

FORMATION AND STRUCTURE OF COKE FROM NON-COKING COALS BY CARBONIZATION IN HYDROGEN

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Introduction

This investigation was made in conjunction with our program on the use of coal to remove coke forming hydrocarbons from residual oils prior to contacting with conventional cobalt molybdate hydrocracking catalysts. It has been found that non-coking coals such as semi-anthracite, sub-bituminous coal and lignite, when added to a low grade hydrocracking feedstock like Athabasca bitumen, act to seed-out the coke formers in the petroleum (1). The evidence obtained from our previous work (4) shows that the coke formed on the surface of the particle originated partly from the hydrocracking of the bitumen, and partly from the partial hydrogenation of the non-coking coal. In the present work, the experimental work has been extended to explore the effect of hydrogenation on the non-coking coals alone (in the absence of oil) and to determine the effect of hydrogenation on the coking properties; fluidity, plasticity, etc. The coals studied were lignite, sub-bituminous coal, oxidized bituminous coal and semi-anthracite.

Experimental

Carbonization experiments were performed in a stainless steel, vertical fixed-bed reactor of 155 ml capacity (1). Approximately 150 gms of sample (-4 to 8 mesh) was loaded into the reactor and electrolytic hydrogen (purity 99.9%) was passed up through the bed at a rate of 2.8 liter (S.T.P.) per minute, at a pressure of 2000 psi. The gas flow was started as soon as the heating cycle for the reactor had begun. The temperature of the reactor was raised to 450°C over a period of one hour and held at temperature for 3 hours. After three hours the reaction bed was allowed to cool overnight in the hydrogen atmosphere. The coal was removed next morning.

In general the material removed from the reactor after hydrogenation showed portions of coal apparently unaffected, cemented together with melted portions of coal resembling pitch. Some of the fused coal showed slight evidence of conversion to coke. The Free Swelling Index, Dilatation test, Proximate and Ultimate Analysis were determined for the hydrogenated coal and the original samples. These are reported in Tables 1 and 2. Microphotographs were taken of both the hydrogenated coal and the corresponding dilatation residues obtained at 550°C (which is termed semicoke). The dilatation tests were carried out in a Ruhr Dilatometer according to German Specification DIN 51739. The rate of heating was 3°C/min and the maximum temperature attained was 550°C.

Results and Discussion

Orakawana Lignite

This lignite subjected to conventional carbonization did not agglomerate, but formed a char. A micrograph of the char produced at 550°C, shown in Figure 1, did not indicate any coke structure. Parts of the hydrogenated lignite from the reactor showed some agglomeration and coke formation (Figure 2). The Spheroidal structures in the hydrogenated product, shown in the micrograph of Figure 3, correspond to one of the initial stages of coke formation. The laminar structure in the semicoke shown in Figure 4 is similar to that described by Mochida et al (2). Mochida obtained spheroidal microstructure at lower temperatures and laminar microstructure at higher temperatures in their studies of the hydrogenation and coke formation of coal tar pitch. Brooks and Taylor also observed a similar phenomenon (3) on heating of pitch.

The Free Swelling Index test applied to the lignite gave no indication of agglomeration; the residue consisted of a powder. The hydrogenated lignite was agglomerated and had a button of 1½. After hydrogenation of the lignite, both dilatation and contraction increased slightly. These properties indicated the development of fluidity and plasticity in the hydrogenated lignite.

Forestburg Sub-bituminous Coal

The Forestburg sub-bituminous coal is a non-agglomerating, non-coking coal. The microstructure of the non-agglomerating char from this coal is shown in Figure 5. After hydrogenation this coal showed agglomeration and coke formation (Figure 6), and the microstructure of this product indicated the formation of numerous small spheroids of a mosaic type (Figure 7). This structure was quite different from that obtained on the hydrogenation of lignite. In the semicoke of the hydrogenated sub-bituminous coal the spheroid structure disappeared completely and a flaky or granular structure developed as shown in Figure 8. The strong bonding between the reactive (fused mass) and the inerts in the semicoke microstructure suggested a similar structure to that obtained in medium volatile coking coals. The Free Swelling Index increased from 1 to 2½ on hydrogenation and the dilatation from nil to 6 indicating a marked improvement in fluidity and plasticity.

Harbour 26 Bituminous Coal (Oxidized)

In general terms a bituminous coking coal

OF 540
75-34-5
ERP/ERL

38
01-219

is converted to a non-coking coal by oxidation as the result of the formation of phenolic-OH and C-O-C ether linkages. For the particular sample used in the present study the Free Swelling Index was only 1 and the Dilatation-nil, which confirmed that this coal was completely oxidized and non-coking. A micrograph of a semicoke obtained from this oxidized coal is given in Figure 9. The hydrogenated product (micrograph shown in Figure 10) indicated agglomeration and coke formation in some particles. The Free Swelling of this coal increased on hydrogenation from 0 to 5½, and the dilatation from 0 to 17%. Microscopic examination of this coal revealed a massive and laminar structure similar to that obtained from tar or bitumen (Figure 11). It appears from the micrograph in Figure 12 that the formation of a few small spheres occurred first by the reaction of hydrogen with the oxidized vitrinite part of the coal, and that these small spheres gradually coalesce to form laminar structure. When a semicoke was made from this hydrogenated product at 550°C, the laminar structure was converted to a grainy structure (Figure 13). The results of the study indicate that this oxidized non-coking coal was transformed into a coking coal by hydrogenation under pressure.

Canmore Semi-Anthracite

This semi-anthracite is non-coking. No significant change in the microstructure occurred on carbonizing to the semi coke stage. The structural changes and the transformation which occurred on hydrogenation are discussed in detail in our previous paper (4). Hydrogenation did produce a change in the coking character of the semi-anthracite and some formation of coke on the surface of semi-anthracite was visible (Figure 14). The microstructure of the hydrogenated coal showed massive and laminar structure (see Figure 15). On heating the hydrogenated product to 550°C in the Ruhr Dilatometer, a coarse grain laminar structure developed in the semicoke (Figure 15). Good bonding appeared to exist between the reactive and inert components. The increase in the Free Swelling Index from 1 to 5 on hydrogenation indicated that sufficient fluidity was developed to form an agglomerated coke.

Conclusion

It can be concluded from the present studies that coking properties can be restored to non-coking coals of all ranks by partial hydrogenation under appropriate conditions of time, temperature and pressure. The conversion of non-coking coal to coking coals in the presence of high hydrogen pressure (200 atm) was reported originally by Lander et al (5) and later by Crawford (6). The present work supports the observations of Lander, Crawford et al for coals ranging from lignite to semi-anthracite and for oxidized bituminous coal.

Infrared analysis of the original oxidized bituminous coal and its hydrogenated product showed the following changes in functional group concentration: (1) a decrease in the aliphatic CH-group, (2) a decrease in the aromatic OH-, C=O group, (3) a decrease in C-O-C oxygen ether group concentration, and (4) a significant increase in the aliphatic CH₂, CH₃ group concentration. The coking properties of the hydrogenated oxidized coal developed probably as the result of the opening of the oxygen ether linkages in the oxidized coal by the action of heat and hydrogen. This is similar to the restoration of the coking properties of oxidized bituminous coal by treatment with K/THF/Naphthalene to open the oxygen ether linkages (7).

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References

1. Ternan, M., Nandi, B.N., and Parsons, B.I., "Hydrocracking Bitumen in the Presence of Coal - A Preliminary Study of Changes Occurring in the Coal", Mines Branch Research Report R 276, Department of Energy, Mines and Resources, Ottawa (1974).
2. Mochida, I., Kudo, K., Takeshita, K., Takahashi, R., Suetsugu, Y., and Furumi, J., Fuel 53, 253 (1974).
3. Brooks, J.D. and Taylor, G.H., "Chemistry and Physics of Carbon", Vol. 4 (Ed. P.L. Walker, Jr.), Edward Arnold, New York, p. 243, (1968).
4. Nandi, B.N., Ternan, M., Parsons, B.I., and Montgomery, D.S., "Coke Formation During Simultaneous Hydrogenation of Coal and Bitumens", Divisional Report ERL 74/96, Energy Research Laboratories, Energy, Mines and Resources, Ottawa, September 1974. Submitted to Fuel, London, (January, 1975).
5. Lander, C., Sinnatt, F.S., King, J.G., and Crawford, A., "Improvements in and Relating to the Treatment of Coal and Like Carbonaceous Material", British Patent Specification 301 720, (1928).
6. Crawford, A., Williams, F.A., King, J.G., and Sinnatt, F.S., "The Action of Hydrogen Upon Coal - I.", Dept. Sci. and Indust. Research, Fuel Research Tech. Paper 29, His Majesty's Stationery Office, London (1931).
7. Nandi, B.N., Wachowska, H.M., and Montgomery, D.S., "Microscopic Studies of Semicoke from Different Macerals after Treatment of the Coal in K/THF/Naphthalene, Fuel 53, 226 (1974).

TABLE 1

Sample	Proximate Analysis			
	#1	#2	#3	#4
	Onakawana Lignite	Forestburg Sub-bituminous	Harbour Seal Bituminous (Oxidized Coal)	Canmore Semi-Anthracite
Moisture I	48.1	17.2	0.64	0.8
Ash I	6.8	10.7	6.10	7.8
Volatile Matter I	21.4	31.1	20.60	13.4
Fixed Carbon I	23.7	51.0	72.60	78.0
	100.0	100.0	100.0	100.0
Free Swelling Index (Original)	1*	1*	1*	1*
" " (Hydrogenated)	1 1/2**	2 1/2	5 1/2	5

* non-agglomerated or powder form
** agglomerated and hard



Figure 1. Lignite char made at 550° C.

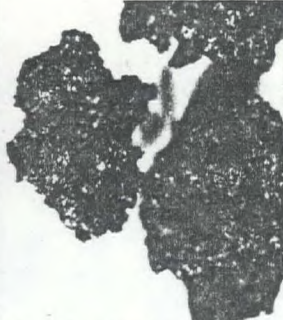


Figure 2. Intermediate hydrogenated product of lignite.

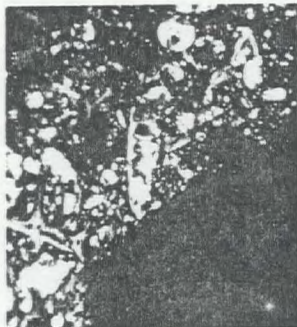


Figure 3. Spheroidal structure in the hydrogenated lignite.



Figure 4. Microstructure of semi-coke from hydrogenated lignite.

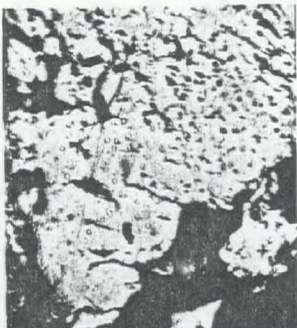


Figure 5. Microstructure of the char from sub-bituminous coal.



Figure 6. Intermediate hydrogenated product of sub-bituminous coal.

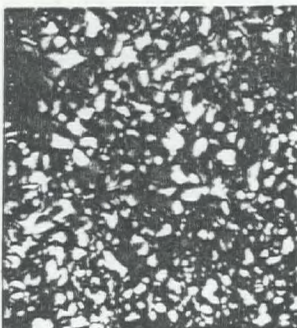


Figure 7. Microstructure of the hydrogenated product showing spheroids.

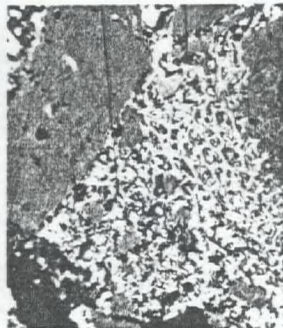


Figure 8. Microstructure of semi-coke from hydrogenated product.

TABLE 2

Sample	Ultimate Analysis					
	#1		#2		#3	
	O	H	O	H	O	H
Carbon	60.39	67.80	64.80	74.70	76.86	85.67
Hydrogen	3.87	3.99	3.98	4.65	4.62	4.31
Nitrogen	0.27	0.64	1.18	1.53	1.39	1.77
	Distillation Test					
Softening point °C	0	300 ⁰	330 ⁰	320 ⁰	336 ⁰	<310 ⁰
Dilatation I	nil	7	nil	6	nil	37
Contraction I	6	11	10	13	10	17

O - Original H - Hydrogenated

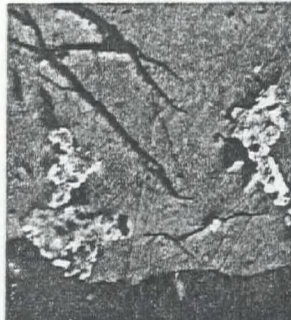


Figure 9. Micrograph of the semi-coke obtained from oxidized coal.



Figure 10. Intermediate hydrogenated product of oxidized coal.



Figure 11. Microstructure of the hydrogenated product of oxid. coal.



Figure 12. Microstructure of the hydrogenated product of oxid. coal - small spheroid in vitrinite (o.v.)

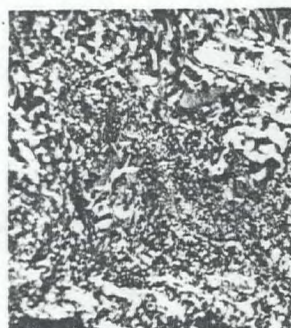


Figure 13. Microstructure of semi-coke from the hydrogenated product.



Figure 14. Intermediate hydrogenated semi-anthracite.



Figure 15. Micrograph product of hydrogenated semi-anthracite.



Figure 16. Microstructure of the semi-coke from hydrogenated semi-anthracite.