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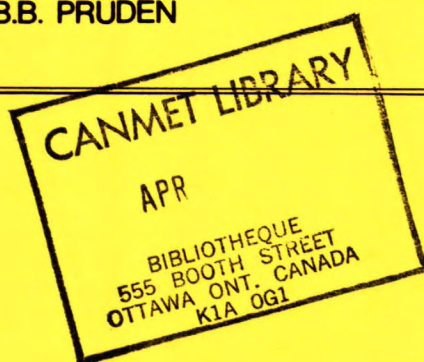
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THERMAL HYDROCRACKING OF ATHABASCA BITUMEN: COMPARISON OF COMPUTER SIMULATED VALUES OF FEED AND PRODUCT VAPORIZATION WITH CANMET PILOT PLANT DATA

D.J. PATMORE AND B.B. PRUDEN



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COMPARISON OF COMPUTER SIMULATED VALUES OF FEED AND PRODUCT
VAPORIZATION WITH CANMET PILOT PLANT DATA

by

D.J. Patmore* and B.B. Pruden**

ABSTRACT

To devise a kinetic model of the CANMET hydrocracking process, it is necessary to know the degree of vaporization of liquid in the reactor. This has been determined for a variety of conditions using a computer simulation. The present study was carried out to compare these results with experimental vaporization data obtained for conditions in the hot separator. In the range of conditions studied - 300 to 400°C and 10.44 to 17.34 MPa - there was reasonable agreement between calculated values (F_C) and experimental data (F_E) considering all the possible experimental errors, 72% of all F_E being within 10% of F_C . The following relationships were found for bitumen and hydro-cracked products respectively:

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

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

There was closer agreement between F_E and F_C at 13.89 MPa than for the other two pressures considered.

The use of vaporization data in the estimation of average liquid residence time is discussed. Calculations for several pilot plant runs emphasize that the discrepancy between spacetime and average liquid residence time can be very large. At a space velocity of $1h^{-1}$ the residence time can be over twice the space-time.

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HYDROCRAQUAGE THERMIQUE DE BITUME D'ATHABASCA:
UNE COMPARAISON DES VALEURS DE L'ALIMENTATION ET LA VAPORISATION
DU PRODUIT SIMULEES PAR ORDINATEUR AVEC LES DONNEES
DE L'USINE PILOTE DE CANMET

par

D.J. Patmore* et B.B. Pruden**

RESUME

Il faut connaître le degré de vaporisation du liquide dans le réacteur avant de créer un modèle cinétique du processus d'hydrocraquage. Il a pu être déterminé selon une variété de conditions à l'aide d'une simulation mécanisée. La présente étude a été effectuée dans le but de comparer ces résultats avec les données de vaporisation expérimentales obtenues pour les conditions du séparateur à chaud. Selon la gamme des conditions étudiées - 300 à 400°C et 10.44 à 17.34 MPa - les valeurs calculées (F_C) et les données expérimentales (F_E) correspondent de façon acceptable si l'on considère toutes les erreurs expérimentales possibles, i.e. 72% de tout le F_E se trouve à 10% du F_C . On a pu observer la relation suivante pour le bitume et les produits d'hydrocraquage respectivement:

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

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

A une pression de 13.89 MPa, le F_E et le F_C correspondent mieux qu'avec les deux autres pressions considérées.

L'utilisation des données de vaporisation pour estimer le temps d'écartement moyen du liquide est discutée. Le calcul de plusieurs parcours de l'usine pilote souligne que l'écart qui existe entre le temps disponible et le temps d'écartement moyen du liquide peut être très grand. A une vitesse de $1h^{-1}$, le temps d'écartement peut être deux fois plus élevé que le temps disponible.

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INTRODUCTION

In keeping with CANMET's aim of ensuring the effective use of Canada's mineral and energy resources, the Energy Research Laboratories have established the viability of a thermal hydrocracking process for the initial refining stage of oil sand bitumen and other heavy oils. This work has been carried out in a one-barrel-per-day pilot plant (1,2).

To scale-up the process to an efficient and economical commercial plant, requires quantitative knowledge of the degree of vaporization of both feed and product under reactor conditions. Such information is needed to calculate hydrogen partial pressures and true liquid and vapour residence times which in turn are necessary for accurate sizing of various plant components as well as for formulating 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 constants, K , for the various components of the system using known or estimated values of thermodynamic properties. Such methods are widely used and work quite well for moderate temperatures and pressures; however, they have not been extensively tested for conditions encountered during thermal hydrocracking of bitumen and heavy oils.

The present study was carried out to test the accuracy of vaporization values calculated using a computer simulation as described in a previous report (3). These values were calculated using the Grayson-Streed modification of the Chao-Seader correlation (4,5).

EXPERIMENTAL

PILOT PLANT RUNS

Pilot plant operation has been described in detail elsewhere (1,2). The process consists of feeding a mixture of hydrogen and bitumen to

the bottom of a long, electrically-heated tubular reactor. The vapour/liquid mixture leaving the reactor enters a hot receiver, or hot catch pot (HCP), where liquid and vapour are separated. The liquid portion or heavy ends (HE) is withdrawn and collected while the vapour portion or light ends (LE) is condensed in a cold receiver and collected. The collected LE and HE weights are recorded at intervals. The ratio of the weight of LE x 100 to the total weight of product (LE + HE) represents the percentage of material vaporized in the HCP at a temperature which is usually below the reactor temperature. This value can then be compared with the value calculated using the computer simulation (3). Total liquid product yields vary typically from 88 to 98% by weight of bitumen feed depending on the severity of hydrocracking conditions. The yield is usually less than 100% because some bitumen is converted to hydrocarbon gases and H_2S and should be considered when calculating the liquid feed rate for products.

Hydrogen concentration in the recycle gas stream is controlled by a scrubbing system which removes H_2S and hydrocarbon gases from the gas leaving the cold receiver. The gas flow rate is measured using an orifice, and is controlled by a gas recycle pump. Fresh make-up hydrogen is added to maintain desired pressure. Gases are removed from the system at four points and their rates and compositions recorded. These off-gases include gases dissolved in HE and LE and scrubber recycle oil, as well as a sample stream removed from the recycle gas.

To compare calculated with experimental values for unreacted bitumen, a series of runs was made employing various gas rates and space velocities, 10.44 MPa pressure, 83 mol % hydrogen, and temperatures of 350 and 370°C, at which very little hydrocracking occurs. The orifice used to measure gas recycle rate was calibrated with 85 mol % hydrogen using a wet test meter.

DATA TREATMENT

Terms and symbols in this report are defined as:

Per cent pitch conversion:

$$= \{[\text{wt \% pitch in feed} - (\text{wt \% pitch in total liquid product} \times \text{wt \% yield})] / \text{wt \% pitch in feed}\} \times 100$$

$$f = \text{wt fraction of liquid vaporized}$$

$$= \frac{\text{wt of liquid in vapour phase}}{\text{total wt of liquid fed}}$$

$$F = \text{weight \% of liquid vaporized} = f \times 100$$

$$G/L = \frac{\text{g mol of gas fed per hour}}{\text{kg of liquid fed per hour}}$$

Vaporization data from a representative selection of pilot plant runs covering a large range of conditions were collected for comparison with calculated values.

For each run considered, G/L values were calculated from the gas recycle rate and the measured liquid rate. The gas rate in litres per hour was converted to NTP and divided by 22.414 to obtain the number of moles of gas per hour.

To calculate the degree of vaporization at any point in the system it is necessary to know the hydrogen concentration in the gas stream at system pressure and 20°C. As all experimental data considered relate to the HCP, composition of the gas leaving the reactor is required. The hydrogen concentration in the gas entering the reactor will be less at this point because of the production of hydrocarbon gases and H₂S and the consumption of hydrogen during the hydrocracking reaction. A reasonable approximation to the hydrogen concentration can be obtained by considering off-gas rates and composition and make-up hydrogen rate using the following equation which is derived in Appendix A:

$$Z_0 = Z_R - \frac{1470}{Q_R P} (I - \sum \frac{Q_i Z_i}{100}), \quad \text{Eq 1}$$

where Q_R = recycle gas rate in ft³/h at P and 20°C

P = pressure in psia

I = H₂ make-up rate in ft³/h at 14.7 psia (0.101 MPa) and 20°C

Q_i = off-gas rate for stream i in ft³/h at 14.7 psia (0.101 MPa) and 20°C

Z_0 = mol % H₂ in reactor exit gas

Z_R = mol % H₂ in recycle gas

Z_i = mol % H₂ in stream i

Data calculated previously were for Athabasca bitumen and three products identified as 94-3-1, 71-1-2 and 81-3-1 corresponding to three essentially different pitch conversions as well as for a fourth product, 82-1-2, which was close in pitch conversion to 71-1-2 (3).

To apply these results to runs at different conversions, data from plots of f vs G/L in (3) were used to construct Fig. 1 to 9, from which F could then be read for a higher and lower conversion at particular conditions. Interpolation was then necessary for intermediate conversions, and a simple linear interpolation was the only feasible method. Although not precise, it introduced no errors larger than experimental. Figures 1 to 9 are plots of calculated values of F against temperature at various G/L values, and pressures; hydrogen concentration was 74 mol % for the feed and 80 mol % for the three products. The G/L values used were 10, 15, 20, 40 and 50; to read F at intermediate values a linear interpolation was used.

The next step was to correct these F values for variations in hydrogen concentration. This was done assuming the following relation to hold at constant pressure.

$$(f_{60}/f_{80})_x = a_x + b_x T, \quad \text{Eq 2}$$

where: f_{60} and f_{80} = f at 60 and 80 mol % H₂

x = G/L value

a_x and b_x = regression coefficients at

G/L = x g mol/kg

T = temperature, °C

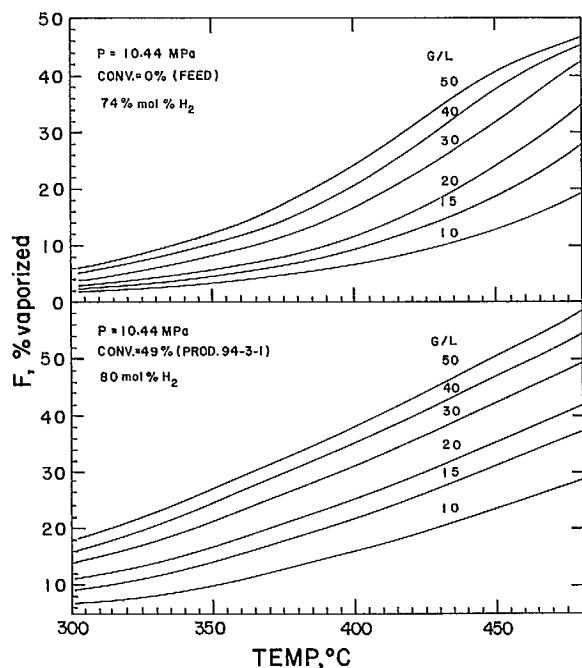


Fig. 1 - Calculated per cent of feed and product 94-3-1 vaporized vs temperature at 10.44 MPa and 74 mol % and 80 mol % H_2 for indicated values of G/L in g mol/kg

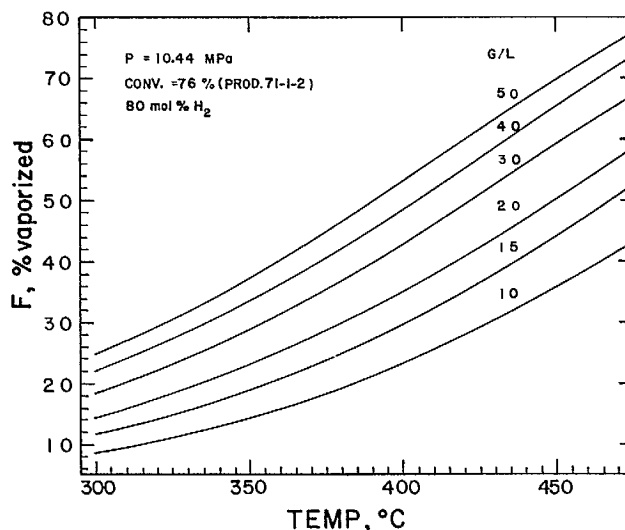


Fig. 2 - Calculated per cent of product 71-1-2 vaporized vs temperature at 10.44 MPa and 80 mol % H_2 for indicated values of G/L in g mol/kg

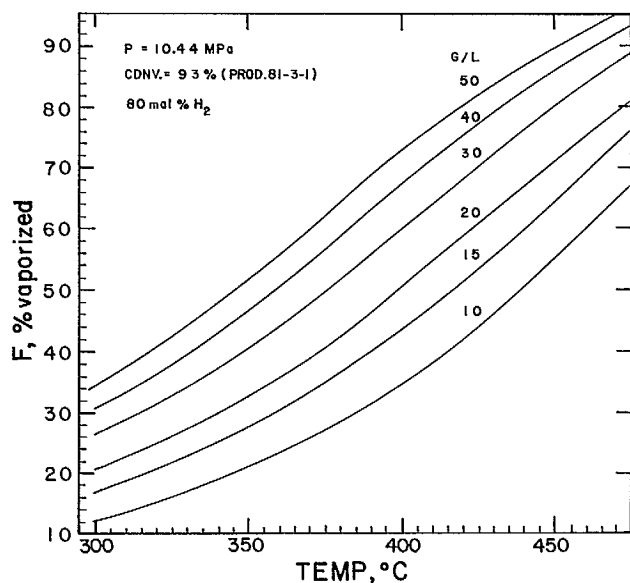


Fig. 3 - Calculated per cent of product 81-3-1 vaporized vs temperature at 10.44 MPa and 80 mol % H_2 for indicated values of G/L in g mol/kg

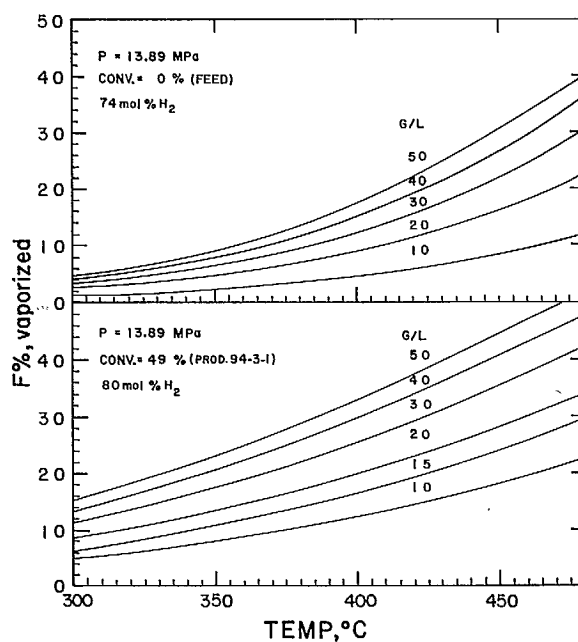


Fig. 4 - Calculated per cent of feed and product 94-3-1 vaporized vs temperature at 13.89 MPa and 74 and 80 mol % H_2 , respectively, for the indicated values of G/L in g mol/kg

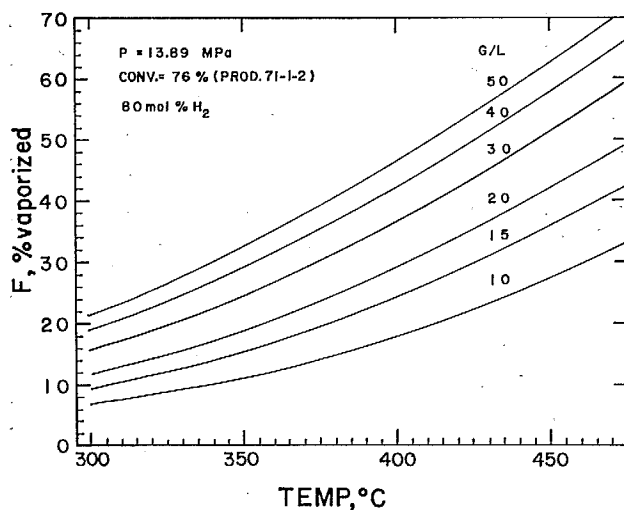


Fig. 5 - Calculated per cent of product 71-1-2 vaporized vs temperature at 13.89 MPa and 80 mol % H_2 for the indicated values of G/L in g mol/kg

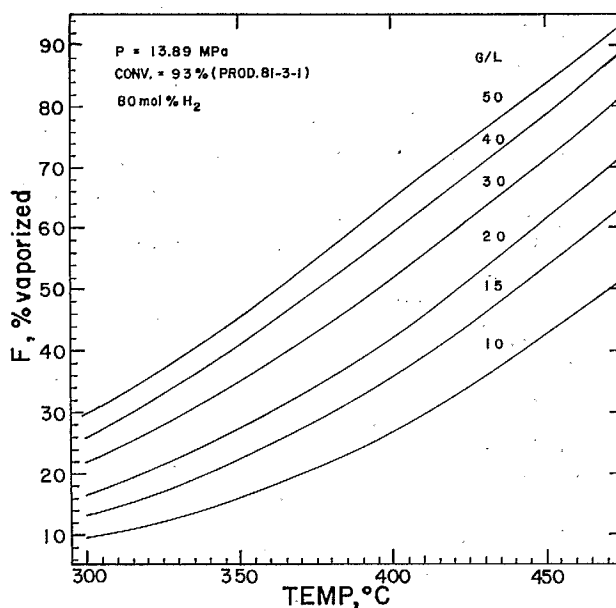


Fig. 6 - Calculated per cent of product 81-3-1 vaporized vs temperature at 13.89 MPa and 80 mol % H_2 for the indicated values of G/L in g mol/kg

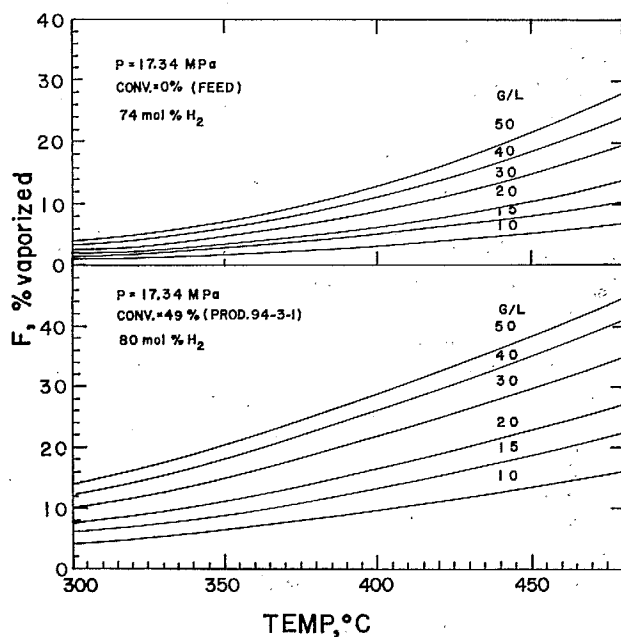


Fig. 7 - Calculated per cent of feed and product 94-3-1 vaporized vs temperature at 17.34 MPa and 74 and 80 mol % H_2 , respectively, for the indicated values of G/L in g mol/kg

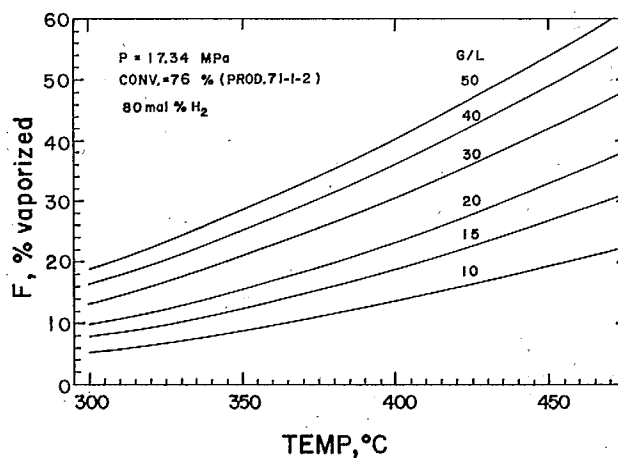


Fig. 8 - Calculated per cent of product 71-1-2 vaporized vs temperature at 17.34 MPa and 80 mol % H_2 for indicated values of G/L in g mol/kg

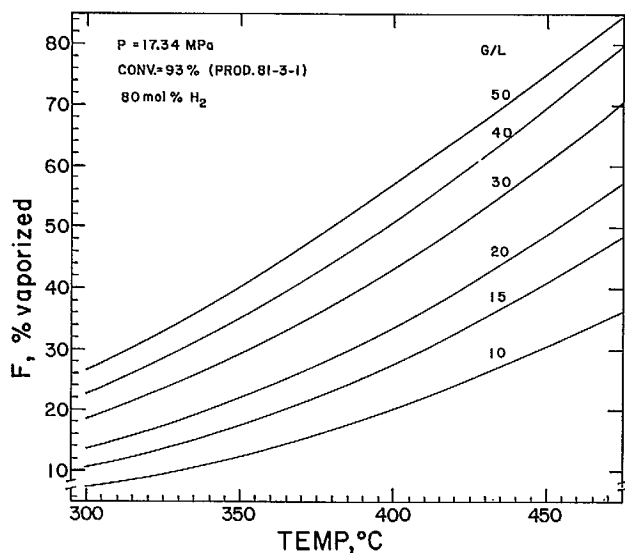


Fig. 9 - Calculated per cent of product 81-3-1 vaporized vs temperature at 17.34 MPa and 80 mol % H₂ for the indicated values of G/L in g mol/kg

Values of a_x and b_x were obtained by first substituting values of T and of f_{60} and f_{80} calculated in (3) in Eq 2 for G/L values of 10 and 50, and then interpolating the regression coefficients for a G/L value of x . These values for a_x and b_x were then substituted in Eq 2 and $(f_{60}/f_{80})_x$ calculated for a particular temperature. The value of f at y mol % hydrogen was then calculated from:

$$f_y = f_{80}(f_{60}/f_{80} - 1)[(80-y)/20] + f_{80} \quad \text{Eq 3}$$

This was done for conversions above and below the conversion of interest, and f was then obtained by linear interpolation.

Calculated values of F were plotted against the experimental values and the best straight line drawn through the points using the method of least squares. The regression coefficients for the equation $F_E = A + BF_C$ were determined together with the coefficient of determination, r^2 , the standard errors in A and B ,

and the standard deviation for F_E , assuming no error in F_C .

RESULTS AND DISCUSSION

The accuracy of the calculated values for the degree of vaporization was tested by comparing with experimentally determined values. The hot receiver was well mixed with excellent gas-liquid contact and thus behaved as an ideal stage. Hence the proportion of light oil to total liquid product gave F directly. Data from runs carried out under various conditions were compiled and compared with the calculated values previously determined (3). Except for the low temperature feed runs and some runs employing heavy oil recycle discussed below, it was not possible to obtain experimental data at the reactor temperature as the hot receiver was operated routinely at temperatures below this value. The temperature range studied was between 300 and 430°C, with 80% of the data below 390°C, and pressure varied between 10.44 and 17.34 MPa, with 50% of the data at 13.89 MPa.

To test the calculated values for unreacted bitumen, a series of runs was carried out at temperatures at which negligible hydrocracking occurs. The conditions employed and the results obtained are listed in Table 1, while F_E and F_C are compared graphically in Fig. 10. A linear regression using these data yielded the following equation for the best line through the points:

$$F_E = (3.3 \pm 0.9) + (0.85 \pm 0.07) F_C \quad \text{Eq 4}$$

The coefficient of determination, r^2 , was 0.954. In every run the experimental value was greater than or equal to the calculated value, the average difference being 12.6% with a standard deviation of 7.9. This discrepancy could be due to several factors, the most likely being (i) hydrocracking was still occurring, even at the low temperatures involved, (ii) systematic experimental errors occurred in weighing LE or HE, and (iii) simulated

Table 1 - Pilot plant runs at sub-hydrocracking temperatures
Comparison of per cent light ends, LE, with per
cent of feed vaporized, F, at 10.44 MPa pressure
and 83 mol % hydrogen

Run no.	T °C ^a	Gas rate ^c	Feed rate	G/L ^d	% LE	F, calc.
	HCP ^b	m ³ /h	kg/h	g mol/kg		%
FVT-1	350	0.03342	4.610	34.2	10.4	8.6
FVT-2	350	0.05041	4.550	52.1	14.1	11.8
FVT-3	350	0.06655	4.500	69.6	16.0	14.6
FVT-4	370	0.03342	4.700	33.6	12.7	10.2
FVT-5	370	0.05041	5.155	50.5	15.7	15.3
FVT-6	370	0.06712	4.525	69.7	19.3	19.3
FVT-7	370	0.03427	9.115	17.6	7.6	6.4
FVT-8	370	0.05041	9.925	23.9	11.4	8.5
FVT-9	370	0.06712	10.400	30.3	11.2	10.3

a - Reactor temperature same as HCP

b - Hot catch pot or hot receiver

c - At pressure and 20°C

d - Gas to liquid flow ratios

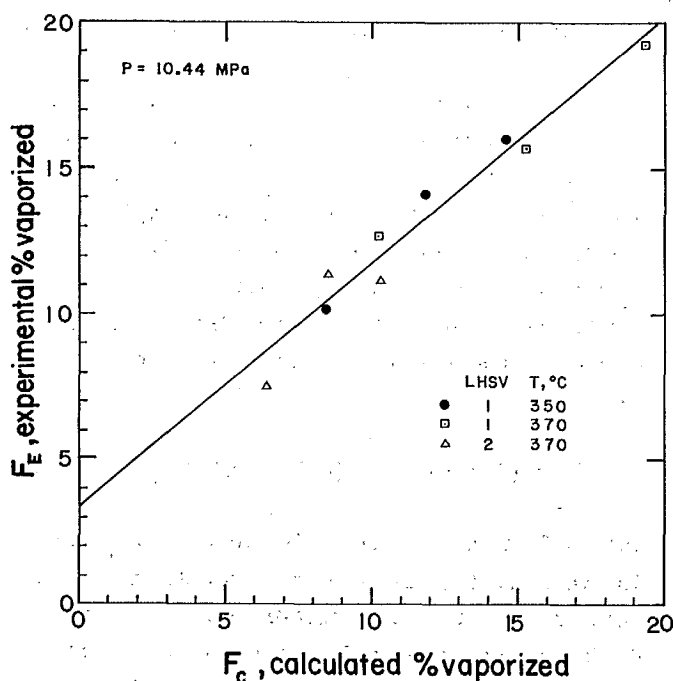


Fig. 10 - Experimental vs calculated per cent of feed vaporized at 10.44 MPa, temperatures of 350 and 370°C and space velocities of 1 and 2 for a reactor volume of 4.5 l

properties of feed do not represent actual properties with enough accuracy. The first two would tend to increase in importance as F decreases, and for values of F above about 15% agreement with experimental data is good.

A similar comparison was made with data from 66 separate pilot plant runs, from which products with a variety of pitch conversions between about 50 and 90% were obtained. A total of 75 data sets were included in the study as more than one set was obtained for several long runs. Complete data for all the runs are included in Tables 2 to 4, whereas graphs of experimental versus calculated per cent of liquid vaporized are shown in Fig. 11 to 16.

A histogram of the per cent difference between F_E and F_C , $100(F_E - F_C)/F_C$, with a normal distribution curve fitted to the data, is shown in Fig. 17. There are approximately equal numbers of experimental values above and below the calculated values; however, the distribution is not symmetrical as shown on page 11.

Table 2 - Comparison of calculated per cent of product vaporized, F, with per cent light ends, LE, observed during pilot plant runs under varying conditions at 10.44 MPa pressure

Run no.	Temp, °C		LHSV ^b / feed kg/h	Gas rate ^c	% H ₂ out	% Pitch conv.	G/L g mol/ kg	% LE	F calc. %
	React.	HCP ^a							
88-1-1	450	402	2/9.062	B	79	68.2	21.4	40.4	33.6
88-2-1	450	402	2.5/11.238	B	80	65.7	17.0	36.5	28.8
88-3-1	450	400	3/13.675	B	80	63.5	14.7	30.4	25.6
88-4-1	450	400	3.5/15.545	C	83	58.7	16.2	30.2	25.0
88-5-1	450	402	4/17.975	D	81	55.5	13.9	24.9	22.2
89-1-1	460	405	3.5/15.822	D	74	71.5	17.6	42.0	32.7
89-2-1	460	403	4/17.888	D	75	63.0	14.1	31.7	25.8
89-3-1	460	405	4.5/20.232	D	77	61.1	13.0	31.4	23.5
91-1-1	450	350	3/13.042	D	79	60.6	19.5	21.7	19.3
97-1-1	450	370	3/13.330	D	64	63.4	19.2	22.3	25.6
97-2-1	455	370	3/13.368	D	64	66.3	19.1	23.3	26.2
98-1-1	430	370	3/12.993	D	88	34.4	19.0	14.3	16.2
98-1-2	430	370	3/13.134	D	86	34.6	18.8	14.7	16.3
77-CG-1	450	365	3/13.368	D	75	54.3	18.8	19.6	21.3
77-CG-2	450	370	3/12.809	D	72	59.4	19.6	21.7	24.3
77-CG-4	450	370	3/13.598	D	74	52.7	18.5	19.6	21.8
77-T-16	430	370	2/9.506	D	85	42.6	25.9	21.5	22.3
77-T-17	440	370	2/9.052	D	82	58.4	27.3	28.6	28.4
77-T-20	450	375	2/9.168	D	78	65.3	27.5	35.7	32.6
56-1-1	445	303	2/7.934	C	71	67.6	30.6	19.2	18.5
56-2-1	450	308	2/8.003	C	69	71.8	30.4	21.2	20.4
56-3-1	455	309	2/8.008	C	65	76.3	30.6	22.3	22.0
56-4-1	460	311	2/8.019	C	62	80.6	31.3	24.0	25.4
56-5-1	465	311	2/7.986	C	64	83.3	31.7	25.3	26.8

a - HCP = Hot catch pot or hot receiver

b - Nominal value of liquid hourly space velocity

c - B = 1.5 ft³/h (0.0425 m³/h) at pressure and 20°C

C = 1.9 ft³/h (0.0538 m³/h) at pressure and 20°C

D = 2.0 ft³/h (0.0566 m³/h) at pressure and 20°C

Table 3 - Comparison of calculated per cent of product vaporized, F_c , with per cent light ends, LE, observed during pilot plant runs under varying conditions at 13.89 MPa pressure

Run no.	Temp., °C		LHSV ^b / feed	Gas rate ^c	% H ₂ out	% Pitch conv.	G/L	% LE	F calc.
	React.	HCP ^a	kg/h				g mol/ kg		%
71-1-2	460	354	2/7.871	B	61	77.9	32.9	29.3	31.0
71-1-2	460	344	2/8.003	B	65	76.1	32.4	28.8	26.6
71-1-2	460	344	2/7.975	B	63	72.8	32.3	27.8	25.8
71-1-2	460	344	2/8.040	B	67	70.7	31.7	25.7	24.7
71-1-3	460	322	2/7.966	B	65	77.7	33.1	24.0	23.3
71-1-3	460	330	2/7.847	B	64	79.8	32.9	25.6	26.3
71-1-3	460	327	2/7.986	B	64	79.4	32.9	24.0	25.5
73-1-1 ^d	460	355	2/7.947	B	74	77.0	32.9	35.8	28.7
73-1-3	460	352	2/7.938	B	65	76.9	32.8	31.4	29.3
77-1-1	450	327	1.5/6.866	A	66	73.2	31.0	23.9	21.6
77-1-1	450	327	1.5/6.968	A	69	72.2	29.9	19.7	20.7
77-1-1	450	327	1.5/6.947	A	71	77.5	30.0	22.2	22.1
82-1-1	450	360	1/4.642	B	84	84.3	56.6	42.9	43.5
82-2-1	450	362	1/4.615	B	79	82.7	56.3	40.5	43.7
82-3-1	450	362	1/4.475	B	73	82.7	57.6	42.2	45.7
82-4-1	450	360	1/4.487	B	67	83.5	56.4	43.5	46.7
82-5-1	450	361	1/4.490	B	58	85.0	57.2	48.4	50.6
82-1-2	450	350	1/4.550	B	82	79.6	58.1	36.5	37.5
82-2-2	450	350	1/4.527	B	80	80.9	57.8	37.6	39.0
82-3-2	450	350	1/4.575	B	76	80.1	57.6	37.8	39.1
82-4-2	450	350	1/4.560	B	70	81.0	56.5	39.2	40.6
82-5-2	450	350	1/4.512	B	59	81.9	58.5	41.2	44.6
82-6-2	450	350	1/4.602	B	48	81.4	56.3	42.6	45.4
82-5-3	450	365	1/4.650	B	42	82.1	54.7	50.4	51.6
82-5-3	450	365	1/4.620	B	48	82.9	56.6	49.0	51.8
82-5-3	450	365	1/4.532	B	49	79.6	56.0	48.1	48.1
93-1-1	420	380	2/8.933	B	85	35.2	27.9	16.6	17.0
93-2-1	420	400	2/8.730	B	82	34.4	27.6	20.1	20.1
93-3-1	420	420	2/9.203	B	82	36.8	26.6	24.8	23.5
94-1-1	430	390	2/8.975	B	77	46.1	27.7	22.9	22.6
94-2-1	430	410	2/9.010	B	79	46.5	27.6	27.5	25.3
94-3-1	430	430	2/9.028	B	77	47.4	27.7	33.5	30.2
87-1-1	460	355	2/8.266	B	63	81.4	31.3	27.3	32.5
55-1-1	440	310	2/7.875	C	79 ^e	61.2	40.8	17.5	17.7
55-2-1	445	312	2/8.012	C	78 ^e	67.1	40.3	19.6	19.4
55-3-1	450	315	2/7.945	C	76 ^e	67.4	40.6	21.1	20.4
55-4-1	455	318	2/8.035	C	75 ^e	74.3	40.7	22.5	23.0
55-5-1	460	318	2/8.000	C	72 ^e	77.6	40.9	23.7	24.6
55-6-1	465	319	2/8.050	C	70 ^e	81.8	41.2	25.4	27.4
55-7-1	470	320	2/8.003	C	67 ^e	85.1	41.9	27.9	30.1
55-1-3	440	401	2/8.212	B	75	57.7	30.9	36.3	30.3
55-3-3	450	405	2/8.080	B	71	67.6	32.0	41.2	36.8
55-5-3	460	406	2/8.180	B	58	76.5	32.1	47.4	43.8
55-7-3	470	410	2/8.185	B	54	83.5	33.1	56.5	54.2

a - HCP = Hot catch pot or hot receiver

b - Nominal value of liquid hourly space velocity

c - A = 1.2 ft³/h (0.0340 m³/h) at pressure and 20°C

B = 1.5 ft³/h (0.0425 m³/h) at pressure and 20°C

C = 1.9 ft³/h (0.0538 m³/h) at pressure and 20°C

d - 8erl saddles in HCP

e - Based on assumed off-gas composition

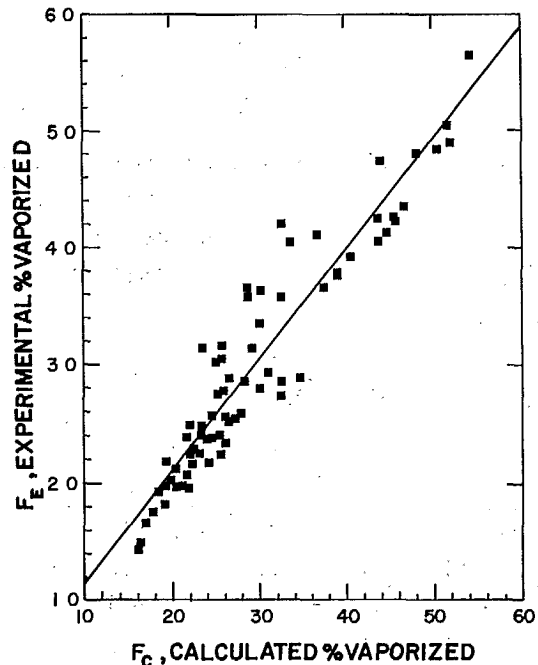


Fig. 11 - Experimental vs calculated per cent of products vaporized for pressures of 10.44 to 17.34 MPa and temperatures of 300 to 430°C

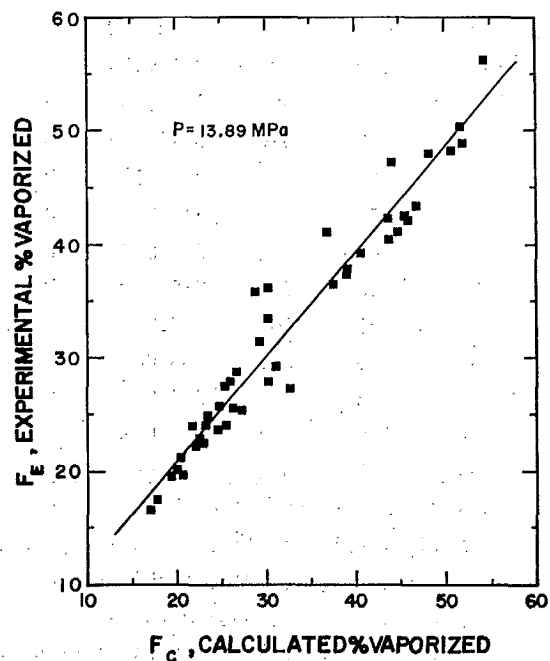


Fig. 12 - Experimental vs calculated per cent of products vaporized at 13.89 MPa and temperatures of 300 to 430°C

Table 4 - Comparison of calculated per cent product vaporized, F , with per cent light ends, LE, observed during pilot plant runs under varying conditions at 17.89 MPa pressure

Run no.	Temp, °C		LHSV ^b / feed kg/h	Gas ^c rate	% H ₂ out	% Pitch conv.	G/L g mol/kg	% LE	F calc. %
	React.	HCP ^a							
54-1-1	440	315	2/7.855	C	77.9	62.4	51.3	18.1	19.2
54-2-1	445	318	2/7.955	C	77.5	70.7	51.1	20.6	21.8
54-3-1	450	319	2/7.970	C	77.3	73.5	51.3	22.5	22.8
54-4-1	455	319	2/8.020	C	77.5	78.0	51.5	23.7	24.3
54-5-1	460	321	2/7.990	C	72.9	81.8	52.0	25.7	28.0
54-6-1	465	321	2/7.967	C	66.4	86.9	53.1	28.5	32.7
54-7-1	470	323	2/8.010	C	67.5	88.5	54.9	28.8	34.7

a - HCP = Hot catch pot or hot receiver

b - Nominal value of liquid hourly space velocity

c - C = 1.9 ft³/h (0.0538 m³/h) at pressure and 20°C

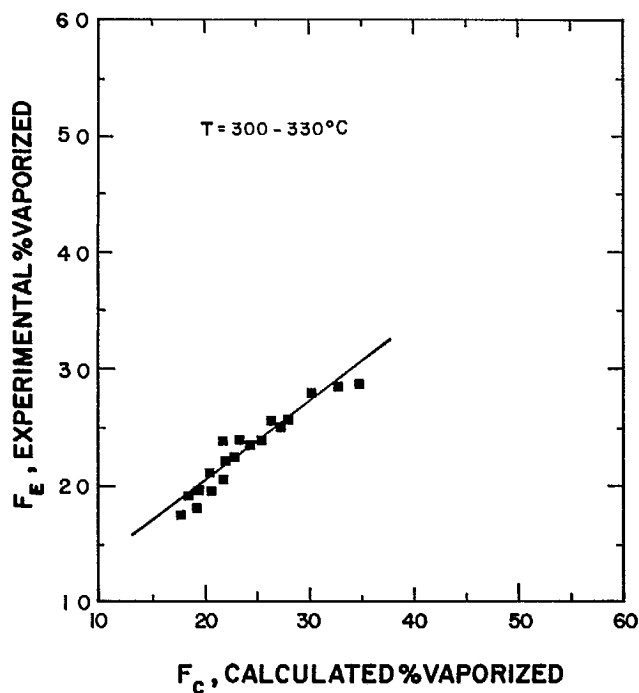


Fig. 13 - Experimental vs calculated per cent of products vaporized for pressures of 10.44 to 17.34 MPa and temperatures of 300 to 330°C

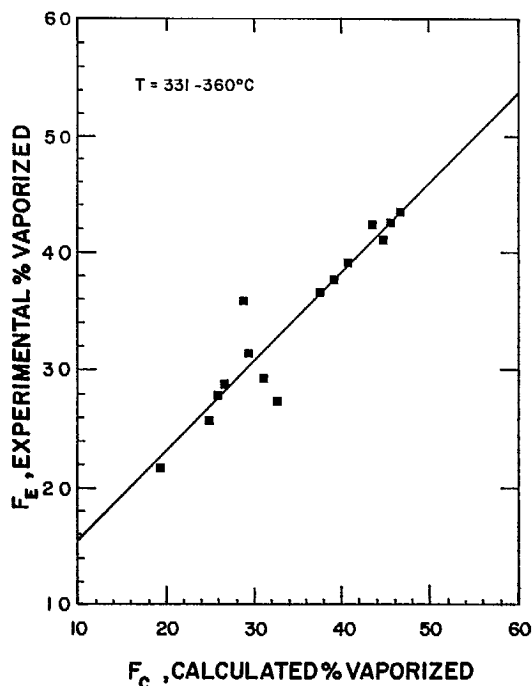


Fig. 14 - Experimental vs calculated per cent of products vaporized for pressures of 10.44 and 13.89 MPa and temperatures of 331 to 360°C

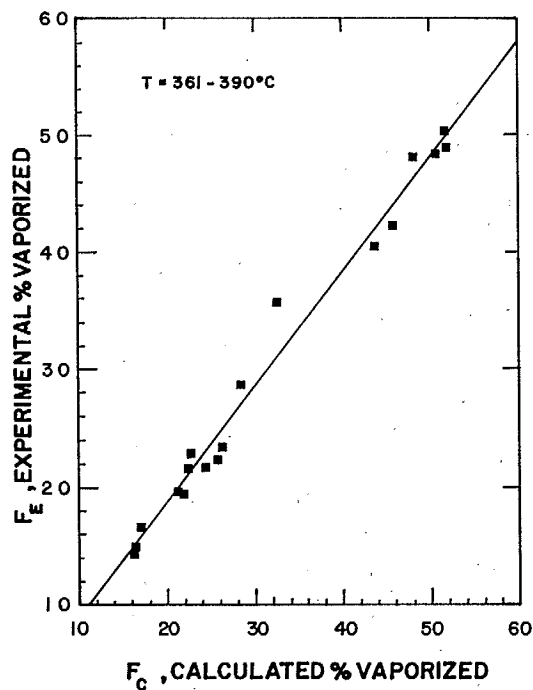


Fig. 15 - Experimental vs calculated per cent of products vaporized for pressures of 10.44 and 13.89 MPa and temperatures of 361 to 390°C

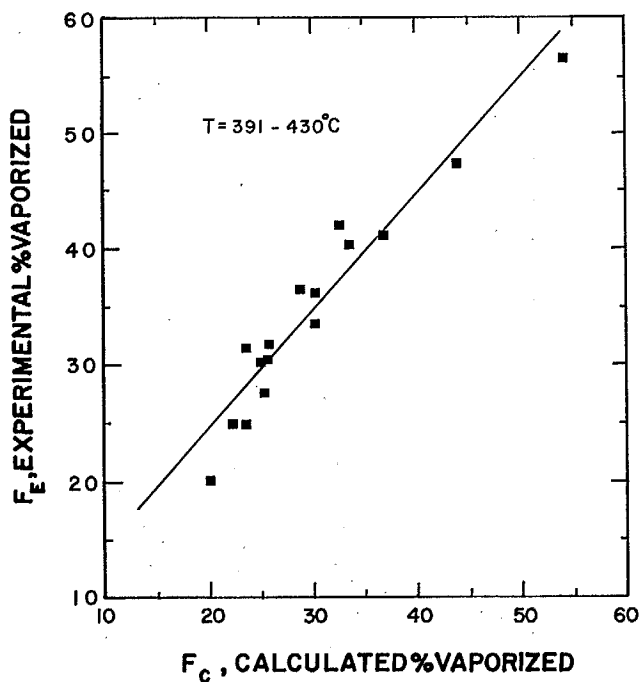


Fig. 16 - Experimental vs calculated per cent of product vaporized for pressures of 10.44 and 13.89 MPa and temperatures of 391 to 430°C

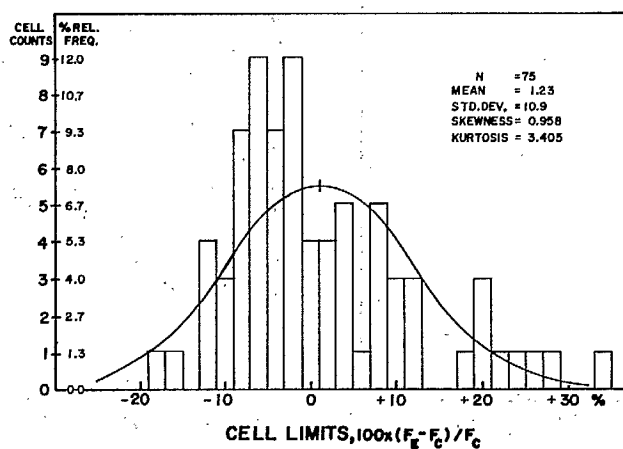


Fig. 17 - Histogram and normal distribution curve for the per cent difference of experimental and calculated per cent product vaporized for all product data listed in Tables 2 to 4

X, %	% of all F_E		
	Between F_C and $F_C + X\%$	Between F_C and $F_C - X\%$	Between $F_C \pm X\%$
5	17.33	21.33	38.67
10	26.67	45.33	72.0
15	33.33	52.0	85.33
20	36.0	54.67	90.67
35	45.33	54.67	100.0

Only 26.7% of all F_E lie between F_C and $F_C + 10\%$ while 45.3% are within F_C and $F_C - 10\%$. Thus 38.7% of all experimental data lie within $\pm 5\%$ of F_C , while 72.0% are within $\pm 10\%$. The mean per cent difference between F_E and F_C is 1.23% with a standard deviation of 10.9.

To investigate the effect of reaction conditions on the agreement between F_E and F_C , eight

different data sets were considered and linear regressions carried out on each to determine the line which best fits the data. Various combinations of three pressure and four temperature ranges were considered as shown in Table 5, which also lists the calculated regression coefficients and standard errors. The closer A and B approach 0.0 and 1.00, the closer the agreement between experimental and calculated values.

Using all the data gives a good fit (Fig. 11), the relationship between F_E and F_C being given by:

$$F_E = (1.8 \pm 1.2) + (0.95 \pm 0.04)F_C \quad \text{Eq 5}$$

although r^2 was only 0.896 because of the relatively large spread in data.

Considering the three pressures separately, the data for 13.89 MPa gives a close fit

Table 5 - Regression coefficients for experimental vs calculated per cent of product vaporized for the pressure and temperature ranges indicated

Pressure MPa	Temp. range °C	n^a	A^b	$S_n(A)^c$	B^b	$S_n(B)^c$	r^{2d}	$\sigma_n(F_E)^e$
10.44-17.34	300-430	75	1.78	1.17	0.948	0.038	0.896	3.113
10.44	300-405	24	- 8.55	3.76	1.416	0.152	0.798	3.286
13.89	310-430	44	2.20	1.18	0.930	0.034	0.945	2.410
17.34	315-370	7	6.43	1.74	0.669	0.065	0.955	0.781
10.44-17.34	300-330	25	6.93	1.08	0.674	0.044	0.909	0.899
10.44-13.89 ^f	331-360	16	7.79	2.53	0.765	0.071	0.842	2.183
10.44-13.89 ^f	361-390	18	- 0.90	1.06	0.982	0.031	0.984	1.611
10.44-13.89 ^f	391-430	16	4.37	2.44	1.010	0.078	0.922	2.503

a - n = number of data points

b - A and B are defined by: $F_E = A + BF_C$

c - $S_n(A)$ and $S_n(B)$ are standard errors in A and B

d - r^2 = coefficient of determination

e - $\sigma_n(F_E)$ is the standard deviation of F_E assuming no error in F_C

f - No 17.34 MPa data in these temperature ranges

(Fig. 12), but for 10.44 MPa and 17.34 MPa the agreement between F_E and F_C is considerably poorer.

If the data for all three pressures are divided into four temperature ranges, the fit tends to improve as temperatures increase (Fig. 12-16), the data at 361-390°C giving the best fit. However this trend must be treated cautiously because of the small number of data in each sub-set.

Considering the approximations involved in interpolating the calculated F values for the particular run conditions, as well as experimental error in pilot plant data, agreement between experimental and calculated values is surprisingly good. As mentioned, 72.0% of all experimental values lie within $\pm 10\%$ of the calculated values. If all data which disagree by more than $+20\%$ are ignored, 78% lie within $\pm 10\%$ of F_C with a mean per cent difference of -1.2 and a standard deviation of 7.8 .

As mentioned, some high temperature data were available for a few runs carried out with recycle of a portion of the heavy ends back to the bottom of the reactor (6). Knowing the feed, LE, HE, and recycle oil flows, it was possible to calculate the per cent of liquid vaporized in the HCP at 450°C. For runs R-2-1-2 and R-2-2-4 this was calculated as 23.9 and 19.7%. Using the per cent of pitch in feed and total liquid product, including recycle oil, an effective pitch conversion was calculated for the total liquid entering the HCP. Calculated values of F could then be interpolated as before. Assuming 80 mol % H_2 in the gas, the calculated values were 23.4 and 21.0%, and were in good agreement with experimental values.

Possible causes of experimental error in the pilot plant data are numerous. Some of the more important are:

- (i) Error in gas recycle rate: this is determined by measuring the pressure drop across an orifice; errors can thus be introduced by partial blockage of the orifice as well as by uncertainties in the gas composition.
- (ii) Errors in measuring light and heavy end rates: these are determined by direct weighing of the receivers, and are thus susceptible to the occasional operator error as well as errors stemming from scale accuracy. Normally, errors of no more than $\pm 2\%$ would be expected, although in extreme cases, in which one weight is very low, this might increase to $\pm 5\%$.
- (iii) Errors in determining off-gas compositions: discrepancies in hydrogen concentrations have been found depending on the method of analysis. An error of 10% in hydrogen concentration in the recycle gas will lead to an uncertainty of approximately 5% in the degree of vaporization.
- (iv) Incomplete separation of liquid and vapour in HCP leading to the carry-over of HE with LE: this could be accentuated if coking of the HCP occurred, leading to greater vapour velocities and the possibility of carrying over HE mist into the cold receiver.

Other errors are also potentially inherent in the computer simulation, e.g., the K values are derived from data on conventional heavy oils and not on bitumen from oil sands. Also the properties of the simulated hydrocarbon fractions may not accurately represent true properties, again because conventional petroleum fractions are the basis of the correlations used to estimate these properties, e.g., MW. Some errors could also be introduced from differences in simulated and true gas composition.

AVERAGE LIQUID RESIDENCE TIME

Accurately determining liquid residence time in the reactor is essential for developing a kinetic model of the hydrocracking reaction. The use of space time ($1/LHSV$) as an estimate for this value can be highly inaccurate as up to 70% or more of the liquid entering the reactor will eventually be vaporized and will rapidly leave the reactor, while the remaining liquid will take much longer to traverse its length. Because the liquid

is being continuously hydrocracked there will be a distribution of residence time, with the more inert components remaining longer in the reactor; however, the following discussion is concerned only with average liquid residence times.

Another factor influencing residence time is the volume of the reactor taken up with gas, usually referred to as voidage. This has the opposite effect of vaporization, causing a reduction in the reactor volume and an increase in the volumetric flow rate. Thus residence time will be proportional to $V(1-\epsilon)$ where V = reactor volume and ϵ = voidage (fraction of reactor volume taken up with gas). The variation of voidage with reactor conditions was studied in detail by Pruden et al (7) who found the following relationship to hold for a tubular unpacked column:

$$\epsilon = 1.54 \times 10^{-7} \times P^{0.18} \times T^{2.11} \times V_g \quad \text{Eq 6}$$

where V_g is the superficial gas velocity in cm sec^{-1} estimated at pressure P and $T^\circ\text{C}$. The voidage was found to be essentially independent of superficial liquid velocity between 0.139 and 0.284 cm sec^{-1} . Values of ϵ range from 0.10 at 10.44 MPa and 300°C , to 0.39 at 17.34 MPa and 470°C , for a gas rate of 2.0 ft^3/h (0.0566 m^3/h) at P and 20°C .

The influence of vaporization on residence time is not so straight-forward, as f is a function of pitch conversion which is itself some function of time. Thus, to obtain accurate residence times, the reaction kinetics must be known. It is therefore necessary to begin with a reasonable approximation of residence time and to use an iterative procedure to determine the reaction kinetics. Taking into account variations in liquid densities, voidage and vaporization, and using the degree of vaporization for entering liquid (feed) and exiting liquid (product), the following equation for the approximate average liquid residence time can be written:

$$t_A = 2Vd_f d_p (1-\epsilon) / \{L[d_p(1-f_f) + d_f(1-f_p)]\} \quad \text{Eq 7}$$

where:

t_A = average residence time

V = reactor volume in m^3

d_f, d_p = feed and product density in $\text{kg}/\%$ at P and T

f_f, f_p = feed and product degree of vaporization

L = liquid feed rate in $\text{g}/\text{unit time}$

ϵ = voidage

and is derived in Appendix B. If we assume that $d_f = d_p = d$, this simplifies to:

$$t_A = dV(1-\epsilon) / \{L[1-(f_f + f_p)/2]\} \quad \text{Eq 8}$$

This equation will give a lower limit for t_A . As the order of the reaction increases from zero, more weight should be given to f_p . In other words, as more of the reaction occurs near the bottom of the reactor, more material will be vaporized in this region, thus increasing the time needed for the remaining liquid to traverse the full length of the tube.

Equation 8 was combined with experimental data obtained for pilot plant runs discussed in detail earlier (1) and from runs 55-N-1 and 56-N-1.

These runs were carried out to examine the effect of changing reactor conditions on pitch conversion. For each set of conditions the calculated degree of vaporization for both feed and final products were determined using the interpolations previously described. These values, together with reaction conditions, were substituted in the voidage and residence time equations described above while liquid density was assumed to be 1.00 $\text{kg}/\%$. The products of average residence times and liquid hourly space velocities were plotted as a function of temperature for each set of conditions. The results, together with the conditions are shown in Fig. 18, which graphically illustrates the large difference between true and nominal residence times, particularly at high temperature and LHSV. The product of residence time

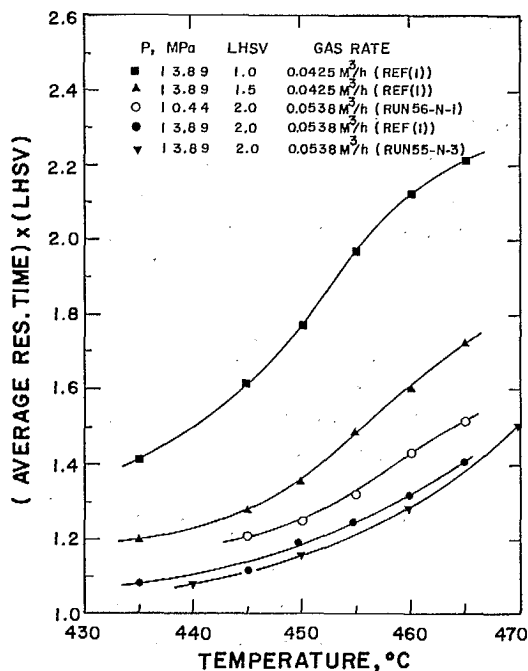


Fig. 18 - Average residence time of liquid in the reactor x LHSV as a function of temperature calculated using data from runs 55-N-3, 56-N-1, and from the data presented in Reference 1

and LHSV was chosen to compare data at different space velocities. If no vaporization were to occur this product would be unity. For a pressure of 13.89 MPa and a gas rate of 1.5 ft³/h (0.0425 m³/h), decreasing the space velocity, especially at high temperatures, considerably increases residence time. Thus for a LHSV of 1.0 at 470°C, residence time increased to 2.27 h from the nominal value of 1 h, while for a space velocity of 2.0 at the same conditions, the residence time only increased to 0.75 h from a nominal value of 0.5 h.

These calculated residence times are only approximate as no allowance has been made for kinetics of the reaction or for variations in density of the liquid at reactor conditions. As shown earlier, the latter can vary considerably with conditions and conversion, although the values

quoted were only estimates of limited accuracy (3). Thus, to achieve the greatest accuracy in residence time estimations, experimental determinations of liquid densities at reactor conditions would be required.

CONCLUSIONS

Data from the hydrocracking pilot plant runs were compared with the computed values of the degree of vaporization. For unreacted bitumen at 350 and 370°C and 10.44 MPa, and for products at temperatures between 300 and 430°C and pressures of 10.44 to 17.34 MPa, the agreement between calculated and experimental per cent of liquid vaporized was reasonably close considering the approximations and experimental errors involved. The relationships between experimental and calculated values were given by the following two equations for feed and product respectively:

$$F_E = (3.3 \pm 0.9) + (0.85 \pm 0.07)F_C \quad \text{Eq 4}$$

$$F_E = (1.8 \pm 1.2) + (0.95 \pm 0.04)F_C \quad \text{Eq 5}$$

For products, the best agreement was for data obtained at 13.89 MPa. If all product data are considered together, 72% of the experimentally determined values for the per cent of liquid vaporized are within $\pm 10\%$ of the calculated values, and 39% within $\pm 5\%$.

For pressures of 10.44 and 17.34 MPa the agreement between experimental and calculated values was considerably less than for 13.89 MPa. However, because of the small number of data points available, it was not possible to determine whether this was a real effect or simply due to experimental errors.

Use of this correlation to predict liquid residence times showed that, for low LHSV, the discrepancy between actual and nominal residence times could be more than 200%.

REFERENCES

1. Merrill, W.H., Logie, R.B. and Denis, J.M. "A pilot scale investigation of thermal hydrocracking of Athabasca bitumen"; Mines Branch [since renamed Canada Centre for Mineral and Energy Technology (CANMET)], Department of Energy, Mines and Resources; Research Report R-281; 1973.
2. Pruden, B.B., Logie, R.B. and Denis, J.M. "Thermal hydrocracking of Athabasca bitumen: Reduction of reactor fouling"; CANMET, Energy, Mines and Resources Canada; CANMET Report 76-33; 1976.
3. Patmore, D.J., Pruden, B.B. and Shah, A.M. "Thermal hydrocracking of Athabasca bitumen - Computer simulation of feed and product vaporization"; CANMET, Energy, Mines and Resources Canada, CANMET Report 78-4; 1978.
4. Chao, K.C. and Seader, J.D. "A general correlation of vapour-liquid equilibria in hydrocarbon mixtures"; Am Inst Chem Eng; 7:4:598-605; 1961.
5. Grayson, H.G. and Streed, C.W. "Vapour liquid equilibria for high temperature, high pressure hydrogen-hydrocarbon systems"; Proc Sixth World Pet Cong, Frankfurt/Main, June 19, Sect. VII, Paper 20, PD7, 233-245; 1963.
6. Khulbe, C.P., Pruden, B.B., Denis, J.M. and Merrill, W.H. "A pilot plant investigation of thermal hydrocracking of Athabasca bitumen: 2. Effect of recycle of heavy oil on product quality"; CANMET, Energy, Mines and Resources Canada; CANMET Report 77-20; 1976.
7. Shah, A.M., Pruden, B.B. and Denis, J.M. "Thermal hydrocracking of Athabasca bitumen: Correlation of reactor voidage in vertical two-phase flow"; CANMET, Energy, Mines and Resources Canada, CANMET Report 77-48; 1976.

APPENDIX A

Below is a simplified flow diagram of the hydrocracking pilot plant showing the various gas rates and hydrogen concentrations around the system. All off-gas rates are at STP. The overall H_2 balance is: mol/h H_2 into reactor - mol/h leaving reactor = total mol/h H_2 added to system.

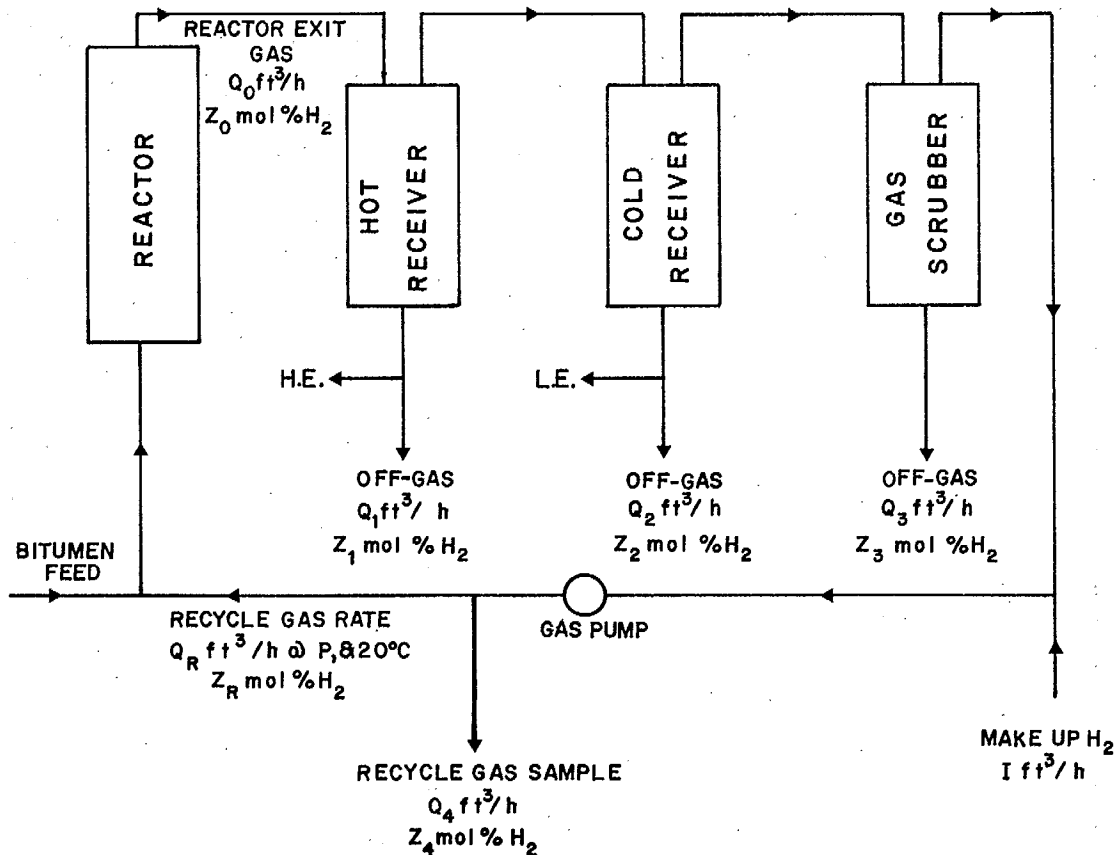
$$\text{i.e., } \frac{Q_R Z_R}{100} \times \frac{P}{14.7} - \frac{Q_0 Z_0}{100} \times \frac{P}{14.7} = I - \sum \frac{Q_i Z_i}{100}$$

$$\frac{Q_0 Z_0 P}{14.7} = \frac{Q_R Z_R P}{14.7} - 100 \left(I - \sum \frac{Q_i Z_i}{100} \right)$$

For a reasonable first approximation assume $Q_0 = Q_R$, i.e., that hydrogen consumption and gas-make are equal

$$\therefore Z_0 = Z_R - \frac{1470}{Q_R P} \left(I - \sum \frac{Q_i Z_i}{100} \right) \quad \text{Eq 1}$$

In practice, hydrogen consumption and gas-make are not necessarily equal, however both values are small compared with the recycle gas rate Q_R , and the error introduced by this assumption is therefore small.



APPENDIX B

Derivation of Residence Time Equation

Let: V = reactor volume in ℓ
 d_f, d_p = feed and product density at P and T
 f_f, f_p = feed and product degree of vaporization
 L = liquid feed rate in kg/unit time
 ϵ = voidage (fraction of reactor occupied by gas).
 In general, residence time, t , is expressed as:

t = effective reactor vol/volumetric liquid flow rate through reactor

Because some reactor volume is taken up by gas, the effective volume is given by $V(1-\epsilon)$, while the liquid flow rate through the reactor for feed and product respectively are given by:

$$L(1 - f_f)/d_f \text{ and } L(1 - f_p)/d_p$$

The residence time is then the effective reactor volume divided by average flow rate, i.e.,

$$t = V(1 - \epsilon) / [L(1 - f_f)/d_f + L(1 - f_p)/d_p] / 2$$

$$= 2V(1 - \epsilon)d_f d_p / [L(1 - f_f)d_p + L(1 - f_p)d_f]$$

Eq 7

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