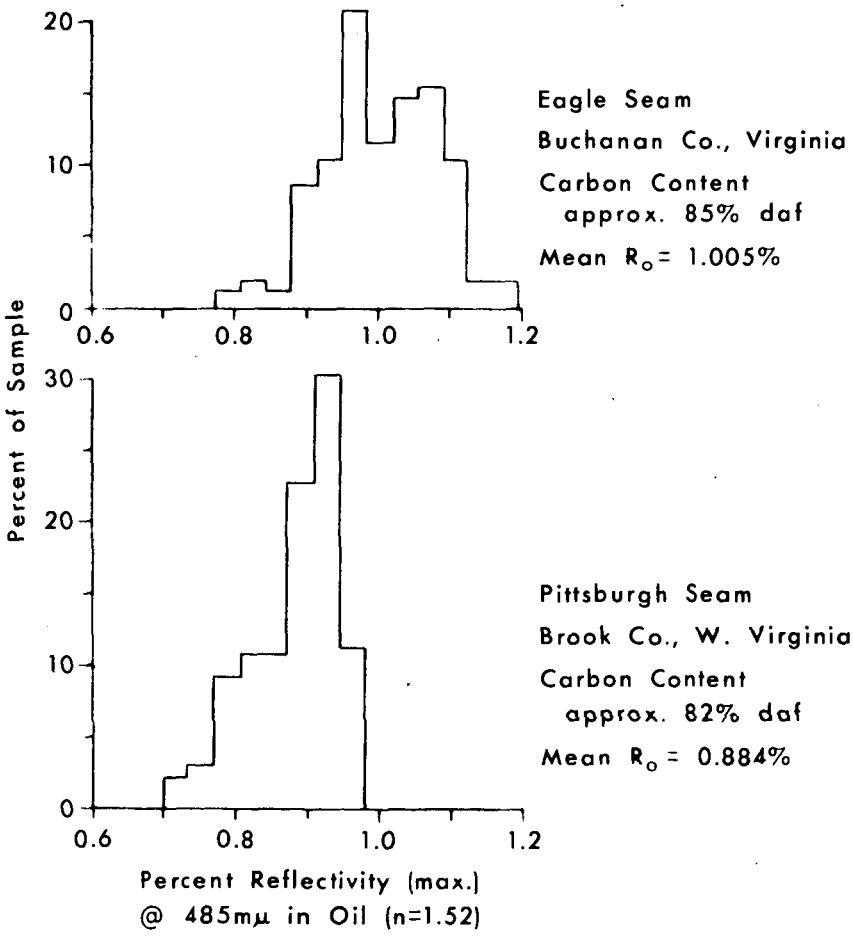

DISTRIBUTION OF MAXIMUM REFLECTIVITY OF VITRINITES IN SMALL (½ inch square) BLOCKS OF BITUMINOUS COAL

Figure 1

A FURTHER STUDY OF THE RELATIONSHIP BETWEEN THE CHEMICAL, PLASTIC, AND PETROGRAPHIC PROPERTIES OF ALABAMA MEDIUM-VOLATILE COALS AND THEIR CARBONIZATION BEHAVIOR

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Introduction

During the past several years, studies have demonstrated that the petrographic properties of coals can be correlated with their carbonization behavior and coking properties.[1,2,3,4,5)*] While coal is being examined petrographically, a measurement is made of the reflectance of the vitrinite in the crushed coal sample. This reflectance has been shown to be directly related to the rank of the coal. Furthermore, it is well known that rank is important in the determination of other carbonization characteristics such as volume change and coking pressure. Since a general relationship prevails between rank and these parameters, a correlation would be better if it were confined to a narrow range of coals or coal blends.[6,7)]

In a previous paper[6)] the authors showed that the volume-change characteristics (expansion-contraction in the sole-heated oven) were related to the plastic and chemical properties of several Alabama medium-volatile coals. In the present paper, the authors demonstrate how not only volume change but also coking pressure are related to the chemical and plastic properties and petrographic characteristics of washed coal samples.

Experimental

The samples consisted of a series of six composites of the daily production from each of several mines operating in the Pratt, American, and Mary Lee seams (Table I). All samples were taken on consecutive days except for those from Mine B in the Pratt seam; the last three samples from this mine were taken six months after the first three.

For the tests in both the 30-lb pressure-test oven and the sole-heated oven, the coals were pulverized to minus 1/4 inch and dried to about 1 percent moisture. These conditions were used to obtain more reliable results in these small ovens and to permit comparisons with the results of the earlier work. The oven designs and heating programs have been described in earlier publications.[6,7,8)] Petrographic, chemical, and plastic properties of the various samples are listed in Table I. Corresponding carbonization data are given in Table II.

* See references.

Relation Between Petrographic and Chemical Characteristics

Since reflectance furnishes a relatively precise measurement of rank,[1] the amounts of the entity types present in the coal as determined petrographically should be related to a chemical-rank parameter, such as volatile matter content. Figure 1 shows the relation between volatile matter content and reflectance of the entities in coals.[3] In general, the exinoids in a coal contain considerably more volatile matter than the vitrinoids of the same rank, and both the exinoids and the vitrinoids contain more volatile matter than the inert semifusinoids, micrinoids, and fusinoids.[4] This is illustrated in Figure 1, in which reflectance of the principal entities is plotted against their volatile matter contents. The different volatile matter contents of the entities are apparent from the lines connecting entities of the same rank. Also one can see how the differences in volatile matter contents become less as the rank increases.

The average vitrinoid reflectance calculated from the quantitative petrographic analysis can be used to calculate the volatile matter content of a coal, by means of the following formula developed by Van Krevelen and Schuyer.[3]

$$VM_c = \frac{E}{100} VM_e + \frac{V}{100} VM_v + \frac{M}{100} VM_m$$

where VM_c is the dry, ash-free volatile matter content of the coal; VM_e, VM_v, and VM_m the dry, ash-free volatile matter contents of the entities; E the percentage of exinoids and resinoids in the coal; V the percentage of vitrinoid plus 1/3 semifusinoids; and M the percentage of inert entities (micrinoids, fusinoids, and 2/3 semifusinoids). In Figure 2 a good correlation is apparent between the volatile matter from the proximate analysis and that obtained by use of the above equation. The calculated volatile matters in Figure 2 are based on the use of the entity volatile matter values published by Van Krevelen and Schuyer.[3] If volatile matter contents are obtained for these entities of the coals being worked with, even better agreement between the calculated values and those from the proximate analysis should be obtained.

Volume-Change Characteristics

Figure 3 shows the relationship of the maximum fluidity of these coals to the average reflectance of the vitrinoids in them. In general, as the average reflectance of the vitrinoids increases, the maximum fluidity decreases. Pratt-seam Mine-B samples exhibit the highest fluidity; Pratt-seam Mine-C and the Mary Lee-seam samples, intermediate fluidities; and Pratt-seam Mine-A and American-seam samples, the lowest fluidities.

Figure 4 shows the relationship between the volume-change characteristics of these coals and the average reflectance of the vitrinoids present. The volume-change data have been corrected[9] to a bulk density of 55 lb of dry coal per cubic foot. This figure indicates that the coals containing vitrinoids with reflectance below about 1.14 percent contract strongly, and that those having vitrinoid reflectance above 1.14 percent are less contracting and show increasing tendency toward expansion as the vitrinoid reflectance increases. It should be noted that the Mine-B Pratt-seam samples showed the widest range in volume change and also the widest range in total inerts (Table I) of all the coals. This range of inerts shows the importance of the inert content of a coal in determining its volume-change characteristics.[5] This is illustrated in Figure 5, in which the volume change of

American-seam coal is plotted against its total inert content. The samples included a very narrow range of rank and had reflectances between 1.206 and 1.223 percent. The transition between contraction and expansion falls between a total inert content of 20 to 21 percent. Beyond this the contraction increases as the amount of inerts increases. Evidently the "pure" coal reactive entities could be expected to be expanding in nature and any increase in the amount of inerts would dilute this effect so that the coal would be less expanding or even contracting. The particle size of the inerts would influence the degree of this effect. Conversely, the opposite effect has been noted wherein if the "pure" coal reactive entities are contracting, the addition of inerts results in less contraction. This would be expected since the inert material, which shows little change in volume during carbonization, would dilute the contracting nature of the "pure" coal reactives.

In the previous study,[6] volume changes of the coals in the sole-heated oven were correlated with their maximum fluidities. This relationship is shown in Figure 6. The band represents the range of values noted in the earlier work,[6] within which the washed coal samples fall. This demonstrates the usefulness of the Gieseler Plastometer in assaying the expansion-contraction properties. Here again, those coals having a maximum fluidity above 10,000 dial divisions per minute should be contracting, and could be expected to give no difficulty in the pushing of the coke if operating practices are under control.

Figure 7 shows the correlation between the volatile matter content and the volume changes for these coals. Because both volatile matter and reflectance are measures of rank, volatile matter would be expected to yield a relationship similar to that obtained in Figure 4. The authors' earlier work[6] indicates that a useful method of estimating the comparative expansion-contraction characteristics of these washed coals should result from a multiple correlation with the ash along with the volatile matter contents. However, because the present washed samples did not show enough variation in ash content between samples from each mine, ash is not significant in the correlation. This does not mean that it should be disregarded in coals that show a greater degree of variability than these samples had. Within a narrow range of ash contents, however, inerts are important, as shown in Figure 5.

Coking Pressure

Since both volume change and coking pressure appear to be the result of the same basic phenomena occurring in coal during heating, these two carbonization characteristics would be expected to correlate under certain conditions. Furthermore, it is generally accepted that coals exhibiting a coking pressure greater than about 2 lb per square inch or having less than approximately 7 percent contraction should not be used.[10] It is not within the scope of this paper to judge the validity of these limits. However, if these or any similar set of limits are used, then some coals will, at a particular operating bulk density, meet one of these limits, but not the other. Therefore, it would be desirable if petrographic, chemical, or plastic properties of these coals could be used to estimate the coking pressure that might develop.

The relationship between coking pressure of the coal and average reflectance of the vitrinoids in the coal is shown in Figure 8. The data on the Mary Lee-seam samples are not shown in this figure nor in those that follow, because these samples had higher oven bulk densities than the samples from the other seams. These higher bulk densities were the result of the coarser particle-size distribution obtained in pulverizing the higher ash Mary Lee coals, even though they were pulverized to

the same top size as the lower ash coals used. In Figure 8, samples having an average reflectance of less than 1.18 percent should not exhibit a coking pressure in excess of the 2 lb per square inch usually considered as the limiting pressure for safe oven operations.

A similar relationship is noted in Figure 9 between coking pressure and volatile matter. In this figure, those coals having a volatile matter greater than 28 percent exhibit coking pressure less than this 2-psi limit, and therefore could be used safely at the bulk densities listed.

The relationship between the coking pressure and the maximum fluidity is shown in Figure 10. Those coals having a Gieseler maximum fluidity in excess of 10,000 dial divisions per minute should not offer any problems with pressure in the oven. Note that this is the same limit that was found for the volume-change characteristics. This lends support to the idea put forth by Potter[11] that these carbonization properties could be expected to correlate under certain conditions.

Summary

The chief finding of this investigation was that reflectance of the vitrinoids, volatile matter content, and maximum fluidity can be used to obtain an estimate of the expansion-contraction behavior and coking pressure exhibited by these medium-volatile coals. Thus, these carbonization characteristics can be estimated from the parameter most readily available.

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* In reference 6 two graphs were reversed and should be corrected as follows: that on page 767 should be titled "Figure 8. Comparison of Site and Zone Samples from the Mary Lee Seam Mine;" and that on page 768 should be titled "Figure 7. Comparison of Site and Zone Samples from American Seam Mine."

Table I

Petrographic, Chemical, and Physical Properties

Coal	Sample No.	Entity Composition of the Coal, volume percent*															Avg R_o	Proximate and Sulfur Analyses, wt percent			
		Reactive Entities										Inert Entities									
		V9	V10	V11	V12	V13	V14	E	R	SF	Total	SF	M	F	MM	Total		Volatile Matter	Fixed Carbon	Ash	Sulfur
Pratt Seam Mine A	1		1.5	18.3	48.8	7.6		3.6	0.2	0.6	80.6	1.2	10.4	3.8	4.0	19.4	1.239	26.3	67.0	6.7	1.29
	2		2.9	18.2	48.1	3.7		2.4	0.2	0.6	76.1	1.3	14.0	4.2	4.4	23.9	1.215	27.6	65.1	7.4	1.38
	3		0.8	16.8	51.2	7.7		2.5		0.5	79.5	1.0	11.4	3.8	4.3	20.5	1.242	26.2	66.6	7.2	1.41
	4		0.8	14.6	49.2	12.3		2.7	0.1	0.8	80.5	1.6	8.9	4.6	4.4	19.5	1.248	25.8	66.8	7.4	1.39
	5		0.8	13.9	47.1	15.5		3.0		0.7	81.0	1.3	9.5	3.7	4.5	19.0	1.250	25.7	66.8	7.5	1.37
	6		0.8	14.2	51.2	12.6		1.6	0.3	0.4	81.1	0.7	8.7	5.3	4.2	18.9	1.244	26.6	66.4	7.0	1.25
Pratt Seam Mine B	1	2.9	17.2	45.8	3.6	2.1		3.8	0.1	0.7	76.2	1.5	12.0	5.9	4.4	23.8	1.125	29.8	63.0	7.2	1.59
	2	0.7	26.6	37.0	4.9	0.7		3.4	0.1	0.8	74.2	1.6	13.5	5.7	5.0	25.8	1.107	30.8	60.9	8.3	1.68
	3	1.5	23.2	46.4	3.0	0.8		3.5	0.1	0.4	78.9	0.7	11.2	5.0	4.2	21.1	1.122	30.2	62.9	6.9	1.57
	4	1.3	23.5	36.9	4.7	0.7		5.1	0.2	0.8	73.2	1.8	15.7	5.1	4.2	26.8	1.116	29.9	63.1	7.0	1.43
	5	2.1	24.8	39.2	2.7			4.8	0.2	0.9	74.7	1.9	14.4	4.8	4.2	25.3	1.114	29.9	63.1	7.0	1.41
	6	1.4	27.5	37.8	1.4	0.7		3.3		0.7	72.8	1.5	14.0	7.3	4.4	27.2	1.109	29.9	62.9	7.2	1.63
Pratt Seam Mine C	1	0.7	13.9	48.5	10.3			2.4	0.2	0.5	76.5	1.1	11.5	6.6	4.3	23.5	1.151	27.9	64.9	7.2	1.46
	2		7.9	42.7	20.1			3.5	0.1	0.5	75.8	1.1	11.8	6.9	4.4	24.2	1.168	27.4	65.3	7.3	1.40
	3	0.7	18.7	43.3	11.2	0.7		3.5	0.1	0.4	78.6	0.8	10.8	5.4	4.4	21.4	1.147	27.7	65.3	7.3	1.40
	4	0.8	14.8	46.0	12.6			3.6	0.2	0.4	78.4	0.9	12.3	4.4	4.0	21.6	1.159	26.0	67.4	6.6	1.45
	5		12.6	48.0	13.3			2.3	0.2	0.6	77.0	1.2	12.2	5.2	4.4	23.0	1.155	27.9	64.9	7.2	1.53
	6		6.7	36.4	30.5	0.7		3.0	0.2	0.6	78.1	1.3	11.3	5.2	4.2	21.9	1.179	27.8	65.2	7.0	1.48
Mary Lee Seam	1	0.7	14.0	32.4	23.6	3.0		5.2	0.1	0.6	79.6	1.1	8.1	4.2	7.0	20.4	1.168	28.0	59.8	12.2	0.75
	2	0.7	14.4	39.6	15.1	2.2		5.4	0.2	0.7	78.3	1.3	8.5	4.8	7.1	21.7	1.152	28.1	59.7	12.2	0.79
	3	2.2	12.3	34.8	20.3	2.9		4.4		0.4	77.3	0.7	10.7	4.4	6.9	22.7	1.162	27.6	60.5	11.9	0.82
	4	1.4	12.9	32.9	22.2	2.2		5.0	0.3	0.5	77.4	0.9	10.1	4.3	7.3	22.6	1.167	27.7	59.7	12.6	0.92
	5		11.8	37.6	20.6	3.7		4.4	0.3	0.7	79.1	1.4	8.2	4.2	7.1	20.9	1.170	28.1	59.7	12.2	0.82
	6	0.7	15.7	38.9	17.9	1.5		3.2	0.1	0.6	78.6	1.3	9.3	3.7	7.1	21.4	1.158	28.2	59.6	12.2	0.80
American Seam	1	0.8	13.7	22.8	24.4	14.4		4.3	0.1	0.6	81.1	1.2	10.3	4.3	3.1	18.9	1.206	27.3	66.8	5.9	0.83
	2	1.5	10.7	26.1	15.4	20.0	3.1	4.4	0.2	0.5	81.9	1.1	9.8	4.2	3.0	18.1	1.210	27.3	67.5	5.2	0.88
	3		13.0	19.5	17.3	19.5	2.9	5.5		0.7	78.4	1.5	12.4	4.4	3.3	21.6	1.223	27.2	67.1	5.7	0.89
	4	3.0	11.9	17.0	24.5	17.1	0.7	4.2		0.6	79.0	1.1	11.3	5.6	3.0	21.0	1.214	27.0	67.8	5.2	0.89
	5	1.4	11.4	20.6	21.3	13.5	2.9	4.1	0.1	1.0	76.3	2.0	12.3	6.1	3.3	23.7	1.211	27.5	66.7	5.8	0.84
	6																	27.4	65.8	6.3	0.85

* Abbreviations for entities:
V = vitrinoids; numeral indicates type.
E = exinoids
R = resinoids
SF = semifusinoids
M = micrinoids
F = fusinoids
MM = mineral matter

Table II

Physical Properties of Indicated Coal and Coke Samples

Coal	Sample No.	Gieseler Plasticity Data: Softening Temp, C	Maximum-Fluidity Temp, C	Solidification Temp, C	Maximum-Fluidity, ddpm	Oven Bulk Density*	Oven Pressure, psi	Sole-Heated Test-Oven Data: Oven Bulk Density*	Volume Change, %: Actual Maximum	Actual Final	Corrected** Maximum	Corrected** Final
Pratt Seam												
Mine A	1	371	452	500	8,300	50	2.0	56	+4.9	+3.6	+3.0	+1.8
	2	369	455	500	7,200	54	2.6	55	+6.9	+4.7	+6.9	+4.7
	3	370	460	501	8,000	51	2.6	55	+2.9	+0.3	+2.9	+0.3
	4	369	453	502	7,200	52	3.6	56	+4.7	+2.6	+2.8	+0.8
	5	372	460	500	6,800	50	2.7	55	+4.1	+1.5	+4.1	+1.5
	6	370	460	502	8,200	50	2.0	54	+3.6	+0.3	+5.4	+2.2
Mine B	1	354	437	493	25,300	50	1.3	53		-8.0		-4.5
	2	351	437	495	19,100	50	0.8	53		-11.9		-8.5
	3	353	437	498	21,200	49	1.3	54		-7.5		-5.7
	4	352	439	ND***	12,900	53	1.3	56		-16.6		-18.0
	5	352	436	ND	13,800	52	1.1	56		-8.4		-10.0
	6	ND	ND	ND	ND	53	1.5	58		-7.9		-12.6
Mine C	1	355	441	499	18,400	52	1.7	56	+2.5	+0.2	+0.7	-1.5
	2	356	442	ND	10,250	53	1.9	56	+3.3	+0.2	+1.5	-1.5
	3	357	440	ND	9,530	52	1.4	56	+2.0	-0.5	+0.2	-2.2
	4	370	449	492	11,000	53	1.6	56	+3.2	-2.5	+1.4	-4.2
	5	358	447	498	9,160	51	1.3	57	+4.6	+3.0	+1.0	-0.6
	6	360	444	495	8,510	54	1.5	57	+4.9	+0.3	+1.3	-3.2
Mary Lee Seam	1	359	452	491	8,400	55	6.3	58	+8.6	+6.8	+3.0	+1.3
	2	357	445	487	9,100	54	5.8	59	+9.7	+7.9	+2.3	+0.6
	3	363	451	487	800	54	4.1	58	+6.9	+4.6	+1.4	-0.8
	4	361	450	487	1,200	54	3.0	58	+5.4	+3.2	+0.0	-2.1
	5	353	445	490	9,400	55	5.1	56	+4.6	+1.6	+2.8	-0.2
	6	354	448	490	11,500	ND	ND	56	+1.8	-1.1	+0.0	-2.8
American Seam	1	365	446	501	4,800	52	4.0	56	+5.6	+3.1	+3.7	+1.3
	2	372	453	500	7,200	50	5.0	54	+5.1	+2.2	+7.0	+4.1
	3	373	451	505	5,700	52	3.1	56	+0.7	-0.8	-1.1	-2.6
	4	373	450	498	6,500	50	4.0	55	+1.6	-0.6	+1.6	-0.6
	5	372	451	499	6,100	ND	ND	56	+0.7	-1.8	-1.1	-3.6
	6	373	449	503	6,100	49	3.8					

* lb dry coal per cu ft.
** At 55 lb per cu ft.
*** Not determined.

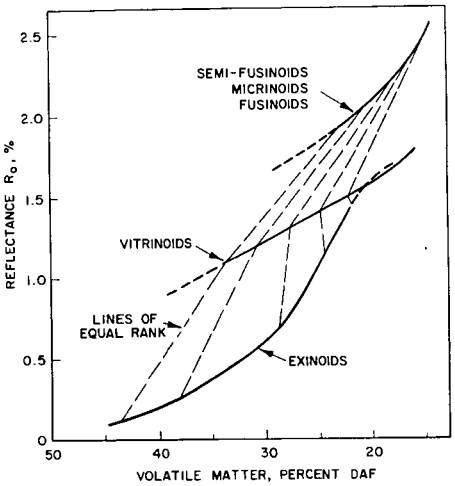

Figure 1. Relationship Between Reflectance and Volatile Matter

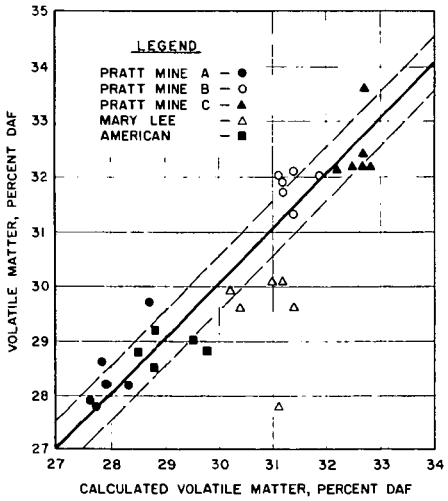

Figure 2. Relationship Between Chemically Determined Volatile Matter and Calculated Volatile Matter

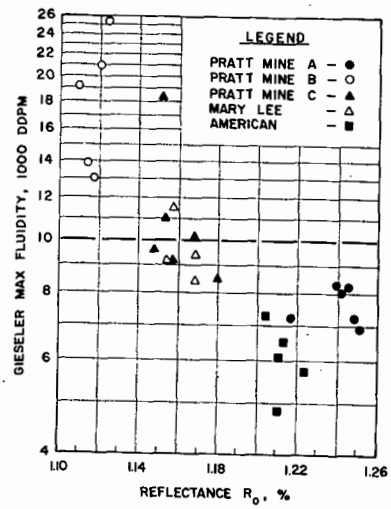

Figure 3. Relationship Between Plasticity and Reflectance

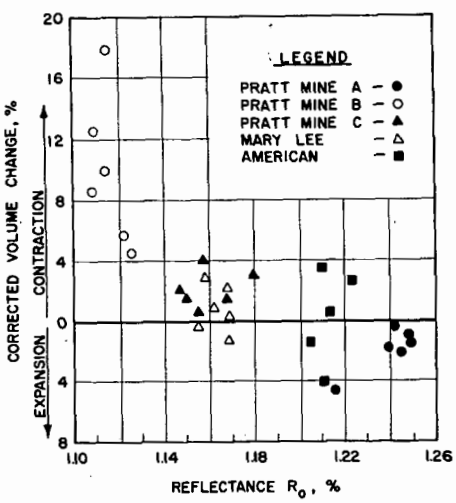

Figure 4. Relationship Between Volume Change and Reflectance

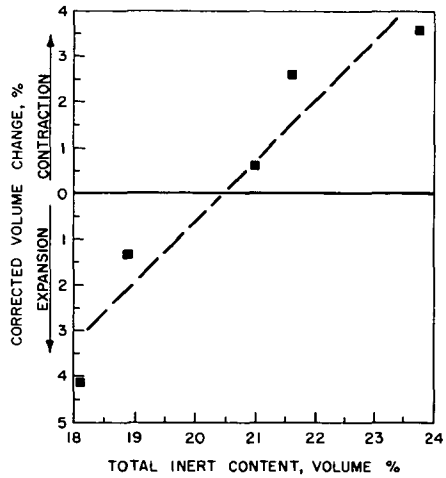

Figure 5. Relationship of Volume Change and Inert Content

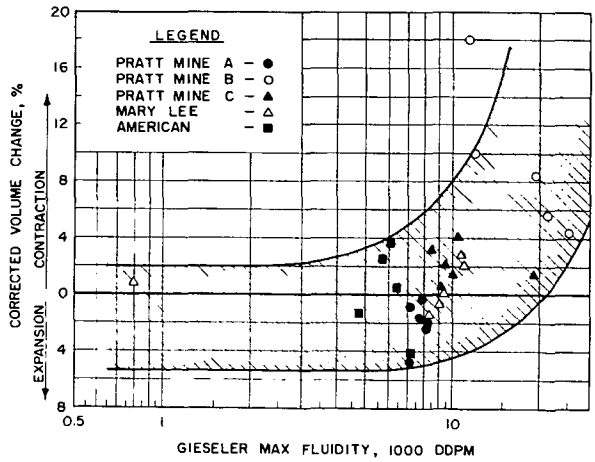

Figure 6. Relationship Between Volume Change and Plasticity

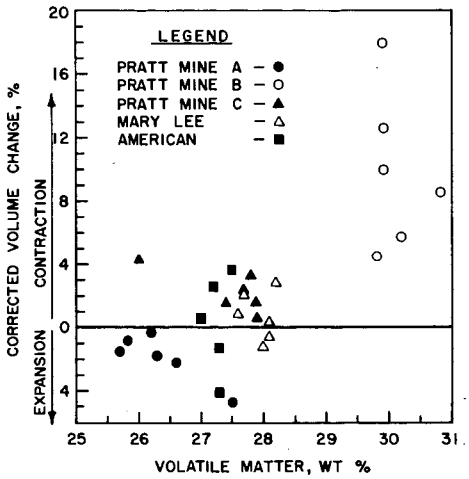

Figure 7. Relationship Between Volume Change and Volatile Matter

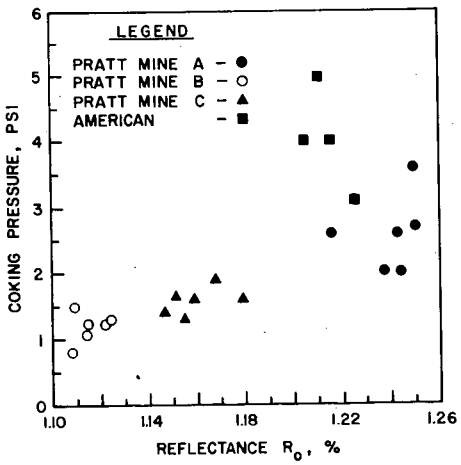

Figure 8. Relationship of Coking Pressure and Reflectance

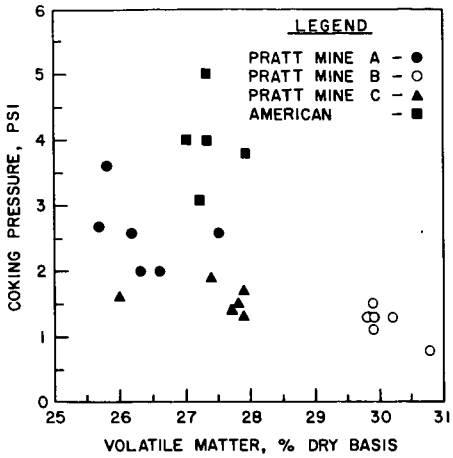

Figure 9. Relationship of Coking Pressure and Volatile Matter

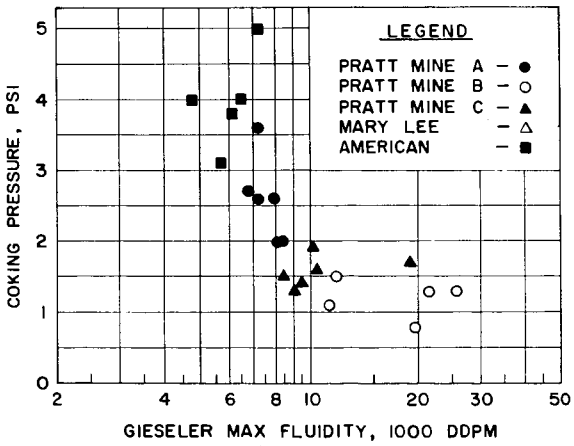

Figure 10. Relationship of Coking Pressure and Plasticity

A NEW METHOD, CAPABLE OF AUTOMATION, FOR THE RAPID CLASSIFICATION OF COALS BASED ON THE RELATION OF TOTAL REFLECTANCE POWER TO COKE QUALITY

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Abstract

The new method of rapid and automatic classification of coals consists in measuring the total reflectance power (P.R.G.) of the surface of a series of "n" pellets formed under strong pressure and without a binder.

Statistically, the total reflectance power varies linearly, increasing with the volatile matter index between 40 and 20 percent, then decreasing between 20 and 13 percent. The thickness of the pellets is least around V.M. = 25 percent.

The ratio $\frac{\text{P.R.G. V.M. = 20\%}}{\text{P.R.G. V.M. = 40\%}}$ reaches 7; the limit of confidence of the mean P.R.G., at 95 percent, is about ± one percent for n = 30 pellets.

A satisfactory correlation between the total reflectance power of coal and the quality of coke has been established from some pilot-plant tests. In standardized conditions of preparation and coking, there is a correlation by type of blend.

INTRODUCTION

The relation between the petrographic composition of coals and their coking properties has received our attention for a decade, first for the Lorraine field from which only coal having a volatile matter index higher than 35 percent was mined, then in the North field where the modern tendency is to limit mining to a small number of pits.

The need for automation of the operation of the mine and for control of the washeries and coking plants led us to seek a rapid, precise and automatic method for classification of coals. Thus, after having rejected the traditional destructive methods based on the behavior of the coal during pyrolysis, we experimented with a non-destructive procedure which consists in measuring the total reflectance power (P.R.G.) of a suitably prepared sample.

I. Brief Description of the Method (1) (2)

The need to arrive at an automatic process made it necessary to abandon the polishing and the selection of fields of vision of the vitrinite usually encountered in the course of measurement of reflectance power (P.R.) with a microscope.

The experimental method consisted in making, under pressure, a series of pellets on which the total reflectance power of the surface was measured with a photometer. A simple visual examination of the pellets thus prepared showed that an important range of intensities of reflectance is available between flaming coals, type 711, and coals called "complement" (d'appoint), type 334, - see Figure 1.

A brief description of the laboratory equipment and of the different steps of the method follows:

- After drying in air, the coal is ground and passed through a screen < 0.5mm.

- A press forms pellets with a diameter of 25mm. A pressure of 4,000 atmospheres is necessary to assure good cohesion without a binder. The pistons and counter-pistons are equipped with tungsten carbide pellets to greatly reduce the rate of wear. The surface of the upper piston must be carefully polished.

- The photometer used functions in the following manner: the light source is a bulb -6V, 5A- which has a stable power source. The light beam is directed vertically towards the surface of the pellet through the use of a semi-transparent plate. The intensity of the reflected light is measured in the same direction by means of a photomultiplier stabilized at 1,400V.

- The intensity of reflection is indicated by a micro-ammeter. Provisionally, micro-amperes have been adopted as the arbitrary unit.

- Two systematic standardizations assure the calibration of total reflectance power in absolute values; a standard substance which can be a relatively stable coal, serves to measure the drift due to wear of the piston and to detect a possible change of the compression force, while a series of glass standards controls the stability of total functioning of the photometer.

The results discussed in the present paper are expressed in the form of a mean total reflectance power in arbitrary units, average of n pellets made at one time from the same sample -- n = 5, 10, 30, or 50, as the case may be -- and of a limit of confidence of the mean at 95 percent may be $\pm\sum = \frac{2\sigma}{n}$ since the dispersion follows a normal law. When n = 30 pellets the relative total precision of measurement of mean total reflectance power is of the order of ± 1 to 1.5 percent. An analysis of variability has shown that a major part of this is due to the preparation of the sample, the formation of the pellets, and the length of time between the completion of the formation of the pellets and the beginning of the photometric measurement. The dispersion of this latter is very small.

II. Factors Influencing the Total Reflectance Power

The principle of the method foresees that the state of the surface of the pellet will depend on the preparation of the sample and on the formation of the pellets, this dependence varying with the physical and chemical properties of the coals.

1. Preparation of the Sample

a. Drying:

Experience has shown that when the moisture in the coal increases the total reflectance power increases, at first quite rapidly, then more slowly as the moisture approaches that of saturation.

b. Grinding

The results obtained with three different degrees of fineness 100 percent < 1, < 0.5 and < 0.2mm indicate that the total reflectance power increases up to 100 percent < 0.5 and that there is no advantage to grinding more finely; the selectivity of the method will not be increased for the porosity of the surface is not lessened any more. In addition, this degree of fineness guarantees that the surface distribution of the macerals will vary very little from one pellet to another.

c. Homogenization of the ground sample is obviously indispensable to assure the stability of the surface structure of all the pellets.

Being given the importance of these three factors, it is necessary to adopt a reproducible method of preparation.

2. Formation of the Pellets

a. Dimensions of the pellet

The diameter must be chosen as a function of the desired precision of measurement and for a given fineness of grinding. We have selected 25mm. The thickness determines the mechanical resistance of the pellet, which is sufficient at 4mm. By giving the compression cavity of the matrix a conical shape the removal of the pellet is made easier and peripheral tearing is avoided. Two other secondary considerations enter into play: The force of the press must increase as the square of the diameter, while the quantity of sample prepared is proportional to the thickness.

b. Pressure

When the force of compression is increased, the total reflectance power increases at first rapidly then holding asymptotically towards a maximum value. Above 4,000 atmospheres the total reflectance power does not vary appreciably. The stability of this pressure can be controlled with the help of an appropriate device.

c. The degree of polishing has an important effect on the value of the total reflectance power. The tungsten carbide surface of the piston is polished with some billiard cloth impregnated with a diamond paste of which the increasing fineness reaches 0.25. Changes in polishing should be evaluated periodically, either indirectly by determining the total reflectance power of a standard material, or directly with an optical device.

3. Photometric Measurement

a. The emission spectral zone of the source

After having sought the existence of absorption bands in the reflected beam from 0.25 to 25μ without success, we have, for reasons of momentary convenience, adopted a lamp with a "punctual" filament which is commonly used in microscopy. This choice is obviously linked to that of the photosensitive detector.

b. The light detector must be very sensitive since the percentage of reflected light remains below one percent. Our laboratory was equipped with some very satisfactory photomultipliers which we have continued to work with. Their spectral sensitivity extends from 3,000 Å to 6,500 Å with a maximum at 4,200 Å.

c. The time interval between formation of the pellets and their photometric measurement must be constant. The total reflectance power of the surface of the pellets falls rapidly during the first two hours and then becomes stable. The explanation of this drop is the object of research. This condition would be easily taken into account with an automatic device.

4. The Physical and Chemical Properties of Coals

a. The tendency to agglomerate without a binder

From about 40 to 20 percent volatile matter, the total reflectance power increases with rank. (Figure 2, Curve 1) This increase is due, on the one hand to the increase of reflectance power of all the macerals, on the other hand to the tendency of coals to orient perpendicularly to the compression, which increases from 40 to 20 percent volatile matter while the porosity of the surface of the pellets (measured with a microscope) decreases from 25 to 10 percent in the same interval. Below 20 percent volatile matter the total reflectance power decreases, in spite of the continued increase in the reflectance power of the macerals, due to the rapid decrease in the capacity to form pellets which disappears completely around 13 percent volatile matter. The minimum thickness of the pellets (Figure 2, Curve 2) corresponds to the maximum capacity to form pellets. This minimum appears to be slightly displaced (25 percent volatile matter) in relation to the maximum total reflectance power (21 percent volatile matter).

b. Pressure coupled with rotation retards the decrease in total reflectance power below 20 percent volatile matter but does not eliminate it. After tests, this technique does not appear to be advantageous to us since the wear of the polished surface of the piston is greatly accelerated.

c. The proportion of mineral matter, characterized by the amount of ash, will have a variable effect on the total reflectance power of the coals depending on the respective levels of the pure coals and that of the mineral matter. Some systematic experiments have shown that in the case of shales or middlings, for which the total reflectance power is little different from coals of low rank, the total reflectance power varies little. Moreover, the amount of ash of most French coals after washing remains constant within about one to two percent. Thus, for low coalification coals

and even for coals whose volatile matter index is close to 20 percent, the normal fluctuations in amount of ash will not noticeably influence the total reflectance power. We have been able to verify this several times.

5. Variations in the Maceral Composition

These will affect the total reflectance power to the extent that the reflectance power of the macerals are very different and there is certainly the possibility of interference with the classification, which it will be proper to examine with care, but we do not yet have enough results to discuss this point.

Still, on the basis of petrographic knowledge accumulated both at Cerchar (4) and in other countries - particularly in Germany, Belgium, and Holland - it is possible to foresee the direction of modifications of the total reflectance power.

a. Above a carbon content of 90-92 percent - corresponding to 22-23 percent volatile matter - the three principle macerals cannot be distinguished by their total reflectance power. It is therefore principally in the case of coals of low rank that the maceral composition could have an influence. In fact, even for a coal with 40 percent volatile matter the reflectance power in air of vitrinite is only slightly greater than that of exinite.

The reflectance power of inertinite on the contrary is already very high. Some important fluctuations in the proportion of inertinite could play an appreciable role. An increase in proportion would be interpreted as an elevation in rank and the coal would act without doubt as if it were lean.

This is valid in fact only for true fusinite, always in low abundance in our coals, in comparison with semi-fusinite which, of variable reflectance power, is the priniiple constituent of the inertinite group.

b. The ratios $\frac{E}{V}$ and $\frac{I}{V}$ generally vary little with rank. When the coal is sampled as it leaves a washery which treats a mixture of many veins situated at different levels, the variations are considerably diminished. This will probably no longer be true if the sampling applies to a single vein.

III. Relation Between the Total Reflectance Power and the Volatile Matter Index of Coals

Experiments with the method on several series of coals of different origins, taken for the most part from cars arriving at a cokery have provided data for the curve in Figure 3 which covers the entire range of rank of coals used in coking.

It is verified that the total reflectance power goes from 1 to 7 when the volatile matter index is reduced by half, that is, between 40 and 20 percent. Below 20 percent the total reflectance power decreases rapidly

for the reasons already presented in paragraph II., 4b., and can no longer be determined below 13 percent. The thickness of the pellets varies in the opposite direction. The dispersion of data is due in part to the fact that at the time of making the measurements, already some time ago, the causes of dispersion had not all been eliminated. The enlargement of the spread of the total reflectance power in comparison to that much more limited spread of the reflectance power of vitrinite - which in the same range varies only from 0.65 to 1.5 - results on the one hand from the summation extended to all the macerals and on the other hand from the important variation in the tendency to agglomerate under pressure, in other words, the hardness of the coals.

The total reflectance power therefore permits the classification of recently washed coals according to an order of classification very near to that which the volatile matter index furnishes.

IV. Relation Between the Total Reflectance Power and Coking Properties of Coals and of Blends

This method of classification has been tried principally with the intention of classifying different coals considered individually according to their coking properties. This objective could appear to be utopian since all of the attempts made till now have only led to the development of methods indicated below (*) and which measure specifically one or the other of two complementary aspects of these properties. The order of the methods of enumeration corresponds to a decreasing tendency to present evidence of these aspects:

Agglutinating Properties	Tendency to Intrinsic Cracking
Swelling in the dilatometer - Gray-King Test	Temperature of resolidification in the plastometer at variable torque
Roga Index or Agglutination Indices	Coefficient of contraction at the temperature of resolidification
Crucible Swelling Index	Volatile Matter Index
Fluidity Index in the plastometers	

*Most of these are used in the International Classification Project which permits definition of the type of coal. (5)

The following remarks should be noted:

- A statistical relation exists between the volatile matter index or rank and the agglutinating properties, which are zero below 13 percent, increase and pass through a maximum around 28 percent, then decrease and become zero

above 40 percent. The maximum is explained by the rapid increase in O_2 content which, above five percent at about 28 percent volatile matter, becomes sufficiently abundant to cause an easier degradation of the agglutinating properties.

- Since the total reflectance power is due chiefly to the vitrinite, which generally makes up 60 to 80 percent of coals, any variation in the chemical composition of this will have an effect on the total reflectance power. In particular, since this maceral contains the major part of the oxygen in coal, an increasing oxygen content will accompany a lowering of the reflectance power. (**)

(**) The oxygen of combustion or exothermic oxidation will certainly not have the same effect on the total reflectance power.

In that which concerns the relation between the coking properties of blends tested by different methods, of which our method is the total reflectance power, and the principal characteristics of the cokes* resulting from these blends, we believe that no general correlation exists; it will be necessary to establish the relation for each type of blend. This prediction follows from the following experimental observations (6):

---

*Independent of the chemical properties of the coke, of the bulk volume and of the grain distribution, the two characteristics used by the siderurgic user are: the M40 index which measures the resistance to cracking and the M10 index which measures the tendency towards degradation by abrasion.

- For a given type of blend - for example, coals 334 and 632 - a relation between the M40 and M10 indices and the proportion of 334 coal exists. As a result, a relation between the quality of the coke and most of the coking properties of these blends can be established. Let us note, however, that the coking properties of the constituent coals are not additive since the quality of the coke improves rapidly at the beginning when the proportion of coal 334 increases, then more slowly around 30 percent and it nearly stabilizes above 50 to 60 percent.

- The logical rule that predicts that the cracking of the coke diminishes when the volatile matter index of the coal is lowered is only verified for the types of mixtures of coals whose swelling in the dilatometer remains sufficient to assure a good agglutination and therefore a good cohesion. When this is reduced below a certain threshold, cracking can increase; the M40 index decreases then because cracking and degradation by abrasion are increased. For the same reasons two blends having the same volatile matter index can result in two cokes of very different quality.

- The presence in the blend of inert substances - mineral matter - or anticracking constituents - coke dust - will affect the characteristics of

the cokes very differently according to their degree of dispersion and their proportion. It is thus that the optimum concentration of coke powder ground < 0.5mm is not the same depending on whether the M40 or the M10 index is considered. In certain cases this concentration can be five percent for the M10 and ten to fifteen percent for the M40.

These lengthy general considerations give an insight into the importance and the number of factors which intervene to alter the relations between the qualities of coals, blends, and cokes.

Fortunately, the complexity of the studies are often reduced when the objective of the classification is limited to the coking problems inherent in one coal seam or one coking plant.

The application of this method for predicting coking properties has not yet been extended very far. We will only mention some systematic laboratory or pilot plant tests whose results are very encouraging.

1. Verification of the additivity of the total reflectance power and a correlation with some other methods of classification (Laboratory)

Two series of blends were prepared in the laboratory. The first was prepared with a base of coal 622 to which coal 333 was added in increasing proportions; the second contained the same base, coal 622, to which coal 434 was added. As predicted, the total reflectance power of the mixture varied linearly with the proportion of coal of increased rank and also with the volatile matter index of the coals, at least up to 75 percent (Figure 5.) Above that the lack of precision of the curve is due to the small number of pellets measured and to the fact that this experiment was carried out at the beginning of testing of the method when the causes of deviation were not all known.

At the same time a good relation was found between total reflectance power and swelling in the dilatometer (Figure 5). It was noted that in the range of low percentages of high rank coal where the deviation of the determination of swelling is quite high, the total reflectance power could be measured with satisfactory precision. Now, taking into account the progress obtained in the application of this method, it is possible to distinguish two blends whose proportions differ by only two percent.

2. Relation between the total reflectance power and the quality of cokes obtained with different blends. First pilot plant test.

Tests of the suitability of the method have been carried out in establishing the relations between the quality of the cokes and the total reflectance power of the blends in collaboration with the Experimental Station for Coking at Marienau. Table 2 on the following page indicates the composition of the blends studied.

Table 2.

Blends	Type and Proportion of Constituent Coals			
	333	434	635	622
Binary	30		70	
	25		75	
	20		80	
	10		90	
Ternary	13	27		60
	12	23		65
	10	20		70
	6	17		75

These blends ground methodically to 100 percent < 3mm, have been oven dried, H_2O = 2%, in the 400 kg oven. For each blend two charges were coked under normal conditions. Total reflectance power was determined on ten pellets of each of the constituents of each blend. The total reflectance power has been calculated starting from that of the constituents, thus permitting the demonstration of additivity.

Examination of the curves in Figure 6 shows that the calculated total reflectance power, therefore the volatile matter index of the blend, is related to the resistance to cracking of the coke, measured by the M40 index, on a single curve although for the abrasion capacity, given by the M10 index, there is a curve by type of blend. The M10 index, well related to the dilatometer swelling, is poorly predicted by the Crucible Swelling Index which has no sensitivity in the zone of volatile matter index between 20 and 33 percent.

The coke quality is located for the most part in the range of French metallurgical cokes for which the M40 index must be above 78 and the M10 index below 8 - 8.5.

The lower level of cohesion of cokes obtained beginning with the binary blends is easily explained by the excess tendency to agglutinate of this type of blend: the cokes contain increasing proportions of froth when the percentage of coal 634 increases.

3. Search for a relationship between the total reflectance power of several coals of the Lorraine field and the quality of the cokes. Second pilot plant test.

After the encouraging results reported above it was proper to verify that the method permitted the evaluation of coking properties of

coals of different origins. The Lorraine field can furnish to steel mill and mine coke plants, four different types of coals: 722, 623, 633, 634/635 listed in increasing order of agglutinating properties. The classification of these coals with the help of total reflectance power has been tested in the case of a moist mixture (H_2O = 10%), placed in an oven after "tamping" and which contained:

Lorraine coal	(634 to 722)	72%
Coal	434	20%
Anticracking coke breeze		8%

The coals were ground to 90 percent < 2mm, the coke breeze to 100 percent < 0.5mm. For each type of coal four charges were placed in the 400kg oven. The mean bulk volume of charging was 970kg/m^3. The coking conditions corresponded to those of the Lorraine mining coke plants. The cokes were removed from the furnace after thermal stabilization was nearly complete, that is, when the middle plane of the charge reached 1,110°C.

The best correlations with the different methods of classification tests are assembled in Figure 7.

It is noted that most of the coals fall along a regular curve for M40 and M10 when the abscissa is the measured total reflectance power of Lorraine coal. The cohesion of the coke M10 is also related to the dilatometer swelling and to the index of agglutination.

Although these results may be again very satisfactory we feel that a more rigorous verification covering a much wider range of quality and a very much larger number of samples is necessary before passing a definitive judgement on the value of the method.

A third series of pilot plant experiments now underway will permit statistical comparison of the different methods of classification which we also consider as valid but for which automation would be more difficult.

V. Conclusions

The interest of this method will result from the balance, not yet definitively established, between its possibilities and its limitations compared with the performance of other methods of classification used in coking and which are based either on the behavior of the coal in the course of pyrolysis, or on the petrographic determination of rank and maceral composition.

In summary, the principle merits of the method can be enumerated according to a scale of rank given by the volatile matter indices:

a. Between 20 and 40 percent volatile matter, the total reflectance power varies statistically in a linear manner.

b. The ratio $\frac{\text{P.R.G. } 20\%}{\text{P.R.G. } 40\%}$ reaches 7.

c. The classification takes into account at the same time the nature and proportions of the macerals, and thus provides a sort of synthesis of coking properties.

d. The precision of the classification can be very great for two reasons: the summation of reflectance power rests on several tens of thousands of particles which in large measure eliminates the sampling error; and through the possibility of automation it is easy to increase the number of pellets measured. Against these advantages, one must note the limits and the weaknesses of the method.

e. Below 13 percent volatile matter the method is no longer applicable without modification which would consist of adding a binder.

f. From 20 to 13 percent the rapid decrease in tendency to agglomerate causes a lowering of the total reflectance power. This results in an ambiguity -- at a single total reflectance power there are two different volatile matter indices. This confusion can be overcome by measuring either the thickness of the pellets or the compression force of the press.

g. Although the method is generally insensitive to the proportion of mineral matter of washed coals, the nature of the mineral matter could in certain cases cause a slight shift in classification.

h. The coal sample subjected to this method must be prepared in a very reproducible way, however this also applies to all other methods of classification.

i. Finally, the classification by quality with the help of total reflectance power could be disturbed in the case where the sampling was practiced in an odd zone of the vein in which the maceral composition differed very much from the mean composition especially as relates to fusinite.

In conclusion: Although this method may be, as the majority of other methods are, susceptible to problems in some particular cases, we think that it will be applicable to classification of coals used in the coking plant after some improvements which will accompany its transfer from the laboratory to industrial scale.

Table 1. Characteristics of Coals Represented in Figure 3.

		Percent Ash	Percent V.M./Ash-Free	Percent V.M./Dry	Swelling Index (Afnor)	Swelling in the dilatometer Percent	Temperature of resolidification	Composition on Ash-Free And Dry Basis				
								C	H	O	N	S
Saint-René		6.5	14.6	13.7	1.25	0	500	91	4.2	2.1	1.3	1
Carolus Magnus	○	6	18.7	17.5	7.5	9		89.7	4.4	2.7	1.6	0.8
Hannibal	◓	4.9	20.7	19.6	8.5	56		89.5	4.7	2.7	1.5	0.95
Bruay-Fauquereuil	△	4.7	22.3	21.4	8.65	74	498	90.5	4.8	3.2	1	0.6
Blumenthal	⊖	6.3	23.4	21.9	8.5	83	498	89.0	4.9	3.4	1.5	1.2
Gayant	×	4.5	24.4	23.4	8.5	75	497					
Sewel	●	5.2	25.5	24.1	8.5	122		88.7	4.9	3.8	1.6	0.8
Courrières	⊙	6.5	28.2	26.3	9	318	499					
Carmaux	△	8.3	30	27.5	8	105		86.9	5.1	5.1	1.4	0.8
Camphausen	△	8.1	36.1	35.6	8	148						
Wendel III	⊘	4.3	34.9	33.4	8.25	98						
St.-Charles	▽	5.5	36.1	34.1	7.5	20	484	86.2	5.5	7.1	1.1	0.7
Ste.-Fontaine	•	6.8	37.4	34.9	6.25	3	475	83.5	5.3	8.7	1	1
Freyming	+	6.6	37.3	35.2	3.75	6	470	84	5.6	9	1	0.9
Roumaux	▼	7	37.2	34.6	2.25	0						
Merlebach	⊕	5.7	39.1	36.9	3.5	45						
La Houve	⦶	7.4	39.1	36.6	1	0						

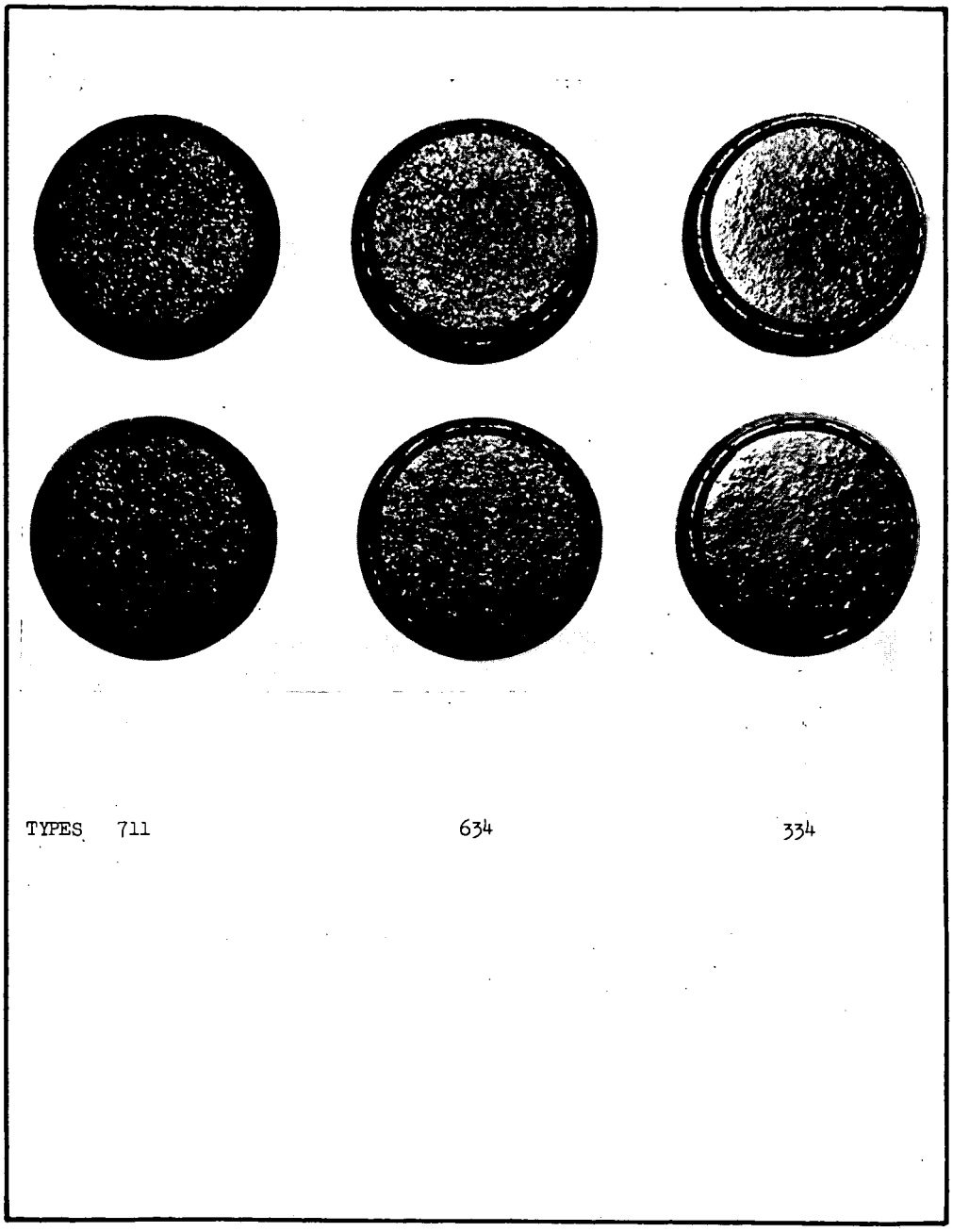


Figure 1. Appearance of Coal Pellets of Different Ranks

ECH. 1 FORMAT ACNS ET.63-31.02 (RBu) 17/6/63 CERCHAR 6899

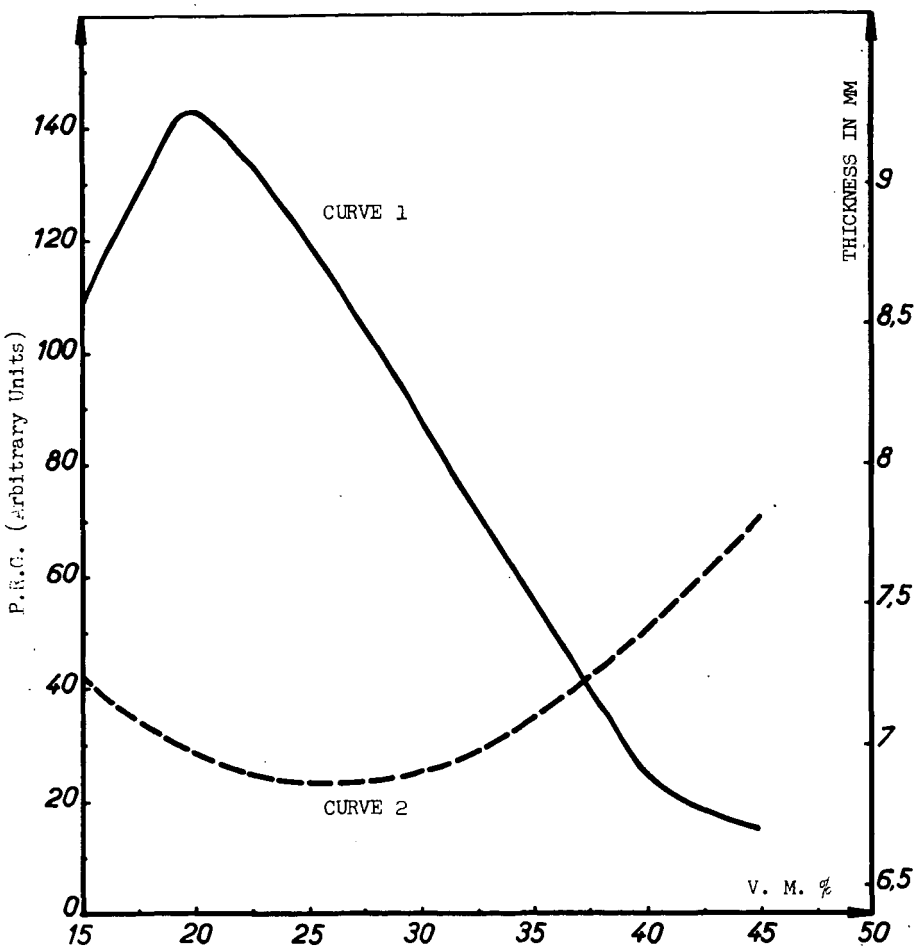


Figure 2. Relation Between P.R.G. (Curve 1), Thickness of Pellets (Curve 2) and Rank

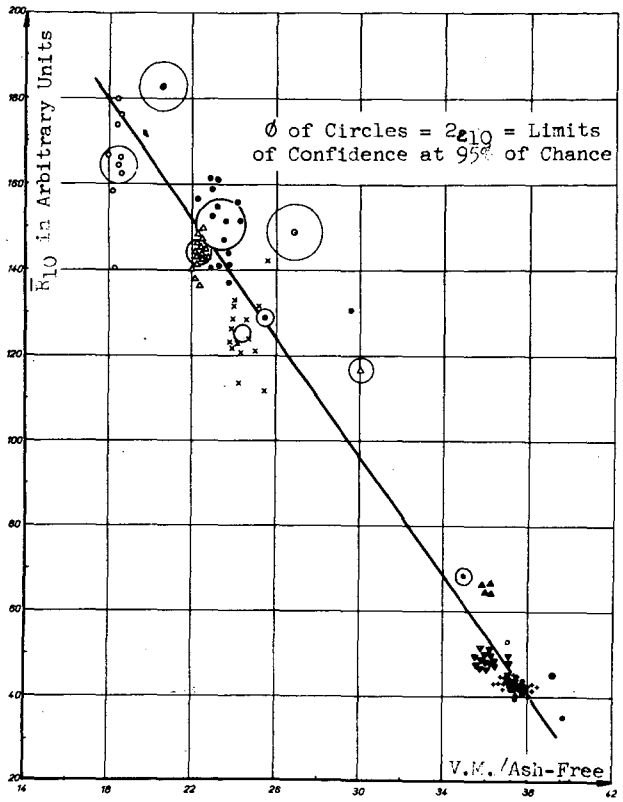


Figure 3. Classification and Quality Variation of Some Coals Used in Coking (See Table 1 for Characteristics of Coals)

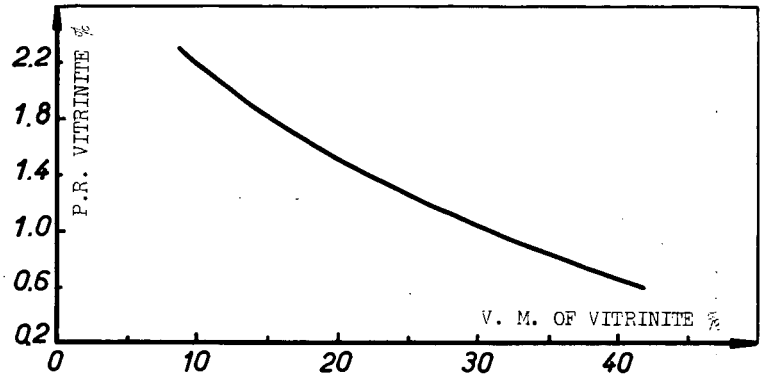
ECH.1 FORMAT ACHS ET.63-31-02 (RBu) 17/6/63 CERCHAR- 6 900-

PRECISION

RELATIVE VALUES

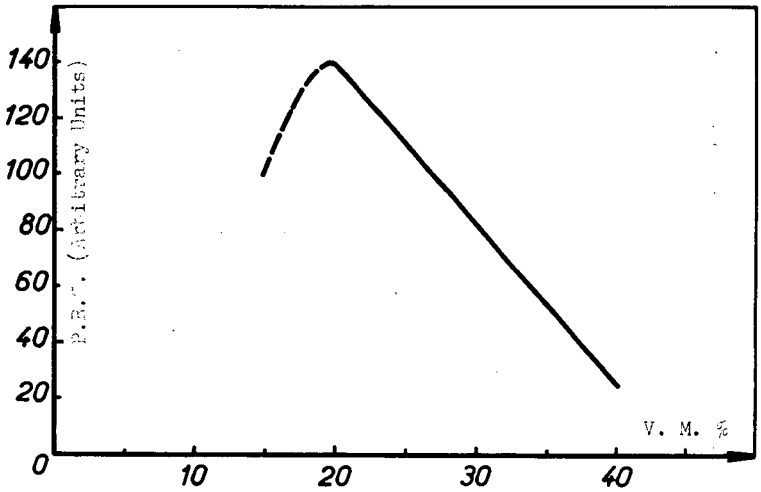
P.R. VITRINITE

$\varepsilon = \frac{2\sigma}{V50} = 0.7\%$



P.R.G.

$\varepsilon = \frac{2\sigma}{V30} = 1\%$



V. M. (AFNOR)

$\varepsilon = \frac{4.3\sigma}{V2} = 1\%$

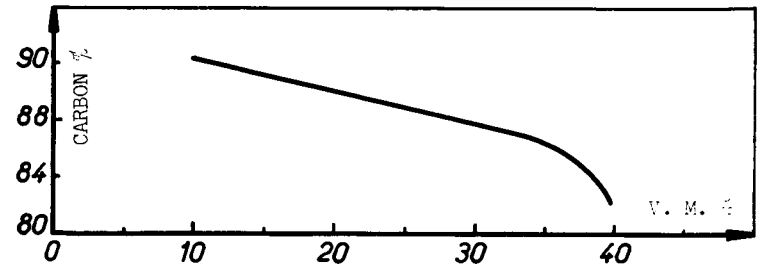
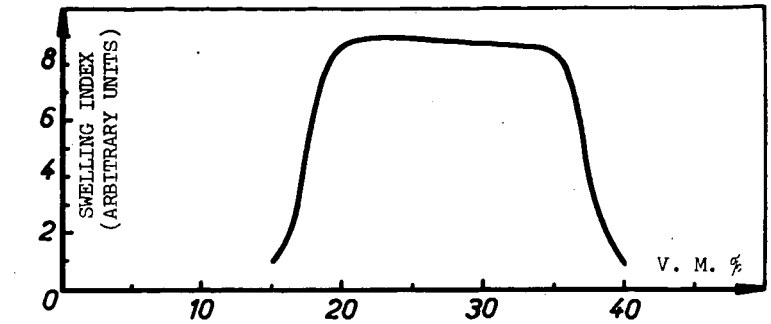


Figure 4a. Comparison of Different Methods of Classification

ECH.1 FORMAT A4 ChS ET.63.31.02 (RBu) 17/6/63 CERCHAR.6901.

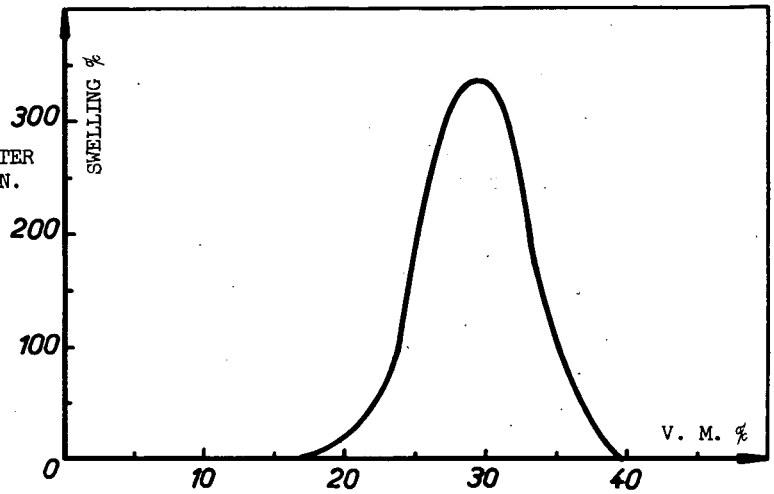
PRECISION

$$\varepsilon = \frac{2{,}8\sigma}{\sqrt{5}} = \frac{1}{4}$$



SWELLING IN THE DILATOMETER
RATE OF HEATING 3°/MIN.

$\varepsilon = 15$ for $G = 200$
$\varepsilon = 5$ for $G = 20$
$(n = 2)$



TEMPERATURE
OF RESOLIDIFICATION
3°/MIN.

$\varepsilon = 3°C$
$(n = 3)$

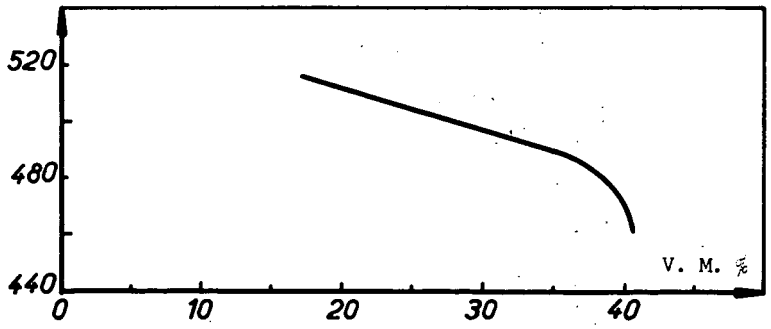


Figure 4b. Comparison of Different Methods of Classification

ECH.1 FORMAT ACHS ET.63.31.02 (RBu) 17/6/63 CFDCHAR- 6902-

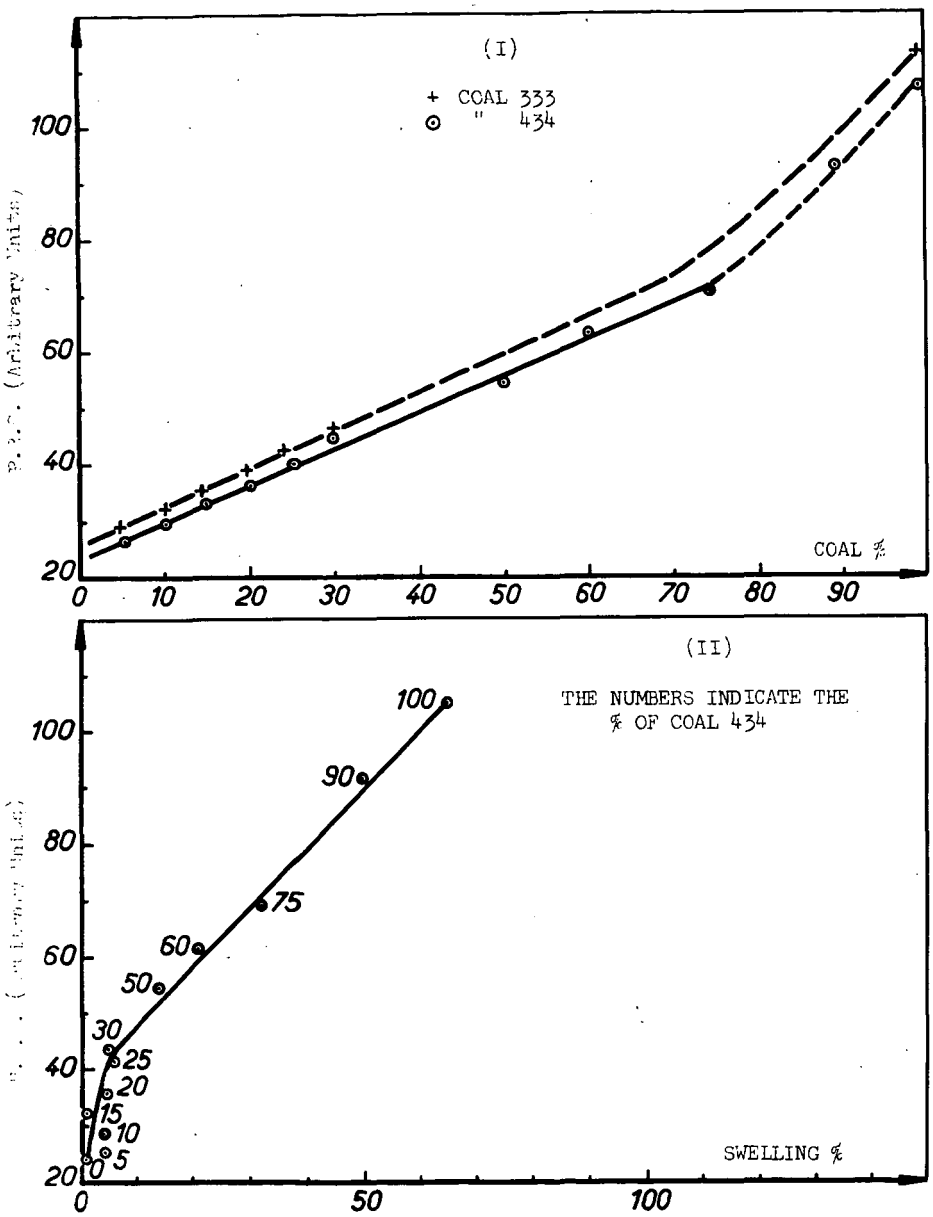


Figure 9. Relation Between P.R.C. and the Composition of Blends (I) and the Swelling in the Dilatometer of the Blend (II)

ECH. 1 FORMAT AChS ET. 63-31.02 (RBu) 17/6/63 CERCHAR. 6903

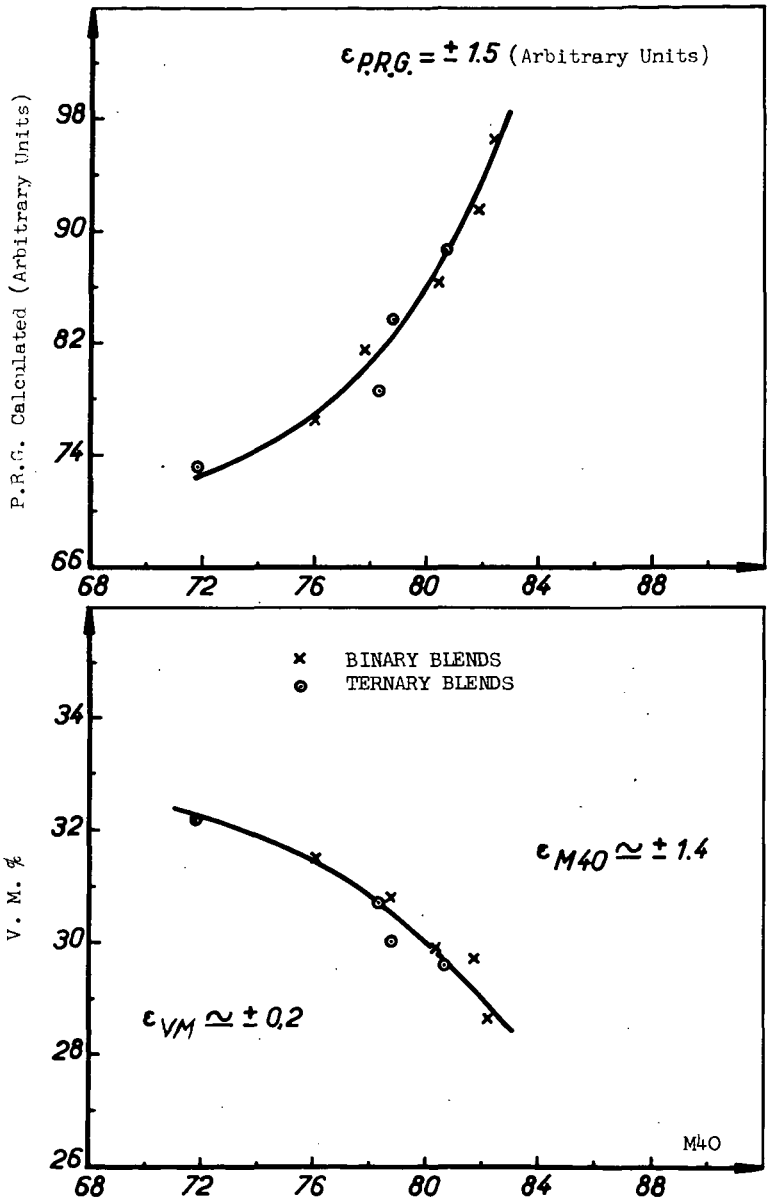


Figure 6a. Relation Between the Tendency of Blends to Crack and the M40 Quality of Cokes

ECH. 1 FORMAT ACHS ET. 63. 31. 02 (RBu) 17/6/63 CERCHAR. 6 904 -

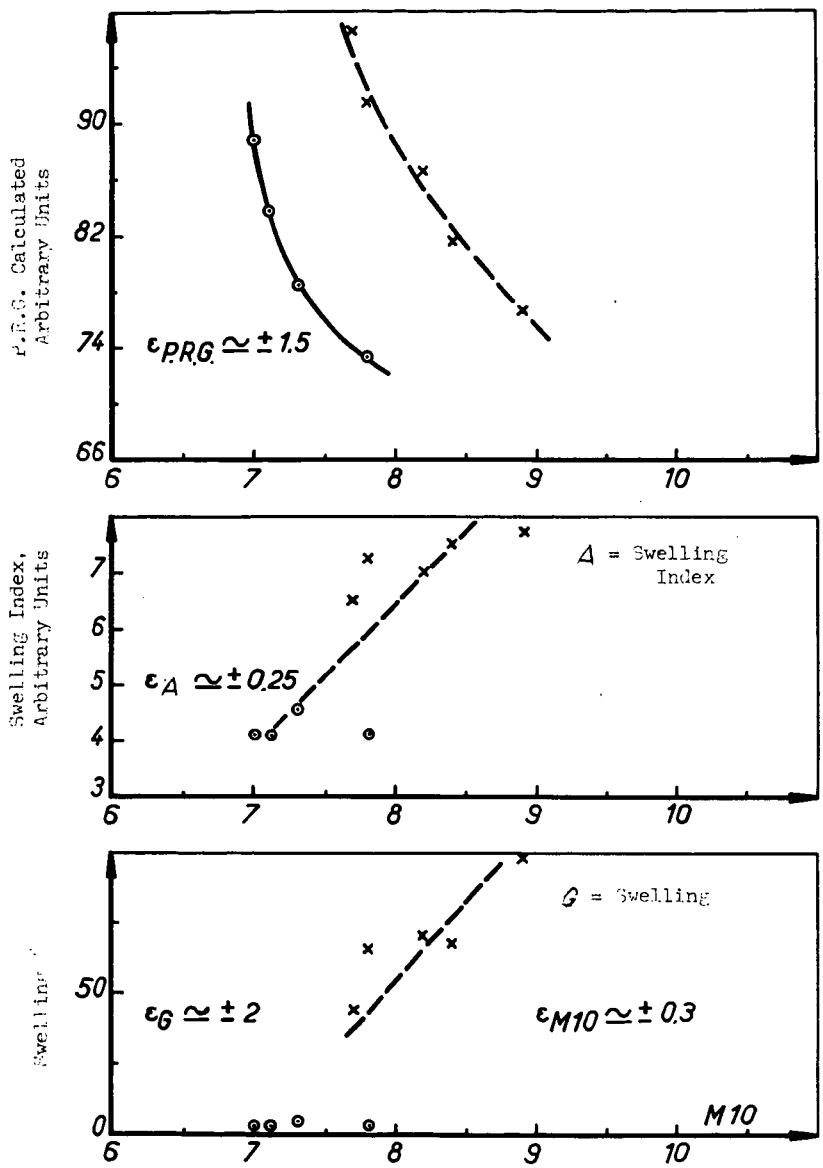


Figure 6b. Relation Between the Tendency of Blends to Agglutinate and the M10 Quality of Cokes

ECH. 1 FORMAT ACh S ET. 63. 31. 02 (RBu) 17/6/63 CERCHAR. 6905

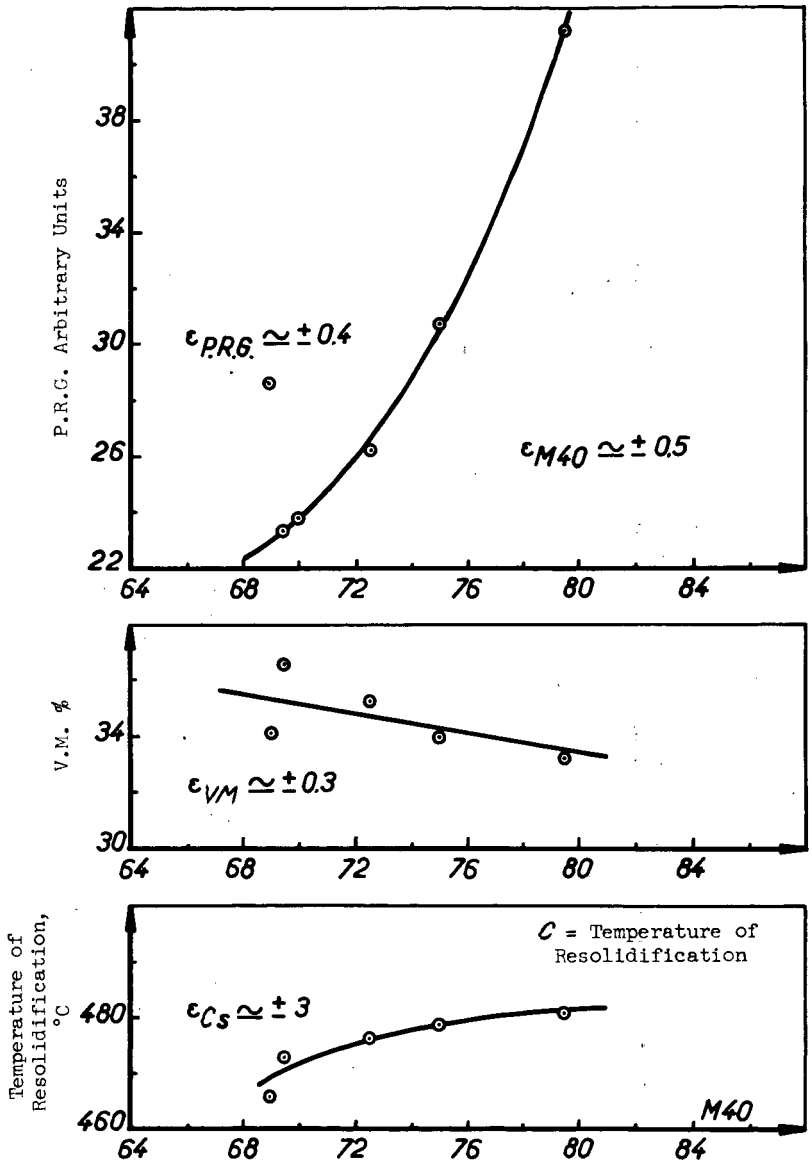


Figure 7a. Relation Between the Tendency of Constituents of Lorraine Coals to Crack and the M40 Quality of Cokes

ECH 1 FORMAT ACh S ET.63. 31.02 (RBu) 17/6/63 CERCHAR. 6 906

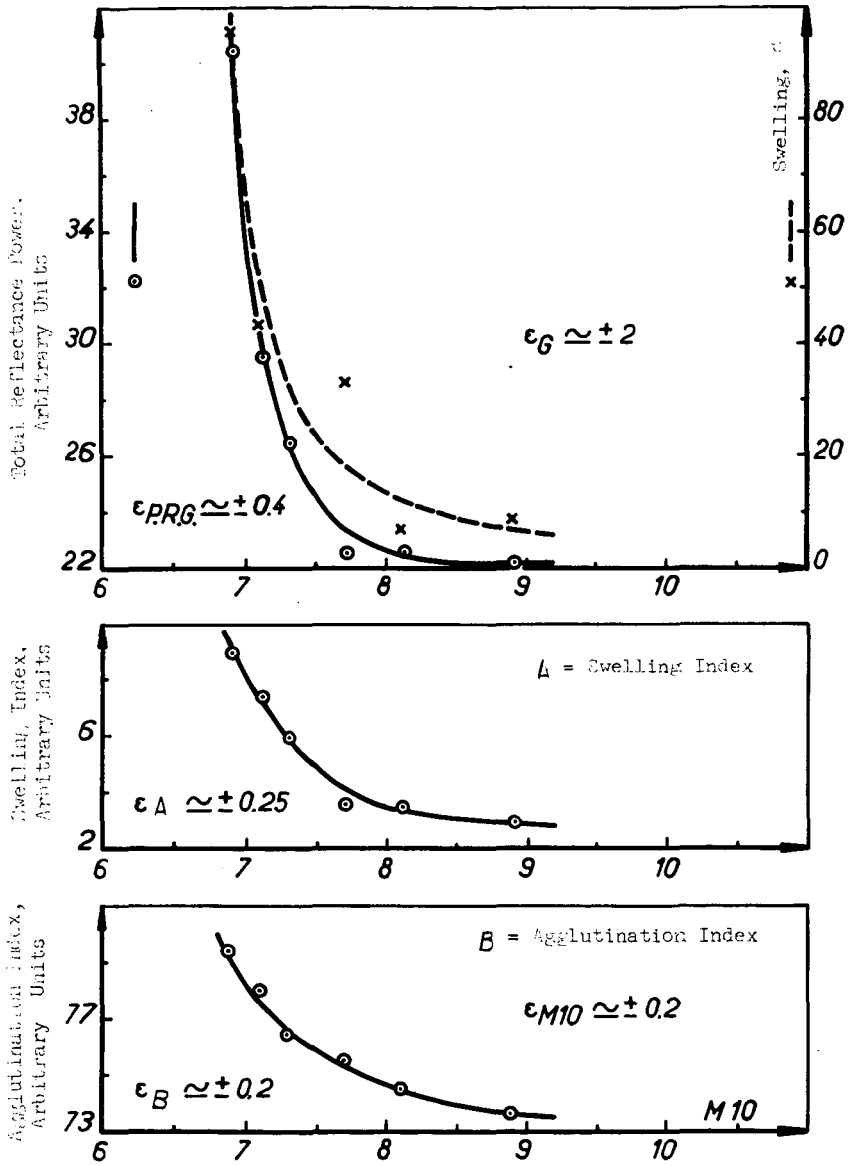


Figure 7b. Relation Between the Tendency of Constituents of Lorraine Coals to Agglutinate and the M10 Quality of Cokes

NOUVELLE METHODE DE QUALIFICATION RAPIDE ET AUTOMATISABLE DES CHARBONS BASEE SUR LEUR POUVOIR REFLECTEUR GLOBAL

RELATION AVEC LA QUALITE DU COKE.

par R. BUSSO et B. ALPERN

Résumé.

La nouvelle méthode de qualification, rapide et automatisable, des charbons consiste à mesurer le pouvoir réflecteur global (PRG) de la surface d'une série de n pastilles agglomérées sous forte pression et sans liant.

Statistiquement le PRG varie d'une façon linéaire, croissante, avec l'indice de matières volatiles (MV) entre 40 et 20 %, puis décroît entre 20 et 13 %. La méthode n'est plus applicable sans modification au dessous de MV = 13 %. L'épaisseur des pastilles est minimum vers MV = 25 %.

Le rapport $\frac{\text{PRG MV = 20 \%}}{\text{PRG MV = 40 \%}}$ atteint 7; la limite de confiance du PRG moyen, à 95 %, est de ± 1 % pour n = 30 pastilles.

Une corrélation satisfaisante entre le PRG du charbon et la qualité du coke a été établie à partir d'essais semi industriels. Dans des conditions normalisées de préparation et de cokéfaction il y a une corrélation par catégorie de mélange.

Introduction.

La relation entre la composition pétrographique des charbons et leurs propriétés cokéfiantes a retenu notre attention depuis une dizaine d'années, d'abord dans le cas du bassin lorrain où l'on n'extrait que des charbons dont l'indice des matières volatiles (MV) dépasse 35 %, puis, plus récemment, dans celui du bassin du Nord où se développe la tendance à la concentration de l'extraction en un petit nombre de puits.

La nécessité de l'automatisation de l'exploitation et du contrôle des lavoirs et des cokeries nous a conduits à rechercher une méthode de qualification des charbons, rapide, précise et automatisable. C'est ainsi qu'après avoir rejeté les méthodes traditionnelles et destructrices basées sur le comportement du charbon en cours de pyrolyse, nous avons expérimenté un procédé de contrôle non destructeur qui consiste à mesurer le pouvoir réflecteur global (PRG) d'un échantillon convenablement préparé.

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I - DESCRIPTION SOMMAIRE DE LA METHODE (1) (2)

Le souci d'aboutir à un procédé automatisable obligeait à abandonner le polissage et la sélection des plages de vitrinite habituellement pratiqués au cours du mesurage du pouvoir réflecteur (PR) au microscope.

La méthode expérimentée consiste à fabriquer, sous une forte pression, une série de pastilles dont on mesure le PRG de la surface à l'aide d'un photomètre. Un simple examen visuel des pastilles ainsi préparées, montre qu'un éventail important d'intensités de réflexion est disponible entre les charbons flambants, type 711, et les charbons dits "d'appoint", type 334, - voir la fig. 1.

Voici une description succincte du matériel de laboratoire et des différentes phases de la méthode :

- Après séchage à l'air le charbon est broyé et tamisé < 0,5 mm.
- Une machine à comprimer fournit des pastilles dont le diamètre est de 25 mm. Une pression de 4000 bars est nécessaire pour assurer sans liant une bonne cohésion. Les pistons et contre-pistons sont munis de pastilles en carbure de tungstène pour réduire fortement la vitesse d'usure. La surface du piston supérieur doit être soigneusement polie.
- le photomètre employé fonctionne de la manière suivante : la lumière issue d'une ampoule - 6V, 5A - dont l'alimentation est stabilisée, est dirigée verticalement vers la surface de la pastille à l'aide d'une lame semi-transparente. On mesure l'intensité de la lumière réfléchie dans la même direction au moyen d'un photomultiplicateur dont l'alimentation sous 1400 V est stabilisée au 1/10 000 ème.
- L'intensité de la réflexion est indiquée par un micro-ampèremètre. Provisoirement les micro-ampères ont été adoptés comme unité arbitraire.
- deux étalonnages systématiques assurent les repérages du PRG en valeur absolue : une substance étalon, qui peut être du charbon peu altérable, sert à mesurer la dérive due à l'usure du piston et à déceler un éventuel changement de la force de compression, tandis qu'une série d'étalons en verre contrôle la stabilité de fonctionnement global du photomètre.

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Les résultats mentionnés dans la présente communication sont exprimés sous la forme d'un PRG moyen en unités arbitraires, moyenne de n pastilles fabriquées à partir d'un même échantillon, - n = 5, 10, 30 ou 50 selon les cas -, et d'une limite de confiance de la moyenne à 95 % soit $\pm\ \varepsilon = \frac{2\sigma}{\sqrt{n}}$ puisque la dispersion suit une loi normale. Lorsque n = 30 pastilles la précision relative globale de mesurage du PRG moyen ε est de l'ordre $\pm$ 1 à 1,5 %. Une analyse de variance a montré que la majeure partie de celle-ci est due à la préparation de l'échantillon, à la fabrication des pastilles et à des décalages chronologiques entre la fin de la fabrication des pastilles et le début du mesurage photométrique. La dispersion de ce dernier est très petite.

II - FACTEURS INFLUENCANT LE PRG.

Le principe de la méthode fait prévoir que l'état de surface des pastilles dépendra de la préparation de l'échantillon et de la fabrication des pastilles, cette dépendance variant avec les propriétés physiques et chimiques des charbons.

1°) Préparation de l'échantillon.

a) Le séchage.

Une expérience a montré que lorsque l'humidité du charbon croît le PRG augmente d'abord très rapidement jusqu'à une humidité voisine de celle de rétention, puis plus lentement.

b) Le broyage.

Les résultats obtenus avec trois degrés différents de finesse 100 % < 1, < 0,5 et < 0,2 mm indiquent que le PRG augmente jusqu'à 100 % < 0,5 mm et qu'il n'est pas avantageux de broyer plus finement, la sélectivité de la méthode n'en serait pas accrue car la porosité de la surface ne diminue plus. En outre ce degré de finesse garantit que la distribution superficielle des macéraux variera assez peu d'une pastille à l'autre.

c) L'homogénéisation de l'échantillon broyé est évidemment indispensable pour assurer la stabilité de la structure superficielle de toutes les pastilles.

Etant donné l'importance de ces trois facteurs il est nécessaire d'adopter un mode de préparation très reproductible.

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2°) Fabrication des pastilles.

a) Les dimensions de la pastille.

Le diamètre doit être choisi en fonction de la précision de mesurage désirée et pour une finesse de broyage donnée. Nous avons adopté 25 mm. L'épaisseur détermine la résistance mécanique de la pastille, celle-ci est encore très suffisante pour 4 mm. En conférant à la cavité de compression de la matrice une forme conique, on facilite l'expulsion de la pastille et on évite les arrachements périphériques. Deux autres considérations secondaires entrent en jeu : la force de la machine à comprimer doit croître comme le carré du diamètre tandis que la quantité de l'échantillon à préparer est proportionnelle à l'épaisseur.

b) La pression.

Lorsque la force de compression augmente le PRG croît d'abord rapidement puis tend asymptoquement vers une valeur maximum. Au dessus de 4000 bars le PRG ne varie plus d'une façon appréciable. La stabilité de cette pression doit être contrôlée à l'aide d'un dispositif approprié.

c) Le degré de polissage a une influence importante sur la valeur du PRG. La surface en carbure de tungstène du piston est polie avec du drap de billard imprégné de pâtes de diamant dont la finesse croissante atteint 0,25 μ. L'altération du poli s'apprécie périodiquement soit indirectement à l'aide d'une substance étalon dont on détermine le PRG, soit directement en utilisant un dispositif optique.

3°) Mesurage photométrique.

a) La zone spectrale d'émission de la source.

Après avoir sans succès cherché l'existence de bandes d'absorption dans le faisceau réfléchi depuis 0,25 μ jusqu'à 25 μ nous avons, pour des raisons de convenance momentanée, adopté une lampe à filament "ponctuel" couramment employée en microscopie. Ce choix est évidemment lié à celui du détecteur photosensible.

b) Le détecteur de lumière doit être très sensible puisque le pourcentage de lumière réfléchie reste inférieur à 1 %. Notre laboratoire étant équipé avec des photomultiplicateurs très satisfaisants, nous avons continué à travailler avec ceux-ci. Leur sensibilité spectrale s'étend de 3000 Å à 6500 Å avec un maximum à 4200 Å.

c) L'intervalle de temps qui sépare la fabrication des pastilles de leur mesurage photométrique, doit être constant, en effet le PRG de la surface des pas-

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tilles diminue rapidement pendant les deux premières heures puis se stabilise ensuite. L'explication de cette dérive fait l'objet de recherches. De toute manière cette condition serait aisément remplie avec un dispositif automatique.

4°) Les propriétés physiques et chimiques des charbons.

a) L'aptitude à l'agglomération sans liant.

De 40 à 20 % de MV environ, le PRG augmente avec le rang (fig. 2, courbe 1). Cette augmentation est due, d'une part à l'augmentation du PR de tous les macéraux, d'autre part à l'aptitude des charbons à s'orienter perpendiculairement à la compression, qui augmente elle aussi de 40 à 20 % MV tandis que la porosité de la surface des pastilles (mesurée au microscope) s'abaisse de 25 à 10 % dans le même intervalle. Au dessous de 20 % de MV le PRG baisse malgré l'augmentation continue du PR des macéraux, ceci étant dû à la décroissance rapide de l'aptitude au pastillage, laquelle disparaît totalement vers 13 % MV. Au maximum de l'aptitude au pastillage correspond le minimum d'épaisseur des pastilles (fig. 2, courbe 2), ce minimum paraissant être légèrement décalé (25 % MV) par rapport au maximum de PRG (21 % MV).

b) La compression couplée à une rotation ralentit la baisse du PRG au dessous de 20 % de MV mais ne la supprime pas. Après essais cette technique ne nous a pas paru avantageuse car l'usure du poli du piston est très accélérée.

c) La proportion des matières minérales, caractérisée par le taux de cendres, influencera différemment le PRG des charbons selon les niveaux respectifs du PRG des charbons purs et celui des matières minérales. Des expériences systématiques ont montré que, dans le cas des schistes ou des mixtes pour lesquels le PRG est peu différent des charbons de bas rang, le PRG varie peu. De plus le taux de cendres de la plupart des charbons français après lavage, reste constant à ± 1 à 2 % près. Ainsi pour les charbons peu houillifiés et même pour les charbons dont l'indice de MV est voisin de 20 % les fluctuations courantes du taux de cendres n'influenceront pas notablement le PRG. C'est ce que nous avons pu vérifier plusieurs fois.

5°) Les variations de la composition macérale.

Elles affecteront le PRG dans la mesure où les PR des macéraux seront très différents et c'est certainement une possibilité de perturbation de la qualification qu'il conviendra d'examiner avec soin, mais nous ne possédons pas encore suffisamment de résultats pour discuter ce point.

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Cependant sur la base des connaissances pétrographiques accumulées tant au Cerchar (4) qu'à l'étranger, - et en particulier en Allemagne, en Belgique, en Hollande -, il est possible de prévoir le sens des modifications du PRG.

a) Au dessus d'une teneur en carbone de 90-92 % - correspondant à 22-23 % de MV - les trois principaux macéraux ne se distinguent plus par leur PRG. C'est donc surtout dans le cas des charbons de rang faible que la composition macérale pourrait avoir une influence. En fait même pour un charbon à 40 % de MV le PR dans l'air de la vitrinite n'est que légèrement plus grand que celui de l'exinite.

Le PR de l'inertinite est au contraire déjà très élevé. Des fluctuations importantes de la proportion d'inertinite pourraient jouer un rôle appréciable. Une augmentation de la proportion serait interprétée comme une élévation du rang et pratiquement le charbon se comportera sans doute comme s'il était amaigri.

Ceci n'est valable en fait que pour la fusinite <u>vraie</u> toujours très peu abondante dans nos charbons par rapport à la semifusinite, celle-ci de PR très variable, est le constituant principal du groupe de l'inertinite.

b) Les rapports $\frac{E}{V}$ et $\frac{I}{V}$ varient généralement peu avec le rang. Lorsque le charbon est prélevé à la sortie d'un lavoir qui traite un mélange de plusieurs veines situées à différents étages les variations sont bien amorties. Ceci ne serait probablement plus vrai si l'échantillonnage portait sur une veine singulière.

III - RELATION ENTRE LE PRG ET L'INDICE DES MV DES CHARBONS.

L'expérimentation de la méthode sur plusieurs séries de charbons d'origines différentes, prélevées pour la plupart dans les wagons à l'arrivée en cokerie a permis de tracer la courbe de la fig. (3) qui s'étend sur tout le domaine de rang des charbons employés en coséfaction.

On constate que le PRG passe de 1 à 7 lorsque l'indice de MV diminue de moitié, soit entre 40 % et 20 %. Au dessous de 20 % le PRG décroît rapidement pour les raisons déjà exposées au paragraphe II 4 b, et ne peut plus être déterminé au dessous de 13 %. L'épaisseur des pastilles varie en sens opposé. La dispersion des données est due en partie à ce qu'à l'époque déjà ancienne de ces mesures toutes les causes de dispersion n'étaient pas éliminées. L'élargissement de l'éventail du PRG par rapport à celui beaucoup plus restreint du PR de la vitrinite, - qui dans le même domaine ne varie que de 0,65 à 1,5 -, résulte d'une part de la sommation étendue à

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tous les macéraux et d'autre part de la variation importante de l'aptitude à l'agglomération sous compression autrement dit : de la dureté des charbons.

Le PRG permet donc de classer les charbons lavés récemment selon un ordre de qualification très proche de celui que fournit l'indice de MV.

IV - RELATION ENTRE LE PRG ET LES PROPRIETES COKEFIANTES DES CHARBONS ET DES MELANGES.

Cette méthode de qualification a été expérimentée principalement en vue de classer les divers charbons considérés isolément selon leurs propriétés cokéfiantes. Cet objectif pouvait paraître utopique puisque toutes les tentatives faites jusqu'à maintenant n'ont conduit qu'au développement des méthodes indiquées ci dessous (*) et qui mesurent spécifiquement l'un ou l'autre des deux aspects complémentaires de ces propriétés. L'ordre des méthodes d'énumération correspond à une aptitude décroissante à la mise en évidence de ces aspects :

Propriétés agglutinantes	Aptitude à la fissuration intrinsèque
Gonflement au dilatomètre - Essai Gray-King	Température de resolidification au plastomètre à couple variable
Indice Roga ou indices d'agglutination	Coefficient de contraction à la température de resolidification
Indice de gonflement au creuset	Indice de matières volatiles
Indices de fluidité aux plastomètres	

En fait il convient de tenir compte des remarques suivantes :

- Il existe une relation statistique entre l'indice des MV ou le rang et les propriétés agglutinantes, celles-ci nulles au dessous de 13 % augmentent et passent par un maximum vers 28 %, puis décroissent et s'annulent au delà de 40 %. Le maximum s'expliquerait par l'accroissement rapide de la teneur en O_2 qui au dessus de 5 % environ pour 28 % de MV devient assez abondant pour provoquer une dégradation de plus en plus efficace des propriétés agglutinantes.

- Le PRG étant dû principalement à la vitrinite, qui constitue généralement 60 à 80 % des charbons, toute variation de la composition chimique de celle-ci aura une influence sur le PRG. En particulier ce macéral contenant la majeure partie de l'oxygène du charbon une teneur croissante en oxygène de constitution s'accompagnera d'une baisse du PR (**).

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(*) La plupart d'entr'elles sont utilisées dans le projet de classification internationale qui permet de définir le type du charbon. (5)

(**) L'oxygène de combustion ou d'oxydation exothermique n'aura sans doute pas le même effet sur le PRG.

En ce qui concerne la relation entre les propriétés cokéfiantes des mélanges évaluées par différentes méthodes, dont notre méthode du PRG, et les caractéristiques principales des cokes (*) issus de ces mélanges, nous pensons qu'il n'existe pas de corrélation générale; il faudra établir la relation pour chaque catégorie de mélange. Cette prévision découle des constatations expérimentales suivantes (6) :

- pour une catégorie donnée de mélanges, - par exemple charbons 334 + 632 -, il existe une relation entre les indices M 40 et M 10 et la proportion de charbon 334. En conséquence on peut établir une relation entre la qualité des cokes et la plupart des propriétés cokéfiantes de ces mélanges. Notons cependant que les propriétés cokéfiantes des charbons constituants ne sont pas additives car la qualité du coke s'améliore rapidement au début lorsque la proportion de charbon 334 augmente, puis plus lentement vers 30 % et elle se stabilise presque au delà de 50 à 60 %.

- La règle logique qui prévoit que la fissuration du coke diminue lorsque l'indice de MV du mélange baisse n'est vérifiée que pour les catégories de mélanges de charbons dont le gonflement au dilatomètre reste suffisant pour assurer une bonne agglutination donc une bonne cohésion. Lorsque celle-ci s'abaisse au dessous d'un certain seuil la fissuration peut croître; l'indice M 40 diminue alors parce que la fissuration et la dégradation par abrasion sont accrues. Pour les mêmes raisons deux mélanges ayant le même indice de MV peuvent fournir deux cokes de qualités très différentes.

- La présence dans le mélange de substances inertes, - matières minérales -, ou de constituants antifissurants, - poussier de coke -, affectera très différemment les ca-

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(*) Indépendamment des propriétés chimiques des cokes, de leur masse volumique et de la distribution granulométrique, les deux caractéristiques utiles pour l'utilisateur sidérurgiste sont : l'indice M 40 qui repère la résistance à la fissuration et l'indice M 10 qui mesure l'aptitude à la dégradation par abrasion.

ractéristiques des cokes suivant leur degré de dispersion et leur proportion. C'est ainsi que la concentration optimum en poussier de coke broyé < 0,5 mm n'est pas la même si l'on considère l'indice M 40 ou l'indice M 10. Dans certains cas cette concentration peut être 5 % pour le M 10 et 10 à 15 % pour le M 40.

Ces longues considérations générales donnent un aperçu de l'importance et du nombre des facteurs qui interviennent pour diversifier les relations entre les qualités des charbons, des mélanges et des cokes.

Heureusement la complexité des études se trouve souvent réduite lorsque l'objectif de la qualification est restreint aux problèmes de coséfaction inhérents à un bassin houiller ou à une cokerie.

L'application de cette méthode à la prévision des propriétés coséfiantes n'étant pas encore très étendue nous ne mentionnerons que quelques expérimentations systématiques de laboratoire ou semi industrielles dont les résultats sont très encourageants.

1°) Vérification de l'additivité du PRG et corrélation avec d'autres méthodes de qualification (en laboratoire).

Au laboratoire on a préparé deux séries de mélanges binaires, l'un à base de charbon 622 auquel on a ajouté une proportion croissante de charbon 333, et l'autre à base du même charbon 622 auquel on additionnait du charbon 434. Comme prévu le PRG du mélange varie linéairement avec la proportion de charbon de rang élevé et aussi avec l'indice des matières volatiles, au moins jusqu'à 75 % (fig. 5). Au delà l'imprécision de la courbe est due au petit nombre de pastilles mesurées et au fait que cette expérience a été faite tout au début de l'expérimentation de la méthode; à cette période les causes de dispersion n'étaient pas toutes connues.

Corrélativement on trouve aussi une bonne relation entre le PRG et le gonflement au dilatomètre (fig. 5), on remarque que dans le domaine des faibles pourcentages de charbon de rang élevé où la dispersion de détermination du gonflement est assez grande, le PRG peut être mesuré avec une précision très satisfaisante.

Maintenant, en tenant compte des progrès obtenus dans l'application de cette méthode il est possible de distinguer deux mélanges dont les proportions d'appoint diffèrent seulement de 2 %.

2°) Relation entre le PRG et la qualité des cokes obtenus avec différents mélanges. Premier essai semi industriel .

Les essais de convenance de la méthode ont été poursuivis en établissant

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les relations entre la qualité des cokes et le PRG des mélanges - en collaboration avec la Station Expérimentale de coséfaction de Marienau. Le tableau ci dessous indique la composition des 8 mélanges étudiés.

Mélanges	Type et proportion des charbons constituants			
	333	434	635	622
binaires	30		70	
	25		75	
	20		80	
	10		90	
ternaires	13	27		60
	12	23		65
	10	20		70
	8	17		75

Ces mélanges broyés méthodiquement 100 % < 3 mm, ont été enfournés secs, H_2O = 2 %, dans des fours de 400 kg. Pourchaque mélange on a cokéfié deux charges dans des conditions normalisées. Le PRG a été déterminé, pour chacun des charbons constituants de chaque mélange, sur 10 pastilles. Le PRG du mélange a été calculé à partir de celui des constituants puisque la démonstration d'additivité le permettait.

A l'examen des courbes de la figure 6 on remarque que le PRG calculé, ainsi que l'indice de MV du mélange, est relié à la résistance à la fissuration des cokes, mesurée par l'indice M 40 par une courbe unique, alors que pour l'aptitude à l'abrasion, donnée par l'indice M 10, il existe une courbe par catégorie de mélange. Le M 10, bien relié au gonflement au dilatomètre est mal prévu par l'indice de gonflement au creuset qui n'a aucune sensibilité dans la zône d'indice de MV située entre 20 et 33 %.

La qualité des cokes se situe, pour la plupart, dans le domaine des cokes métallurgiques français pour lesquels l'indice M 40 doit être supérieur à 78 et l'indice M 10 inférieur à 8 - 8,5.

Le niveau plus bas de cohésion des cokes obtenus à partir des mélanges binaires s'explique bien par l'excès d'aptitude à l'agglutination de cette catégorie de mélange : les cokes contiennent des proportions croissantes de mousses lorsque le pourcentage de charbon 634 augmente.

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3°) Recherche d'une relation entre le PRG de plusieurs charbons du bassin lorrain et la qualité des cokes. Deuxième essai semi-industriel.

Après les résultats encourageants rapportés ci dessus il convenait de vérifier que la méthode permettait d'évaluer les propriétés coséfiantes des charbons d'origines diverses. Le bassin lorrain peut fournir aux cokeries sidérurgiques et minières quatre types différents de charbons : 722 - 623 - 633 et 634/635 énoncés par ordre croissant des propriétés agglutinantes. La qualification de ces charbons à l'aide du PRG a été expérimentée dans le cas d'un mélange humide (H_2O = 10 %) enfourné après pilonnage et qui contenait :

charbon lorrain (634 à 722)	72 %
charbon d'appoint 434	20 %
poussier de coke antifissurant	8 %

Les charbons étaient broyés 90 % < 2 mm, le poussier de coke 100 % < [redacted] 0,5 mm. Pour chaque catégorie de charbon on a enfourné 4 charges en fours 400 kg. La masse volumique de chargement moyenne était 970 kg/m^3. Les conditions de coséfaction correspondaient à celles des cokeries minières lorraines. On défournait les cokes après stabilisation thermique presque complète, c'est à dire lorsque la température dans le plan médian du saumon atteignait 1110°C.

Les meilleures corrélations avec les différentes méthodes de qualification essayées sont rassemblées dans la figure 7.

On remarque que la plupart des charbons se classent selon une courbe régulière en M 40 et M 10 lorsqu'on porte en abscisse le PRG mesuré du charbon lorrain. La cohésion du coke M 10 est aussi bien reliée au gonflement au dilatomètre, à l'indice d'agglutination.

Bien que ces résultats soient à nouveau très satisfaisants nous estimons qu'une vérification plus rigoureuse portant sur un domaine de qualité plus vaste et sur un nombre d'échantillons beaucoup plus grand est nécessaire avant de porter un jugement définitif sur la valeur de la méthode.

Une troisième série d'expériences semi industrielles, en cours d'exécution permettra de comparer statistiquement les différentes méthodes de qualification que nous considérons aussi comme valables mais pour lesquelles l'automatisation serait plus difficile.

V - CONCLUSIONS.

L'intérêt de cette méthode résultera de la balance, pas encore définitivement établie, entre ses possibilités et ses limites comparativement aux performances

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des autres méthodes de qualification employées en cokéfaction et qui sont basées soit sur les comportements de la houille en cours de pyrolyse, soit sur les déterminations pétrographiques du rang et de composition macérale.

En résumé on peut énumérer les principaux mérites de la méthode évalués par rapport à une échelle de rang donnée par les indices de MV :

a) - Entre 20 et 40 % de MV le PRG varie statistiquement d'une manière linéaire;

b) - le rapport $\frac{\text{PRG 20 \%}}{\text{PRG 40 \%}}$ atteint 7;

c) - la qualification tient compte à la fois de la nature des macéraux et de leurs proportions, ce qui fait une sorte de synthèse des propriétés cokéfiantes;

d) - la précision de qualification peut être très grande pour deux raisons : la sommation des PR porte sur plusieurs dizaines de milliers de particules ce qui élimine en grande partie l'erreur d'échantillonnage, de plus par la possibilité d'automatisation il est aisé de multiplier le nombre de pastilles mesurées.

En regard de ces mérites, il convient de préciser les limites et les susceptibilités de la méthode :

e) au dessous de 13 % de MV la méthode n'est plus applicable sans une adaptation nouvelle qui pourrait consister à ajouter un liant;

f) de 20 à 13 % de MV la diminution rapide de l'aptitude à l'agglomération entraîne une baisse du PRG. Il en résulte une ambiguité, à un même PRG il correspond deux indices de MV différents. Cette confusion peut être supprimée en mesurant soit l'épaisseur des pastilles, soit la force de compression de la machine à comprimer du type mécanique;

g) bien que la méthode soit généralement peu sensible à la proportion de matières minérales des charbons lavés, la nature de celles-ci pourrait dans certains cas particuliers provoquer un léger déclassement.

h) l'échantillon de charbon soumis à la méthode doit être préparé d'une façon très reproductible, mais cela est aussi indispensable pour toutes les autres méthodes de qualification.

i) Enfin le classement par qualité à l'aide du PRG pourrait être perturbé dans le cas où l'échantillonnage aurait été pratiqué sur une zone singulière du gisement dans laquelle la composition macérale s'écarterait beaucoup de la composition moyenne notamment en ce qui concerne la fusinite.

<u>En conclusion</u> : bien que cette méthode soit, comme la majorité des autres méthodes, susceptible d'être infirmée dans quelques cas particuliers, nous pensons qu'elle sera applicable au classement des charbons utilisés dans les cokeries après quelques perfectionnements qui accompagneront son transfert du laboratoire dans la

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pratique industrielle.

Nous exprimons notre reconnaissance et nos remerciements à Monsieur le Président W. Berry qui a accepté de présenter à notre place cette communication.

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Microstructure Variation in Pilot Oven Coke

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INTRODUCTION

Techniques of microstructure analysis have been employed in defining coke types and quality for some time.[1,*2,3] However, there has been little effort expended to determine the microstructure variations between samples taken from various locations in large coke masses or the number of fingers that should be analyzed to adequately characterize coke structure. Coke microstructure data have been useful in explaining variations in physical properties,[2] reactivity,[3] and blast furnace behavior[4] of various coke types. Therefore, it is important that the limitations and reproducibility of microstructure analysis be determined if coke microstructure analyses are to be used to quantitatively characterize coke quality and behavior. Consequently, this investigation was initiated to determine the location and number of coke fingers needed to characterize the microstructure of coke produced in a 750-pound pilot coke oven and to evaluate our present coke sampling procedures.

As part of The Youngstown Sheet and Tube Company's program of coke evaluation, two duplicate charges of 100 per cent high volatile A bituminous coal were carbonized for this investigation. Samples were collected from each charge according to a statistically designed sampling plan. The coke finger samples were mounted and polished and their microstructure determined utilizing a six spindle integrating stage. The resultant microstructure data were then statistically evaluated.

PREPARATION OF COAL FOR CARBONIZATION

In order to provide coal for two duplicate charges, a bulk sample (1500 lbs.) of high volatile A bituminous coal was collected. This bulk sample (1" x 0" fraction) was pulverized to approximately 82 per cent minus 1/8" (Table I) in a Pennsylvania Type C reversible hammer-mill-impactor. All of the pulverized coal was then blended in a Model GD Patterson-Kelly, 30 cubic foot capacity twin shell blender for two hours. After homogenization of the coal, samples were removed for screen and chemical analyses. Prior to withdrawing the coal for carbonization, the bulk density and moisture were adjusted and the coal was blended for an additional hour.

CARBONIZATION

Duplicate carbonization tests were made in a Bethlehem type pilot coke oven having a coking chamber 36 inches long, 18 inches wide, and 36 inches high. To insure duplication of these tests, the oven was stabilized for 24 hours before each charge. At charging time, a 750-pound sample of coal was withdrawn from the blender and placed in the oven. Pertinent carbonization data for these oven tests are given in Table I.

SAMPLING PROCEDURE AND EXPERIMENTAL DESIGN OF SAMPLING PLAN

A sampling plan was selected in order to provide data for an adequate appraisal of the microstructure of the resultant coke, as well as providing data for a

* See References.

comprehensive statistical evaluation. Although twelve oriented samples and one quench car "grab" sample were collected from each charge, only six oriented samples and the quench car sample were examined for each charge. This procedure was followed since it was believed that one sample from a particular location on the fixed wall would be the mirror image of the one immediately across from it on the movable wall or vice versa. The areas from which the samples were taken are shown on Figure 1. The remaining twelve samples were retained as reserve samples for additional studies. The coke side and push side samples were pulled from the charge with steel tongs after the "horseshoe" had been raised. The center samples were collected after half of the charge had been pushed from the oven. Each coke finger was immediately water quenched and labeled. The quench car sample was collected after the entire charge had been pushed and quenched.

Depending on viewpoint, the experimental design of the sampling plan can be considered either as (1) a full 3 x 2 x 2 factorial with replicates, or as (2) a fractional 3 x 2 x 2 x 2 factorial with replicates. The reason for the above difference depends on whether one considers the location of "mirror image" coke fingers as a replication or as a factor. This location refers to whether the coke finger sample was taken from the "fixed wall" or "movable wall" side of the oven. The above consideration was only of secondary importance in the initial analysis since samples had been taken for the full 3 x 2 x 2 x 2 factorial. However, only half of the original samples were microscopically analyzed for the initial analysis but the other half can be analyzed at a later date if it should prove statistically necessary to do so. Thus, the initial analysis distinguishes the confounded effect of charge and oven side rather than the independent effect of each. The factors referred to in the 3 x 2 x 2 x 2 factorial are (1) oven length location at three levels, (2) oven height location at two levels, (3) oven charge at 2 levels, and (4) oven side location at two levels. The experiment was designed to satisfy two objectives:

1. To determine the inherent errors of the various measurement categories associated with a microscopic analysis of coke.

2. To determine whether sampling errors were attributable to oven location and to determine if the present sampling procedures are adequate.

With respect to the first objective, it was necessary that a replicate transect be made on each coke finger, such that an adequate estimate of the "within coke finger" variability could be obtained. Although only 12 coke finger samples were analyzed, a total of 24 transects were taken by making two independent transects per coke finger. Thus, the "within coke finger" variability of each of the categories is based on 12 degrees of freedom and can be considered as the pooled within variance of the six locations and the two oven charges.

With respect to the second objective, it was necessary that samples be taken at various locations within the oven and also from more than one oven charge, such that it would be possible to determine whether differences due to oven location were independent of the oven charge. Since two transects per coke finger were necessary to satisfy the first objective and two oven charges were also necessary, it was felt that only six oven locations could be incorporated into the plan because of the time involved in making the individual transects. For this reason, the six oven locations were chosen, such that they would reflect large rather than small location differences and also provide an adequate representation of the entire oven. The oven was divided into a cross section of three vertical and three horizontal plots for a total of nine plots, but only the top three and the bottom three plots were used in the plan for a total of six samples per charge. The samples were then taken at random from somewhere within each of these six locations for each of the two charges.

The data were analyzed by use of the analysis of variance technique, such that the various sources of variability could be distinguished and compared.

The .05 significance level was used throughout the analysis to determine whether observed differences were "real" or not. For the purpose of this report, a "real" difference indicates that the risk of making an incorrect decision based on this significance level would be five times in 100.

SAMPLE PREPARATION

A section one-half inch thick was cut from the center through the entire length of each finger. In all cases, the full length of each finger (approximately nine inches), from the cauliflower to the tar end was maintained. The width of the fingers varied from two to three inches. To facilitate ease of handling, mounting, and polishing, the 9-inch slabs were cut in half. These sections, each representative of 1/2 finger, were then placed in molds, impregnated with an epoxy resin, and polished for microstructure analyses.

ANALYTICAL PROCEDURES

A Leitz Ortholux microscope (Figure 2) equipped with a Leitz six spindle integrating stage, cross hair, and an ocular micrometer was employed in these microstructure analyses. All of the measurements were carried out at 160X magnification. Four transects covering the entire length, from the cauliflower to the tar end, were completed on a single surface of each finger. Each transect was oriented perpendicular to the cauliflower or tar end, depending upon which half was being examined. During the first transect, the pores which fell within five arbitrarily chosen size categories were recorded on five of the spindles. The sixth spindle was used to record the total cell wall area transversed during the transect. At the end of the initial transect, the specimen was returned to the original starting position. A similar transect was then completed over the same area, and the cell wall sizes were differentiated and the total space occupied by pores was recorded on the sixth spindle. This procedure was repeated twice on each finger. The arbitrarily chosen categories (Table II) were selected from those presented by Abramski and Mackowsky.[2] The average cell wall thickness and pore diameter calculations (Table III) are those proposed by Daub[2] and are based on the supposition that the true average for any of the categories approaches that of the mid-point of the particular category in question. Although the authors have not completed a statistical confirmation of this assumption, they do feel it is a reasonable estimate of the average. The density values are expressed in terms of the ratio of the volume per cent of pores to cell walls in the coke.

RESULTS AND DISCUSSION

In Table I, the carbonization data for both charges indicate that the coal charges were subjected to essentially identical coking conditions. The thermocouple readings (Tables IV, V) taken at charging and pushing time do exhibit some variation. However, these temperature differences are normal for the oven in question, and ovens of this size and type. The statistical evaluation presented herein has not included the specific effect of temperature variation. However, it would be possible in future work to determine statistically the effects of temperature variation and oven location on coke microstructure by an analysis of co-variance of these factors.

A high volatile A bituminous coal was selected for this study because previous studies have shown that this rank of coal would produce a coke possessing considerable variation in microstructure. The authors believe that the variation in the microstructure of this coke type would be greater than that obtained on coke from other coals used at our Company coke plants. In general, higher rank metallurgical coals produce cokes with larger percentages of cell walls and pores per unit area and it is reasonable to assume that the degree of reliability would increase with increasing rank of the coal. This observation has been confirmed in our laboratory and is based

on frequency measurements of cell walls and pores in cokes produced from various ranks of coal.

In Table VI, the variability limits at the 95 per cent confidence level for the cell wall and pore diameter categories are given. In addition, the limits are given for the average cell wall thickness, average pore diameter, and density measurements. The "within finger" variability consists of the inherent variability of the material, plus the analytical variability.

The within variability limits listed for the 95 per cent confidence level are the limits developed for comparison of individual fingers, each of which was transversed twice. The "within finger" variabilities of the various measurement categories were statistically compared, and it was found that:

1. The within variability of the three cell wall categories of 0.1 to 0.2 mm, 0.2 to 0.5 mm, and +0.5 mm did not differ significantly among themselves. Also the three pore diameter categories of 0.2 to 0.5 mm, 0.5 to 1.0 mm, and +1.0 mm did not differ significantly among themselves. It is also interesting to note that there was no significant difference between these cell walls and pore diameter categories.

2. The two cell wall categories of -0.05 mm and 0.05 to 0.10 mm did not differ significantly from each other nor from the two pore diameter categories of -0.1 mm and 0.1 to 0.2 mm which also did not differ significantly from each other.

3. In comparing the categories in 2 above, the -0.05 mm cell walls and both of the pore diameter categories were significantly different at the .05 significance level from all the categories in 1 above. However, the 0.05 mm to 0.10 mm cell walls were only significant at the .10 level from the categories in 1 above, which would not be considered significant in this analysis.

Even though the analytical variability was not separated out of the "within finger" variability, it is believed that it would be much smaller than the "within" limits. Variations due to the positioning of the transect on the coke fingers were noted, but it was not separated out in these statistical analyses.

The values listed under "total variability" are the limits of reproducibility that would be obtained if a completely random finger were analyzed without any knowledge of its original position in the oven or the charge from which it was sampled. These limits are much greater than those given for the "within finger" variability. Therefore, it is important that the microscopist realize that this variability exists when microstructure analyses are completed on a completely random, pilot oven finger. The degree of reproducibility is reduced markedly when such a finger is analyzed. It is also interesting to note that for the two cell wall categories of 0.05 mm to 0.10 mm and 0.1 mm to 0.2 mm, the sampling variability due to oven location and charge was not significantly different from the variability within a single coke finger. This degree of homogeneity was not found to exist in any of the other categories.

In Table VII, the mean value for the twelve fingers taken from both charges are compared to the mean value for various locations in the oven. The average pore diameter for the top fingers was significantly larger than that of the bottom fingers. The percentages of pores in the -0.1 mm, 0.1 to 0.2 mm, and 0.2 to 0.5 mm categories were found to be significantly smaller in the samples from the top of the oven as compared to the samples from the bottom (Figure 3). For the +1.0 mm pore diameter category, the samples from the top of the oven had a significantly larger percentage than those from the bottom. Although the 0.5 to 1.0 mm category had a larger percentage

for the top samples than those from the bottom, this difference was not sufficiently large to be termed significant. Although the height in the oven had significant and marked effects on the pore diameter measurements, the height in oven was found to have little or no significant effects on the cell wall measurements (Figure 3).

The low density values for the top fingers are directly related to the increase in the percentage of large pores and total area occupied by pores. A highly significant difference was found between the density of the top and bottom samples. The density is expressed in terms of the ratio of the volume per cent of pore space to that occupied by cell walls. The increase in pore diameter and larger pores may be related to a decrease in bulk density of the coal at the top of the oven. The loosely packed coal would permit the formation of frothy coke. It is less restricted in the plastic state, and gas evolution would proceed more freely in the upper portion of the charge than at the bottom. These data also show that a given coal may produce a coke with markedly different microstructures within the same coke mass.

The variations in the microstructure of the coke side, middle, and push side samples are shown in Table VII and illustrated graphically in Figures 4 and 5. The increase in average cell wall thickness toward the center from both ends of the oven may be the result of variations in bulk density. The coal in the center of the oven would have a higher bulk density, since it lies directly below the charging hole, whereas, the coal next to the doors would have a lower bulk density.[5,6] Note in Figure 4 that the distribution of the various cell wall sizes varies from the ends to the middle fingers. It was found that this difference was significant, however, for only two cell wall categories: the -0.05 mm and the 0.2 to 0.5 mm categories. In Figure 5 the percentage of plus 1.0 mm pores for the end samples was significantly higher than that of the middle fingers. Coincident with the increase in larger pores, is the decrease in density of the end fingers (Table VII). This decrease in density is also statistically affected by the height-length relationship. All of these data indicate that coal bulk density, oven temperature and other variables not considered here may affect the resultant microstructure.

In Table VIII the microstructure analyses of each charge are listed. The significance of these data are as follows:

1. The mean values for the microstructure analyses of the six fingers taken from each of the charges compared quite favorably and did not exhibit any significant statistical differences.

2. Apparently the carbonization conditions and the composition of the coal were similar, as a result reproducible data were obtained.

3. Even though there are microstructure variations, the mean values are remarkably similar.

In order to determine if our present sampling plan was adequate to characterize a 750-pound charge, routine "grab" samples were collected and analyzed. Our present sampling of coke for microstructure analysis is as follows:

1. The entire charge is pushed and quenched.

2. A single finger exhibiting a cauliflower and a tar end and four fractured surfaces is selected from the top of the quench car by the lab technician.

3. It is labeled and forwarded to the anthracology laboratory for analyses.

In Table VIII and Figures 6 and 7, microstructure analyses of the two "grab" samples are compared to the mean values for their respective charges. These data show that all the values except the -0.05 mm cell wall category for the second "grab" sample, fall

within the 95 per cent confidence limits. This is true only if two transects are completed on each "grab" sample. Although the "grab" sample from the second charge is statistically outside the variability band in the -0.05 mm category by 0.21 per cent this could legitimately be adjusted by taking two "grab" samples from the quench car and making two transects on each sample. The authors feel that this minor variation is insignificant in view of the magnitude of the measurements involved and the practical aspects of these data. It is interesting to note that an examination of the four sample locations (top middle, bottom middle, top push side, and bottom push side) indicated that a sample representative of the charge could be obtained at a position somewhere within the central third plot and between the push side and middle third plots of the oven. This, incidentally, was the approximate area from which the present "grab" sample was being taken. Consequently, the present method of selectively collecting coke samples for microstructure analysis should be continued. However, this present method should be checked periodically by making additional transects on samples taken from the six locations as defined in the experimental design.

In Table IX the microstructure of cokes produced from various ranks of coal and petroleum, as well as form coke, are compared to the microstructure of the high volatile coal used in this study. Although there are no differences in certain cell wall and pore categories, there are marked differences among other categories. There are significant differences in average cell wall thickness and average pore diameter among the coke types and in certain categories a relationship to coal rank is evident.

SUMMARY

Microstructure analyses were completed on 12 oriented coke fingers collected from duplicate pilot oven tests of a single high volatile A bituminous coal. A selected "grab" sample was also collected from each charge and its microstructure determined. Duplicate transects were made on all coke fingers. These data show that from a practical viewpoint an analysis of a single selective sample adequately characterized the microstructure of coke produced in the 750-pound oven. The criterion of adequateness was satisfied, from a statistical viewpoint, in all but one of the measurement categories on one of the oven charges. Two selected "grab" samples should completely satisfy the adequateness criterion. Even though variations were noted because of sample location in the oven, the single "grab" samples compare favorably with the mean values for the charges.

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TABLE I - CARBONIZATION DATA

	1ST CHARGE	2ND CHARGE
Net charge weight	665 lbs.	673 lbs.
Net coking time	18 hrs. 37 min.	18 hrs. 45 min.
Oven bulk density	47.50 lbs./Ft.^{3}	48.07 lbs./Ft.^{3}
Kopper's cone	42.0 lbs./Ft.^{3}	40.6 lbs./Ft.^{3}
Per cent moisture	5.4	5.5
Per cent pulverization	82.8% - 1/8 inch	82.8% - 1/8 inch
Controlling Flue temp.	2460°F	2460°F
ASTM stability factor	43.54	42.14
ASTM hardness factor	55.35	55.55

TABLE II - SAMPLE CALCULATIONS OF PERCENTAGES OF PORES AND CELL WALLS IN THE INDICATED CATEGORIES

CELL WALL SIZE CATEGORIES	SPINDLE VALUES (mm)	PER CENT
0 - 0.05 mm	13.81	15.45
0.05 - 0.1 mm	16.36	18.31
0.1 - 0.2 mm	32.54	36.41
0.2 - 0.5 mm	24.15	27.03
+ 0.5 mm	2.50	2.80
Total cell wall	89.36	100.00

PORE SIZE CATEGORIES	SPINDLE VALUES (mm)	PER CENT
0 - 0.1 mm	21.90	8.59
0.1 - 0.2 mm	18.51	7.26
0.2 - 0.5 mm	59.99	23.55
0.5 - 1.0 mm	49.93	19.59
+ 1.0 mm	104.50	41.01
Total pore	254.83	100.00

TABLE III - SAMPLE CALCULATIONS OF AVERAGE PORE DIAMETER AND CELL WALL THICKNESS

CELL WALL SIZE CATEGORIES	SPINDLE VALUES (mm)		MID POINTS (MP)		NUMBER OF CELL WALLS
0 - 0.05 mm	13.81	÷	0.025		552.40
0.05 - 0.1 mm	16.36	÷	0.075		218.13
0.1 - 0.2 mm	32.54	÷	0.15		216.93
0.2 - 0.5 mm	24.15	÷	0.35		69.00
+ 0.5 mm	2.50	÷	0.75		3.33
Total cell wall	89.36 mm			Total	1059.79

Average cell wall thickness = $\frac{89.36}{1059.79}$ = .084 mm

PORE SIZE CATEGORIES	SPINDLE VALUES (mm)		MID POINTS (MP)		NUMBER OF PORES
0 - 0.1 mm	21.90	÷	0.05		438.00
0.1 - 0.2 mm	18.51	÷	0.15		123.40
0.2 - 0.5 mm	59.99	÷	0.35		171.40
0.5 - 1.0 mm	49.93	÷	0.75		66.57
+ 1.0 mm	104.50	÷	1.50		69.67
Total pore	254.83 mm			Total	869.04

Average pore diameter = $\frac{254.83}{869.04}$ = .293 mm

TABLE IV - COMPARISON OF TEMPERATURE READINGS TAKEN AT CHARGING TIME

THERMOCOUPLE	1ST CHARGE FIXED WALL	2ND CHARGE FIXED WALL	1ST CHARGE MOVABLE WALL	2ND CHARGE MOVABLE WALL
1	1870°F	1850°F	1760°F	1760°F
2	1870	1860	1820	1800
3	1850	1840	1800	1840
4	1950	1960	1890	1900
5	1900	1890	1900	1880
6	out	out	1820	1860
7	1780	1700	1860	1860
8	1860	1840	1920	1910
9	1850	1880	1600	1610
Average	1866°F	1853°F	1819°F	1824°F

TABLE V - COMPARISON OF TEMPERATURE READINGS TAKEN AT PUSHING TIME

THERMOCOUPLE	1ST CHARGE FIXED WALL	2ND CHARGE FIXED WALL	1ST CHARGE MOVABLE WALL	2ND CHARGE MOVABLE WALL
1	1860°F	1800°F	1890°F	1840°F
2	2000	1900	2070	2060
3	2020	2020	1980	1990
4	1980	1970	2000	1970
5	2140	2110	2170	2150
6	out	out	2140	2100
7	1760	1770	1940	1890
8	1980	1840	2040	2020
9	1930	1870	1880	1800
Average	1959°F	1910°F	2012°F	1980°F

THERMOCOUPLES IN COKE MASS	1ST CHARGE	2ND CHARGE
#3 Fixed wall	1920°F	1900°F
#4 Movable wall	1920	1900
#5 Center	1890	1870

TABLE VI - "WITHIN FINGER" AND TOTAL VARIABILITY ERRORS AT THE 95 PER CENT CONFIDENCE LEVEL FOR ONE AND TWO TRANSECTS

CATEGORIES	"WITHIN FINGER" VARIABILITY PER CENT		TOTAL VARIABILITY* PER CENT	
CELL WALLS	ONE TRANSECT	TWO TRANSECTS	ONE TRANSECT	TWO TRANSECTS
- 0.05 mm	± 2.477	± 1.752	± 5.169	± 5.014
0.05 - 0.1 mm	± 3.716	± 2.628	± 3.569	± 3.022
0.1 - 0.2 mm	± 5.596	± 3.957	± 5.849	± 5.102
0.2 - 0.5 mm	± 5.553	± 3.926	± 8.275	± 7.773
+ 0.5 mm	± 5.900	± 4.172	± 6.327	± 5.562
PORES				
- 0.1 mm	± 1.782	± 1.260	± 4.933	± 4.849
0.1 - 0.2 mm	± 2.777	± 1.964	± 8.248	± 8.124
0.2 - 0.5 mm	± 5.127	± 3.626	±13.101	±12.197
0.5 - 1.0 mm	± 6.119	± 4.327	± 8.804	± 8.230
+ 1.0 mm	± 5.288	± 3.739	±22.487	±22.324
Average Cell Wall Thickness mm	.00919	.00650	.01554	.01482
Average Pore Diameter mm	.02534	.01792	.08957	.08863
Density**	.08669	.0613	.1731	.1673

* Total variability error: expect error if a random sample is analyzed without any knowledge of its original position in the oven.

** Ratio of volume per cent pore area to volume per cent cell wall area in coke.

TABLE VII - COMPARISON OF MEAN VALUES BY SAMPLE LOCATION AND CATEGORIES TO THE GRAND MEAN FOR BOTH CHARGES

CATEGORY	GRAND MEAN FOR BOTH CHARGES	TOP SAMPLES	BOTTOM SAMPLES	COKE SIDE SAMPLES	MIDDLE SAMPLES	PUSH SIDE SAMPLES
CELL WALLS						
- 0.05 mm	14.96	14.57	15.34	14.16	13.71	17.00
0.05 - 0.1 mm	18.62	18.79	18.45	18.73	18.15	18.98
0.1 - 0.2 mm	33.43	33.62	33.25	33.86	34.02	32.42
0.2 - 0.5 mm	28.24	28.15	28.33	29.89	29.46	25.37
+ 0.5 mm	4.75	4.87	4.63	3.36	4.66	6.23
Per Cent	100.00	100.00	100.00	100.00	100.00	100.00
Average Cell Wall Thickness mm	0.087	0.088	0.086	0.089	0.091	0.082
PORES						
- 0.1 mm	10.68	8.63	12.72	10.80	11.30	9.92
0.1 - 0.2 mm	13.66	10.08	17.25	12.94	14.11	13.94
0.2 - 0.5 mm	31.15	25.84	36.47	29.51	32.71	31.24
0.5 - 1.0 mm	24.43	25.51	23.35	24.77	24.82	23.71
+ 1.0 mm	20.08	29.94	10.21	21.98	17.06	21.19
Per Cent	100.00	100.00	100.00	100.00	100.00	100.00
Average Pore Diameter mm	0.236	0.275	0.196	0.238	0.223	0.247
Density $\left(\frac{\text{Vol. \% Cell Walls}}{\text{Vol. \% Pores}}\right)$	0.466	0.398	0.534	0.471	0.486	0.441

TABLE VIII - COMPARISON OF EACH GRAB SAMPLE TO THE MEAN VALUES FOR THE RESPECTIVE CHARGES

CATEGORY	MEAN 1ST CHARGE	LIMITS	1ST CHG. GRAB SAMPLE	MEAN 2ND CHARGE	LIMITS	2ND CHG. GRAB SAMPLE
CELL WALLS						
- 0.05 mm	14.08	15.83 - 12.33	12.65	15.82	17.57 - 14.07	13.86*
0.05 - 0.1 mm	18.97	21.60 - 16.34	18.76	18.21	20.84 - 15.58	16.89
0.1 - 0.2 mm	34.18	38.14 - 30.22	36.21	32.67	36.63 - 28.71	35.86
0.2 - 0.5 mm	29.09	33.02 - 25.16	29.44	27.48	31.41 - 23.55	28.81
+ 0.5 mm	3.68	7.85 - 0	2.94	5.82	9.99 - 1.65	4.58
Per Cent	100.00		100.00	100.00		100.00
PORES						
- 0.1 mm	10.58	11.84 - 9.32	11.14	10.74	12.00 - 9.48	9.97
0.1 - 0.2 mm	13.61	15.57 - 11.65	12.56	13.68	15.64 - 11.72	14.87
0.2 - 0.5 mm	31.92	35.55 - 28.29	29.68	30.42	34.05 - 26.79	30.26
0.5 - 1.0 mm	24.41	28.74 - 20.08	24.29	24.46	28.79 - 20.13	24.35
+ 1.0 mm	19.48	23.22 - 15.74	22.33	20.70	24.44 - 16.92	20.55
Per Cent	100.00		100.00	100.00		100.00
Average Cell Wall Thickness mm	.089	.0955 - .0825	.092	.085	.0915 - .0785	.090
Average Pore Diameter mm	.233	.2509 - .2160	.228	.238	.2559 - .2201	.232
Density (Vol. % Cell Walls / Vol. % Pores)	.473	.534 - .412	.418	.459	.520 - .398	.459

* Only value which does not fall within the variability limits.

TABLE IX - VARIATION IN MICROSTRUCTURE OF INDICATED COKE TYPES.

CATEGORY	High Vol.	High-Med. Vol.	Low-Med. Vol.	Low Vol.	Petroleum Coke	Form Coke
CELL WALLS						
- 0.05 mm	13.25	16.09	18.84	29.49	0.19	15.45
0.05 - 0.1 mm	17.83	21.35	20.68	23.20	0.12	25.38
0.1 - 0.2 mm	36.04	38.71	34.33	27.89	1.03	40.50
0.2 - 0.5 mm	29.12	20.49	18.79	13.67	6.52	16.45
+ 0.5 mm	3.76	3.36	7.36	5.75	92.14	2.22
Per Cent	100.00	100.00	100.00	100.00	100.00	100.00
Average Cell Wall Thickness mm	0.091	0.080	0.076	0.058	0.635	0.078
PORES						
- 0.1 mm	10.55	17.23	15.62	23.62	1.98	23.76
0.1 - 0.2 mm	13.72	16.68	21.88	24.63	3.72	29.16
0.2 - 0.5 mm	29.97	37.66	40.09	37.20	15.03	34.91
0.5 - 1.0 mm	24.32	19.86	17.63	10.66	17.05	12.17
+ 1.0 mm	21.44	8.57	4.78	3.89	62.22	-
Per Cent	100.00	100.00	100.00	100.00	100.00	100.00
Average Pore Diameter mm	0.230	0.168	0.167	0.132	0.583	0.127
Density $\left(\frac{\text{Vol. \% Cell Walls}}{\text{Vol. \% Pores}}\right)$	0.439	0.569	0.589	0.534	1.59	0.747

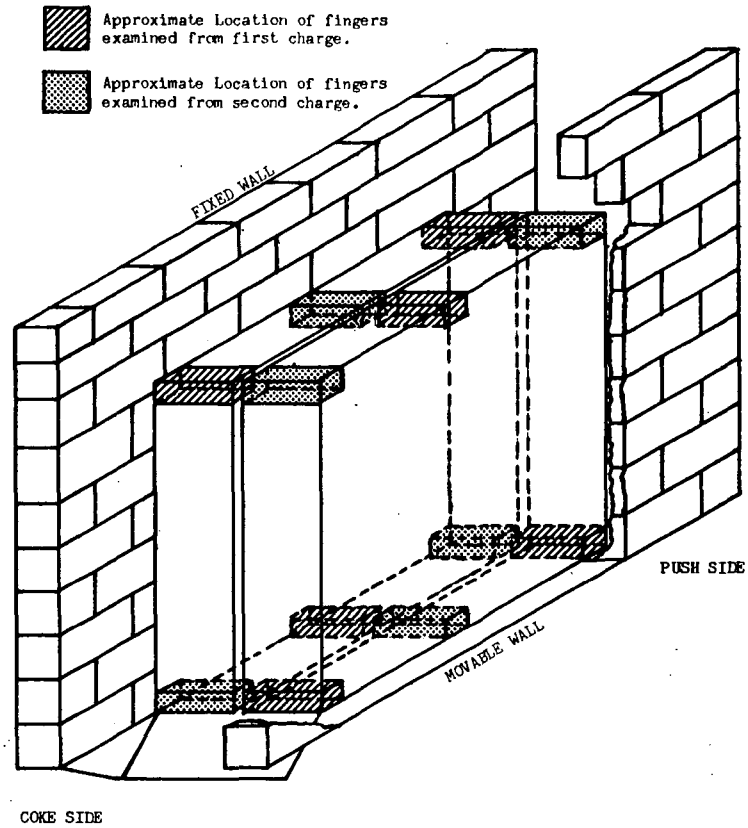

FIGURE 1 - SCHEMATIC OF 750 POUND OVEN SHOWING APPROXIMATE LOCATION OF COKE FINGERS EXAMINED FROM DUPLICATE CHARGES.

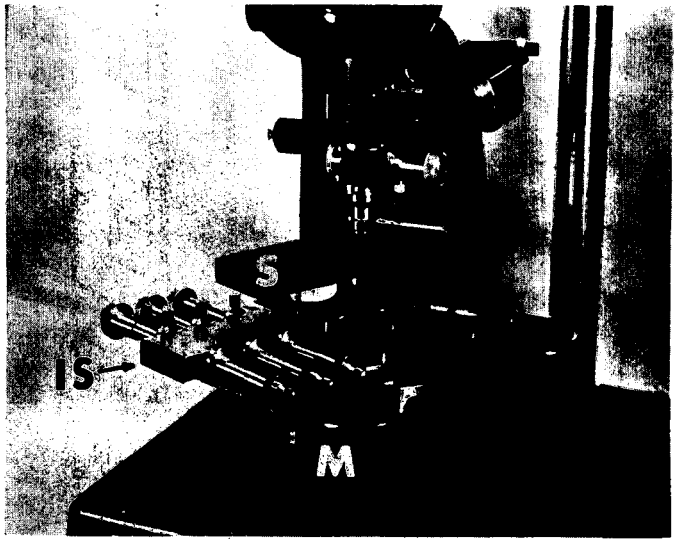

FIGURE 2 - PHOTOGRAPH OF MICROSCOPE AND INTEGRATING STAGE EMPLOYED IN MICROSTRUCTURE ANALYSES (1/4 X). INTEGRATING STAGE (IS), SPECIMEN (S), AND MICROSCOPE STAND (M).

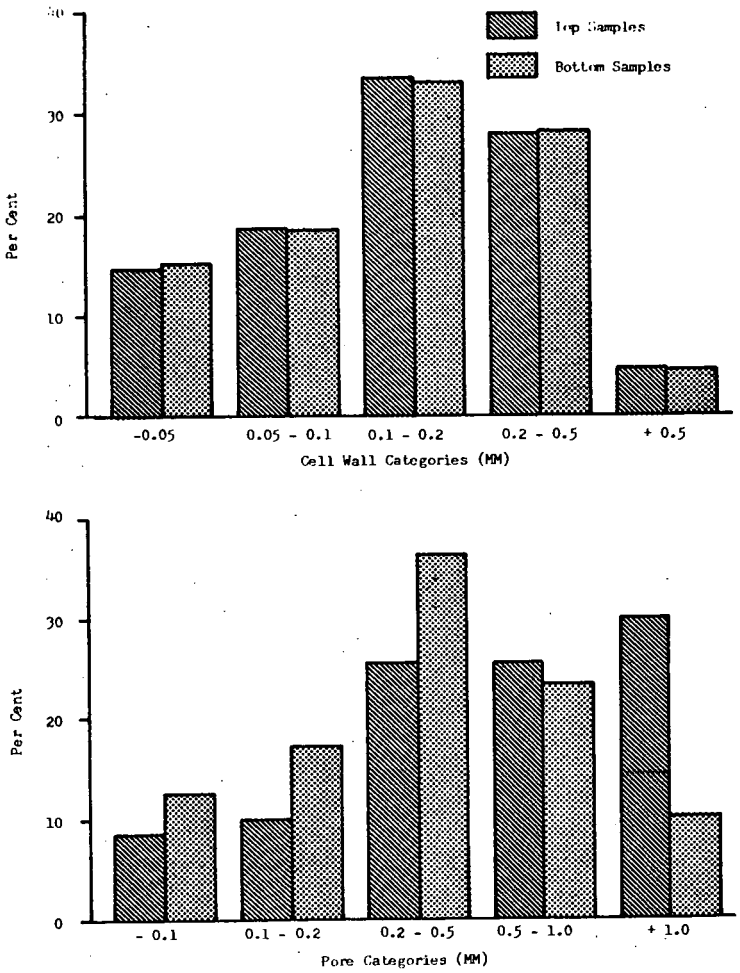

FIGURE 3 - COMPARISON OF FINGERS TAKEN FROM TOP OF THE OVEN TO THOSE TAKEN FROM BOTTOM OF OVEN FOR BOTH CHARGES

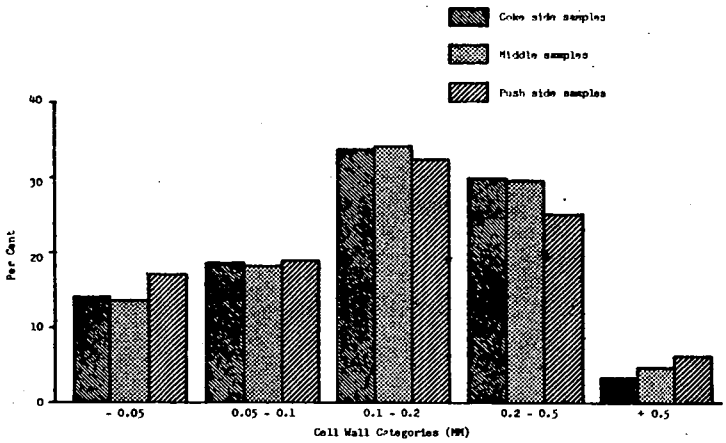

FIGURE 4 - COMPARISON OF PER CENT CELL WALLS IN THE INDICATED CATEGORIES FOR THE COKE SIDE, MIDDLE, AND PUSH SIDE SAMPLES.

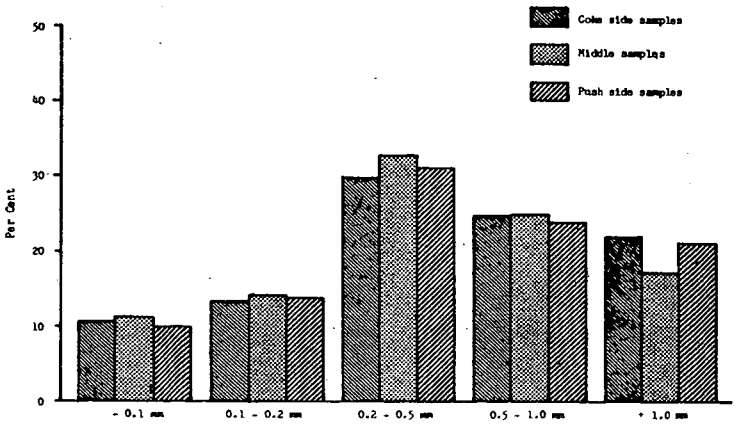

FIGURE 5 - COMPARISON OF PER CENT PORES IN THE INDICATED CATEGORIES FOR THE COKE SIDE, MIDDLE, AND PUSH SIDE SAMPLES.

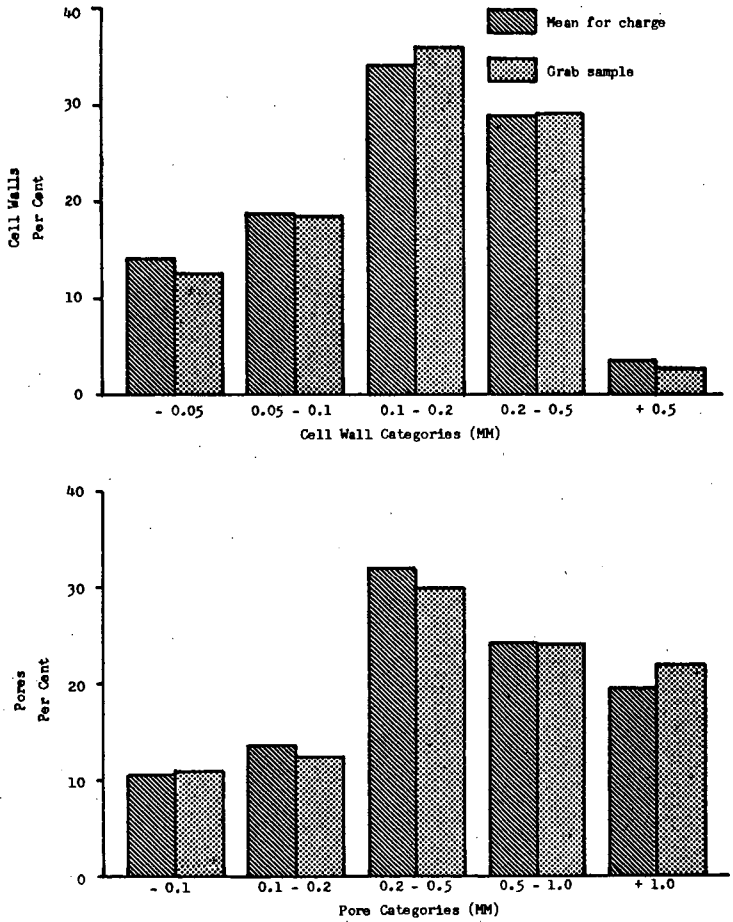

FIGURE 6 - COMPARISON OF MEAN VALUES FOR 1ST CHARGE TO THE MEAN VALUES FOR THE SINGLE GRAB SAMPLE TAKEN FROM THIS CHARGE.

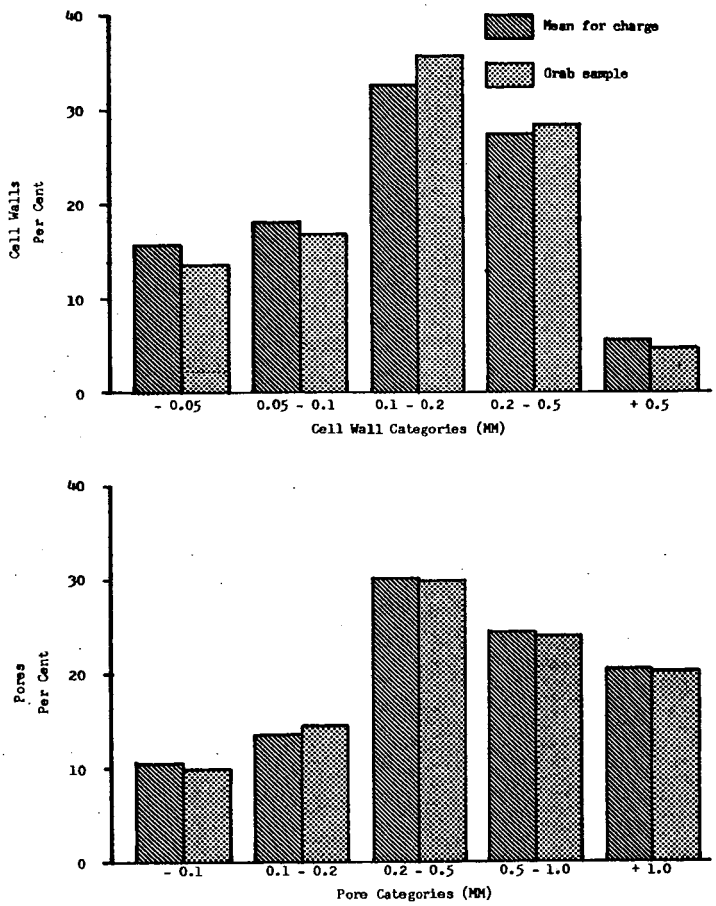

FIGURE 7 - COMPARISON OF MEAN VALUES FOR 2ND CHARGE TO THE MEAN VALUES FOR THE SINGLE GRAB SAMPLE TAKEN FROM THIS CHARGE.

Investigation Into the Effect of Particle Size and Apparent Bulk Density on Coke Structure

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During the past thirty years, there has been a great effort in the science of coal petrography which has led to the use of this science in the solution of certain coking coal problems. The specific works of F. L. Kuhlwein, E. Hoffmann, H. Hoffmann, E. Burstlein, C. Abramski, D. W. Van Krevelen, and many others (1, 3, 9, 10, 18) show over and over that it is difficult to take into consideration all of the influences which affect the carbonization of coal. Amosov and Eremin, Harrison and Shapiro, Gray and Eusner (2, 7, 16) have in their work, which is based upon the maceral analysis of seam coals, been able to ascertain experimentally the optimum ratio of the reactive to inert components in the coal rank range between 16 and 40 percent volatile matter. These workers were able to derive a suitable formula which will allow the prediction of the coking strength of a coal or coal blend, in terms of stability, with sufficient accuracy for use in the prediction of coke strength characteristics of metallurgical coal blends. The assumptions necessary for such a calculation were a constant size consist of the coal, as well as a constant apparent density, and, of course, constant coking conditions. However, ability to predict stability is not completely useful in every case. In the Ruhr district of Germany, for example, coals from numerous coal seams with very different rank classifications are in the feed at the same time from one shaft installation. Since the feeds to such a coal product cannot be changed - due to operating technique and raw material supplies - it is difficult to assure a constant coke quality.

In a situation such as that with the Ruhr Valley coals, the question arises as to how, with a given raw material situation and therefore a given maceral composition of a coking coal, the quality of the coal produced can be influenced by changing the particle size structure and/or the apparent bulk density of the coal charge. Preliminary work along this line has been published by Marshall and Harrison (13). Using this work as a basis, during the last year we have investigated thoroughly the effect of size and apparent bulk density on the coke structure. For the purposes of this study, different size consists of seam coals were coked, varying the bulk density and keeping the coking rate as consistent as possible under laboratory conditions.

First, a very granular coal, with an apparent bulk density of 0, was used. The bulk density of 0 was assumed since, for all practical purposes, each grain was coked alone without contact with the others. In a second series of experiments, using a small coking oven developed by H. Ritter and G. Juranek (14), an apparent bulk density of approximately 0.5 was used. The third series was coked using the dilatometer with a very highly compressed coal in which the apparent bulk density was about 1.

The experimental results will be discussed briefly in order to show that such research can produce a worth-while complement to the work of Amosov and Eremin (2) on one hand, and to that of Shapiro, Gray and Eusner (15, 16) and Harrison (7) on the other hand. For the sized coals, the screen sizes of 5 to 3, 3 to 1, 1 to 0.5, 0.5 to 0.2, and minus 0.2 millimeter were used on coals from seams with volatile matter contents of from 15 to 37 percent. On the basis of petrographic analysis, the ratio of the reactive to inert components was calculated. The data for all the samples examined are summarized in Figure 1. Figure 1 shows that in other than sample 1 (with 31.7 percent volatile matter), the ratio of the reactive to the inert component in the screen size 5 to 3 millimeters and the screen size less than 0.2 millimeters is approximately equal, or perhaps a little larger, than in the finer grained material. This indicates clearly that a poorer coking capacity is surely not caused by maceral composition but can only be caused by the grain size.

The individual screen sizing of coals of different stages of coalification were examined when coked, and the proportion of pore-showing grains was determined quantitatively. From Figure No. 2, it appears that in the screen sizing of 5 to 3 millimeters, all grains - independent of the stage of coalification - possessed degassing pores. However, the size and shape of these degassing pores are quite different in coals of different stages of coalification, as shown in Figure No. 3. With increasing fineness of size consist, the proportion of pore-showing grains becomes smaller. The decrease in the pore-showing grains is especially great in the poorer coking coals (Samples 1 and 5), while the decrease becomes apparent in the good coking coals only in the screen sizes under 0.5 millimeters. The basis for this reduced pore structure with decreasing screen size is that a degassing pore can only evolve in the temperature range of the plastic zone when the gas volume set free by the decomposition is larger than the gas volume escaping at the same time from the interior of the grain by diffusion. Consequently, there is an excess pressure in the interior of the grain, and at the same time a pressure drop from the inside to the outside of the grain. Since in the smaller grains the diffusion route and, therefore, the diffusion resistance is smaller, fewer degassing pores will result in small grains.

In another investigation series, shown in Illustration No. 4, the pore count per grain and the mean pore size diameter were ascertained for each of the different screen sizes (Illustration No. 5). The pore count per grain and the mean pore diameter were ascertained because it was thought that the mean pore diameter is not only dependent on grain size, but is primarily dependent upon the degree of coalification and is, therefore, related to the softening capacity of the coals. In the smaller screen sizes of the best coking coals, the largest pore diameter is shown, and consequently, the smallest number of pores per grain. Therefore, pore size and pore count are not in direct relation to the volatile matter content of the initial coal. The pore size is probably dependent upon the gas volume split off in the plastic zone and the viscosity of the plasticized coal, and perhaps also the permeability of the coal when in a plastic state. If these assumptions are correct, then a low viscosity melt might have a poorer gas permeability than a coal with a high viscosity melt. However, the work has not progressed far enough to provide experimental data on these assumptions. If one were to consider not only the small screen sizes for each of the coals examined, but all screen sizes of an individual coal, it appears that in

coals with 37.1 percent volatile matter and 20.6 percent volatile matter, the mean pore diameter from the coarsest to the finest sizes decreases approximately one-half. In coals with 15.1 percent volatile matter, the pore diameter remains practically constant, only the pore count per grain is changed. On the other hand, in good coking coals, the mean pore diameter falls off only from one-sixth to one-tenth of the value of the coarsest screen size. An explanation of this phenomenon does not seem to be possible on the basis of a microscopic analysis. Therefore, a systematic physical-chemical investigation became necessary. However, it should be pointed out that it is conceivable that in good coking coals in which a relatively strong degassing occurs in the plastic zone, the ratio of the volume of released gas to that carried off by way of diffusion shifts more strongly than in coals which have low degassing in the plastic zone, and at the same time a proportionately higher viscosity of the plasticized coal.

In order to attempt to explain the occurrence of the undesirable sublimation phenomenon in the coking process, the idea of the strong shift of the ratio of released gas volume to the diffusion gas volume in good coking coal was tested by coking and determining the mean coal grain diameter before and after coking. For these experiments, only the screen sizes under 1 millimeter could be used, since only in these sizes were there a sufficient number of grains to allow a statistical evaluation of the resulting data. The results are shown on Illustration No. 6. It must be stated, however, that in the microscopic determination of the mean grain diameter, the values of diameter were always too small, since the coal grains were cut randomly and were not always cut in the plane of the largest grain diameter. However, the results are useful since the raw material and the end product were examined by exactly the same method. Screen analysis did not enter into the question, because the screened materials presented only small changes in the mean grain diameter, and the mechanical resistance of the swollen granular coked material was so low that it had to be measured without screening because of the induced breakage by screening. Illustration No. 6 shows the variation in grain diameter of the three screen sizes related to the stages of coalification. If one disregards the results of the sample with 32.5 percent volatile matter, it is obvious that for the grain sizes 1 to 0.5 millimeter, the mean grain diameter of the coke samples clearly increases up to the range of 20 percent volatile matter and then decreased again. In the finest screen sizes, it cannot be said that there is a clear increase of the mean grain diameter for the coke sample. This distinct behavior of the screen sizes of a coal has the same cause as the pore structure, that is, the ratio of gas volume released in a unit time to the gas volume diffused out is the reason for this phenomenon.

The different behavior of the sized grains (for example, the grain size between 1 and 0.5 millimeters) with an increasing stage of coalification, is explained in the following manner. In the various coalification stages, the swelling of the coal caused by the pore formation is compensated for by a shrinking phenomenon, following plastic state. As a rough simplification, it can be said that the shrinking property of a coal decreases with increasing stage of coalification. Strong swelling in conjunction with a low shrinkage, or after-shrinkage, leads to a distinct problem which can result in the difficult working of a coking oven. The decrease of bulk density associated with a larger grain size, which is often undesirable, affects the oven pressure less than has often been supposed. It is possible, by the addition of oil to the coal, to raise the initial value of bulk density of the coal. This is essentially the same as grinding the coal to a finer size, and will lower the oven pressure without the necessity of doing anything more to the coal.

It is possible that the lesser shrinkage of a coal with a greater stage of coalification can be explained by the changes in the microstructure of the coal. Through the investigations of Hirsch (8) it is known that in the course of the second phase of the coalification, the specific concentration and the degree of order of the condensed ring systems contained in the coal increases. This means that with increasing degree or stage of coalification, the distance of the aromatic lamella from each other becomes smaller. If the distance of the aromatic lamella from each other is made equal to the theoretical maximum shrinkage capacity, it is comprehensible that coals with 20 percent volatile matter will have less shrinkage than coals with 30 percent or more volatile components. In a coal with less than 20 percent volatile matter, the volume increase of the grains of the 1 to 0.5 millimeter size range decreases again in coking, so it can be said that these coals with a low swelling will offset the capacity of poor after-shrinkage.

The strong increase in the mean grain diameter of the screen size 1 to 0.5 millimeter of a coal with 32.2 percent volatile matter cannot be explained on the basis of the relationships heretofore discussed. In this screen size, the ratio of reactive to inert is 10 to 1, and is especially high. It does not appear possible to find an explanation of the high volume increase with the help of a maceral analysis. It can be surmised that in this type of coal the aromatic lamella are better arranged, and this should manifest itself in a normally higher reflectance anisotropy. This, however, could not be established, and there must be further research into why the otherwise ascertainable relationship between the degree of coalification on the one hand and the swelling on the other hand could not be determined by comparison of the same particle sizes.

In the second experimental series, coal samples with different stages of coalification were again coked in the experimental furnace of Ritter and Juranek. For this series, bulk density was held constant. Working on the constant bulk density basis, it was not possible to coke the individual screen sizes as separates, but rather a mixture of the following composition was established:

		Millimeters		Percent
Screen Size	-	5 to 3	-	20
"	-	3 to 1	-	30
"	-	1 to 0.5	-	30
"	-	0.5 to 0.2	-	10
"	-	under 2	-	10

Since the coked sample could be sectioned as a whole, data became possible in this experimental series on the variable conditions of individual, different sized particles. The results of the first series were confirmed qualitatively in the second series. Quantitatively, a few noteworthy differences were determined. The greater tightness of packing causes the particles to cement together, since they tend to swell strongly during the formation of the coke. Owing to this cementing, the particles are limited in their swelling capacity.

This results in clearly lower mean pore diameters, especially in the finer particles, with a lower pore count per particle. This lower possibility of deformation can work out favorably in the relation of swelling to after-shrinkage. However, this does not imply that in all cases the coals known as "dangerous oven pressure producing coals" are related to a larger grain size consist because this series of tests showed that there is apparently no greater oven pressure related to an increase of the mean grain size particle diameter. Direct measurement of the oven pressure cannot be undertaken in the small experimental equipment.

In the third experimental series, an ultra-high tightness of packing (apparent bulk density about 1) was used. As before, the results of this series confirmed the results of the first series so far as the coal samples were examined. Quantitatively, the experimental results were again different from the results of the first experimental series because of the very high tightness of packing. The particles cemented together immediately at the start of softening. The pore formation set in generally only after this cementing. The cementing was again demonstrated to be more in the coarse particles than in the fine particles. However, the mean pore diameter, and also the pore count per particle, were clearly reduced in comparison to those of the first two experimental series, so that one could no longer properly speak of a normal coke structure, especially if coals of a very high or low stage of coalification were charged. This again is traced back to the fact that with an apparent bulk density as high as was used in this third series, the pore formation combined with an increase in volume of the particle is only possible if the whole coke button was deformed. Therefore, an essentially higher internal gas pressure is necessary for the deformation of the whole sample than for the deformation of a single particle, or for the deformation of particles in a relatively loose charge (an apparent bulk density of 0.5), in which, even after the cementing of the particles together, there still remains the possibility of swelling in the relatively large spatial volume.

In Illustration No. 7, three cokes from the three experimental series are compared. The illustration shows clearly the difference in mean pore diameter and the pore count per particle. Further, it is apparent that in the very low and the very high bulk density charges there is no normal coke structure formed.

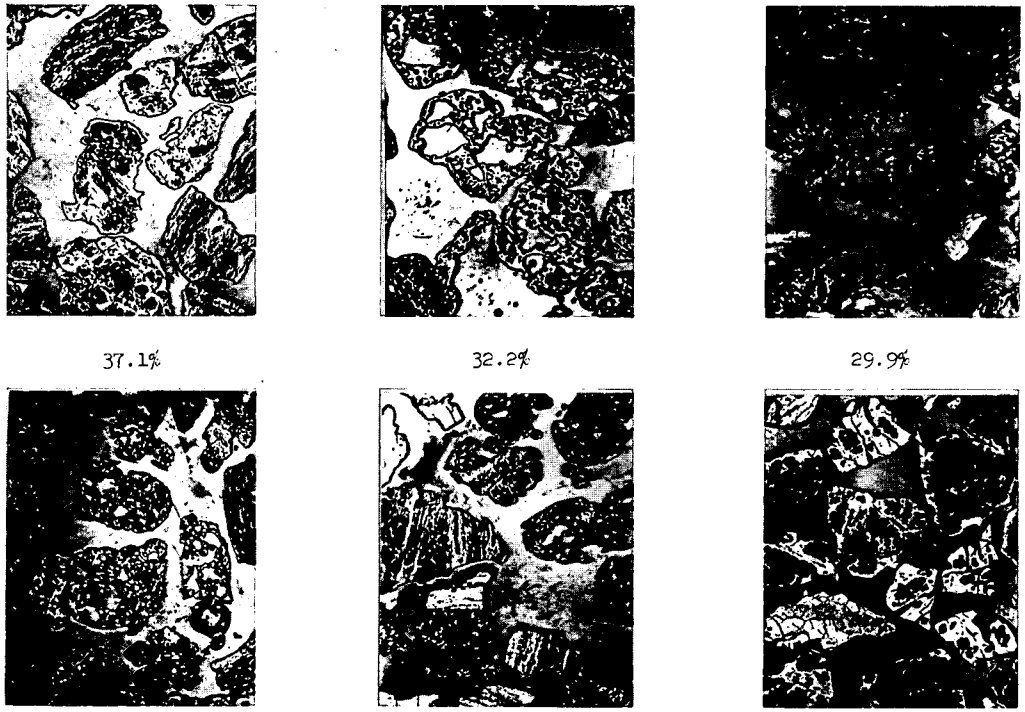
If conclusions usable in practice are to be drawn from these three experimental series, one conclusion is that crushing a coal too fine can lead to a lowering of coke quality. In good coking coal, particles under 0.2 millimeter are too fine, and with poor coking coals, particles under 0.5 millimeter appear to be too fine. At these sizes, the pore formation necessary for coke formation is greatly reduced and in many cases is completely absent. On the other hand, the results also show that too high a proportion of coarse particles, (particles between 2 and 3 millimeters) especially with a very good coking coal, lead to a very porous coke whose strength is not satisfactory. Further, it can be shown from the three experimental series that a high density packing (the high bulk density) does not positively lead to an increase in the strength of coke, since with a bulk density of about one, a good coke structure can no longer be formed.

Samples	1	2	3	4	5	6
Volatile Components of Raw Material in Weight %, Water and Ash Free	37.1	32.2	29.9	23.7	20.6	15.1
5 - 3 mm	6.1	3.0	2.8	3.2	2.1	3.8
3 - 1 mm	7.3	3.8	3.0	5.6	3.0	4.9
1 - 0.5 mm	6.7	10.1	6.7	4.9	5.2	5.3
0.5 - 0.2 mm	5.7	4.6	4.3	4.9	5.2	9.0
< 0.2 mm	3.2	3.3	3.0	3.8	4.3	6.1

Illustration No. 1. The Ratio R/I for the Coal Charge for Granular Coking, Distributed According to Screen Size

Volatile Components of Raw Material in Weight %, Water and Ash Free	37.1	32.2	29.9	23.7	20.6	15.1
5 - 3 mm	100	100	100	100	100	94
3 - 1 mm	98	100	100	100	100	95
1 - 0.5 mm	98	100	100	100	100	78
0.5 - 0.2 mm	62	94	95	88	89	23
< 0.2 mm	23	41	37	30	25	-

Illustration No. 2. Portion of Coked Screen Sizes in Particles With Degassing Pores (fusite and mineral-free coking material)



Bergbau-Forschung, 1962, TR 1739

Illustration No. 3 (X2). Granular Coking of a Coalification Series
(Volatile components in percent, water and ash free)
Screen Size: 5 - 3 mm

Volatile Components of Raw Material in Weight %, Water and Ash Free	37.1	32.2	29.9	23.7	20.6	15.1
5 - 3 mm	14	7	5	9	10	10
3 - 1 mm	7	7	3	3	3	4
1 - 0.5 mm	3	3	2	2	3	2
0.5 - 0.2 mm	2	2	1	1	1	1
< 0.2 mm	2	1	1	1	1	-

Illustration No. 4. Pore Frequency per Particle in Particles With Degassing Pores

Volatile Components of Raw Material in Weight %, Water and Ash Free	37.1	32.2	29.9	23.7	20.6	15.1
5 - 3 mm	0.1	0.3	0.6	0.3	0.1	0.16
3 - 1 mm	0.09	0.2	0.3	0.2	0.2	0.1
1 - 0.5 mm	0.05	0.1	0.1	0.2	0.1	0.2
0.5 - 0.2 mm	0.08	0.1	0.1	0.09	0.09	0.15
< 0.2 mm	0.06	0.05	0.06	0.05	0.06	-

Illustration No. 5. Mean Pore Diameter in mm

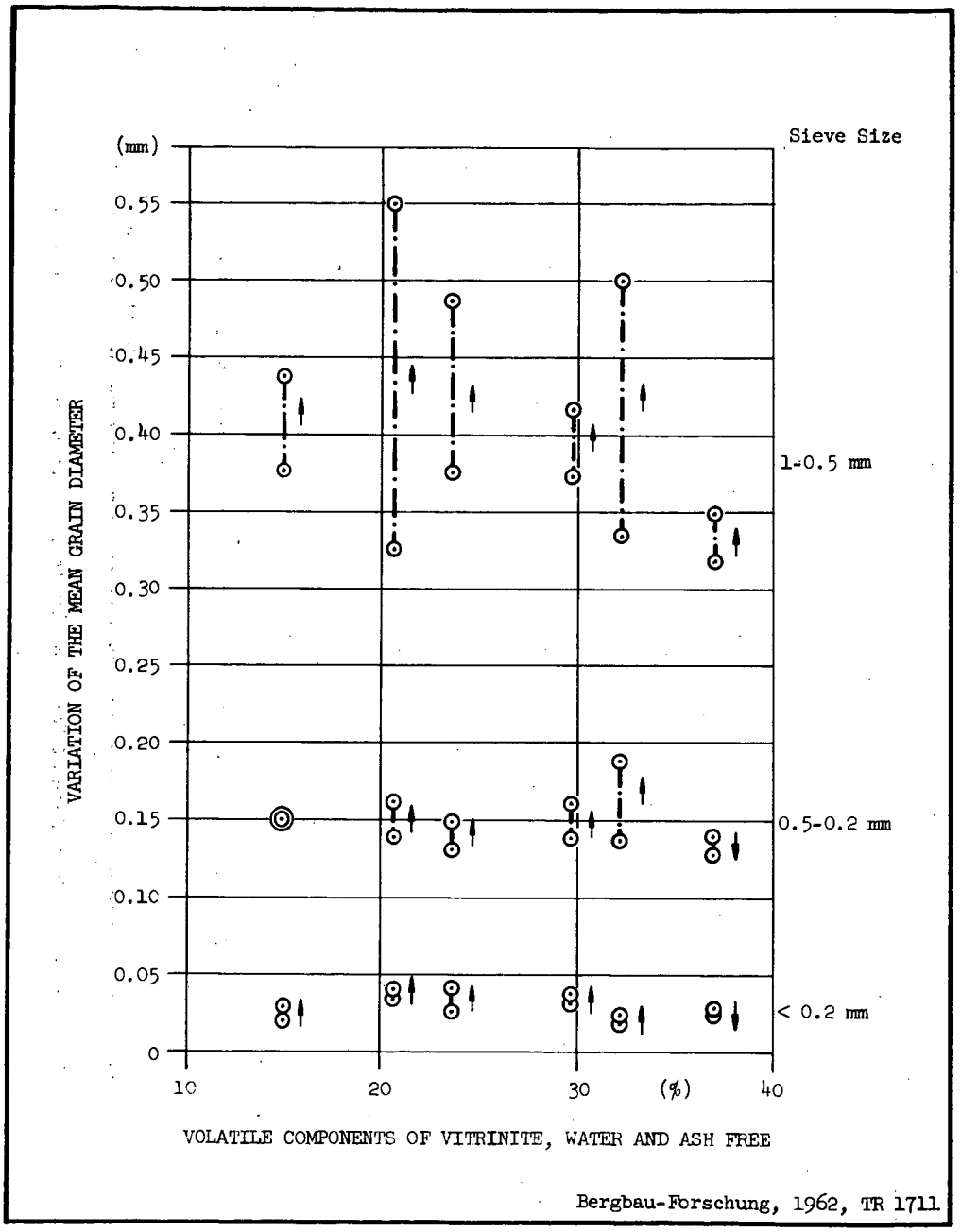


Illustration No. 6. Particle Diameter of the Granular Coking Material

Bulk Density: ca. 1 kg/l wf	ca. 0.5 kg/l wf	0
Particle Size: < 1 mm	1 - 0.5 mm	1 - 0.5 mm

X220 Oil

Volatile Components of Raw Material: ca. 24.0 percent, water and ash free

Bergbau-Forschung, 1963, TR 1835

Illustration No. 7. Variation of Pore Size and Count in Relation to Bulk Density

Untersuchungen über den Einfluß von Korngröße und Schüttgewicht auf die Koksbildung

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In den vergangenen 30 Jahren hat es nicht an Versuchen gefehlt, die Bedeutung der Kohlenpetrographie für Verkokungsprobleme herauszustellen. Es sei hier nur an die Arbeiten von F. L. Kühlwein, E. Hoffmann, H. Hoffmann, E. Bürstlein, C. Abramski, D.W. van Krevelen u.v.a. erinnert (1, 3, 9, 10, 18). In diesen Arbeiten zeigt sich immer wieder, daß es sehr schwierig ist, die Vielfalt der Einflüsse insgesamt zu berücksichtigen und dennoch zu klar überschaubaren Ergebnissen zu kommen. Amosov, Eremin, Harrison, Schapiro, Gray und Eusner (2, 7, 16) haben nun den Versuch unternommen, ausgehend von der Mazeralanalyse verschieden hoch inkohlter Flözkohlen das optimale Verhältnis von reaktiven zu inerten Bestandteilen im Inkohlungsbereich zwischen etwa 40-16 % Flüchtigen Bestandteilen experimentell zu ermitteln und anschließend Formeln aufzustellen, mit deren Hilfe auch bei Vorliegen von Kohlemischungen die Koksfestigkeit mit befriedigender Genauigkeit errechnet werden kann. Aufgrund dieser Arbeiten ist es möglich geworden, die rohstoffliche Zusammensetzung einer Kokskohle ohne Zusätze zu verbessern. Vorraussetzung für derartige Berechnungen ist ein konstanter Körnungsaufbau der Kohle, ein konstantes Schüttgewicht und selbstverständlich konstante Verkokungsbedingungen, also gleichbleibende Heizzugstemperatur und damit gleichbleibender Verkokungsfortschritt, wenn in Koksöfen gleicher Ausmessung, vor allem gleicher Kammerbreite verkokt wird.

Die von den russischen und amerikanischen Autoren aufgezeigte Möglichkeit hat in den Fällen große praktische Bedeutung, in denen die Möglichkeit besteht, die Zusammensetzung der Kokskohle durch Veränderung der prozentualen Beteiligung der an ihrem Aufbau beteiligten Flöze oder Mazeralgruppen zu verändern. Diese Möglichkeit ist jedoch nicht in jedem Fall in ausreichendem Maße gegeben, besonders dann nicht, wenn, wie z... i[illegible] ist,

zahlreiche Flöze mit recht verschiedenem Inkohlungsgrad auf einer Schachtanlage zugleich in Förderung sind. Ihr Förderanteil kann aus betriebstechnischen und rohstofflichen Gründen nicht in weiten Grenzen verändert werden, da dann, auf lange Sicht gesehen, eine gleichbleibende Koksqualität nicht zu garantieren ist. Bei einer derartigen Situation gewinnt die Frage, wie bei gegebener rohstofflicher Situation, also gegebener Mazeralzusammensetzung und gegebener inkohlungsmäßiger Zusammensetzung der Kokskohle die Koksqualität durch Veränderung des Körnungsaufbaus und des Schüttgewichts beeinflußt werden kann. Ähnliche Ideen wurden auch schon von Marshall und Harrison geäußert (13). Aus diesem Grunde haben wir in den letzten Jahren in verstärktem Maße den Einfluß von Körnung und Schüttgewicht auf die Koksbildung untersucht. Zu diesem Zweck wurden verschiedene Siebstufen oder auch verschiedene Körnungen von Flözkohlen in unterschiedlicher Packungsdichte bei annähernd gleichem Verkokungsfortschritt im Laboratoriumsmaßstab verkokt. Bei der sogenannten Granularverkokung wurde mit einem Schüttgewicht von 0 gearbeitet, da praktisch jedes Korn, ohne das andere zu berühren, allein verkokt wurde. In einer zweiten Versuchsserie wurde in dem von H. Ritter und G. Juranek (14) entwickelten kleinen Verkokungsofen bei einem Schüttgewicht von etwa 0,5 gearbeitet und in der dritten Versuchsreihe im Dilatometer mit hochverdichteten Kohlen, deren Schüttgewicht etwa bei 1 lag.

Im folgenden sollen nun kurz die Versuchsergebnisse besprochen werden, um zu zeigen, daß derartige Untersuchungen gegebenenfalls eine wertvolle Ergänzung der Arbeiten von Amosov und Eremin (2) einerseits und von Schapiro, Gray, Eusner (15, 16) und Harrison (7) andererseits darstellen können. Für die Granularverkokung wurden die Siebstufen 5-3, 3-1, 1-0,5, 0,5-0,2 und unter 0,2 mm aus Flözen zwischen 37-15 % Flüchtigen Bestandteilen untersucht. Aufgrund von Mazeralanalysen wurde der Quotient reaktive zu inerten Bestandteilen errechnet, der für alle untersuchten Proben in Abb.-Nr. 1 zusammengestellt ist. Die Abb.-Nr. 1 zeigt, daß abgesehen von Probe 1 mit 37,1 % Flüchtigen Bestandteilen i. waf. der Quotient R/I in den Siebstufen 5-3 mm und unter 0,2 annähernd gleich oder im

Feinkorn sogar größer ist, so daß ein schlechteres Verkokungsvermögen im Feinkorn sicher nicht durch die Mazeralzusammensetzung bewirkt wird, sondern nur durch die Korngröße.

Die einzelnen Siebstufen der Flöze verschiedenen Inkohlungsgrades wurden nach der Granularverkokung unter verschiedensten Gesichtspunkten untersucht. Als 1. wurde der Anteil an porenzeigenden Körnern quantitativ ermittelt. Aus der Abb.-Nr. 2 geht hervor, daß in der Siebstufe 5-3 mm alle Körner unabhängig vom Inkohlungsgrad Entgasungsporen aufweisen. Die Größe und Form dieser Entgasungsporen ist jedoch, wie Abb.-Nr. 3 zeigt, in den verschiedenen Inkohlungsbereichen verschieden. Mit zunehmender Kornfeinheit wird der Anteil an porenzeigenden Körnern kleiner. Diese Abnahme ist besonders stark bei den schlechter kokenden Kohlen(Probe 1 und 5), während sie sich bei den gut verkokbaren Kohlen zwischen 30 und 20 % Flüchtigen Bestandteilen erst im Korn unter 0,5 mm deutlich bemerkbar macht. Der Grund für diese verminderte Porenbildung mit sinkender Korngröße ist darin zu sehen, daß eine Entgasungspore nur dann entstehen kann, wenn im Temperaturbereich der plastischen Zone die in der Zeiteinheit durch Zersetzung freiwerdende Gasmenge größer ist als die in der gleichen Zeit vom Korninnern durch Diffusion entweichende. Auf diese Weise kommt es zu einem Überdruck im Korninnern und zugleich zu einem Druckgefälle von innen nach außen. Da bei kleinen Körnern der Diffusionsweg und damit auch der Diffusionswiderstand kleiner ist, entstehen in kleinen Körnern weniger Entgasungsporen als in größeren. In weiteren Untersuchungsreihen wurde, wie die Abb.-Nr. 4 zeigt, die Porenzahl pro Korn und der mittlere Porendurchmesser in den verschiedenen Siebstufen ermittelt (Abb.-Nr.5) da vermutet wurde, daß vor allem der mittlere Porendurchmesser nicht nur Kornfrökenabhängig ist, sondern vor allem abhängig vom Inkohlungsgrad und damit von dem Erweichungsvermögen der Kohle. Aus den Abbildungen ist zu ersehen, daß in den kleinen Siebstufen immer die am besten verkokbaren Kohlen die größten Porendurchmesser aufweisen und damit die kleinste Porenzahl je Korn. Porengröße und Porenzahl stehen also nicht in direkter Beziehung zum Gehalt an flüchtigen Bestandteilen in der Ausgangskohle. Die Porengröße ist

aller Wahrscheinlichkeit nach in erster Linie von der in der plastischen Zone abgespaltenen Gasmenge, der Viskosität der erweichten Kohlen und vielleicht auch von der Permeabilität der Kohlen im plastischen Zustand abhängig. Sind diese Vermutungen richtig, dann müßte eine niedrig viskose Schmelze eine schlechtere Gasdurchlässigkeit haben als eine hochviskose. Hierfür liegen jedoch noch keine experimentellen Ergebnisse vor. Betrachtet man nun nicht nur die kleinen Siebstufen für alle untersuchten Flözkohlen sondern alle Siebstufen einer einzelnen Kohle, so zeigt sich, daß bei den Kohlen mit 37,1 und 20,6 % Flüchtigen Bestandteilen der mittlere Porendurchmesser von der gröbsten zur feinsten Siebstufe auf etwa den halben Wert fällt. Bei der Kohle mit 15,1 % Flüchtigen Bestandteilen bleibt er praktisch konstant, Es ändert sich nur die Porenzahl je Korn. Bei den gut kokenden Kohlen sinkt der mittlere Porendurchmesser dagegen von 1/6 bis 1/10 des Wertes für die grobe Siebstufe. Eine Erklärung dieses Phänomens ist aufgrund der mikroskopischen Analyse nicht möglich. Hierfür sind systematische physikalisch-chemische Untersuchungen erforderlich. Es ist jedoch denkbar, daß bei den gut kokenden Kohlen, bei denen eine verhältnismäßig starke Entgasung in der plastischen Zone stattfindet, sich das Verhältnis von freiwerdender zu über Diffusion abtransportierter Gasmenge stärker verschiebt als bei den Kohlen mit geringer Entgasung in der plastischen Zone und zugleich verhältnismäßig hoher Viskosität der erweichten Kohle.

Als letztes wurde im Zusammenhang mit der Granularverkokung noch versucht, die Veränderung der mittleren Korndurchmesser durch die Verkokung zu ermitteln, um auf diese Weise eine Erklärung für das Auftreten von unerwünschten Treiberscheinungen bei dem Verkokungsprozeß zu geben. Für diese Untersuchungen konnten nur die Siebstufen unter 1 mm herangezogen werden, da nur bei ihnen eine ausreichende Anzahl von Körnern für die statistische Auswertung zur Verfügung stand. Die diesbezüglichen Ergebnisse sind der Abb.-Nr. 6 zu entnehmen. Zu Ihrem Verständnis muß vorausgeschickt werden, daß bei der mikroskopischen Bestimmung der mittleren Korndurchmesser stets im Mittel zu kleine Werte ermittelt werden, da die Körner nur selten in der Ebene des größten Korndurchmessers geschnitten werden.

Dennoch sind die Ergebnisse brauchbar, da Ausgangsmaterial und Endprodukt mit der gleichen Methode untersucht wurden. Siebanalysen kamen nicht infrage, da einmal mit ihr kleine Verschiebungen im mittleren Korndurchmesser nicht erfaßt werden können, zum anderen war die mechanische Widerstandsfähigkeit des z.T. stark geblähten, granularverkokten Materials so gering, daß bei einer Siebung mit einer unkontrollierbaren Zerkleinerung gerechnet werden mußte. Die Abb.-Nr. 6 zeigt die Veränderungen der mittleren Korndurchmesser für 3 Siebstufen in Abhängigkeit vom Inkohlungsgrad. Wenn von der Probe mit 32,5 % Flüchtigen Bestandteilen abgesehen wird, ist für das Korn 1-0,5 mm festzustellen, daß der mittlere Korndurchmesser der verkokten Proben mit steigendem Inkohlungsgrad bis in den Bereich um 20 % Flüchtige Bestandteile deutlich zunimmt, um dann wieder abzunehmen. Bei den beiden feineren Siebstufen kann von einer deutlichen Zunahme des mittleren Korndurchmessers für die verkokten Proben nicht mehr gesprochen werden. Dieses unterschiedliche Verhalten der Siebstufen einer Flözkohle hat die gleiche Ursache wie die Porenbildung. Es wirkt sich also auch hier das Verhältnis von in der Zeiteinheit freiwerdender zu abtransportierter Gasmenge aus. Das verschiedenartige Verhalten einer Körnung, z.B. der Körnung 1-0,5 mm bei steigendem Inkohlungsgrad, ist dadurch zu erklären, daß in den verschiedenen Inkohlungsbereichen das durch die Porenbildung bedingte Blähen der Kohle in unterschiedlichem Maße durch ein ebenfalls in der plastischen Zone einsetzendes Schwinden kompensiert wird. In grober Vereinfachung kann gesagt werden, daß das Schwindvermögen einer Kohle mit steigendem Inkohlungsgrad abnimmt. Starkes Blähen, verknüpft mit einem nur geringfügigen Schwinden, führt zu Treiberscheinungen, die einen schweren Ofengang bedingen können. Die Untersuchungsbefunde führen demnach zu dem Ergebnis, daß das Treiben einer Kohle durch Zerkleinerung aufgefangen werden kann. Die mit zunehmender Kornfeinheit stets verbundene Verminderung des Schüttgewichts, die vielfach unerwünscht ist, beeinflußt den Treibdruck weniger als vielfach angenommen wurde. Es ist möglich, durch Olzugabe das Schüttgewicht einer Kohle, die zur Verminderung des Treibdrucks feiner aufgemahlen wurde, wieder auf den Ausgangswert anzuheben, ohne daß die Kohle wieder treibt.

Möglicherweise läßt sich das verminderte Schwinden einer Kohle mit steigendem Inkohlungsgrad durch die Veränderungen in der Feinstruktur in der Kohle erklären. Durch die Untersuchungen von Hirsch (8) ist bekannt, daß sich im Laufe der zweiten Phase der Inkohlung die spezifische Konzentration und auch der Ordnungsgrad der in der Kohle enthaltenen kondensierten Ringsysteme erhöht. Das bedeutet, daß mit steigendem Inkohlungsgrad der Abstand der Aromatlamellen voneinander kleiner wird. Wird nun der Abstand der Aromatlamellen voneinander dem theoretisch maximalen Schwindvermögen gleichgesetzt, so ist es verständlich, daß Kohlen mit 20 % Flüchtigen Bestandteilen schlechter schwinden als solche mit 30 % Flüchtigen Bestandteilen oder mehr. Daß bei Kohlen mit weniger als 20 % Flüchtigen Bestandteilen die Volumenzunahme der Körner der Siebstufe 1-0,5 mm bei der Granularverkokung wieder abnimmt, ist ohne weiteres so zu deuten, daß bei diesen Kohlen dem schlechten Schwinden auch ein geringfügiges Blähen gegenübersteht.

Die starke Vergrößerung des mittleren Korndurchmessers der Siebstufe 1-0,5 mm der Kohle mit 32,2 % Flüchtigen Bestandteilen läßt sich aufgrund der diskutierten Zusammenhänge nicht erklären. Da in dieser Siebstufe der Quotient R/I mit 10,1 besonders hoch liegt, scheint es nicht möglich zu sein, mit Hilfe der Mazeralzusammensetzung eine Erklärung für die starke Volumenzunahme zu finden. Die Vermutung, daß in dieser Kohle die Aromatlamellen besser als normal geordnet sind, müßte sich in einer normal hohen Reflexionsanisotropie äußern, die jedoch nicht festgestellt werden konnte. Es muß deshalb weiteren Untersuchungen vorbehalten bleiben, warum der sonst feststellbare Zusammenhang zwischen dem Inkohlungsgrad einerseits und dem Blähen andererseits, sofern gleiche Korngrößen miteinander verglichen werden, bei einigen Kohlen nicht festzustellen ist.

In der zweiten Versuchsserie wurden wiederum Flözkohlen verschiedenen Inkohlungsgrades mit einem Schüttgewicht von 0,5 in dem Versuchsverkokungsofen von Ritter und Juranek verkokt. Für diese Versuchsserie war die Einhaltung eines konstanten Schüttgewichtes erforderlich. Aus diesem Grunde war es nicht möglich, die einzelnen Sieb-

stufen getrennt zu verkoken. Es wurde vielmehr eine Mischung nachstehender Zusammensetzung eingesetzt:

Siebstufe	5 - 3 mm	20 %
"	3 - 1 mm	30 %
"	1 - 0,5 mm	30 %
"	0,5 - 0,2 mm	10 %
"	unter 0,2 mm	10 %
		100 %

Da die verkokte Probe als Ganzes angeschliffen werden kann, werden auch in dieser Versuchsserie Angaben über das unterschiedliche Verhalten der einzelnen, verschieden großen Körner möglich. Qualitativ wurden in dieser Versuchsserie die Ergebnisse aus der Granularverkokung bestätigt. Quantitativ lassen sich jedoch einige bemerkenswerte Unterschiede feststellen. Durch die deutlich größere Packungsdichte der Körner verkitten diese miteinander, da während der Porenbildung die Körner aufblähen. Durch die Verkittung sind die Körner in ihrer Ausdehnungsmöglichkeit behindert. Die Folge sind deutlich verminderte mittlere Porendurchmesser und vor allem bei den feineren Körnern auch eine verminderte Porenzahl je Korn. Diese verminderte Deformationsmöglichkeit kann sich für das Verhältnis von Blähen zu Schwinden günstig auswirken, führt aber keineswegs zu der Konsequenz, daß die bei der Granularverkokung wegen der starken Vergrößerung des mittleren Korndurchmessers in den groben Siebstufen als treibgefährlich erkannte Kohlen nun keinen Treibdruck mehr aufweisen. Direkte Messungen der Treibkraft bzw. des Treibdruckes konnten allerdings in der kleinen Versuchsapparatur nicht vorgenommen werden.

In der dritten Versuchsserie wurde nun mit einer extrem hohen Packungsdichte (Schüttgewicht etwa 1) gearbeitet. Auch in dieser Versuchsserie bestätigten sich, sofern Flözkohlen untersucht wurden, qualitativ die Ergebnisse der Granularverkokung. Quantitativ waren die Untersuchungsbefunde noch unterschiedlicher zu den Ergebnissen der ersten Versuchsreihe als zu denen der Kleinverkokung. Durch die

sehr hohe Packungsdichte der Körner verkitten diese miteinander unmittelbar nach dem Erweichungsbeginn. Die Porenbildung setzt in der Regel erst nach der Verkittung ein. Sie war wiederum in den groben Körnern stärker als in den kleinen. Der mittlere Porendurchmesser und auch die Porenzahl je Korn waren jedoch im Vergleich zu denen der ersten beiden Versuchsserien deutlich reduziert, so daß eigentlich nicht mehr von einem normalen Koksgefüge gesprochen werden konnte, insbesondere dann, wenn Kohlen geringen oder hohen Inkohlungsgrades eingesetzt wurden. Dies ist darauf zurückzuführen, daß bei einer so hohen Schüttdichte die mit einer Volumenvergrößerung verbundene Porenbildung in den Körnern nur dann möglich ist, wenn der ganze Kokskuchen deformiert wird. Dafür ist ein wesentlich höherer Gasinnendruck erforderlich als für die Deformation eines einzelnen Kornes (Granularverkokung) oder für die Deformation der Körner in relativ loser Schüttung (Kleinverkokungsofen, Schüttgewicht 0,5), bei der selbst nach dem Verkitten der Körner untereinander die Möglichkeit einer Deformation in das verhältnismäßig große Lückenvolumen verbleibt. In der Abb.-Nr. 7 sind 3 Kokse aus 3 Versuchsserien einander gegenübergestellt. Die Abbildung zeigt deutlich die Unterschiede im mittleren Porendurchmesser und der Porenzahl je Korn. Man sieht weiter, daß bei zu loser Schüttung und zu hoher Schüttung sich kein normales Koksgefüge ausbildet.

Werden nun aus den drei Versuchsserien für die Praxis verwertbare Schlußfolgerungen gezogen, so kommt man zu dem Ergebnis, daß eine zu feine Aufmahlung der Kokskohle zu einer Verminderung der Koksqualität führt, da bei gut kokenden Kohlen im Korn unter 0,2 mm, bei schlechter kokenden Kohlen schon im Korn unter 0,5 mm die zur Koksbildung unbedingt erforderliche Porenbildung stark vermindert, wenn nicht sogar unmöglich geworden ist. Zum anderen zeigten vor allem die Ergebnisse der Granularverkokung, daß ein zu hoher Anteil an grobem Korn (Korn über 3-2 mm) vor allem bei sehr gut kokenden Kohlen zu einem sehr schaumigen Koks führt, dessen Festigkeit nicht befriedigt. Auf der anderen Seite kann aus den drei Versuchsserien abgeleitet werden, daß eine hohe Packungsdichte nicht zwangsläufig

zu einer Festigkeitssteigerung der Kokse führen muß, da bei einem Schüttgewicht von etwa 1 sich wegen der zu dichten Lagerung der Körner kein gutes Koksgefüge mehr ausbilden kann.

Interessanterweise wurden ganz unabhängig von diesen Versuchsreihen von Echterhoff und Simonis (5) aufgrund von halbtechnischen Versuchsverkokungen mit Kokskohlenmischungen verschiedener Körnung und verschiedenem Schüttgewicht, als auch aufgrund theoretischer Überlegungen die gleichen Feststellungen gemacht. Hierdurch dürfte bewiesen sein, daß diese an Flözkohlen im Laboratorium erarbeiteten Ergebnisse sich für die Praxis nutzbar machen lassen und daß sie nicht nur für Flözkohlen sondern auch für Mischungen verschiedener Kohlearten miteinander verwendbar sind.

Die Ausführungen sollten zeigen, daß durch Veränderung der Kokskohlenkörnung und Veränderung der Packungsdichte Verbesserungen der Koksqualität bei gleichbleibendem rohstofflichem Verhältnis möglich sind, so daß die Meinung vertreten wird, daß diese Untersuchungsergebnisse eine wertvolle Ergänzung der Arbeiten von Amosov und Eremin (2, 3) einerseits, und Schapiro, Gray, Eusner (16) und Harrison (7) andererseits darstellt.

Zum Schluß möchte ich nicht versäumen, meinen Mitarbeitern, speziell Fräulein E.-M. Wollf, für ihre Mitarbeit zu danken. Desgleichen gilt mein Dank einigen Kollegen der Abteilung Physikalisch-Chemische Verfahrenstechnik der Bergbau-Forschung für ihre Unterstützung bei den vorliegenden Arbeiten.

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Proben	1	2	3	4	5	6
Flücht. Best. d. Einsatzkohle i. Gew.-% waf	37,1	32,2	29,9	23,7	20,6	15,1
5 - 3 mm	6,1	3,0	2,8	3,2	2,1	3,8
3 - 1 mm	7,3	3,8	3,0	5,6	3,0	4,9
1 - 0,5 mm	6,7	10,1	6,7	4,9	5,2	5,3
0,5 - 0,2 mm	5,7	4,6	4,3	4,9	5,2	9,0
0,2 mm	3,2	3,3	3,0	3,8	4,3	6,1

Abbildung-Nr. 1: Das Verhältnis R/I für die Einsatzkohlen zur Granularverkokung, aufgeteilt nach Siebstufen.

PETROGRAPHIC COMPOSITION AND THE PLASTIC PROPERTIES OF COAL

by

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Abstract*

This investigation was initiated to determine the effects of coal petrographic composition on its plastic properties as determined by dialatometric and plastometric measurements. In addition, the effects of crucible design of the Gieseler plastometer were investigated in terms of their effect on the resultant readings. The optical changes and reflectance of the semi-coke residues were determined in order to evaluate the effects of temperature on the petrographic components as the coal is being carbonized. A wide range of metallurgical coking coals were evaluated in these studies. The results show that: (1) Modifications of the Gieseler crucible and testing procedures improved the results of the tests; (2) The petrographic composition of the coal correlates well with the plastic properties as determined by the modified techniques; (3) Normal ASTM Gieseler data do not measure the actual plastic properties of coals or coal blends; (4) Heating rate drastically affects the behavior of the petrographic entities during plasticity tests; and (5) Petrographic and reflectance studies of the semi-coke residues proved to be useful in explaining certain phenomena taking place during carbonization.

* Complete manuscript not received in time for inclusion in Divisional Preprints. Single copies of the complete paper will be available at the Sessions in New York for those who desire one. Others may write the authors for a copy.

MECHANICAL AND RELATED PROPERTIES OF SOME EASTERN COALS

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In the mining, preparation, handling, and utilization of coal, the mechanical characteristics of the coal influence both its breakage and the operation of the equipment used. Numerous methods have been developed to measure the hardness, strength, and grindability properties of coal.[1,2,3]* One of these methods, the Hardgrove grindability test, has been widely used to determine the relative ease of grinding coals. This grindability index measures the hardness, strength, and fracture characteristics of coal.[1,4] Further evidence that this empirical index measures a physical coal property was proposed by Brown.[5] Consequently, the Applied Research Laboratory of U. S. Steel determined the Hardgrove grindability indexes of channel samples from mines in the Pittsburgh seam in the Pocahontas seam, and in eastern Kentucky seams (High Splint seam, Winifrede seam, and C seam). These data were obtained to provide information for the selection of face equipment in mining and of facilities for the preparation of coal. In addition, the relative abrasiveness, microtumbler strength,** and Brabender hardness (power required in grinding) of each coal were determined, because these characteristics should also have an important bearing on the selection of equipment.

This paper presents the data obtained from the four types of tests; the results of each test are related to the chemical and petrographic properties of the coals and also compared with one another. In addition, the paper presents a brief discussion of the application of mechanical properties to the coal industry.

The sources of the coal samples used in this investigation are listed in Table I. All samples were full-length channel samples. The Mine No. A, B, C, and D samples from the Pittsburgh seam represent four channel samples that were blended without crushing. The other channel samples were treated as single samples. The samples, which weighed about 200 pounds each, were processed by the method shown schematically in Figure 1. All samples were air-dried to about 1 percent moisture content. The proximate and sulfur analyses, listed in Table II, were determined by ASTM procedures. The petrographic analyses, Table III, were conducted according to the standard method developed by U. S. Steel.[6]

The Hardgrove grindability test was conducted according to ASTM standard D409-51. The Hardgrove apparatus has eight 1-inch balls that roll on a stationary ring and are driven by a rotating ring above. The index represents the weight of material passing 200-mesh sieve after 60 revolutions in the machine. The reproducibility of the index obtained on a sample should check within 2 percent.

The Brabender hardness test was conducted in the Brabender Plastograph adapted for operation as the hardness tester.[7,8] This instrument has a cone mill and an electrodynameter to rotate the grinding element. A 200-gram sample of minus 4 mesh or 16- by 30-mesh coal was fed into the crusher. The power required by the crusher in grinding the coal was recorded in respect to time by the electrodynameter

* See references.
** Also known as microstrength index.

in the form of a diagram. The area drawn in this diagram is used as the hardness index, which is expressed in kilogrammeters. The standard deviation for the entire range was found to be ± 6.5 index points.

The microtumbler test (resistance to degradation by abrasion and impact) was conducted in an apparatus consisting of 2 stainless steel tubes, 1 inch in internal diameter and 12 inches long.[9] The two tubes are mounted on a frame that can be rotated at a constant speed. Duplicate 2-gram samples of 14- by 28-mesh coal were placed in the tubes with twelve 5/16-inch diameter steel balls and tumbled for 800 revolutions. The breakage was then determined by a sieve analysis and the amount of plus 100-mesh material was recorded as the microtumbler strength. In this test using coal, the standard deviation was ± 1.3 index points.

The abrasion test was conducted on an apparatus consisting of a mortar that holds the charge of coal, a shaft, an arm assembly to hold the wearing blades, and a drill press to provide rotation.[10] The test consists of rotating the four removable blades at 1500 rpm for 12,000 revolutions in a 4-kilogram sample of minus 4-mesh air-dried coal. After each test the wearing blades are thoroughly cleaned and weighed. The weight loss sustained by the blades in milligrams is used as the index of abrasion. The standard deviation was ± 1.7 index points over the range tested.

Mechanical Tests

The results obtained from each of the four tests used to measure the mechanical properties of the coal are presented in Table IV and compared with one another in the following discussion.

In the Hardgrove grindability test the Pittsburgh-seam coals showed indexes from 59 to 63, the eastern Kentucky coals from 41 to 51, and the Pocahontas-seam coals from 90 to 105. Note that the lower the index, the more difficult it is to grind the coal. These data are in good agreement with those reported by the Bureau of Mines.[11]

The Brabender hardness test gives a measure of the power requirement in grinding the coals; thus, the index represents the work done in grinding the sample. The higher the number the more power is required to grind the sample. As expected, an inverse relationship exists between the Brabender hardness index and the Hardgrove grindability index (Figure 2, Table IV). The correlation with the values obtained from the minus 4-mesh coal was much better than with those from the 16- by 30-mesh coal, even though the Hardgrove grindability test requires 16- by 30-mesh coal. This test showed the differences among the coals from three different locations, as well as considerable variability within each location (Figure 2). This variability may be significant since the extreme values ranged more than would be expected by the standard deviation.

Since the microtumbler strengths of coal indicate the resistance to degradation by abrasion and impact, the natures of this test and the Hardgrove test are very similar. This similarity is clearly shown in the excellent correlation obtained between the results of these two tests (Figure 3). Hence, this test can be used to calculate the Hardgrove grindability index, or vice versa.

The results of the abrasion test are also presented in Table IV. Comparison with the previous work[10] is limited since that investigation included only one coal,

a Pittsburgh-seam coal, in common with the present study. However, the indexes for coking coals were similar. The relationship between the index of abrasion and grindability is shown in Figure 4. From this relationship, these tests must be measuring different properties of the sample. The comparison of these results will be discussed further hereafter.

Factors Affecting the Hardness, Abrasion, and Grindability of Coal

Because of the similarity of the Hardgrove grindability, Brabender hardness, and microtumbler-strength tests, only the results relating the grindability index with the chemical and petrographic analyses of the coals are presented. The relationships of the index of abrasion and the chemical and petrographic analyses are discussed separately.

Hardgrove Grindability

Figure 5 shows the relationship of coal rank (expressed by volatile-matter content) to the grindability index. Confirming published data,[1,4] the index increased as the volatile-matter content decreased. The trend is then reversed with coals having volatile-matter contents of less than 23 percent. Since the average reflectance of the vitrinoids correlate with the volatile-matter content,[6] a similar relationship was obtained in Figure 6 between the average reflectance and the grindability index. This relationship of rank and grindability index may be associated with the porosity[12,13] and elastic properties[13,14] of the various rank coals.

The effect of ash content on grindability is shown in Figure 7. The low-volatile coals tended to become more difficult to grind when the ash content increased. However, ash content had no apparent effect on the grindability of the high-volatile coals. The low-volatile coals are much softer or more friable than the high-volatile coals and relatively easy to grind; therefore, an increase in hard ash material would make the low-volatile coals harder to grind. In contrast, a higher percentage of ash in the high-volatile coals would have little influence on the grindability, since the coal substance is apparently harder than the ash. Other investigators reported that additions of ash to coals having indexes from 60 to 110 tended to increase or decrease the index to 75.[15] However, ash content per se does not exert a primary effect on the resistance to grinding, because the type of mineral matter is the main determining factor.

The effect of petrographic constituents on the hardness or strength of coal has been known for some time.[1,2] In a more recent investigation Harrison discussed the effects of petrographic composition in the breakage of coal.[16] At the ARL,[17] the total tough coal was related with the microtumbler strength, which has been shown to correlate well with the grindability index. Therefore, the summation of the micrinoids, resinoids, and exinoids (previously termed total tough coal) was correlated with the Hardgrove grindability indexes. The relationship is shown in Figure 8. A good correlation was obtained with the high-volatile coals from the Pittsburgh seam and eastern Kentucky, where the grindability index decreased as the amount of micrinoids, exinoids, and resinoids increased. In the low-volatile coal samples from the Pocahontas seam, the grindability index increased as these macerals increased. An examination of the data of these low-volatile coals (Tables II and III) indicates that those samples with the least amount of micrinoids, exinoids, and resinoids are associated with the highest rank (Figure 5) and highest ash contents (Figure 7) of these low-volatile coals; whereas those with the greatest

amount of micrinoids, exinoids, and resinoids are associated with the lowest rank (Figure 5) and lowest ash contents (Figure 7). Therefore, the correlation obtained for the high-rank coals is doubtful, particularly when the small range (approximately 8 to 14 percent) of the amounts of these entities are considered.

Index of Abrasion

The test results indicated that the rank or the petrographic composition of the coal did not show significant relationships with the index of abrasion, the ash or foreign material in the coal being mainly responsible for the abrasion. The relationship of ash content and index of abrasion is shown in Figure 9. Other investigators have reported similar conclusions.[1,10] However, the difference at the same ash content level for coal of similar characteristics are significant, as indicated by the standard deviation of the test. Additional studies are required to determine the causes for this variation.

Referring to Figure 4, the relationship of these two indexes can most likely be associated with rank for the grindability index and ash content or mineral matter for the index of abrasion. For example, the eastern Kentucky samples possessed the lowest grindability index with the highest volatile matter and tough coal, while the index of abrasion of these samples was low because of their very low ash contents.

Application of Mechanical Properties

At the ARL the power required by a mining machine to rip coal was qualitatively related to petrographic properties of the Pittsburgh-seam coal and microtumbler strength.[17,18] Because of the excellent correlation between the grindability index and the microtumbler strength, the Hardgrove grindability index should also show the power required for mining coal with a continuous miner. Since the petrographic analyses showed only a good relationship with the grindability index of high-volatile A coals, additional studies would be required on higher rank coals to determine the influence that their petrographic composition has on the strength of coal or the power requirements for mining this type of coal.

It is interesting to note that the British have been studying the rheological behavior of coal to provide basic data in the design of coal-winning machinery. Some fundamental studies have related coal plowing force,[19] dust formation,[20] and the penetration resistance to a wedge[21] to the strength properties of the coal. Evans came to the conclusion that friable coal fails in shear and hard coal fails in tension. His results indicate that blades should be kept very sharp to efficiently plow hard coal, sharp blades not being so necessary for friable coals.[22] In another study, the friction between coal and metal surfaces was found to be influenced by the rank of coal.[23] The relationship to rank was similar to that obtained with heat of wetting, Knoop hardness, compressive strength, tensile strength in bending and impact strength. Brown and Hiorns have summarized this British work.[2]

This investigation as well as others[24] indicate that the basic information on the strength properties should be useful in the design, selection, and operation of equipment used in the mining, preparation, handling, and utilization of coal. Of particular interest in the last-named field has been the study of the breakage or comminution of coal.[2,5]

Summary

The test results showed that the Hardgrove grindability indexes of the low-volatile coals from the Pocahontas seam were from 90 to 105, those of the high-volatile coals from the Pittsburgh seam from 59 to 63, and those of the coals of eastern Kentucky from 41 to 51. The Brabender hardness indexes and the microtumbler strengths of these coals correlated with the grindability indexes. However, the Brabender hardness index did show considerable variability between samples from the same seam or location. The index of abrasion appeared to measure different properties of the samples and did not show a significant relationship with the other indexes.

The rank of the coal influenced the grindability index as shown in the published data. The index increased as rank decreased; but the trend was reversed with coals having volatile-matter contents (dry ash-free basis) of less than 23 percent. The ash content appeared to decrease the index of the low-volatile coals but did not have an effect on the index of high-volatile coals. In contrast, the amount of micrinoids, exinoids, and resinoids correlated well with the grindability index of these high-volatile coals, but their influence on the index of low-volatile coal is doubtful.

In the index of abrasion, the coal substance apparently contributed little to the abrasion, the ash or foreign material in the coal being mainly responsible for the abrasion.

Previous work at the ARL had shown qualitatively that the petrographic composition and microtumbler strength could be related to the power required by a continuous miner. In this investigation the grindability index has been correlated with both microtumbler strength and petrographic composition, so that this index could also be used. Additional study would be necessary for relating the indexes of high-rank coals to actual practice in the mine.

These results and those of other investigators have indicated that basic information on the mechanical properties of coal should be useful in the design, selection, and operation of equipment in the mining, preparation, handling, and utilization of coal.

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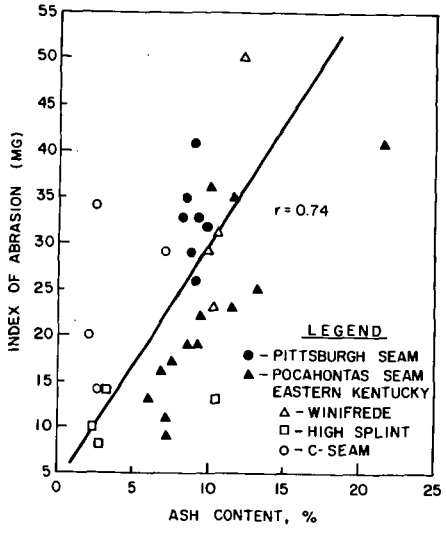

Figure 9. Effect of Ash on the Index of Abrasion

Table I

Channel Sample Identification

Seam	Code Mine	Code Section	County, State
Pittsburgh	A	Composite of 4 channel samples	Greene, Pa.
Pittsburgh	B	Composite of 4 channel samples	Greene, Pa.
Pittsburgh	C	Composite of 4 channel samples	Greene, Pa.
Pittsburgh	D	Composite of 4 channel samples	Washington, Pa.
Pittsburgh	E	1	Washington, Pa.
Pittsburgh	E	2	Washington, Pa.
Pittsburgh	E	3	Washington, Pa.
Pittsburgh	E	4	Washington, Pa.
Eastern Kentucky			
C Seam	F	1	Harlan, Ky.
C Seam	F	2	Harlan, Ky.
C Seam	F	3	Harlan, Ky.
C Seam	F	4	Harlan, Ky.
High Splint	G	1	Harlan, Ky.
High Splint	G	2	Harlan, Ky.
High Splint	G	3	Harlan, Ky.
High Splint	G	4	Harlan, Ky.
Winifrede	H	1	Harlan, Ky.
Winifrede	H	2	Harlan, Ky.
Winifrede	H	3	Harlan, Ky.
Winifrede	H	4	Harlan, Ky.
Pocahontas No. 3	I	1	McDowell, W. Va.
Pocahontas No. 3	I	2	McDowell, W. Va.
Pocahontas No. 3	I	3	McDowell, W. Va.
Pocahontas No. 3	I	4	McDowell, W. Va.
Pocahontas No. 3	J	1	McDowell, W. Va.
Pocahontas No. 3	J	2	McDowell, W. Va.
Pocahontas No. 4	K	1	McDowell, W. Va.
Pocahontas No. 4	K	2	McDowell, W. Va.
Pocahontas No. 4	K	3	McDowell, W. Va.
Pocahontas No. 4	K	4	McDowell, W. Va.
Pocahontas No. 3	L	1	McDowell, W. Va.
Pocahontas No. 3	L	2	McDowell, W. Va.
Pocahontas No. 3	L	3	McDowell, W. Va.
Pocahontas No. 3	L	4	McDowell, W. Va.

Table II

Proximate Analysis of Mine Channel Samples

Seam	Mine Code & Section	Proximate Analysis*, percent (minus 4 mesh) VM	VM, (daf) basis	FC	Ash	Sulfur, percent	Proximate Analysis, percent (16 by 30 mesh) VM	VM, (daf) basis	FC	Ash	Sulfur, percent
Pittsburgh	A	36.6	40.5	53.7	9.7	2.47	36.8	40.5	54.1	9.1	2.10
Pittsburgh	B	36.3	39.8	54.8	8.9	2.52	36.7	40.0	55.1	8.1	2.00
Pittsburgh	C	36.4	39.7	55.4	8.2	2.31	37.1	40.4	54.7	8.2	2.26
Pittsburgh	D	29.3	38.8	46.2	24.5	1.29	30.1	39.6	45.8	24.1	1.11
Pittsburgh	E-1	34.9	38.4	56.0	9.1	0.98	35.0	38.1	56.9	8.1	0.95
Pittsburgh	E-2	36.4	40.2	54.2	9.3	1.82	35.8	38.8	56.4	7.8	1.43
Pittsburgh	E-3	34.4	37.6	57.2	8.4	1.14	34.3	37.4	57.5	8.2	1.02
Pittsburgh	E-4	34.4	37.8	56.7	8.8	1.73	35.0	38.0	57.1	8.9	1.62
Eastern Kentucky											
C Seam	F-1	35.0	37.6	58.0	7.0	0.53	34.8	37.5	58.0	7.2	0.50
C Seam	F-2	36.3	37.1	61.6	2.0	0.43	36.6	37.3	61.5	1.9	0.41
C Seam	F-3	37.2	38.2	60.1	2.7	0.48	37.3	38.3	60.2	2.5	0.46
C Seam	F-4	36.1	37.0	61.5	2.4	0.44	36.6	37.3	61.4	2.0	0.40
High Splint	G-1	36.5	37.7	60.3	3.2	0.50	37.6	38.8	59.3	3.2	0.51
High Splint	G-2	35.0	39.1	54.6	10.4	0.56	36.2	40.3	53.7	10.1	0.54
High Splint	G-3	37.8	38.7	59.8	2.4	0.46	38.6	39.5	59.1	2.3	0.47
High Splint	G-4	38.5	39.6	58.7	2.8	0.50	39.0	40.1	58.2	2.8	0.50
Winifrede	H-1	34.1	38.1	55.4	10.5	2.32	34.5	38.3	55.5	10.0	1.78
Winifrede	H-2	34.6	39.4	53.3	12.1	1.81	34.8	39.3	53.7	11.5	1.65
Winifrede	H-3	35.4	39.4	54.4	10.2	1.07	35.9	39.8	54.3	9.8	0.99
Winifrede	H-4	36.1	40.0	54.1	9.8	1.69	36.7	40.5	53.9	9.4	1.60
Pocahontas No 3	I-1	15.9	17.2	76.5	7.6	0.67	15.7	17.0	76.6	7.7	0.64
Pocahontas No. 3	I-2	15.4	16.5	77.7	6.9	0.60	15.6	16.8	77.4	6.9	0.61
Pocahontas No. 3	I-3	15.0	17.0	73.4	11.6	0.68	14.8	16.6	74.2	11.0	0.63
Pocahontas No. 3	I-4	14.7	16.9	72.1	13.2	0.89	14.4	16.6	72.1	13.5	0.89
Pocahontas No. 3	J-1	17.1	18.4	75.7	7.2	0.61	17.1	18.5	75.2	7.7	0.58
Pocahontas No. 3	J-2	17.2	19.4	71.3	11.5	0.52	16.6	18.8	71.6	11.8	0.51
Pocahontas No. 4	K-1	15.2	17.8	70.1	14.7	1.23					
Pocahontas No. 4	K-2	15.0	16.6	75.6	9.4	0.61					
Pocahontas No. 4	K-3	15.2	16.9	74.8	10.0	0.82					
Pocahontas No. 4	K-4	14.1	18.0	64.4	21.5	0.69					
Pocahontas No. 3	L-1	19.0	20.8	72.4	8.6	0.51					
Pocahontas No. 3	L-2	20.0	21.3	74.0	6.0	0.56					
Pocahontas No. 3	L-3	21.4	23.6	69.2	9.3	0.58					
Pocahontas No. 3	L-4	20.5	22.1	72.4	7.2	0.57					

* VM - volatile matter FC = fixed carbon

Table III

Petrographic Analysis* of Mine Channel Samples

Seam	Code Mine & Section	Vitrinoid Type 7	8	9	10	11	12	13	14	15	16	17	18	19	SFR	SFI	F	Tough Coal M	E	R	Total	MM
Pittsburgh	A	7.0	46.2	16.8											0.6	1.2	6.3	9.3	5.5	1.0	15.8	6.1
Pittsburgh	B	5.1	34.7	31.1	1.4										1.2	2.5	5.5	7.2	4.9	0.8	12.9	5.6
Pittsburgh	C	0.7	38.7	29.7											1.3	2.7	6.5	9.8	5.1	0.4	15.3	5.1
Pittsburgh	D		26.4	36.3	0.7	1.3	0.7	0.7							1.1	2.2	4.4	5.8	4.4	0.8	11.0	15.2
Pittsburgh	E-1		20.9	45.5	5.0										0.9	1.7	5.6	8.8	5.8	0.8	15.4	5.3
Pittsburgh	E-2		35.8	34.4											1.2	2.3	4.6	10.7	5.3	-	16.0	5.7
Pittsburgh	E-3	0.7	23.0	42.4	3.5										1.2	2.3	5.4	11.1	5.1	0.4	16.6	4.9
Pittsburgh	E-4		15.2	56.6	0.7										0.8	1.7	3.9	9.8	5.1	0.8	15.7	5.4
Eastern Kentucky																						
C Seam	F-1		1.3	34.9	27.3										1.3	2.5	6.7	12.6	8.6	0.7	21.9	4.1
C Seam	F-2		2.7	28.0	35.4	0.7									1.3	2.5	5.0	14.6	8.0	0.6	23.2	1.2
C Seam	F-3		1.9	24.6	38.1										1.2	2.4	6.0	15.5	8.0	0.8	24.3	1.5
C Seam	F-4		0.6	27.7	36.1										0.9	1.5	6.8	16.2	8.2	0.4	24.8	1.4
High Splint	G-1	3.6	25.0	22.4											2.9	5.8	7.1	22.7	8.3	0.4	31.4	1.8
High Splint	G-2	14.3	24.4	11.7	0.5										3.0	6.0	6.7	18.0	8.8	0.7	27.5	5.9
High Splint	G-3	0.9	18.3	26.5											3.8	7.6	5.3	23.3	11.4	1.5	36.2	1.4
High Splint	G-4	11.9	26.4	15.6											2.1	4.1	7.0	21.8	8.2	1.3	31.3	1.6
Winifrede	H-1	0.6	24.0	32.7											2.7	5.5	4.6	14.7	7.5	1.2	23.4	6.5
Winifrede	H-2	1.0	25.9	24.3	0.5										2.3	4.7	7.1	17.0	8.3	1.3	26.6	7.6
Winifrede	H-3		28.8	25.4	3.5										2.1	4.2	6.0	16.4	6.3	1.4	24.1	5.9
Winifrede	H-4	0.5	27.7	24.5											2.0	3.9	6.6	19.9	8.2	1.3	29.4	5.9
Pocahontas No. 3	I-1											38.0	32.3		-	5.5	8.2	11.7	-	-	11.7	4.3
Pocahontas No. 3	I-2										0.7	42.5	25.8	0.7	-	6.0	9.8	10.2	0.4	-	10.6	3.9
Pocahontas No. 3	I-3											33.3	31.3	3.4	-	7.3	8.3	9.7	0.1	-	9.8	6.6
Pocahontas No. 3	I-4											21.5	41.0	7.0	-	5.7	9.2	7.5	0.4	-	7.9	7.7
Pocahontas No. 3	J-1										42.5	30.7			1.3	5.4	6.2	9.7	0.1	-	9.8	4.1
Pocahontas No. 3	J-2									21.5	42.4	5.6			-	7.6	6.5	9.5	0.4	-	9.9	6.5
Pocahontas No. 4	K-1								0.7	1.4	6.4	24.1	31.9	6.4	0.9	3.7	6.2	9.3	0.3	-	9.6	8.7
Pocahontas No. 4	K-2											18.7	33.5	14.7	-	5.9	9.3	12.4	0.2	-	12.6	5.3
Pocahontas No. 4	K-3										0.7	24.7	36.5	6.9	-	6.5	6.4	12.5	0.1	-	12.6	5.7
Pocahontas No. 4	K-4										15.1	32.3	18.4		0.9	3.7	5.6	10.9	0.1	-	11.0	13.0
Pocahontas No. 3	L-1								33.7	33.0	3.5				1.2	4.6	5.2	13.3	0.6	-	13.9	4.9
Pocahontas No. 3	L-2							1.4	35.5	30.8	0.7				1.2	4.7	8.2	13.2	0.6	-	13.8	3.7
Pocahontas No. 3	L-3							8.4	52.9	8.4					1.8	7.0	3.4	12.8	-	-	12.8	5.3
Pocahontas No. 3	L-4							1.5	45.1	26.2					0.7	3.0	5.8	13.2	0.4	-	13.6	4.1

* M = micrinoids
E = exinoids
R = resinoids

SFR = semifusinoids, reactive
SFI = semifusinoids, inert
F = fusinoids
MM = mineral matter

Table IV

Comparison of Various Methods to Determine Hardness and Grinding Properties of Coal

Seam	Code Mine & Section	Hardgrove Grindability Index	Brabender Hardness Index Minus 4 Mesh	Brabender Hardness Index 16 by 28 Mesh	Microstrength Index	Index of Abrasion
Pittsburgh	A	63.5	98.1	145.9	37.8	32
Pittsburgh	B	60.1	77.6	145.0	39.5	41
Pittsburgh	C	62.0	87.6	131.1	--	33
Pittsburgh	D	60.8	84.9	52.4	44.5	99
Pittsburgh	E-1	59.4	108.5	141.7	--	26
Pittsburgh	E-2	60.3	101.1	50.3	41.0	33
Pittsburgh	E-3	60.3	91.2	127.8	--	35
Pittsburgh	E-4	60.9	109.7	139.1	38.7	29
Eastern Kentucky						
C Seam	F-1	50.9	125.4	144.0	39.4	29
C Seam	F-2	49.5	129.9	145.1	--	20
C Seam	F-3	50.8	139.9	125.5	--	14
C Seam	F-4	52.3	97.0	132.5	44.3	34
High Splint	G-1	43.2	127.8	114.0	--	14
High Splint	G-2	42.2	94.7	124.3	49.9	13
High Splint	G-3	41.6	108.3	111.8	--	10
High Splint	G-4	42.9	97.0	116.2	47.1	8
Winifrede	H-1	46.5	126.7	102.7	48.4	31
Winifrede	H-2	45.1	108.4	126.6	--	50
Winifrede	H-3	44.9	129.1	139.3	49.1	23
Winifrede	H-4	45.3	163.4	141.5	--	29
Pocahontas No. 3	I-1	98.4	70.1	138.0	11.1	17
Pocahontas No. 3	I-2	95.1	64.3	129.8	--	16
Pocahontas No. 3	I-3	91.3	65.2	110.5	--	35
Pocahontas No. 3	I-4	89.9	77.1	93.6	13.7	25
Pocahontas No. 3	J-1	97.6	52.5	139.3	--	9
Pocahontas No. 3	J-2	101.1	86.1	151.6	10.8	23
Pocahontas No. 4	K-1	93.4	42.7	89.0	18.5	--
Pocahontas No. 4	K-2	100.3	40.5	102.7	--	22
Pocahontas No. 4	K-3	93.2	28.4	98.1	13.3	36
Pocahontas No. 4	K-4	94.2	54.2	102.5	--	41
Pocahontas No. 3	L-1	104.1	33.6	75.2	--	19
Pocahontas No. 3	L-2	102.2	29.6	78.7	8.7	13
Pocahontas No. 3	L-3	102.1	48.6	77.8	--	19
Pocahontas No. 3	L-4	105.2	32.0	80.0	8.6	11

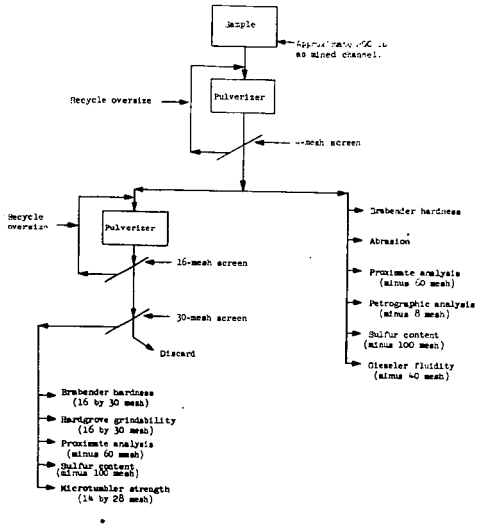

Figure 1. Sampling Procedure

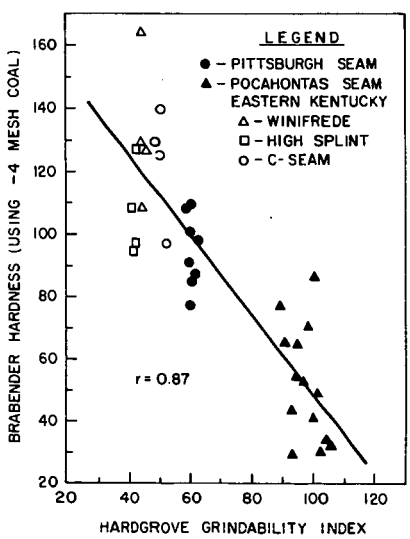

Figure 2. Relationship of Brabender Hardness and Hardgrove Grindability Index

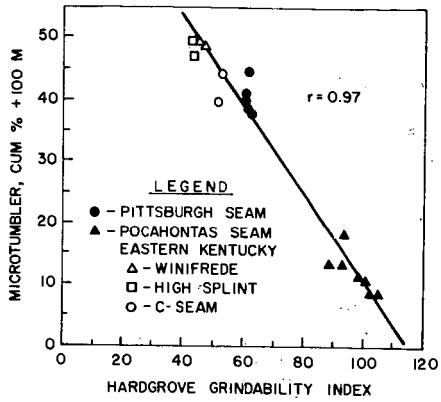

Figure 3. Relationship of Microtumbler Strength and Hardgrove Grindability Index

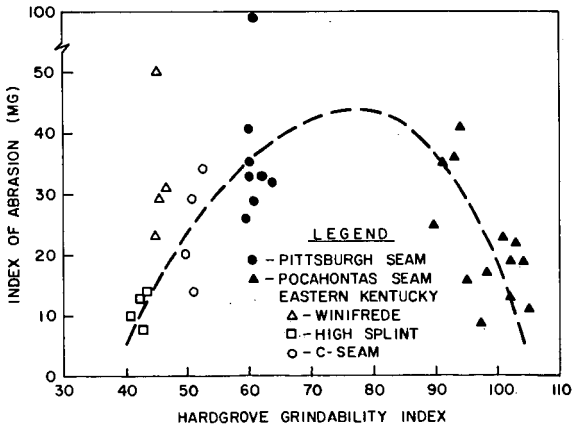

Figure 4. Relationship of Index of Abrasion and Hardgrove Grindability Index

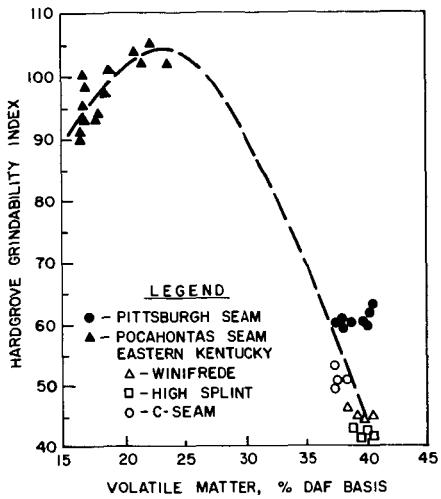

Figure 5. Relationship Between Hardgrove Grindability and Coal Rank

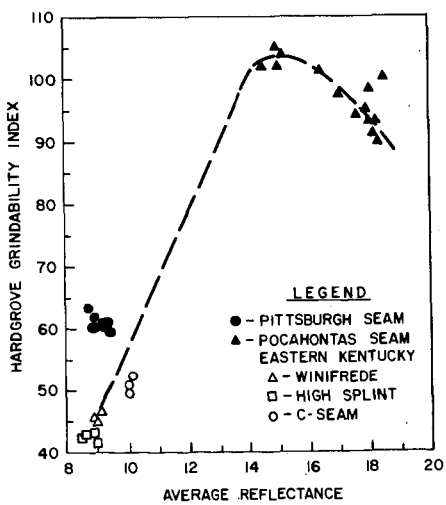

Figure 6. Relationship Between Hardgrove Grindability Index and Rank

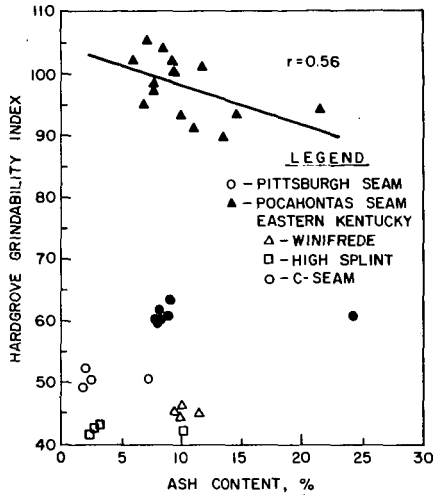

Figure 7. Effect of Ash on Hardgrove Grindability Index

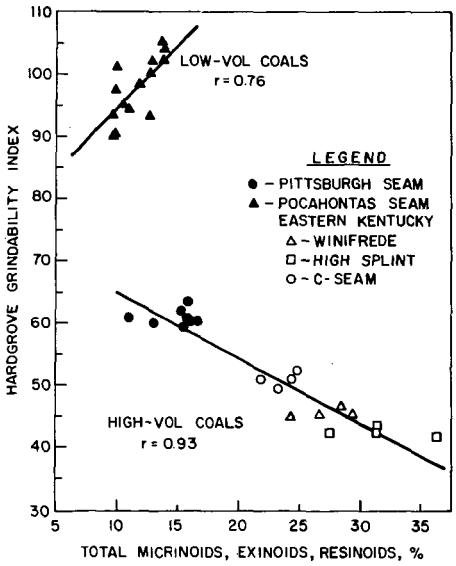

Figure 8. Effect of Petrographic Composition on the Hardgrove Grindability Index

EFFECT OF IGNEOUS INTRUSIVES ON THE CHEMICAL, PHYSICAL, AND OPTICAL PROPERTIES OF SOMERSET COAL

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Introduction

Examination of exploratory drill cores taken from a limited area near Somerset, Colorado, disclosed some coal beds associated with sills, or horizontal bodies, of monzonite and diorite rock. These sills, or igneous intrusions, were formed when the rock, in a molten state, invaded the coal-bearing strata. The coals range in rank from high-volatile bituminous through anthracite to natural coke. The material transformation of coal to coke produces chemical, physical, and petrographic changes. This investigation was conducted to determine to what extent variations in the chemical, physical, and petrographic data can be used to assess the deleterious effect of the intrusives on the coking quality of the coal.

Materials and Experimental Work

Samples of coals and natural coke were selected from three 6-inch cores from exploratory diamond-drill holes near Somerset, Colorado. A map of the Somerset area of Delta County, Colorado, Figure 1, shows the location of the holes from which the cores were obtained. The B-1 coal was sampled from holes 1 and 2, the B-2 and C coals were sampled from hole 3. A thin coal between the B-1 and A coals was sampled in hole 1. The 35 core segments sampled were chosen to include similar material and to accent major changes in the coal seams.

Proximate and ultimate chemical analyses and reflectance, and resistivity measurements were performed for each sample. Since these chemical and physical properties of coal change by thermal treatment, these properties are used as indications of the degree of thermal metamorphism. Ordinarily, chemical data alone should suffice to indicate the degree of thermal alteration; however, the coal samples frequently proved to be of high ash yield and not suitable for routine coal-chemical tests.

To relate the temperature involved in the thermal alteration of coal by igneous intrusions, samples of unaltered coal from the seams were thermally treated in the laboratory. Ten 15-gram samples of minus 8-mesh Somerset coal were carbonized in covered crucibles in an electric box furnace at a heating rate of 5.4 F per minute to predetermined temperatures ranging from 212 F to 1832 F. A portion of each carbonized sample was then analyzed for reflectance, resistivity, and hydrogen content.

The following analytical procedures were followed in analyzing both the drill-core and laboratory-carbonized samples. The average reflectance in oil was based on 50 reflectance determinations per sample. The resistivity values were

determined for half-gram, minus 65-mesh samples dried for 24 hours at 212 F and tested at 20,000 psi. All chemical data were determined by standard laboratory procedures.

Equations were developed and correlation coefficients were determined for the relationships of temperature with reflectance, resistivity, and hydrogen content of the coals, Table I.

Results and Discussion

When coal and/or associated rocks in place in the earth are invaded by molten rock, the resulting alteration of the coal is similar to the thermal alteration produced in commercial carbonization processes. For this reason chemical and physical changes produced in laboratory-carbonized coals can be compared with similar changes in coals that have been thermally altered by igneous intrusions. In addition, the thickness of the intrusion and its distance from the coal seam have been related to the degree of coal alteration so that the damage sustained by the coal or coals can be approximated with a minimum of analytical test data.

In the following discussion the physical and chemical properties of the drill-core samples are compared with those of coals carbonized in the Laboratory at various temperatures. Following this, the relation of the degree of coal alteration to the source of heat is discussed.

Physical and Chemical Changes in Thermally Altered Coal

The optical reflectance, electrical resistivity, and hydrogen content were determined for Somerset high-volatile coal carbonized at different temperatures in the laboratory. The reflectance increases and the resistivity and the hydrogen content decrease as the carbonization temperature increases, as shown in Figure 2. The Somerset high-volatile rank coal, which has not been altered thermally, has a reflectance of about 0.7 percent, a resistivity of about 4.2×10^{11} ohm-cm, and a hydrogen content of about 5.9 percent. When coal has been altered to a reflectance greater than 2.0 percent, a resistivity of 6.5×10^{7} or more, and a hydrogen content of less than 4.0 percent, it can be considered as non-coking. In the laboratory samples the variations in the reflectance, resistivity properties, and hydrogen content have been related to the temperature of carbonization because temperature was the variable in the sample preparation. The correlation coefficients for the relation of temperature to both reflectance and hydrogen is $R^2 = 0.99$ and for the temperature-to-hydrogen relation is $R^2 = 0.96$. The reflectance, resistivity, and hydrogen measurements on the drill specimens from the cores were used to estimate the temperature to which the coal had previously been heated, Figure 3. Equations expressing the relationships of temperature with reflectance, resistivity, and hydrogen content, Table I, developed for coal carbonized in the laboratory were used in calculating temperature involved in the thermal altering of the coal and coke in the core samples. The core samples range from virtually unaltered coal to coke that has been thermally altered at a maximum temperature of not less than 1580 F or more than 2200 F. Indirectly determined temperatures in and near intrusions[1)*] and directly determined temperatures for lava[2)] are within this range. It appears that coal may be used as a maximal geothermometer. However, the temperatures calculated from reflectance are higher than those calculated from resistivity and these in turn are higher than those calculated from the hydrogen content, Figure 3.

* See references.

Part of this discrepancy is due to the large percentage of ash-forming materials, which affect the resistivity and hydrogen measurements. Reflectance is considered as the most accurate indicator of rank changes resulting from thermal alteration since it is not affected by ash-forming minerals in the samples. However, when coals of different rank are carbonized under the same conditions, the highest-rank coal will produce coke with the highest reflectance. In this study, the coal carbonized in the laboratory is the same rank as the unaltered coal recovered in the drill core.

The visible changes that occur in the transformation of coal to coke are shown in Figure 4. The reflectance, resistivity, and hydrogen data are also shown to associate these changes with the visible changes in the coal and coke structure. The photomicrographs shown in Figure 5 illustrate altered and unaltered coal in a single sample of coal, pyrolytic carbon (carbon from cracked hydrocarbon gases) and mineral matter intruded into the coal.

Relation of the Thermal Alteration of Coal
To the Position and Thickness of the Intrusive

The changes in reflectance, hydrogen and volatile-matter content with distance from the intrusions in the samples taken from different depths in the four drill holes are shown in Figures 6, 7, 8, and 9. In hole 1, B-1 seam (Figure 6) is intruded near the top by two sills of nearly equal thickness for a total of 1.5 feet. The heat from the sills was sufficient to bring 8.0 feet of the 14-foot seam to a reflectance of 2 percent or more. In the middle of the coal column the reflectance drops abruptly (in only 0.8 foot) from more than 5 to less than 2 percent. The base of the seam, consisting of about 6.0 feet of coal, was only slightly altered by metamorphism and can be considered as coking coal.

In hole 3, B-2 seam (Figure 7) is in contact near the top with an 8.5-foot sill overlaid by 2.8 feet of shale and 3.7 feet of coke, which is in turn overlaid by 11.2 feet of intrusive rock. In this coal column, the entire 7.8 feet of coal has coked completely. The reflectance decreases as the distance from the sill increases.

In hole 3, C-seam (Figure 8) is thermally metamorphosed in the bottom third of an 11.6-foot coal column. Comparison of the sample intervals with the driller's log shows that 1.2 feet is unaccounted for at the base of the column. It was assumed that the intrusive occurs in this position. Approximately 3.6 feet of the basal portion of the column exceeds 2 percent reflectance. The remaining 8.0 feet of coal is only slightly altered and should be considered coking coal. The reflectance drops from 5 to less than 2 percent in an interval of about 2.0 feet. Thus the change from coke to coal is abrupt.

In hole 2, B-1 seam (Figure 9) is not in direct contact with an intrusion but is separated from an overlaying sill by 38.6 feet of shale. The intrusion totals 26.9 feet; however, a 7.5-foot unit of natural coke splits the sills and only 15.9 feet of sill was considered effective in the thermal metamorphism of the coal. The entire 11.4-foot column has been altered to anthracite and is non-coking. There are virtually no vesicles developed in this coal. This coal has probably been subjected to less rapid heating or greater pressures than the coals in which the coke structure developed.

The graphic presentations show that intense changes in a coal by contact with intrusions extend only a short distance from the contact. However, the amount of coal alteration, while undoubtedly related to the temperature of the intrusion, is also related to the thickness of the intrusion and its distance from the coal. Blignault,[3] in his investigation of the dolerite intrusions in the Natal Coalfields, found that as the ratio of the distance (D) from the coal to the thickness of the intrusive (T) decreases, the volatile matter (daf)* of the coal decreases from the unaltered coal. For these relationships to hold true, the intrusive temperature must have been nearly constant. Data from the present investigation were used to test the applicability of Blignault's findings, but reflectance was used as the rank parameter in preference to volatile matter.

The relation of D/T to the reflectance is shown in Figure 10. Distance is taken from contact of the intrusion to the center of the individual coal units. The following sill thicknesses were used in the calculation: 1.5 feet for B-1 seam in hole 1, 8.5 feet for B-2 seam, and 1.2 feet for C seam in hole 3, and 15.9 feet for B-1 seam in hole 2. The data shown in Figure 10 indicate that the ratio of the distance of the intrusive from the coal to the thickness of the intrusion increases as reflectance decreases.

Coal alteration in coal-bearing strata associated with intrusions should be useful in establishing distance from intrusive centers and the direction of the leading edge of an intrusive body as well as in establishing the deleterious effects sustained by the individual coals in a coalfield.

Summary

Examination of coal-bearing strata obtained from drill-core samples taken from the Somerset area indicated that portions of the coal have been thermally altered as a result of exposure at some time to molten rock (igneous intrusion). The degree of alteration of the coal was such that the coking properties of the coal have been affected. In the investigation, it was found that measurements of reflectance, electrical resistivity, and hydrogen content could be used to determine the degree of alteration of the coal. The data indicate the alteration of the coal was related to thickness and distance of the intrusive from the coal bed. In addition it was found that, within limits, coal may be used as a maximal geothermometer.

References

1. T. S. Lovering, "Temperatures In and Near Intrusions," Economic Geology, Fiftieth Anniversary Volume, pp. 249-281, 1955.

2. E. Ingerson, "Methods and Problems of Geologic Thermometry," Economic Geology, Fiftieth Anniversary Volume, pp. 341-410, 1955.

3. J. J. G. Blignault, "Field Relationships of the Dolerite Intrusions in the Natal Coalfields," Transactions of the Geological Society of South Africa, Volume 55, pp. 19-31, 1952.

* dry, ash free.

Table I

Equations Used to Express the Relationships of Temperature with Reflectance, Resistivity, and Hydrogen Content

1. Temperature, $F = 222.6514 + 641.1268\ R_o - 147.9204\ R_o^2 + 12.6124\ R_o^3$

   R_o = maximum reflectance in oil

2. Temperature, $F = 1497.4304 - 75.9517\ R - 5.9162\ R^2 - 0.5102\ R^3$

   R = electrical resistivity in ohm-cm

3. Temperature, $F = 2279.1012 - 749.1191\ H + 178.4985\ H^2 - 17.0855\ H^3$

   H = hydrogen content, weight percent (daf)

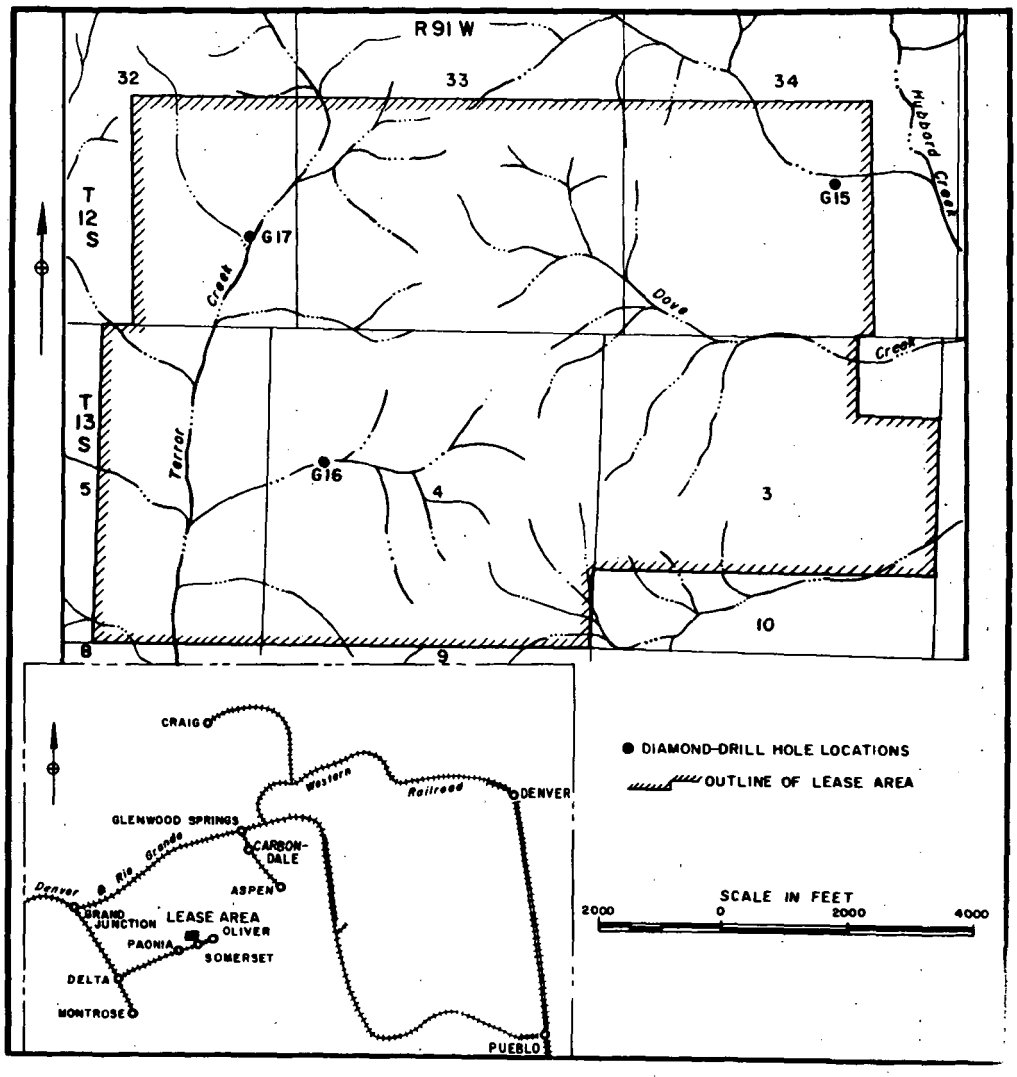


Figure 1. Location of Diamond-Drill Holes in Somerset Area, Colorado

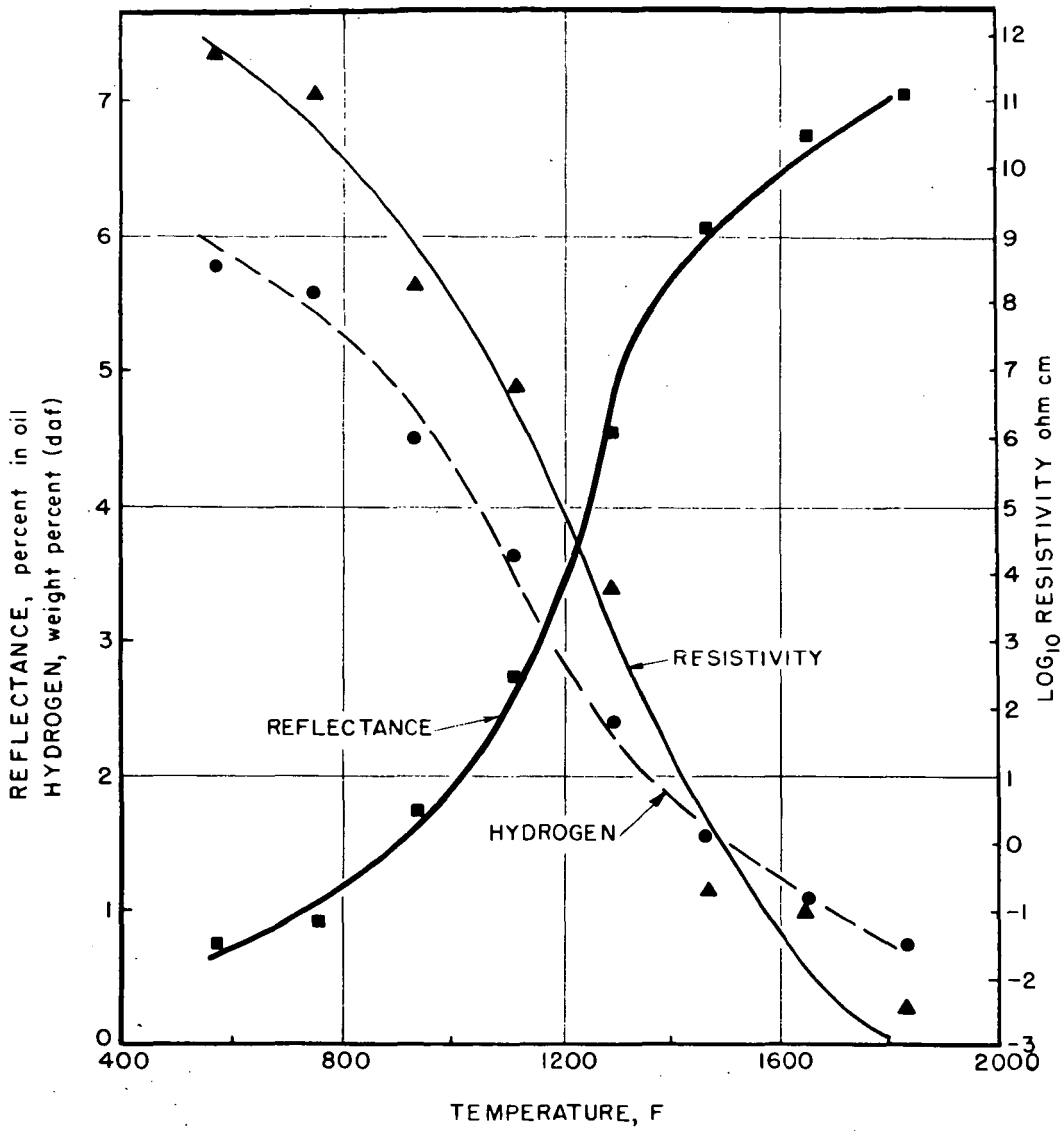


Figure 2. Relation of Temperature to Reflectance, Resistivity, and Hydrogen for Coal Carbonized in the Laboratory

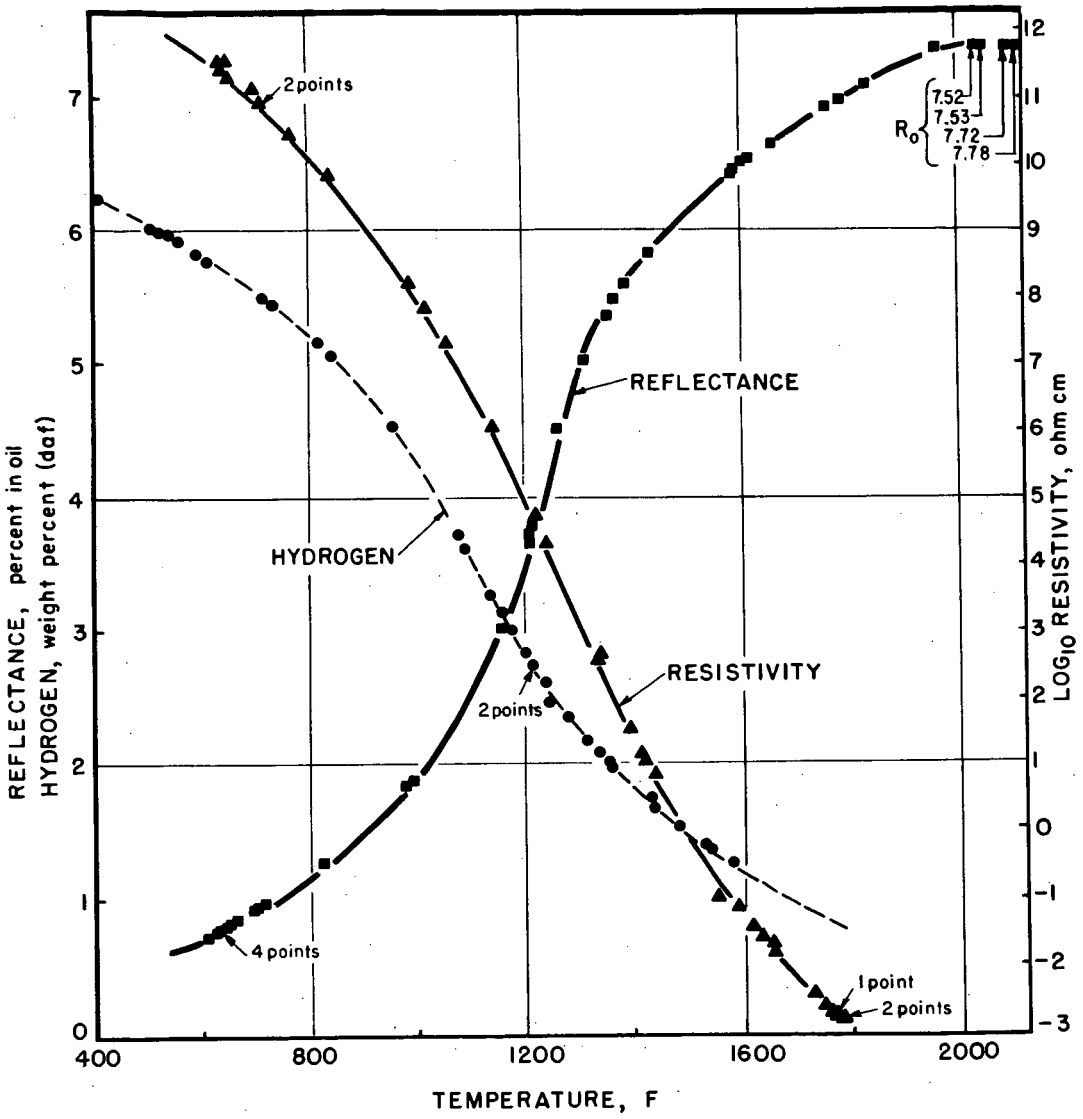
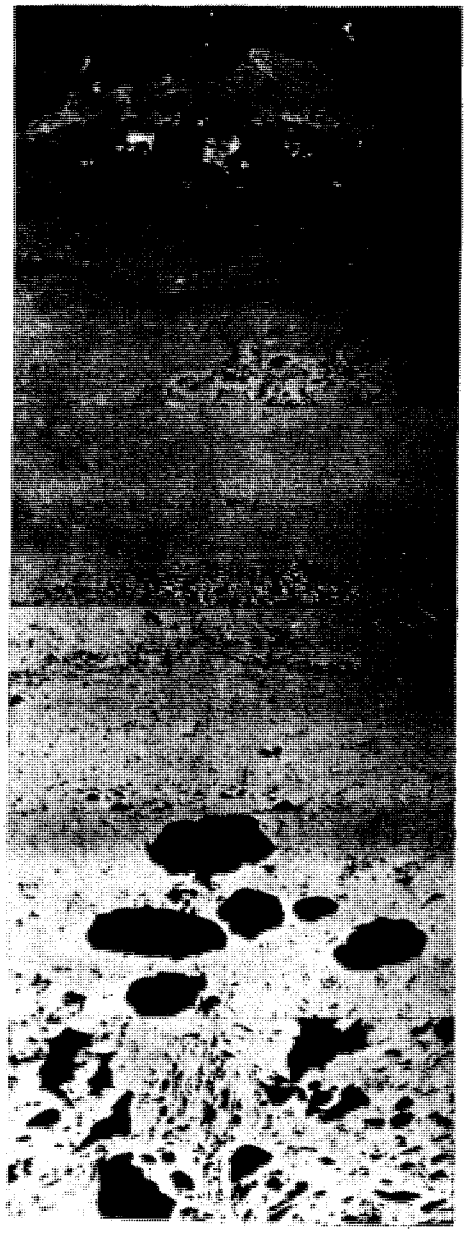


Figure 3. Relation of Calculated Temperature to Reflectance, Resistivity, and Hydrogen for Drill Core Samples of Coal



Reflectance, percent	Resistivity, ohm cm	Hydrogen, wt percent	Description
0.7	3.0 x 10"	6.2	Coal is unaltered
0.9	8.4×10^{10}	5.5	Coal increases in reflectance but vacuole development has not occurred.
3.0	2.1×10^{7}	3.6	Small pinpoint vacuoles develop.
4.5	2.0×10^{4}	2.8	Vacuoles increase in size.
5.6	1.3 x 10	2.5	Vacuoles continue to increase in size.
7.5	2.9×10^{-2}	1.3	Anisotropic coke structure develops.

Figure 4. As the Thermal Metamorphism of Coal Increases, the Extent of Vacuole Development Increases and the Reflectance Increases, While Resistivity and Hydrogen Decrease. Reflected light, X300.

Particles of coal showing wide variation in reflectance in a single sample representing a 1.7-foot coal interval. This is evidence of abrupt changes in the degree of thermal metamorphism.

Coke (pyrolytic carbon) produced from cracking of hydrocarbons or incomplete combustion of gas.

Mineral matter derived from the diorite intruded into the coal.

Figure 5. Photomicrographs Show Thermally Metamorphosed Coal, Pyrolytic Carbon, and Intruded Mineral Matter. Reflected light, X300.

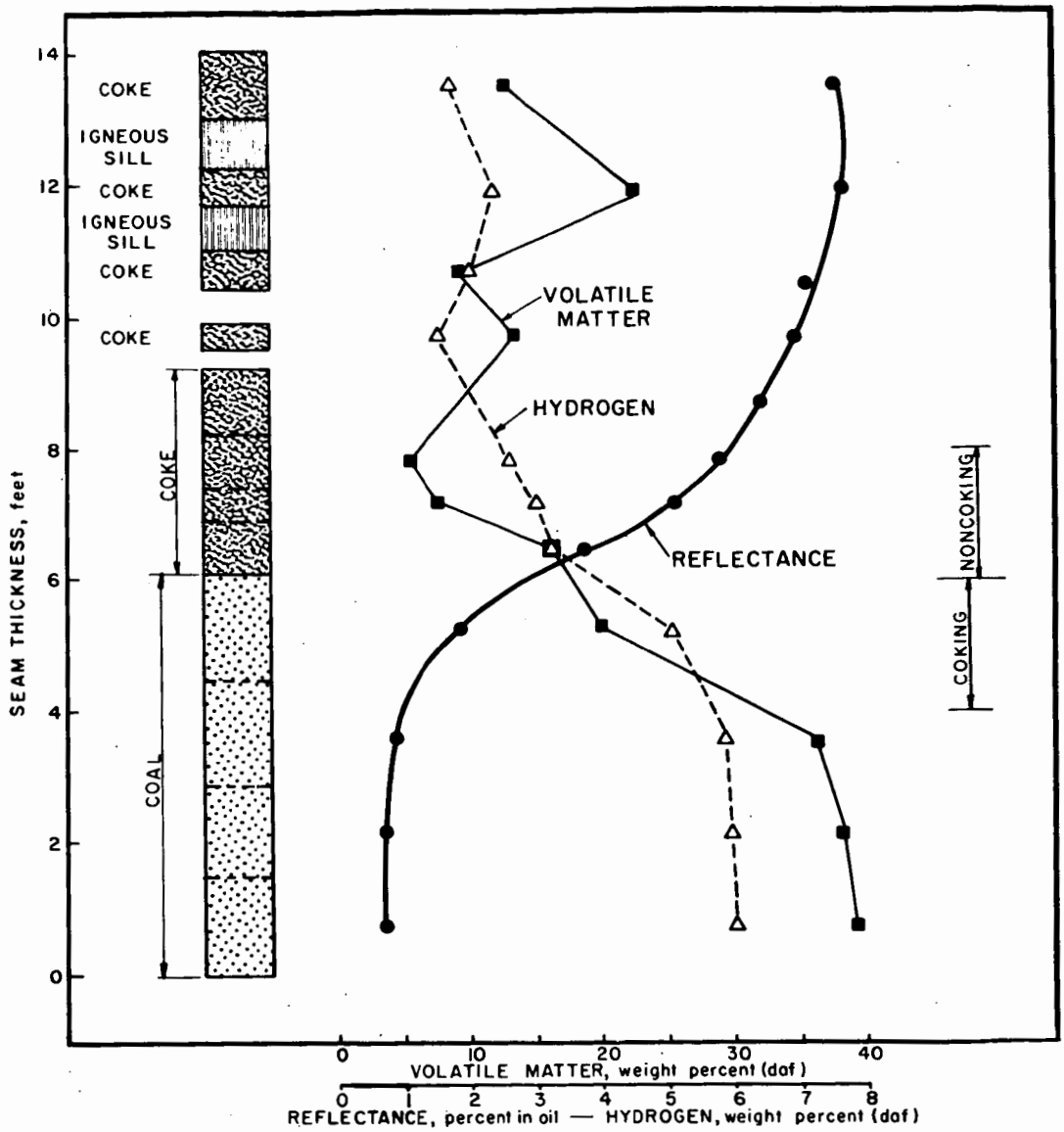


Figure 6. Profile of Coal and Sills with Reflectance, Hydrogen, and Volatile Matter for Indicated Coal Units, B-1 Seam, Hole G-15.

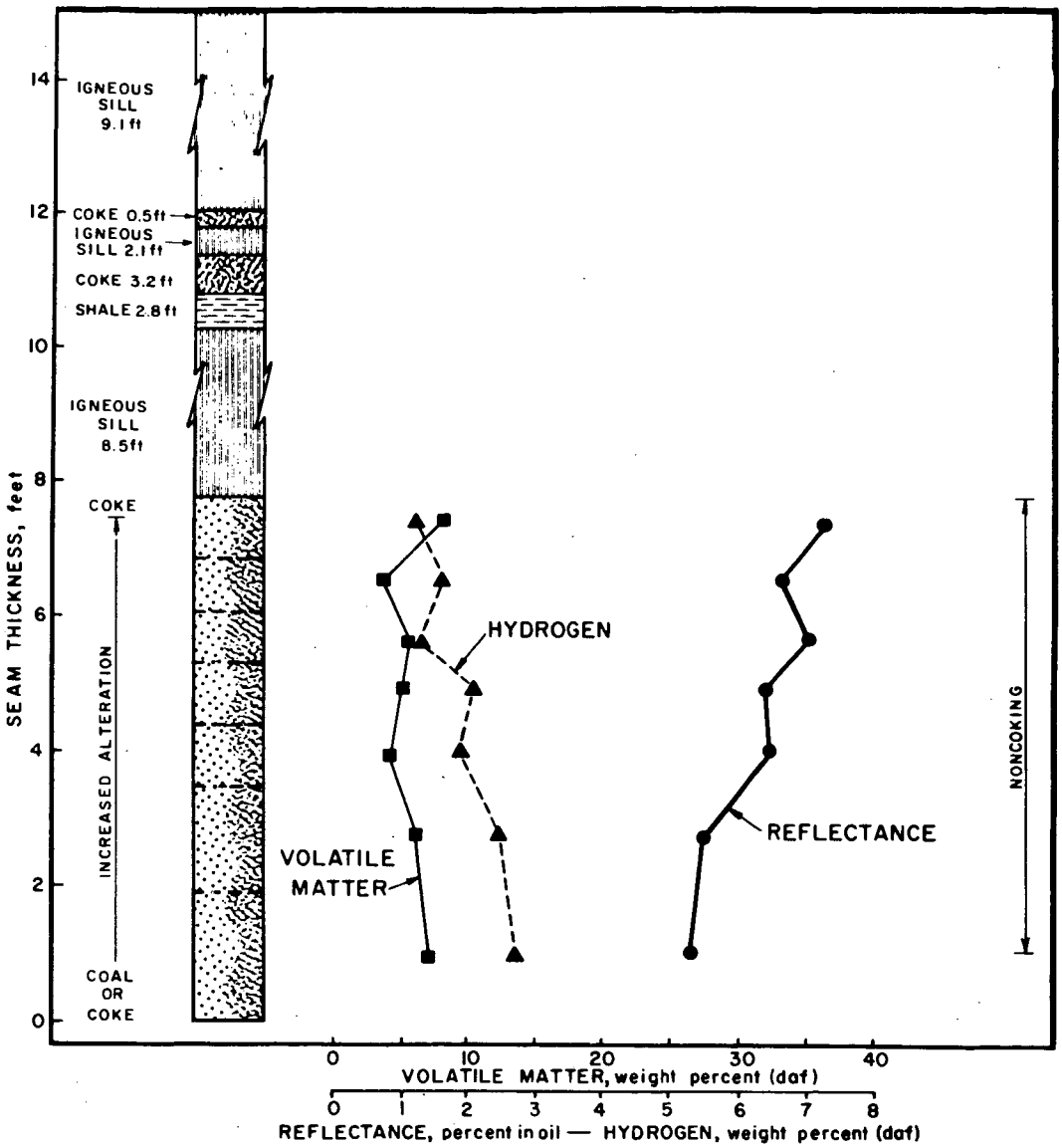


Figure 7. Profile of Coal and Sills with Reflectance, Hydrogen, and Volatile Matter for Indicated Coal Units, B-2 Seam, Hole G-16.

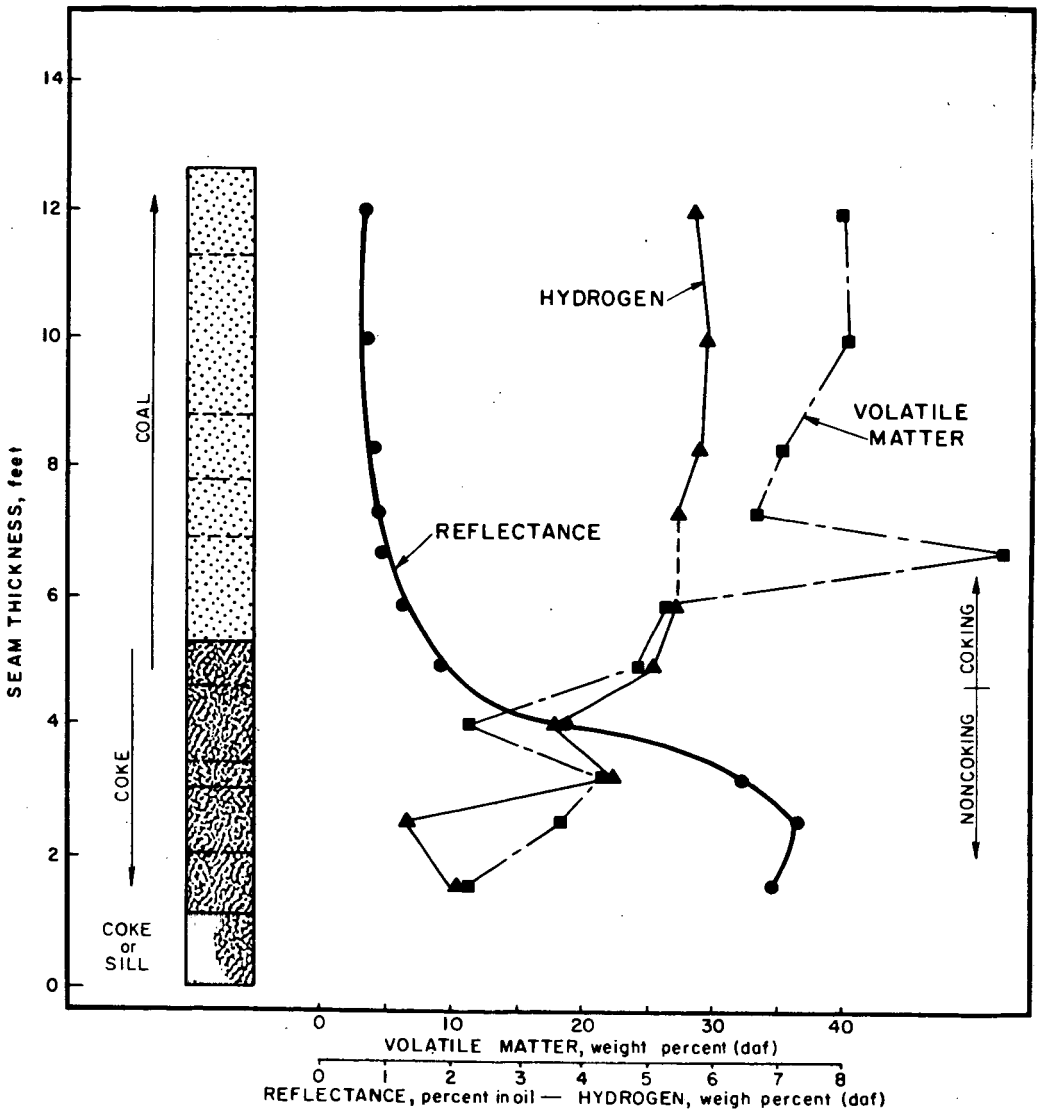


Figure 8. Profile of Coal and Sills with Reflectance, Hydrogen, and Volatile Matter for Indicated Coal Units, C Seam, Hole G-16.

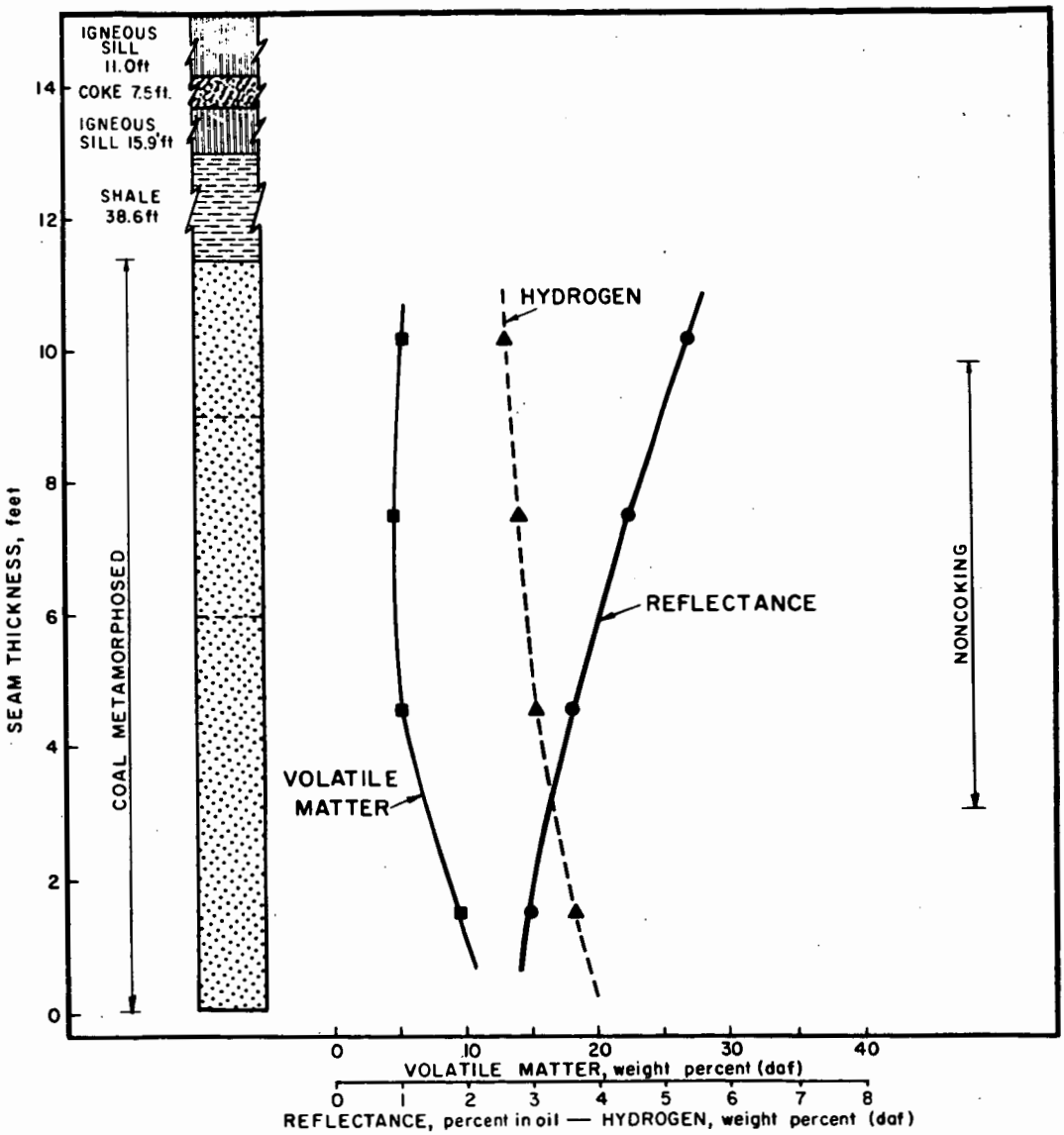


Figure 9. Profile of Coal and Sills with Reflectance, Hydrogen, and Volatile Matter for Indicated Coal Units, B-1 Seam, Hole G-17.

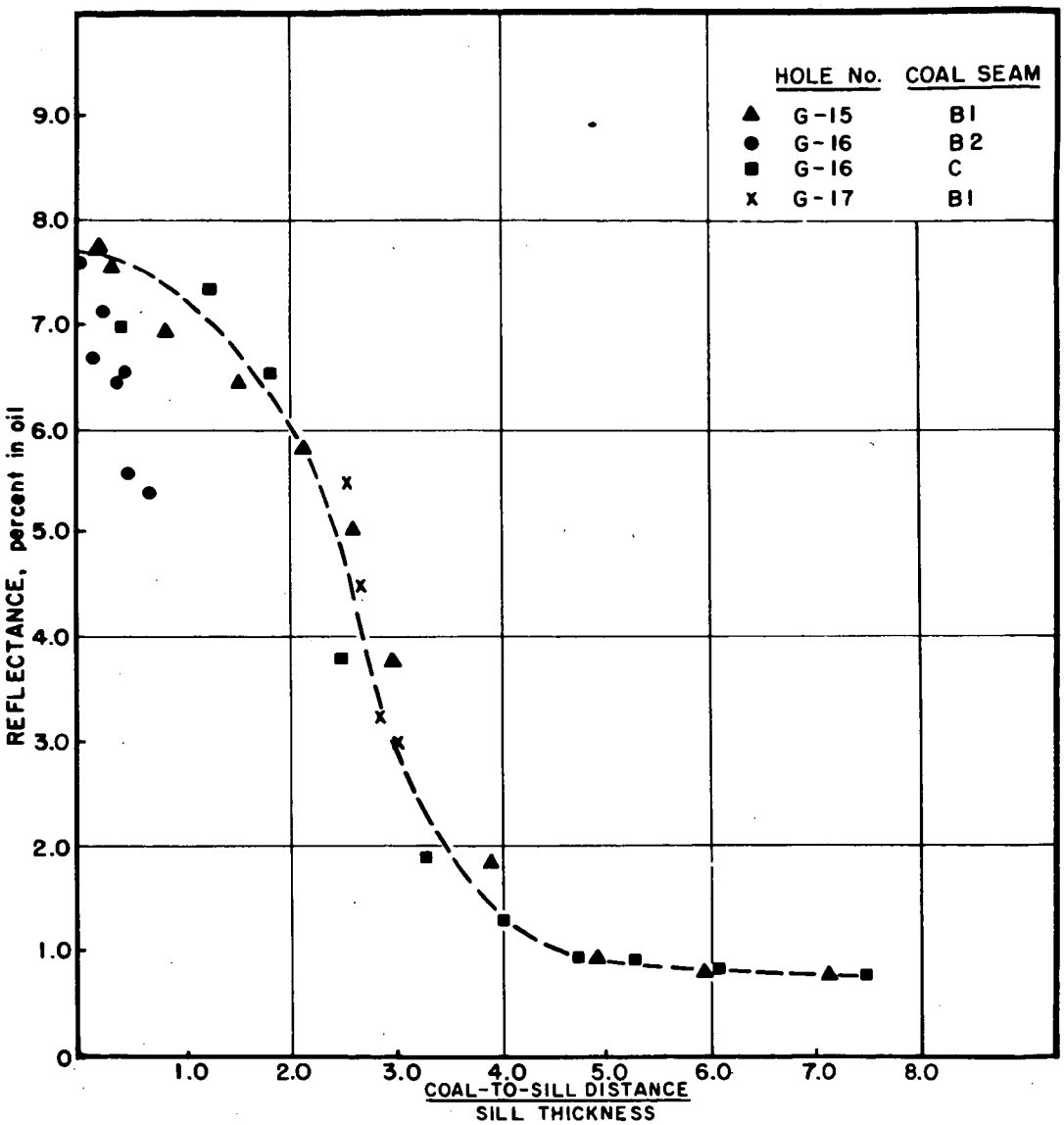


Figure 10. Reflectance Versus Ratio of Coal-to-Sill Distance to Sill Thickness for Thermally Altered Somerset Coal

THE EFFECT OF MACERAL COMPOSITION ON THE BINDERLESS BRIQUETTING OF HOT CHAR

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1. INTRODUCTION

The process of hot char briquetting now being developed and exploited by the National Coal Board consists of the direct briquetting of hot fluid-bed carbonised char. The principal process variables have already been discussed by Habberjam and Gregory (1), and this paper concerns an extension of their work.

The coal seams so far considered for the hot char briquetting of low rank coal have been of similar petrographic composition, i.e. about 60% vitrinite, 17% exinite, and the remainder composed of micrinite 1 and 2, fusinite, shale and pyrite. There is no reason why other coal seams should not be examined, particularly since certain coal preparative treatments, e.g. selective froth flotation and dense medium separations, have the effect of concentrating one particular maceral or group of macerals at the expense of the others. It was considered that coals of unusual maceral composition might exhibit a new range of briquetting properties.

Although work has been published on the thermal changes occurring in individual coal macerals, no systematic survey has been made using British low rank coals heated in fluid-bed conditions.

Many workers, notably Kröger (2) and Fitzgerald (3) have shown the pyrolysis behaviour of the individual coal macerals to be different. They, as well as Permitina (4) and Amnosov (5), were working under coke oven conditions; Permitina, using polished microscope sections of Russian coking coal chars, showed that only vitrain, and vitrainised masses and spores, contributed significantly to caking behaviour. Permitina also showed that fusainised micro-components, xylene* and minerals, made no contribution, whilst xylo-vitrain and partially fusainised attrition particles had low caking properties. Ergun (6), working with a microscope hot-stage, has confirmed that vitrinites and exinites undergo visible changes during carbonisation, and that the other constituents remain comparatively inert. Taylor (7) studied the thermal properties of the Stopes concentrates during carbonisation, and lists a considerable quantity of relevant literature.

In this work the maceral system of coal component classification will be used. The components analysed will be:

vitrinite, exinite, total inertinite, shale and pyrite.

The inertinite will be further divided into micrinite 1, micrinite 2, and fusinite.

* The word "xylene" is taken directly from a translation of Permitina's paper. It probably implies xylo-fusain.

The detailed objects of the present study were:

(a) to devise a method for estimating volume changes in the macerals of low rank coal chars heated in a fluid bed;

(b) to show whether variations in the maceral compositions of the coal feed would affect the char briquetting process;

(c) to follow any changes occurring in the macerals of chars in the range 380° to 500°C.

2. EXPERIMENTAL

2.1. Coal sample preparation

Samples of four low rank, high volatile coals were used. An analysis of these coals is given in Table 1.

TABLE 1

Analyses of coals used

Colliery	Seam	Commercial grade	Moisture % as received	Ash % as received	Volatile matter d.a.f.
Calverton	High Main	Washed smalls	7.59	11.68	36.83
Denby Hall	Mixed	Washed smalls	5.25	16.50	37.80
Birch Coppice	Mixed	Washed smalls	5.53	11.11	41.19
Dexter	Mixed	Washed special beans	6.18	1.66	38.03

Samples of one coal, namely Calverton CRC.902, were used to prepare maceral concentrates. Hards, brights and fusinised materials were manually selected, and further refined by flotation and crushing, followed by selection under a low-power lens. Three basic samples were prepared in this way, the proximate analyses being given in Table 2.

TABLE 2

Proximate analyses of basic samples

	Durain	Vitrain	Fusain
Moisture	5.99%	12.47%	4.55%
Ash (dry basis)	7.67%	1.07%	10.29%
Volatile matter (d.a.f)	38.49%	35.61%	24.80%

Ten mixes were prepared from the three basic samples, the vitrain, durain and fusain samples being listed as Sample Nos. 1, 8 and 10 respectively (Table 3).

TABLE 3

Analyses of Calverton coal maceral concentrate blends

Sample No.		1	2	3	4	5	6	7	8	9	10
Vitrinite	Vol. %	97.9	74.7	51.4	67.4	50.9	33.3	35.7	14.5	16.7	23.9
Exinite	"	1.7	9.8	28.6	5.7	21.0	33.2	14.8	51.1	34.4	5.4
Total inertinite	"	0.4	15.5	19.3	26.9	27.7	33.0	49.3	34.4	48.5	70.3
Micrinite 1	"	0.3	7.5	12.7	14.7	18.6	17.9	27.2	26.8	31.0	33.7
Micrinite 2	"	0.1	4.8	6.5	7.8	7.4	12.2	15.2	7.3	12.1	24.3
Fusinite	"		3.2	0.1	4.4	1.7	2.9	6.9	0.3	5.4	12.3
Shale	"			0.7		0.3	0.5	0.2		0.4	0.1
Pyrite	"					0.1					0.3

2.2. Apparatus

Two systems of fluid-bed carbonisation were used:

(1) A 2-inch laboratory-scale fluid-bed of the design described by Habberjam and Gregory (1). This apparatus was used for the study of the pyrolysis of macerals. Two carbonisation periods were used in this fluid bed, i.e. 8 and 30 min., the first 4 min. of each period being the heating time. Nitrogen was used as the fluidising gas.

(2) A miniature fluid-bed and briquetting mould. This apparatus consisted of a 0.5-inch diameter tapered mould and hardened steel plunger mounted in the jaws of a hydraulic jack. A tightly fitting funnel was placed in the top of the mould, so that the mould and funnel together acted as a fluid-bed, the funnel being removed from the mould for briquette production. Air and nitrogen were used as the fluidising gases.

One carbonisation period was used in the miniature bed, i.e. 5 min., including a 2 min. heating period.

2.3. Testing and analysis of samples

The briquettes prepared at 6 tons/sq.in. were tested for their bulk density and mechanical strength by the method described by Habberjam and Gregory (1).

The samples for maceral analysis were ground as coal to -10 B.S.S. and reduced to 30 gm. using an Otto Microsplitter (8). These samples were then carbonised in the 2-inch fluid-bed, the chars being further reduced to approximately 1 gm. samples before impregnation and mounting in blocks with cold-setting polyester resin. A flat surface was ground on the blocks, using several grades of carborundum powder on glass plates, and a high polish was obtained with fine alumina powder on a Bolting silk lap.

A statistical method of analysis, based on a technique first described by Delesse (9) was used to determine the relative volume of macerals in the coals and chars. This was based on the fact that, in a cross-section of rock, the ratio of the area occupied by one mineral to the total cross-sectional area is a reliable estimate of the total volume percentage of that mineral.

Several methods of measuring the relative areas of minerals in cross-section have been proposed, but the most reliable was taken as the 'point counter' technique described by Glagolev (10). In theory, the cross-section is covered with a grid and the mineral occurring under each intersection is recorded. The ratio of the number of points at which the particular mineral occurs to the total number of points of the grid may be reliably taken as the ratio of the area of the mineral to the total measured area. A mathematical proof of these statements is given by Chayes (11). In practice, instead of moving from point to point on a grid, the polished coal section is moved in successive steps along a number of traverses, and the mineral under the crosswires is recorded at each step. In order to limit the error to ± 3% at 75% and to ± 1% at 5%, a total of 1,000 points is analysed on each sample.

In order to estimate the changes in the volumes of the macerals with respect to the original coal, it is necessary to have some body or bodies present which remain inert during carbonisation. Since their volume does not change, comparison is possible with the changing maceral volumes. Where a natural inert material is present in reasonable percentages, this may be used. More than 10% must be present, however, to ensure that the errors are less than the probable error in the maceral analysis.

For the coals Calverton, Denby Hall and Birch Coppice, micrinite 2, fusinite and minerals were regarded as standard inerts. In the case of Dexter, a percentage of gas coke ground to -10 B.S.S. was added to the original coal charge. The porosities, also found by a 'point counter' method, are a derived figure (see section 3, Discussion). Sections of briquettes were also mounted in resin, and photomicrographs of sample chars were made with a Vickers projection microscope. (See photos. 1 through 12.)

3. RESULTS AND DISCUSSION

The experimental conditions for briquetting and for maceral analysis were unavoidably different. The briquetting trials using the very small quantities of sample available were carried out using a miniature fluid bed which allowed for heating rates of approximately 200°C/min. Three minutes after the attainment of carbonisation temperature, i.e. 5 min. after sample introduction, the briquettes were formed. In the maceral analysis larger samples were available, and a more convenient and conventional fluid bed was employed. The rate of heating in this bed was approximately 100°C/min. and samples were analysed 4 min. and 26 min. after they had attained carbonisation temperature, i.e. total residence times of 8 and 30 min. respectively. Previous work had shown that briquettes formed in the miniature fluid bed after heating for 5 min. had a similar performance to those after 8 - 10 min. in the more conventional bed.

The results of the briquetting of maceral concentrates are given in Figures 1 to 3. Calverton coal (C.R.C. 902, V.M. 37% d.a.f.) was used and the three methods of briquette assessment employed, i.e. shatter index, abrasion index and bulk density, gave similar results. Maceral concentrates rich in inertinite produced poor briquettes, whilst both exinite and vitrinite rich mixtures produced good briquettes. Exinite rich mixtures containing over 25% micrinite 1 produced good briquettes, whereas inertinite rich mixtures with the same concentration of micrinite 1 produced poor briquettes. It was therefore unlikely that micrinite 1 contributed to the production of strong briquettes. An interaction between exinite and micrinite was possible and this was not ruled out by the microscopic study of the macerals (Fig. 4). Micrinite 1 underwent some swelling between 375° and 400° C, the swelling being greater after 30 min. carbonisation than after 8 min. This swelling occurred for all

the coals considered (Figs. 5 and 7).

Samples containing practically pure vitrinite (97.9% by volume) produced strong compacts throughout the range of temperatures at the short carbonisation time studied, the shatter and abrasion strengths falling slightly at the higher temperatures. A photomicrograph of a 97.0%"pure" vitrinite briquette (Photo.11) illustrates the way in which the vitrinite grains appear to 'jig-saw' into one another. The maceral analyses show a series of expansions and contractions throughout the range which are only qualitatively followed by the other coals studied.

The exinite rich mixtures (up to 51% volume) did not produce strong briquettes before 410°C, but above this temperature the exinite played an important role in briquetting, either alone or in combination with vitrinite or micrinite 1. The quality of exinite rich compacts rose to a maximum at about 440°C and then fell gradually. A photomicrograph (Photo.12) of a 'whole' coal briquette (exinite 17%, vitrinite 66%, micrinite 17%, and micrinite 2 plus fusinite 10%) shows definite bridging of coal grains by melted exinite. As a maceral the exinite appeared to be lost, both with respect to increasing temperature and carbonisation time. Its disappearance as a recognisable maceral would not preclude its impregnation into the microstructure of remaining coal substance. The changes in the maceral structure were coincident with porosity changes. There was no significant difference for nitrogen and air fluidisation.

The porosities of the chars (Fig. 8) rose steeply with temperature and increased with period of carbonisation. In determining the porosities of chars, three separate types of pores were measured: rounded holes, angular holes and natural holes. It was probable that the rounded holes were formed as the gases resulting from the decomposition of exinite and vitrinite attempted to escape through the plastic or semi-plastic vitrinite, and that the angular holes were cracks formed after carbonisation when the material contracted on cooling. The third classification of holes, natural holes, occurred in fusinite and semi-fusinite grains. The porosities shown in Fig. 8 are 'rounded hole' porosities.

Table 4 below illustrates the relative importance of the rounded, angular and natural holes in Calverton coal.

TABLE 4

Porosity Analyses of Calverton Chars

Calverton 8 min. N_2	Rounded holes	Angular holes	Natural holes	Total porosity
350°C	0.1	1.6	2.4	4.1
375°C	1.4	1.6	1.8	4.8
400°C	0.7	2.2	2.3	5.2
425°C	21.6	3.9	3.0	28.5
450°C	43.4	3.2	1.1	47.7
475°C	51.7	3.5	1.1	56.3
500°C	60.5	2.6	1.0	64.1
30 min. N_2				
350°C	0.4	2.0	1.1	3.5
375°C	0.4	1.9	1.3	3.6
400°C	10.2	3.8	2.0	16.0
425°C	32.3	4.0	1.9	38.1
450°C	47.3	3.5	1.2	52.0
475°C	52.8	3.4	0.3	56.5
500°C	59.4	2.6	1.2	63.2

Photomicrographs of chars heated in air and in nitrogen illustrate the formations of these holes and the relative changes in the macerals. (See photos. 1 through 10)

On a commercial scale, the results of these investigations illustrated the danger of highly selective coal preparative treatments. Changes of the maceral composition of the coal feed to a char briquetting plant might well affect the operation of the process, e.g. the addition of froth flotation fines would lower overall quality and a change of exinite/vitrinite ratio might well affect the optimum temperature of operation.

On the laboratory scale, the work has illustrated that changes in the volume of individual macerals can be estimated by comparison with naturally inert material in coal, and that results using this method are similar to those using an artificial inert additive.

4. CONCLUSIONS

(i) The maceral volume changes in coal chars can be estimated by the use of naturally occurring inert material where over 10% is present in the original coal. Where this naturally inert material is not present, an artificial additive, e.g. high temperature coke, may be used.

(ii) On a commercial scale, sudden or gradual changes of the maceral composition of coal feed to a char briquetting plant may well affect the operation of the process. High inertinite content raw material will lower overall strength, and any change in exinite/vitrinite ratio may affect the optimum operational temperature.

(iii) For a non-coking high volatile coal, exinite, vitrinite and micrinite 1 were shown to undergo changes in the range 350°C to 500°C. The vitrinite, and to a lesser extent, micrinite 1, swell and contract in this range, whilst the exinite is lost completely as a recognisable maceral.

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CAPTIONS TO PHOTOMICROGRAPHS OF CHAR GRAINS

Photomicrographs of 30 minute Calverton Chars C.P.S.1855/16

(Magnification approximately X 120)

Photo. No.

1. 350°C N_2 Fluidisation

The exinite appears unaltered at this temperature. The vitrinite shows cracking around the inert fusinite mass, which indicates that there may be contraction.

2. 350°C Air Fluidisation

The exinite appears unaltered except where it lies on the margins of grains and has been oxidised. The vitrinite is cracked, and has fairly wide oxidised margins extending up the open cracks.

3. 400°C N_2

The exinite is disappearing, leaving irregular holes in the micrinite and vitrinite. The megaspore in the larger durain grain has become liquid and some of it has migrated to the edge of the grain, cementing a triangular vitrinite grain to it. The micrinite and fusinite are unaltered, and the vitrinite remains angular, with fine cracks.

4. 400°C Air

A large megaspore has become oxidised and has cracked away from the durain grain which contains it. Within this megaspore there is a small area of unoxidised volatile matter which is boiling off. There is unoxidised exinite boiling off in both durain grains. In the triangular grain the megaspores have been partially oxidised and the transition between volatile and non-volatile exinite is shown. The vitrinite is just beginning to become plastic enough for rounded bubbles to develop in some of the grains.

5. 425°C N_2

Most of the exinite has disappeared. The vitrinite grains are becoming plastic, and some grains are filled with gas bubbles. The inertinites are still unaffected, except by escaping from enclosed vitrinite and exinite.

6. 425°C Air

The vitrinite appears to be considerably more plastic than in N_2 at this temperature. The grains are considerably swollen and their margins are rounded. There is still some exinite present in the durain grain. The inertinites remain as in the 400°C sample. It can be seen that the margins of the vitrinite grains are still sealed, since the bubbles have no oxidation rims, indicating that the margins must still be quite plastic.

7. 450°C N_2

The large durain grain has remained inert, except for a vitrinite band which is boiling out. The microspores and megaspores have gone, leaving a skeleton of micrinite, which has not even collapsed into the space left by a megaspore. The pure vitrinite grains are swollen, but the ones shown in this micrograph still have fairly thick walls.

8. 450°C Air

Again the decomposition of vitrinite appears to be in a later stage than in the 450°C N_2 chars. Some of the bubbles contain oxidised margins, and some are unoxidised, being still enclosed.

9. 500°C N_2

The vitrinite grains have become quite rounded, consisting of a network of thin-walled bubbles. Bands of micrinite 2 have remained with their original structure.

10. 500°C Air

The stage reached is very similar to that of the N_2 char at this temperature, except for the oxidation of the grain and pore margins. Again, the micrinite 2 and fusinite appear to have its original structure. Most of the bubbles have been oxidised, showing that the surface of the grains has been broken, and that the oxidised vitrinite has become brittle at this temperature.

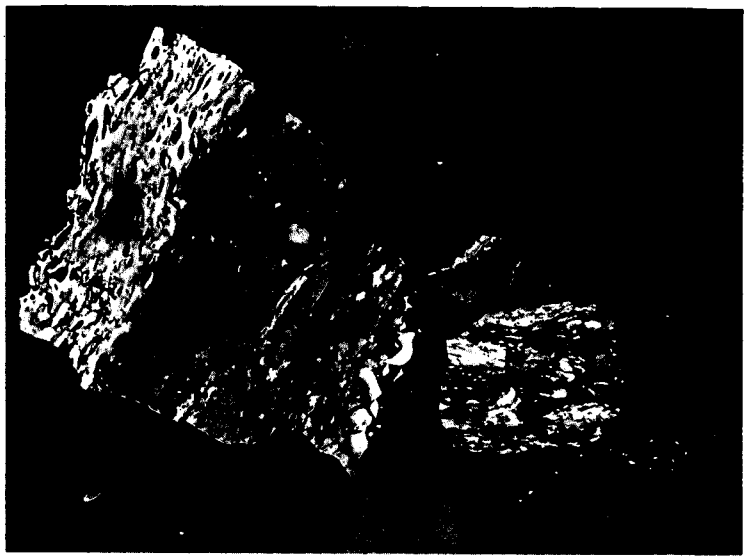
ACKNOWLEDGMENT

The work described in this paper was carried out as part of the research programme of the Scientific Department of the National Coal Board. The views expressed are those of the authors, and not necessarily those of the Board.

1. 350°C N_2

2. 350°C Air

3. 400°C N_2

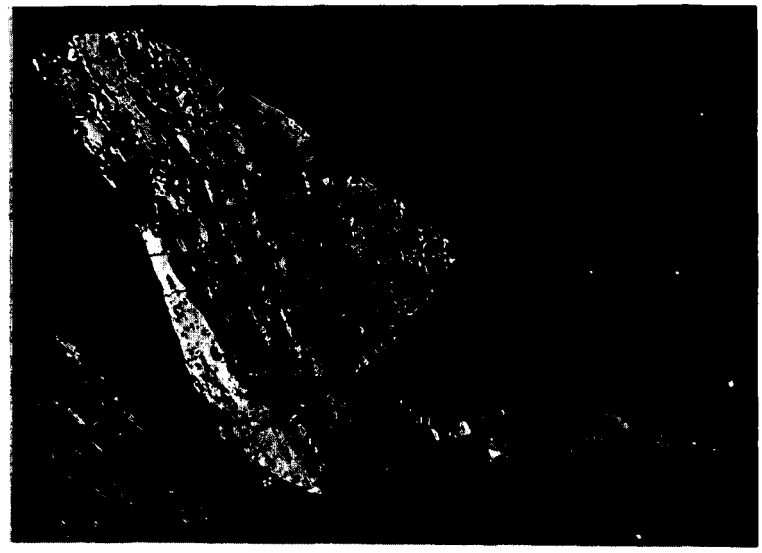


4. 400°C Air

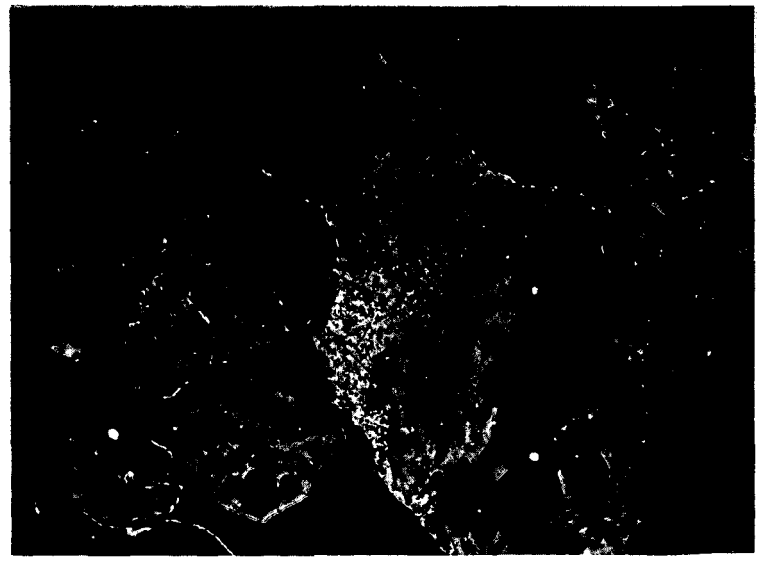
5. 425°C N_2

6. 425°C Air

7. 450°C N_2

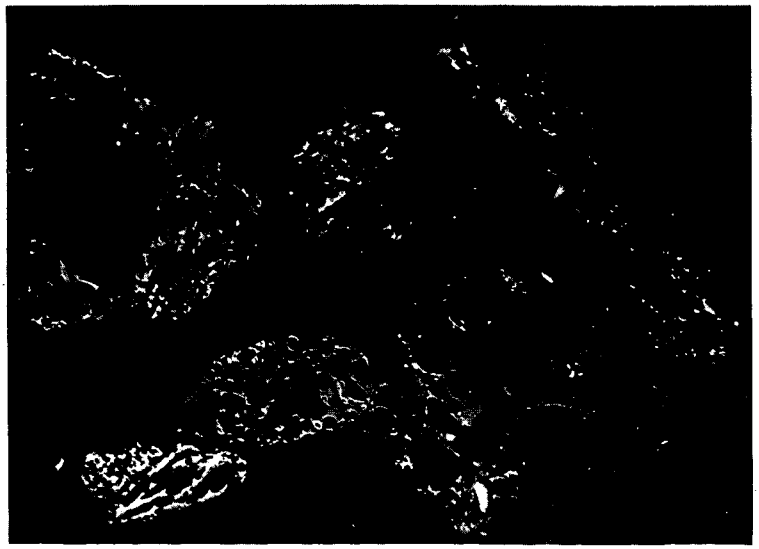


8. 450°C Air

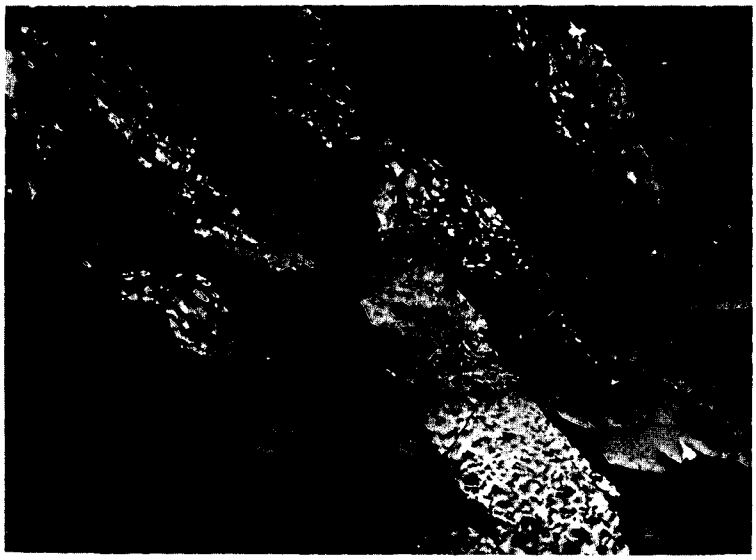


9. 500°C N_2

10. 500°C Air



11. A 420°C "pure" vitrinite briquette



12. A 420°C "whole coal" briquette

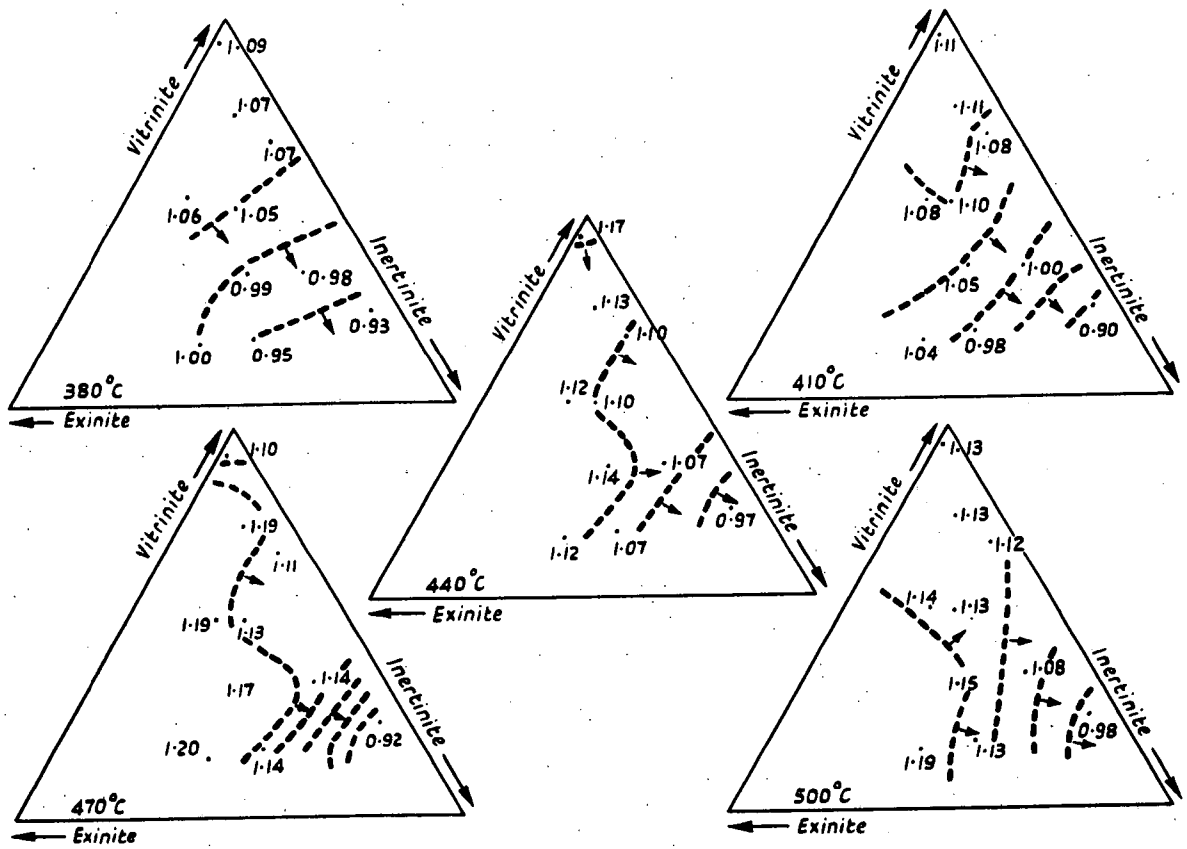


FIG. I. DENSITY OF CHAR BRIQUETTES, g/cc.

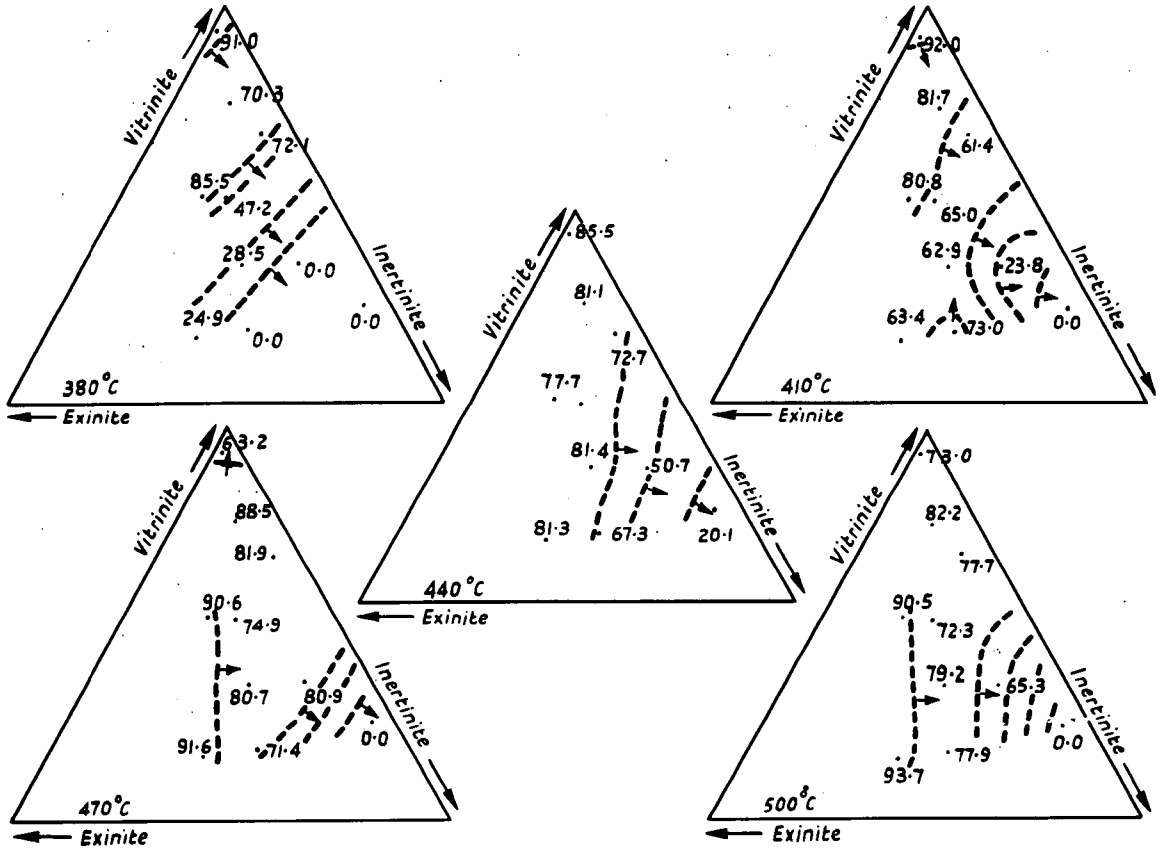


FIG. II. VARIATION OF ABRASION INDEX WITH TEMPERATURE AND COMPOSITION.

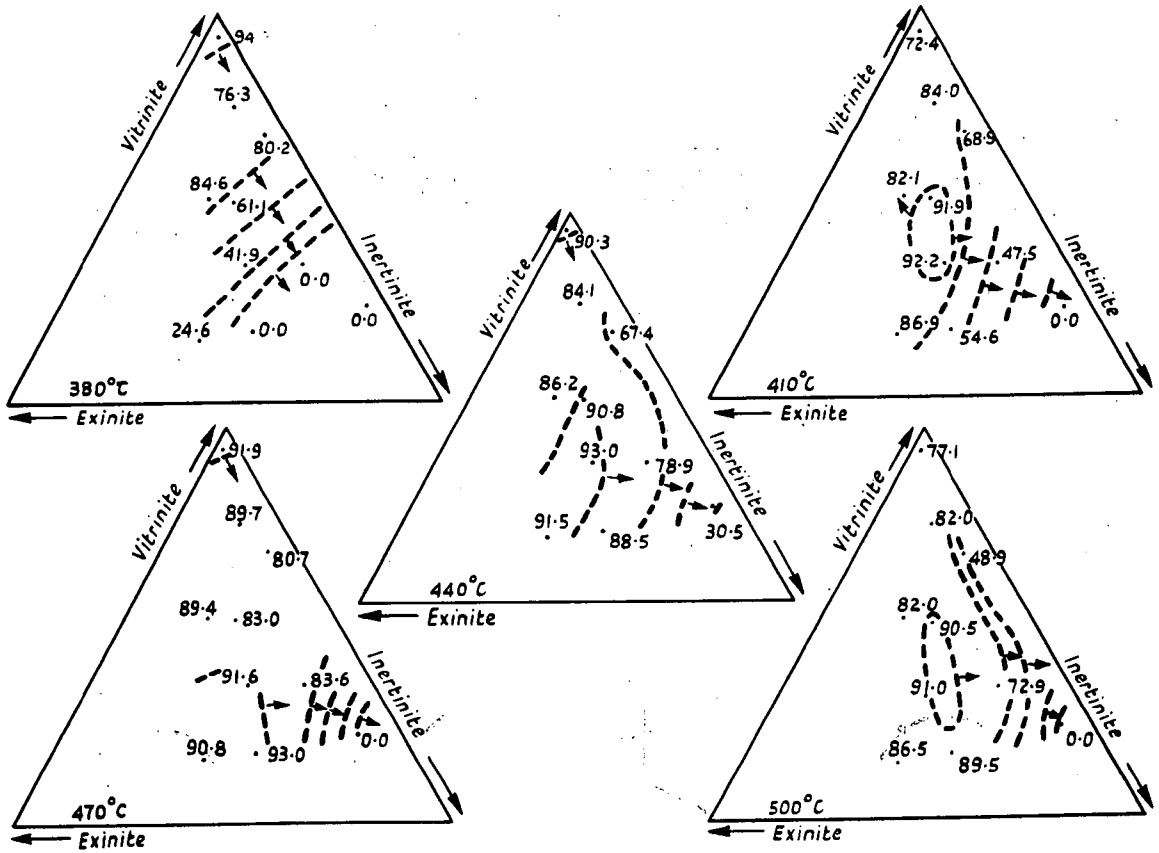


FIG. III. VARIATION OF SHATTER INDEX WITH TEMPERATURE AND COMPOSITION

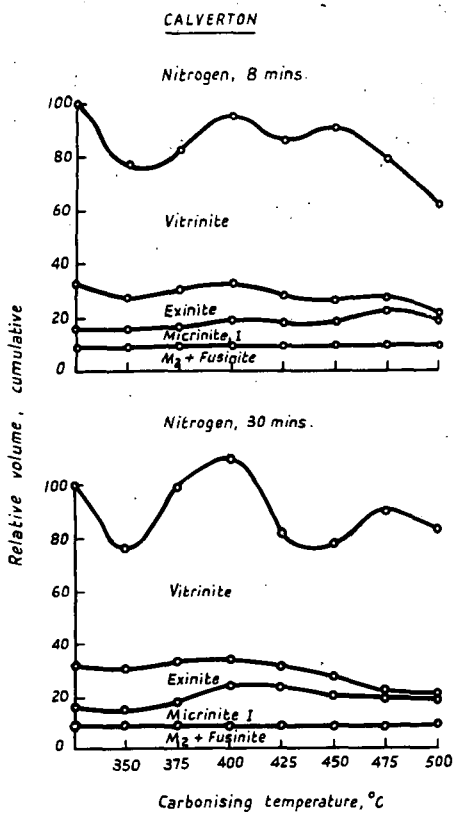


FIG. IV. RELATIVE VOLUME OF MACERALS.

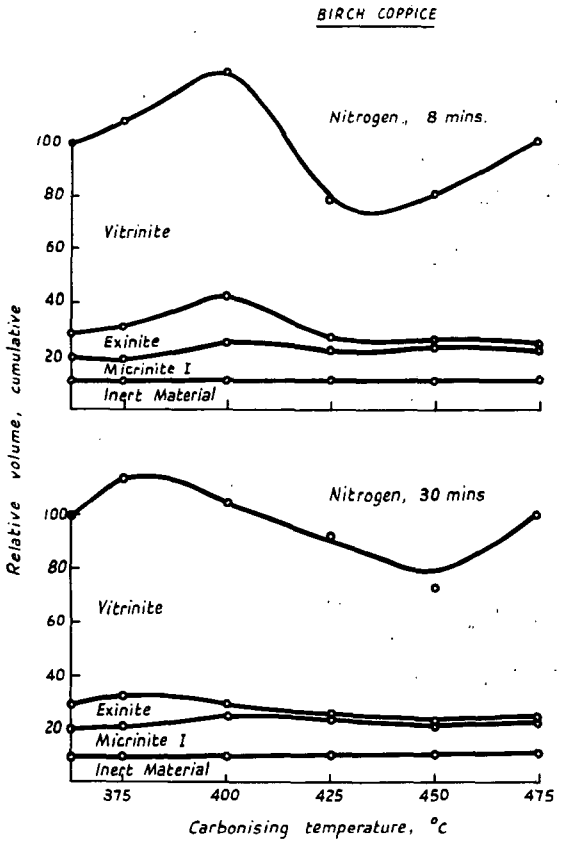


FIG. V RELATIVE VOLUME OF MACERALS.

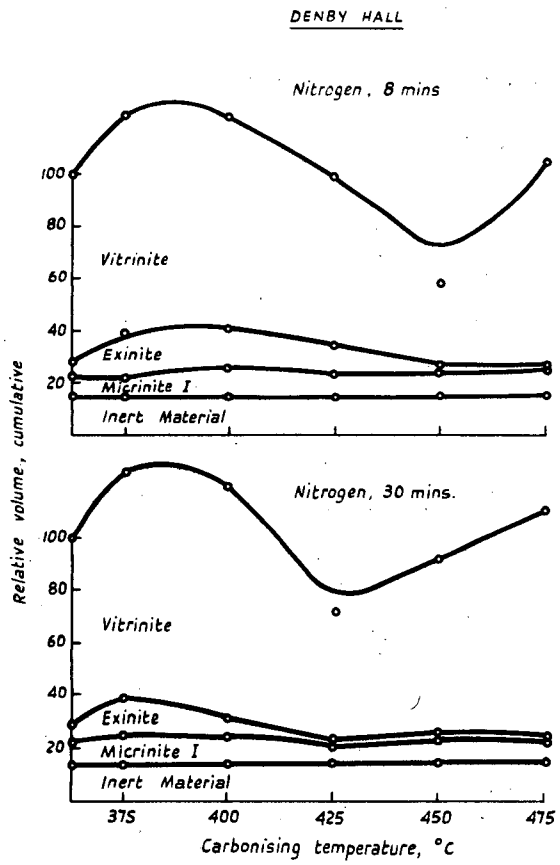


FIG. VI RELATIVE VOLUME OF MACERALS.

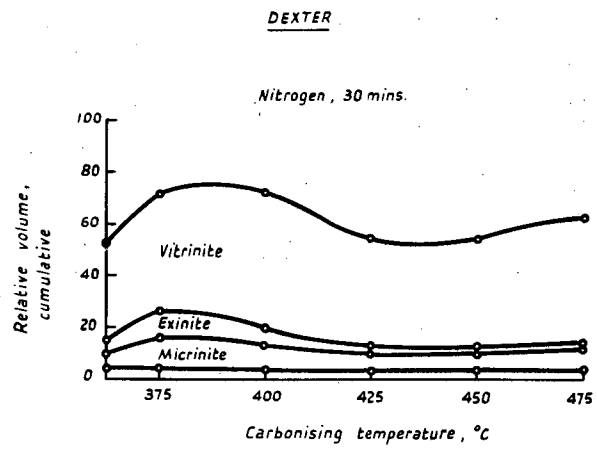


FIG. VII. RELATIVE VOLUME OF MACERALS.

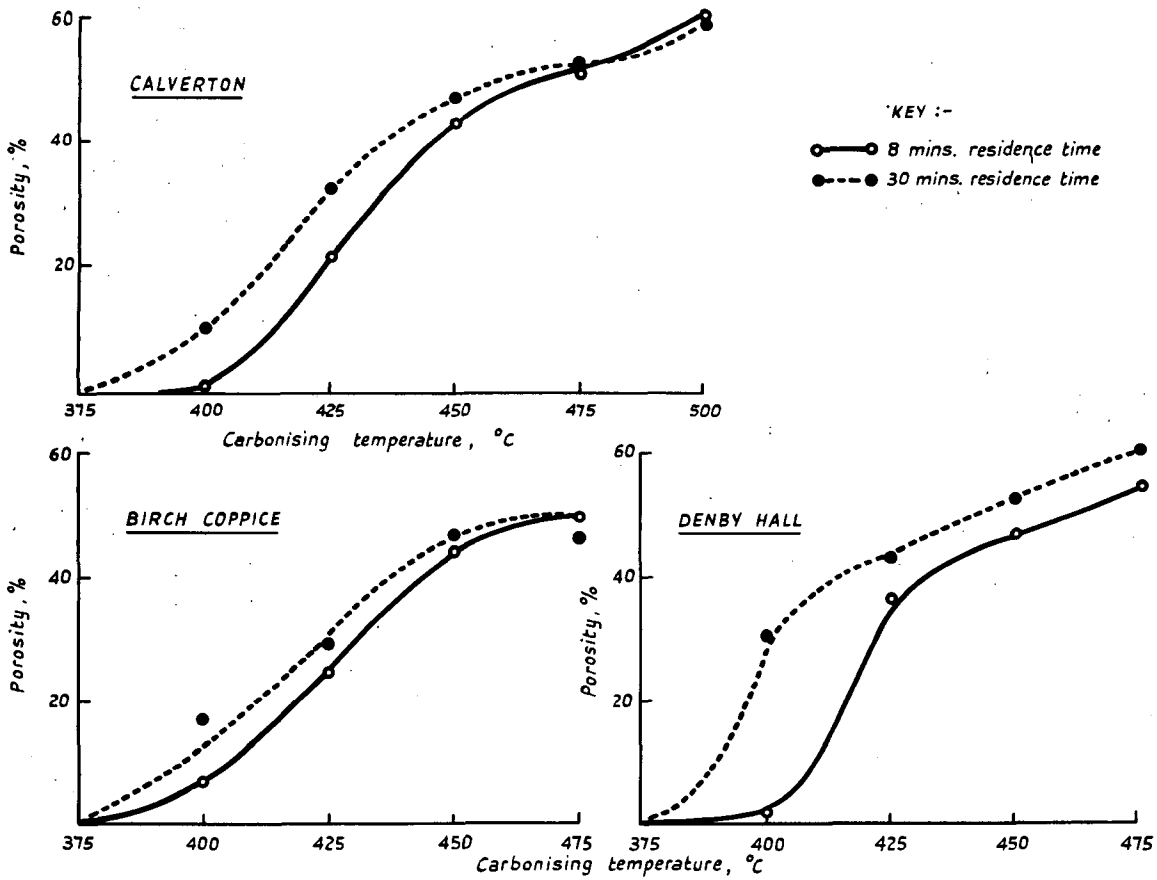


FIG. VIII. POROSITY OF CHARS FROM THREE LOW RANK COALS.

Selective Chemical Reactions for the Study of Coal Macerals

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That the petrological classification of coal components in four main groups, known as vitrinite, exinite, micrinite and fusinite, has chemical and physical significance, as well as practical importance, is already established. There is petrographic and palaeobotanic evidence indicating that each of these groups is complex and that several varieties of each exist, but little chemical work has been carried out to supplement and consolidate this evidence. Such work is in progress in this laboratory; so far, attention has been paid mostly to the development of experimental techniques, but a start has been made in applying them to the study of vitrinite structure.

It is obvious that structural differences between two or more "vitrinoids"[1] found in the same coal will be more subtle than the differences between, say, vitrinite and exinite. A comparison of vitrinoids from different coals but of similar rank will also require subtle distinctions. If these distinctions can be established and understood, our understanding of the concepts of rank and metamorphosis should be strengthened considerably, and knowledge of the relation of constitution to behavior increased. Research of this kind clearly requires particularly sensitive techniques, and any chemical reactions used must be as selective and as informative as possible. In this paper the extension and improvement of two such chemical reaction techniques are described, together with their application to some purified vitrinitic materials.

Samples Studied.

In some of the preliminary experiments designed to elucidate the mechanism of the dehydrogenation reaction, a sample of vitrain from the Bruceton mine of the Pittsburgh seam was used. The elementary analysis is shown in Table 1; the petrographic analysis of a block from the same batch of coal is: vitrinite, 85%; semifusinite, 6%; fusinite, 2%; exinite, 4%; micrinite, 2%; and pyrite, 1%.

The other samples were pure vitrinites separated by float-and-sink techniques from the bright bands in selected vitrains. Their properties are collected in Table 1. Samples MP 10a and 10b were taken from different levels in one pillar section of the same seam, but differ appreciably in reflectance, and represent different vitrinoids in the classification of Schapiro and Gray.[2] Samples MP 11 and 17 have similar reflectances and represent the same vitrinoid V 9 according to Schapiro and Gray; they are, however, of quite different geological age and derived from different types of plant material, since MP 11 is an Appalachian coal laid down in the Pennsylvanian period of the Palaeozoic and MP 17 is younger, have been laid down in the Cretaceous period of the Mesozoic (ages approximately 300 and 120 x 10^6 years respectively).

The hydroxyl contents of the samples are included in Table 1 for completeness; they are repeated from an earlier publication.[3] It seems clear that samples MP 11 and 17 do differ somewhat in elementary analysis, but the carbon content of MP 17

may be somewhat too high*.

The infra-red spectra of all four vitrinites have been obtained. The spectra of MP 10a and 10b do not differ significantly, except that a difference of the intensity of the hydroxyl band at 3400 Å is observed, paralleling the hydroxyl contents determined chemically. The spectra of MP 11 and 17 also resemble one another closely; here again the hydroxyl bands differ in intensity, and the distribution of hydrogen between aromatic and aliphatic structures is evidently somewhat different (see Table 3 below).

Table 1. Analyses of Samples Studied

Sample No.	Source seam and location	Av. Reflectance in oil, %	Per cent d.a.f. C	H	N	S	O*	O as OH
MP 10a	Lower Freeport West Sunbury, Pa.	0.743	82.6	5.4	1.6	1.4	9.0	5.6
MP 10b	Lower Freeport West Sunbury, Pa.	0.630	83.8	5.3	1.6	1.1	8.2	3.9
MP 11	Upper Freeport, Maysville, Pa.	0.995	84.9	5.2	1.5	0.8	7.6	3.2
MP 17	Frederick, Valdez, Colo.	0.934	86.6	5.5	1.9	0.8	5.2	2.0
-	Pittsburgh Bruceton Vitrain	-	83.6	5.6	1.7	2.0	7.3	-

*by difference

Reduction with Lithium.

Lithium in aliphatic amines is a powerful reducing agent for aromatic systems, naphthalene, for example, being reduced to the octa- or deca-hydro derivative. The reaction proceeds, depending on the solvent, at 18 or 100°, and breakage of carbon-carbon bonds, such as occurs in catalytic hydrogenation, is not found. Both ethylamine[4] and ethylene diamine[5,6] have been used as the amine component in the application of the reaction to coals; the latter causes somewhat more extensive reduction of the coal, but is much more toxic and is impossible to remove completely from the coal after reaction. The extent of reduction varies strongly with rank, passing through a sharp maximum with vitrains of about 89% carbon content.[4,5] The solubility of the coal in pyridine is always increased by the reaction, and the magnitude of the increase varies with rank in a manner closely parallel to the extent of reduction. The marked variation with rank of the effects of reaction suggest that here we have one suitable technique for investigating close distinctions among vitrinitic materials.

Hitherto in the study of the reduction of coals, attention has been chiefly concentrated on the variation of extent of reaction with rank, and little work has been done on the chemistry of the products. One interesting possibility is the

* The analyses quoted were made by United Analysts Ltd., East Boldon, Co. Durham, England, a laboratory experienced in coal analysis, and they are believed to be the most reliable data available. The samples have also been analysed in two other laboratories, with results that do not altogether agree with those quoted; however, these laboratories did not observe certain precautions now believed important (see Appendix), which were observed by United Analysts.

study of hydrogen distribution in the product by nuclear magnetic resonance spectroscopy. To get the maximum advantage from this technique, the material must be in solution, preferably in a solvent that contains no hydrogen. Deuteropyridine has been used for this purpose with solvent extracts of untreated vitrinites[7] and reduced products.[8] However, it is extremely expensive and the small proportion of isotopic impurities found in all commercial samples interferes with estimation of aromatic hydrogen in the solute. We have now found that 40-75% of that part of the reduction products of four vitrinites soluble in pyridine is also soluble in chloroform. A large number of solvents have been tested, most of which dissolved very little; piperidine, chloroform, dimethylformamide and dimethylsulfoxide dissolved significant quantities of product. Deuterochloroform is relatively inexpensive, and since any isotopic impurity interferes little with the coal spectra, it is an excellent solvent for n.m.r. studies. So far we have only been able to run one spectrum in the solvent; the result is discussed later.

Four pure vitrinites have been reduced by the lithium-ethylamine technique. The amount of hydrogen added and the solubilities of the products in pyridine and chloroform are shown in Table 2. All the samples are of lower rank than that at which maximum reduction occurs; it will be seen that the pyridine solubilities are higher for the two samples of higher carbon content. Moreover the two samples MP 10a and 10b, taken from different levels in a single pillar section of a seam, behave differently; so also do the pair of vitrinites of the same reflectance but from different seams. The nitrogen contents of the products and the weak methyl absorption band at 1375 cm^{-1} in the infrared spectra show that the ethylamine is not retained by the products. Good oxygen balances were also obtained, showing that oxidation did not occur. Some pick-up of oxygen did occur, however, in some of the solvent extractions.

Table 2. Reduction of Vitrinites with Lithium

	Reduced Vitrinites			
	MP 10a	MP 10b	MP 11	MP 17
H atoms per 100 C atoms in product	115	87	107	91
H atoms added per 100 C atoms	37	11	31	15
Pyridine solubility, %	37	41	61	53
Chloroform solubility, %	27	18	45	16*

*Low solubility may in part be due to exposure to air.

The infrared spectra of the untreated vitrinite MP 11, the chloroform-and pyridine-soluble and -insoluble parts of the reduced products are shown in Fig. 2. It will be seen that all fractions of the product show increased aliphatic C-H absorption at about 2920 cm^{-1} and 1450 cm^{-1} (3.45μ and 6.9μ), the chloroform-soluble part showing the greatest increase. The extinction coefficients of the absorption at 2920 cm^{-1} calculated from the per cent transmission and the concentration in the potassium bromide discs (gm./gm.), are shown in Table 3, together with the H_{ar}/H_{al} ratios for the raw coals calculated from the absorptions at 3030 cm^{-1} and 2920 cm^{-1}. and an assumed $\epsilon_{ar}/\epsilon_{al} = 0.44$ (see refs. 9-11). The extinction coefficients for the products from different coal samples are approximately consistent with the extent of reduction derived analytically. The use of the extinction coefficient ratios must not be pushed too far as the value of the extinction coefficients is dependent not only on the concentration but also on structural factors.

In the spectra of all the reduced products, the absorption in the aromatic carbon-hydrogen bending region, 650-950 cm^{-1} (11-15μ) was considerably weaker than

Table 3. Spectral Studies of Hydrogen Distribution

	Sample	Vitrinite MP 10a	MP 10b	MP 11	MP 17
H_{ar}/H_{al}	Raw Coal	0.32	0.36	0.41	0.34
ϵ_{2920} cm^{-1}	Raw Coal	0.11	0.12	0.12	0.16
$\frac{\epsilon_{2920}\ (\text{Product})}{\epsilon_{2920}\ (\text{Raw Coal})}$	Crude Reduction Product	3.2	2.1	3.5	1.6
"	Pyridine Extract	3.6	1.5	3.6	1.3
"	Pyridine Insolubles	1.2	0.5	1.2	0.6
"	Chloroform Extract	3.6	2.7	3.5	2.2
"	Chloroform Insolubles	1.8	1.6	---	1.2

that in the untreated coals, and the C-H stretching vibration at 3030 cm^{-1} could not be distinguished at all in the spectra of any of the products but MP 17. A broad band centered at 1250 cm^{-1} and a broad shoulder and 1050 cm^{-1} were noticeable in the spectra of all the products. Similar but not identical spectra have been shown previously by Reggel et al.[5] for the reduced products; these authors do not report spectra of solvent extracts of the products.

The n.m.r. spectrum of the chloroform-soluble part of the product of reduction of sample MP 10b is shown in Fig. 1. Owing to instrumental difficulties, it has not been possible to re-run this spectrum nor to run other samples or a solvent blank. However, the infrared spectrum of the solvent showed very high isotopic purity and little sign of the presence of hydrogen. The most striking feature of the spectrum is the extremely sharp doublet at chemical shifts of 2.87 and 2.95 p.p.m. (referred to tetramethylsilane). These peaks are in the position expected for hydrogen atoms on carbon in the α-position to an aromatic ring or double bond. Absorption in this region has been previously reported for certain coal derivatives, and so its presence here is not surprising. However the sharpness and the fact that the area under the peak is 50% of the total area under all peaks is surprising. As already noted, this result still awaits checking, but it is very difficult to imagine any possible impurity that could give a large sharp peak here but no similar sharp peaks elsewhere. Other peaks were observed corresponding to methyl and other aliphatic hydrogen (0.87, 1.25 and 1.45-2.0 p.p.m.) and aromatic and phenolic hydrogen (8.06 p.p.m.).

Dehydrogenation

It is already established that much of the aliphatic hydrogen in vitrinites and spore exinites is present in hydroaromatic rings.[12,13] It has been argued that these rings play an important part in the structural make-up of these macerals[14] and that they govern much of the maceral chemistry. The study of hydroaromatic structures by dehydrogenation is therefore important in any detailed study of macerals, but no fully satisfactory method has yet been reported. Peover[12] has described the use of benzoquinone as a dehydrogenating agent; it is efficient, but in a side-reaction, which Peover believed to be addition by a Diels-Alder reaction, a considerable proportion of quinone combines with the coal and cannot be removed. Peover mentions the use of triphenylmethyl perchlorate, but gives few details. Raymond et al.[13] report catalytic dehydrogenation with palladium on calcium carbonate and other catalysts, in high boiling solvents such as phenanthridine. This method permits direct and accurate determination of the hydrogen removed, but it requires a rather high temperature (over 300°C) and there is apparently some difficulty in removing catalyst and solvent if the products are wanted for further study.

We have used 3,5,3',5'-tetramethyldiphenoquinone as a dehydrogenating agent for the Bruceton vitrain under the same conditions as Peover used for benzoquinone, thinking that this bulky molecule would not readily undergo Diels-Alder addition to the coal. The spectrum of the product showed little change from the untreated coal, except that a band at 1190 cm^{-1} (8.4μ) appeared. This band is in the region expected for either ether oxygen or carbonyl vibrations, and suggest some addition of the quinone to the coal; however, no carbonyl stretching absorption at 1660-1700 cm^{-1} was observed, in contradistinction to the situation when benzoquinone was used.

We have also used the free radical diphenylpicrylhydrazyl, $(C_6H_5)_2 \cdot NHN \cdot C_6H_2(NO_2)_3$, which is reported to be an effective dehydrogenating agent for hydroaromatic rings.[15] The infrared spectrum of the product indicated that some dehydrogenation probably occurred, but in most cases some addition of the hydrazyl to the coal took place. In one experiment a relatively small amount of the hydrazyl was used; it was found that in the ultra-violet spectrum of the filtered reagent solution after reaction the strong band at 3330 Å characteristic of the hydrazyl had been completely replaced by a band at 3200 Å characteristic of its reduction product, the hydrazine. We conclude that the reagent does dehydrogenate coal, but not very effectively.

It is believed that in dehydrogenation with the quinones, the hydrazyl and triphenylmethyl perchlorate, the first step in all cases is a transfer of hydride ion, H^-, from the hydroaromatic system to the reagent. This step would leave a carbonium ion, and the first stage of reaction must then be completed by loss of a proton, H^+, so that the net result is elimination of a hydrogen molecule. Further hydrogen molecules are removed in the same way until the ring has become aromatic. Now some carbonium ions are known to be stable, and so it is possible that in the reaction of coals a proportion of the H^- loss is not followed by elimination of H^+. The carbonium ions in the coal could then react with some species derived from the reagent, in an addition reation. For example, if a quinone takes up H^-, the hydroquinone mono-anion is formed, and if this reacted with a carbonium ion, a covalently-bonded ether would result. If triphenylmethyl perchlorate is the reagent, then a coal carbonium perchlorate would result, in which the bonding is essentially ionic. We have, therefore, a possible explanation of why all four reagents add to the coal to some extent, which in the case of quinones would replace the Diels-Alder hypothesis. In the case of the perchlorate reaction, it should be possible on the above hypothesis to remove the perchlorate ion and a proton from the coal, thus completing the dehydrogenation step, by treatment of the product with a suitable base. We have investigated the use of triethylamine for this purpose.

Peover[12], and Cunningham, Given and Wyss (unpublished observations) found that the products of dehydrogenating some British vitrains with triphenylmethyl perchlorate weighed 30-50% more than the coal originally taken. J. K. Brown (unpublished) found absorption in the infrared spectra of the products characteristic of the perchlorate ion, but could find no sign of the presence of the triphenylmethyl group. We have dehydrogenated the Bruceton vitrain and the vitrinites MP 10a and 10b with the reagent, washed the product thoroughly with acetone, and find the weight increases shown in Table 4. The products were refluxed with triethylamine (b.p. 89.5°C) and suffered the losses in weight shown in the Table. It will be seen that with the two vitrinites the addition of reagent was relatively small, but nearly the whole of it was apparently eliminated by amine treatment.

In the infrared spectra of all the dehydrogenated products, the aliphatic C-H bands at 2920 and 1420 cm^{-1} (3.45 and 6.90μ) were decreased in intensity. All the spectra showed a broad region of absorption between 1030 and 1120 cm^{-1} (8.9 to 9.7μ), that is, in the position where the perchlorate ion absorbs strongly. This absorption was completely removed by the amine treatment. The products also showed well-defined absorption in the aromatic C-H bending region at 698 and 745 cm^{-1}, which was not removed by amine treatment. The triphenylmethyl group in the perchlorate and the alcohol absorbs strongly at 698 and 753-760 cm^{-1}; in spite of the fact that the second frequency is somewhat higher than that in the spectrum of the coal products, this suggests

that some triphenylmethyl anion or triphenyl methane is retained by the coal. On the other hand, dehydrogenation will increase the aromaticity of the coal, and this should cause increased absorption in this general region.

Table 4. Weight Changes in Dehydrogenations with Triphenylmethyl Perchlorate

	Bruceton vitrain	Vitrinite 10a	Vitrinite 10b
Wt. gain in reaction, %	36	16	18
Wt. loss on amine treatment, % of wt. of untreated coal	12	14	17

There were indications in the spectra that vitrinite MP 10b was somewhat more extensively dehydrogenated than 10a.

There is therefore some support for the suggestion that the perchlorate ion at least is retained in the coal products on carbonium ions which are intermediate products of the dehydrogenation, though perhaps it should not yet be regarded as proved. Amine treatment is fairly effective in removing the ion. The matter is under further investigation.

As an alternative approach to the study of dehydrogenation, we are using C^{14}-labelled benzoquinone, in the hope that a radiochemical determination of quinone retained will permit us to correct elementary analyses of the products to a quinone-free basis. The method will also facilitate study of the removal of the quinone.

General Discussion and Conclusions

We believe that the introduction of chloroform as a solvent for vitrinites reduced with lithium in an amine represents a significant advance, which should facilitate further study of the chemistry of the reaction and the application of n.m.r. techniques. It should prove particularly useful with vitrinites of higher rank than those used here, where higher solubility is to be expected, and on the present evidence the study of the reaction and its products does provide a sensitive means of distinguishing between closely related macerals. The single n.m.r. spectrum of a reduced product so far obtained suggests a number of detailed interpretations with most interesting implication for coal structure, but these will not be discussed until more data are available.

Some contribution to the understanding of the mechanism of dehydrogenation reactions has been made, but it cannot be claimed that a fully satisfactory procedure has yet been found. Information merely about the amount of hydrogen removable, without any further study of the products, would be useful in the study of macerals, and of the methods available at present for obtaining it, the catalytic method[13] is perhaps the best.

There is now available a fairly detailed set of data on two pairs of highly purified vitrinitic materials. It has been established that between the members of each pair there are significant differences in elementary composition, in distribution of hydrogen and of oxygen functional groups, and in response to lithium reduction. In the case of the pairs from the same pillar section, the chemical differences are matched by a difference in reflectance. The reflectances of the two coals of different geological age do not differ much, but we must conclude that in spite of this the samples are of somewhat different rank in a chemical sense. This apparent discrepancy between petrographic and chemical rank may be associated with the difference in age and origin.

The results throw some light on the problem of the heterogeneity of the vitrinite group of macerals, but more data are obviously required before firm conclusions can be stated.

Experimental

Spectra. All infra-red spectra were run in a Perkin-Elmer Model 21 Spectrophotometer; the samples were dispersed in KBr pellets, a blank KBr window being placed in the reference beam. In order to obtain reliable optical densities, the weight of samples was taken to the nearest 0.01 mg. on a micro-balance, and the window thickness was measured with a micrometer. Peak heights were measured by the base-line technique.

The n.m.r. spectrum was run on an approximately 2% solution of material in deuterochloroform. A Varian A-60 spectrometer was used.

Lithium Reductions. The procedure previously described[4] was followed; approximately 1 gm. coal samples were taken in each experiment, and 8 hrs. reaction time was allowed. The extractions of the products were run on 0.1 - 0.2 gm. samples, which were shaken mechanically with 4-6 ml. solvent at room temperature for 24 hours. To recover the extracts, solutions were evaporated slowly under nitrogen and the residues dried in vacuum at 100°.

Dehydrogenations. 3,5,3',5'-Tetramethyldiphenoquinone was prepared by the oxidation of 2,6-xylenol with benzoyl peroxide in chloroform.[16] In the dehydrogenation reactions, 0.3 gm. coal was refluxed with 1.2 gm. of the quinone in 30 ml. dimethylformamide under nitrogen for 5-1/2 hours.

In the use of diphenylpicryl hydrazyl, 0.1 gm. coal was refluxed with 0.3 gm. hydrazyl in 30 ml. of either pyridine or chloroform for various lengths of time up to 24 hours.

The above methods were applied only to the Bruceton vitrain.

The reactions with triphenylmethyl perchlorate were run as follows. About 1 gm. coal was refluxed with 10 gms. perchlorate in 50 ml. glacial acetic acid for 30-35 minutes. After cooling the liquid was poured into acetone (to dissolve the triphenylmethane formed and any unchanged perchlorate) and filtered. The residue on the filter was shaken mechanically in a further 100 ml. acetone for 5-8 hours, filtered, washed on the filter with more acetone, and dried. A portion of the product (about 0.2 gm.) was refluxed with triethylamine for 2 hours; the liquid was cooled, and filtered, and the product was washed thoroughly with methanol and dried.

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Appendix: Elementary Analysis of Coal Samples

As a result of experience accumulated during the research reported here, we have reached certain conclusions about the preparation of samples for analysis and about analytical procedure, which we wish to place on record.

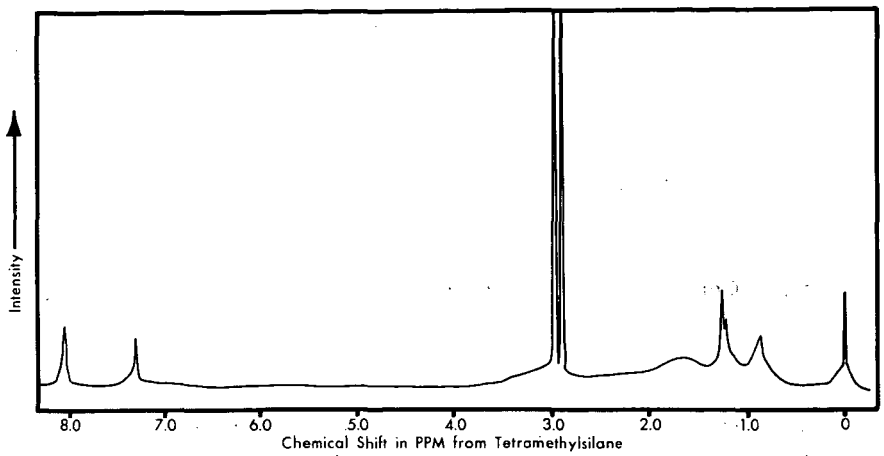
1. Samples should be submitted for analysis and analysed in an undried condition. The moisture content should be determined carefully at the same time as the other determinations, and the hydrogen and oxygen contents corrected appropriately.

In conditions of medium to high humidity and relatively low temperature, well dried coals are very hygroscopic and can absorb moisture from the air while being handled and weighed.

2. Freshly mined samples and samples that have been separated by float-and-sink in organic solvents should be thoroughly dried, and then allowed to come to equilibrium with moist nitrogen at a suitably controlled humidity. This prevents methane, solvents, etc. being determined as moisture. The controlled humidity can be chosen so that any change of weight on exposure to moist air is slow.

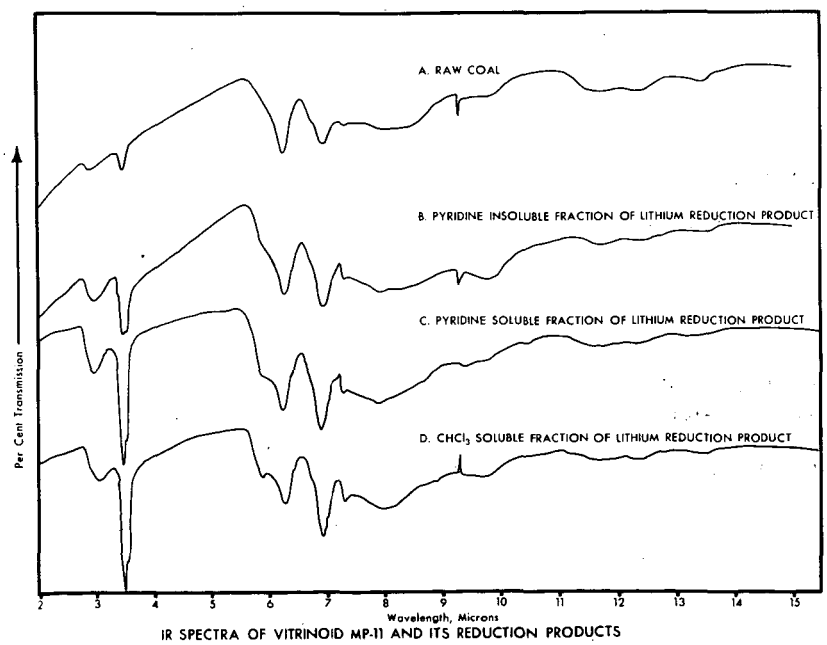
3. Ash should be determined separately, as in a proximate analysis; weighing the residue after the combustion for the C and H determination is not reliable.

4. Wherever possible, oxygen should be determined directly; by comparing the sum of the various determinations with 100% a valuable check on the correctness of the whole analysis is obtained.



NMR SPECTRUM OF $DCCl_3$ EXTRACT OBTAINED FROM Li REDUCED MP-10b

Figure 1



IR SPECTRA OF VITRINOID MP-11 AND ITS REDUCTION PRODUCTS

Figure 2

HEATING OF COAL WITH LIGHT PULSES

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Introduction

The carbonization of coal is normally carried out under conditions of relatively slow heating, the process taking many hours. During the past decade, interest has arisen in faster heating rates. Thus, the use of fluidized beds[1], circulating heated pebbles[2], and hot-gas[3] carbonization treatment has reduced the heating periods into the time range of seconds or less. Investigators have reported in detail carbonizations in time ranges as low as 60 milliseconds[3]. Nelson reported the use of flash heating on coal samples but did not detail his findings[4]. His technique resulted in one to three milliseconds exposure. The present work was undertaken to obtain further information on the effect of flash-heating on coal using even shorter exposures.

Experimental

The flash unit consisted of a flashtube holder, four 100μF capacitators, and a 4000V power supply. A GE FT524-Xenon-filled quartz helix flashtube was used. The flash unit was incorporated into a gas-handling system as shown in Figure 1.

The duration of flash is a function of the electrical circuit, particularly the capacitance and the resistance of the flashtube. By definition, the flash duration is considered to be the time from the initial 1/3-peak power to the final 1/3-peak. With a given tube, the length of the flash varies with the capacitance. The flash duration was determined from data supplied by the manufacturer[5], Table I.

TABLE I

Flash Characteristics

Capacity	Time above 1/3 power, μ sec. Max.	Min.	Input, joule	Output, j/sq. cm.*
100μF	230	195	800	3.7
200	-	305	1600	7.5
300	-	415	2400	11.2
400	800	520	3200	15

*The internal surface of the helix is 62 sq. cm.

The input energy dissipated in the flash was computed from the formula $E = 1/2\ CV^2$, where E is the energy in joules, C is capacitance in microfarads, and V is voltage in kilovolts. Thus, the FT524 tube emits 15 optical joules/sq. cm. for an energy input of 3200 joules. But, as seen above, the light energy output is considerably less than the input energy. Approximately 30 percent of the input energy was radiated into the test cylinder.

The experimental system used is shown in Figure 1. Usually 10 mg. of pulverized coal (less than 10 microns in size) were transferred into the quartz reactor and suspended on the walls by rotating the reactor. The reactor was then carefully placed into the helix of the flashtube, connected to the manifold, and evacuated. After flashing at the desired energy level, the pressure rise was measured and a gas sample was taken. The residual solids were sampled or weighed when necessary.

As the characteristics of both the lamp and the quartz reactor tended to change with time, test series designed to achieve specific goals were run closely together.

Results

A series of coals having increasing volatile matter content were studied. Their compositions and proximate analysis are shown in Table II.

TABLE II

Composition of Coals Used

Coal	Elkol[1]	Federal No. 1[2]	Kopperston No. 2[2]	Colver[2]
Proximate Analysis, %, dry basis				
Volatile Matter	40.7	37.7	31.6	25.3
Fixed Carbon	54.6	56.8	63.9	68.5
Ash (dry)	4.7	5.5	4.5	6.2
Ultimate Analysis, %, dry basis				
Carbon	70.6	78.4	85.1	80.6
Hydrogen	5.4	4.9	6.2	5.3
Sulfur	1.0	1.9	0.7	0.8
Nitrogen	1.2	1.5	1.5	1.5
Oxygen	17.1	7.8	2.0	5.6
Ash	4.7	5.5	4.5	6.2

[1]Kemmerer Coal Co., Frontier, Wyoming

[2]Eastern Gas and Fuel Associates, Pittsburgh, Pa.

The composition of the evolved gases from the last three coals is shown in Figure 2 through 4. As the energy of the flash is increased, the gas composition changes. Hydrogen increases, the volume percentage of C_2H_2 remains nearly constant, while the more saturated hydrocarbons decrease. CO_2 decreases, while CO increases.

The gas-composition trends are consistent with increased cracking of the evolved gases with the higher temperatures associated with the increased energy. Thus, the more saturated ethane and ethylene are replaced by acetylene. Also, methane may crack to acetylene. However, the acetylene may decompose to carbon and hydrogen.

It is of interest to relate the product concentration to the volatile matter of the coal. The younger coals show less hydrogen and methane in the product gas. However, increasing the energy input increases the concentration of both of these gases, Figure 5.

Tests were also run to determine the effect of various atmospheres on the product distribution. As stated previously, most of the experiments were run in vacuum. In a departure from this usual practice, nitrogen was added to serve as an absorber for the high energy believed existent in the products. It is seen in Table III that 10 mm. of N_2 had no significant effect, when compared with the vacuum runs.

TABLE III

Effect of Increased Pressure

200- x 325-mesh Elkol particles, 3200 joules input

Gas Composition, mol %	10 mm N_2	Control (vacuum 0.1 mm)
H_2	44.5	42.4
CH_4	0.9	0.7
C_2H_2	20	20.7
CO	24.5	25

The effect of hydrogen in repressing the decomposition reactions was investigated next. Two pressure levels were investigated. It is seen in Table IV that increasing the H_2 pressure decreases the C_2H_2 while increasing the CH_4. This is consistent with inhibiting the reaction.

$$2CH_4 \rightarrow C_2H_2 + 3H_2$$

Some saturation of the C_2H_2 could also have occurred. Increasing the pressure increased the effect. Two sets of control runs are quoted because the tests were run at different times and the physical conditions of the reactor, light, etc. had changed.

TABLE IV

Effect of Hydrogen

Elkol 5-10μ, 3200 joules energy input

	Mole % (on H_2-free basis)			
	Higher pressure comparison		Lower pressure comparison	
Gas Composition	160 mm H_2	control (0.1 mm vacuum)	10 mm H_2	control (0.1 mm vacuum)
CH_4	4.8	0.8	0.4	0.4
C_2H_2	9.5	25.0	25	37.8
CO	85	65.5	71	49

The effect of steam on the reaction was studied by adding a drop of water to the coal. As shown in Table V results are similar to those obtained with H_2.

TABLE V

Effect of Water

Elkol, 3200 joules energy input

Gas Composition, mol %	With H_2O	Without H_2O
H_2	48	59
CH_4	2.6	1.0
C_2H_2	8.2	14.7
CO	30.1	21.4
C_2's	4.9	2.7

In the above results, all changes were attributed to variation of the energy input. However, the exposure time varied concurrently. With the available set-up, it was not practical to vary the electrical circuitry. Mechanical screening of the coal proved most practical as a means of varying the energy at constant exposure time. The technique consisted of using a double quartz reactor and interposing three layers of 18- x 14-mesh metal screen between to cut down the adsorbed energy without affecting the time, Table VI. It is seen that the screen, by reducing the impinging energy, reduces cracking reactions.

TABLE VI

Effect of Energy Variation on Yield

Double Quartz Walls
Elkol coal, average particle size 5-10μ

	With Screen	Without Screen	Without Screen
Electrical Energy input	3200j	3200j	800j
Gas Composition, mol %			
H_2	16	59	44
CH_4	5.5	1.0	3.0
C_2H_2	4.2	14.7	12.0
CO	53	21.5	18
CO_2	7.7	0.4	2.3
C_2's	8.9	2.7	6.6
C_3's	2.0	-	1
C_4H_2	0.2	0.7	0.8

Mass balances around the reactor show recoveries of 74 to 110 percent. The weight of gas was determined from the pressure rise. The solid residue was washed into a Celite filter-aid bed for weighing. In none of the tests was there any evidence of tar formation. As seen in Table VII, the amount of gas produced varied randomly, reflecting poor reproducibility in exposing all of the coal to the flash. Some of the coal invariably fell to the bottom of the reactor during handling. Also, some coal obviously was blown from the reactor wall during the volatile-matter release.

TABLE VII

Mass Balances

All runs at 3200 joules energy input

Coal	Wt. Charged, mg.	Recovery, mg. Wt. Solid	Wt. Gas	% Recovered
Elkol	10.6	5.4	3.2	81
Elkol (N_2 run)	10.2	5.5	6.2	115
Elkol (H_2 run)	10.4	6.9	4.0	105
Elkol (H_2 run)	11.3	8.6	3.8	108
Johnstown	9.7	8.5	1.7	105
Johnstown	10.7	6.7	1.8	80
Johnstown	10.1	8.5	2.5	110
Powhattan	10.1	6.3	2.9	92
Powhattan	10.0	7.6	2.8	104
Illinois No. 6	10.4	8.8	1.4	98
West Virginia	10.3	4.8	2.8	74
West Virginia	9.7	6.0	2.6	89

Since the distribution of solids and gas did not give a realistic estimate of the percentage of coal volatilized, various other techniques for obtaining this parameter were investigated, but none were successful.

Microscopic examination of the residues showed the presence of carbon-black particles. The presence of these particles could be interpreted as being the residue of almost completely vaporized coal particles or the final product of a hydrocarbon-cracking sequence. A variety of tests were therefore devised to clarify this point.

1) In order to preserve as much of the hydrocarbons as possible, an even faster quench was attempted. A special reactor vessel with a central cooling thimble was constructed by suspending a small 4-inch test tube within

a larger one. The thimble was filled with either a dry ice-acetone mixture or liquid nitrogen. At first, the cold thimble was placed above the top of the flash tube. Black sooty material was found all over the condenser indicating that gas-phase decomposition could have occurred. The thimble was lowered until it was finally completely within the flash zone. When liquid nitrogen was used, the thermal shock shattered the glass apparatus. However, the sooty appearance of the condensed particles persisted.

2) Attempts were made to distinguish microscopically between unreacted coal, char and acetylene black. The fineness of the starting material made direct decision among the possibilities impossible. Attempts to produce very uniformly sized coal were essentially unsuccessful. It was finally decided to attempt direct comparison by photographing specific areas of slides before and after flashing. The results are shown in Figure 6. The A designation indicates that the picture was taken before flashing, the B, after flashing. The grid was superimposed on the slides during printing and serves to locate points of interest. It can be seen that large clumps of coal were blown off the slide by the flash. For example, compare Figure 6A - B areas 7D, 2F. Some glass was blistered as in Figure 6B, areas 8D, 9F. Important observations can be made in Figure 6A - B, areas 8D, 8E - F. Here particles can be identified before and after exposure (note in particular the particle shaped like the state of New Jersey in the upper center of 8D). The particles are essentially similar in shape before and after the flash, thus indicating that complete decomposition of the coal has not occurred. Obviously these coals were not screened from the flash, as any particle which could be seen by the camera should also have been exposed to the flash. The conclusion therefore must be that only partial vaporization or decomposition of the coal particles occurred. However, the exact magnitude cannot be determined since the coal particles expand during the coking process.

Conclusions

Flash heating is a practical technique to produce short periods of high temperature in coal particles. The percentage of coal volatilized could not be determined, but microscopic examination suggests that total vaporization did not take place. No liquids were recovered, but the gases, whether produced directly or indirectly by cracking of precursor tars, contained many valuable constituents.

Acknowledgment

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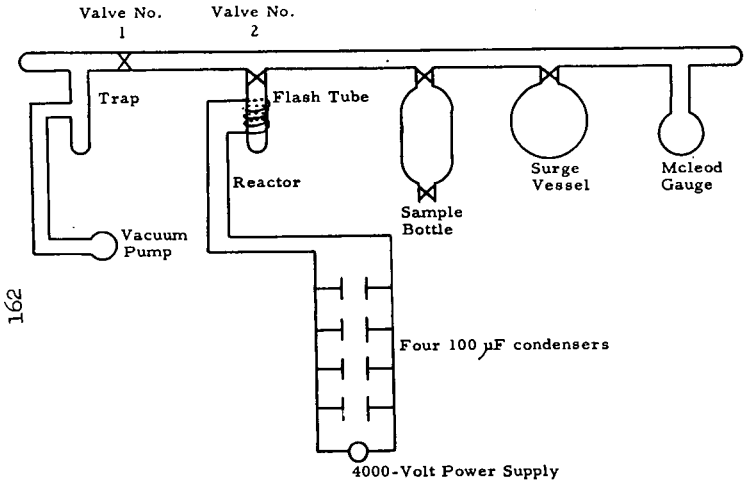


FIGURE 1: Flash heating system

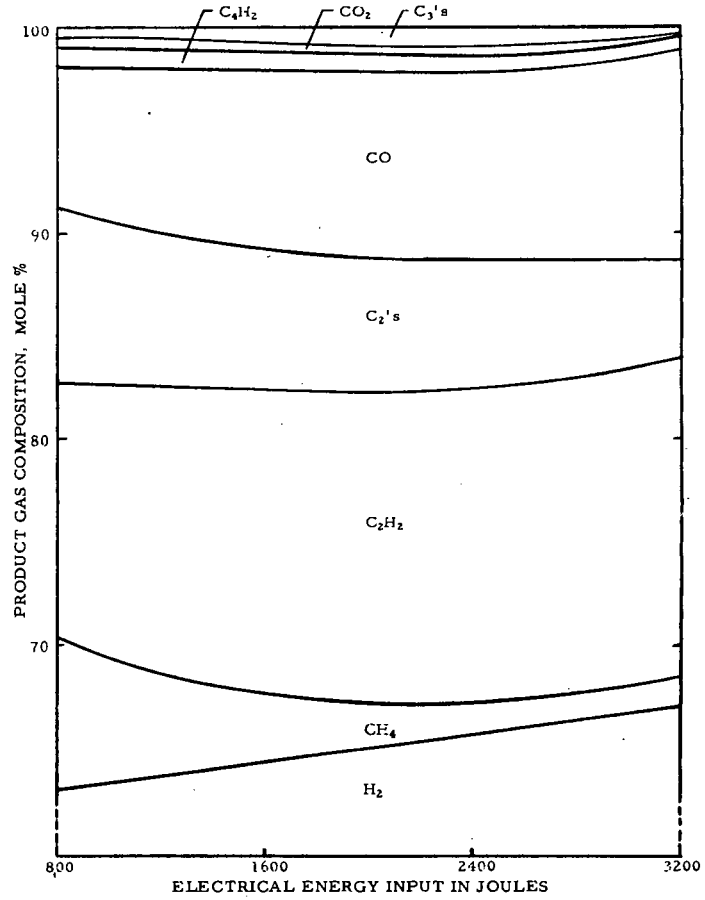


FIGURE 2: Gas composition from flash heating of Federal No. 1 coal (-400 mesh then pulverized), Quartz reactor

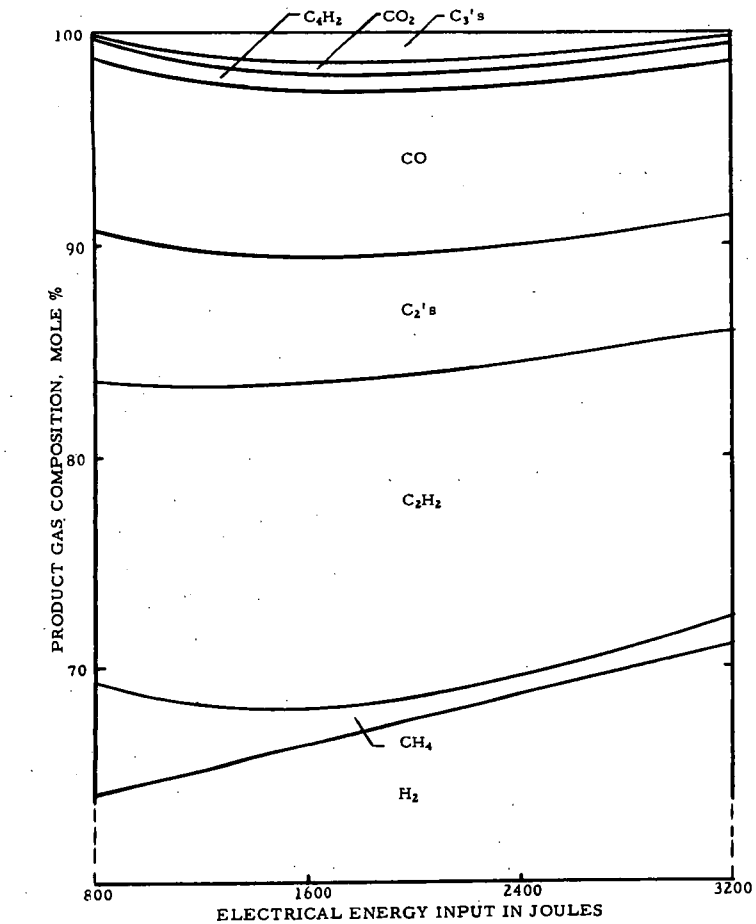


FIGURE 3: Gas composition from flash heating of Kopperston coal (-400 mesh then pulverized), Quartz reactor

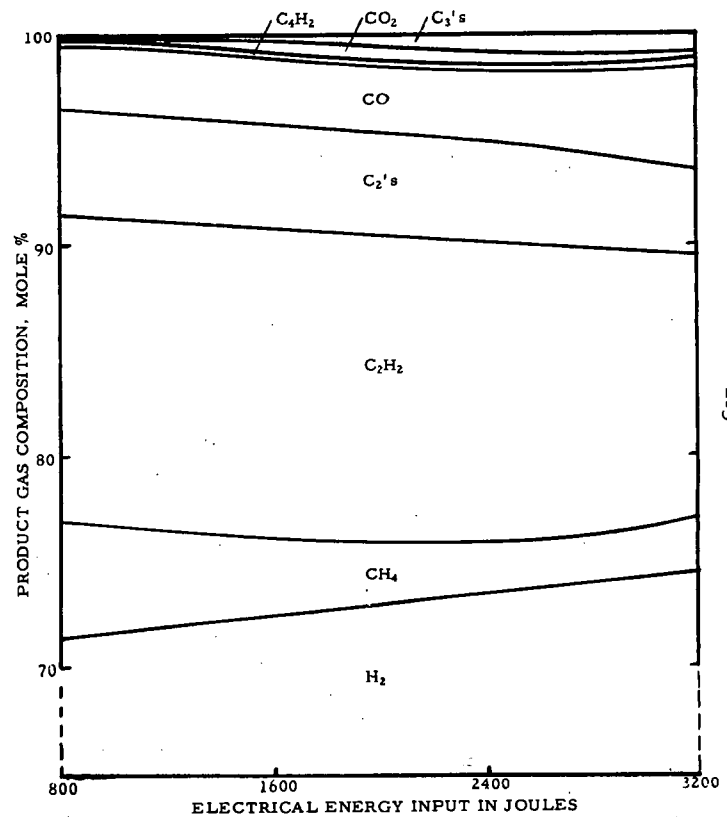
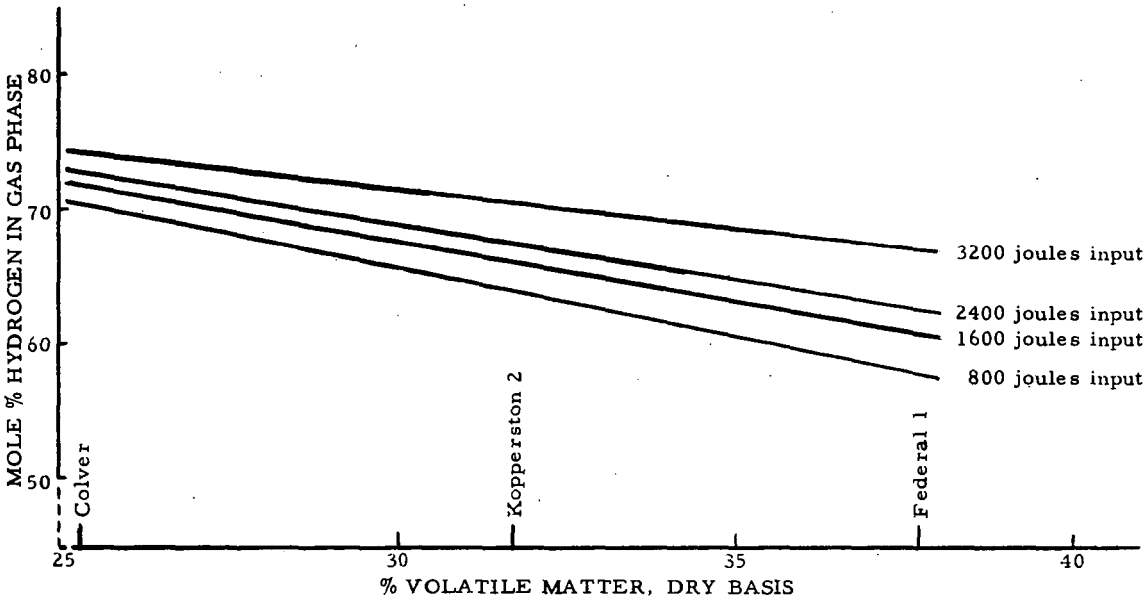


FIGURE 4: Gas composition from flash heating of Colver coal (-400 mesh then pulverized), Quartz reactor



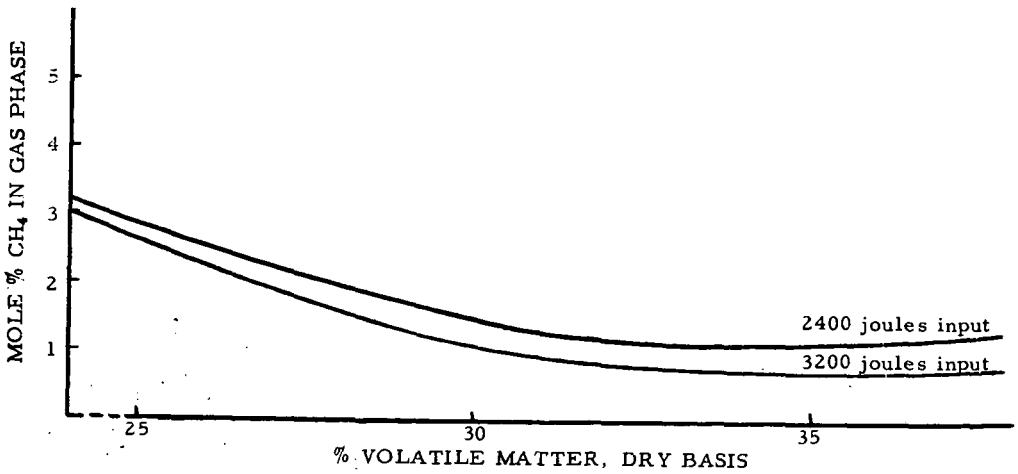


FIGURE 5: Relationship of H_2 and CH_4 concentrations to volatile matter of coals

FIGURE 6A: Before flash Each scale division = 2 microns
Energy of flash 3200 joules.
Elkol, powdered, then twice elutriated to separate out the fines; average particle size about 5 microns.

FIGURE 6B: After flash Each scale division = 2 microns
Energy of flash 3200 joules.
Elkol, powdered, then twice elutriated to separate out the fines; average particle size about 5 microns.

Extensive Reduction of Coal by a New Electrochemical Method

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In recent years electrolytic methods have been employed in the reduction and structural elucidation of coal (1, 2). The usefulness of these methods is limited by the fact that the benzene ring (that is, the isolated benzene ring as in benzene or tetralin) which may represent a large portion of the coal structure, has not previously been reduced electrolytically. Work in this laboratory has shown that reduction of benzene can be achieved by electrolysis in ethylenediamine saturated with lithium chloride (3). The same method has now been successfully applied to the reduction of a high rank coal and has resulted in the addition of 36 hydrogens per 100 carbon atoms. The best electrochemical reduction achieved (2) prior to this amounted to the addition of 14 hydrogens.

EXPERIMENTAL

Six grams of the coal (Pocahontas vitrain ground to pass 325 mesh) suspended in 100 milliliters of ethylenediamine containing 1.4 grams of lithium chloride was electrolyzed at 33° between carbon electrodes at 0.5 amperes and 115 volts. Apparatus and technique of electrolysis (3) and recovery of the reduced coal (4) were the same as described previously. Current efficiency at the beginning of the electrolysis was 46 percent and dropped to 10 percent after 16 hours. The electrolysis was continued for an additional 15 hours during which time the current efficiency remained practically constant. The reduced coal was recovered from the solution, analyzed and subjected to a second electrolytic reduction. The current efficiency at the beginning of the second electrolytic reduction was 20 percent and dropped to 8 percent after 16 hours. The electrolytis was continued for 15 hours during which time the current efficiency remained at 8 percent. Recovery of the reduced coal was 95 percent. The reduced coal was tan-gray in color and 73 percent soluble in pyridine; the solubility of the unreduced coal was only 3 percent. The analyses of the original and reduced samples are shown in Table 1. The ratio of total hydrogen taken up by the coal to lithium chloride used was about 2:1.

DISCUSSION

Perhaps the most interesting result is the fact that the solubility of the electrolytically reduced coal in pyridine at room temperature (73 percent) is higher than that of the same coal reduced chemically (4) with excess lithium in ethylenediamine at 90-100°. In the latter case, 45 hydrogens were added but the solubility was only 63 percent. It is conceivable that chemical reduction at elevated temperature, in contrast to electrolytic reduction at room temperature, is accompanied by polymerization resulting in a decrease in solubility.

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TABLE 1. - Electrochemical reduction of Pocahontas vitrain

Substance	C	H	N	S	Ash	H atoms added[a] per 100 C atoms in starting material
Original vitrain	87.94	4.53	1.12	1.01	3.10	
	88.09	4.58	1.15	0.97	2.98	
First reduction	81.82	6.29	2.93	1.12	3.97	21.1
	81.77	6.15	3.29	1.21	3.76	
Second reduction	80.81	7.21	3.82	0.31	3.85	36.1
	80.73	7.19	3.80	0.51	3.21	

[a] Method of calculation as described in reference 4.

Destruction of the Caking Quality of Bituminous Coal in a Fixed Bed

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INTRODUCTION

Production of a high-Btu pipeline gas from coal appears to have great potential for consuming coal in large quantities. Fixed-bed pressure gasification with steam and oxygen is highly attractive for the production of high-Btu gas because a gas with a high methane content is made with comparatively low oxygen requirements. However, strongly caking coals cannot be gasified efficiently in a fixed bed because they agglomerate and fuse when heated through their plastic range. This would render a fixed-bed gasifier inoperable. Most coals found in the East and Midwest, where the largest markets for pipeline gas exist, are highly caking.

Numerous commercial processes[1, 2, 3] have produced a noncaking fuel from bituminous coal for many years; however, each was developed for a specific purpose other than for fixed-bed gasification, and was not particularly suited as a preliminary to gasification. Consequently an experimental pilot plant program was initiated by the Bureau of Mines to develop a process for pretreating a caking bituminous coal specifically for fixed-bed gasification. Based upon the general knowledge that thermal or oxidative treatment or a combination of the two destroys the caking property of coal, a process was envisioned which would utilize the above. An integrated pretreatment and gasification scheme appeared advantageous whereby all or part of the feed gases to be fed to the gasifier, or the hot, raw product gas could be used in the pretreatment, and the volatile matter evolved during pretreatment could be returned as fuel to the gasifier.

Use of thermal pretreatment in an oxidizing atmosphere for treating a highly caking coal of granular or small lump size in a fixed bed presented difficult problems. To make particles of this size nonagglomerating, the treatment would have to be drastic enough not only to affect the surface, but also the interior. Furthermore, because the coal expands on heating, compaction in a fixed bed would be difficult to avoid.

Therefore, the purpose of this investigation was first to determine whether the caking properties could be destroyed sufficiently in a fixed bed, and secondly to determine the conditions requiring the minimum time and

effecting the minimum loss of coal. The criterion of successful pretreatment would be that the pretreatment could be completed without agglomeration, and that after pretreatment the coal would not agglomerate in a hydrogen-rich atmosphere at conditions of temperature and pressure similar to those in a fixed-bed gasifier.

EXPERIMENTAL EQUIPMENT AND PROCEDURE

Description of Apparatus

The schematic flow diagram of the pilot plant for coal pretreatment given in figure 1 consists primarily of a gas heater and a vessel in which the coal can be heated and exposed to various atmospheres at controlled rates. The vessel is a 4-foot long, 3-1/2-inch diameter schedule 80 pipe made from 347 stainless steel. It is shown in figure 2. A ring joint blind flange served as a charge port and closure at the top of the vessel. The bed of coal was supported by a perforated stainless steel plate located 2 inches above the bottom of the vessel as shown in figure 3. During all pretreatment tests the coal was always heated externally by electric heaters and internally by the pretreating gas. The gas was heated by passing it through a coiled tube located in an electric furnace.

Gases flow normally up through the coal and out of the top of the vessel; however, several tests were performed with gases flowing down through the bed. Either nitrogen, carbon dioxide, or steam, or a mixture of these gases was satisfactory for pretreatment. In the remainder of this report the term "inert gas" is used to represent any of these gases. In some steps oxygen was also required, and this is specified in the procedure.

Temperatures of the bed were measured by thermocouples inserted in thermowells located in the center and at the periphery of the pretreater vessel. Thermocouples were adjustable and normally measured the temperature of the top, center, and bottom of the bed. The thermowells entered the bottom of the vessel and extended within one foot of the top flange. A differential pressure instrument measured and recorded the pressure drop across the fixed bed of coal. Temperature, pressure, and flow control are provided for at the panel shown in figure 4.

Procedure

The following steps of pretreatment destroyed the caking property of a bituminous coal in a fixed bed,

1. Coal, from 1/8- to 1-1/2-inch size, was heated from ambient temperature to its initial softening temperature as rapidly as possible with an inert gas. This temperature varies with the type or rank of coal, and usually is higher than the softening temperature indicated by the Giesler Plastometer Test (ASTM D-1812-60T).

2. Coal was held at softening temperature for about 1 to 3 hours with an inert gas containing about one volume percent of oxygen. About 17 percent of the volatile matter was removed during this step.

3. Coal was heated through its plastic range in about 1/2 to 1 hour with a superficial linear gas velocity that varied from 0.6 to 12 feet per second, depending upon the pressure and the oxygen content of the inert gas. An additional 33 percent of the volatile matter was removed, leaving about 50 percent of the original volatiles in the pretreated char.

As an alternate to steps 2 and 3, the coal could be effectively pretreated by gradually heating through its plastic range in about 3 hours. A pretreatment was considered successful after the coal was heated through its plastic range without agglomeration in a fixed bed. The char so produced flowed as freely as the original coal.

Testing of Chars and Coals

An arbitrary test was devised in which chars produced by pretreatment were exposed in a fixed bed to hydrogen or hydrogen-rich atmospheres for 1 hour at 400 psig and 600° C. The hydrogen-rich atmospheres contained nigrogen, steam, carbon dioxide, and carbon monoxide. These tests simulated gas compositions and conditions which would be found in a coal gasifier. Chars produced from coals heated through their plastic range without caking in a fixed bed never caked during these tests, indicating a strong probability that a char so produced would not cake in an actual gasifier. Coals not heated through their plastic range invariably caked during the hydrogen test.

Free swelling index (FSI) ASTM Test D-720-57 values of about 1.5 or less, which is usually indicative of a noncaking coal, were recorded for all chars made from coals pretreated through their plastic range. Chars with FSI values were used as a guide in estimating the caking property of chars produced during pretreatment. The ultimate and proximate analyses of coals tested and chars produced were performed according to ASTM procedure D-271-48.

Material

High-volatile A bituminous (hvab) coal from the Pittsburgh seam, one of the most strongly caking coals, was used in most of the pretreatment tests. Hvab coals from Sewickley, Upper Freeport, and Taggart seams, in addition to a high-volatile (hvbb) coal from the Illinois No. 6 seam and a low-volatile bituminous (lvb) coal from the Pocahontas No. 4 seam, were also tested and successfully pretreated. Analyses of coals tested are shown in table 1.

RESULTS

An example describing a successful pretreatment is as follows: A Pittsburgh seam coal was heated with steam, at atmospheric pressure, containing about 1 percent oxygen and flowing at a superficial velocity of 3 feet per second, to its initial softening temperature of 360°-370° C and maintained at that temperature for 3 hours. It was then heated through its plastic range of 370° to 430° C in about 1/2 hour with the same gas at the same velocity and pressure. The treatment was terminated with nitrogen

TABLE 1.- Source, analysis, free swelling index, rank, and heating value of coals tested

County, bed, mine	Proximate, percent				Ultimate, percent					Heating value, Btu (dry basis)	Free swelling index	Rank 1/
	Moisture	Volatile matter	Fixed carbon	Ash	H	C	N	O	S			
Illinois												
Franklin Illinois #6 Old Ben #21	8.0	35.4	50.0	6.6	5.5	70.6	1.7	14.7	0.9	13,550	4.5	hvbb
Pennsylvania												
Allegheny Pittsburgh Federal Bureau Mines, Experimental	2.5	35.6	54.3	7.6	5.3	75.8	1.5	8.2	1.6	13,960	8.5	hvab
Butler Upper Freeport Coal Hollow #2	1.7	35.3	55.9	7.1	5.3	76.9	1.5	7.9	1.3	14,020	8.0	hvab
Virginia												
Wise Taggart Dixiana	1.4	33.8	62.3	2.5	5.3	82.8	1.5	7.2	0.7	14,980	8.5	hvab
West Virginia												
McDowell Pocahontas #4 Bartley #1	2.7	14.8	76.5	6.0	4.4	88.3	1.3	4.5	0.5	14,660	6.5	lvb
Monongalia Sewickley Christopher #5	1.1	36.7	50.9	11.3	5.1	73.3	1.5	6.2	2.6	13,400	8.0	hvab

1/ American Society of Testing Materials, Standard Specifications for Classification of Coals by Rank: ASTM Designation D-388-38 ASA M20.1-1938.

cooling the char to less than 100° C in about 1/2 hour. An inert gas containing nitrogen and carbon dioxide was also used to cool the pretreated coal during other tests. A free flowing char was produced with a FSI indicative of noncaking coal. The treated coal expanded about 50 percent above its original volume.

Heating coal with this same gas through its plastic range in 3 hours also produced free flowing char. Replacing steam with nitrogen or nitrogen plus carbon dioxide or a combination of all three gases plus a small amount of oxygen destroyed the caking property of coal in a fixed bed as effectively as the steam-oxygen mixture.

Heating coal, as described previously, with a gas containing 0.2 percent oxygen plus 11 to 40 percent hydrogen and the remainder nitrogen, carbon dioxide, and steam produced a solid mass of char with no evidence of pretreatment. This was an attempt to pretreat coal with a gas similar in composition to a gas produced in a coal gasifier.

The pretreatment technique developed in a 6-inch bed depth at atmospheric pressure with gas flowing up through the bed also proved effective in an 18-inch bed depth with the gas flowing up or down. The bed expanded less during the tests with the gas flowing down; however, the char produced was free flowing and showed no evidence of fusion.

Pretreatment at pressures of 50, 150, and 300 psig in a 6-inch bed depth also was effective. Char produced at elevated pressures normally exhibited less expansion than that made at atmospheric pressure.

The caking quality of hvab coal from the Sewickley, Upper Freeport, and Taggart seams was as effectively destroyed as the Pittsburgh seam coal. Of the four hvab coals tested, Pittsburgh and Upper Freeport seams required about 180 minutes of treatment at 360° to 430° C as compared to about 190 and 200 minutes, respectively, for the Taggart and Sewickley seams. The volatile matter of all hvab coals decreased during pretreatment from about 36 to 20 percent. Pretreatment of the hvbb coal from the Illinois No. 6 seam with a high inherent moisture content of about 8 percent was relatively easy, requiring only 80 minutes at 360° to 430° C. A low-volatile bituminous (lvb) coal from the Pocahontas No. 4 seam containing about 15 percent volatile matter was successfully pretreated at its plastic range of 470° to 510° C in about 2 hours with steam plus oxygen. The volatile matter content decreased from 15 to 9 percent during pretreatment. Analyses of chars produced from these coals during typical pretreatment are shown in table 2.

Expansion of coal during pretreatment was related to gas velocity and pressure. Low velocities or high pressures produced less expansion. Coals with high volatile matter content appeared to expand more. Pretreatment appeared more difficult for hvab coals with a low oxygen content.

Pretreatment at gas velocities approaching fluidization velocities of about 13 feet per second appeared easier and required about 2 hours at 360° to 430° C as compared to 3 hours at a velocity of 3 feet per second. At high gas velocities, the oxygen concentrations in the pretreating gas were varied

TABLE 2.- Analysis, free swelling index and heating value of chars produced during pretreatment with steam containing 1 to 3 volume percent oxygen at atmospheric pressure

Char prepared from bed	Proximate, percent				Ultimate, percent				
	Moisture	Volatile matter	Fixed carbon	Ash	H	C	N	O	S
Illinois #6	0.7	23.3	66.4	9.6	4.3	75.2	1.9	8.1	0.9
Pittsburgh	.3	20.9	71.9	6.9	4.1	78.9	1.7	7.4	1.0
Upper Freeport	.5	22.6	66.8	10.1	4.2	76.0	1.7	6.6	1.4
Taggart	.2	23.1	73.2	3.5	4.4	83.6	1.6	6.3	0.6
Pocahontas #4	.8	8.9	81.8	8.5	3.1	82.8	1.3	3.8	.5
Sewickley	.6	22.1	62.9	14.4	4.0	71.8	1.6	6.4	1.8

Char prepared from bed	Heating value, Btu (dry basis)	Free swelling index	Maximum pretreatment, temp., °C
Illinois #6	13,220	NC[1/]	430
Pittsburgh	13,580	NC	430
Upper Freeport	13,300	1.0	430
Taggart	14,560	1.5	430
Pocahontas #4	13,830	NC	510
Sewickley	12,460	1.5	430

1/ NC = Noncaking.

from 0.5 to 4.0 percent with good results, whereas at gas velocities of 3.0 feet per second, oxygen content was limited to a range of about 1.0 to 3.0 percent. Low oxygen concentration in the gas is desirable because it allows for close control of the temperature. In tests with oxygen concentrations above 5 percent, temperature control was difficult because of excessive localized combustion.

Figure 5 shows a typical raw coal used plus a char from a successful pretreatment, and the same char after exposing it to a hydrogen flow at 400 psig and 600° C for 1 hour in a fixed bed. There was no evidence of fusion and the char flowed as freely as raw coal. All chars produced during successful pretreatment and subjected to this test did not fuse, or show any evidence of fusion.

Char produced in the manner described from a Pittsburgh seam coal was successfully gasified in a bench-scale, fixed-bed reactor with steam at 800° C and atmospheric pressure at the Bureau of Mines Coal Research Center in Morgantown, W. Va. There was no evidence of caking during gasification, and the results indicate that the char is quite reactive. Even mildly caking coals agglomerated in similar tests.

Tests performed by the Direct Coal-Conversion group at the Bureau of Mines Coal Research Center in Bruceton, Pa., in bench-scale equipment show that the same char as above could be hydrogenated at 3,000 psig and 750° C in free-falling bed without agglomerating. The char was crushed to a 30 x 50 U.S. Tyler mesh size for the hydrogenation tests.

DISCUSSION OF RESULTS

Results from tests performed at conditions other than those outlined in the procedure for successful pretreatment indicate the need for close adherence to the procedure. Several of these tests are described: Coal particles heated directly through their plastic range with inert gas in a fixed bed fused into a solid mass as shown in figure 6. Coal particles heated slowly through their plastic range with a gas containing 11 to 40 percent hydrogen plus 0.2 percent oxygen and the remainder nitrogen, carbon dioxide, and steam, also fused into a solid mass similar to the one shown in figure 6. This test was an attempt to pretreat coal with a gas which was similar in composition to a gas produced in a coal gasifier.

Coal heated at its softening temperature of 360° to 370° C with inert gas plus oxygen for 3 to 8 hours, and not heated through the plastic range, also fused upon subsequent exposure to hydrogen at 400 psig and 600° C; however, as shown in figure 7, there was some evidence of pretreatment since discrete coal-char particles were discernible in the fused mass.

Investigators[4, 5] have shown that oxygen was necessary for the reduction or destruction of the caking quality of coal in fluidized or moving fixed beds; however, evidence of complete and relatively rapid destruction of the caking property of coal in a stationary fixed bed was lacking. Consequently, the techniques as previously described were developed using small amounts of oxygen and a controlled heating cycle to destroy the caking quality of coal

in a fixed bed. The role that oxygen plays in helping to destroy the caking property of coal in a fixed bed is not precisely known. However, it is theorized that the "sticky" matter which is normally formed when coal is heated through its softening and plastic range is oxidized to a "nonsticky" material.

The apparent differences in pretreatment time for the coal tested can also be attributed to oxidation. According to Radmacher[6] the rate of oxidation; that is, "the rate of decaking", is generally dependent on the oxygen content of the coal. On the other hand, Schmidt[7] reports that a lvb coal with a low oxygen content was also relatively sensitive to oxidation. This appears to confirm our findings since the hvbb coal from the Illinois No. 6 seam, having the highest oxygen content of about 9.0 percent, required a minimum pretreatment time of about 80 minutes. A pretreatment time of about 120 minutes was required for the lvb coal from the Pocahontas No. 4 seam, which contained about 2.4 percent oxygen.

Pretreatment time for the hvab coals generally was related to the oxygen content. The Pittsburgh and Upper Freeport coals, having an oxygen content of about 7.0 percent, required about 180 minutes of pretreatment, followed by about 190 minutes for the Taggart seam and 200 minutes for the Sewickley seam. Both Taggart and Sewickley seams had a slightly lower oxygen content of about 6.0 percent. The slight difference in pretreatment time for these two coals could be attributed to the differences in volatile matter content, since the Taggart seam had a volatile matter content of about 35 percent compared to 42 percent for the Sewickley seam.

Chars produced from hvab and hvbb coals containing a volatile matter content of 20 percent or less always had a FSI indicative of a noncaking coal. On the other hand, even after it was heated at temperatures that destroyed the caking quality of hvab coals, a lvb coal with a volatile matter content of about 16 percent maintained a FSI of about 5.0 that is indicative of a good caking coal. This would indicate that the caking quality of a coal or char was not directly dependent upon the quantity of volatile matter it contained.

To get an insight into what was occurring to the volatile matter content and FSI of a coal during pretreatment, a series of tests was performed at different maximum temperatures. Each test of the series was performed with a 600-gram batch of Pittsburgh seam coal treated with steam plus 1 percent oxygen at atmospheric pressure at a gas velocity of 3 feet per second. Each batch was heated directly to 360° C in 25 minutes. After reaching 360° C, each individual batch of coal was heated to a designated temperature at 10° C intervals from 360° to 430° C. The coal was heated at a rate of 10° C per 25 minutes. Each test was concluded by rapid cooling with nitrogen as previously described.

Analysis of char taken at 10° C intervals during the gradual heating of a Pittsburgh seam coal through its plastic range indicates little change in the FSI from 360° to 400° C. Heating to 410°, 420°, and 430° C effected a rapid decline in the FSI of the coal-char to 4.5, 2.5, and 1.5, respectively. As shown in figure 8, the volatile matter content of the coal rapidly

decreased, following the same pattern as the FSI for every 10° C increase above 400° C. Each 10° C increase was accompanied by an increase in pretreatment time of 25 minutes; thus devolatilization was a function of both temperature and time.

The pretreatment technique developed offers promise, from an economic standpoint, as part of an integrated coal pretreatment and high pressure steam-oxygen-coal gasification process. The pretreatment can be performed at gasification pressure and part or all of the steam and a small part of the oxygen fed to the gasifier can be used as in the pretreatment. Furthermore, the gases and tars produced in pretreatment can be fed directly to the gasifier as fuel. Not only would this conserve energy, it would solve the effluent or off-gas problem from the pretreater. It is also conceivable that the pretreater vessels could serve as feed lock-hoppers for the pressure gasifiers, thus decreasing the net capital investment of the pretreatment.

CONCLUSIONS

A pilot plant study has shown that the caking property of a bituminous coal can be eliminated by pretreatment in a fixed bed. The caking quality of hvab, hvbb, and lvb coals was destroyed either by prolonged heating at the softening temperature followed by rapid heating through the plastic range with an inert gas containing a small amount of oxygen or by rapid initial heating followed by prolonged heating through the plastic range.

There was some variation in the conditions required for treating each coal, but generally hvab coals required about 180 minutes of pretreatment as compared to about 80 minutes for the hvbb coals. The chars produced did not cake when exposed to a hydrogen atmosphere at 600° C and 400 psig, indicating their suitability for use in fixed-bed gasification. The FSI served as a guide to indicate that the coal was no longer agglomerating. For most chars there was no agglomeration when the FSI declined to about 1.5 or lower.

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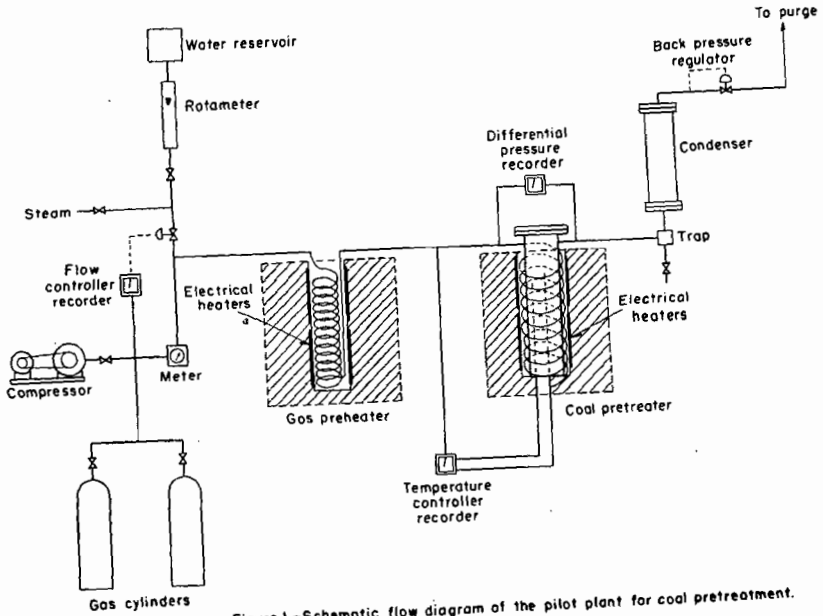

Figure 1.–Schematic flow diagram of the pilot plant for coal pretreatment.

Figure 2

A View of the Vessel in Which the Coal is Pretreated.

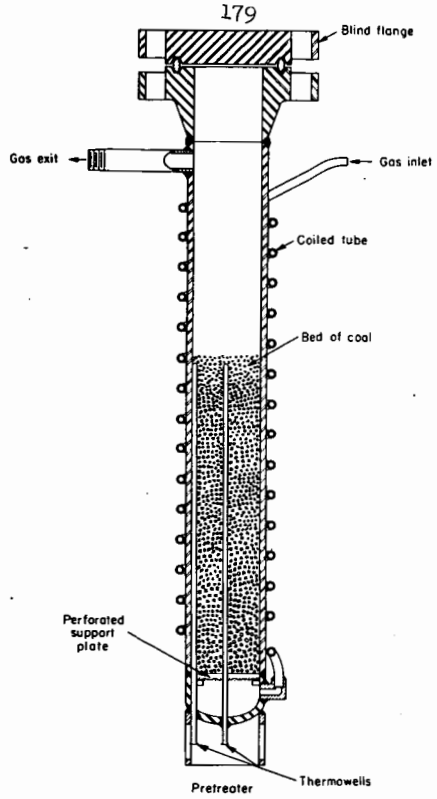

Figure 3.—Cross-sectional view of the coal pretreater vessel.

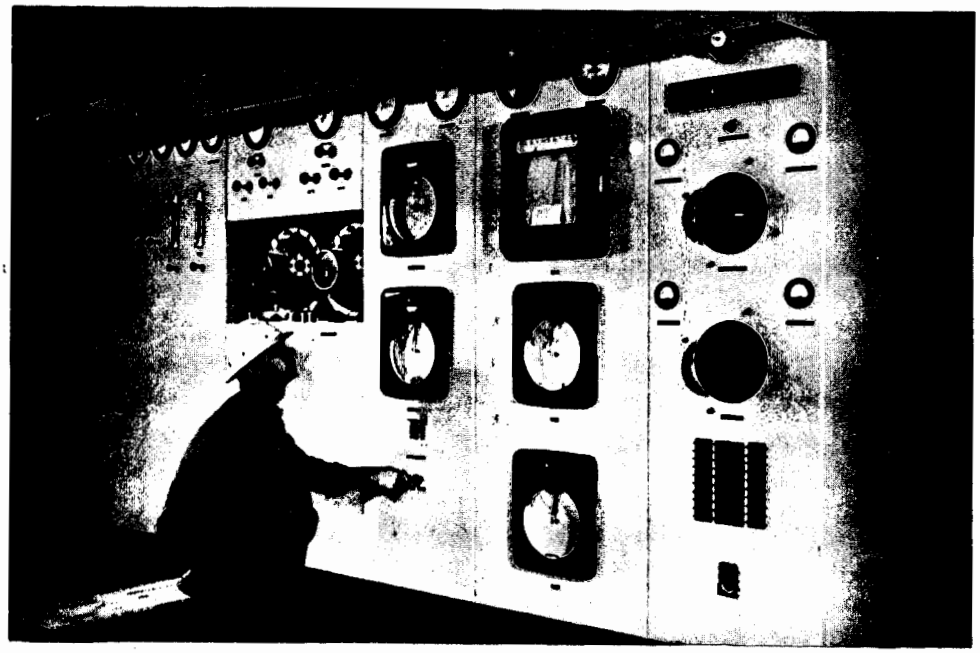

Figure 4. A view of the control panel for the coal pretreating pilot plant.

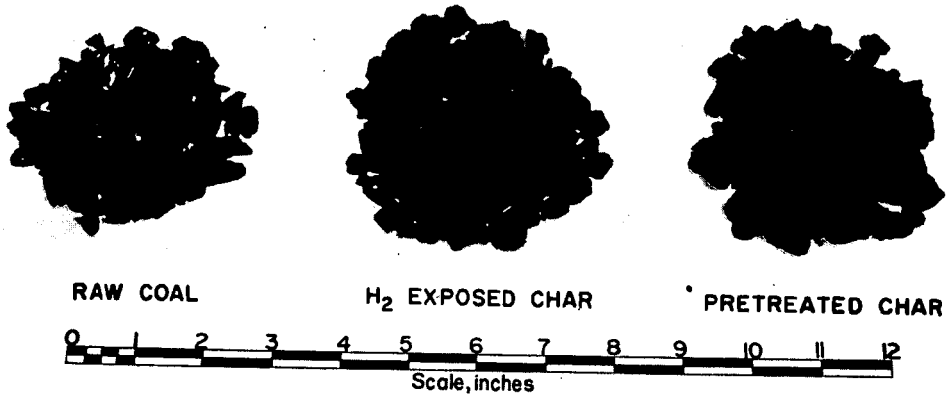

Figure 5. Raw coal used plus char from a typical pretreatment at 430 C and the same char exposed to hydrogen for 1 hour at 600 C and 400 psig.

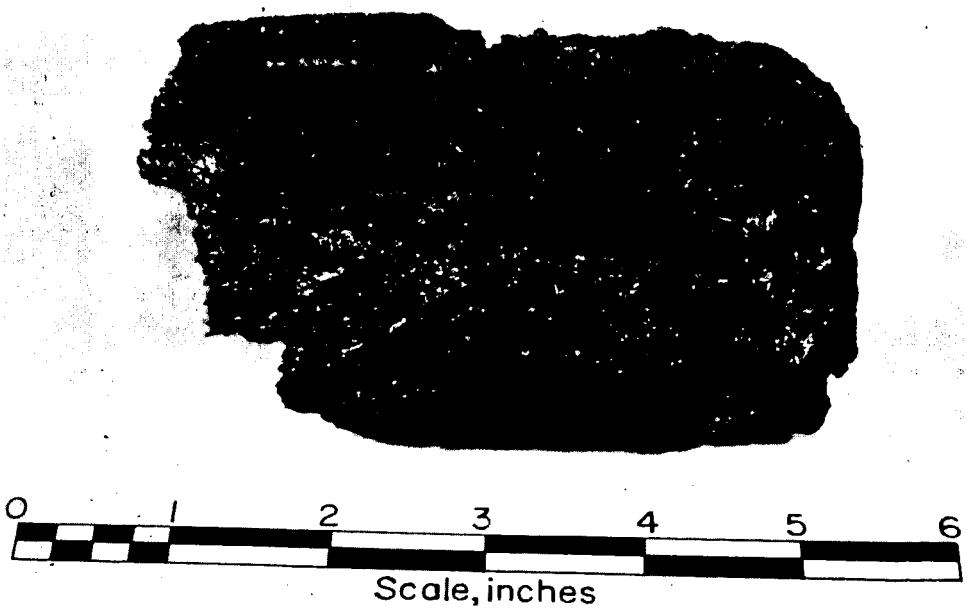

Figure 6. Solid mass of char made from coal with no pretreatment.

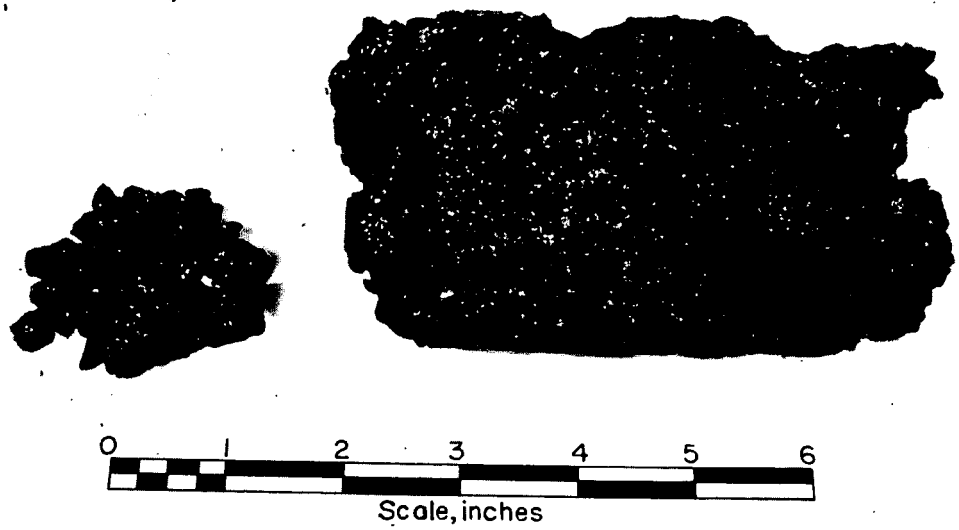

Figure 7. Mass of char containing discrete coal-char particles made from coal with some pretreatment.

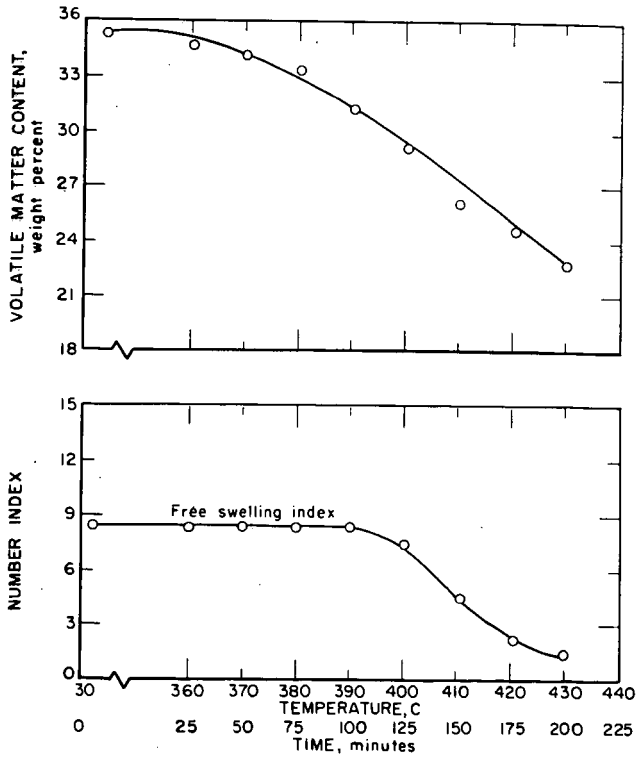

Figure 8.—Effect of temperature and pretreatment time on the free swelling index and volatile matter content of a Pittsburgh seam coal.

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The Destruction of the Caking Properties of Coal By Pretreatment in a Fluidized Bed

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INTRODUCTION

Gasification of coal to make a synthesis gas that can be converted to fluid fuels is a means of supplementing the country's liquid and gaseous fuel supplies while at the same time increasing the market for coal. A large market for these fuels exists near the eastern coal-fields, but, unfortunately, eastern coals do not readily yield to gasification in commercial fixed-bed and fluidized-bed gasifiers. They become plastic and agglomerate when heated to the gasification temperature, the permeability of the bed to gas is reduced, and objectionable channeling occurs. The Bureau of Mines is investigating methods of pretreating coals to destroy their caking properties in order to overcome these obstacles to gasification. The ultimate objective is to develop a low cost process. The first phase of the work consisted of pretreatment studies in a fluidized bed using various fluidizing gases and operating conditions. The studies were conducted with strongly caking coals, typical of those in the East. The results of the study and the operating requirements necessary to destroy the caking properties of the selected coals are reported.

Other research has been done on methods to destroy the caking properties of these coals. Chanabasappa and Linden[1] pretreated coal to make a char for hydrogasification. They operated at 400° to 700° F using a steam feed of 4-5 standard cubic feet per pound bituminous coal. The time of treatment was 60-75 minutes. Nathan[2] patented a fluidized process for pretreating coal at a temperature of 316° to 441° C, requiring 10-60 minutes and using 0.02-0.08 pound of oxygen per pound coal feed. Char was recycled for temperature control. Karl[3] preheated bituminous coal to less than 400° C with a gas containing oxygen. Sylvander[4] also preheated coal, to a temperature below the plastic range, using oxygen. Welinsky[5] operated a fluidized carbonizer, the first stage at temperatures within the plastic range of the coal (725° to 825° F).

Recycle char from the second stage is added to the feed in the first. Foch[9] carbonized coal in a three-stage system. He dried and preheated coal to 570° to 750° F in the first stage using gases resulting from partial combustion of pyrolysis gases from the second stage. The preheated coal in the second stage is carbonized using preheated air. The char is cooled in the third stage.

When a caking coal is heated it becomes viscous and plastic at a given temperature range that is characteristic of the coal. This property makes caking coals nonusable in fluidized-bed and fixed-bed gasifiers because the coal sticks to the walls and the particles agglomerate. The Bureau investigated a combined thermal and mild oxidation treatment to destroy in a fluidized bed the caking properties of typical coals found in the eastern United States. Although the method described in this paper was successful it is not known definitely why the pretreatment makes the coal nonagglomerating. It cannot be attributed entirely to oxidation of the surface of the particles, because the resultant char contains less oxygen than the original coal. (See table 1.) Rapid thermosetting of the liquid phase as it forms may be an explanation, but this needs to be confirmed by experimental studies that are beyond the objectives of the investigation.

A variable study was made to determine operable conditions for pretreating the coal to a nonagglomerating state in the minimum time with the least loss of valuable components.

APPARATUS AND EXPERIMENTATION

A flowsheet of the bench-scale unit is shown in figure 1 and a photograph of the unit is shown in figure 2. The reactor is a 1-inch diameter stainless steel tube with an effective length of 18 inches. It is surrounded by electric heaters capable of heating the reactor to 900° C. Thermocouples are inserted both from the bottom and the top of the reactor. The usual method of operation is to heat the reactor while setting the proper gas velocity to give fluidization. This velocity was determined by experimentation in a glass tube at atmospheric temperature and pressure and then was corrected for the operational conditions. After the desired temperature is reached, the coal is charged to the reactor. The gases are collected after leaving the reactor and passing through a condenser and flask to remove the tars. When inert gas is used for treating the coal, the exit gas is not collected because the gas originating from the coal is too highly diluted by the inert gas to give significant results.

Different conditions of operation were tried in the development of the process. The following fluidizing gases were used:

Steam
Steam plus air
Inert gas (N_2 + CO_2 + 0.1-1.0 percent O_2)
Nitrogen (contains 0.1-0.3 percent O_2)
Prepurified nitrogen (essentially O_2-free)
Helium (essentially O_2-free).

Heat was transferred to the coal through the reactor wall (gas entering cold) and from the preheated gas (reactor wall maintained at the same temperature as the bed).

Pittsburgh seam coal from the Bruceton mine was used principally, but Pocahontas, Illinois, Sewickley, and Taggart coals also were treated. The rank and analyses of the coals are shown in table 1. The free swelling indices of these coals range from 4.5 to 8.5. The free swelling index is indicative of the caking qualities of the coals. If the index is reduced below 2 by pretreatment, the residue is usually noncaking.

To supplement the indicated results from the free swelling index, another test was devised to verify that the char was nonagglomerating.[7] A sample of the char was placed in a ceramic boat and the boat placed in a quartz tube in an electric furnace. The char was heated to 600° C while pure hydrogen was passed through the tube. The char was considered noncaking if after hydrogen treatment it flowed freely out of the boat. Later, to test it more severely, the char was exposed to hydrogen at 900° C. Usually if the free swelling index was less than 2, the hydrogen test indicated noncaking also.

Because this pretreatment process was developed primarily to make a nonagglomerating fuel for a gasification process, the hydrogen test is more pertinent than the free swelling index test. As the char is fed into the gasification unit, it will come in contact with hot hydrogen-containing product gases of the gasifier, a condition simulated by the hydrogen test at 600° or 900° C.

DISCUSSION OF RESULTS

Initially Pittsburgh seam coal, 10-14 mesh, was used with inert gas or nitrogen as the treating gas. The gas velocity for fluidizing at atmospheric pressure was about 2.5 feet per second, and the expansion of the bed was about 100 percent. Early tests showed that the individual coal particles expanded 100 percent or greater at temperatures of 400° to 450° C. Because of the expansion of the treated particles and the fluidized bed, the size of the charge was limited to 35 grams (60 cc). When the fluidized bed of coal was heated indirectly by transfer through the reactor wall, the coal particles agglomerated and adhered to the wall, making the unit inoperable. However, when the heat was supplied by direct transfer from the

gas while the reactor wall was maintained at a temperature for adiabatic conditions, the coal's caking properties were destroyed by the treatment and the unit was operable. The coal particles swelled and became globular. Pretreatment was successful when inert gas, steam plus air, or nitrogen was used, whereas agglomeration occurred at the same operating conditions when helium, steam, or prepurified nitrogen was the treating gas. This difference in results was traced to the presence of a small quantity of oxygen (0.1-0.3 percent) in the inert gas and nitrogen, and the absence of a measurable quantity of oxygen in the other gases.

The effect of temperature on the caking properties of Pittsburgh seam coal is shown in figure 3. Four mesh sizes of coal were fluidized with an inert gas containing 0.8-1.0 percent oxygen. Plotted are the increase in volume, the weight loss of the coal, and the free swelling index of the resultant char with variation in treatment temperature. These results are more relative than absolute, but the trends of the different sizes are realistic. The larger particles were exposed to more oxygen than the smaller ones because the linear velocity was higher for the fluidization of the larger particles. The coal was maintained at the test temperature for 30 minutes in all tests. Poor fluidization occurred in all tests at 450° C, and with the 8-10 and 10-14 mesh sizes at 425° C. The 28-48 and 48-100 mesh were successfully pretreated at 425° C, as were all sizes at 400° C. While the fluidization of the coals was satisfactory in the reactor at 375° C, the chars caked when they were tested at 600° C with hydrogen, indicating insufficient treatment. The free swelling index test corroborates the hydrogen tests because the index was higher than 2 at 375° C and no higher than 2 for all tests at 400° C, and below 2 at 425° and 450° C. As the temperature of treatment increased, the weight loss increased as more of the volatiles were removed. There was a greater increase in bulk volume with increasing temperature. These tests showed that the caking quality of Pittsburgh seam coal of 28-48 and 48-100 mesh was destroyed at 400° to 425° C in 30 minutes.

The effect of pressure on the caking properties of Pittsburgh coal is shown in figure 4. During these tests a 48-100 mesh size coal was fluidized with an inert gas containing 0.8 to 1 percent oxygen for 30 minutes at 400° C. Chars made at all pressures were noncaking. The volumetric expansion became less as the pressure increased from 0 to 300 psig. The weight loss decreased as the pressure was increased from 0 to 75 psig, then did not change with further increase in pressure. A linear gas velocity of about 0.4 foot per second was necessary for fluidization of 48-100 mesh coal at all the pressures, so that at the higher pressures a larger quantity of gas flowed through the coal. Generally, there was no significant change due to pressure. The only novel effect occurred when the pressure was released when the char was removed from the reactor. Some of the particles seemed to explode, probably because trapped gas was released due to depressurization. This effect was observed at all pressures above atmospheric.

Varying the time of pretreatment of Pittsburgh seam coal of 18-100 mesh produced the results shown in figure 5. Nitrogen containing 0.2 percent oxygen was the treating gas, and operating temperatures were 400° and 425° C. As shown in this figure, the char made by treating at 425° C for five minutes could be subjected to a hydrogen atmosphere at 900° C without caking. The free swelling index of this char was 1.5. The weight loss of the coal was 10 percent. Pretreatment for only 1 minute at 425° C was enough to produce a char that did not agglomerate at 600° C with hydrogen. However, the free swelling index of the char was 6-1/2, still indicative of a caking coal. Apparently the test with hydrogen at 600° C is not severe enough to determine if the coal has been rendered noncaking throughout. Some difference between the free swelling index and hydrogen exposure tests can be expected because the char is ground for the free swelling index test but is used in its original state in the hydrogen tests. The weight loss in the 1-minute test was 8 percent. When the coal was treated at 400° C, the minimum pretreatment time was 20 minutes for the char to remain nonagglomerating in the hydrogen test at either 600° or 900° C. The free swelling index was 2, indicative of noncaking. The weight loss was 10 percent. Since the weight loss at both 400° and 425° C was about 10 percent, the higher temperature is more desirable because less time is required for treatment.

The effect of temperature on the volume and composition of the gas made during coal treatment with pure steam for 30 minutes at 375°, 400°, and 425° C is shown in figure 6. As the temperature increased, the hydrogen yield increased from about 5 to 9 cubic centimeters of gas per gram of coal charged. The methane yield increased from about 1 to 5 cubic centimeters per gram, and the C_2 yield increased also. The yields of carbon dioxide, nitrogen, carbon monoxide, and oxygen remained relatively constant. A gas of higher heating value was made at the higher temperature of operation.

The effect of varying the temperature of pretreatment of Pocahontas No. 4 (lvb), Taggart (hvab), Illinois No. 6 (hvbt), and Sewickley (hvab) coals is shown in figure 7. Nitrogen containing about 0.2 percent oxygen was used at a linear velocity of about 0.8 foot per second to fluidize the 28-48 mesh particles. Chars, made from Pocahontas or Illinois coal that had been treated at 375°, 400°, or 425° C, did not cake when subjected to a hydrogen test at 900° C. Taggart coal required treatment at 425° C to be satisfactory, while Sewickley could be treated at 400° only, as it agglomerated during pretreatment at 425° C and was ineffectively pretreated at 375° C. Taggart and Sewickley coals are similar in rank to Pittsburgh seam, all being hvab.

Pocahontas No. 4 and Illinois No. 6 require less drastic treatment than the hvab coals. This is not surprising for the lower rank Illinois coal, which has a free swelling index of 4.5 compared to 8-8.5 for the hvab coals. While the Pocahontas coal has the highest rank, it may respond to milder pretreatment because of its low volatile content. Taggart coal required treatment at 425° C. This coal also showed a drastic change in expansion as plotted in figure 7, having 0 percent volume increase at 375° C and 100 percent at 425° C.

These tests showed that the technique of pretreatment utilizing fluidization with gases containing small quantities of oxygen is applicable to several caking coals. However, conditions of pretreatment cannot be fixed exactly by the rank of coal; each coal must be tested to determine the most satisfactory temperature for pretreatment.

CONCLUSIONS

The caking properties of coals tested could be destroyed by fluidizing the coal with a gas such as nitrogen, nitrogen plus carbon dioxide, or steam, containing at least 0.2 percent oxygen at 400° or 425° C. In a batch system, a thoroughly nonagglomerating char could be produced at 425° C in a 5-minute treatment using 18-100 mesh size coal. The caking property cannot be destroyed by the treatment described if oxygen is absent. It is desirable and may be necessary to heat the coal internally by the treating gas to prevent the particles from adhering to the wall of the reactor.

To obtain data that will permit a more exact evaluation of the process and estimate of the cost of this method of pretreatment, a study of a continuous system is needed. We plan to modify the bench-scale equipment for continuous feed of coal and removal of char. This will allow a realistic determination of the optimum feed gas-to-coal ratio and minimum average residence time required for pretreatment. In a fluidized bed all the coal is not pretreated for a uniform length of time because of the rapid mixing of the raw coal and treated char. The discharged solids will contain particles treated to different degrees because the residence time of the individual particles varies. The results of the batch study will be used as a guide for the continuous studies, but the optimum solids residence time and conditions of operation may be different from those obtained in the present investigation.

References

1/ Chanabasappa, K. G., and H. R. Linden. Fluid-Bed Pretreatment of Bituminous Coals and Lignite. Ind. and Eng. Chem., 50, No. 4, 637-644 (April 1958).

2/ Nathan, M. F. U.S. patent 3,032,477, May 1, 1962.

3/ Karl, Alfred. German patent 1,041,192, Oct. 16, 1958.

4/ Sylvander, N. E. U. S. patent 3,070,515, filed May 6, 1957.

5/ Welinsky, Irving H. U. S. patent 2,955,077, Oct. 4, 1960.

6/ Foch, Pierre. U. S. patent 3,011,953, Dec. 5, 1961.

7/ The treated or processed coal is designated as char in this report.

TABLE 1.- Analyses of coals and chars from pretreatment tests

Classification[1]	Pocahontas #4 lvb		Taggart hvab		Illinois #6 hvbb		Sewickley hvab		Pittsburgh hvab	
	Raw	Char	Raw	Char	Raw	Char	Raw	Char	Raw	Char
Proximate analysis, percent[2]										
Moisture	2.7	0.4	1.1	0.1	6.1	0.5	1.3	0.4	1.7	0.8
Volatile matter	14.8	13.7	35.1	24.4	33.8	26.1	36.8	24.2	36.6	26.0
Fixed carbon	76.5	78.6	61.8	73.1	53.2	66.4	52.9	64.3	55.5	66.7
Ash	6.0	7.3	2.0	2.4	6.9	7.0	9.0	11.1	6.2	6.5
Ultimate analysis, percent[2]										
Hydrogen	4.4	4.0	5.4	4.7	5.2	4.4	5.2	4.4	5.3	4.6
Carbon	83.3	84.3	83.8	84.6	70.8	77.6	75.3	75.0	77.3	78.9
Nitrogen	1.3	1.3	1.5	1.6	1.7	1.9	1.6	1.7	1.6	1.7
Oxygen	4.5	2.6	6.6	6.0	14.3	8.1	6.5	5.2	8.4	7.2
Sulfur	0.5	0.5	0.7	0.7	1.1	1.0	2.4	2.6	1.2	1.1
Ash	6.0	7.3	2.0	2.4	6.9	7.0	9.0	11.1	6.2	6.5
Free swelling index	6.5	1.5	8	1.5	4.5	1.5	8.5	2	8.5	2
Heating value, Btu/lb	14,660	14,410	14,950	14,700	12,530	13,550	13,630	13,240	13,780	13,740

1/ American Society for Testing Materials, Standard Specifications for Classification of Coals by Rank. A.S.T.M. Designation D-388-38; A.S.A. M20.1-1938.

2/ As received basis.

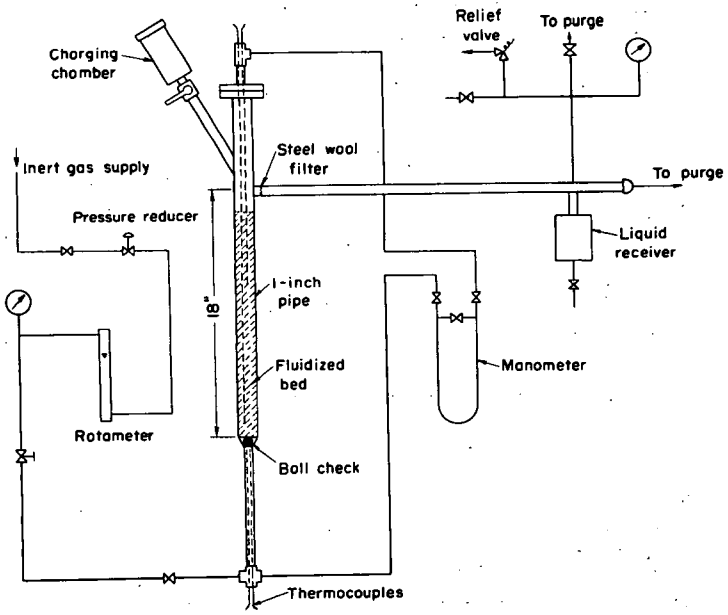
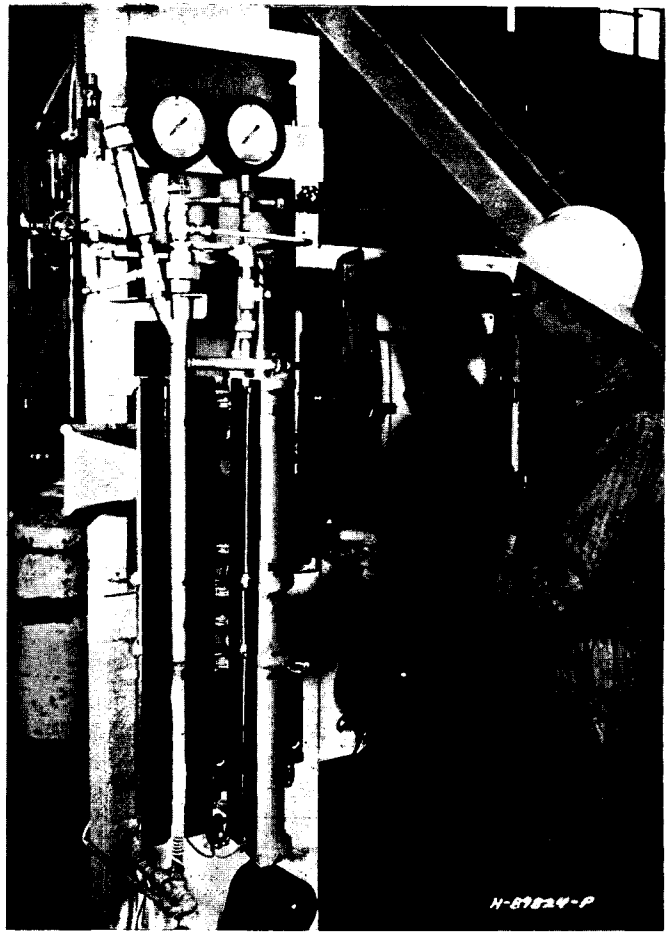


Figure 1.- 1-inch reactor for pretreating coal in a fluidized bed. L-79



The Bench-Scale Unit for the Destruction of Coking Properties of Coal.

Figure 2.

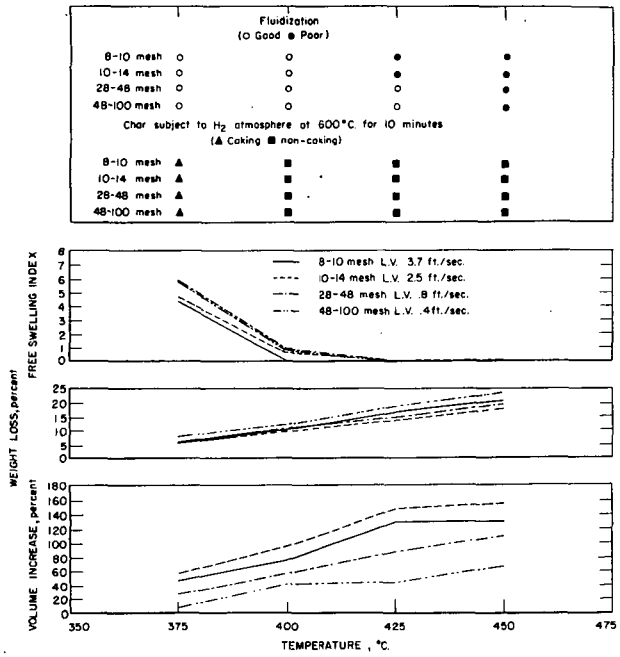


Figure 3.- Coking tests of Pittsburgh seam coal-temperature and size consist effect (coal held at indicated temperatures 30 minutes. Fluidization medium-inert gas containing 0.8-1.0% oxygen-atmospheric pressure).

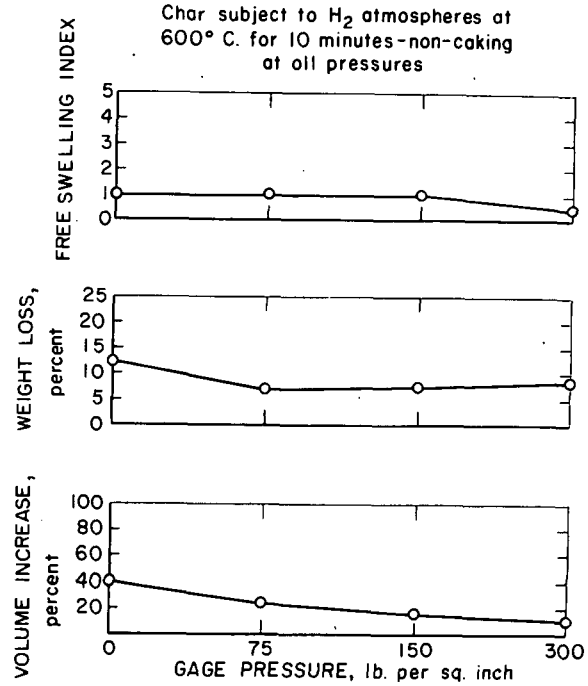


Figure 4. - The effect of pressure on the caking properties of Pittsburgh seam coal, and (48-100 mesh; coal held at 400° C. 30 minutes. Fluidization medium-inert gas containing 0.8-1.0% oxygen.)

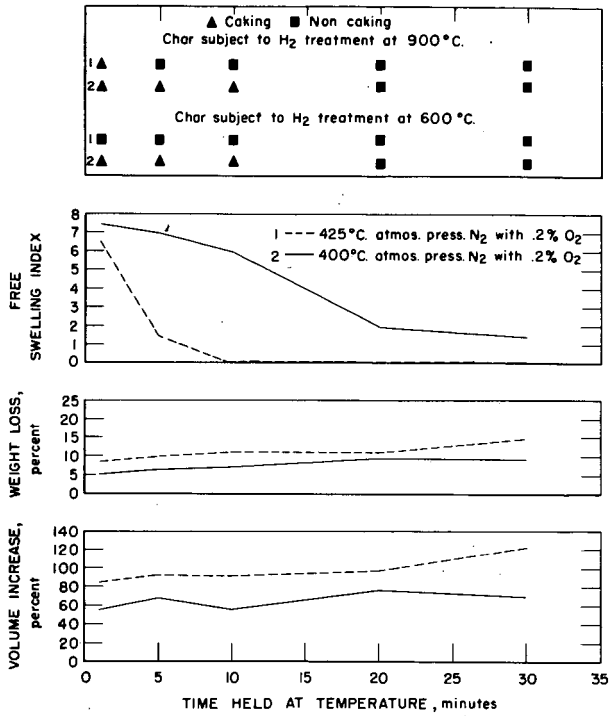


Figure 5.-The effect of time of pretreatment on the caking properties of Pittsburgh seam coal (18-100 mesh)

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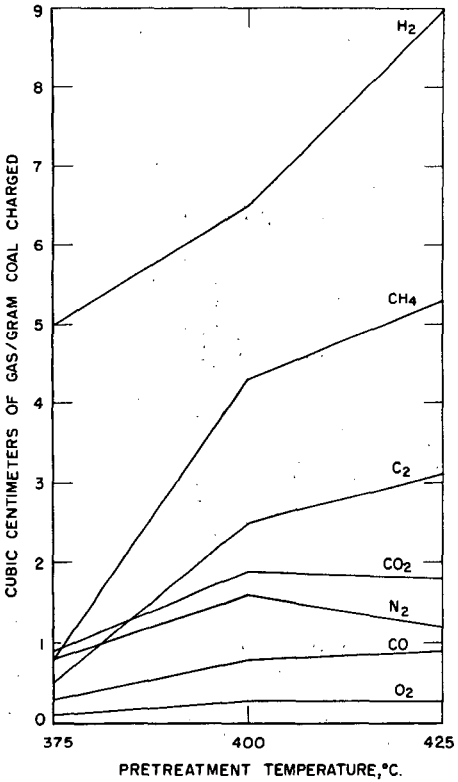

Figure 6.-The effect of temperature on the off gas made during steam pretreatment of Pittsburgh seam coal of 28-48 mesh. (Time of pretreatment 30 minutes).

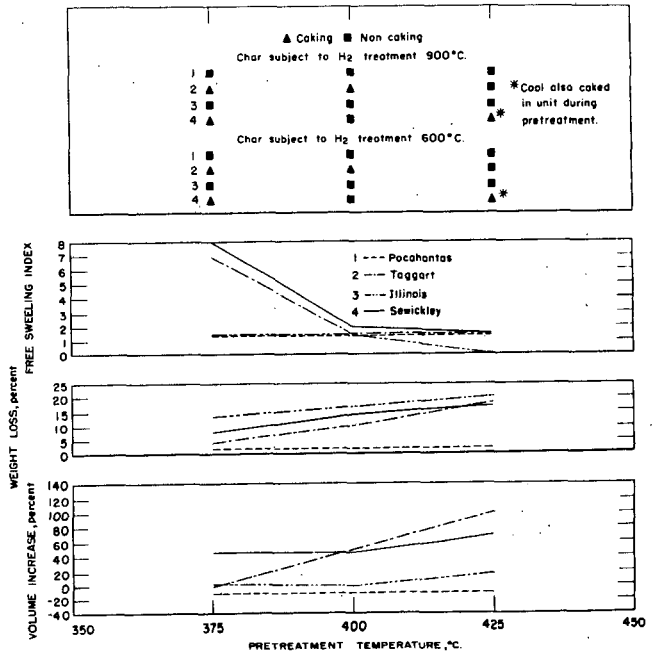

Figure 7.-The effect of temperature of pretreatment on caking properties of various coals 28-48 mesh. (Time of pretreatment 30 minutes.)

FLAMMABILITY CHARACTERISTICS OF METHYLACETYLENE, PROPADIENE AND PROPYLENE MIXTURES[1/]

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INTRODUCTION

Methylacetylene and propadiene are used as welding and cutting fuels, as intermediates in chemical production, and as rocket fuels. Mixtures containing these combustibles in the gas phase are potentially hazardous because their vapors can decompose exothermally and propagate flame in the absence of oxygen. Heat from surroundings may be sufficient to effect their decomposition and ignition. With increasing temperature and pressure their thermal stability may be expected to decrease. The present investigation was conducted to determine the flammability characteristics of gas or liquefied gas mixtures containing these materials together with a hydrocarbon diluent, such as propylene or propane.

The fundamental properties of the methylacetylene decomposition flame at elevated pressures have been studied recently. Hall and Straker (1)[2/] report that its burning velocity is about 2 cm/sec between 10 and 40 atmospheres - a relatively low value in comparison to most known flames. They report a critical pressure for flame propagation of 43 psig (lower pressure limit) at about 20° C, in a 4-inch diameter tube. This may be compared with the critical pressure limit of 50 psig, in a 2-inch diameter tube, reported by Fitzgerald (2). Methylacetylene is more stable than acetylene which also forms a decomposition flame. The low pressure limit of acetylene in a 2-inch tube is only about 6 psig (3). Although little information is available on the stability of propadiene, recent experiments indicate that the energy requirements for the ignition of propadiene-methylacetylene mixtures are comparable to those required for the ignition of methylacetylene alone (4).

Like acetylene, methylacetylene and propadiene can be stabilized in a system at a specified temperature and pressure by adding inert gases or hydrocarbons that do not decompose under the given conditions. Fitzgerald (2) reports ethane to be a much better stabilizer than either methane or nitrogen. In the present study, the use of propylene and propane as diluents is examined because of the current interest in these hydrocarbons as stabilizers for methylacetylene and for methylacetylene-propadiene mixtures. The flammability characteristics of such mixtures (vapors) are shown to be sensitive to temperature and pressure, as well as to the size of the reaction chamber.

1/ The work upon which this report is based was done under a cooperative agreement between the Bureau of Mines, U. S. Department of the Interior and The Dow Chemical Company.

2/ Numbers in parentheses indicate references at end of paper.

EXPERIMENTAL APPARATUS AND PROCEDURE

Limit of Flammability Measurements

Flammability limits of the methylacetylene-propadiene-propylene system were determined at elevated temperatures and pressures in cylindrical stainless steel bombs measuring 1-, 2-, 4- and 12-inches in diameter, respectively, and in a spherical bomb of 24-inch diameter. The cylinders were about 42 inches long, except for the 12-inch diameter one which was 17 inches long. All of the bombs were insulated with asbestos and heated externally with Nichrome[3/] ribbon elements (see figure 1). Chromel-Alumel thermocouples (22-gage), located near the top and bottom of each bomb, were used to follow the heating of the test mixtures introduced into the vessels; thermocouple outputs were measured by a potentiometer. The partial pressure of each mixture component was measured by a mercury manometer or a Bourdon gage which also served to indicate if ignition occurred. A continuous pressure record was obtained during each experiment with an SIM Kistler transducer system whose output was fed to an oscilloscope equipped with a camera. In most determinations, the ignition source consisted of about 1 inch of 38-gage platinum wire located at the bottom of the test vessel.

In preparing for an experiment, a vapor mixture from the liquefied gases was made up in an explosion bomb which had previously been evacuated. To facilitate transfer of the gases from their supply cylinders, the latter were immersed in a water bath maintained at a selected temperature between 20° and 45° C; the explosion bomb was kept at the same temperature. Generally, at least one of the gases was introduced in two increments and alternately with the other gas or gases. To effect mixing, a thermal gradient of about 60 C° was maintained for at least one hour between the top and bottom of the bomb. Calculated mixture compositions, corrected for compressibility, were in close agreement with mass spectrometric analyses made for a few sample mixtures.

After the gases were mixed, the bomb was heated to the desired temperature and the platinum wire was fused. Ignition and extent of flame propagation was determined from the pressure measurements and from the amount of carbon formed. In some instances, complete analyses of the cooled product gases were made. Most of the experiments were performed at 120° C and at pressures of 50 and 100 psig.

The flammability of commercial mixtures (vapor) of liquefied gases was determined in much the same way. However, many of the flammability experiments were conducted at pressures greater than 100 psig and necessitated the transfer of appreciable quantities of the sample mixture to the bomb as a liquid. This was accomplished by first transferring a measured volume of liquid from the supply cylinder to an evacuated stainless steel sphere (523 cc); both were precooled with dry ice. The small sphere was then heated to force the liquid mixture into the bomb where the initial test pressure was controlled by varying the sample volume and bomb temperature. The subsequent procedure was similar to that in the previous experiments.

Two representative commercial mixtures were examined; their compositions are given in table 1. According to the manufacturer's analyses, mixture No. 1 contained about 41 volume-percent diluents, (mostly propane and propylene); mixture No. 2 contained about 32 volume-percent diluents (mostly propane). Mass spectrometric analyses of mixture No. 2 by the Bureau of Mines gave a diluent content of 43 volume-percent for the vapor sample and 29 volume-percent for the liquid sample. This variation can be attributed to the preferential distillation of the lighter diluent components.

3/ Reference to specific brands, and make or models of equipment is made to facilitate understanding and does not imply indorsement of such items by the Bureau of Mines.

TABLE 1. - Composition of representative commercial mixtures of liquefied gases (volume-percent)[1/]

	Mixture No. 1	Mixture No. 2		
	Mfg.'s analysis (Liquid)	Mfg.'s analysis (Liquid)	BuMines analysis[2/] (Liquid)	(Vapor)
Methylacetylene	36.1	27	(71	(57
Propadiene	23.3	41	(	(
Propane	22.5	28	22	37
Propylene	10.8	---	--	2
C_4-Carbon cpds.	7.3	4	7	4

1/ Supplied by The Dow Chemical Company.
2/ Mass spectrometric analyses.

The methylacetylene used in this work had a minimum purity of 95 percent and could contain as much as 4 percent nitrogen according to the vendor's specifications; mass spectrometer analysis of our sample showed about 2 percent nitrogen present. The propadiene and propylene were about 97.5 and 99 percent pure, respectively; propylene was the main impurity in the propadiene.

RESULTS AND DISCUSSION

Flammability Limits of the Methylacetylene-Propadiene-Propylene System

Mixtures of methylacetylene and propadiene vapors were found to be flammable (in the absence of air) in all proportions at 120° C and 50 psig. Addition of propylene to either of these components produced limit mixture compositions which were dependent upon the temperature and pressure as well as on the vessel diameter. Limit compositions found at 120° C and at 50 or 100 psig are given in table 2 for vessel diameters of 1 to 24 inches. The data in table 2 were used to make up the ternary diagram shown in figure 2. This figure shows the approximate range of flammable mixtures for the methylacetylene-propadiene-propylene system under the experimental conditions noted. In any given vessel, the range of flammable mixture compositions is greatest with high concentrations of propadiene. For example, propadiene-propylene mixtures containing up to 31.3 percent propylene are flammable in the 12-inch diameter bomb at 100 psig; 21.9 percent is the limiting propylene concentration for methylacetylene-propylene mixtures.

The propadiene used in this investigation propagated flame at pressures in excess of 16 psig at 120° C in a 2-inch diameter bomb; the methylacetylene required pressures greater than 39 psig. Other investigators have reported similar pressure limits of 31 psig at 120° C and about 45 psig at 150° C for methylacetylene in 2-inch and 1-1/4-inch diameter bombs, respectively (2,4). It is not altogether surprising that methylacetylene should be more stable than propadiene, because the former contains a methyl group that provides increased resistance to thermal degradation. Pyrolysis experiments (400-650° C) by Meinert and Hurd (5) indicate the same order of stability for these liquefied gases. They also obtained evidence that methylacetylene first converts to propadiene, which then polymerizes and eventually decomposes.

TABLE 2. - Flammability limits of methylacetylene-propylene-propadiene mixtures at 120° C in various size vessels.1/

Initial Pressure psig	Methylacetylene Vol.-%	Propylene Vol.-%	Propadiene Vol.-%
	1-inch ID Bomb (0.47 liter)		
100	92.8	7.2	--
100	--	19.8	80.2
	2-inch ID Bomb (2.03 liters)		
50	94.7	5.3	--
50	--	15.3	84.7
100	90.4	9.6	--
100	--	23.8	76.2
100	39.4	21.5	39.1
	4-inch ID Bomb (7.86 liters)		
100	84.5	15.5	--
100	--	28.7	71.3
	12-inch ID Bomb (31.0 liters)		
100	78.1	21.9	--
100	--	31.3	68.7
	24-inch ID Bomb (118.7 liters)		
100	>76	<24	--
100	--	32.5	67.5

1/ Ignition source consisted of 1-inch of 38-gage platinum fuse wire.

The flammable range of the mixtures was noticeably greater at 100 psig than at 50 psig (figure 2). In view of the lower explosion pressure limits given above for methylacetylene and propadiene, it was to be expected that the flammability of the mixtures would be pressure-sensitive under the experimental conditions; even propylene will propagate flame at sufficiently high temperatures and pressures. It was also to be expected that an increase in temperature would widen the limits of flame propagation. In some preliminary experiments at 60° C and 50 psig, mixtures of methylacetylene and propylene failed to ignite in the 2-inch diameter bomb with the ignition source used (1 inch of 38-gage platinum wire); these mixtures ignited readily at 120° C and 50 psig in the same bomb. It is possible that with other ignition sources these mixtures would ignite and propagate flame at the lower temperature (60° C) since ignition energy requirements become most critical near the limiting pressure condition for flame propagation.

The effects of initial pressure, vessel diameter, and mixture composition were also reflected in the pressure measurements. Pressure-time records from experiments in the 1-, 2- and 4-inch diameter bombs with near-limit mixtures of propadiene-propylene and methylacetylene-propylene are shown in figure 3 (A and B); pertinent data from these records are given in table 3. The rates of pressure rise and the maximum explosion pressures developed decrease markedly with a decrease in bomb diameter. For example, the initial rates of pressure rise for the propadiene-propylene mixtures were 60 and 250 psi/sec in 1 and 4-inch diameter bombs, respectively; the

corresponding ratios of maximum explosion pressure to initial pressure were 2.15 and 5.82. Comparable data were obtained with methylacetylene-propylene mixtures. It was evident from these and other results that the heat losses were greatest for the smallest vessel. The quenching diameter for methylacetylene flames is reported to be less than 0.3 cm at 15 psia and 120° C (1); with propylene as diluent, the quenching diameter should be greater under the same conditions.

Explosion pressure-time histories for the flammability determinations conducted in the 2-inch diameter bomb with propadiene and methylacetylene at various initial pressures are also shown in figure 3 (C and D). Maximum explosion pressures were attained more rapidly with propadiene than with methylacetylene, at a given initial pressure. At the explosion pressure limit for propadiene (16 psig), the initial and maximum rates of pressure rise were only 25 and 55 psi/sec, respectively (table 3). These rates, and those obtained for mixtures of these gases with propylene, increased noticeably as the initial pressure and the diameter of the vessel were increased. Because of the relatively low rates of pressure rise observed in most of these determinations, the times required to reach a given pressure were long, as compared to those that are generally observed with combustible-oxidant mixtures in similar bombs. As noted in table 3, the times required to attain maximum pressures were greater than 1 second except in experiments conducted in the 4-inch diameter bomb; these data indicate the slow development and propagation of flame that can be expected in the decomposition of these materials.

The effect of vessel size on the flammability limits of methylacetylene-propylene mixtures at 120° C and 100 psig is illustrated in figure 4. The concentration of diluent (propylene) required to produce limit mixtures increased with an increase in vessel diameter from 1 to 12 inches; above 12 inches the diameter had little effect. The following equations were found to fit the experimental data by the method of least squares for the range of vessel diameters, d, indicated:

Methylacetylene-propylene mixtures:

$$\text{Vol.-\% propylene} = 4.1 + 3.2\,d - 0.14\,d^2; \qquad 1'' \leq d \leq 12'' \qquad (1)$$

Propadiene-propylene mixtures:

$$\text{Vol.-\% propylene} = 18.3 + 3.0\,d - 0.16\,d^2; \qquad 1'' \leq d \leq 12'' \qquad (2)$$

The volume percent of propylene is the amount required to obtain a limit mixture.

The vessel diameter effect observed for these mixtures can be attributed largely to the slow flame propagation obtained with these materials. During most of the burning period, the burning velocities probably did not exceed about 2 cm/sec, the value reported by Hall and Straker (1) for pure methylacetylene at 10 atmospheres. With such a low burning velocity, the total heat losses to the walls by conduction and radiation can be significant enough to cause flame extinction. It is to be expected that such effects would be most evident, as is the case here, for the smallest diameter vessels or those with the greatest contact area-to-volume ratio. Judging from the burning velocities and flame temperatures, heat losses due to radiation appear to be very important in the propagation of decomposition flames through methylacetylene and acetylene; observed flame temperatures are much less than values calculated assuming no radiation losses (6,7). However, it has not been established whether such heat losses alone determine the explosion pressure limits of these flames.

The main (cooled) decomposition products from methylacetylene and propadiene were found to be carbon, hydrogen and methane (table 4); small or trace quantities of ethane, ethylene and unreacted gas were also present. Similar results have been obtained with methylacetylene and with acetylene by other investigators (1,2).

TABLE 3. - Pressure data from flammability experiments with methylacetylene-propylene-propadiene mixtures at 120° C and at various pressures.

Propylene Vol.-%	Bomb Diameter inches	Initial Pressure, P_1 psig	Maximum Pressure, P_2 psig	Pressure Ratio, P_2/P_1 psia/psia	Time to Max. Pressure[1/] sec	Initial Rate of Pressure Rise psi/sec	Maximum Rate of Pressure Rise psi/sec
				Methylacetylene			
None	2	45	233	4.18	1.295	70	320
"	"	100	610	5.46	1.190	160	1060
				Propadiene			
None	2	16.5	68	2.67	2.070	25	55
"	"	18.5	89	3.17	1.335	35	115
"	"	22	226	6.62	1.240	65	440
"	"	100	600	5.37	1.020	150	1180
				Methylacetylene + Propylene			
6.9	1	82	173	1.95	2.020	50	60
5.0	2	50	289	4.71	1.330	90	470
7.9	2	90	458	4.53	1.310	115	630
15.0	4	100	690	6.24	0.790	270	1510
				Propadiene + Propylene			
19.3	1	100	231	2.15	1.830	60	100
21.5	2	100	304[2/]	2.79[2/]	0.945[2/]	160	430[2/]
27.9	4	100	652	5.82	0.810	250	1490
				Methylacetylene (40.1%) + Propadiene (39.7%) + Propylene (20.2%)			
20.2	2	100	419[2/]	3.78[2/]	1.195[2/]	145	810[2/]

1/ Times measured from point of initial pressure rise.
2/ Maximum pressures were not observed.

TABLE 4. - Decomposition products in flammability experiments with methylacetylene-propylene-propadiene mixtures at 120° C and at various pressures

Initial Propylene Content, Vol.-%	Bomb Diameter, inches	Initial Pressure, psig	Carbon Formed, gms	Gaseous Products (Vol.-%)						Hydrogen - Carbon Mole Ratio		Carbon Conversion[1/] %
				Hydrogen	Methane	Ethane	Ethylene	Nitrogen & Carbon Monoxide	Unreacted Gas	Input	Output	
						Methylacetylene						
None	2	42	6.61	71.0	25.4	0.3	0.2	1.8	1.3	1.33	1.44	71
"	"	45	6.92	--	--	--	--	--	--	--	--	71
"	"	60	9.19	--	--	--	--	--	--	--	--	74
"	"	100	13.89	73.4	19.0	0.1	0.1	1.8	5.6	1.33	1.48	73
						Propadiene						
None	2	16.5	2.89	61.5	29.8	0.6	2.3	0.7[2/]	5.1	1.33	1.36	58
"	"	18.5	3.48	--	--	--	--	--	--	--	--	67
"	"	50	7.65	72.7	20.9	0.3	0.3	2.3	3.5	1.33	1.40	74
"	"	100	15.69	81.7	16.3	0.1	0.1	--	1.8	1.33	1.42	82
						Methylacetylene + Propylene						
6.9	1	82	1.52	--	--	--	--	--	--	--	--	40
7.9	2	90	12.28	--	--	--	--	--	--	--	--	70
15.0	4	100	60.68	79.1	18.2	--	--	1.7	1.0	1.43	1.75	82
						Propadiene + Propylene						
19.3	1	100	1.80	--	--	--	--	--	--	--	--	42
23.3	2	"	13.90	--	--	--	--	--	--	--	--	75
27.9	4	"	56.81	--	--	--	--	--	--	--	--	80
						Methylacetylene (50%) + Propadiene (50%)						
None	2	50	7.58	--	--	--	--	--	--	--	--	74
						Methylacetylene (40.1%) + Propadiene (39.7%) + Propylene (20.2%)						
20.2	2	100	13.55	--	--	--	--	--	--	--	--	74

1/ Mole percent of available carbon converted to free carbon.
2/ Benzene.

However, acetylene generally undergoes more complete decomposition to the elements, (carbon and hydrogen) at the temperatures and pressures employed here. Hydrogen production increased with an increase in initial pressure whereas the methane content decreased. Ethane and ethylene were barely detectable in the products formed at the maximum pressure (100 psig), but they were present in significant amounts (0.6 percent ethane and 2.3 percent ethylene) in the experiment with propadiene at a pressure of 16.5 psig; benzene (0.7 percent) was also found at this low pressure. The same gases form as products of the explosive decomposition of ethylene at elevated temperatures and pressures (8). Hurd and Meinert also report similar products from the pyrolysis of propylene between 600° and 955° C (9); however, they did not find any evidence of aromatic hydrocarbons in the pyrolysis of methylacetylene or propadiene between 400° and 650° C (5).

Figure 5 shows that the amount of free carbon formed was nearly insensitive to mixture composition and increased linearly with initial pressure; these data were obtained at 120° C in the 2-inch diameter bomb. The experimental carbon yield is compared to that which would be expected from the assumed reactions that identify the three curves given in this figure. It is seen that the experimental data fall essentially between the bottom and middle curves which correspond to carbon yields of 2 and 2-1/2 moles, respectively, per mole of methylacetylene ($HC \equiv C\text{-}CH_3$) or propadiene ($H_2C{=}C{=}CH_2$). However, the gas compositions of the cooled combustion products were not altogether consistent with those of the reactions assumed here.

Material balances based on the complete analyses of the combustion products from methylacetylene and propadiene are given in table 5. As the decomposition products were largely carbon, hydrogen and methane, small quantities of ethane, ethylene, etc. were neglected. Best material balances were obtained in the experiments at 100 psig.

TABLE 5. - Products formed by the explosive decomposition of methylacetylene, propadiene, and methylacetylene-propylene mixtures at 120° C and various initial pressures

Initial Pressure psig	Bomb Diameter inches	Reactants (moles)1/	Carbon moles	Hydrogen moles	Methane moles
42	2	(1)$HC \equiv C\text{-}CH_3$	2.16	1.08	0.39
100	"	"	2.34	1.34	0.35
16.5	"	(1)$H_2C{=}C{=}CH_2$	1.86	0.75	0.36
50	"	"	2.36	1.19	0.34
100	"	"	2.54	1.44	0.29
100	4	(1)$HC \equiv C\text{-}CH_3$ + (0.175)$H_2C{=}CH\text{-}CH_3$	2.96	2.00	0.46

1/ Numbers in parentheses indicate moles of reactant.

essentially, only small amounts of additional carbon are needed to obtain agreement between the input and output materials at this pressure. The mole ratio of total hydrogen to carbon was 1.33 for both reactants; it was between 1.36 and 1.48 for their reaction products, including minor constituents such as ethane, ethylene, etc. (table 4). The apparent shortage of carbon may be ascribed to the fact that all of the carbon formed in the reaction vessel was not removed and weighed. The amount of hydrogen and other gaseous products combined or adsorbed in the carbon probably did not introduce a serious error.

The combustion products from an ignition in the 4-inch diameter bomb with 85 percent methylacetylene and 15 percent propylene at 100 psig and 120° C were also analyzed (table 4). The products were again chiefly carbon, hydrogen and methane, and the material balance was much like that observed with methylacetylene or propadiene alone (table 5).

The relative concentrations of hydrogen and methane that were found in the decomposition products may be explained partly by consideration of the decomposition of methane as follows:

$$2\ CH_4 \longrightarrow C_2H_2 + 3H_2 \qquad (3)$$

$$C_2H_2 \longrightarrow 2C + H_2 \quad . \qquad (4)$$

According to thermodynamic data, little methane should exist at about 1500° C (10); therefore, maximum conversion of methane to carbon and hydrogen should occur at temperatures equal to or greater than this value. Since the observed flame temperatures for the decomposition of methylacetylene are about 1300° C (6), noticeable methane concentrations should then be expected in the end products. With decreasing pressure and vessel size, the heat losses increase and the ratio of methane to hydrogen should increase, as it actually did. In comparison, the decomposition of acetylene is associated with higher flame temperatures which account in part for the small amount of methane that is generally found in the decomposition of this material.

Flammability Characteristics of Representative Commercial Mixtures of Liquefied Gases

Vapors of commercial mixture No. 1 (41% diluents) did not propagate flame without air in the 2-inch diameter explosion bomb at temperatures extending from 18° to 187° C and at corresponding pressures of 80 to 390 psig; the only evidence of reaction was the presence of small quantities of liquid products and of carbonaceous soot near the ignition element. In most of these experiments, the ignition element consisted of two platinum wires (38-gage and 1-inch long) and 50 mg of guncotton.

Commercial mixture No. 2 (32% diluents) showed little evidence of reaction in flammability tests conducted in the 24-inch spherical bomb at 126° C and pressures up to 116 psig. However, at about 215° C and 285 psig, the mixture decomposed explosively in the 4-inch diameter cylindrical bomb, and the maximum pressure developed was greater than 1000 psig. Ignition occurred without fusion of the ignition source indicating that the mixture temperature (215° C) was sufficient to ignite the guncotton; spontaneous ignition of the mixture was unlikely in the absence of air at the above temperature and pressure.

According to the data obtained for various mixtures of methylacetylene, propadiene and propylene, commercial mixture No. 1 should not be flammable under the experimental conditions used here because of its high diluent content (22.5% propane, 10.8% propylene, and 7.3% 4-carbon atom hydrocarbons). Figure 2 shows that this mixture composition does not fall in the flammable range, assuming that the diluents are as stable as propylene. However, a moderate increase of the methylacetylene or propadiene concentration would tend to make the mixture flammable. Moreover, the mixtures will tend to be more unstable at higher temperatures and pressures. As the composition of commercial mixture No. 2 falls close to the range of flammable methylacetylene-propadiene-propylene mixtures (figure 2), its behavior at high temperatures and pressures is not surprising.

The ability of paraffin hydrocarbon diluents to stabilize liquefied gases appears to depend partly upon the heat of formation of the diluent. For example, the stability of methylacetylene (2) and acetylene (3) increases with the addition of paraffins of increased molecular weight and decreased heat of formation (negative). The effectiveness of these diluents and of nitrogen decreases in the following order:

Butane > propane > ethane > methane > nitrogen .

Thus, butane and propane should be preferred as stabilizers for these commercial mixtures; they should also be favored over propylene which has a positive heat of formation. The ability of the diluents to absorb heat can also be an important factor here and probably accounts to a large extent for the greater effectiveness observed with hydrocarbons than with nitrogen.

CONCLUSIONS

Mixtures of methylacetylene and propadiene vapors are flammable in all proportions at an initial temperature of 120° C and a pressure of 50 psig. Nonflammable mixtures are formed by adding propylene and are dependent on such variables as temperature, pressure, vessel diameter, and ignition energy. The range of flammable mixtures increases when the initial pressure is increased from 50 to 100 psig. It increases also when the diameter of the reaction vessel is increased from 1 to 12 inches; above 12 inches the diameter has little effect.

The low pressure (explosion) limits are about 16 psig for propadiene, and 39 psig for methylacetylene at 120° C in a 2-inch diameter bomb. Initial rates of pressure rise following ignition of the test materials are very low and are indicative of unusually low burning velocities. These rates increase with an increase in vessel diameter and pressure.

The end products formed by explosive decomposition of methylacetylene between 42 and 100 psig and of propadiene between 16 and 100 psig are chiefly carbon, hydrogen and methane; methylacetylene-propylene mixtures give similar products. An increase in pressure increases the percentage of hydrogen and decreases the percentage of methane. Decomposition of these liquefied gases to their elements was less complete than that of acetylene at the same conditions.

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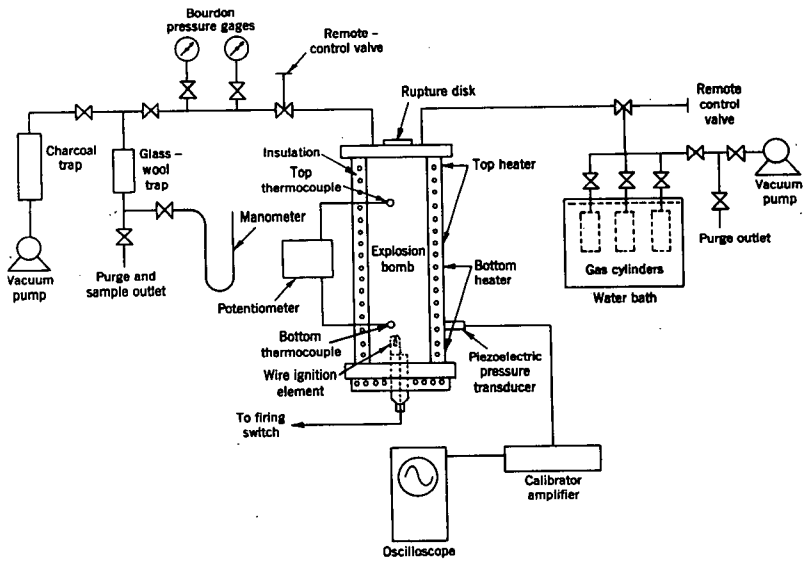

Figure 1. - Experimental setup for flammability determinations.

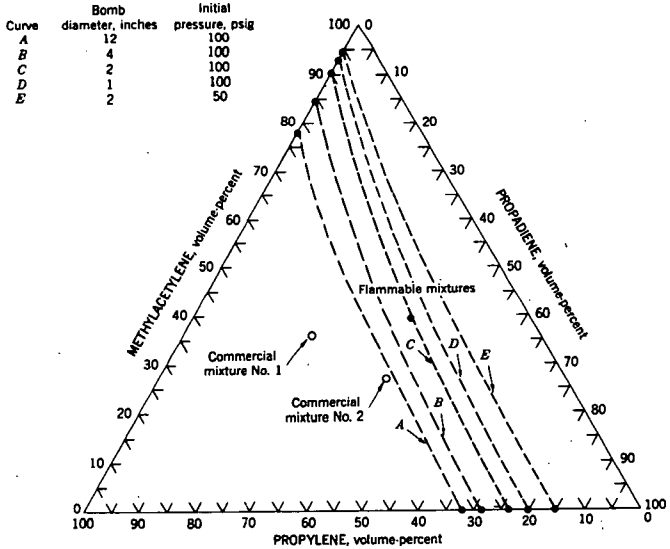

Figure 2. - Range of flammable mixtures for the methylacetylene-propadiene-propylene system at 120° C and at 50 and 100 psig.

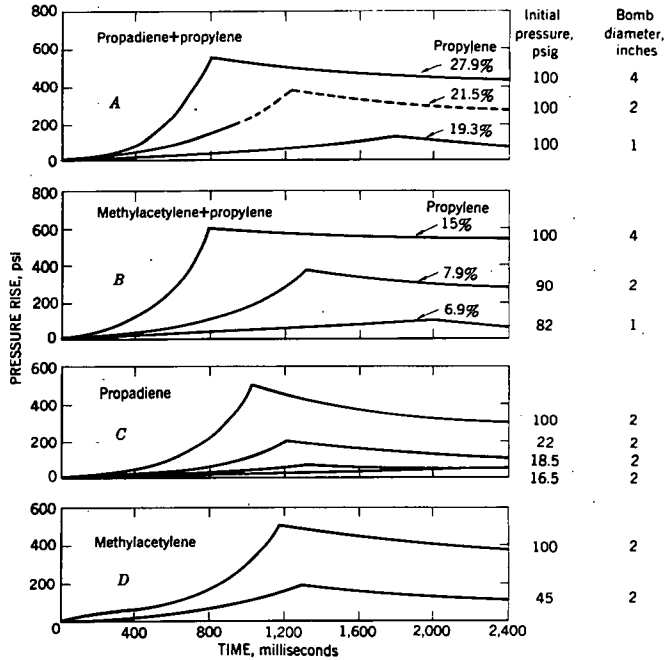

Figure 3. - Pressure-time records following the ignition of methylacetylene, propadiene and propylene mixtures at 120° C and various initial pressures.

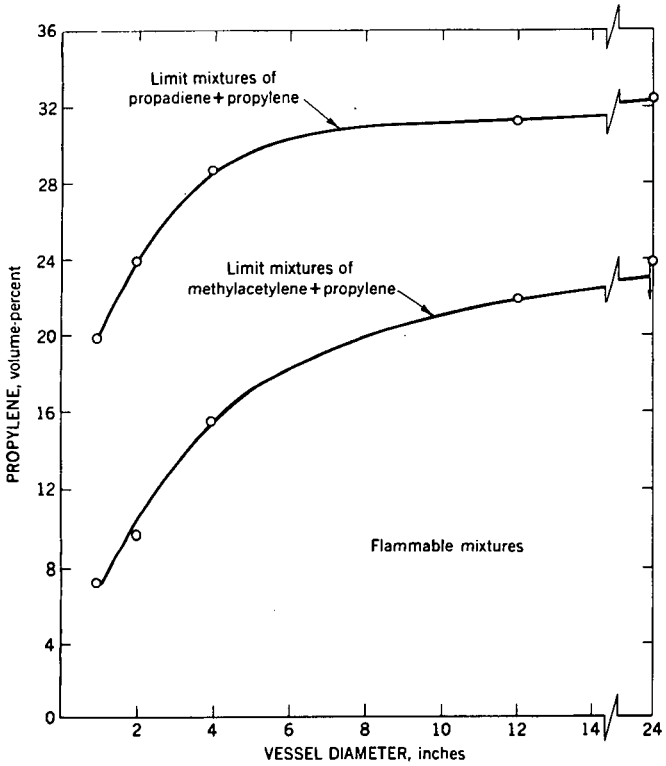

Figure 4. - Effect of vessel diameter on limits of flammability of methylacetylene-propylene and propadiene-propylene mixtures at 120° C and 100 psig.

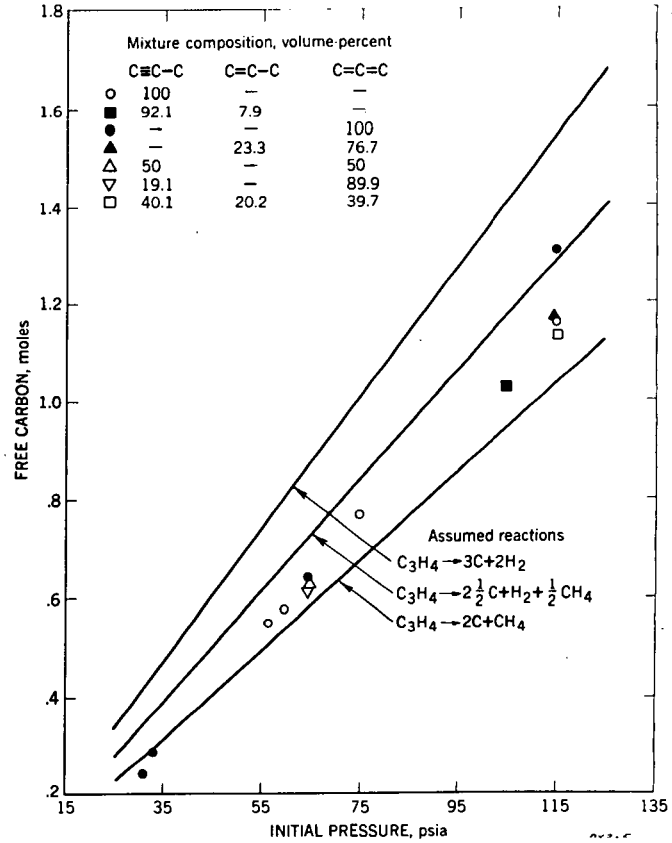

Figure 5. - Free carbon formed in explosive decomposition of methylacetylene, propadiene and propylene mixtures at 120° C and various initial pressures (2-inch diameter bomb).