

01-12056



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JUNE 1985

For Presentation at the International Symposium on Mining and Technology  
of Coal, Xuzhou, Jiangsu Province, China. September 1985

ENERGY RESEARCH PROGRAM  
ENERGY RESEARCH LABORATORIES  
DIVISION REPORT ERP/ERL 85-42 (OPJ)

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# USE OF LIGNITE AS BLENDING COAL FOR BLAST FURNACE COKE

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**SUMMARY** A novel process has been developed to convert lignite (non-coking) to coking type coal for the production of metallurgical coke. Low-rank coals generally contain high levels of carboxyl groups, ether linkages and alkyl groups. The absence of plasticity and fluidity precludes the use of such coal for blending with coking coal. This paper describes a process to induce coking propensities by eliminating oxygen functional groups, e.g. carboxyl, using blast furnace gas and steam, thereby allowing mesophase formation. Chemical, physical and petrographic properties along with the microscopic structure of coke are discussed. Coking propensity in lignite is observed.

## Introduction

The greater part of the world's huge coal deposit is lignite (non-coking coal) which cannot be used for the production of metallurgical coke. Because of the limited availability of high-grade coal, the development of new technologies to utilize low-grade coal for steel production is highly desirable. Unless new technologies are developed that can alleviate the need for high-grade coal, a shortage of coking coal throughout the world is likely to occur.

Lignite generally contains considerable amounts of oxygen functional groups<sup>1</sup> (ether linkages, hydroxyl, carbonyl and carboxyl groups) and is devoid of plasticity or fluidity. The absence of these properties precludes the use of lignite for blending with good coking coals. Nandi and Ternan<sup>2</sup> developed a process to increase the coking propensities of lignite and other non-coking coals by partial thermal hydrogenation. They also observed structural changes from infrared spectroscopic analysis of the partially hydrogenated lignite: an increase in aliphatic CH<sub>2</sub> and CH<sub>3</sub> groups, a decrease in CH, OH, C=C and ether groups along with an increase in coking propensities such as fluidity, plasticity and mesophase formation on pyrolysis of the hydrogenated product. This is tantamount to the enhancement of the reactive nature of the lignite to the level of bituminous coking coal.

The use of hydrogen alone to upgrade inexpensive material such as lignite would be costly. The water-gas shift reaction ( $\text{CO} + \text{H}_2\text{O}$ ) on the other hand appears to be both an economical and feasible alternative. Reppe<sup>3</sup> had demonstrated a direct

role of CO acting upon the surface oxides along with the opening of C=C bonds and C-O-C linkages. There is also an indirect role of CO which in the presence of H<sub>2</sub>O undergoes the shift reaction generating "active hydrogen"<sup>7</sup>. This might act as a scavenging agent for free radicals produced by extensive dealkylation at high temperatures.

Liquefaction of coal and peat using carbon monoxide and water has been studied extensively by others.<sup>2-6</sup> Recently, successful technological processes to convert non-coking coals<sup>7</sup>, subbituminous coal and lignite have been developed by the authors to induce structural and chemical changes in the coal macerals. Processed coal exhibits improved rheological properties such as fluidity and plasticity as well as initial development of mesophase on heating and subsequently agglomerates with formation of anisotropic coke on pyrolysis.

The economics of using carbon monoxide in this process is not very favourable because the production of carbon monoxide by gasification is expensive. Hence the cost of the processed lignite would not compete with that of bituminous coking coal. An eventual viable process appears to depend on the utilization of inexpensive byproducts such as blast furnace gas which typically contains 25-30% carbon monoxide and 50% nitrogen.

The present study is an extension of previous work<sup>7</sup> on the water-gas shift reaction on coals of higher rank. The objective of this work was to investigate the validity of the concept of using blast furnace gas to replace carbon monoxide. Carbon

monoxide is replaced by simulated blast furnace gas (30% CO and 70% N<sub>2</sub>).

### Experimental

Experiments were conducted in an Inconel 600 vibrating autoclave having a nominal capacity of 250 cc. A schematic of the autoclave system is presented in Fig. 1. In a typical run, 20-30 g of lignite having an average moisture content of about 30% was put into a basket inside the autoclave. No direct contact existed between the lignite and the autoclave walls. A vibrating system allows shaking of the autoclave to induce reasonable gas-solid mixing. The available gaseous volume in the autoclave was too small, i.e., gas/solid ratio excessively low when using the autoclave alone. Thus a 1.1 L ballast volume connected to the vibrating autoclave was added to the experimental system.

The autoclave was rapidly heated by immersion into a sodium nitrite/nitrate bath. Heating of the ballast was provided by electrical resistances. At the end of the prescribed reaction time, the autoclave was quenched using a water bath. A coil through which cold water was recirculated ensured rapid cooling of the ballast. Temperatures were monitored by thermocouples located in the salt bath, the inside of the ballast, the inside of the autoclave and the bottom of the basket holding the lignite in the autoclave.

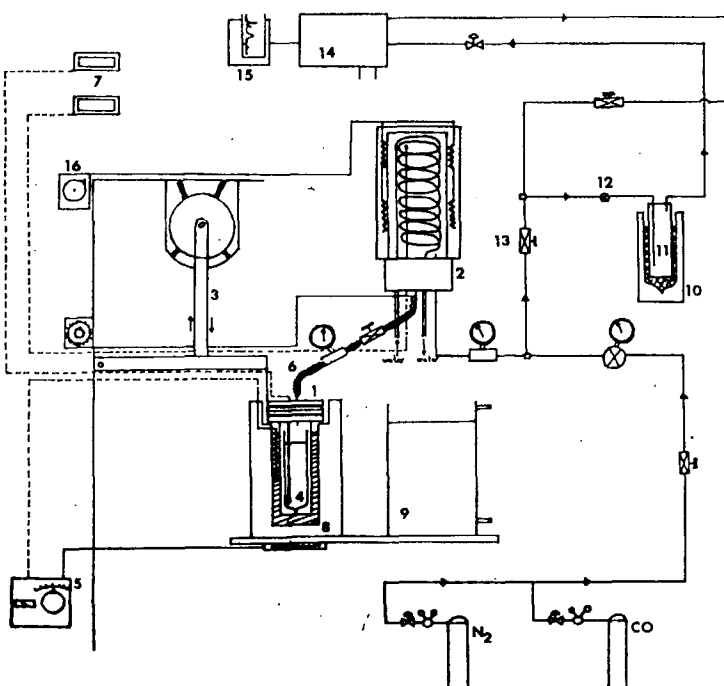
In a typical experiment the lignite was deposited in the basket, the closures put in place and the gas mixture (70% N<sub>2</sub>, 30% CO, i.e., simulated blast furnace gas) introduced at room temperature. As compressibility factors of N<sub>2</sub> and CO are very similar at 25°C, it was assumed that the relative amount of each gas introduced in the system was the same as the relative pressure ratios, i.e., individual gas percentages of the initial pressure. Chromatographic analyses were carried out during the experiments. A small amount of gas was bled through a condensing trap and cooled to room temperature for analysis.

After the prescribed reaction time, the salt bath was removed and the autoclave was quenched in a water bath and cooled to 25°C. At this point the final temperature and pressure were precisely determined to evaluate the amount of gas produced. This required a perfect determination of the initial gas volume which was done before the experiment. At 25°C, the system was depressurized to 1.4 MPa (200 psig) and a chromatographic determination was made. Careful consideration must be given to the fact that this gas composition is not fully representative of the gas inside due to adsorption-desorption

equilibria. Full gas depressurization and collection in an enclosed volume followed by subsequent analysis will solve the uncertainty.

The autoclave was weighed before and after each experiment. Water content was determined on raw (~30%) and treated lignite. The pH of the small aqueous phase resulting from the operation was also measured. It was slightly acidic, pH ≈ 5.

Samples of treated lignite were subsequently subjected to evaluation by physical, chemical, microscopic and dilatometric (Ruhr) analyses.



1. Autoclave 2. Ballast 3. Vibrating system  
4. Stainless system 5. Heating system  
6. Heating tap 8. Salt bath 9. Water bath

Figure 1 Schematic of autoclave system  
Results and Discussion

A series of 26 experiments have been conducted so far. The range of operating parameters in the autoclave is shown in Table 1.

Table 1  
Range of Operating Parameters

Temperature	= 340-400°C
Reaction time	= 15-120 min
Reaction pressure	= 24-28 MPa
Gas compositions	= CO/N <sub>2</sub> molar ratio: 30/70
	CO/Ar molar ratio: 30/70
	CO/H <sub>2</sub> molar ratio: 50/50
	CO : 100%

Major gases detected after CO/N<sub>2</sub> treatment were: H<sub>2</sub> (1.5-2.5%); N<sub>2</sub> (41-65%); CO (44-27%) and CO<sub>2</sub> (12.4-5.3%). Some aliphatic hydrocarbons are also present as minor components.

Few operational problems occurred in the batch autoclave experiments although problems were encountered in the still imprecise temperature control ( $\pm 10^{\circ}\text{C}$ ); the gas/solid mixing patterns which are unknown and probably poor due to the limitations of the vibrating system used for agitation; and the gas analysis which has been conducted during depressurization taking 1.4 MPa as the reference point.

Proximate and ultimate analyses and the results of dilatation tests are given in Table 2. Microscopic examination of the semicoke from the dilatation residue of the original and processed lignite were made to assess coking propensities of the processed material.

Table 2  
Western Canadian Lignite

#### Proximate analysis

	wt % dry basis	
	Original	Processed
Ash	11.3	-
Volatile matter	42.7	-
Fixed carbon	46.0	-
	100.0	

#### Ultimate analysis

Carbon	63.64	66.34
Hydrogen	4.14	4.60
Sulphur	0.59	-
Nitrogen	1.33	1.02
Oxygen (by difference)	19.01	
Oxygen (determined)	22.74	12.58
H/C	0.78	0.83
Heating value (MJ/kg)	24.02	

#### Ruhr dilatometer tests

Softening Temperature $O_s$ ( $^{\circ}\text{C}$ )	nil	253
Contraction C(%)	nil	22
Temp. of max. contraction $O_c$ ( $^{\circ}\text{C}$ )	nil	485
Plasticity index = $\frac{C}{O_c - O_s}$	nil	0.10

#### Dilatometric analysis

Significant changes in the softening behaviour ( $253^{\circ}\text{C}$ ) and contraction (22%) in the processed lignite were observed whereas they were absent in the original lignite. From the above analysis it is indicated that coking propensity, plasticity and fluidity were developed in the processed lignite possibly owing to the overall decrease of elemental oxygen by 50% suggesting the release of oxygen functional groups during the water-gas shift reaction.

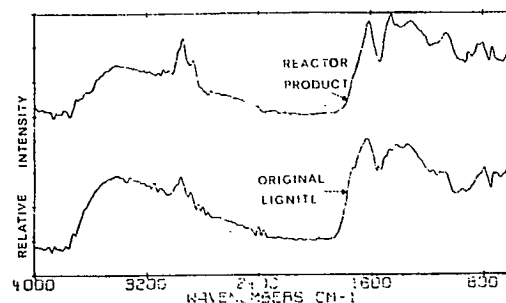


Figure 2 FTIR spectra of original and processed lignite. Spectra were obtained on - 100 mesh powdered samples, dried in a vacuum, using photo-acoustic detection.

#### Infrared Spectroscopic Analysis

Fourier transform infrared spectra using photo-acoustic detection were obtained for the original and processed lignite (Fig. 2). The most notable differences involved oxygen functional groups. The carbonyl ( $1690\text{ cm}^{-1}$ ) and carboxylate ( $1575\text{ cm}^{-1}$ ) bands which were very prominent in the original lignite were significantly decreased in the processed lignite. In addition an increase in aliphatic C-H ( $\approx 3050\text{ cm}^{-1}$ ) in the processed lignite was observed. This is in agreement with the ultimate analysis data of Table 2, (as well as with our previous work<sup>1</sup>) where it is seen that overall loss of oxygen along with a slight increase in the atomic H/C ratio (0.78 to 0.83) occurs upon processing.

#### Microscopical Examination of the Semicoke from Original and Processed Lignite

The residues obtained from the dilatometer tube at  $550^{\circ}\text{C}$  (semicoke) from the original and processed lignite were embedded in lucite plastic and polished for microscopic examination at 600X. The original lignite on pyrolysis neither agglomerates nor forms coke (Fig. 3) - it is termed as char. The dilatometer residue from the processed lignite exhibits both isotropic and anisotropic coke structure (Fig. 4).

Both original and processed lignite were carbonized to  $550^{\circ}\text{C}$  under identical conditions. The original lignite does not show any sign of fusion of masses or coke formation (Fig. 5 OL) whereas the processed lignite produces hard agglomerated coke similar to that which may be obtained from coking bituminous coal (Fig. 5 PL).

For the sake of comparison, the original lignite was treated with 100% CO and water using the conditions given in Table 1. The coke obtained from this process (Fig. 6) is very similar to that (Fig. 4) produced from simulated blast furnace gas.



## CONCLUSIONS

Studies on lignite using the water-gas shift reaction and simulated blast furnace gas have provided the following inferences:

1. A direct role of CO to remove the carboxyl and other oxygen functional groups leading to the development of plasticity and fluidity in the processed lignite is indicated from the FTIR spectra and dilatation tests.
2. The formation of mesophase at the initial stage of heating of processed lignite and agglomerated coke structure during final stage of pyrolysis have been confirmed by microscopic examination and dilatometric tests.
3. The treatment with simulated blast furnace gas ( $\text{CO/N}_2 = 30/70\%$ ) can at  $340^\circ\text{C}$  induce necessary changes resulting in the conversion of non-coking to coking properties in lignite.
4. The concept of using inexpensive blast furnace gas to replace costly carbon monoxide to improve coking propensities of lignite has been validated. This may become an economically viable process.



Figure 3 - Micrograph of Dilatation residue of original lignite at  $550^\circ\text{C}$  X600



Figure 4 - Micrograph of Dilatation residue of processed lignite at  $550^\circ\text{C}$  showing agglomerated coke formation



Figure 5 - Photograph of pyrolysis product at  $550^\circ\text{C}$ . O.L. - original lignite  
P.L. - processed lignite

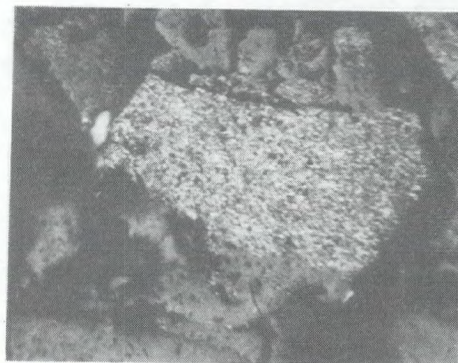


Figure 6 - Micrograph of dilatation residue at  $550^\circ\text{C}$  of processed lignite with 100% CO X600

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## Acknowledgements

This work is supported by the International Development and Research Centre, Ottawa, Canada to develop coking propensities in Turkish lignites.

The authors are grateful to B. LeCorre of the University of Sherbrooke for the experimental assistance and L.A. Ciavaglia, S.E. Nixon and B.H. Mofatt of Energy Research Laboratories for their help in the evaluation and analyses.