

Both stages require the use of hydrogen at moderately high pressures (16 MPa). The high oxygen content of the low rank coal means that excessive quantities of expensive hydrogen are needed to convert the oxygen to water, in addition to hydrogen uptake by the coal and bitumen. Although Alberta presently has ample supplies of natural gas for this purpose.

Earlier work^{3,4,5} has proven that CO/H₂O is more efficient than hydrogen at solubilization of coal in bitumen at temperatures below 400°C. More coal is dissolved and the reaction proceeds much more rapidly. The water gas shift reaction does not go to completeness during coal liquefaction or coprocessing. Equilibrium concentrations of carbon monoxide may exceed 50% with the bulk of the remaining gases being carbon dioxide and hydrogen. In a commercial operation it would be necessary to remove the carbon dioxide and recycle the unconverted carbon monoxide and any produced hydrogen. This present study was carried out to compare the efficiency of carbon monoxide/hydrogen mixtures with pure carbon monoxide for the solubilization of coal in bitumen and to establish the maximum permitted limit of hydrogen in the recycle gas steam. In addition, simulated two-stage experiments allowed a comparison of carbon monoxide and hydrogen in the overall coprocessing operation.

EXPERIMENTAL

Coprocessing experiments have been performed at ARC in miniautoclaves, 1 litre batch autoclaves, a hot charge-discharge unit and a 2 litre/hour bench unit. Since this work was restricted to the batch autoclaves, a brief description of the procedures will be given. Two modes of operation were employed: single stage and simulated two-stage.

In the single stage process coal, bitumen and an aqueous solution of potassium carbonate (shift reaction catalyst) were loaded into the autoclave. The autoclave was charged to 5.2 MPa (750 psi) with the gas mixture and heated to run temperature at about 5°C/minute. Operating conditions are listed in Table 1. When the run was complete the reaction mixture was cooled rapidly to 350°C by passing water through an internal cooling coil. The gaseous components were discharged at this elevated temperature through a condenser immersed in ice water. Gas volume was measured by a dry gas meter and its composition was determined by gas chromatography. The hot discharge eliminated foaming problems, due to dissolved carbon dioxide, which occurred when the unit was depressurized at room temperature.

In the simulated two-stage mode the process initially duplicated the single stage operation. Upon completion of the first stage a cracking catalyst, potassium molybdate/dimethyldisulfide (DMDS), was injected into the autoclave through a port in the head. The unit was repressurized with hydrogen 8.6 MPa (1250 psi) and a second heating cycle was completed. As before the gases were discharged at 350°C. The condensed oils and water from the two stages were combined prior to product distillation while the gas samples were analyzed individually.

A standard laboratory product separation procedure was established (Figure 1) to give distillable oil yield to 525°C, pyridine soluble organic material and insoluble organic material (IOM) remaining in the ash. Coal conversion was defined as
$$\frac{\text{Input coal} - \text{IOM}}{\text{Input coal}} \times 100\%$$

Properties of Highvale coal and Athabasca bitumen are given in Table 2. Both single and simulated two-stage experiments were performed in duplicate.

RESULTS AND DISCUSSION

A. Single Stage Experiments

Coal conversion and product distribution are summarized in Table 3 and Figure 2. The coal conversion can be seen to decline as the carbon monoxide content of the initial gas mixture was reduced. The pure carbon monoxide was much superior to the pure hydrogen while 50% carbon monoxide was still equal to the latter. These results ignore any pressure effects. Run pressure was lower at the lower carbon monoxide concentrations since the initial pressure was fixed. However, the partial pressure of the more active gas, carbon monoxide, was not constant. The initial pressure in the pure hydrogen run was 8.2 MPa (1200 psi) which could explain why it gave better coal conversion than 25% carbon monoxide.

Little evidence of upgrading of the coal or bitumen was observed apart from coal solubilization. Hydrocarbon gas and distillable oil yields were constant suggesting that thermal rather than chemical effects were responsible for their production. The distillable oil yield was essentially unchanged from that derived from the bitumen in the feedstock (33%); ie 525+°C conversion was zero. The only measurable change occurred in the formation of pyridine soluble organics, where pure carbon monoxide was most effective. Pyridine solubles declined in parallel with the coal conversion at the lower carbon monoxide concentrations. This confirmed earlier work that showed carbon monoxide was more effective than hydrogen for the solubilization of coal below 400°C due to the increased reactivity of the reducing species produced by the shift reaction, compared with molecular hydrogen.

Carbon monoxide conversion to carbon dioxide and hydrogen, varied little, being 61 ±1% for all experiments except the 25% carbon monoxide run (Table 4). As expected carbon dioxide production exceeded that of hydrogen in all cases although they should be equimolar if both were derived solely from the shift reaction. The coal had a high oxygen content, part of which is converted thermolytically to carbon dioxide upon heating. Produced hydrogen was below that expected from the shift reaction plus that initially present; consumption ranged from .4 to .7 moles per 100g of feed with a suggestion of a downward trend at lower carbon monoxide concentrations.

Hydrogen sulphide production was relatively constant at 0.2% MAF feedstock except for the pure hydrogen run where the higher partial pressure of reducing gas may have contributed to giving a slightly higher value, 0.3%. Thermal effects again appeared to outway chemical effects.

Product quality, expressed as elemental analyses was independant of the reducing gas composition. Hydrogen to carbon ratios were 1.6 for the distillable oils and 1.25-1.35 for the pyridine extract, sulfur was 2.6-2.8% and 3.4-4.1% respectively. Approximately 10% of the sulfur in the feedstock was converted to hydrogen sulfide, while little or none was present in the insoluble organic matter and ash. The majority of the input sulfur (96%) was derived from the bitumen and it remained within those fractions where the

bitumen products were concentrated, ie. the distillable oil and pyridine solubles. Little or no upgrading in terms of heteroatom removal could be attributed to the carbon monoxide solubilization process.

Simulated distillations of the distillable oils showed little variation (Table 5). The naphtha fraction accounted for $\approx 10\%$ while the medium oil fraction was $\approx 55\%$. Class analyses of the pyridine extracts, ie. non-volatile hydrocarbon, asphaltenes and preasphaltenes gave interesting results. The hydrocarbon content decreased as a percentage of the pyridine solubles as the carbon monoxide increased but the mass was relatively constant. Asphaltenes increased both in percentage and absolute terms. This suggested that the hydrocarbons required lower operating severity (less carbon monoxide) to solubilize, increased severity would result in more asphaltenes in the pyridine extract. More experimentation is required to confirm this observation because of the high scatter in the data.

B. Two Stage Experiments

Gas composition and conversion were discussed for the first stage in the previous section. Consumption of hydrogen in the second stage was not altered by the reducing gas used in the first stage. Hydrogen sulfide and hydrocarbon gas production were also constant, once more the result of thermolytic reaction pathways (Table 6). The difference in carbon oxides was quite marked, a factor of 10 greater for the carbon monoxide and 3 for the carbon dioxide in the carbon monoxide runs. It is most likely that these gases remained dissolved in the bitumen/coal liquids when the autoclave was vented at 350°C and were subsequently released in the second stage.

Product yields and distribution (Table 7) were not altered by the nature of the reducing gas present in the first stage. Overall coal conversion improved to approximately 90%. A high degree of upgrading took place with no difference attributable to the improved coal solubilization found in the carbon monoxide first stage. Pyridine extractable material declined from almost 60% to 22% of the product. Most of this material was converted to distillable oils. The hydrocarbon gas yield was high, combined first and second stage gas production being 10%. Conversion of the 525+°C material was 63% in both experimental modes.

CONCLUSIONS

Carbon monoxide was superior to hydrogen for the solubilization of coal in bitumen at temperatures below 400°C. However, it provided no benefit in a two stage process in terms of coal conversion, 525+°C conversion, and product quality. It does offer some potential economic benefits since lower temperatures can be employed in the first stage.

Coal solubilization could still approach 80% if the carbon monoxide stream contained hydrogen. Up to 25% hydrogen could be tolerated before a significant reduction in solubilization was observed. If the syngas mixtures function as rapidly as the pure carbon monoxide, then process improvements over pure hydrogen would include reduced first stage residence time and thus a smaller reaction vessel.

REFERENCES

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Table 1
Operating Conditions

	1st Stage	2nd Stage
Gas	CO/H ₂ or H ₂	H ₂
Pressure (MPa)	5.2 or 8.2	8.5
initial reaction	15.6-20.7	15.3-19.0
Temperature (°C)	390	440
Reaction time (min.)	30	60
Feed	Highvale Coal/ Athabasca Bitumen	non distillables from Stage I
Ratio	1:2.5	-
Catalyst	K ₂ CO ₃	K ₂ MoO ₄ /DMDS

Table 2
Properties of Feedstocks

	Highvale Coal	Athabasca Bitumen
Moisture	6.4%	-
Ash (as is)	13.5	-
Carbon	75.0	82.0%
Hydrogen	4.3	10.6
Nitrogen	1.1	0.6
Sulphur	0.2	4.5
Oxygen ¹	19.3	2.3
Distillables (525°C)	N/A	46
Pyridine Solubles	N/A	54
Hydrocarbons	-	29
Resins	-	48
Asphaltenes	-	23

¹ by difference

Table 3
Coal Conversion and Product Distribution -
Single Stage Experiments

Carbon Monoxide Concentration (%)	100	87	75	50	25	0 ¹
Coal Conversion (% MAF coal)	85	76	75	65	47	65
Product Distribution(g/100 g MAF feed)						
Hydrocarbon gases (C ₁ -C ₅)	1	1	1	1	1	1
Distillable Oils (up to 525°C)	31	32	32	32	32	31
Pyridine Soluble Organics	57	54	51	50	47	53

¹ Initial pressure 8.2 MPa (1200 psi)

Table 4
Gas Production and Consumption

Carbon Monoxide Content	100 ¹	87	75	50	25	0 ¹
CO conversion %	62	63	60	62	44	-
Gas Production (moles)						
Carbon dioxide	1.26	1.06	1.00	.62	.36	.11
Carbon monoxide	-.97	-.86	-.67	-.49	-.18	-
Hydrogen	.52	.56	.48	.46	.36	-.25
Hydrogen Sulfide	.013	.011	.009	.009	.009	.017

¹ from 1st stage of 2 stage experiments

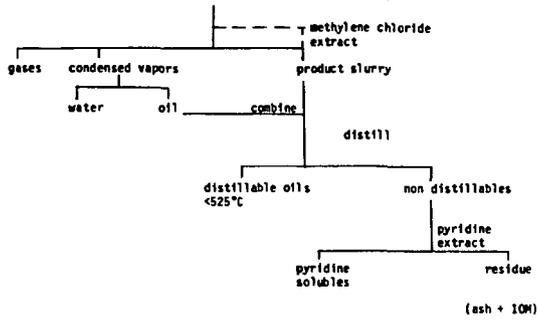
Table 5
Product Qualities - Single Stage Experiments

Carbon Monoxide %	100 ¹	87	75	50	25
A. Distillable Oil ²					
Naphtha		9	7	10 ¹	11 ¹
light gas oil		55	54	58	60
heavy gas oil		36	39	32	29
sulfur	2.6	2.6	2.7	2.7	2.8
hydrogen:carbon	1.65	1.6	1.6	1.6	1.6
B. Pyridine Extract					
hydrogen:carbon	1.35	1.3	1.25	1.25	1.25
nitrogen	2.3	1.6	1.2	1.1	1.3
sulfur	3.4	3.8	4.1	3.7	4.0
C. Class Analysis					
hydrocarbons		49	45	61 ¹	60
asphaltenes		43	50	31	31
preasphaltenes		8	5	7	9

¹ single analysis

² all percent except hydrogen to carbon ratio

Figure 1
Product Work-up Procedure



Analysis performed

gases	:	composition, C_1-C_5
water	:	none
distillable oils:		C, H, N, S , simulated distillation
pyridine extract:		C, H, N, S , class analysis
residue	:	proximate

Figure 2: Coprocessing Product Yields as a Function of Reducing Gas Composition

