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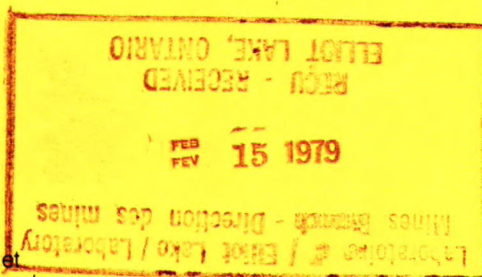
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THERMAL HYDROCRACKING OF ATHABASCA BITUMEN: COMPUTER SIMULATION OF FEED AND PRODUCT VAPORIZATION

D.J. PATMORE, B.B. PRUDEN AND A.M. SHAH

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THEMAL HYDROCRACKING OF ATHABASCA BITUMEN:
COMPUTER SIMULATION OF FEED AND PRODUCT VAPORIZATION

by

D.J. Patmore*, B.B. Pruden** and A.M. Shah***

ABSTRACT

A computer simulation was carried out to determine the fraction of feed and product vaporized during the hydrocracking of Athabasca bitumen. The program utilized the Grayson-Streed modification of the Chao-Seader equation of state. It was found that as much as 75% or more of the liquid fed to the reactor can be in the vapour phase at reactor outlet conditions. The effect of temperature, pressure, gas-to-liquid ratio, mol % H₂ in the gas and pitch conversion on the degree of vaporization were investigated.

It was found that the ratio of gas to liquid fed to the reactor has a large initial effect on the degree of vaporization, but the rate of increase drops off sharply at high G/L values.

Changes in temperature and pressure have significant effects on the degree of vaporization. Thus for a product at 76% pitch conversion at 10.44 MPa, 80 mol % H₂ and a G/L value of 20 g mol/kg, an increase in temperature from 400 to 450°C causes the percentage of liquid vaporized to increase from 34 to 52%. Similarly at 13.89 MPa, the same temperature increase causes the percentage to increase from 28 to 42%.

Increasing the mol % of hydrogen in the gas causes a linear decrease in the degree of vaporization. Changing the mol % of hydrogen from 60 to 80 causes the degree of vaporization to drop by approximately 10%.

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L'HYDROCRAQUAGE THERMIQUE DU BITUME DE L'ATHABASCA:
SIMULATION PAR ORDINATEUR DE L'EVAPORATION DU PRODUIT
ET DE LA CHARGE D'ALIMENTATION

par

D.J. Patmore*, B.B. Pruden** et A.M. Shah***

RESUME

On a effectué une étude de simulation par ordinateur afin de déterminer le niveau d'évaporation du produit et de la charge d'alimentation qui se produit lors de l'hydrocraquage du bitume de l'Athabasca. Le programme comprenait la modification Grayson-Streed apporté à l'équation d'état de Chao-Seader. Les auteurs ont constaté que 75% ou plus du liquide avec lequel on alimente le réacteur peut être en phase vapeur aux conditions de sortie du réacteur les effets de la température, de la pression, du rapport gaz à liquide, du % mol de H₂ dans le gaz et de la transformation du brai sur le degré de vaporisation ont été analysés.

Les auteurs ont remarqué que le rapport du gaz au liquide avec lequel on alimente le réacteur, a un effet initial important sur le degré de vaporisation, mais que le taux décroît rapidement lorsque le rapport du G/L est élevé.

Les changements de température et de pression ont des effets significatifs sur le degré de vaporisation. Dans le cas d'un produit ayant une transformation du brai de 76% à 10.44 MPa, 80% mol H₂ et un rapport G/L de 20 g mol/Kg, une augmentation de la température de 400 à 450°C occasionnera une augmentation du pourcentage de liquide évaporé de 34 à 52%. De même qu'à 13.89 MPa, cette même augmentation de température occasionnera une augmentation du pourcentage du liquide évaporé de 28 à 42%.

Lorsque le % mol d'hydrogène est augmenté dans le gaz, il en résulte un décroissement linéaire du degré de vaporisation. En élevant le % mol d'hydrogène de 60 à 80, le degré de vaporisation baissera d'environ 10%.

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INTRODUCTION

In keeping with the aims of the Energy Research Program of the Canada Centre for Mineral and Energy Technology (CANMET), Department of Energy, Mines and Resources, and its policy of ensuring the effective use of Canada's mineral and energy resources, the Energy Research Laboratories has established the viability of thermal hydrocracking for the initial refining stage of tar sand bitumen and other heavy oils. This work has been carried out using a one-barrel per day pilot plant (1,2).

To achieve an efficient and economical scale-up of this process to a commercial-size plant, a quantitative knowledge of the degree of vaporization of both feed and product under reactor conditions is essential. Such information 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 their known or estimated values of thermodynamic properties. Such methods are used quite extensively, and work well for moderate temperatures and pressures. However, these methods have not been tested extensively for conditions encountered during thermal hydrocracking of bitumen and heavy oils.

The present study was carried out using the Grayson-Streed modification of the Chao-Seader correlation employing the principle of corresponding states (3,4). In this correlation, K -values are calculated by the equation

$$K = Y_i/X_i = v_i^{\circ} \gamma_i/\phi_i,$$

where: Y_i = mole fraction of component i in the gas phase

X_i = mole fraction of component i in the liquid phase

v_i° = fugacity coefficient of pure component i in the liquid phase

γ_i = activity coefficient of i in the liquid mixture

ϕ_i = fugacity coefficient of i in the vapour mixture

Values of ϕ_i were calculated with reasonable accuracy using the Redlich-Kwong equation of state (5), while γ_i values were calculated from Hildebrand's equation (6) using solubility parameters and liquid molar volumes. The liquid fugacity coefficient, v° , is a well-defined thermodynamic property when the component actually exists as a liquid, and may be calculated from generalized correlations in terms of reduced temperatures and pressures. If conditions are such that the component does not occur as a pure liquid, e.g., above the critical temperature of the pure component, v° becomes hypothetical and the usual correlations cannot be used. Chao and Seader (3) developed a correlation that could be extended to such conditions. They correlated fugacities with reduced pressure and temperature using experimental vapour-liquid equilibrium data.

To extend the temperature range of the Chao-Seader correlation, Grayson and Streed (4) carried out a series of experimental determinations of vapour-liquid equilibria which are actually measured during the hydrocracking of gas oils. They were able to extend the temperature range of their correlation to about 480°C, although it was increasingly uncertain above 430°C. The pressure range studied by them was 3.45 MPa to 20.68 MPa.

The present study involves a computer simulation using this correlation for feed (unreacted bitumen) and four different product compositions under a variety of conditions likely to be encountered during the hydrocracking operation. A companion study is in preparation to compare these computed values with data obtained in a pilot plant using Athabasca bitumen (7).

EXPERIMENTAL

COMPUTER PROGRAM

The computer simulations were carried out by Saturn Engineering, Calgary, using the DISTILL program licensed by the Chem Share Corporation, Houston, Texas. This program employs the Grayson-Streed modification of the Chao-Seader correlation based on the principle of corresponding states (3,4). This program had been used previously (8); an improvement in the temperature dependence of the liquid phase activity coefficients was subsequently made. Thus there are some discrepancies in calculated f values between that study and the present work. The present values should be more accurate. It must be borne in mind that f values obtained for temperatures above about 430°C are of increasing uncertainty.

Definition of symbols and terms

f = degree of vaporization

$$= \frac{\text{weight of liquid vaporized}}{\text{total weight of liquid feed}}$$

F = per cent of liquid vaporized = 100 f

G/L = Gas to liquid flow rate ratio

$$= \frac{\text{g mol of gas fed/h}}{\text{kg of liquid fed/h}} = \text{g mol/kg}$$

$LHSV$ = liquid hourly space velocity

= number of reactor volumes of liquid fed per hour

P = pressure, MPa

T = temperature, °C

Subscripts: C = calculated

E = experimental

F = feed

P = product

Feed = unreacted bitumen

Product = bitumen after hydrocracking: combined liquid product, excluding butane and lighter components

INPUT DATA

Feed and product properties

The reactor conditions used to prepare the products are listed in Table 1. The composition and properties of the liquid feed and products were simulated by ten fractions with mean average boiling points (MABP's) ranging from 65.5°C (150°F) to 648.9°C (1200°F) as shown in Tables 2 and 3. These were derived from modified Hempel distillation of the feed and products (9) together with specific gravities of the cuts, using standard correlation procedures for petroleum fractions.

The composition of the gas at NTP was approximated as shown in Tables 4 and 5. These compositions refer to the gas before mixing with liquid at the particular point in the system at which the liquid-vapour equilibrium is to be calculated: at the bottom of the reactor for feed, and at the top for product. Ideally, a different gas composition should be used for each set of conditions. As this is not feasible, an average representative composition was chosen.

Conditions

A series of computer studies were carried out for a representative selection of operating conditions. Variation of temperature, pressure, G/L values, and hydrogen concentration were studied. The particular conditions for each case are listed below.

Case A - Feed vaporization

P = 10.44, 13.89, 17.34 and 20.79 MPa

T = 300, 350, 400, 450 and 470°C

G/L = 4, 10, 40, 80, 120, 160 and 200 g mol/kg

Mol % H_2 = 74

Gas composition listed in Table 4

Case B - Effect of gas compositionon Vaporization of Feed

P = 13.89 MPa

T = 400, 450, 470°C

G/L = 10, 50, and 80 g mol/kg

Mol % H₂ = 80, 90 and 100 (Cases B1, B2
and B3, respectively)

Gas composition listed in Table 4

G/L = 10, 50, 80 and 120 g mol/kg

Mol % H₂ = 60 and 80

Gas composition listed in Table 5

Case D - Product vaporization

P = 10.44, 13.89 and 17.34 MPa

T = 300, 350, 400 and 450°C

Case D2 - Effect of gas composition on
vaporization of product 82-1-2

P = 13.89 MPa

T = 350°C

G/L = 20, 40, 60, and 80 g mol/kg

Mol % H₂ = 50, 70 and 90

Gas composition listed in Table 5

Table 1: Reactor conditions for pilot plant runs used to
prepare products used in computer simulation

Reactor Conditions	Run Number			
	94-3-1	71-1-2	82-1-2	81-3-1
Temperature °C	430	460	450	480
Pressure MPa	13.89	13.89	13.89	20.79
Gas Rate ^a	1.5	1.5	1.5	1.5
LHSV	2.0 ^b	2.0 ^c	1.0 ^b	2.0 ^b
Mol % H ₂	85	83	96	89
Feed lot ^d	111	98	111	109
Length of Run h	4	455	12	4
Pitch Conversion %	49	76	81	93

a - ft³/h at pressure and 20°C; 0.0425 m³/h = 1.5 ft³/h

b - Reactor volume = 4.5 l

c - Reactor volume = 4.0 l

d - GCOS bitumen lot number

Table 2: Simulated composition and component properties of feed

Component	MABP ^o C ^a	wt %	Sp Gr ^b	MW ^c
1	65.6	0.22	0.713	82
2	121.1	0.11	0.763	109
3	176.7	0.48	0.840	140
4	232.2	0.43	0.867	180
5	287.8	3.11	0.893	222
6	343.3	11.00	0.922	275
7	398.9	11.31	0.949	334
8	454.4	11.26	0.977	392
9	510.0	11.54	1.005	450
10	648.9	50.53	1.073	1508

a MABP - Mean average boiling point

b Sp Gr - Specific gravity 15.6/15.6^oC

c MW - Molecular weight

Table 3: Input data used to simulate liquid product compositions

Comp. No.	MABP ^o C	Product 1 (94-3-1)			Product 2 (71-1-2)			Product 3 (82-1-2)			Product 4 (81-3-1)		
		wt %	Sp Gr	MW	wt %	Sp Gr	MW	wt %	Sp Gr	MW	wt %	Sp Gr	MW
1	65.6	1.95	0.690	85	3.54	0.683	86	3.43	0.696	85	6.07	0.682	85
2	121.1	4.65	0.782	109	5.40	0.765	107	5.04	0.770	107	6.79	0.763	107
3	176.7	4.73	0.823	136	8.09	0.810	137	7.94	0.810	137	12.62	0.813	137
4	232.2	8.25	0.864	177	11.69	0.855	174	13.01	0.853	174	14.33	0.864	172
5	287.8	10.87	0.905	212	14.55	0.902	213	13.93	0.895	214	17.89	0.912	211
6	343.3	14.20	0.938	259	15.52	0.942	258	14.40	0.928	262	17.98	0.955	253
7	398.9	14.22	0.971	310	15.86	0.983	303	14.96	0.965	310	12.40	1.004	295
8	454.4	9.68	0.999	360	9.62	1.032	350	11.02	1.012	355	5.58	1.064	332
9	510.0	7.41	1.020	422	4.69	1.074	395	7.63	1.057	400	3.19	1.110	380
10	648.9	24.05	1.100	550	11.03	1.100	550	8.64	1.100	550	3.15	1.200	550

Table 4: Gas composition^a input data^b for computer simulation of feed vaporization

Component	Case A ^c	Case B1	Case B2	Case B3
H ₂	74.20	80.01	90.00	100.00
H ₂ S	2.05	0.00	0.00	0.00
CH ₄	16.07	13.54	6.77	0.00
C ₂ H ₆	4.36	3.68	1.84	0.00
C ₃ H ₈	2.14	1.82	0.91	0.00
n-C ₄ H ₁₀	0.94	0.76	0.38	0.00
n-C ₅ H ₁₂	0.26	0.20	0.10	0.00

a - vol %

b - Before mixing with liquid and equilibration

c - See experimental section for description of cases

TREATMENT OF DATA

Output from the computer program consisted of liquid and vapour compositions and properties for each combination of conditions together with values for f , the degree of vaporization. These calculated values of f , listed fully in Tables 6-12, were then plotted as functions of conditions and smooth lines were drawn through all the points. These graphs were then used to interpolate f values for conditions other than those used as input data.

RESULTS AND DISCUSSION

Because pitch conversion is mainly dependent on space velocity and only to a small extent on gas rate at a specified temperature and pressure, fixing the reactor volume and feed rate will also fix the conversion. Thus if LHSV is used as a variable, calculations of f for the reactor for conditions other than those corresponding to the four products used in this study would be hypothetical. To make the calculations as general as possible and independent of reactor size, the ratio of gas rate to liquid feed rate was therefore chosen as a variable.

Calculations of the degree of vaporization were carried out for feed and for four representative products covering a range of pitch conversions from 49% to 93%. These values for all the cases studied are listed in Tables 6 to 12 and are presented graphically in Fig. 1 to 28.

Figures 1 to 4 illustrate the influence of G/L values on f for feed for different temperatures and for pressures of 10.44, 13.89, 17.34 and 20.79 MPa. A notable feature is the initial very strong dependence of f on G/L especially at higher temperatures and lower pressures. Thus to estimate f accurately, G/L must be known accurately under these conditions. At lower pressures there is a greater tendency for the curve to flatten out and approach a constant value of f ; this reflects the composition of bitumen which consists of about 50% of relatively non-volatile high molecular weight material. For any particular temperature and G/L value, f increases as pressure decreases. This is illustrated graphically in Fig. 5 to 7 where f is plotted vs G/L with P as a parameter for $T = 400^{\circ}\text{C}$ to 470°C . Thus pressure has a pronounced effect on the degree of vaporization of feed — halving

Table 5: Gas composition input data for computer simulation
of product vaporization^a

Case D								
Component	94-3-1		71-1-2		82-1-2		81-3-1	
H ₂	60.00	80.00	60.00	80.00	60.00	79.99	60.00	80.00
H ₂ S	12.83	6.42	8.72	4.36	8.60	4.30	9.40	4.70
CH ₄	9.32	4.66	14.08	7.04	14.28	7.14	15.13	7.56
C ₂ H ₆	8.24	4.12	5.68	2.84	5.88	2.95	5.81	2.90
C ₃ H ₈	5.81	2.90	4.96	2.48	5.24	2.62	4.51	2.26
n-C ₄ H ₁₀	2.51	1.25	4.96	2.48	4.48	2.24	4.01	2.00
n-C ₅ H ₁₂	1.29	0.65	1.60	0.80	1.52	0.75	1.15	0.58

Component	Case D2 - Product 3		
H ₂	50.00	70.00	90.00
H ₂ S	10.75	6.45	2.15
CH ₄	17.85	10.71	3.57
C ₂ H ₆	7.35	4.41	1.47
C ₃ H ₈	6.55	3.93	1.31
n-C ₄ H ₁₀	5.60	3.36	1.12
n-C ₅ H ₁₂	1.90	1.14	0.38

a - All values in mol %, gas composition before mixing. See experimental section for description of cases.

the pressure from 20.79 MPa to 10.44 MPa increases f by a factor of approximately 2 to 3 at 450°C.

Figures 8 to 11 illustrate the variation of f with G/L for product 94-3-1 at 10.44, 13.89 and 17.34 MPa and 60 and 80 mol % H_2 . The pitch conversion for this material was 49%, and was the lowest of the four products. Again, an initial rapid increase can be seen in f with G/L , especially at high temperatures. However, the increase is not as steep as that observed in the feed case discussed above and the curve does not tend to flatten out so rapidly. This is because feed has been topped to 260°C while the product contains a wider range of lower boiling fractions produced during hydrocracking. Again, increasing the pressure causes f to decrease.

Similar sets of curves are presented in Fig. 12 to 18 for products 71-1-2, 82-1-2 and 81-3-1 with pitch conversions of 76%, 81% and 93%, respectively. The results for 71-1-2 and 82-1-2 are very similar because of the closeness of their pitch conversion, thus complete data for both products are not presented. The shape of the curves for products 94-3-1, 71-1-2 and 82-1-2 are very similar while those for 81-3-1 tend to flatten out more and approach $f = 1$ at high temperatures. For all four products, increasing pressure reduces f . The degree of vaporization also decreases on increasing the mol % of H_2 in the gas. An increase of 60 to 80 mol % H_2 causes a reduction in f of approximately 10%. This will be discussed in more detail below.

Table 6: Fraction of feed vaporized, f , as a function of G/L , temperature and pressure for % $H_2 = 74\%$

P, MPa	T, °C		300	350	400	450	470
	G/L, g mol/kg						
10.44	4		0.00635	0.0133	0.0269	0.0529	0.0692
	10		0.01533	0.0329	0.0674	0.1321	0.1722
	40		0.04784	0.1032	0.2036	0.3760	0.4313
	80		0.0806	0.1689	0.3222	0.4580	0.4770
	120		0.1075	0.2193	0.3998	0.4773	0.4921
	160		0.1305	0.2611	0.4369	0.4869	0.5016
	200		0.1508	0.2973	0.4545	0.4934	0.5091
13.89	4		0.0045	0.0088	0.0167	0.0296	0.0366
	10		0.0117	0.0240	0.0468	0.0850	0.1073
	40		0.0376	0.0788	0.1505	0.2653	0.3266
	80		0.0638	0.1309	0.2407	0.3968	0.4379
	120		0.0855	0.1713	0.3072	0.4445	0.4660
	160		0.1043	0.2046	0.3591	0.4631	0.4786
	200		0.1210	0.2331	0.3971	0.4732	0.4864
17.34	4		0.0031	0.0057	0.0097	0.0145	0.0162
	10		0.0090	0.0176	0.0323	0.0543	0.0648
	40		0.0299	0.0605	0.1114	0.1853	0.2211
	80		0.0510	0.1019	0.1814	0.2918	0.3426
	120		0.0686	0.1344	0.2328	0.3632	0.4093
	160		0.0839	0.1613	0.2739	0.4080	0.4405
	200		0.0976	0.1844	0.3081	0.4336	0.4567
20.79	4		0.0021	0.0034	0.0047	0.0044	0.0031
	10		0.0069	0.0127	0.0215	0.0321	0.0358
	40		0.0238	0.0462	0.0814	0.1274	0.1467
	80		0.0407	0.0788	0.1357	0.2073	0.2376
	120		0.0548	0.1047	0.1761	0.2637	0.3003
	160		0.0672	0.1265	0.2084	0.3071	0.3468
	200		0.0783	0.1452	0.2353	0.3418	0.3813

Table 7: Fraction of feed vaporized, f , as a function of G/L, temperature and mol % hydrogen at 13.89 MPa pressure

% H ₂	T, °C		400	450	470
	G/L g mol/kg				
80	10		0.0447	0.0821	0.1028
	50		0.1684	0.2951	0.3592
	80		0.2301	0.3852	0.4313
90	10		0.0419	0.0777	0.0979
	50		0.1574	0.2786	0.3425
	80		0.2155	0.3680	0.4213
100	10		0.0393	0.0736	0.0931
	50		0.1470	0.2628	0.3255
	80		0.2016	0.3500	0.4095

Table 8: Calculated fraction vaporized, f , for product 94-3-1 as a function of G/L, temperature, pressure and mol % hydrogen

% H ₂		60 %				80 %				
P, MPa	T, °C		300	350	400	450	300	350	400	450
	G/L g mol/kg									
10.44	10		0.0682	0.1115	0.1741	0.2587	0.0631	0.1030	0.1611	0.2410
	50		0.1928	0.2912	0.4113	0.5336	0.1758	0.2679	0.3838	0.5077
	80		0.2416	0.3562	0.4851	0.6009	0.2204	0.3288	0.4561	0.5774
	120		0.2879	0.4143	0.5445	0.6484	0.2630	0.3843	0.5161	0.6283
13.89	10		0.0556	0.0896	0.1372	0.1984	0.0505	0.0813	0.1248	0.1827
	50		0.1733	0.2595	0.3650	0.4763	0.1540	0.2331	0.3333	0.4447
	80		0.2201	0.3221	0.4392	0.5509	0.1956	0.2905	0.4044	0.5201
	120		0.2645	0.3788	0.5009	0.6061	0.2355	0.3434	0.4654	0.5782
17.34	10		0.0458	0.0719	0.1059	0.1453	0.0412	0.0646	0.0959	0.1342
	50		0.1573	0.2319	0.3219	0.4167	0.1367	0.2044	0.2890	0.3836
	80		0.2019	0.2917	0.3948	0.4938	0.1756	0.2581	0.3573	0.4612
	120		0.2444	0.3463	0.4569	0.5571	0.2130	0.3081	0.4172	0.5237

Table 9: Calculated fraction vaporized, f , for product 71-1-2 as a function of G/L, temperature, pressure and mol % hydrogen

% H ₂		60 %				80 %			
P, MPa	T, °C G/L g mol/kg	300	350	400	450	300	350	400	450
10.44	10	0.0932	0.1572	0.2530	0.3884	0.0865	0.1452	0.2334	0.3601
	50	0.2692	0.4066	0.5722	0.7295	0.2450	0.3736	0.5336	0.6980
	80	0.3367	0.4931	0.6642	0.7950	0.3086	0.4573	0.6279	0.7730
	120	0.3996	0.5688	0.7329	0.8331	0.3670	0.5302	0.7003	0.8177
13.89	10	0.0750	0.1252	0.1986	0.2997	0.06836	0.1133	0.1794	0.2724
	50	0.2418	0.3639	0.5126	0.6658	0.2141	0.3259	0.4667	0.6223
	80	0.3071	0.4486	0.6086	0.7489	0.2742	0.4063	0.5627	0.7143
	120	0.3682	0.5237	0.6846	0.8013	0.3296	0.4772	0.6403	0.7751
17.34	10	0.0608	0.0988	0.1506	0.2143	0.0548	0.886	0.1353	0.1955
	50	0.2190	0.3259	0.4547	0.5910	0.1894	0.2858	0.4061	0.5420
	80	0.2819	0.4080	0.5520	0.6891	0.2461	0.3623	0.5008	0.6446
	120	0.3409	0.4816	0.6321	0.7571	0.2986	0.4304	0.5799	0.7193

Table 10: Calculated fraction vaporized, f , for product 82-1-2 as a function of temperature, pressure, G/L and mol % hydrogen

		60 mol % H ₂				80 mol % H ₂			
P, MPa	T, °C G/L g mol/kg	300	350	400	450	300	350	400	450
10.44	10	0.0916	0.1558	0.2509	0.3832	0.8486	0.1438	0.2315	0.3553
	50	0.2679	0.4032	0.5641	0.7279	0.2452	0.3727	0.5281	0.6947
	80	0.3351	0.4871	0.6555	0.8023	0.3074	0.4524	0.6185	0.7754
	120	0.3968	0.5601	0.7271	0.8480	0.3651	0.5226	0.6917	0.8284
13.89	10	0.0734	0.1236	0.1961	0.2934	0.0668	0.1118	0.1771	0.2670
	50	0.2401	0.3601	0.5034	0.6559	0.2138	0.3250	0.4613	0.6133
	80	0.3050	0.4424	0.5970	0.7453	0.2726	0.4017	0.5519	0.7060
	120	0.3651	0.5146	0.6731	0.8065	0.3278	0.4701	0.6278	0.7740
17.34	10	0.0593	0.0970	0.1477	0.2077	0.0534	0.0864	0.1328	0.1902
	50	0.2167	0.3217	0.4447	0.5753	0.1887	0.2846	0.4007	0.5300
	80	0.2793	0.4015	0.5383	0.6750	0.2441	0.3578	0.4895	0.6289
	120	0.3374	0.4720	0.6163	0.7494	0.2964	0.4236	0.5654	0.7065

Results for the four products at 13.89 MPa and temperatures of 400 to 450°C are compared in Fig. 19 for 80 mol % H₂. Increasing the pitch conversion from 49% to 93% causes an approximate two-fold increase in f at these conditions.

The effect of pressure on f for the feed and products is illustrated in more detail in Fig. 20 and 21 where f is plotted vs P at 450°C and various G/L values. Feed shows a relatively complex behaviour, while products show an essentially linear relationship between f and P . For feed at G/L = 40 g mol/kg, increasing P from 10.44 to 17.34 MPa results in a 51% decrease in f , while for products at G/L = 50 g mol/kg, the percentage decrease becomes less as the pitch conversion increases. Thus for 94-3-1, it drops by 22% while for 81-3-1, the reduction is only 12%. For lower G/L values, however, the percentage drop in f is about the same. Thus at G/L = 10 g mol/kg, f decreases by 54% for feed, 45% for 94-3-1, and 45% for 81-3-1.

The effect on f of hydrogen concentration in the gas was studied and the results presented in Fig. 22 to 28. The range of H₂ concentrations investigated was 80 to 100 mol % for the feed, and 50 to 90 mol % for product 82-1-2. The results for the feed are shown in Fig. 22 to 25. The first two show how hydrogen concentration influences f as a function of G/L, while Fig. 24 and 25 show f as a function of mol % H₂ for three temperatures and G/L values, all at 13.80 MPa. From the last two graphs it is seen that f is a linear function of mol % H₂, and that an increase of 80 to 100 mol % H₂ causes the degree of vaporization to drop by approximately 10% under the conditions studied, i.e., G/L = 10 to 80 g mol/kg, and T = 400 to 470°C.

Figures 26 and 27 illustrate the results for case D2 for product 82-1-2 for 50 to 90 mol % H₂ at 350°C and 13.89 MPa. Again a linear relationship can be seen between f and mol % H₂, and an approximate 10% drop in f for a rise in mol % H₂ of 20. This value was about the same for all products except where f was greater than about 0.8 when the percentage drop was much less. This is illustrated for product 81-3-1 in Fig. 28, and can be seen in Tables 6 to 12.

Calculated degree of vaporization for typical ERL pilot plant conditions

In the operation of the hydrocracking pilot plant, the conditions that are controlled are temperature, pressure, gas volumetric recycle rate and concentration, and the liquid hourly space velocity. To illustrate the way in which f varies with temperature and LHSV, Fig. 29, 30, 31 and 32 were constructed, showing f vs temperature with LHSV as a parameter for feed and product vaporization. These figures apply to a fixed gas rate in each case. Figures 29 and 30 show the expected feed vaporization in the CANMET pilot plant hydrocracker. Figures 31 and 32 show the expected product vaporization. To use these graphs, the temperature and LHSV to give, for example, a product similar to 94-3-1 (49% pitch conversion), are plotted and f determined. For thermal hydrocracking in the CANMET pilot plant, with no additive, there is only one temperature for each LHSV to give 49% conversion. However for catalytic systems, systems with solids addition, or systems with different mixing conditions, other combinations of LHSV and temperature are possible. This is because LHSV is based on the empty reactor volume even if catalyst or inert solids fill a large portion; and different conversions are obtained in a fully stirred or a plug flow reactor which have mixing characteristics at either end of the mixing spectrum.

Figures 29 through 32 show that temperature has a more pronounced effect on f for feed than for products, and that for the two higher conversion products, the relationship is approximately linear at temperatures above about 350°C.

The effect of LHSV on the degree of vaporization of feed as a function of pressure at 450°C is shown in Fig. 33. For a feed rate of 4.5 kg/h, doubling the pressure decreases f by 33%.

Composition of liquid and vapour phases

The DISTILL program calculates values for the concentrations of individual components in the liquid and vapour phase for each specified set of conditions. More than 200 sets of such data were generated in the present study and it was not possible to list them all in this work. However,

Table 11: Calculated fraction vaporized, f , for product 81-3-1, as a function of G/L, temperature, pressure and mol % hydrogen

P, MPa	T, °C G/L g mol/kg	60 mol % H ₂				80 mol % H ₂			
		300	350	400	450	300	350	400	450
10.44	10	0.1301	0.2256	0.3757	0.5462	0.1205	0.2076	0.3448	0.5517
	50	0.3704	0.5575	0.7692	0.9164	0.3403	0.5172	0.7276	0.8975
	80	0.4599	0.6656	0.8584	0.9464	0.4237	0.6218	0.8253	0.9374
	120	0.5420	0.7541	0.9105	0.9595	0.5007	0.7105	0.8877	0.9543
13.89	10	0.1043	0.1802	0.2992	0.4763	0.0946	0.1617	0.2665	0.4267
	50	0.3340	0.5032	0.7034	0.8748	0.2987	0.4550	0.6487	0.8377
	80	0.4213	0.6119	0.8083	0.9271	0.3781	0.5578	0.7585	0.9068
	120	0.5019	0.7039	0.8771	0.9441	0.4522	0.6478	0.8380	0.9387
17.34	10	0.0838	0.1417	0.2271	0.3433	0.0752	0.1253	0.1995	0.3050
	50	0.3037	0.4542	0.6343	0.8090	0.2652	0.4017	0.5723	0.7556
	80	0.3886	0.5619	0.7496	0.8923	0.3408	0.5015	0.6878	0.8549
	120	0.4673	0.6550	0.8330	0.9318	0.4118	0.5903	0.7785	0.9105

Table 12: Fraction of product 82-1-2 vaporized, f , as a function of G/L and mol % hydrogen for P = 13.89 MPa and T = 350°C

G/L g mol/kg	% H ₂ = 50	% H ₂ = 70	% H ₂ = 90
20	0.2263	0.2022	0.1818
40	0.3401	0.3058	0.2755
60	0.4120	0.3725	0.3370
80	0.4643	0.4216	0.3826

representative examples of feed and product liquid compositions are listed in Table 13 for 450°C, 13.89 MPa, a G/L value of 50 (40 for feed), and 80 mol % H₂ (74 for feed). This table lists both mol % and wt % of each component. The program also calculates specific gravities of the liquid and vapour at reactor conditions, thus although these gravities are of limited accuracy, it is possible to calculate the concentration of any component of interest in moles or kg/l.

One of the objects of the present study was to generate data that would aid in the development of a kinetic model for the hydrocracking reaction. As one of the main reactions of inter-

est is the conversion of pitch to material boiling below 524°C (975°F), the concentration of this material in the liquid phase in the reactor is of importance. Obviously other reactions can occur which involve lower boiling fractions. However, for simplicity, the discussion will be confined to pitch, the conversion of which, together with S and N removal, is of great interest in the CANMET hydrocracking process.

The wt % data for a few representative conditions were converted to concentrations in kg/l for the 649°C (1200°F) fraction using the calculated gravities and the results listed in Table 14.

Table 13: Computed composition of product liquids at P = 13.89 MPa, T = 450°C, G/L = 50 g mol/kg and mol % H₂ = 80

Component	Feed ^a		94-3-1		71-1-2		81-3-1	
	mol %	wt %	mol %	wt %	mol %	wt %	mol %	wt %
H ₂	33.58	0.17	25.08	0.21	24.80	0.23	23.58	0.24
H ₂ S	0.99	0.08	2.52	0.35	1.67	0.26	1.71	0.29
CH ₄	7.34	0.29	1.63	0.11	2.16	0.16	2.45	0.20
C ₂ H ₆	3.85	0.29	2.81	0.35	1.89	0.26	1.82	0.27
C ₃ H ₈	1.80	0.20	1.81	0.33	1.51	0.31	1.28	0.28
n-C ₄ H ₁₀	0.80	0.12	0.99	0.24	1.88	0.51	1.42	0.41
n-C ₅ H ₁₂	0.25	0.04	0.61	0.18	0.74	0.25	0.50	0.18
65.6°C ^b	0.07	0.01	0.53	0.19	0.91	0.36	1.50	0.64
121.1°C	0.03	0.01	1.35	0.61	1.56	0.77	1.87	1.01
176.7°C	0.12	0.04	1.55	0.87	2.56	1.63	3.82	2.64
232.2°C	0.12	0.05	2.95	2.16	4.15	3.35	4.97	4.31
287.8°C	1.01	0.56	4.84	4.24	6.35	6.27	7.84	8.33
343.3°C	4.79	3.28	8.28	8.87	9.24	11.07	11.58	14.75
398.9°C	6.93	5.75	10.78	13.82	13.28	18.67	12.74	18.93
454.4°C	9.16	8.93	8.75	13.04	10.38	16.87	9.04	15.11
510.0°C	11.05	12.36	6.85	11.96	5.71	10.47	7.04	13.48
648.9°C	18.09	67.81	18.67	42.47	11.18	28.55	6.83	18.91

a - Calculated for P = 13.89 MPa, 450°C, G/L = 40 g mol/kg and 74 mol % H₂

b - 65.6°C, etc. are hydrocarbon fractions with MABP = 65.6°C, etc.

Table 14: Reactor liquid specific gravity and pitch concentration in liquid at reactor outlet

T °C	P MPa	G/L g mol/ kg	Feed		94-3-1		71-1-2		81-3-1	
			Sp Gr	kg/ℓ	Sp Gr	kg/ℓ	Sp Gr	kg/ℓ	Sp Gr	kg/ℓ
450	10.44	10	-	-	0.78	0.244	0.722	0.123	0.666	0.0462
450	10.44	50	-	-	0.848	0.408	0.818	0.293	0.844	0.251
450	13.89	50	1.372 ^a	0.930 ^a	0.874	0.371	0.825	0.236	0.813	0.154
20	0.101	0 ^b	1.00	0.505	0.963	0.232	0.931	0.103	0.898	0.0283

^a No conversion; calculated

^b This corresponds to Sp Gr and pitch concentration in bitumen or total liquid product at STP.

The main point to note from these data is the considerable variation of actual pitch concentration for any particular product or feed as the conditions are varied. This is more noticeable for the high conversion product 81-3-1 but is still considerable for the other products. Unfortunately no detailed composition data were obtained for the feed at pressures other than 13.89 MPa. The pitch concentration in feed and products at STP and zero G/L is also listed for comparison.

Pitch concentration is strongly dependent on G/L values, temperature, and pressure. Thus for product 71-1-2 at a conversion of 76%, the concentration increases by a factor of 2.38 when G/L increases from 10 to 50; it increases by a factor of 1.64 when temperature increases from 400 to 450°C, and it drops by a factor of 0.81 when pressure increases from 10.44 to 13.89 MPa. These effects are greater for 81-3-1 and less for 94-3-1. Any kinetic model must obviously take these variations of pitch concentration into account.

Table 13 also lists the concentrations of hydrogen in the liquid phase. This is of importance not only for kinetic studies but also for practical considerations of coking. Coking reactions become more important as the concentration of hydrogen decreases. The partial pressure of

hydrogen in the gas phase is usually considered in this respect, but the more important factor is really the concentration in the liquid phase which can vary depending on conditions at constant pressure. This is illustrated below where hydrogen concentrations are calculated in moles/litre. Again the absolute values should be treated with caution because of uncertainties in the density values calculated at reactor conditions (Table 15).

Table 15: Hydrogen concentration in reactor liquid at reactor conditions

T, °C	P, MPa	G/L g mol/ℓ	Feed	94-3-1	71-1-2	81-3-1
				values in g mol/ℓ		
400	10.44	50	-	0.532	0.556	0.584
450	10.44	50	-	0.568	0.597	0.616
450	10.44	10	-	0.616	0.624	0.606
450	13.89	50	1.146	0.909	0.949	0.967
450	13.89	10	1.079	0.938	0.921	0.824

Pressure has the greatest influence on hydrogen concentration — increasing system pressure from 10.44 MPa to 13.89 MPa increases the

hydrogen concentration by 50%. Variation of temperature and G/L values have much less effect. For G/L values of 50, H₂ concentrations increase as conversion increases, while for a G/L value of 10, hydrogen concentration decreases. This effect reflects the greater decrease in density with increasing conversion at lower G/L values. Increasing the temperature from 400 to 450°C has a smaller effect, hydrogen concentrations increasing by only approximately 7%; again this is a reflection of gravity changes.

The influence of pressure on hydrogen concentration, which was noted above, is consistent with the observation that coking is alleviated by increasing the pressure, and that at pressures below 10.44 MPa, coking problems become serious.

In the above discussion, no account was taken of the effect of diffusion; however, the possibility of diffusion control of coking and hydrocracking reactions should not be ignored. If this effect is important, the hydrogen concentrations could be considerably lower than indicated above, and G/L values could have a greater effect, e.g., on the degree of gas-liquid mixing in the reactor.

The hydrogen concentration in the vapour phase at the top of the reactor at equilibrium will be dependent on the degree of vaporization. This is illustrated below for typical reactor conditions at 450°C and 80 mol % H₂ in the recycle gas (Table 16).

Table 16: Hydrogen concentration in vapour phase at equilibrium

P, MPa	G/L g mol/kg	Feed mol %	94-3-1 mol %	71-1-2 mol %	81-3-1 mol %
10.44	10	-	69.9	65.2	58.9
10.44	50	-	76.1	75.0	72.6
13.89	10	72.2	71.8	67.6	61.5
13.89	50	72.6 ^a	76.5	75.5	73.0

^a at G/L = 40

It can be seen that G/L values and pressure influence hydrogen concentration, the effect being greater for higher conversion products. The interesting point to note is that although the hydrogen concentration in the vapour phase decreases for increasing conversion, the opposite trend was found for the concentration of H₂ in the liquid phase for G/L values of 50 (although for values of 10, the same trend is seen). This, however, could be merely a reflection of inaccuracies in specific gravity estimations.

CONCLUSIONS

Between 20 and 80% of the liquid fed to the reactor can be in the vapour phase depending on the conditions and pitch conversion. For instance, for feed at 460°C, 13.89 MPa, an LHSV of 2.0, a gas rate of 0.0425 m³/h (1.5 ft³/h), and 74 mol % H₂, 34% of the material will be in the vapour phase while for product 71-1-2 under the same conditions, 56% will be vaporized. Increasing the gas rate to 0.0564 m³/h (2.0 ft³/h) will increase *f* for product 71-1-2 by 12.5% to 0.63.

The ratio of gas to liquid fed to the reactor has a large initial effect on the degree of vaporization, but the rate of increase of *f* drops off sharply at high G/L values. Typical pilot plant conditions generally fall within the area of rapid increase in *f*.

Temperature has a significant effect on vaporization, particularly above about 350°C, while pressure also has a considerable effect. Thus at 450°C and 80 mol % H₂, an increase in pressure from 10.44 to 17.34 MPa reduces *f* by the following amounts: 51% for feed at a G/L value of 40, 22% for 94-3-1, and 12% for 81-3-1 at G/L value of 50 for both products.

Increasing the mol % of hydrogen in the recycle gas causes a linear decrease in the degree of vaporization. Changing mol % H₂ from 60 to 80 causes *f* to drop by approximately 10%.

From calculated compositions of the liquid phase in the reactor, it was noted that pitch concentration is dependent to a marked degree on conditions. This has particular significance for the development of a kinetic model.

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 R281; 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. 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.
4. Grayson, H.G. and Streed, C.V. "Vapour liquid equilibria for high temperature, high pressure hydrogen-hydrocarbon systems"; Proceedings of the 6th World Petroleum Congress, Frankfurt/Main, June 1926, 1963, Section VII, Paper 20, PD7, p 233-245; 1963.
5. Redlich, O., and Kwong, J.N.S. "The thermodynamics of solutions. V. An equation of state. Fugacities of gaseous solutions"; Chem Rev, 44:233; 1949.
6. Hildebrand, J.H. and Scott, R.L. "The solubility of non-electrolytes"; 3rd ed. Reinhold, New York; 1950.
7. Patmore, D.J. and Pruden, B.B. "Thermal Hydrocracking of Athabasca bitumen - a comparison of computer simulated feed and product vaporization with pilot plant data"; CANMET, Energy, Mines and Resources Canada, CANMET Report 78-19.
8. Pruden, B.B. and Denis, J.M. "Heat of reaction and vaporization of feed and product in the thermal hydrocracking of Athabasca bitumen"; CANMET, Energy, Mines and Resources Canada, CANMET Report 76-30; 1976.
9. Smith, N.A.C., et al. "The Bureau of Mines routine method for the analysis of crude petroleum I: The analytical method"; U.S. Bureau of Mines, Bulletin 490; 1951.

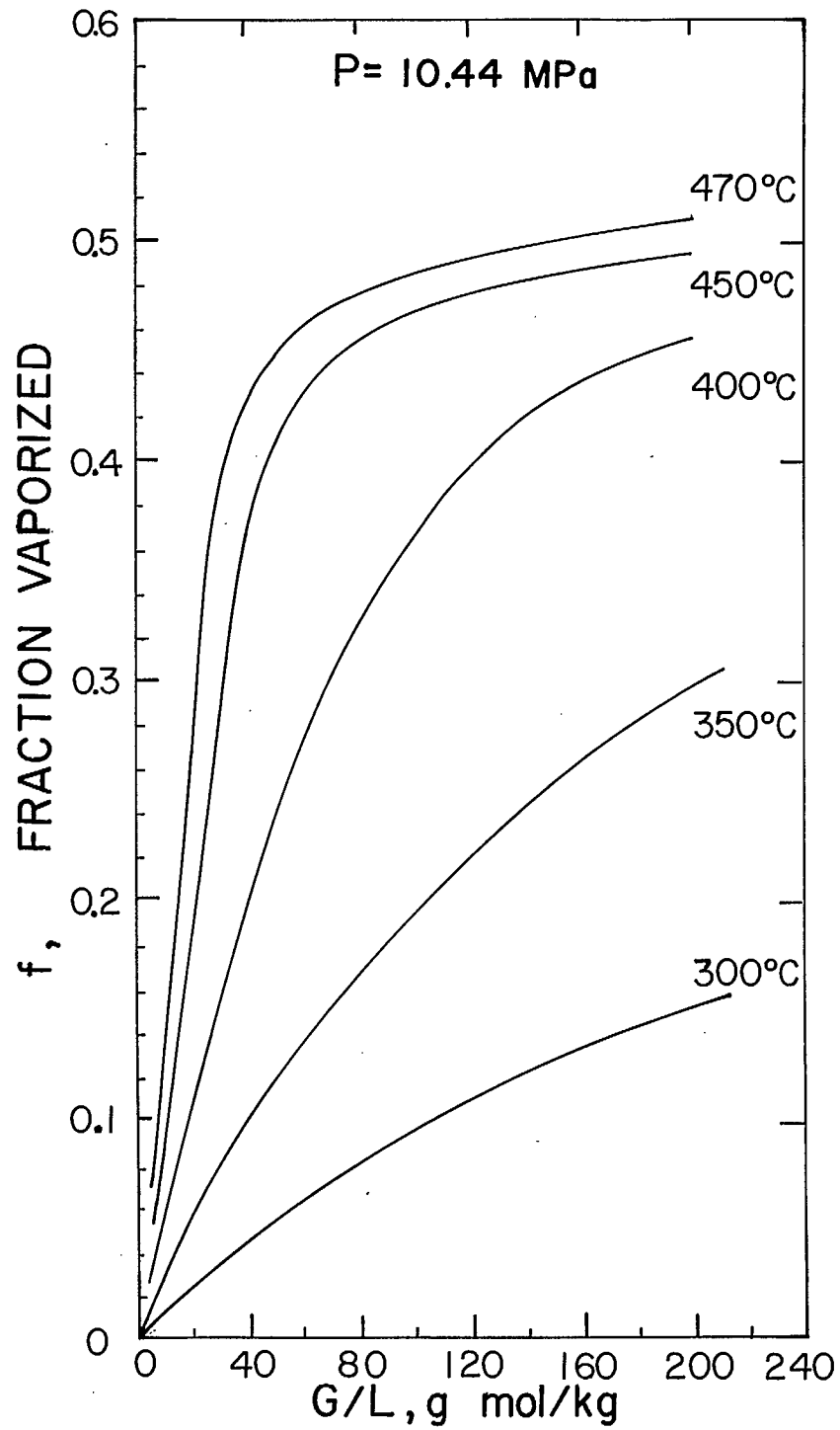


Fig. 1 - Calculated fraction of liquid feed vaporized, f , vs g mol of gas per kg feed, G/L , at 10.44 MPa and 74 mol % H_2 for temperatures of 300 to 470°C

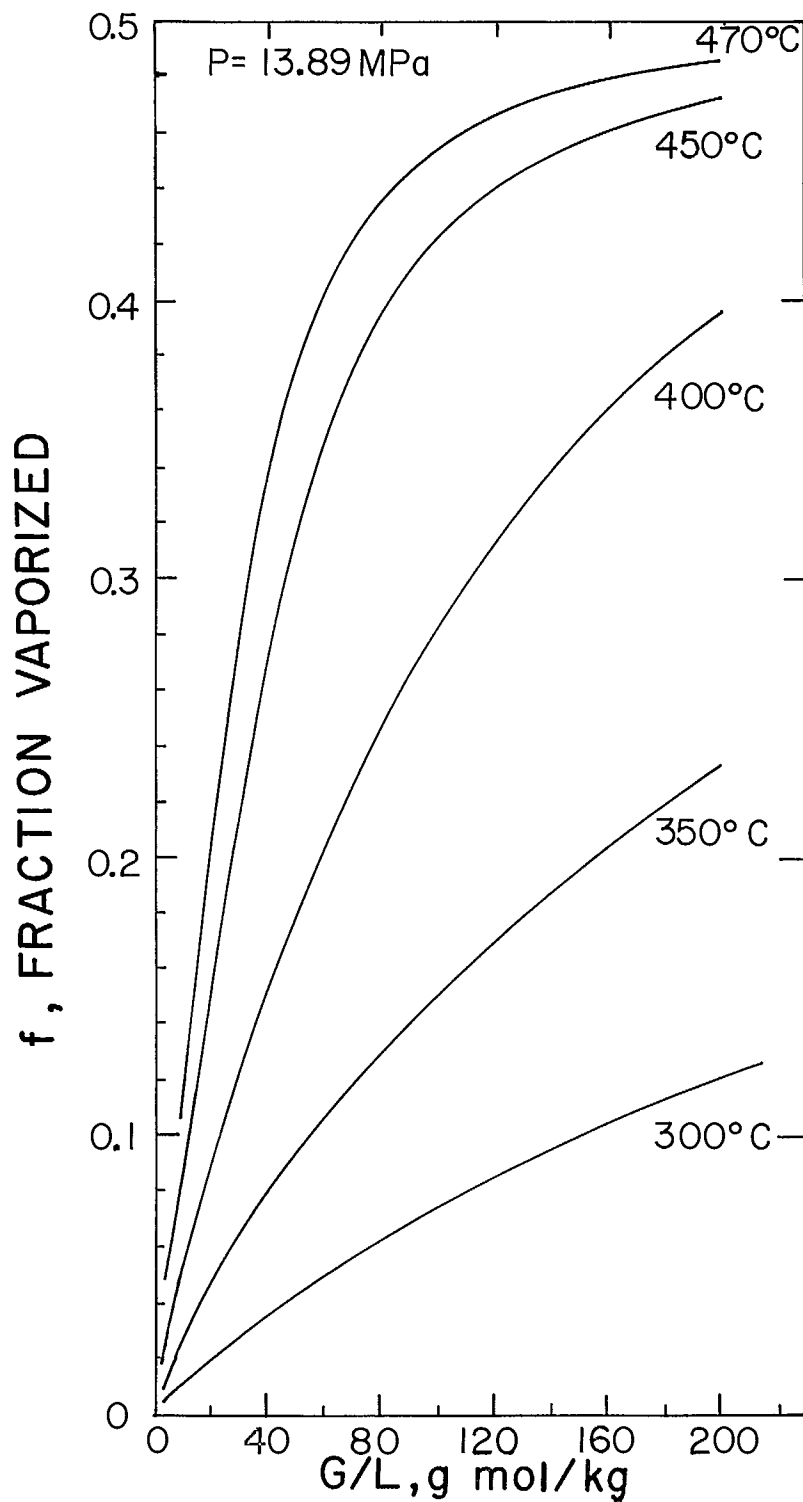


Fig. 2 - Calculated fraction of liquid feed vaporized, f , vs g mol of gas per kg of feed, G/L , at 13.89 MPa and 74 mol % H_2 for temperatures of 300 to 470°C

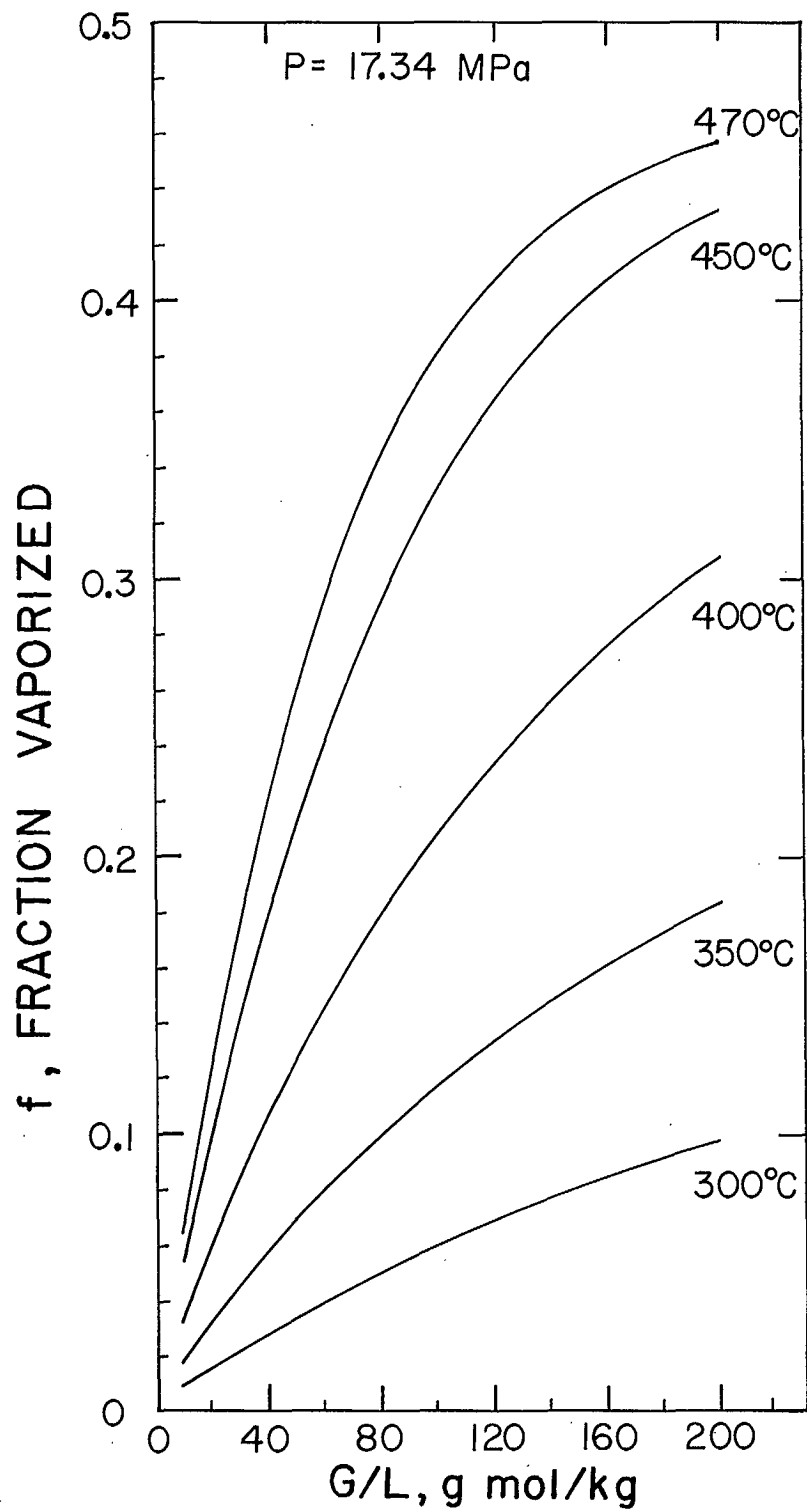


Fig. 3 - Calculated fraction of liquid feed vaporized, f , vs g mol of gas per kg of feed, G/L , at 17.34 MPa and 74 mol % H_2 for temperatures of 300 to 470°C

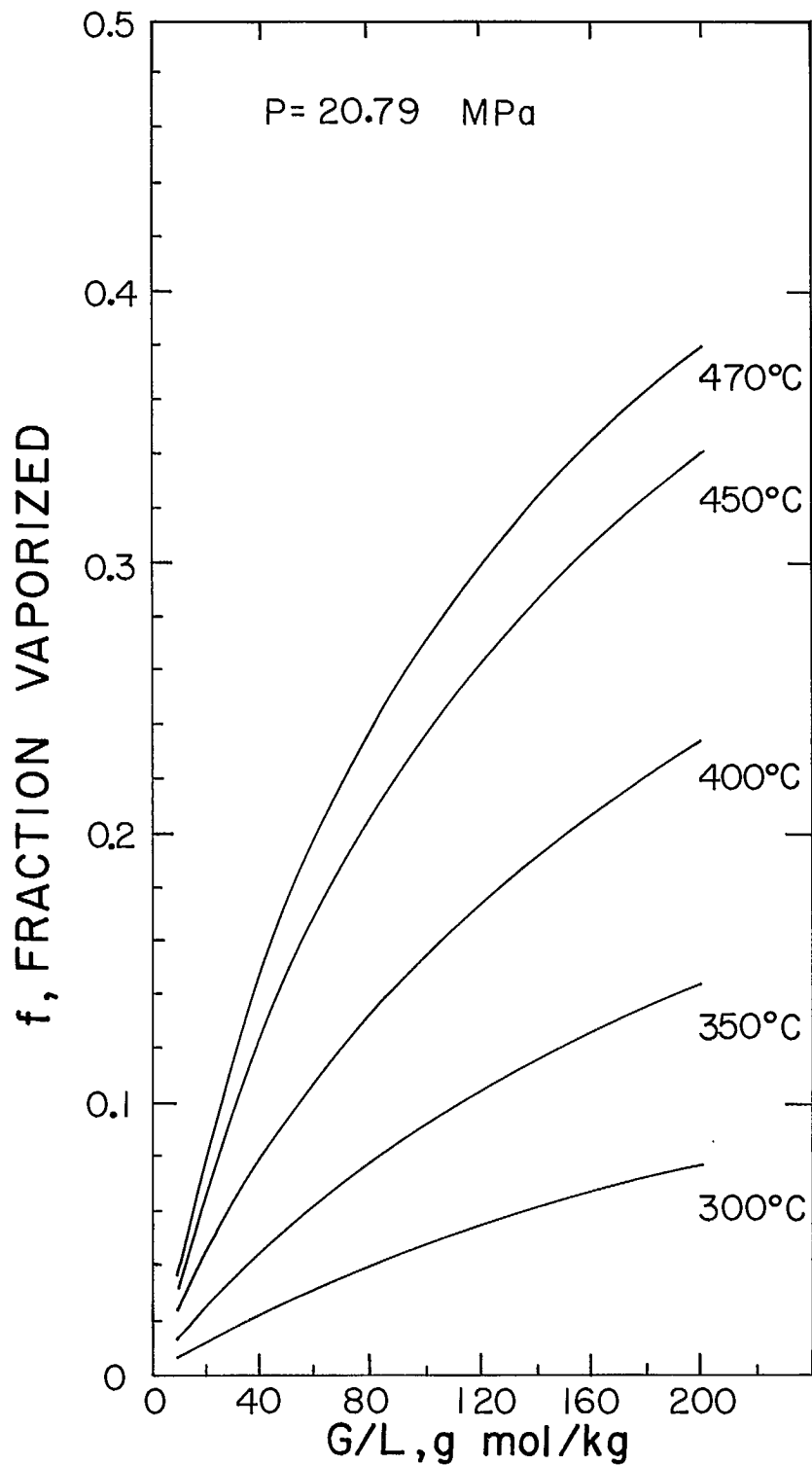


Fig. 4 - Calculated fraction of liquid feed vaporized, f , vs g mol of gas per kg of feed, G/L , at 20.79 MPa and 74 mol % H_2 for temperatures of 300 to 470°C

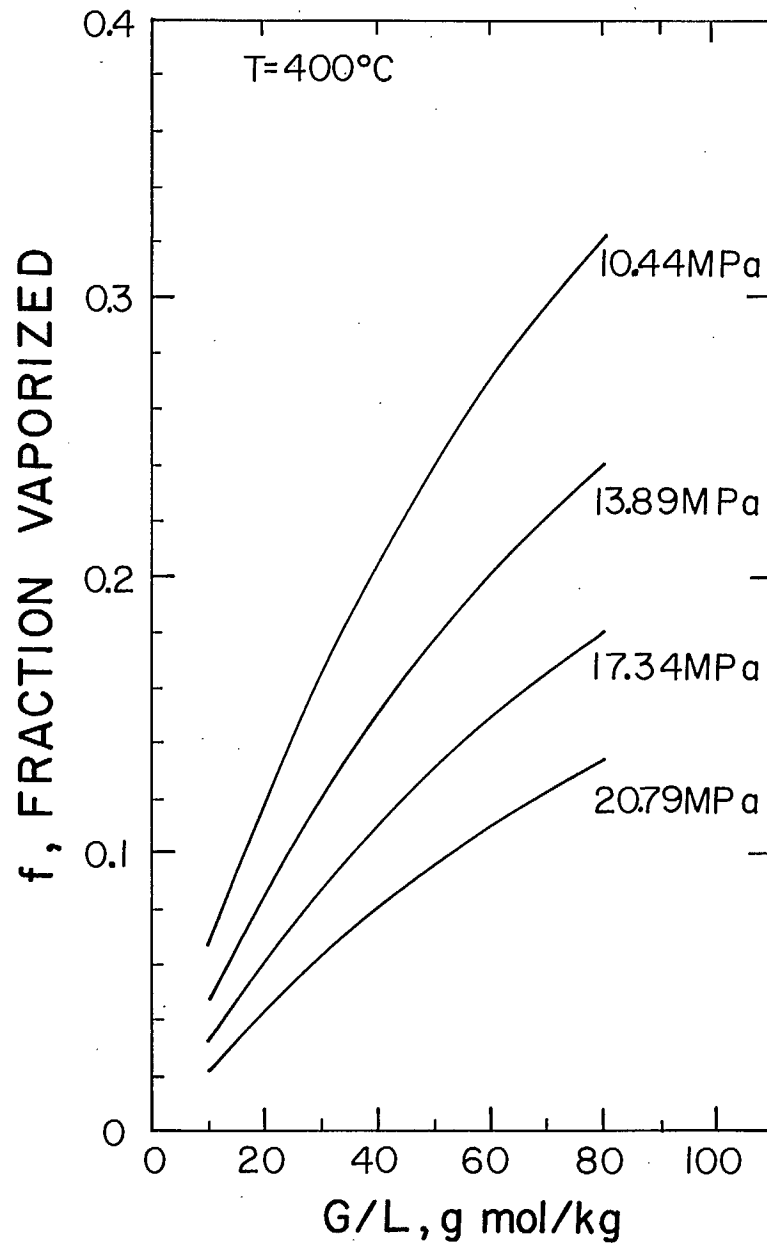


Fig. 5 - Effect of pressure, in MPa, on calculated fraction of liquid feed vaporized, f , vs g mol of gas per kg of feed, G/L , at 400°C and 74 mol % H_2

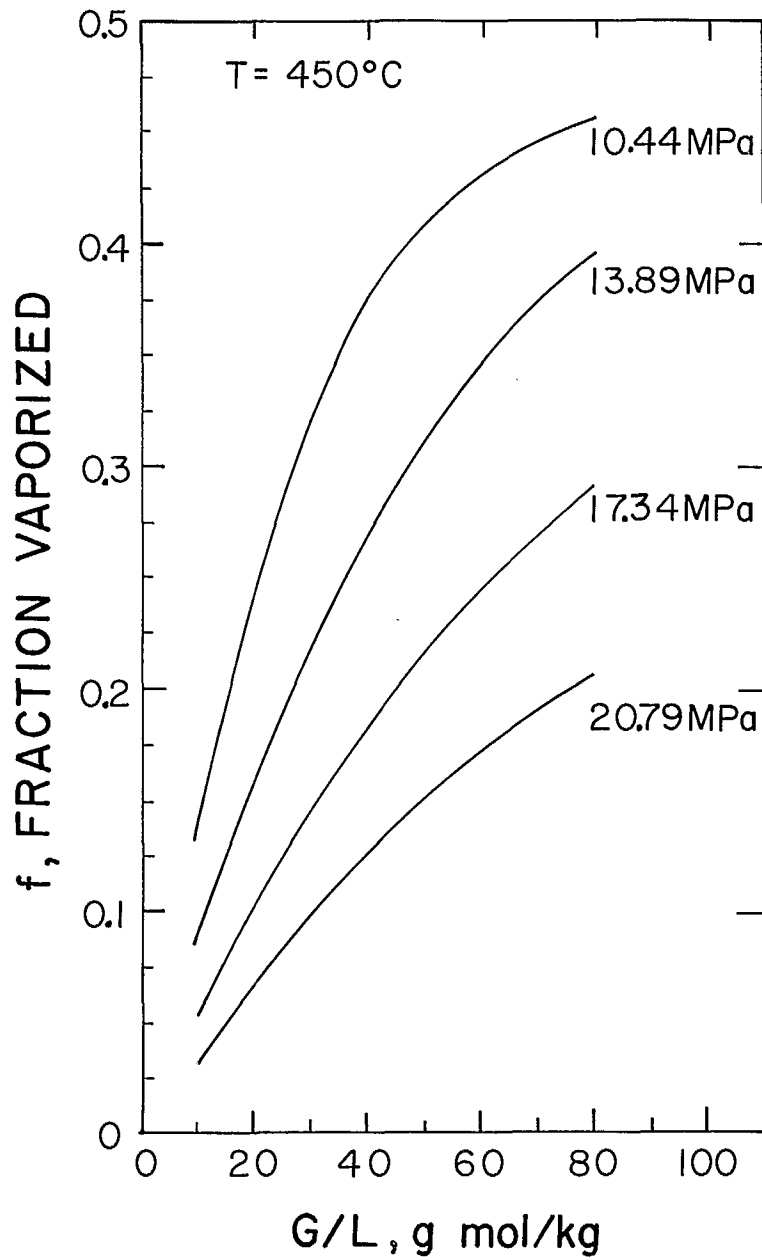


Fig. 6 - Effect of pressure, in MPa, on calculated fraction of liquid feed vaporized, f , vs g mol of gas per kg of feed at 450°C and 74 mol % H_2

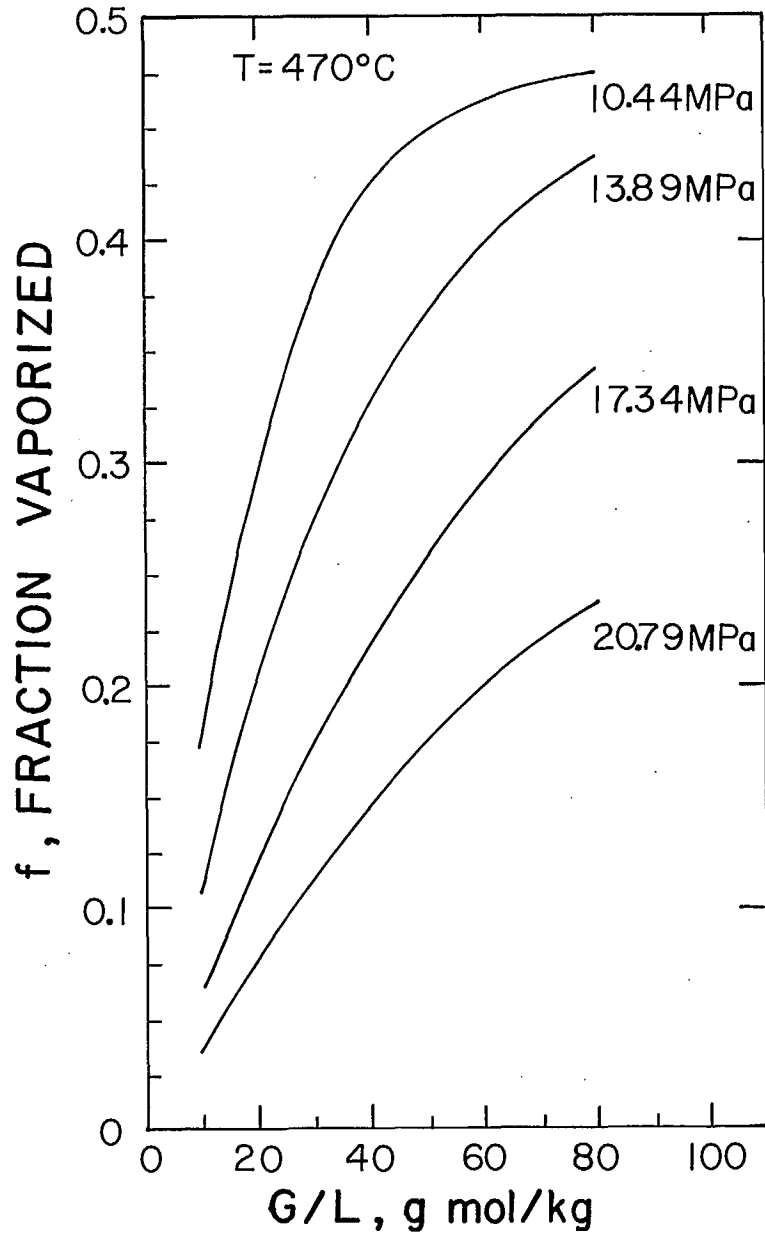


Fig. 7 - Effect of pressure, in MPa, on calculated fraction of feed vaporized, f , vs g mol of gas per kg of feed, G/L , at 470°C and 74 mol % H_2

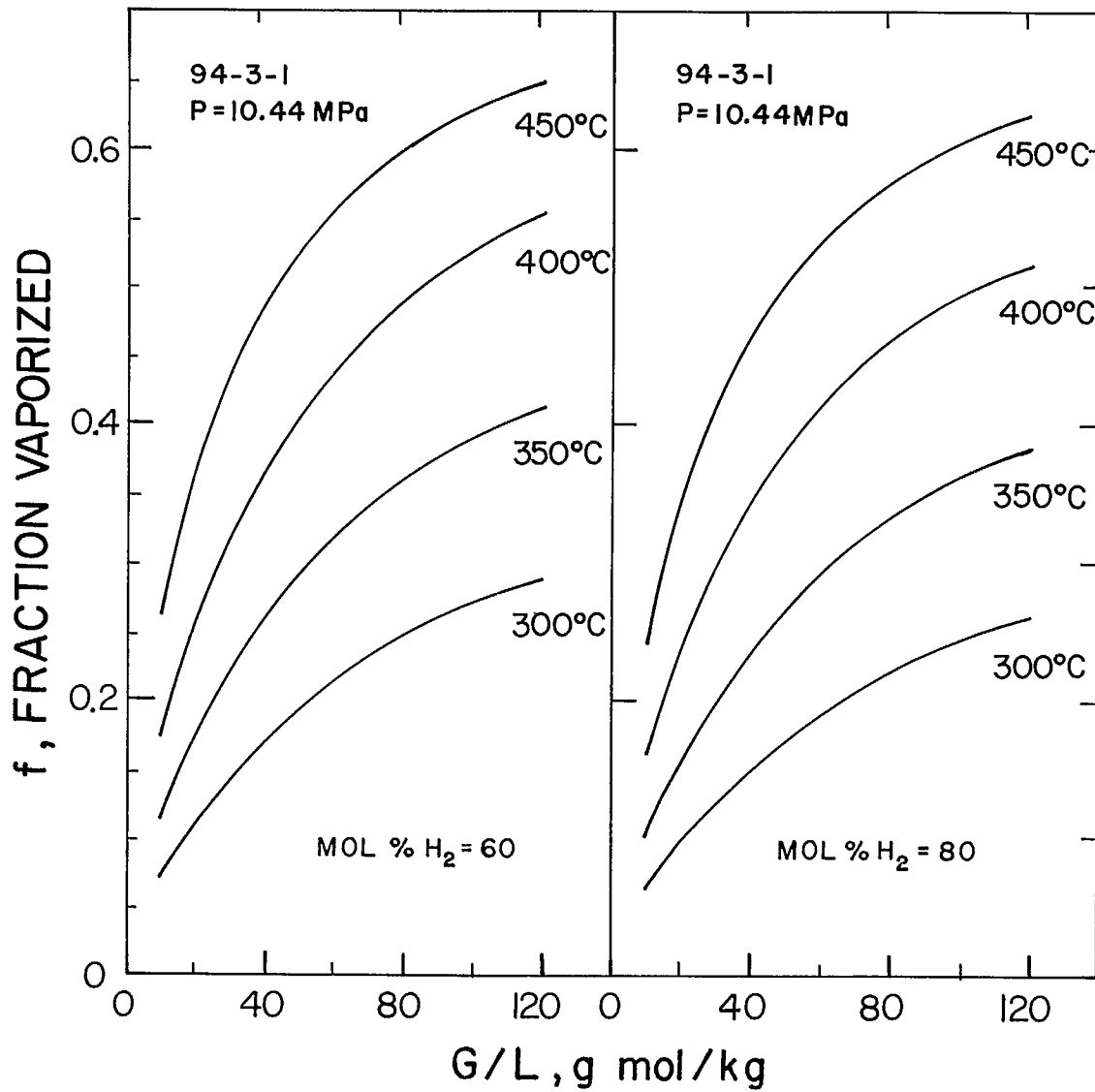


Fig. 8 - Calculated fraction of liquid product 94-3-1 vaporized, f , vs g mol of gas per kg of product fed, G/L , at 10.44 MPa, for 60 and 80 mol % H_2 and temperatures of 300 to 450°C

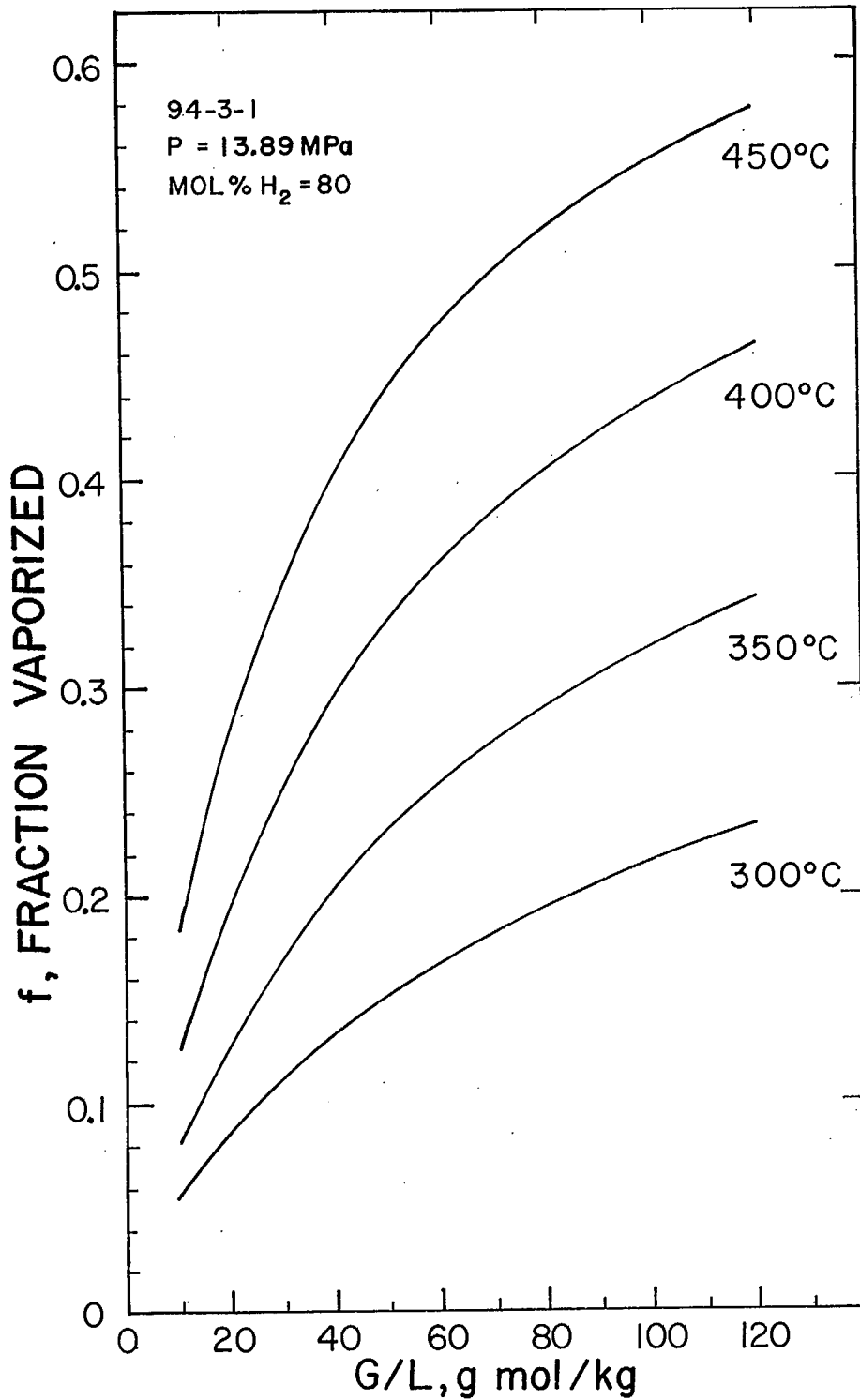


Fig. 9 - Calculated fraction of liquid product 94-3-1 vaporized, f , vs g mol of gas per kg of liquid product fed, G/L , at 13.89 MPa for temperatures of 300 to 450°C and 80 mol % H₂

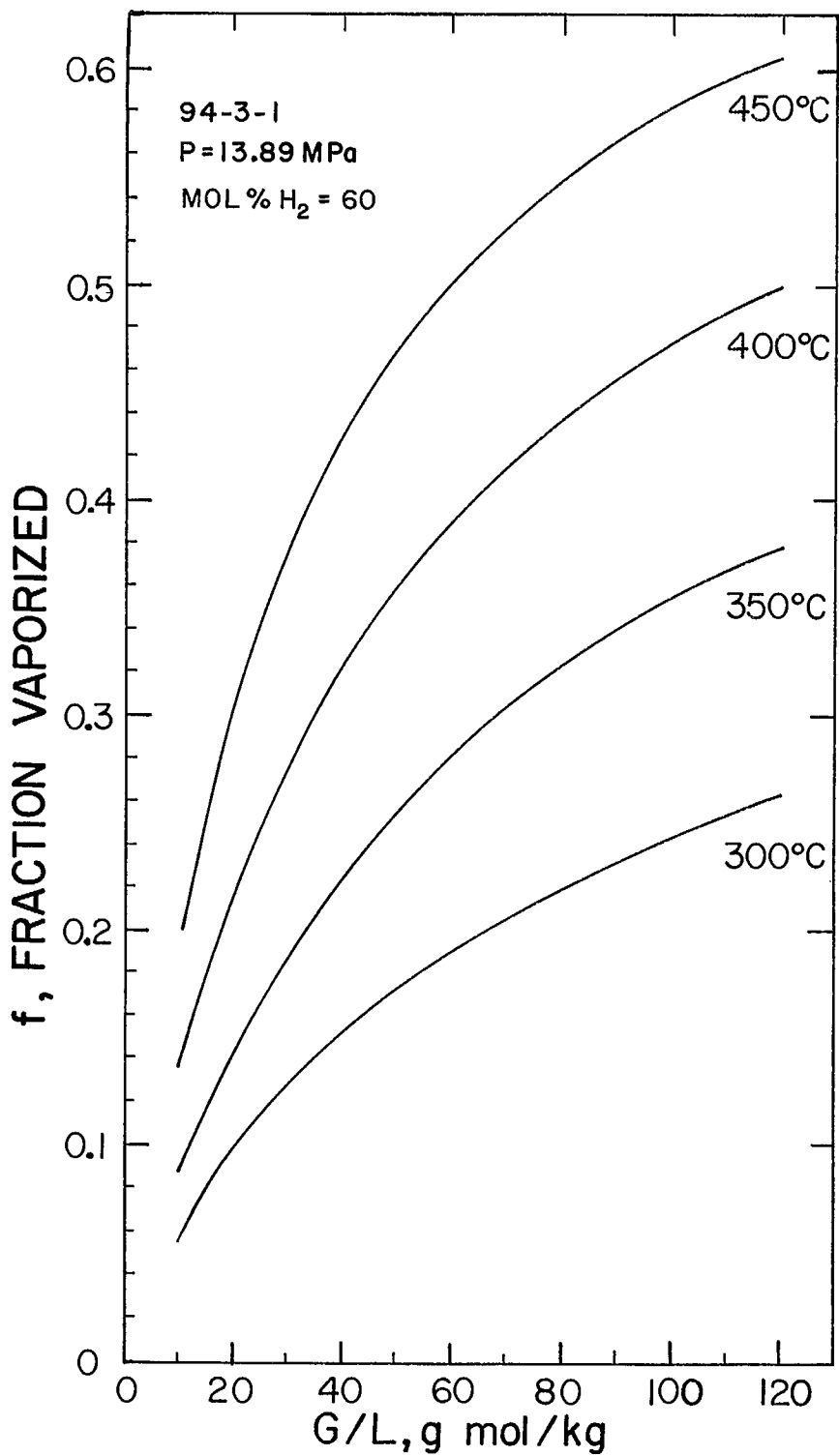


Fig. 10 - Calculated fraction of liquid product 94-3-1 vaporized, f , vs G/L , g mol/kg of product fed, for 60 mol % H₂, a pressure of 13.89 MPa, and temperatures of 300 to 450°C

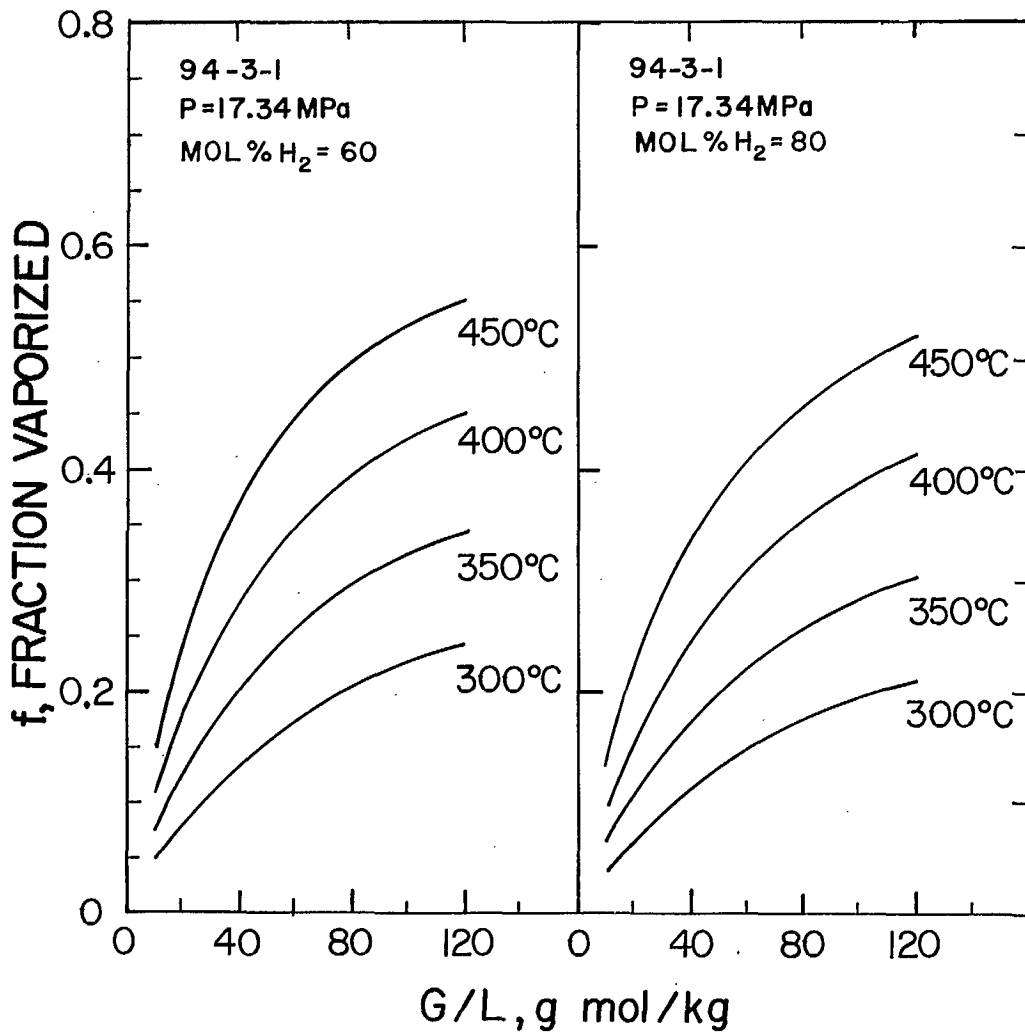


Fig. 11 - Calculated fraction of liquid product 94-3-1 vaporized, f , vs g mol of gas per kg of product fed, G/L , at 17.34 MPa for 60 and 80 mol % H₂ and temperatures of 300 to 450°C

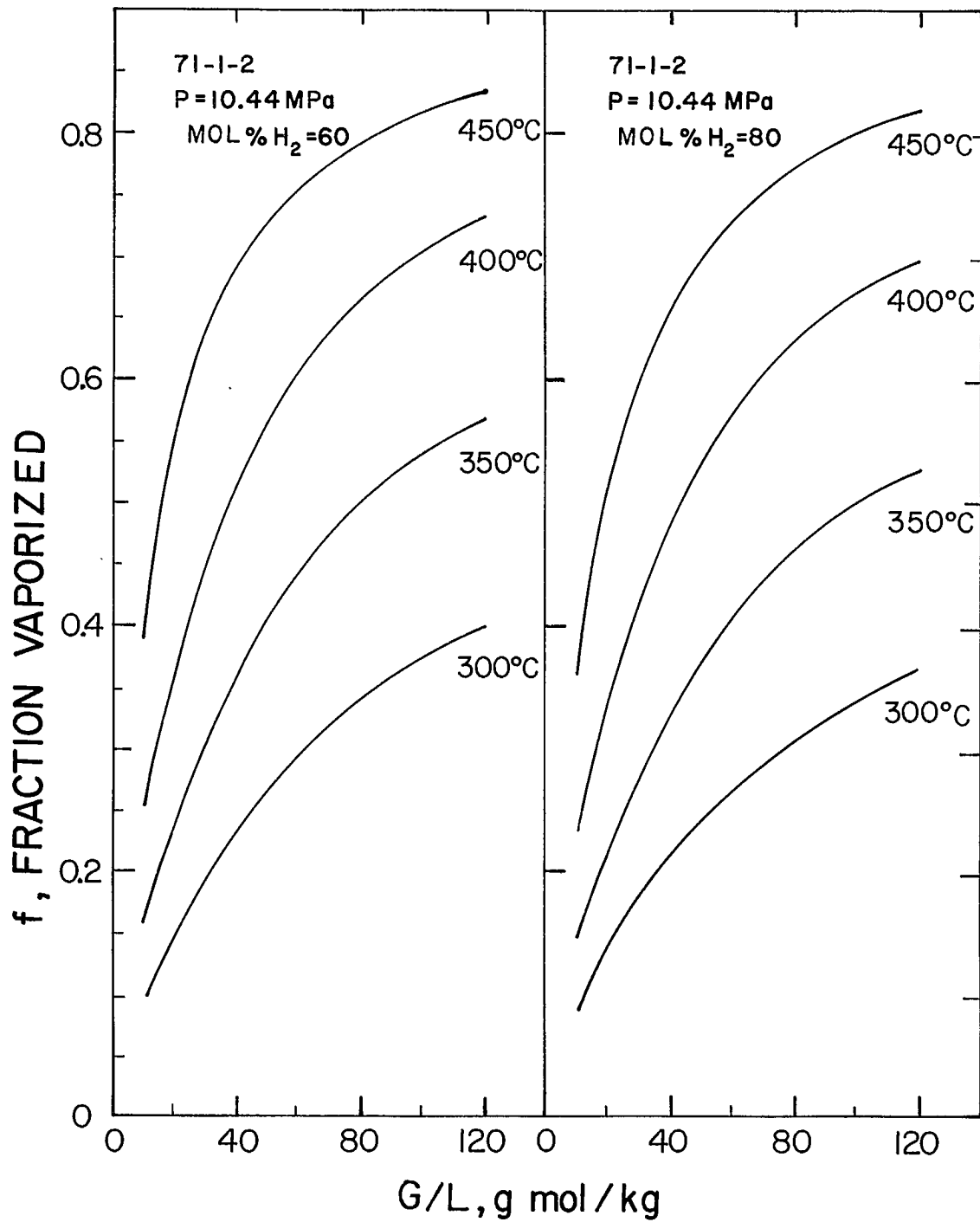


Fig. 12 - Calculated fraction of liquid product 71-1-2 vaporized, f , vs g mol of gas per kg of product fed, G/L , at 10.44 MPa for 60 and 80 mol % H_2 and temperatures of 300 to 450°C

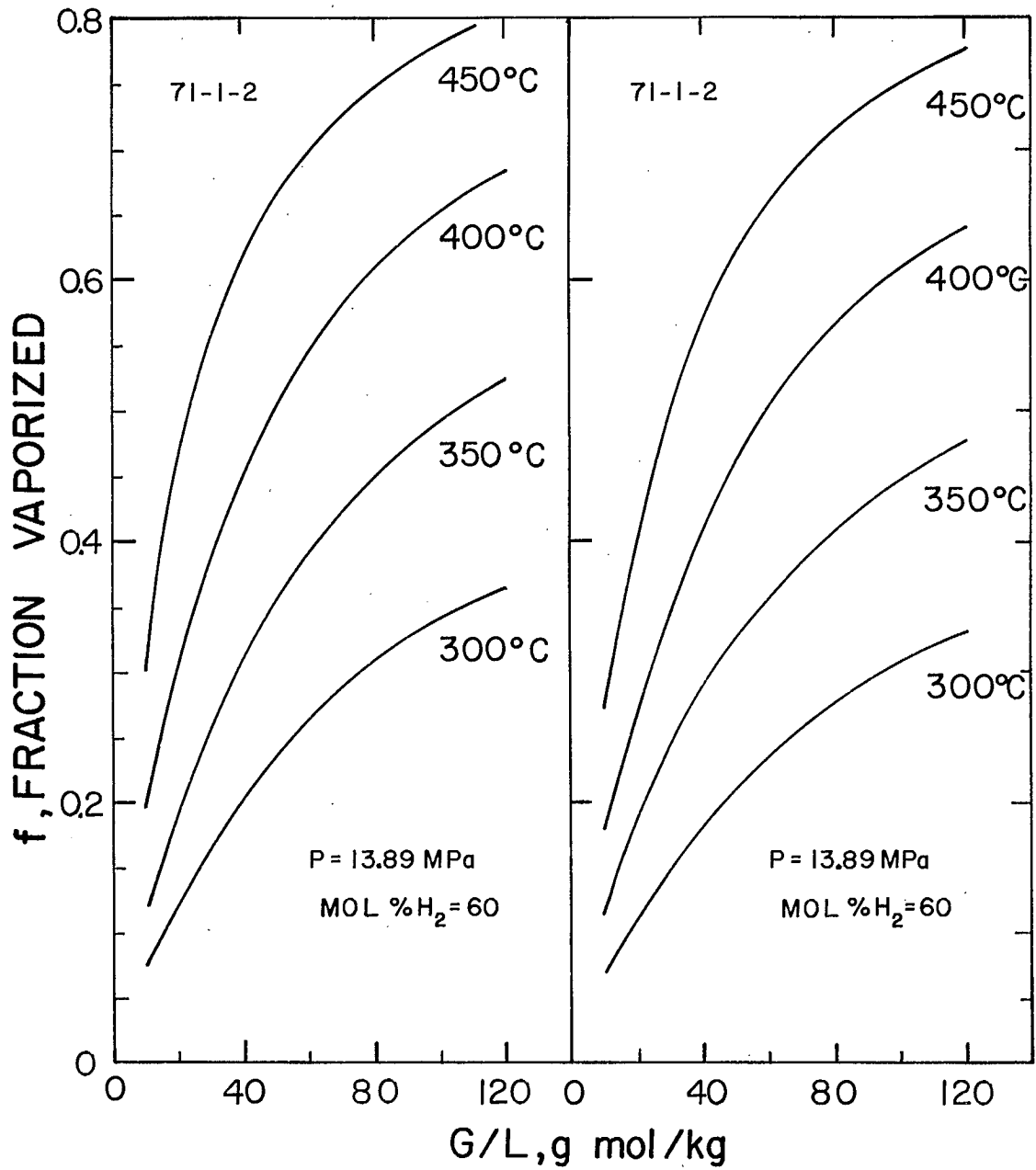


Fig. 13 - Calculated fraction of liquid product 71-1-2 vaporized, f , vs g mol of gas per kg of product fed, G/L, at 13.84 MPa for 60 and 80 mol % H_2 and temperatures of 300 to 450°C

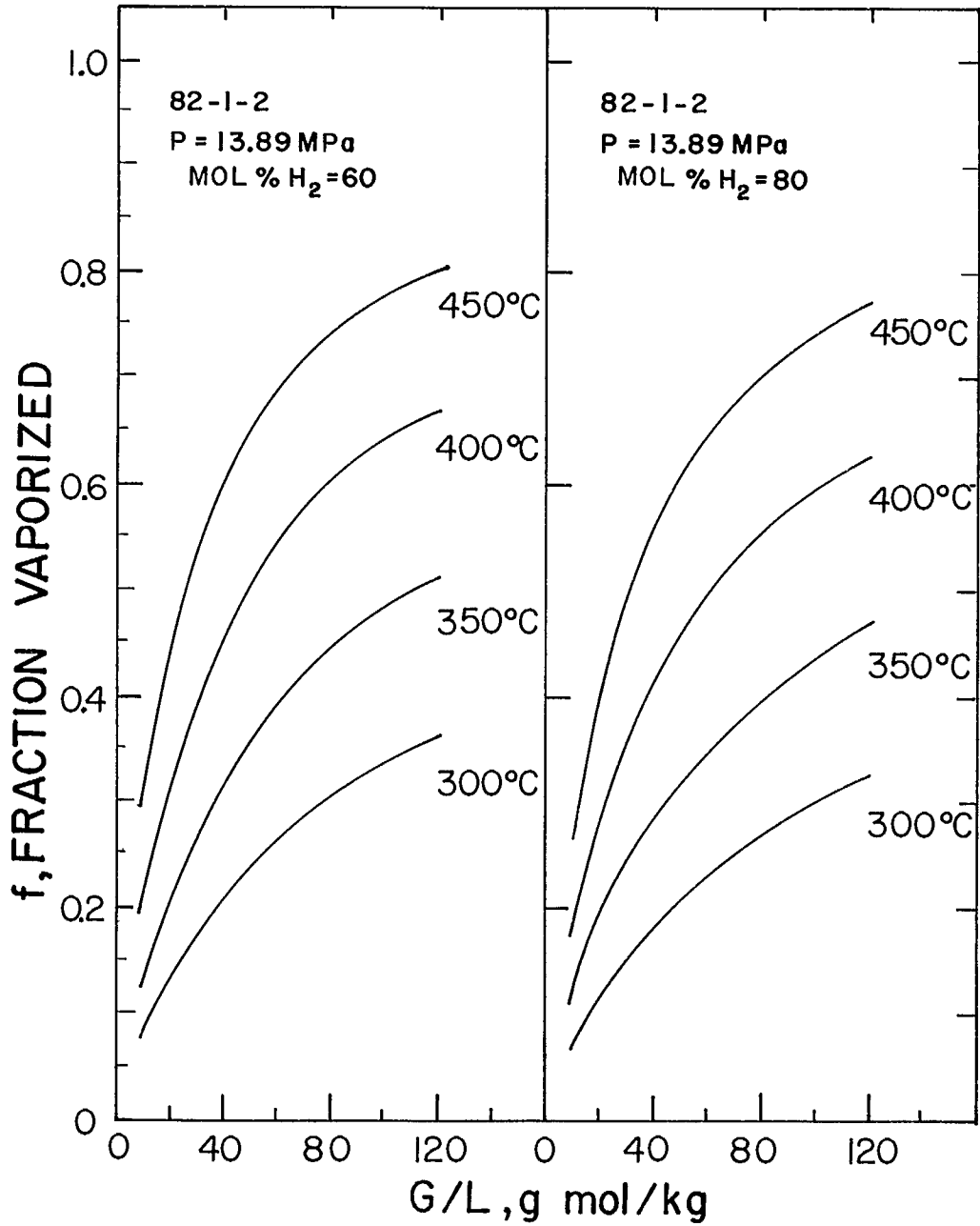


Fig. 14 - Calculated fraction of liquid product 82-1-2 vaporized, f , vs g mol of gas per kg of product fed, G/L , at 13.89 MPa for 60 and 80 mol % H_2 and temperatures of 300 to 450°C

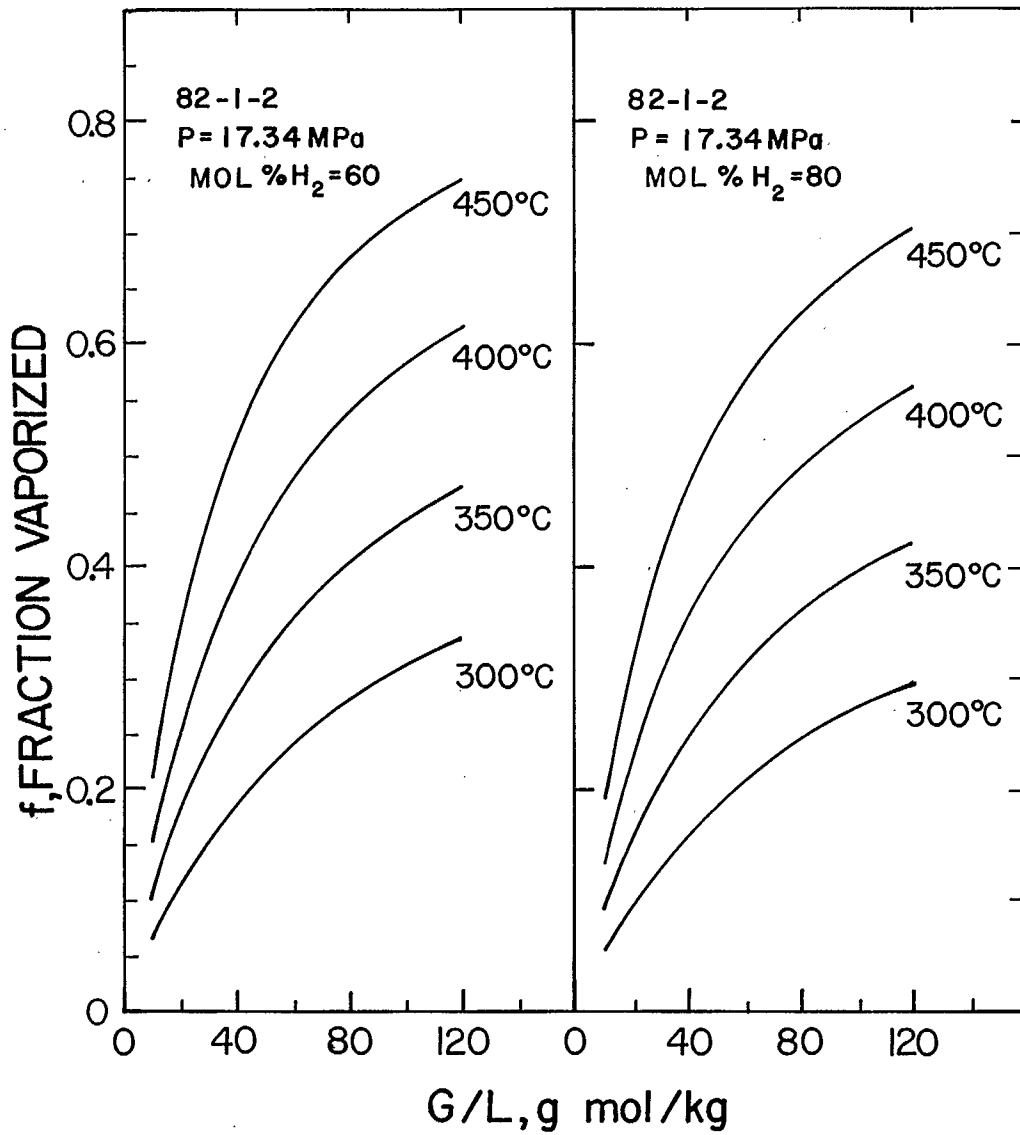


Fig. 15 - Calculated fraction of liquid product 82-1-2 vaporized, f , vs g mol of gas per kg of product fed, G/L at 17.34 MPa for 60 and 80 mol % H_2 and temperatures of 300 to 450°C

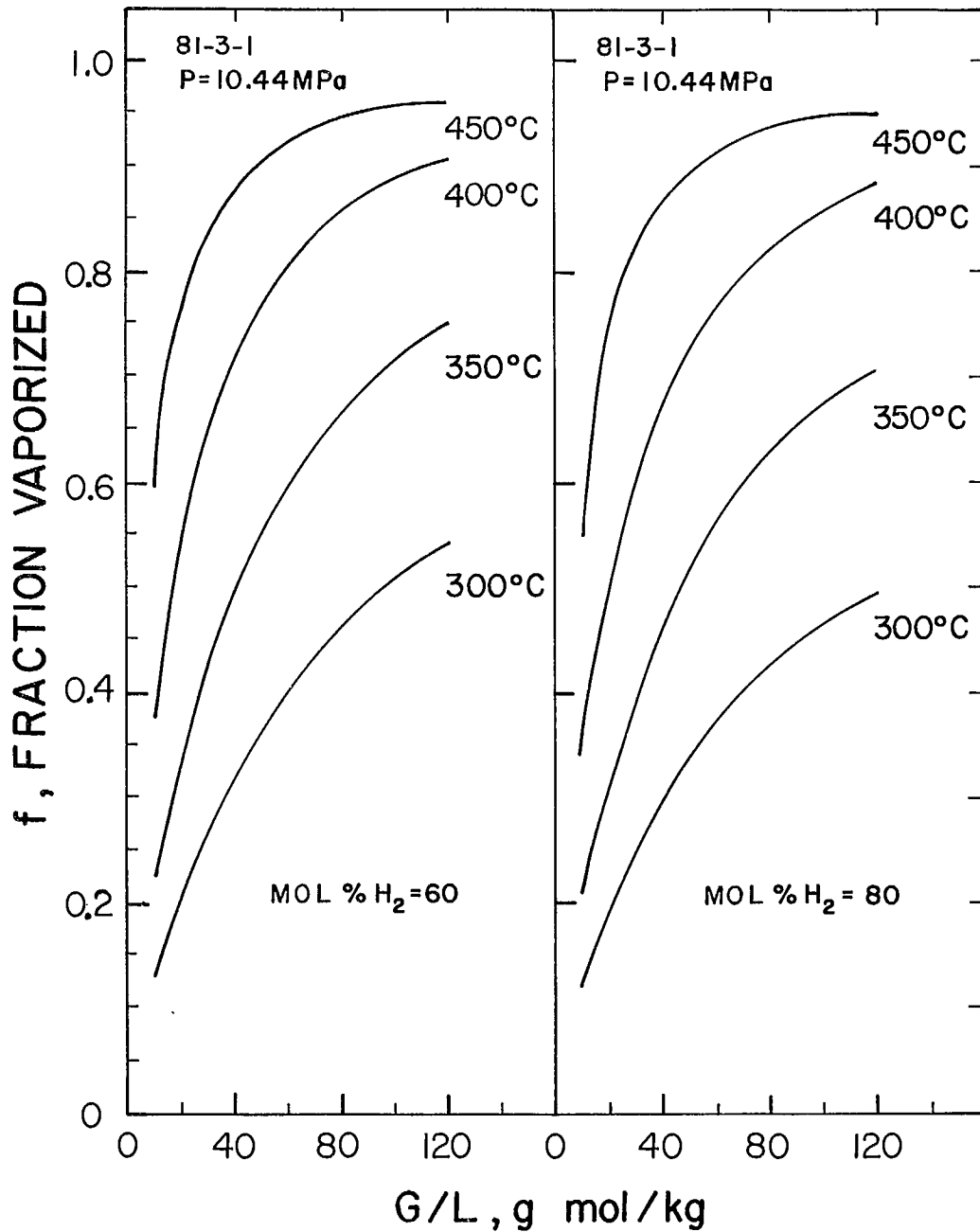


Fig. 16 - Calculated fraction of liquid product 81-3-1 vaporized, f , vs g mol of gas per kg product fed, G/L , at 10.44 MPa for 60 and 80 mol % H_2 and temperatures of 300 to 450°C

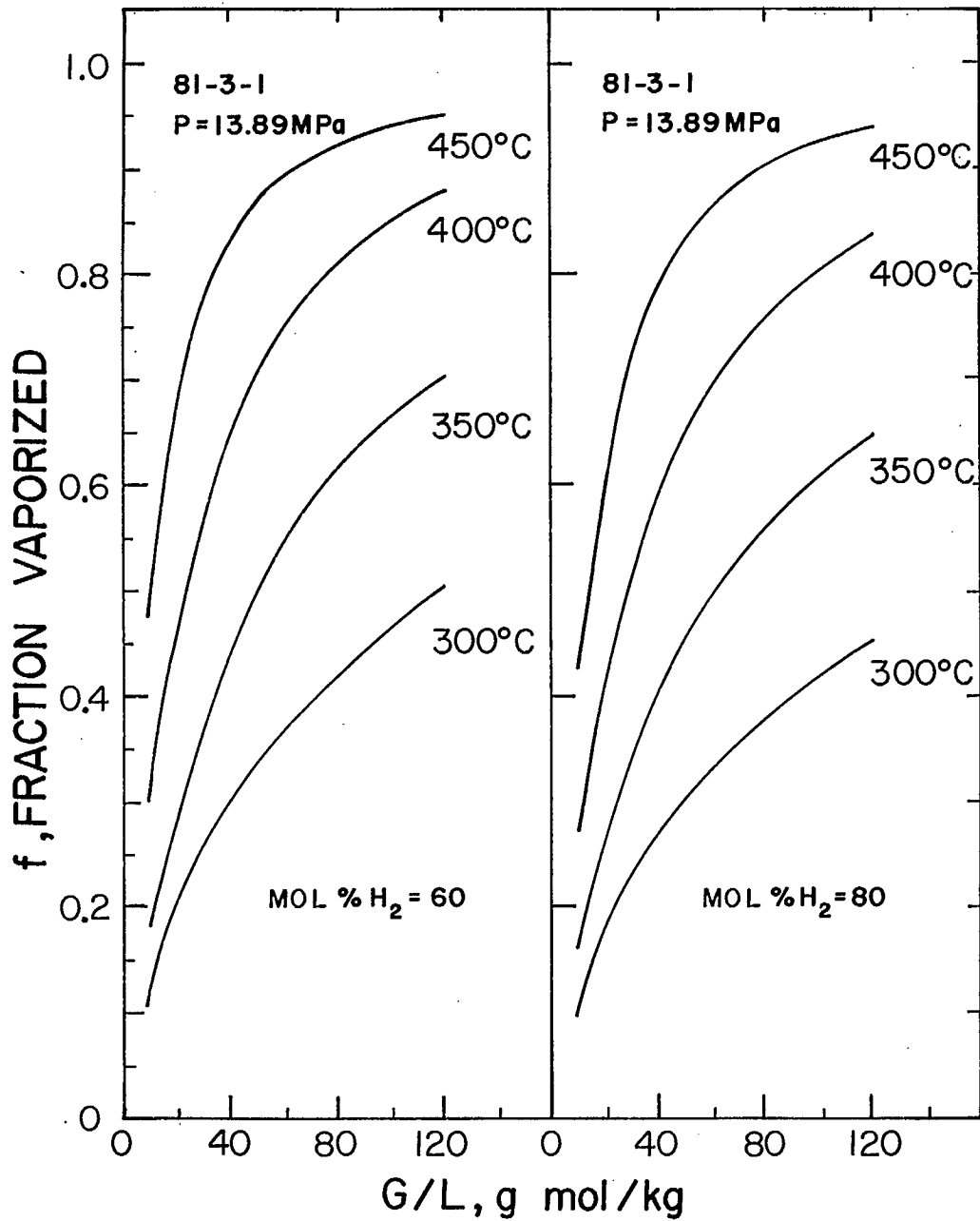


Fig. 17 - Calculated fraction of liquid product 81-3-1 vaporized, f , vs g mol of gas per kg of product fed, G/L, at 13.89 MPa for 60 and 80 mol % H₂ and temperatures of 300 to 450°C

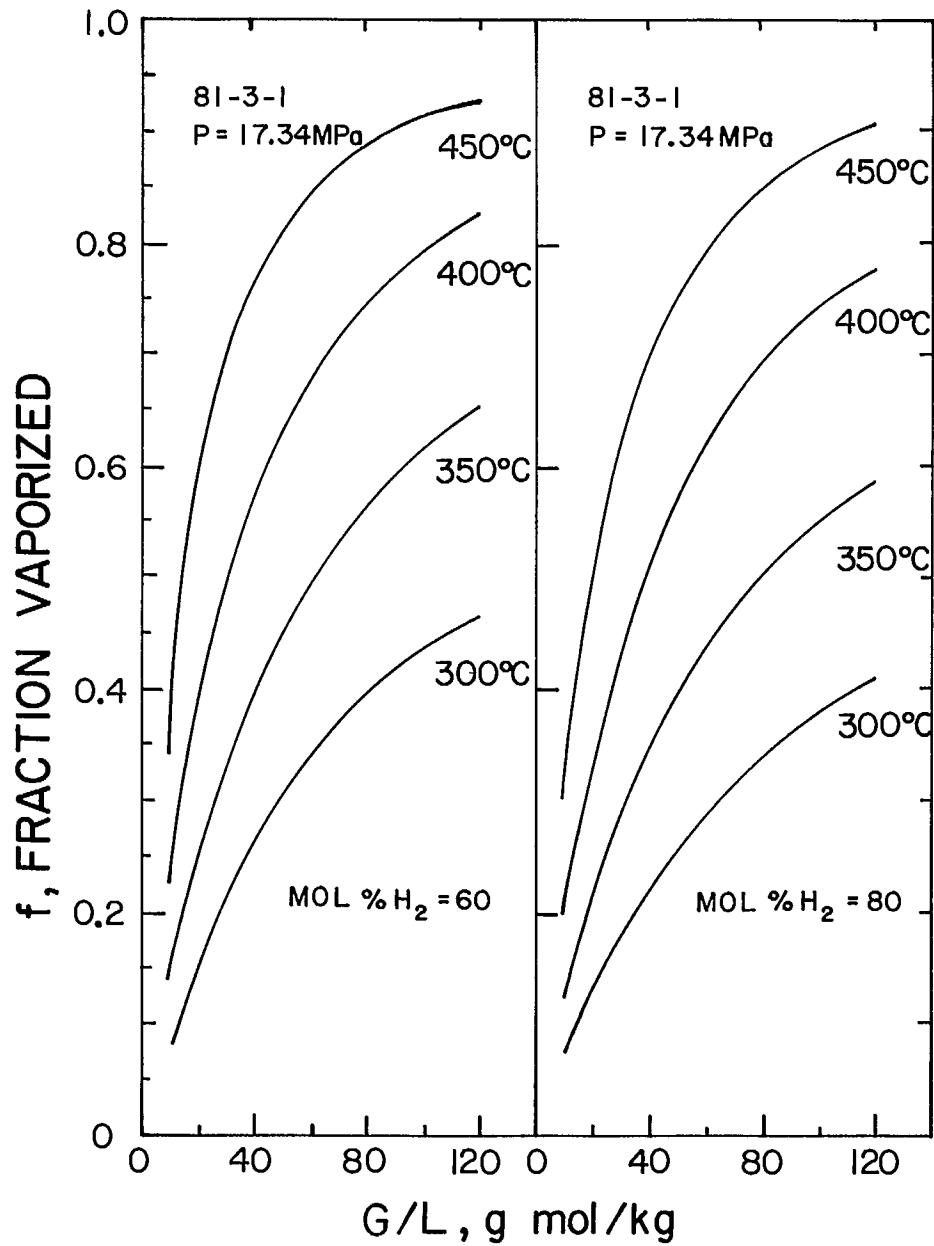


Fig. 18 - Calculated fraction of liquid product 81-3-1 vaporized, f , vs g mol of gas per kg of product fed, G/L , at 17.34 MPa for 60 and 80 mol % H_2 and temperatures of 300 to 450°C

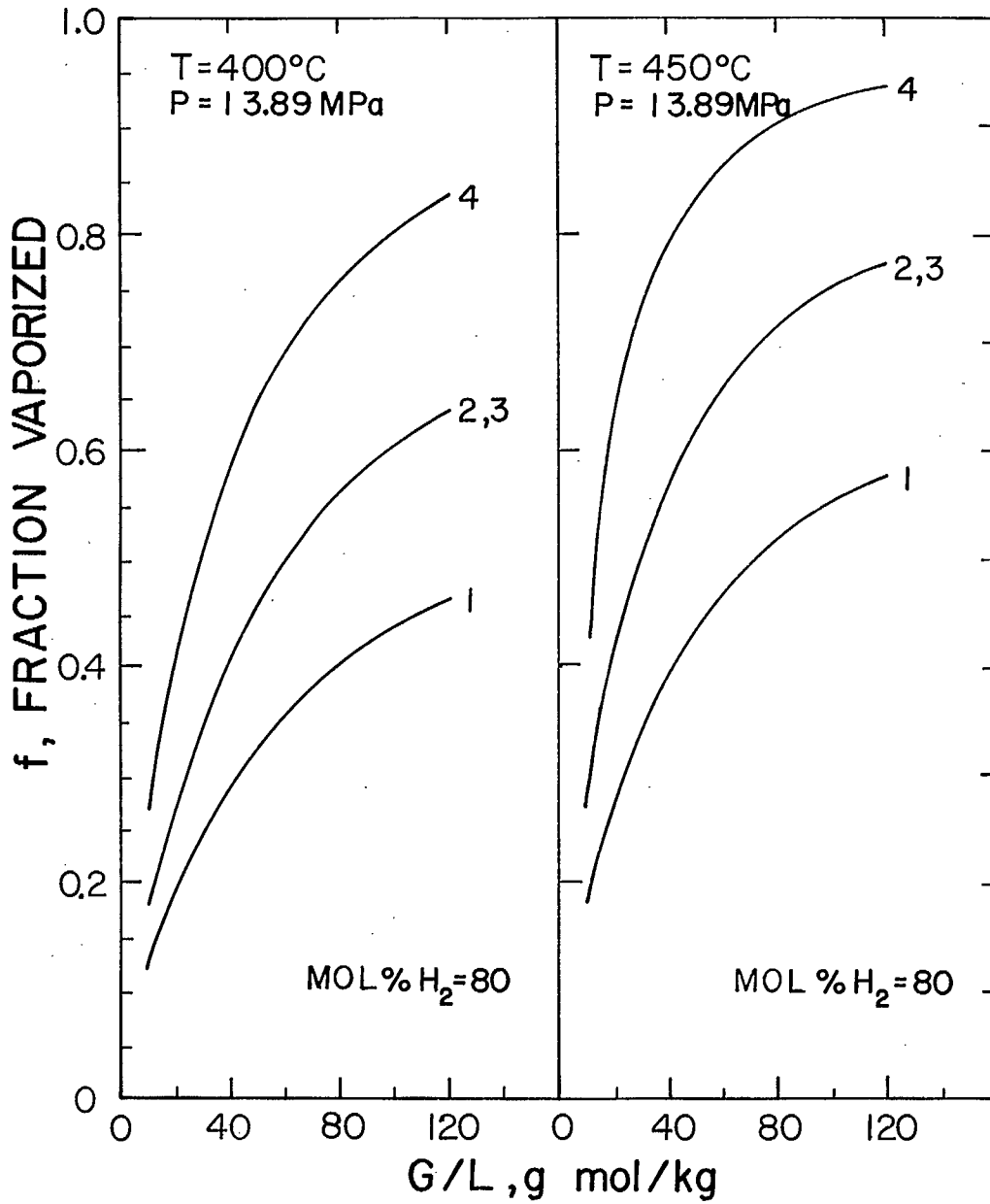


Fig. 19 - Calculated fraction of product vaporized, f , vs g mol of gas per kg of product fed, G/L, at 400°C and 450°C, and 13.84 MPa for the products: 1, 94-3-1; 2, 71-1-2; 3, 82-1-2; 4, 81-3-1; and 80 mol % H_2

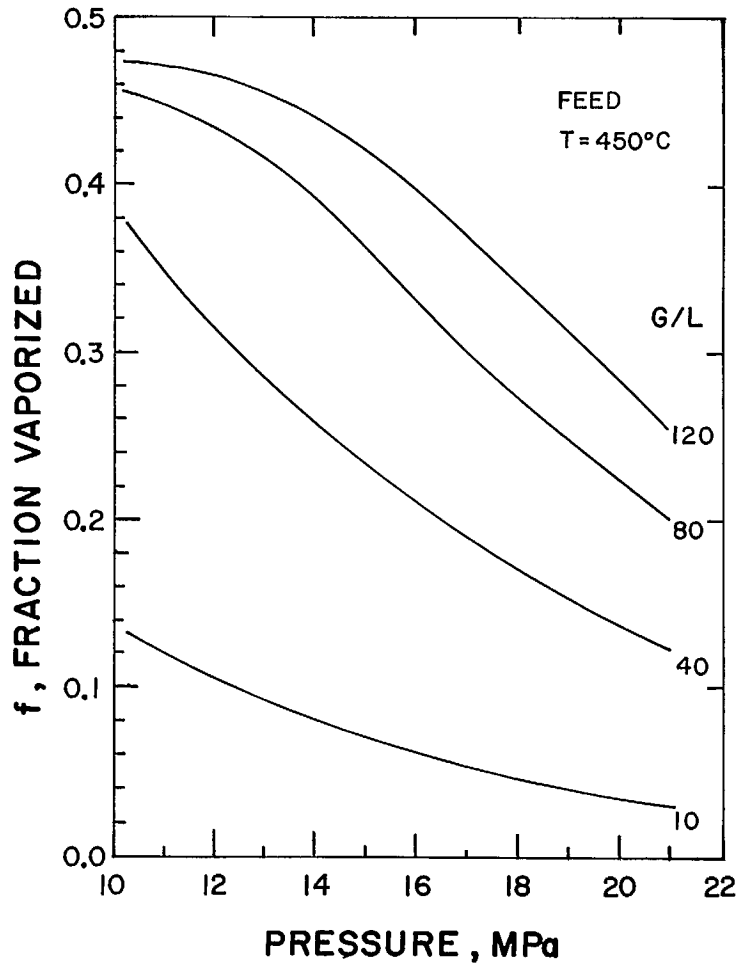


Fig. 20 - Calculated fraction of feed vaporized, f , vs pressure at 450°C and $74 \text{ mol } \% \text{ H}_2$ for G/L values of 10 to 120 g mol of gas per kg of feed

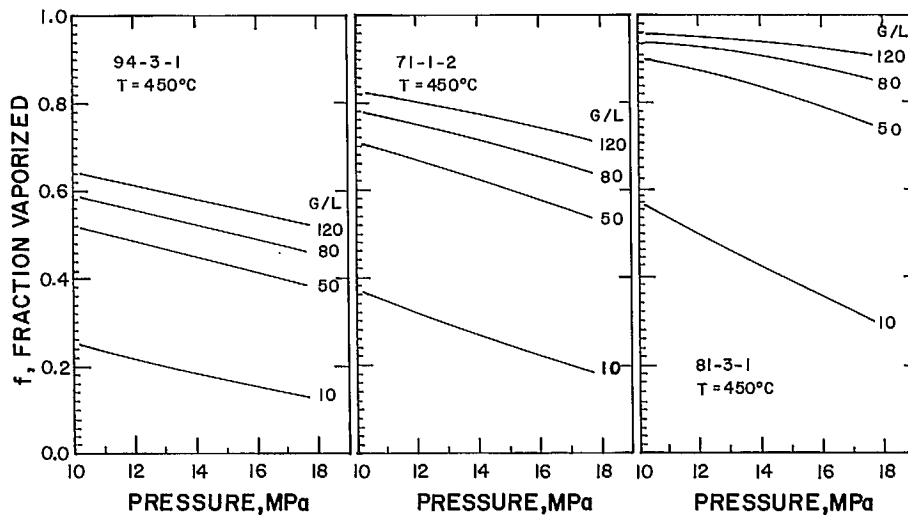


Fig. 21 - Calculated fraction of product vaporized, f , vs pressure at 450°C for $80 \text{ mol } \% \text{ H}_2$, G/L values of 10 to 120 g mol/kg, and products 94-3-1, 71-1-2 and 81-3-1

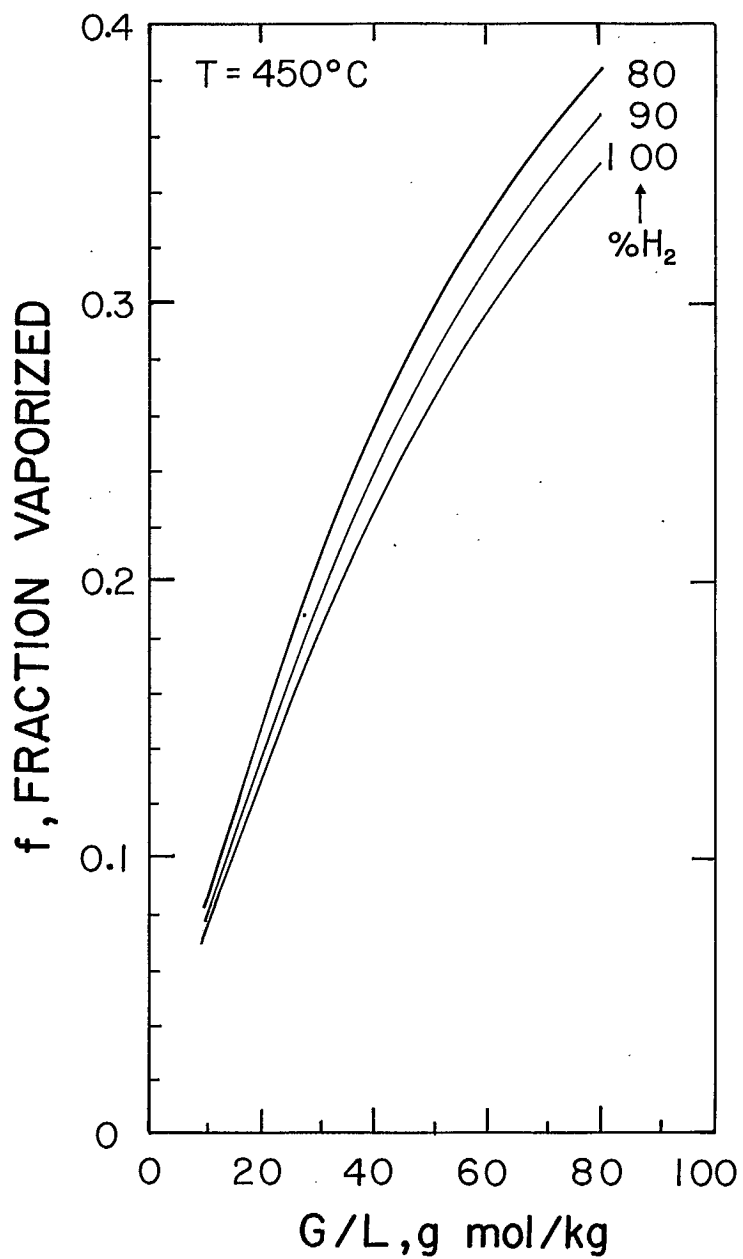


Fig. 22 - Calculated fraction of feed vaporized, f , vs g mol of gas per kg of feed at 13.89 MPa and 450°C for 80 to 100 mol % H_2

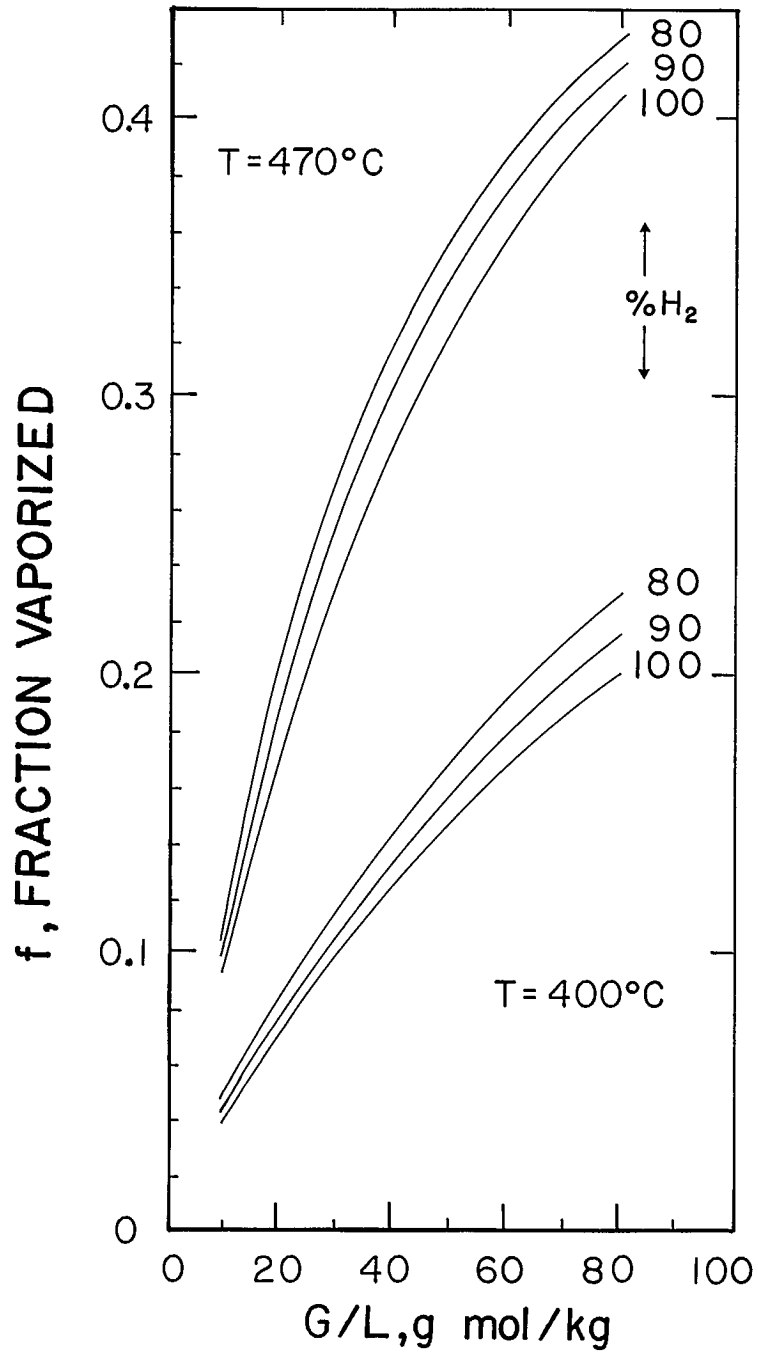


Fig. 23 - Calculated fraction of feed vaporized, f , vs g mol of gas per kg of feed G/L , at 13.89 MPa and 400 and 470°C, for 80 to 100 mol % H_2

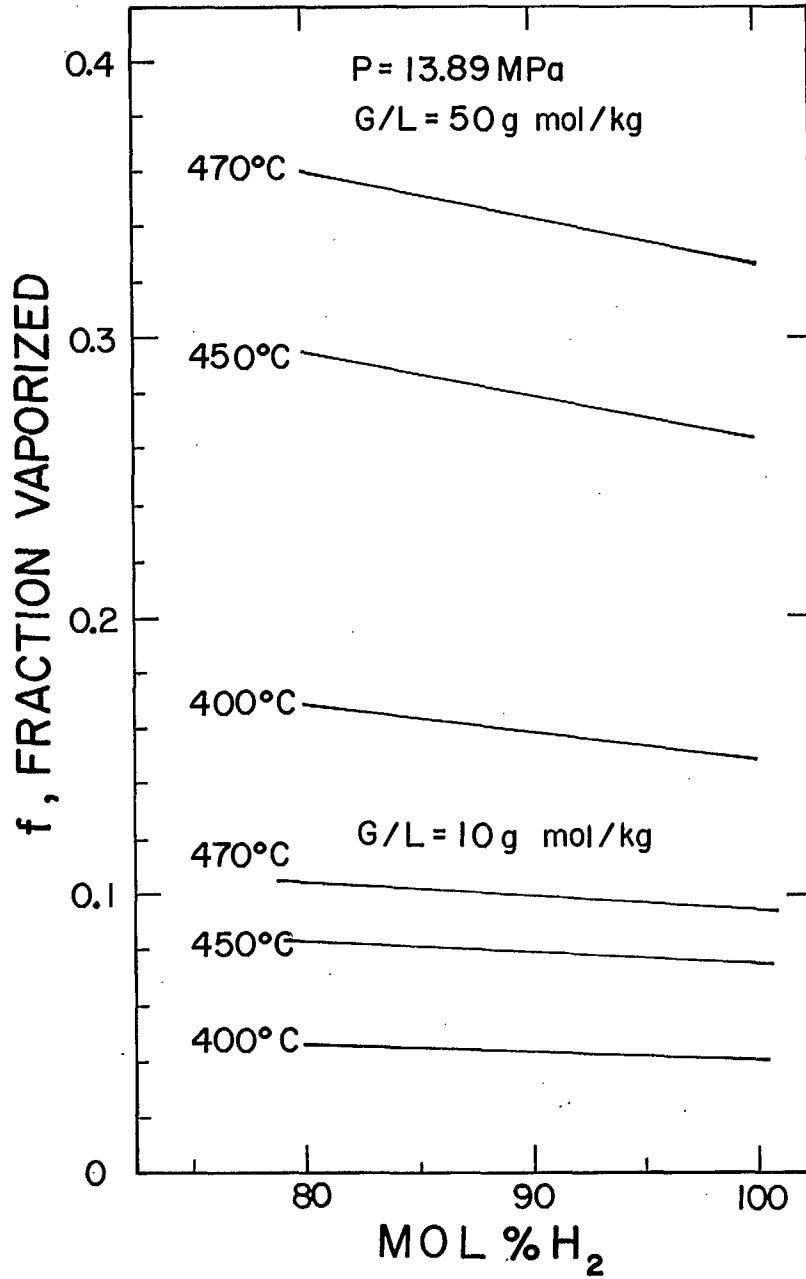


Fig. 24 - Effect of mol % H_2 on the calculated fraction of liquid feed vaporized, f , at temperatures of 400 to 470°C and G/L values of 10 and 50 g mol of gas per kg of feed, at 13.89 MPa

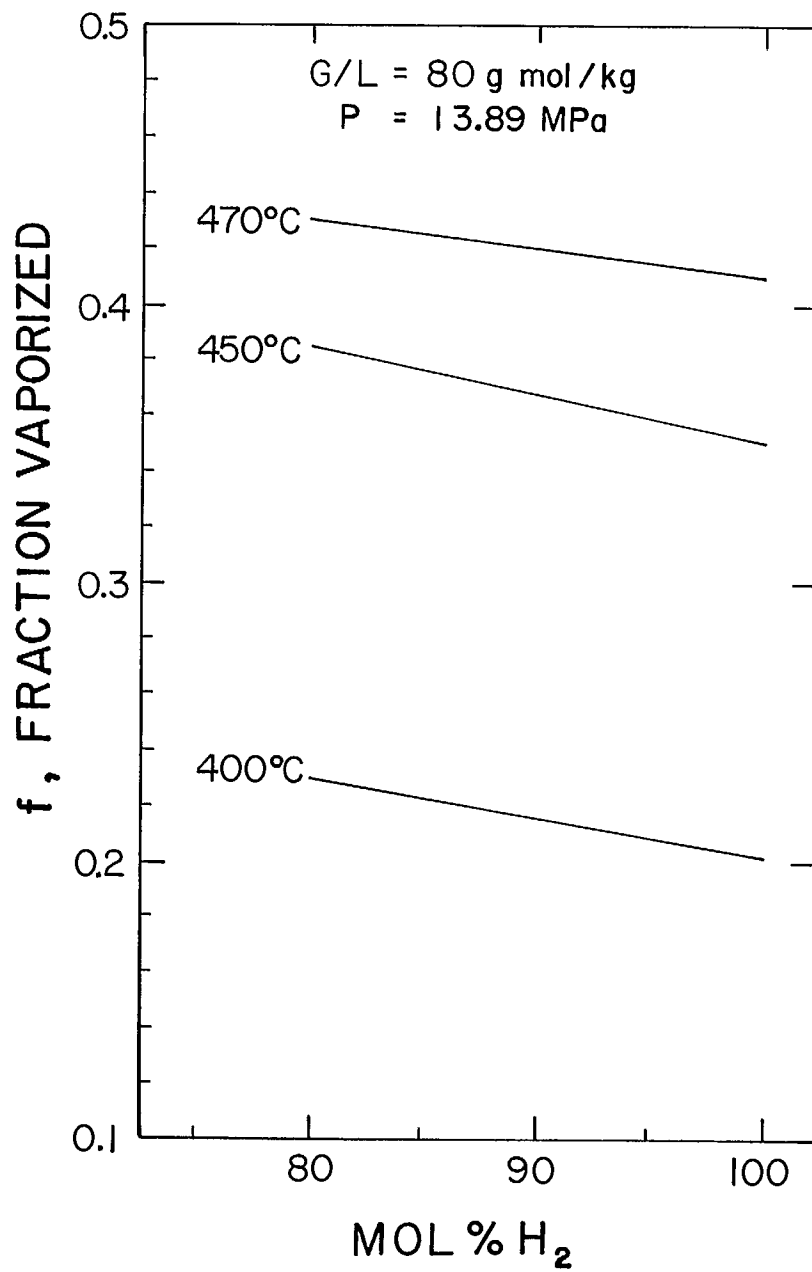


Fig. 25 - Effect of mol % H_2 on the calculated fraction of liquid feed vaporized, f , at 13.89 MPa and 80 g mol of gas per kg of feed for temperatures of 400 to 470°C

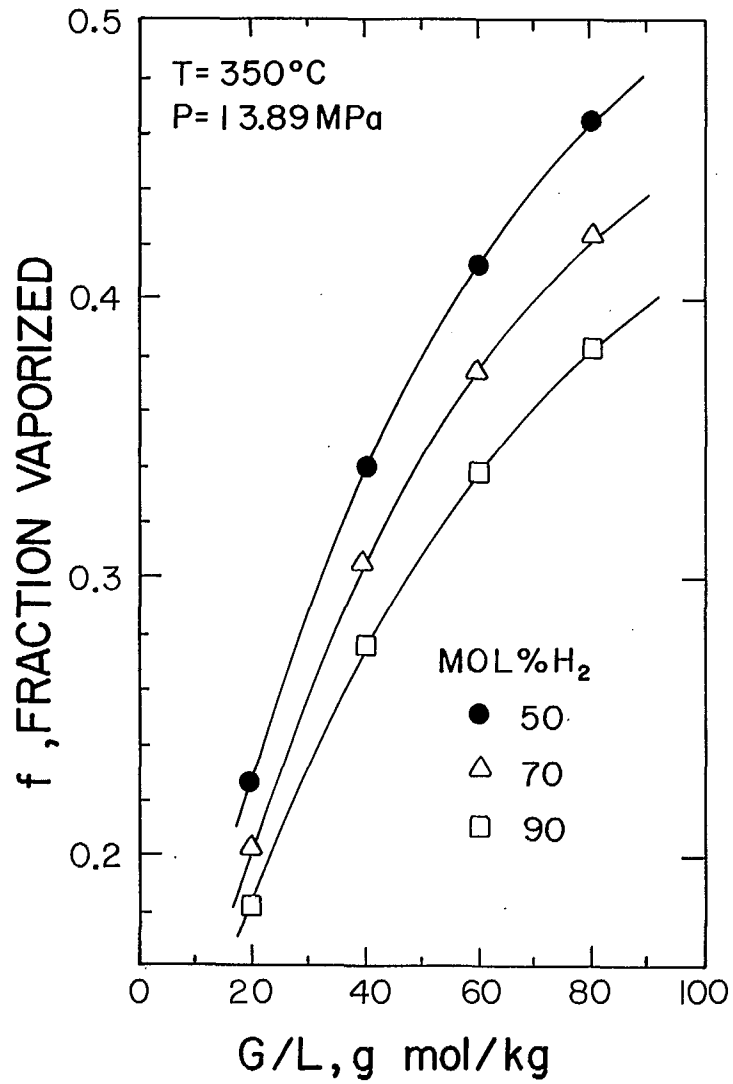


Fig. 26 - Calculated fraction of product 82-1-2 vaporized, f , vs g mol of gas per kg of product fed, G/L , at 350°C and 13.89 MPa for 50 to 90 mol % H_2

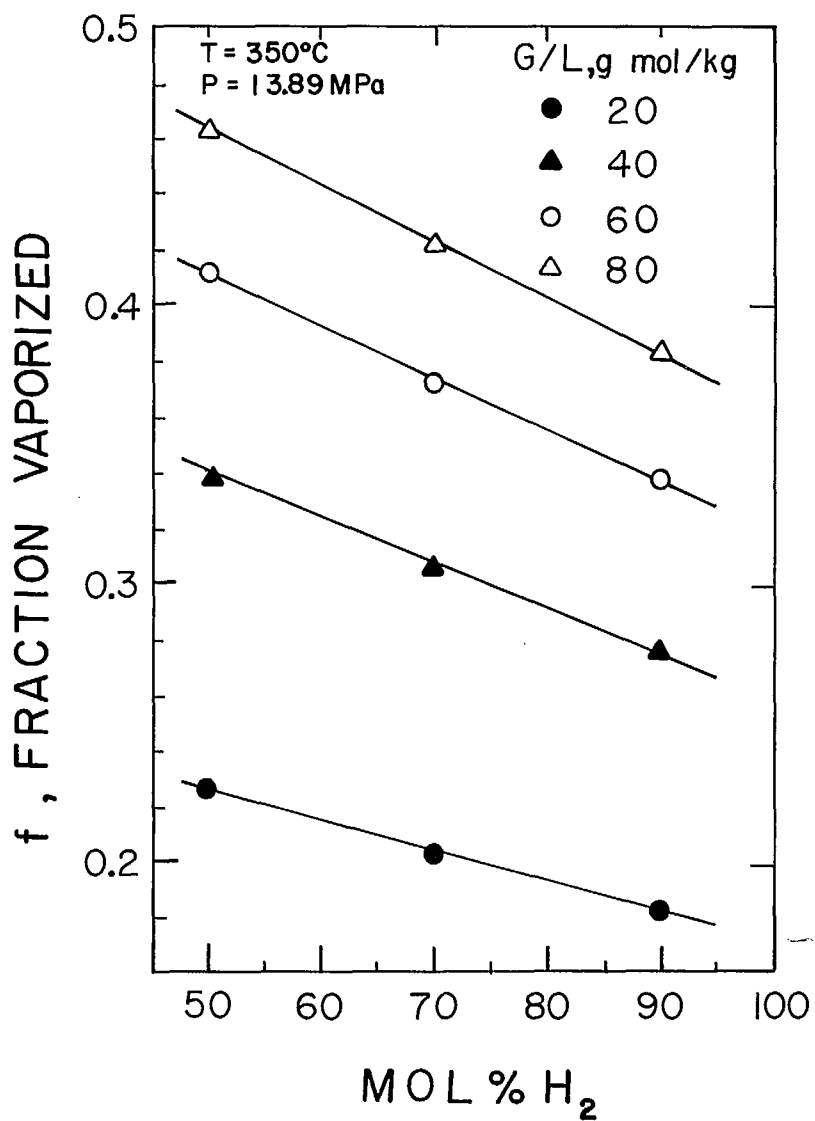


Fig. 27 - Effect of mol % H_2 on the calculated fraction of liquid product 82-1-2 vaporized, f , at 350°C and 13.89 MPa for G/L values of 20 to 80 g mol per kg of product fed

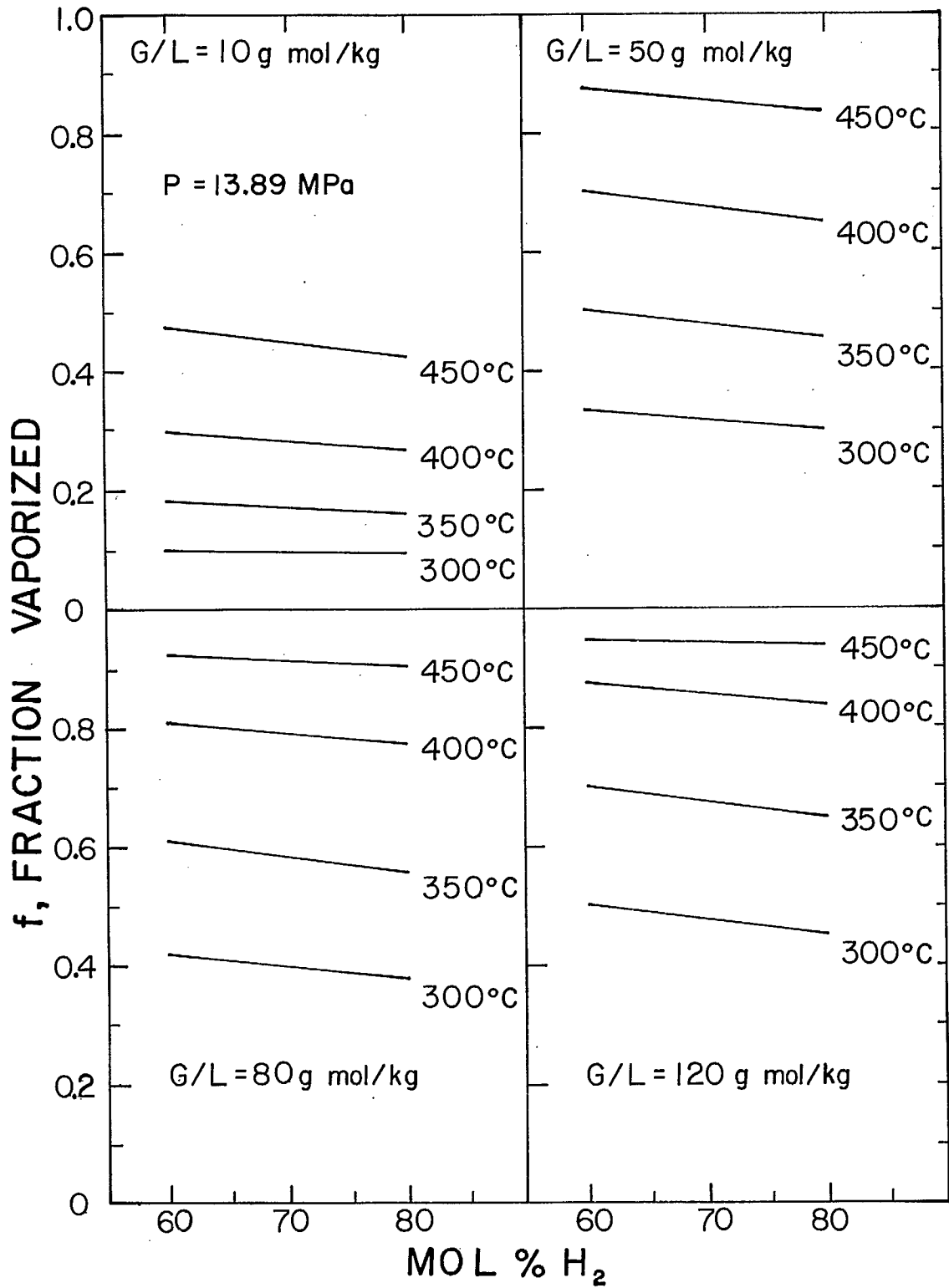


Fig. 28 - Effect of mol % H₂ on the calculated fraction, f , of product 81-3-1 vaporized at 13.89 MPa for temperatures of 300 to 450°C and G/L values of 10 to 120 g mol per kg of product fed

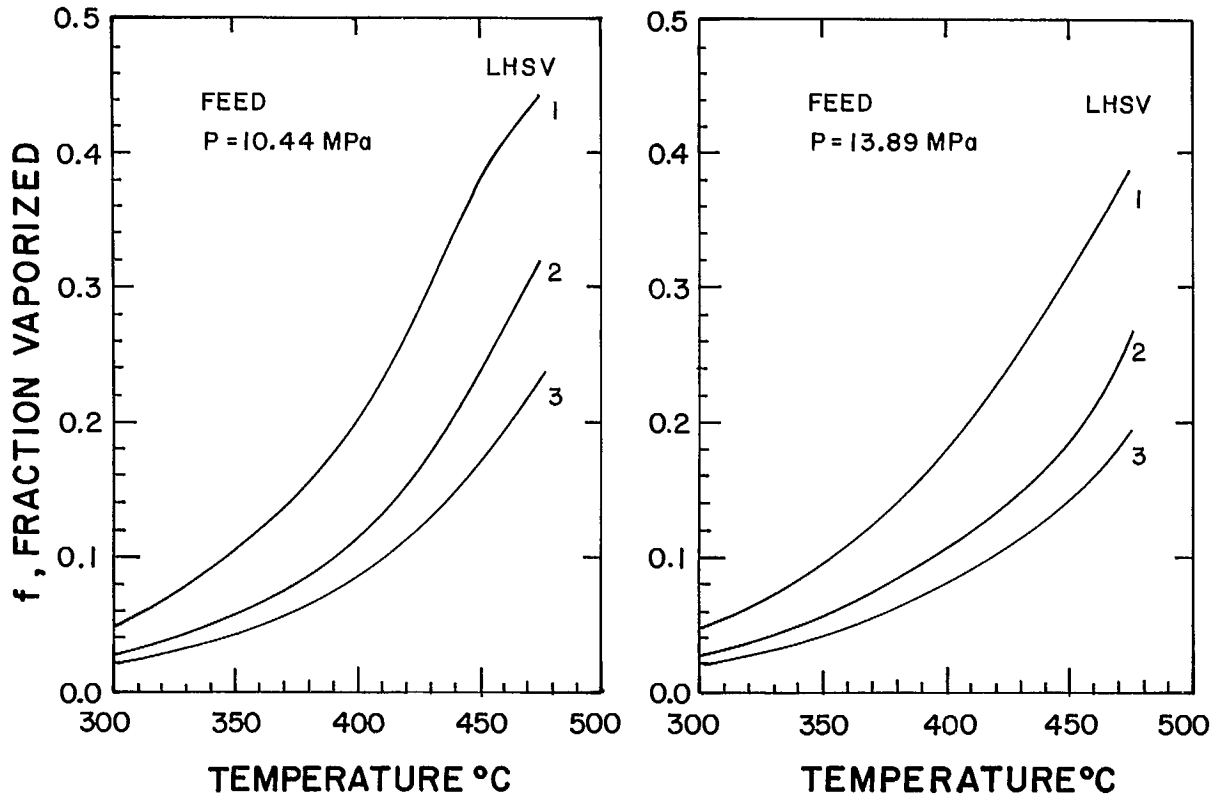


Fig. 29 - Calculated fraction of feed vaporized, f , vs temperature at 10.44 MPa and 13.89 MPa for liquid hourly space velocities (LHSV) of 1 to 3 at a gas recycle rate of 1.5 ft³/h (0.0425 m³/h) at pressures and 20°C, and 74 mol % H₂; reactor volume is 4.5ℓ

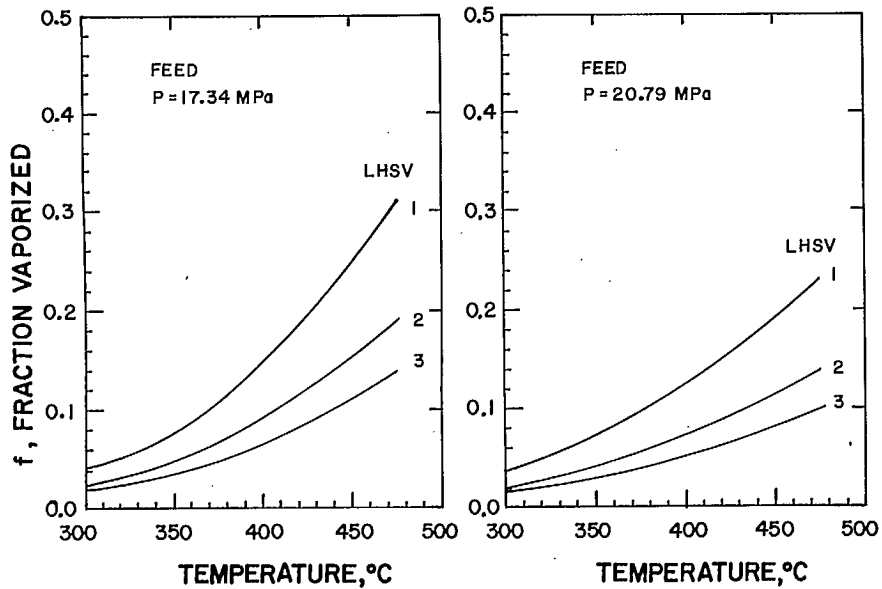


Fig. 30 - Calculated fraction of feed vaporized, f , vs temperature at 17.34 MPa and 20.79 MPa for liquid hourly space velocities (LHSV) of 1 to 3 at a gas recycle rate of 1.5 ft³/h (0.0425 m³/h) at pressures and 20°C, and 74 mol % H₂; reactor volume is 4.5ℓ

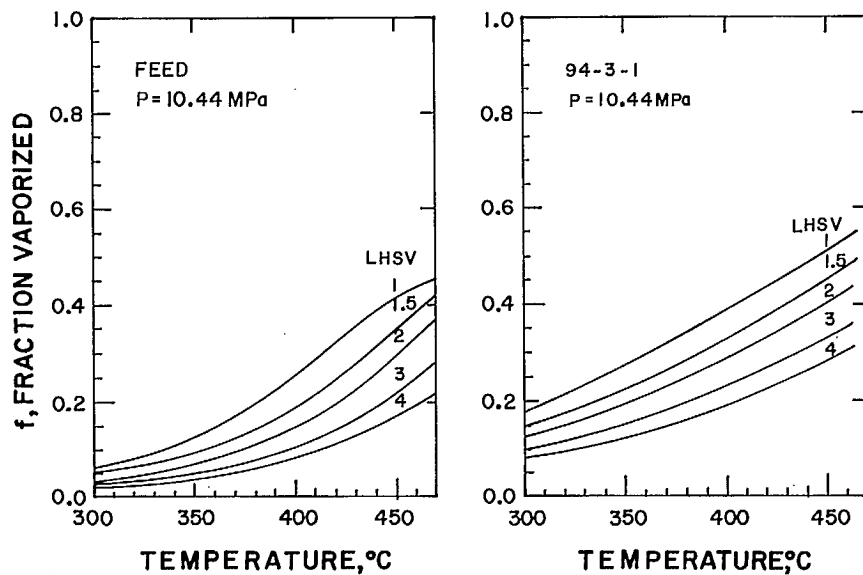


Fig. 31 - Calculated fraction of feed and product 94-3-1 vaporized, f , vs temperature, at 10.44 MPa for 74 and 80 mol % H₂ respectively, and LHSV values of 1 to 4 at a gas rate of 2.0 ft³/h (0.0566 m³/h) at pressure of 10.44 MPa and 20°C; reactor volume is 4.5ℓ

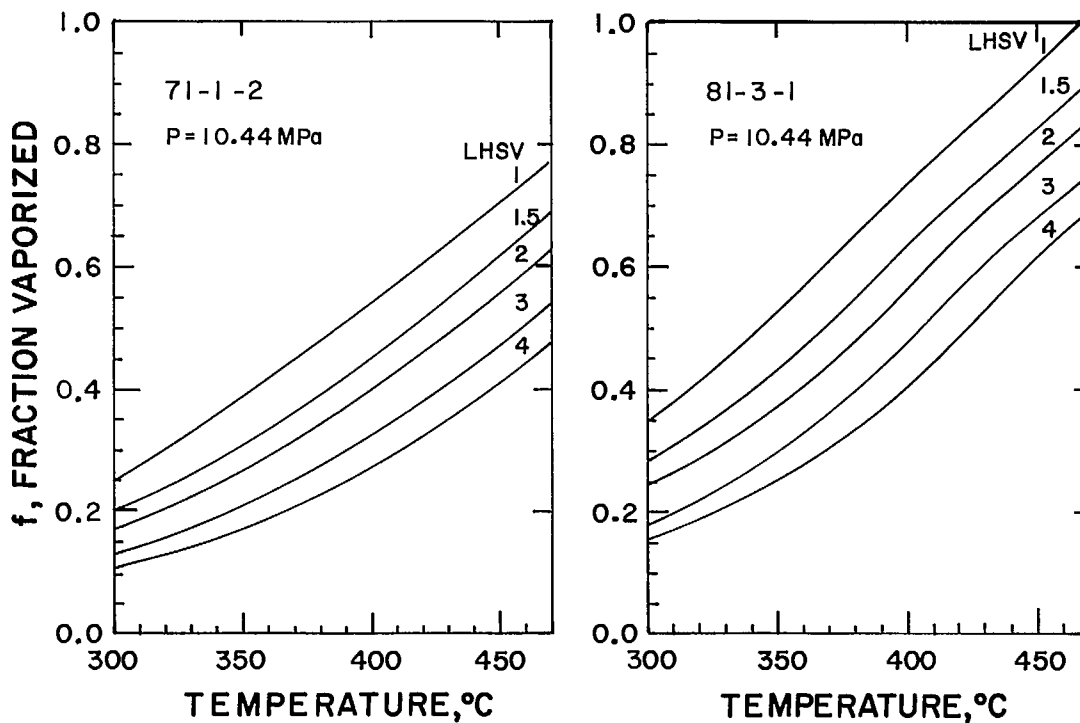


Fig. 32 - Calculated fraction of products 71-1-2 and 81-3-1 vaporized, f , vs temperature at 10.44 MPa for 80 mol % H_2 and LHSV values of 1 to 4 at a gas rate of 2.0 ft³/h (0.0566 m³/h) at pressure of 10.44 MPa and 20°C; reactor volume is 4.5ℓ

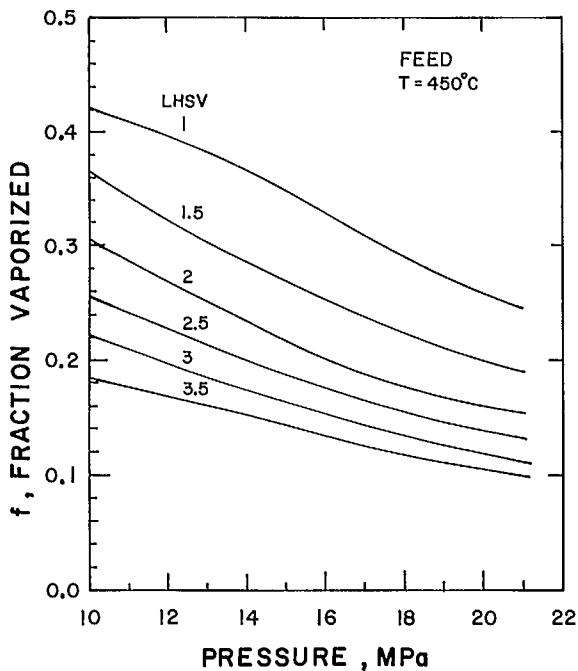


Fig. 33 - Calculated fraction of feed vaporized, f , vs pressure at 450°C, and 74 mol % H_2 for LHSV values of 1 to 3.5 and a gas rate of 2.0 ft³/h (0.0566 m³/h) at pressure and 20°C; reactor volume is 4.5ℓ

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