

## MATHEMATICAL MODELLING OF COPROCESSING KINETICS

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### INTRODUCTION

CANMET has played a major role in heavy oil/coal coprocessing since the late 1970's. CANMET has conducted studies on determining characteristics of the products and residues from the coprocessing of heavy oil and coal, development of high performance catalysts for the coprocessing of heavy oils and coal, and demonstrating the feasibility of coprocessing Canadian feedstocks. An ongoing experimental program using a continuous bench-scale reactor system has generated a significant amount of scientific and engineering information on process performance and operation. These data were previously reviewed and analyzed for reaction engineering models (1). As a continuation of that study, CANMET and Lobbe undertook a program on computer simulation of coprocessing with special emphasis on studying the effects of coal and additives on the yield and selectivity of coprocessing products, and development of a Coprocessing Simulator as a tool for further work (2).

### EXPERIMENTAL

The experiments were conducted in a continuous-flow unit. A detailed description of the unit is given elsewhere (3). Forestburg subbituminous coal from Alberta and Cold Lake + 454°C cut vacuum bottoms were used in the experiments. The coal was ground to -200 mesh and slurried with heavy oil at concentrations of 5 to 30 percent, daf slurry basis. A disposable iron sulphide catalyst was added in amounts from 0.5 to 1.0 percent (w/w Fe on daf slurry). Methods used for catalyst preparation were described previously by Fouda and Kelly (4).

The coprocessing runs were conducted over a temperature range of 400 to 450°C, nominal slurry space velocity 0.5 to 1.5 kg/l/hr, reactor pressure 2000 to 3000 psig, and run duration of 80 to 120 minutes each. The coprocessing workup procedures and product analysis are depicted in Figure 1. The relationships between pitch and distillate yields, and product selectivity are shown in Figures 2 and 3.

#### MODELLING COPROCESSING KINETICS

Previous publications and reports (1) (2) (5) have shown that despite the limitations of lumping procedures (grouping of the product components) in describing kinetics of complex reaction mixtures like heavy oil/coal, the lumping approach can provide a good approximation of the behavior of various product groups in coprocessing. The performed analyses showed that the characteristics of the model components in Figure 4 are independent of the severity of coprocessing and, therefore, they can be used as a definition of pseudo-components in kinetic analysis. Typical predictive capabilities for low and high severity runs of the developed kinetic models (1) (2) are shown in Table 1. The differences between Model A and Model B pertain to the difference in kinetic rate constants only and not the model structure. This was due to the fact that rate constants for formation of Naphtha and other lighter components were weak functions of temperature and required small adjustments for coprocessing experiments conducted over a wide temperature range as shown in Table 1.

In the current work, a simulator capable of optimizing coprocessing parameters was developed. The simulator included lumped kinetic models for coprocessing reactants and product, coke formation models and hydrogen consumption models as a function of feed composition, additive concentration and reactor operating parameters. Selected examples of product yield simulation over a range of temperatures, for three space velocities, are depicted in Figures 5 to 8. The data shows strong interdependence of temperature and space velocity, over the range studied, and the presence of localized maxima and minima product yield and selectivity, over the reactor operating parameters studied.

Interesting features of coprocessing results are presented in Figure 9, depicting simulation of distillate yield over a range of coal concentration, with and without adjustment of the process model for relative volatility of coprocessing feed and product components. It is shown that the extent of product/feed flashing (adjusted  $\phi$  constants) affects the residence time distribution (RTD) of the heavy components and results in apparent synergistic effects between heavy oil and coal. These effects are particularly strong at low coal concentration and low process severity.

An interesting effect was also shown by optimization studies using derived coke formation and hydrogen consumption models for coprocessing. Table 2 gives optimized results for two different constraints (limits) on coke formation. The data show relatively similar product slate composition despite significant differences (by an order of about 20) in the amount of coke being formed.

#### SUMMARY

Detailed modelling of the coprocessing of heavy oil bottoms and subbituminous coal, and an evaluation of the effects of coal and additive concentration on product yields and selectivity were completed for the CANMET process. Also, a computer simulation package was developed for simulating and optimizing heavy oil and coal coprocessing kinetics, refining kinetic models and assisting reaction engineering studies for various feedstocks.

Simulation studies revealed: 1) the synergistic effects between heavy oil and coal could be explained, in part, by simulating variant mean residence time distribution (RTD) for the feed and product components; 2) the maximum in the yield of preasphaltenes was shown to shift to lower temperature with increasing residence time; and 3) the extent of product/feed flashing strongly affected the RTD of the heavy components with the RTD effects being most pronounced at low coal concentration and low process severity.

Optimization studies showed that hydrogen consumption was not the key optimization variable at the process conditions studied, i.e., at relatively high heavy gas/oil yield. Also, the studies showed that coke formation and its sensitivity to temperature made optimization of the product slate difficult, i.e., coke formation was a monotonic function of the initial coal and additive concentration, while temperature acted like a threshold variable above which coke was formed rapidly.

## REFERENCES

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**Table 1. COPROCESSING PRODUCT YIELD FOR MODEL A AND MODEL B RATE CONSTANTS**

	<u>MODEL A</u>	<u>MODEL B</u>	<u>EXPERIMENT</u>
<b>LOW SEVERITY RUN</b>			
THFI	15.7	15.2	14.7
Preasphaltenes	5.1	5.0	1.8
Asphaltenes	14.1	15.3	13.7
Oil	40.1	39.7	37.9
HGO 1&2	13.6	15.2	13.7
LGO	7.3	7.7	6.3
Naphtha	3.5	1.7	4.0
C <sub>1</sub> -C <sub>4</sub>	0.3	0.3	---
<b>HIGH SEVERITY RUN</b>			
THFI	2.5	1.3	4.3
Preasphaltenes	5.2	2.7	1.8
Asphaltenes	8.3	8.7	1.5
Oil	6.8	5.6	6.7
HGO 1&2	22.4	31.3	32.6
LGO	18.3	26.1	25.7
Naphtha	28.0	18.1	15.3
C <sub>1</sub> -C <sub>4</sub>	8.6	6.1	6.4

**Table 2. OPTIMIZATION RESULTS FOR FORESTBURG AND COLD LAKE FEED**

Product Slate Optimized	<u>SPECIFIED CONCENTRATIONS FOR COKE</u>	
	<u>&lt; 2%</u>	<u>&lt; 5%</u>
THFI	0.9	0.8
PA	2.9	2.8
A	6.5	6.3
O	4.0	3.8
HGO	28.4	28.3
LGO	25.5	25.1
NAPHTHA	24.9	25.7
C <sub>1</sub> -C <sub>4</sub>	6.9	7.1
Hydrogen Consumption	3.52	3.59
Estimated Coke	0.19	3.55

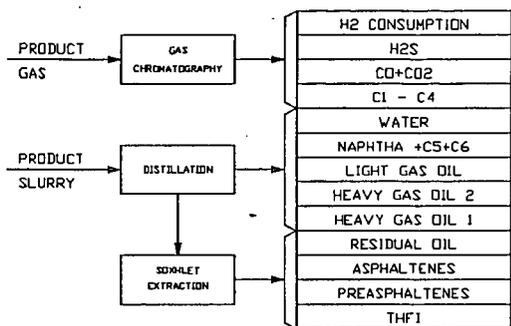


Figure 1. SUMMARY OF PRODUCT ANALYSES

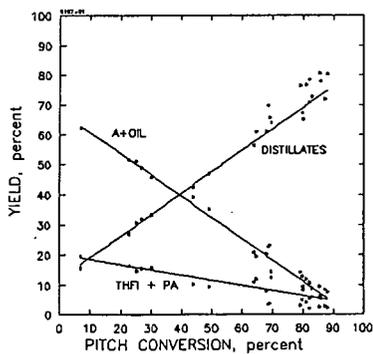


Figure 2. SELECTIVITY OF COPROCESSING PRODUCTS

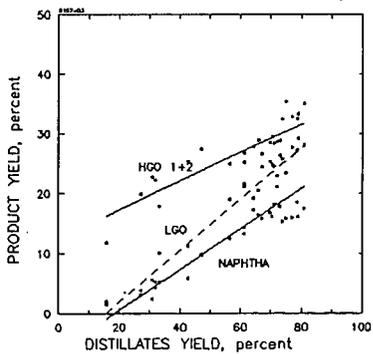


Figure 3. SELECTIVITY OF DISTILLATE FRACTIONS

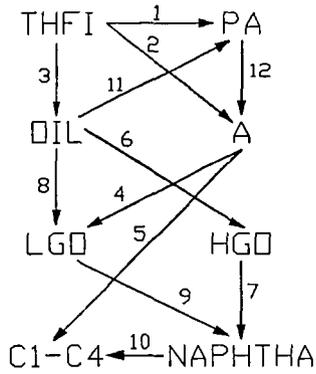


Figure 4. CANMET COPROCESSING MODEL INCORPORATING ADDUCT FORMATION

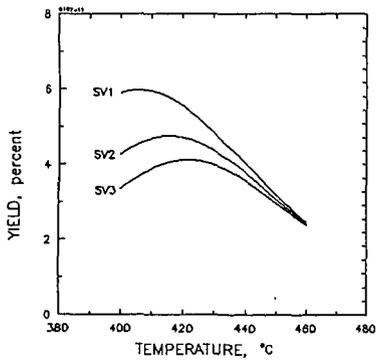


Figure 5. EFFECT OF TEMPERATURE ON PREASPHALTENES YIELD AT THREE SPACE VELOCITIES

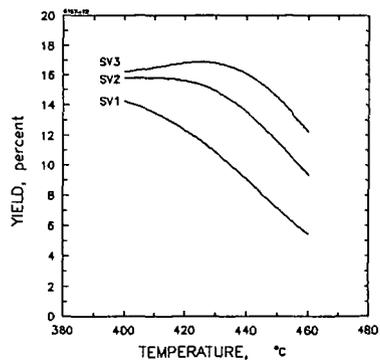


Figure 6. EFFECT OF TEMPERATURE ON ASPHALTENES YIELD AT THREE SPACE VELOCITIES

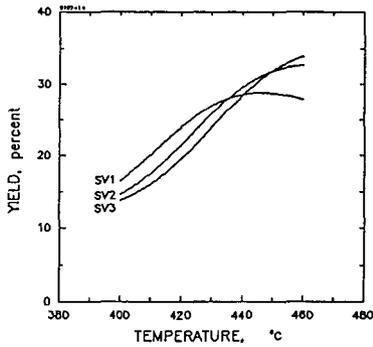


Figure 7. EFFECT OF TEMPERATURE ON HEAVY GAS OIL (1&2) YIELD AT THREE SPACE VELOCITIES

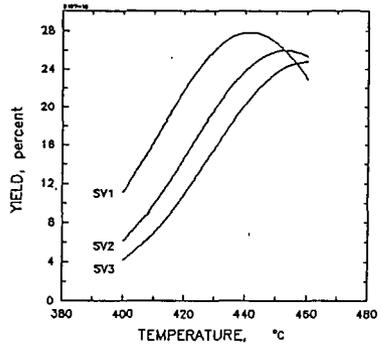


Figure 8. EFFECT OF TEMPERATURE ON LIGHT GAS OIL YIELD AT THREE SPACE VELOCITIES

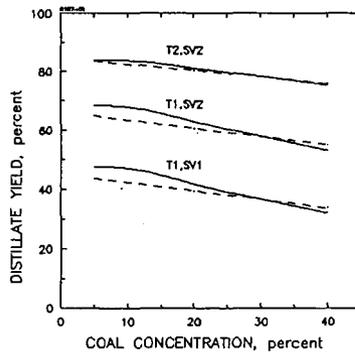


Figure 9. SIMULATED EFFECT OF COAL CONCENTRATION ON TOTAL DISTILLATE YIELD (solid lines for adjusted  $\phi$  constants)