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THE IMPROVEMENT OF LIQUEFACTION PROPENSITIES OF LOW GRADE  
OXIDIZED COAL FROM WESTERN CANADA VIA THE WATER-GAS REACTION

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THE IMPROVEMENT OF LIQUEFACTION PROPENSITIES OF LOW GRADE OXIDIZED COAL  
FROM WESTERN CANADA VIA THE WATER-GAS SHIFT REACTION

by

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SYNOPSIS

In western Canada many of the Cretaceous coals suffered oxidation during metamorphosis subsequent to the Rocky Mountain upheaval. These coals are also rich in inert macerals due to the shearing stress and strain of the mountain movement. Large scale conversion of oxidized coal to liquid by hydrogenation processes is hampered by coke formation. Development of mesophase in the early stages of hydrogenation reduces the oil yield. A new approach involving initial upgrading of this inert-rich oxidized Cretaceous coal using the water gas shift reaction ( $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$ ) to improve the rheological properties and softening characteristics has been developed. The conversion to oil of the inert-rich oxidized coal by hydrogenation is increased considerably by pre-treatment of the coal using the water-gas shift process. Supporting evidence from microscopy, rheology, chemical analysis and nmr spectroscopy are discussed.

Coal deposits in Canada originate from two different geological ages: in eastern Canada the coals are from the Carboniferous period, while in Western Canada they belong to the Cretaceous period. Because of the influence of different vegetation, the eastern Canadian coals contain a higher portion of reactive macerals (vitrinite and exinite) whereas in the west more inert (semi fusinite and fusinite) and less litpic macerals are found. During metamorphosis, the Cretaceous coal seams were subjected to tectonic pressures of the Rocky Mountains giving rise to faults and cracks observed in these seams. Large amounts of these coals were oxidized or weathered "in-situ" in the presence of water containing dissolved oxygen and carbonates seeping through these cracks. Moreover, owing to the shearing stress and strain of the mountain formation, a large quantity of inert macerals was formed in these coals.

Some of these coals are not only rich in inert macerals but also the major part of the vitrinites are highly oxidized. These inert-rich oxidized coals produce a high proportion of unburnt carbon in the residue and fly-ash from pulverized fuel boilers<sup>1</sup>. The direct conversion of these oxidized coals to liquid products using hydrogen, with or without catalyst, is often hampered by coke formation<sup>2</sup>. In gasification, large quantities of inert macerals remain unaltered because of graphite-like structures<sup>3</sup>.

The Carboniferous coals of eastern Canada are prime coking coals. Their one drawback is the high sulphur content, mainly in the form of pyrite. These high-fluid, high-volatile coals possess large quantities of vitrinite and exinite and are also considered suitable for coal conversion processes.

Our previous published work has shown the formation of mesophase spheres, precursor to coke<sup>4,5,6</sup>, in the solid residue from hydrogenation of naturally oxidized coal. The non-coking nature of the oxidized coal has been previously ascribed to oxygen functional groups (ether linkages, hydroxyl and carbonyl groups) by Montgomery<sup>7</sup>, et al. Nandi and Ternan<sup>5</sup> observed from infra-red studies of partially oxidized coal,

treated with hydrogen, an increase on aliphatic  $-CH_2$ ,  $-CH_3$  groups and a decrease in CH, OH, C = C and C-O-C ether groups, along with an increase in coking properties (fluidity and plasticity). Yang, Sethi and Steinberg<sup>8</sup> also reported a decrease in ether linkages which would explain their results in the transformation of non-coking coal to coking coal: in other words, the restoration of the reactive nature of the oxidized vitrinite.

- The use of hydrogen alone to upgrade oxidized coal would be very uneconomical. Considerable work has been carried out on this process<sup>4-6</sup>. Alternatively, the present approach involves the water-gas<sup>9-11</sup> shift reaction ( $CO + H_2O \rightleftharpoons CO_2 + H_2$ ) for initial upgrading of the low-grade oxidized coals to improve the rheological properties such as fluidity and plasticity as well as solubility in liquids or gases. This process may represent a more economic alternative to the use of hydrogen alone<sup>9-10</sup>. The laboratory scale batch process for the treatment of western Canadian inert-rich oxidized Cretaceous coals with  $CO + H_2O$  has already been discussed in detail in our previous publications<sup>11</sup>.

Processed coals obtained via the water-gas shift reaction exhibit an improvement in rheological properties (plasticity and fluidity) and show very little initial development of mesophase on heating to 370°C<sup>11</sup>. Extensive mesophase formation reduces conversion yields drastically and renders the liquefaction of low-grade oxidized coal difficult due to the formation of large amounts of coke in the reactor<sup>2</sup>. In view of this problem the effect of liquefaction with hydrogen without catalyst on both original and processed coals was investigated.

## EXPERIMENTAL

### WATER-GAS SHIFT REDUCTION PROCESS

The details of this process have been published elsewhere<sup>11</sup> but a short description of the  $CO + H_2O$  treatment of oxidized coals is given here. After charging the rocking autoclave (0.1ℓ parr) with 100-150 g coal, (particle size <250µm dried overnight at 100°C) water (adjusted to between 12 - 17% of the coal charged) was added. In all cases the

heating rate was  $9^{\circ}\text{C}/\text{min}$ ; operating pressure and temperature varied from 24 to 35 MPa and 350 to  $465^{\circ}\text{C}$  respectively. Rapid quenching followed the prescribed reaction time, comprised between 0.3 and 60 min. The reaction products were cooled to  $200^{\circ}\text{C}$  in 2 min. and from  $200^{\circ}\text{C}$  to  $25^{\circ}\text{C}$  in 12 minutes. Once at room temperature, the autoclave was rocked to homogenize the cooled gas mixture which was vented off and measured with a wet test meter.

Subsequent to withdrawal from the autoclave the processed coal was put into a small glass container, flushed with argon and stored prior to physical and chemical analysis and relevant testing. The processed coal was then subjected to hydrogenation under the conditions described below.

#### COAL LIQUEFACTION PROCESS

A 0.1L stainless steel batch reactor, mounted on a shaking mechanism at a  $45^{\circ}$  angle to the axis of motion was used. The reactor was charged with approximately 25 g of feed and after closure was tested for pressure at 13.8 MPa and flushed with hydrogen. It was then pressurized with hydrogen to 6.9 MPa, heated at a rate of  $3^{\circ}\text{C}/\text{min}$  to the desired temperature and maintained at this temperature for 2 hours; the heating was then discontinued and the reactor was allowed to cool to room temperature<sup>2</sup>.

#### PRODUCT ANALYSIS

On completion of each experiment, a sample of gas was collected for analysis and the reactor contents were removed and weighed. The reacted coal (residue in autoclave) was then extracted with toluene in a Soxhlet extraction apparatus for at least 20 hours.

The toluene-soluble product was recovered by removing the toluene at a low pressure in a rotary evaporator. The conversion was calculated from the weight of the toluene insolubles.

## MICROSCOPIC EXAMINATION OF UNREACTED RESIDUE

The toluene-soluble portion of the hydrogenated coal from each experiment was subjected to microscopic examination. The residues were mounted in epoxy resin and polished by standard methods. Microscopic examination was carried out using a Leitz reflected light microscope. All micrographs were taken at 600 x magnification using an oil immersion lens.

The proximate, ultimate and petrographic analyses were carried out according to the ASTM specification. Dilatation test was conducted according to DIN No. 51739.

## RESULTS AND DISCUSSION

At the beginning of this work, fresh and naturally oxidized coal (exposed for 30 years in mine) from the same eastern Canadian seam (sample no. PH-1 and PH-2) were selected for hydrogenation in order to study the conversion to liquid and the nature of hydrogenation residues. The petrographic, physical and chemical analyses and dilatation tests are given in Table 1.

The conversion to liquid of the oxidized coal (PH-1) and fresh coal (PH-2) was carried out at 13.8 MPa, and 400°C for 2 hours. The conversion yield of toluene solubles for non-oxidized and oxidized coals was 40.9% and 12.8% respectively.

Microscopic examination of the residue after hydrogenation of the oxidized coal (PH-1) shows a large proportion of mesophase and formation of coke (Figure 1) whereas neither mesophase spheres or coke were detected in the hydrogenation residue of the fresh coal (PH-2) (see Figure 2). Conversion was about 28% higher for fresh coal than for oxidized coal even though both samples were treated with hydrogen under identical conditions. Indications are that naturally oxidized coal (or oxidized in-situ) on hydrogenation produces more coke than oil.

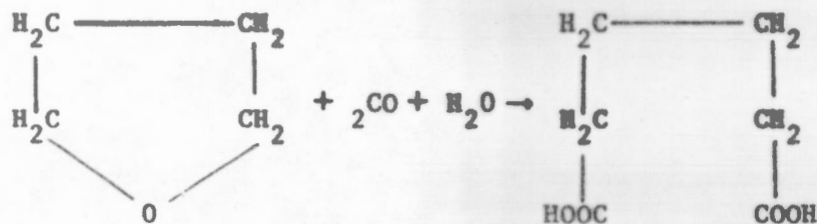
In view of the above observation, two inert-rich oxidized (in-situ) Cretaceous coals from western Canada were selected in order to investigate behaviour during hydrogenation under similar conditions. The

properties of these two coals, given in Table 2, are very similar to each other except that sample BR-1 has higher oxygen content (7.7%) and more inert macerals (59%) than sample CR-1.

On hydrogenation under the same conditions as above (except for a pressure of 13.0 MPa for BR-1) the conversion of CR-1 and BR-1 to liquids was 12.5% - 0.8% respectively. Microscopic examination of hydrogenation residues of both original samples of coal BR-1 and CR-1 show mesophase and coke formation shown in Figures 3 and 4 respectively.

The high oxygen content in these oxidized coals is partly due to ether linkages (C-O-C), hydroxyl groups (-O-H) and carboxyl groups (COOH). These may either be removed or broken down by the water-gas shift reaction in the following manner.

1. A direct role of CO acting upon the surface oxides and yielding  $\text{CO}_2$ .
2. A direct role of  $\text{CO} + \text{H}_2\text{O}$  on the opening of C-O-C linkages<sup>12</sup>.



3. An indirect reaction of CO which, in the presence of  $\text{H}_2\text{O}$ , undergoes the shift reaction generating "active hydrogen". This active hydrogen acts as a scavenging agent for free radicals and is responsible for the extensive dealkylation. Dealkylation not only increases the aromatics but also helps formation of mesophase.

It has also been reported by the authors that the rheological properties of the oxidized coals were improved and the aromaticity increased by the process<sup>11</sup>.

The coals CR-2 and BR-2 processed using the water-gas shift reaction showed significant increase in rheological properties and aromaticity ( $^{13}\text{C}_{\text{NMR}}$ ), (Table 2) and a concomitant decrease in softening temperature. These phenomena correlate with the restoration of the reactive nature of vitrinite and semi-fusinite and subsequent increase in conversion to oil during hydrogenation using the laboratory batch method described in the experimental part. Both processed coals showed improved conversion to oil compared with the original coals. The yield of oil for CR-2 increased from 12.5 to 17.6% and for BR-2 from 0.8 to 10.2% respectively (see Table 2). Figure 5 and 6 show the micrographs of the hydrogenation residues of BR-2 and CR-2. Very little mesophase or coke formation was observed.

### CONCLUSIONS

From the limited experimental data the following trends are noted:

1. During hydrogenation, the oxidized coal generally produced spherical mesophase and coke and very little oil compared with non-oxidized coal, which gave more oil and less coke.
2. The oxidized vitrinite and inert rich macerals (specifically fusinite) play a negative role in hydrogenation. This type of coal (high inert-rich) may not be suitable for liquefaction processes because of the presence of ether linkages and other oxygen functional groups.
3. The water-gas shift reaction ( $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$ ) plays a positive role in the opening of C-O-C linkages and also in removing alkyl groups. This process is able to restore the reactive nature of inert vitrinite (oxidized) and semi-fusinite.
4. Clear evidence of significant increase in oil yield on hydrogenation of oxidized coal, pretreated by the water-gas shift process, was observed in this work.

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EASTERN CANADIAN COAL

Table 1

Proximate Analysis

	PH-1 Naturally Oxidized	PH-2 Fresh
Moisture	2.6	1.7
Ash	2.0	3.9
Volatile Matter	32.4	35.2
Fixed Carbon	63.0	59.2
	<u>100.0</u>	<u>100.0</u>
Fluidity dd/min	0.9	11,700.
Oxygen (detd)	8.4	6.2
$f'_a$ (C aromaticity)	0.64	0.71

Dilatometric Test

Softening point $\theta_S$ ( $^{\circ}\text{C}$ )	362	350
Contraction C	25	24
Temperature of Max. Contraction ( $\theta_C$ ) ( $^{\circ}\text{C}$ )	447	401
Dilatation	nil	185
Temp. of max. dilatation	-	449
Plasticity Index = $C/(\theta_C - \theta_S)$	0.29	0.47
Conversion to liquid at $\theta_S$ 13.8 MPa & 400 $^{\circ}\text{C}$ for 2 hours (%)	12.8	40.9

Petrographic Analysis (vol %)

Vitrinite	86.4	80.4
Exinite	5.2	8.0
Mictinite	2.0	2.4
Fusinite	3.2	4.0
Semifusinite	3.2	3.2
Pyrite	-	<u>2.0</u>
	<u>100.0</u>	<u>100.0</u>

WESTERN CANADIAN COALS

TABLE 2

Proximate Analysis

	<u>CR-1</u> <u>Original</u>	<u>CR-2</u> <u>Processed</u>	<u>BR-1</u> <u>Original</u>	<u>BR-2</u> <u>Processed</u>
Moisture	1.7	1.7	1.9	0.5
Ash	8.6	9.5	16.1	15.2
Volatile Matter	22.4	25.8	24.9	25.2
Fixed Carbon	67.3	63.1	57.1	59.1

Ultimate Analysis

Carbon	79.3	78.0	72.2	74.1
Hydrogen	4.4	4.2	4.2	4.6
Sulphur	0.7	0.7	0.6	0.6
Nitrogen	1.2	0.8	1.0	0.8
Ash	8.8	9.7	16.4	15.3
Oxygen (diff)	5.6	6.6	5.6	4.6
	<u>100.0</u>	<u>100.0</u>	<u>100.0</u>	<u>100.0</u>
Oxygen (detd)	5.2	5.8	7.7	6.7
f <sub>a</sub> (C aromaticity)	0.63	0.77	-	-

Dilatometric Test

Softening Point $\theta_S$ ( $^{\circ}\text{C}$ )	411	337	411	280
Contraction C (%)	5	19	7	18
Temp of Max.				
Contraction $\theta_C$ ( $^{\circ}\text{C}$ )	486	435	500	451
Dilatation (%)	nil	-18	nil	nil
Temp. of Max.				
Dilatation ( $^{\circ}\text{C}$ )	-	464	-	-
Plasticity Index - C/( $\theta_C - \theta_S$ )	0.07	0.19	0.08	0.15
Conversion after Hydrogenation %	12.5	17.6	0.8	10.2

Petrographic Analysis (vol %)

	<u>CR 1</u>	<u>BR 1</u>
Vitrinite	51.8	40.6
Exinite	0.2	0.0
Micrinite	2.6	6.4
Fusinite	11.2	35.2
Semifusinite	<u>34.2</u>	<u>17.8</u>
	100.0	100.0

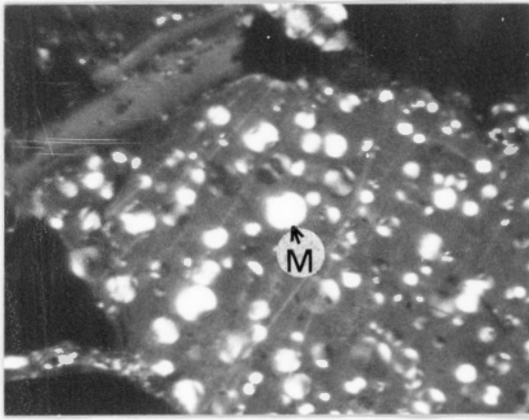


Fig. 1 Hydrogenation residue of oxidized coal PH-1 showing formation of mesophase spheres.

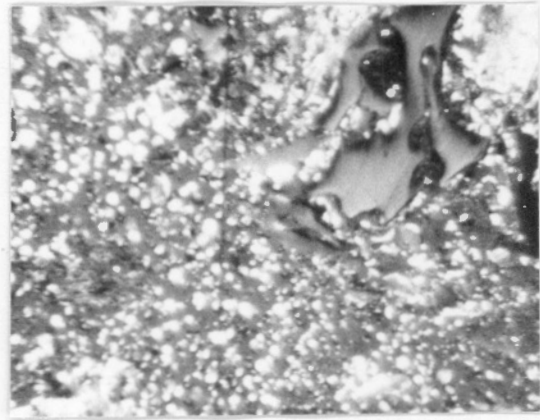


Fig. 4 Hydrogenation residue of oxidized coal CR-1 showing mesophase formation similar to Fig. 1.

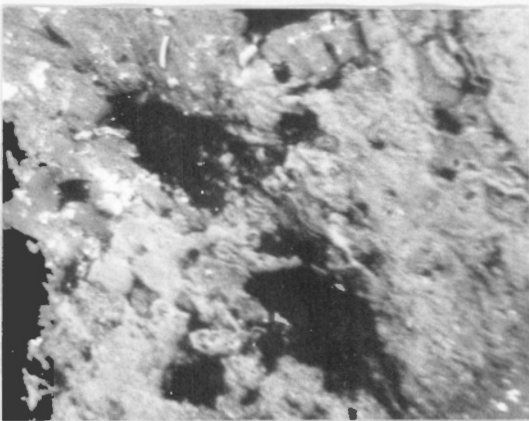


Fig. 2 Hydrogenation residue of non-oxidized coal PH-2 showing deterioration effect of  $H_2$  on vitrinite. No evidence of mesophase formation.

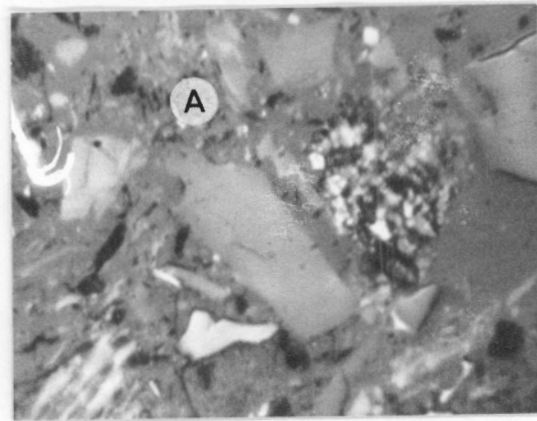


Fig. 5 Hydrogenation residue of oxidized coal BR-2 (processed) showing attack of hydrogen on vitrinite (A) and very little mesophase formation.

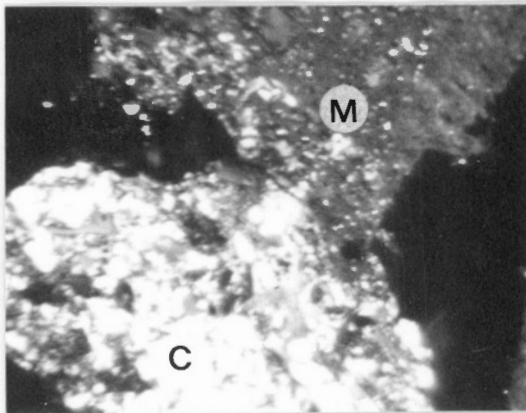


Fig. 3 Hydrogenation residue of oxidized coal BR-1 showing coke (C) formation and small mesophase (m).

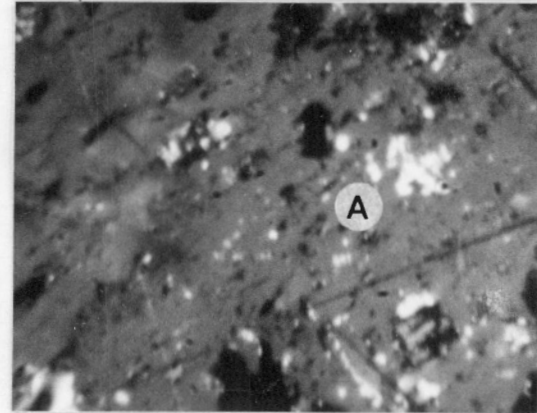


Fig. 6 Hydrogenation residue of CR-2 (processed). Hydrogen altered vitrinite (A) - Low reflectance. No mesophase or coke formation.