# INFLUENCE OF REDUCING GAS IN THE COPROCESSING OF COAL AND BITUMEN

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## INTRODUCTION

Coprocessing of bitumen/heavy oils with coals can offer a viable route for production of synthetic crudes. Under certain conditions these low grade materials can have mutual beneficial synergistic effects during hydroprocessing. Also, additional synthetic crudes become available from coal during the upgrading of bitumen/heavy oils. There is an added advantage over the conventional coal liquefaction process in that no solvent recycling is required. A comparison is made between synthesis gas and hydrogen as reducing gases for the coprocessing of an Alberta subbituminous C coal and Cold Lake vacuum bottoms. Product yields and qualities are compared at two levels of processing severity.

## EXPERIMENTAL

The feed was a mixture of Cold Lake vacuum bottoms containing 83.2% pitch (+525°C material) and subbituminous C coal from Alberta (1). This slurry was processed under two different reducing feed gases: pure hydrogen and synthesis gas (30 mol % carbon monoxide in hydrogen). The liquid products were obtained at 60% and 70% pitch conversion. Pitch is defined as the material boiling above 525°C and pitch conversion is a measure of the difference in pitch concentration before and after coprocessing (1).

The products were distilled to obtain a naphtha fraction (<205°C), a distillate fraction (205°C-525°C) and a residue. This residue was further characterized by solubility in order to quantitate the residual oil (pentane-soluble), the asphaltenes (pentane-insoluble, toluene-soluble) and the preasphaltenes (toluene-insoluble, tetrahydrofuran-soluble).

The distillate portion (205°C-525°C) was combined with the residual oil (pentane-soluble residues) and hydrocarbon-type separation was performed using a modified API procedure developed by Sawatzky et al. (2). A column was packed with silica-alumina adsorbents. The solvents and the sequence of elution of the different fractions are shown in Table 1.

The polyaromatic fraction from hydrocarbon-type separation was separated by HPLC on a bonded amino column in order to quantitate the triaromatics, the tetraaromatics and molecules having five or more aromatic rings (3,4).

Fractions from hydrocarbon-type separation and polyaromatic subfractions from HPLC were characterized by gas chromatography equipped with a Dexsil 300 packed column and FID detector. Molecular weights of all aromatic fractions and concentrations of HPLC subfractions were determined from these runs according to a method published elsewhere (4).

## RESULTS AND DISCUSSION

The primary characterization of the products is shown in Table 2. As expected, higher processing severity leads to lighter products. Gas and distillate yields are significantly higher for the high conversion products whereas residue levels were definitely lower.

Table 2 shows that the use of hydrogen results in less residue and leads to a higher coal conversion at both levels of severity. Also, the naphtha yield is significantly higher when using hydrogen especially under lower pitch conversion. Conversely, distillates over 200°C are favored by the synthesis gas especially at higher pitch conversion. This may indicate that when using hydrogen larger molecules are cracked into smaller units to a greater extent. However, most of these results are not indicative of a definite trend for designating the best reducing gas but they indicate that synthesis gas does not have an adverse effect on the quality of the products. Nevertheless, the use of synthesis gas resulted in less hydrogen equivalent consumption particularly at lower severity. This is also a positive aspect of the use of synthesis gas.

Besides product slate, quality of the products is obviously an important factor. Hydrocarbon-type separations were thus performed on each of the four samples in order to assess the quality of some of the products. Only distillates over 200°C combined with the residual oil were used in this chromatographic separation. Table 3 shows that the distribution of the recovered samples is similar for the two reducing gases. Gas chromatographic runs of the various fractions showed very similar chromatograms for the same concentration. Since the chromatograms were very similar, the calculated average molecular weights were also practically the same for all aromatic fractions. In some of the chromatograms, we noticed the presence of unresolved peaks having a high retention time. However, the concentration of these compounds was not high enough to affect the average molecular weights or the molecular weight distribution.

The most important feature about the hydrocarbon-type separation is that recoveries of material from the column were much higher for the synthesis gas. This would indicate that synthesis gas induces a higher conversion of very polar/basic molecules at both conversion levels. Compounds that can be strongly retained on such a system are highly polar and basic material or very heavy molecules similar to asphaltenes. In order to explain the differences between the material recoveries noted in Table 3, elemental analysis was performed on the samples that were separated on the hydrocarbon-type columns (Table 4). Unfortunately, the differences in heteroatomic levels cannot be significantly related to the column holdback. Sulphur levels seem to indicate that pure hydrogen is slightly better for eliminating sulphur compounds. Nitrogen levels are the same within experimental error and oxygen levels do not designate a particular gas. Although the elemental analysis results do not explain the differences in recovery between the two reducing gases, these recoveries strongly indicate that there is a significant difference between the two products. The higher recoveries using synthesis gas cannot be explained at

this point but they are reproducible indicating that the use of pure hydrogen produces a strong adsorption of very polar or heavy material on the column. This might be an indication that pure hydrogen and synthesis gas would react with the slurry feed in different ways thus leaving molecules of different polarity and basicity in the products. For example, it is known that carbon monoxide interacts directly with oxygen functionality in low-rank coals. A similar behaviour could be expected in subbituminous coals. In any case, the strongly retained compounds can be assumed to be undesirable material in view of production of synthetic fuels therefore the use of synthesis gas has advantages. Since the composition of the recovered material is not significantly different for the two reducing gases, we can at least conclude that the use of synthesis gas would not be deleterious. Moreover, in cases where carbon monoxide is cheaper than hydrogen, synthesis gas would be an advantageous alternative.

## CONCLUSIONS

This study shows how the use of synthesis gas in coprocessing of coal and bitumen could be advantageous over hydrogen. Although most results indicate that pure hydrogen and synthesis gas have similar hydrocarbon yields, synthesis gas seems to be advantageous for the cracking/hydrogenation of very polar undesirable molecules that could be present in the valuable products. Compared with hydrogen it also enhances the formation of distillates. Finally, synthesis gas shows a significantly lower hydrogen equivalent consumption especially under moderate operating severity.

## REFERENCES


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Table 1 - Hydrocarbon-type separation procedure

| Solvent | Quantity | Fraction |
|---|---|---|
| Pentane | 250 mL | Saturates |
| 5% toluene/pentane | 300 mL | Monoaromatics |
| 15% toluene/pentane | 300 mL | Diaromatics |
| Toluene | 100 mL | Polyaromatics |
| Methanol/toluene (50/50) | 100 mL | Polars |
| Methanol | 100 mL | Polars |

Note: The column is flushed with pentane at the end of the sequence to ensure complete elution of the methanol.

Table 2 - Composition of products from coprocessing

| | Severity | | | |
|---|---|---|---|---|
| | 60% pitch conversion | | 70% pitch conversion | |
| Reducing gas | $H_2$ | $H_2/CO$ | $H_2$ | $H_2/CO$ |
| $H_2$ equivalent consumption (%) | 3.32 | 2.0 | 3.15 | 2.90 |
| Coal conversion (%) | 74.0 | 73.7 | 83.8 | 78.5 |
| **Fractionation:** | | | | |
| $C_1$-$C_4$ yield (%) | 5.3 | 5.0 | 6.6 | 7.2 |
| Naphtha (%) | 16.3 | 9.7 | 15.2 | 13.1 |
| Distillate +205°C (%) * | 45.1 | 46.5 | 49.7 | 54.2 |
| Residual oil (%) | 15.0 | 16.2 | 11.2 | 11.8 |
| Asphaltenes (%) | 6.3 | 9.3 | 5.7 | 5.8 |
| Preasphaltenes (%) | 3.8 | 3.4 | 1.6 | 2.1 |
| Residue (%) ** | 32.5 | 37.1 | 23.4 | 26.3 |

* In hydrocarbon-type separation, the distillates are combined with the residual oil.

** The residue includes residual oil, asphaltenes and preasphaltenes and tetrahydrofuran insolubles (unreacted coal).

Table 3 - Hydrocarbon-type separation of coprocessing products (distillates 205-525°C + residual oil)

| Fractions | 60% pitch conversion | | 70% pitch conversion | |
|---|---|---|---|---|
| | $H_2$ | $H_2/CO$ | $H_2$ | $H_2/CO$ |
| Saturates (%) | 30.4 | 35.0 | 38.8 | 36.7 |
| Monoaromatics (%) | 11.1 | 10.4 | 9.7 | 12.3 |
| Diaromatics (%) | 12.9 | 13.8 | 10.9 | 10.9 |
| Polyaromatics (%) * | 12.0 | 13.6 | 15.4 | 15.3 |
| Triaromatics (%) | 5.0 | 6.2 | | |
| Tetraaromatics (%) | 4.0 | 4.7 | | |
| Higher aromatics (%) | 3.0 | 2.7 | | |
| Polars (MeOH/Tol) (%) | 18.6 | 20.4 | 11.9 | 19.0 |
| Polars (MeOH) (%) | 1.9 | 1.8 | 1.6 | 2.9 |
| Recovery ** | 86.9(3) | 95.0(2) | 88.3(2) | 97.1(2) |

* Polyaromatics = triaromatics + tetraaromatics + higher aromatics.
** The number in parenthesis indicates the number of replicates.

Table 4 - Elemental analysis of products (distillates 205-525°C + residual oil, wt %)

| | 60% pitch conversion | | 70% pitch conversion | |
|---|---|---|---|---|
| | $H_2$ | $H_2/CO$ | $H_2$ | $H_2/CO$ |
| Carbon | 84.60 | 84.93 | 84.90 | 84.35 |
| Hydrogen | 10.43 | 10.56 | 10.40 | 10.43 |
| Sulphur | 2.02 | 2.32 | 2.07 | 2.46 |
| Nitrogen | 0.60 | 0.55 | 0.68 | 0.64 |
| Oxygen (by difference) | 2.35 | 1.64 | 1.95 | 2.12 |