THERMAL HYDROCRACKING OF ATHABASCA BITUMEN: COMPARISON OF COMPUTER-SIMULATED FEED AND PRODUCT VAPORIZATION VALUES WITH PILOT PLANT DATA

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INTRODUCTION

The Energy Research Laboratories of the Canada Centre for Mineral and Energy Technology (CANMET) are engaged in a continuing upgrading project involving the hydrocracking of Canadian oil sand bitumen and heavy oil. Such upgrading is necessary to remove sulphur and to reduce the viscosity of the bitumen to facilitate transport by pipeline to the refinery. Currently upgrading is accomplished on a commercial scale by Great Canadian Oil Sands Limited using a coking process which converts up to 20% of the bitumen to char. One aim of the CANMET work is to develop an economical process which would convert all of the bitumen to usable products, and thus reduce the waste of a valuable resource. For this purpose a one-barrel-per-day pilot plant was built and has been operated successfully with a variety of feedstocks. This work has concentrated on both plant operability, in particular the prevention of reactor coking (1), and on the effect of operating conditions on yields and product qualities (2).

Efficient and economical scale-up of this process to a commercial-size plant requires quantitative knowledge of both the degree of vaporization of feed and product and the fraction of the reactor occupied by gas under reactor conditions. The latter, usually referred to as voidage, has already been investigated in detail (3). Such knowledge is needed to calculate hydrogen partial pressures and true liquid and vapour residence times. These in turn are necessary to accurately estimate the size of various plant components as well as to formulate a kinetic model for the thermal hydrocracking reaction.

Because it is not feasible to measure liquid and vapour compositions in the reactor directly, recourse must be made to computational methods. These involve estimating the equilibrium vaporization constant, K, for various components of the system using known or estimated values of their thermodynamic properties.

Computations for the present study were carried out using the Grayson-Streed modification of the Chao-Seader correlation employing the principle of corresponding states (4,5). A package program was employed.

Vapour-liquid equilibrium data were obtained from measurements in a hot separator downstream of the pilot plant reactor. This well-mixed separator, which was temperature controlled, was assumed to behave as a single stage contactor, and measurements of liquid and vapour flows and concentrations were taken at steady state conditions.

EXPERIMENTAL

The pilot plant is shown schematically in Fig. 1. Bitumen and hydrogen are fed at the bottom of a long unpacked heated tubular column (3.81 cm diam. x 3.95 m long). The hydrocracked products are led from the top of the reactor to a hot separator kept at a temperature below that of the reactor. The heavy oil product is withdrawn and the vapour passed into a cold receiver and condensed. The light oil product is again withdrawn and collected. The hot separator was well mixed as the reactor products entered below the liquid level, and there was a high ratio of gas to liquid. It follows that the fraction of liquid vaporized, f, was the weight of light oil product divided by the total liquid product. The hot separator was temperature controlled so that the above ratio could be obtained as a function of temperature. The gas flow was metered using the orifice, and the gas composition at the reactor inlet controlled by scrubbing. Accordingly the actual gas composition and flow in the hot separator could be computed by using these data along with dissolved gas flows and compositions, reaction hydrogen requirements and hydrocarbon gas make.

Athabasca bitumen containing 51% pitch (material boiling above 524°C equivalent atmospheric boiling temperature) was fed in all cases. Products are identified by the amount of pitch conversion based on feed. Further details are given in Reference 6.

The computer simulation was carried out for CANMET by Saturn Engineering, Calgary, Alberta, using the DISTILL program licensed by the Chem Share Corporation, Houston, Texas. Simulations were carried out for Athabasca bitumen and four typical hydrocracked products covering the range 49 to 93% pitch conversion. Input to the program consisted of liquid and gas rates, compositions and properties. The composition and properties of liquid feed and product were approximated by ten fractions with mean average boiling points ranging from 65.5°C (150°F) to 648.9°C (1200°F). These fractions were derived from Hempel distillations and gravities of each cut, using standard correlation procedures for petroleum fractions.

For each specified temperature and pressure combination the program calculated f, the weight fraction of liquid that vaporizes under the specified conditions, as a function of specified values of G/L, the ratio of gas rate at STP (in g mol/h) to liquid rate at STP (in kg/h). Gas composition was also entered and treated as a parameter.

RESULTS AND DISCUSSION

Calculated values of the degree of vaporization were plotted as functions of G/L and temperature (Figs. 2 to 5). From these graphs interpolations can be made to obtain f values at conditions other than those specified. Figures 2 and 3 illustrate the effect of G/L on f for different pressures and temperatures for bitumen and for a hydrocracked product with 93% pitch conversion. The trend is an initial rapid increase in f followed by a general flattening out of the curve, a trend which becomes more pronounced at higher temperatures and pressures. This reflects the presence of a very high boiling fraction (pitch) which is vaporized to only a small extent. A similar trend is seen when f is plotted against temperature as shown in Figs. 4 and 5 for bitumen and 3 hydrocracked products (49, 76 and 93% pitch conversion) at 10.44 MPa and various G/L values. The degree of vaporization in the high conversion case reached very high values.

The effect of pressure on f is also illustrated in Figs. 2 and 3. For typical conditions of 450°C and G/L = 40 g mol/kg, increasing pressure from 10.44 to 17.34 MPa decreases f by 50% from 0.37 to 0.185 for Athabasca bitumen, and by 20%,

from 0.86 to 0.69 for product hydrocracked to 93% conversion; while for G/L = 10, f is decreased by 54% and 44% respectively.

Another factor which influences the degree of vaporization is the gas composition; increasing the concentration of hydrogen causes a decrease in f. This is illustrated in Fig. 6 for 350°C and 13.89 MPa for a product hydrocracked to 83% conversion. In the range 50 to 90 mol % H_2, f is linearly proportional to hydrogen concentration. For all hydrocracked products, f was calculated for both 60 and 80 mol %; for most cases studied an increase of 33% from 60 to 80 mol % H_2 caused an approximate 10% decrease in f.

Average liquid residence times (t) can be calculated from these vaporization figures by taking average values for bitumen and hydrocracked product, after making allowance for the fraction of reactor volume occupied by gas (voidage), as follows:

t = [(reactor vol)x(1-voidage)]/[(vol of liquid fed per h)x(1-ave.fraction vaporized)]

Such calculations were carried out for a series of pilot plant runs as shown in Fig. 7, where the product of average residence time and liquid hourly space velocity (LHSV) were plotted against the temperature at which each hydrocracked product was obtained. The average fraction vaporized was taken as the average of f for bitumen and for product. As each product represented a different pitch conversion, and as the computer simulation gave vaporization values only for a limited number of products at fixed conversions, a linear interpolation was used to calculate values for these intermediate conversions. A similar interpolation was also used to correct for different hydrogen concentrations. Figure 7 shows that the calculated residence times are very sensitive to reaction temperature, and become increasingly higher than the nominal space time as temperature and space velocity increase.

Although experimental vaporization data for the reactor were not available, it was possible to test the computer simulation by comparing the calculated values of f with experimental data obtained at lower temperatures for the hot separator where vapour/liquid ratios are routinely measured. Again the f values calculated by computer were interpolated to correct for pitch conversion and hydrogen concentration for each run considered. To test the data for bitumen itself a series of runs were carried out with both reactor and hot separator at 350°C and 370°C at which temperatures hydrocracking reactions occur to only a limited extent (≃ 3% pitch conversion at 370°C). Calculated values were plotted against experimental data (Fig. 8). The best line fitted the equation:

$$F_E = (3.3 \pm 0.9) + (0.85 \pm 0.07)F_C$$

where F_E and F_C are experimental and calculated values of the per cent of liquid vaporized. The agreement is reasonable considering all the possible sources of experimental error, and in fact F_E and F_C are in close agreement above about 15%.

The results for hydrocracked products are shown in Fig. 9, in which 75 data from pilot plant runs carried out under a variety of conditions are compared with calculated values. Pressure ranged from 10.44 to 17.34 MPa, and temperature from 300 to 430°C. Although there is considerable spread in the data, the best line lies close to the diagonal and is given by the equation:

$$F_E = (1.8 \pm 1.2) + (0.95 \pm 0.04)F_C$$

It is believed that much of the spread is caused by experimental error, particularly in measurements of gas rate and composition where errors of ± 5% or

more can occur. Errors can also occur in weighing and in temperature determinations. The following Table illustrates the sensitivity of f to variations in G/L and temperature for typical values of these variables.

Sensitivity of f to Variations in G/L and Temperature

	G/L = 20 g mol/kg					G/L = 40 g mol/kg				
	400°C	δ, %[a]	450°C	δ, %[a]	Δ, %[b]	400°C	δ, %[a]	450°C	δ, %[a]	Δ, %[b]
Bitumen	0.1175	8.5	0.241	8.3	105.1	0.205	10.0	0.378	4.2	84.4
93% Prod.	0.505	4.6	0.712	3.2	29.1	0.672	4.2	0.860	1.7	28.0

[a] Percentage increase in f for a 12.5% increase in G/L.
[b] Percentage increase in f for a 12.5% increase in T.

It is seen that for a 12.5% increase, temperature has a greater effect than G/L. However, as the accuracy of temperature measurements is much greater than those of G/L determinations, the errors are probably of similar magnitude.

Errors can also be introduced by the approximations used in the interpolations for pitch conversion and hydrogen concentrations, as well from discrepancies between simulated and actual liquid and gas properties.

CONCLUSIONS

Comparison of calculated values of liquid vaporization using a computer simulation with experimental data indicated that such computational methods will give reasonably accurate values for the degree of vaporization, considering the approximation and experimental errors involved, for a very heavy oil such as tar sand bitumen and its hydrocracked products.

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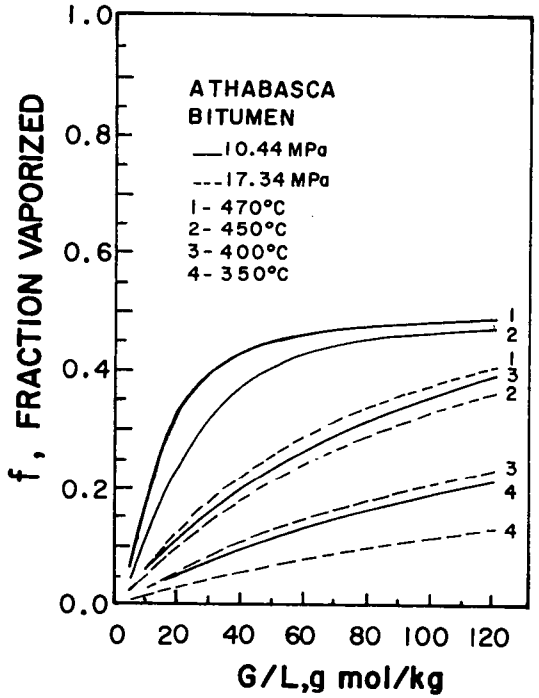

FIGURE 2 - Fraction of Liquid Vaporized, f, as a Function of Gas to Liquid Feed Rate Ratio, G/L g mol/kg, for Bitumen at 10.44 to 17.34 MPa and 350 to 470°C

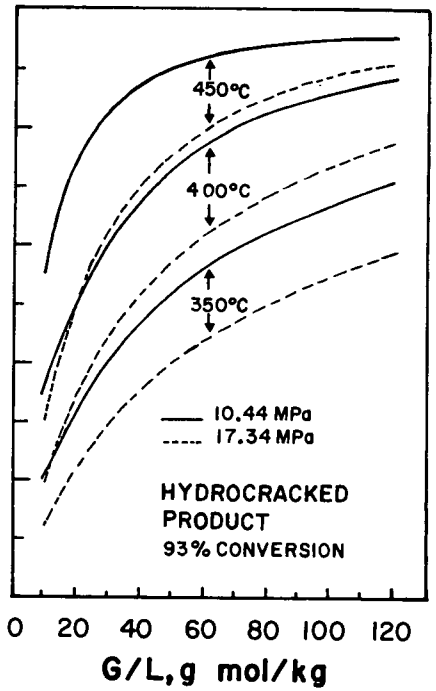

FIGURE 3 - Fraction of Liquid Vaporized, f, as a Function of Gas to Liquid Feed Rate Ratio, G/L g mol/kg, for 93% hydrocracked product at 10.44 to 17.34 MPa, and 350 to 450°C

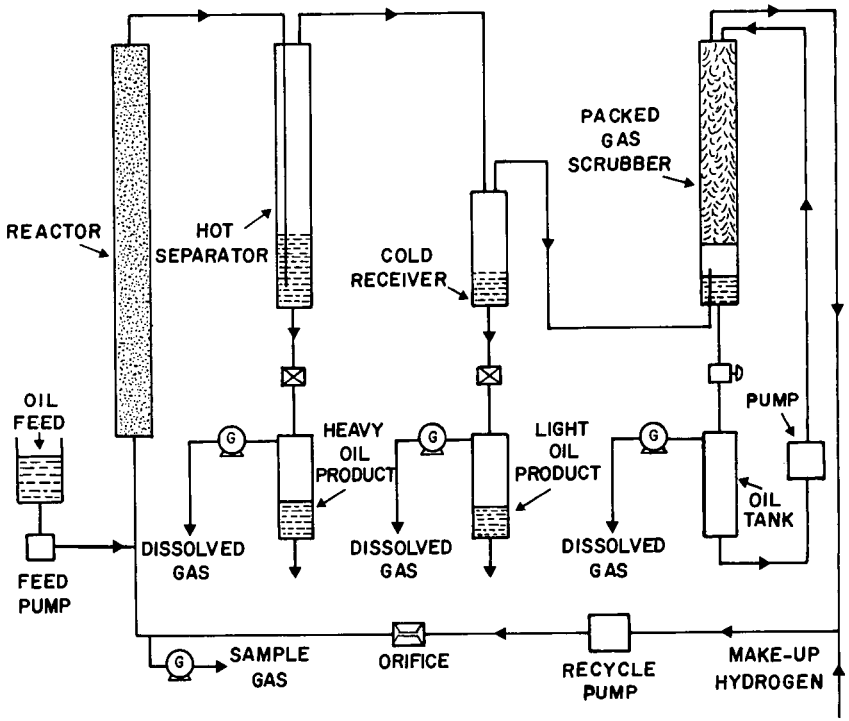

FIGURE 1 - Schematic Diagram of CANMET Hydrocracking Pilot Plant

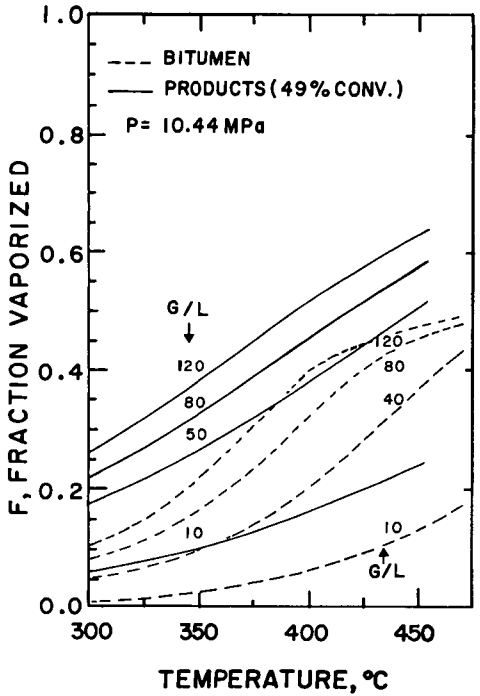

FIGURE 4 - Fraction of Liquid Vaporized, f, as a Function of Temperature for Bitumen and 49% Hydrocracked Product at 10.44 MPa and G/L Values of 10 to 120 g mol/kg

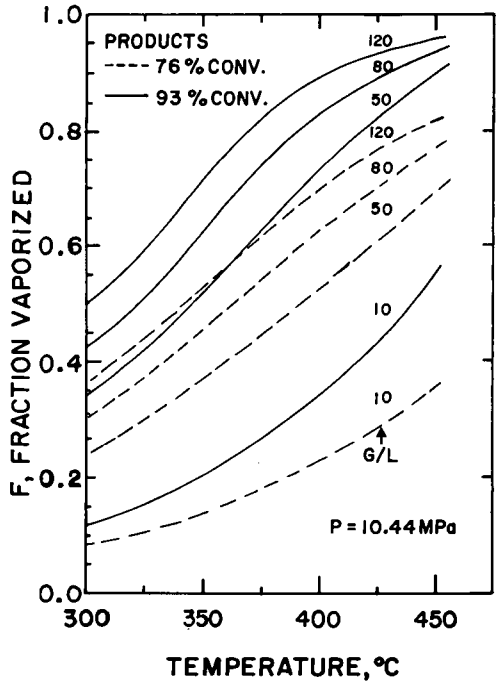

FIGURE 5 - Fraction of Liquid Vaporized, f, as a Function of Temperature for 76 and 93% Hydrocracked Products at 10.44 MPa and G/L Values of 10 to 120 g mol/kg

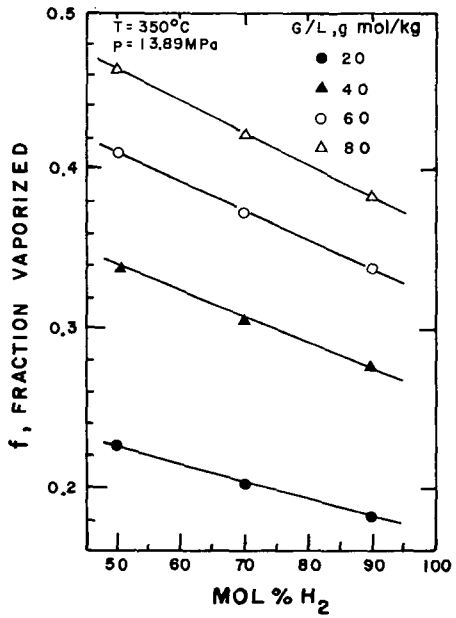

FIGURE 6 - Fraction of Liquid Vaporized, f, vs mol % H_2 for 83% hydrocracked product at 350°C, 13.89 MPa and G/L Values of 20 to 80 g mol/kg

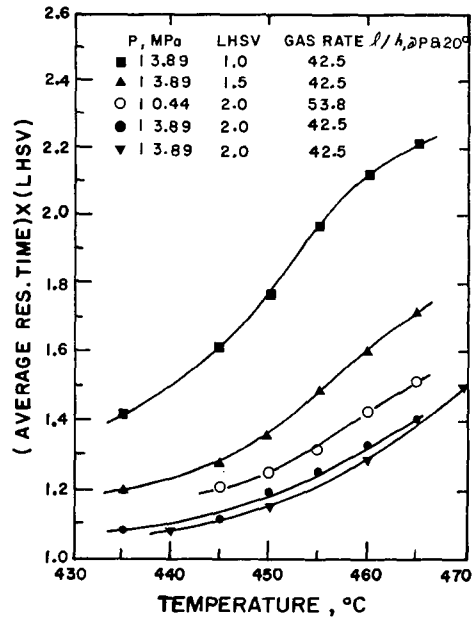

FIGURE 7 - Product of Calculated Average Liquid Residence Time and Liquid Hourly Space Velocity vs Temperature for a Series of Hydrocracked Products Obtained Under the Indicated Conditions

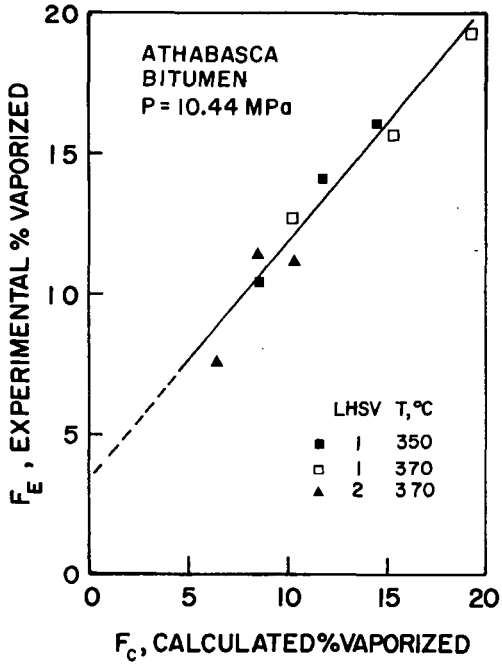

FIGURE 8 - Experimental vs Calculated Per Cent of Liquid Vaporized for Athabasca Bitumen at 10.44 MPa

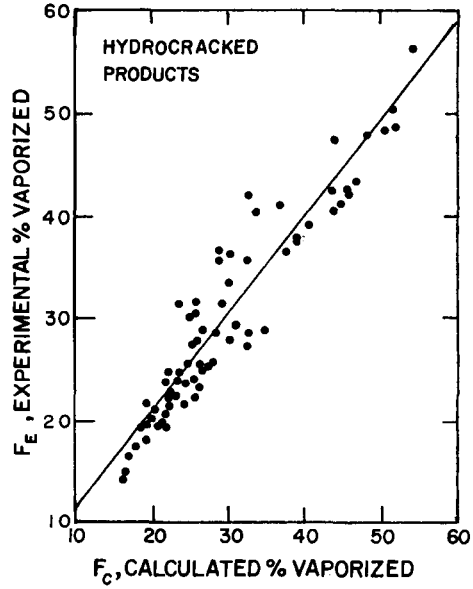

FIGURE 9 - Experimental vs Calculated Per Cent of Liquid Vaporized for 75 Hydrocracked Products for Pressures of 10.44 to 17.34 MPa and Temperatures of 300 to 430°C.