

Reactivities of Low Rank Coals

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During the past years, various investigations were undertaken at the University of Wyoming on the utilization of low rank coal. In several of these, the reactivity of the coal products was important and therefore was given consideration. In connection with the development work on reducing carbon, the reaction of the carbon to CO_2 was tested and in connection with the use of processed coal for barbecue briquets, the reactivity to air was investigated. Results of this work are reported here as they appear of general significance.

Carbon Dioxide Reactivity

In order to show results from as wide a rank of coals as possible, three Wyoming coals were chosen, ranking from high volatile C Bituminous to subbituminous C. These coals were carbonized in a closed retort to 950°C . The heating rate was 5°C per minute. Table I shows the proximate and ultimate analyses, also the heating values of the chars. Listed are also the coals from which the chars are derived and two commercial cokes, one Western coke furnished by the Colorado Fuel and Iron Corporation and one Eastern coke furnished by Pittsburgh Coke and Chemical Company.

TABLE I
ANALYSES OF COKES, CHARS AND COALS
(Moisture Free, in Percent)

NAME AND RANK			VM	FC	Ash	H_2	C	O_2	N_2	S	Btu/lb.
Cokes	Pitt. Foundry	Hvab	0.4	93.9	5.7	0.2	91.2	1.4	1.0	0.4	13140
	C F and I	Hvab	3.5	83.6	13.1	1.1	83.5	0.8	1.0	0.5	12250
950° Chars											
	DOClark	Hvab	1.1	93.4	5.5	0.7	91.0	1.4	0.9	0.5	13580
	Elkol	Subb	2.5	93.2	4.3	1.0	90.7	2.2	1.4	0.4	13510
	Wyodak	Subc	2.1	82.2	14.7	1.1	80.6	1.3	0.9	0.4	12400
Coals	DOClark	Hvcb	39.3	57.0	3.7	5.8	72.2	15.4	1.6	1.3	13220
	Elkol	Subb	43.0	54.5	2.5	5.0	72.4	17.8	1.5	0.8	12580
	Wyodak	Subc	42.3	47.7	10.0	4.5	65.6	17.8	1.1	1.0	11340

The reactivity of the char to carbon dioxide was measured by conducting CO_2 over the char and measuring the proportion of CO to CO_2 in the effluent. As it is known that the surface area often is closely related to the reactivity, the densities, in methanol as well as in mercury, were also measured. From the densities, the porosities were calculated. Results are shown in Table II.

The chars from a lower rank coal have a higher reactivity than the chars from a higher rank coal and all are higher than the reactivities of the cokes. In Figure I, this relationship is shown graphically. The lower the rank of the coal, the higher the reactivity of the carbon residue.

TABLE II
 Reactivity, Density and Porosity
 of
 Chars and Cokes
 Moisture Free

Rank	Rank	Reactivity		Density	Porosity
		CO ₂	McOH	Hg	
Hvab	Foundry Coke	13.3	2.031	1.736	0.145
Hvab	C F & I Coke	71.8	1.869	1.617	0.135
Hvcb	DOClark Char	119.1	1.820	1.415	0.223
Subb	Elkol Char	137.5	1.840	1.382	0.249
Subc	Wyodak Char	146.0	1.810	1.100	0.392

It appears that this tendency is related to the porosity of the material. The higher porosity of the low rank chars facilitates the access of the oxidizing gas to the carbon surfaces. It is widely believed that diffusion is a limiting factor in reaction rates when gas reacts with a porous solid. It would perhaps be more to the point to say that the reactivity is governed by the concentrations of CO₂ and CO at the surfaces regardless how these concentrations were achieved. It would appear logical to assume that the rough low rank surfaces are more open to attack by the CO₂ than the glossy surfaces of the coke. The surface area of the lowest rank char under study, Wyodak, is about 27 m² per g whereas those of the two cokes are 2 and 3 m² per g respectively.^{1.)} Diffusion deeply into the piece of coke or char may take place but reaction is retarded by mounting concentrations of the product gas, CO, within the particle. The concentrations of the two gases are affected by the rate at which the one is supplied and the other is removed, and by the relative concentrations which prevail.

Milliken^{3.)} has suggested that the micelles of the lower rank coals may be composed at least partially of di-phenyl linkages and that these linkages are oriented about sixty degrees from planar. This results in steric hindrance which prevents formation of large blocks of oriented and planar molecules, thus leaving a greater random porosity. It also should be considered that the lower rank coals yield much water and carbon dioxide while being carbonized in the lower temperature ranges. There are thus many carbon-to-OH and carbon-to-oxygen linkages broken and probably left in a condition which encourages reaction of the peripheral carbon molecules with the oxidizing gas. The higher rank coke, never having been freed of such an amount of water and oxygen, has fewer sites open for attack and thus a lower reactivity.

In order to examine the possibility that the analysis of the coal substance would throw some light on these differences in reactivity, the ultimate analyses of the moisture and ash free chars and cokes are shown in Table III. As will be seen carbon and hydrogen content is similar down the columns. Oxygen, determined by difference, is not significant. As has been pointed out by Peters^{2.)}, it would appear that the chemical analysis gives no explanation for the differences in reactivity.

The two commercial cokes shown in Figure I were made under conventional coking conditions which involve comparatively slow temperature rise and longer periods at maximum temperature. The longer period at coking temperature, this so-called soaking period, also affects the CO₂-reactivity of the coke. Extended periods at high temperature reduce the CO₂-reactivity. Thus the two points, 1 and 2, would have been higher, closer to the level of the chars, if the cokes had been made at the same conditions as the chars.

TABLE III
 Ultimate Analyses of Chars and Cokes
 (Moisture and Ash Free)

Rank	Name	H ₂	C	O ₂	N ₂	S
Hvab	Foundry Coke	0.6	96.8	1.2	1.0	0.4
Hvab	C F & I Coke	1.0	96.3	1.3	0.9	0.5
Hvcb	DOClark Char	0.7	96.4	1.5	0.8	0.6
Subb	Elkol Char	1.0	95.0	2.2	1.4	0.6
Subc	Wyodak Char	1.2	95.8	1.1	1.0	0.5

To examine the effect of heat soak on reactivity, a char from DOClark coal was heat soaked for various periods, and then subjected to the reactivity test. The results are shown in Figure II. Heat soaking for 3 hours reduced the reactivity by about 15% and soaking for 48 hours by 35%. It is known that any char and any coke shrinks with continued heat soaking. This, of course, results in higher densities and lower porosities, and it must be expected that such changes result in closure or partial closure of openings and a reduction of the reaction surface. Thus, reactivity to CO₂ and doubtless to other gases is decreased with extended heating cycles. However, the nature of the surface of the char made from subbituminous coal is so open that no amount of heat soaking will lower its reactivity to that of a metallurgical coke.^{4.)}

The higher reactivity of the chars made from lower rank coals must be ascribed to their surface structure, and such chars must find applications where high reactivity is an advantage.

Reactivity Measured by Ignitability of Smokeless Briquets

Several investigations were made on the suitability of processed coal for barbecue briquets. Such briquets should be easy to ignite and should develop a reasonable amount of heat. Further, they should burn with a minimum of odor or smoke. The amount of heat, intensity of smoke and odor are outside the scope of this discussion. Remains the ignitability. This is determined to a large extent by the shape and size of the briquet, and especially by the degree of compaction which affects the apparent specific gravity. If, however, these and other factors of processing are kept uniform, the ignitability can serve as measure of the reactivity of the carbon substance.

In the ignition test, 5 briquets of uniform pillow shape are placed on a brick, four in a square, one-fourth inch apart, and one on top. The brick is placed off the floor. Room temperature is kept uniform and noticeable draft is avoided. 30 ml of lighter fluid is poured over the briquets uniformly and the briquets are ignited. The percentage of surface burning is estimated at close intervals for each briquet, and the average recorded. The time elapsed when 80% of the surface is burning is termed "Ignition time". It is not too difficult to train an operator within a few days so that the estimating can be done with reasonably close reproducibility.

Figure III shows the ignitability relative to the volatile content. The coal used was air-dry North Dakota lignite with 9.6% of moisture, 36.0% of volatile matter and 10.2% of ash. The coal was carbonized to various volatile contents, and the char briquetted with cereal binder. As will be seen from the curve, the optimum ignition time was achieved with 15 to 18% of volatile matter. At this stage, the volatile matter of the coal has been reduced by about 80%. All carbon dioxide has been evolved, and there is apparently an optimum compounded of the amount of volatile matter retained by the char and the quality of this volatile matter.^{1.)} It had been known for a long time that in the stated volatile range, the coal is best suited for

effective combustion at ordinary furnace temperatures. It may be surprising, however, that under the stated extreme conditions where the low ambient temperature slows the combustion, the same volatile content indicated the highest reactivity.

A great number of various lignites were carbonized, the char briquetted, and the briquets subjected to the ignition test. Processing conditions were uniform. There were again considerable variations in ignition time. Some were traced to variations in ash content, some to aggregate size. Yet there remained distinct differences. These were traced finally to the structure of the coal. In every instance, the lower ignition time was achieved with char from a coal with laminated structure, at least in part of the coal. Figure IV shows samples of the laminated and of the more compact structure. The former is black and has a shiny, velvety appearance, the latter is dull and often brownish. The one apparently originates from either leafy or bark matter, and the other from solid wood.

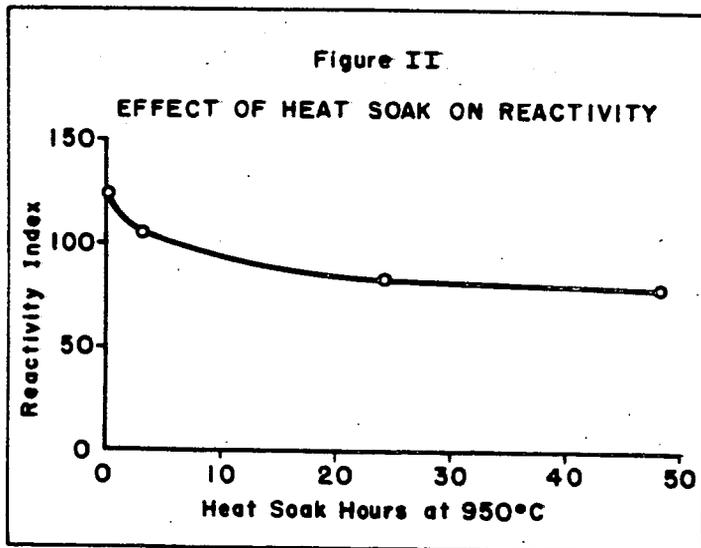
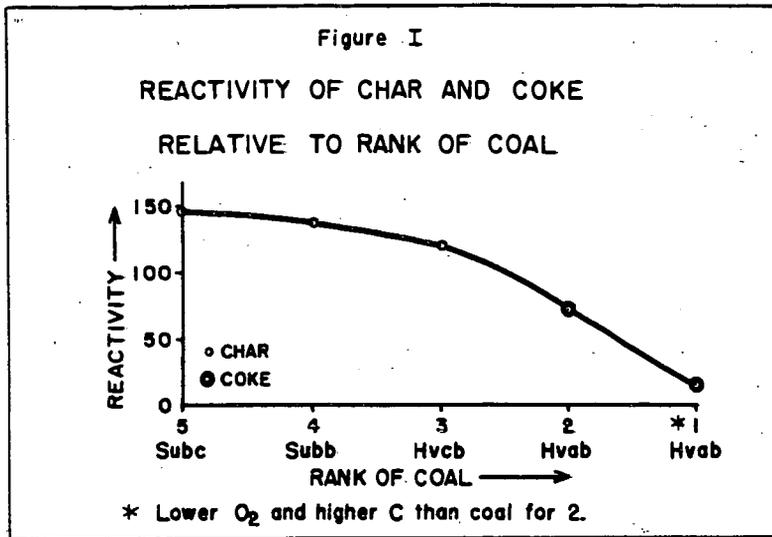
In another investigation, briquets were tested which were produced from char derived from subbituminous C coal. The volatile matter was kept uniform, also the ash content. To vary the amount of reaction surface, the size of the aggregate was varied. Changes in ignitability obtained with changes in aggregate size are shown in Figure V. The aggregate sizes shown are nominal. All aggregates were graded, and uniform grading was used in each case. It will be seen that the tests were confined between U.S. No. 20 and 70 screen sizes. Sizes beyond these limits had to be ruled out for reasons of operating procedures. Within the stated limits, the ignitability increased with decreasing aggregate size.

All the reported results point to the importance of sufficient reaction surface. However, there are, apparently, other factors involved. Many briquets of commercial production were tested which showed an ignition time of 40 minutes. Good smokeless briquets usually showed an ignition time of less than 30 minutes. Very good briquets showed 20, 19, or even 18 minutes ignition time. But this seemed to be the minimum. Any possible introduction of promoters or oxidizing agents is ruled out here and only the reactivity of the coal substance and the oxygen of the air is considered. It appeared that further reduction in aggregate size or further reduction in ash content did not lower the ignition time further.

The oxidation of the char is of course a heterogeneous process^{5.)}, and rather complicated. To accomplish it, however, there must be not only sufficient reaction surface but also sufficient open space for the air to enter and for the products of combustion to leave. For this reason the amount of specific surface beyond a certain optimum cannot be utilized.

References

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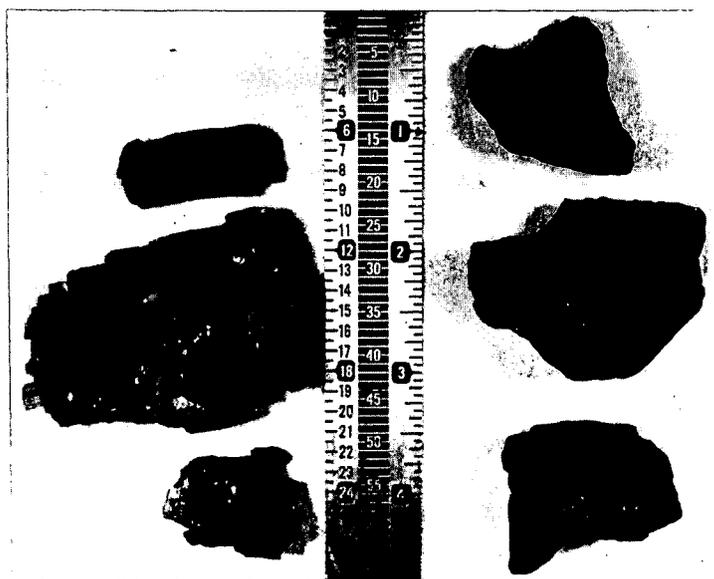
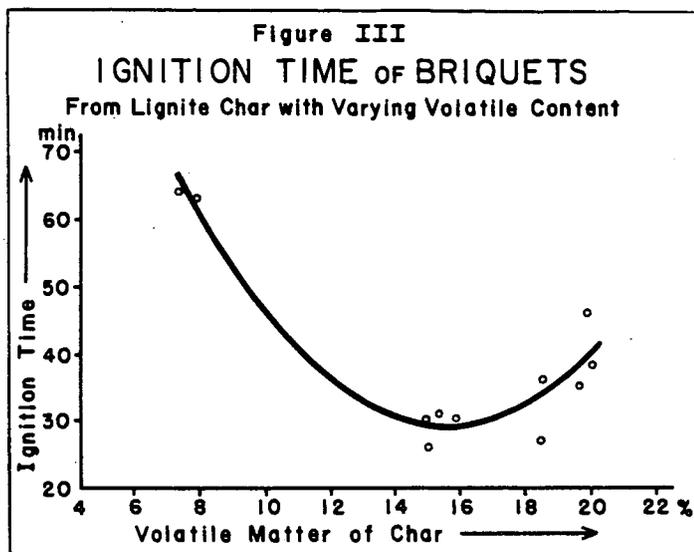


FIGURE IV

