



Energy, Mines and
Resources Canada

Énergie, Mines et
Ressources Canada

CANMET

Canada Centre
for Mineral
and Energy
Technology

Centre canadien
de la technologie
des minéraux
et de l'énergie

MR. 37

HEAT OF REACTION AND VAPORIZATION OF FEED AND PRODUCT IN THE THERMAL HYDRO- CRACKING OF ATHABASCA BITUMEN

B.B. Pruden and J.M. Denis
Canadian Fossil Fuel Research Laboratory
Process Engineering Section

APRIL 1976

ENERGY RESEARCH PROGRAM
ENERGY RESEARCH LABORATORIES
CANMET REPORT 76—30

© Minister of Supply and Services Canada 1976

© Ministre des Approvisionnements et Services Canada 1976

Available by mail from:

En vente par la poste:

Printing and Publishing
Supply and Services Canada,
Ottawa, Canada K1A 0S9

Imprimerie et Édition
Approvisionnement et Services Canada,
Ottawa, Canada K1A 0S9

CANMET
Energy, Mines and Resources Canada,
555 Booth St.,
Ottawa, Canada K1A 0G1

CANMET
Énergie, Mines et Ressources Canada,
555, rue Booth
Ottawa, Canada K1A 0G1

or through your bookseller.

ou chez votre libraire.

Catalogue No M38-13/76-30 Price: Canada: \$1.25
ISBN 0-660-00691-X Other countries: \$1.50

N° de catalogue M38-13/76-30
ISBN 0-660-00691-X

Prix: Canada: \$1.25
Autres pays: \$1.50

Price subject to change without notice.

Prix sujet à changement sans avis préalable.

Title: Heat of Reaction and Vaporization of Feed and Product in the
Thermal Hydrocracking of Athabasca Bitumen

Authors: B.B. Pruden and J.M. Denis

PAGE 16, TABLE 3, should read

Nickel, as Ni	ppm	68
Ash	wt %	0.56

PAGE B4, FIGURE B-2, should read

$$f_p = 0.096$$

$$f_R = 0.29$$

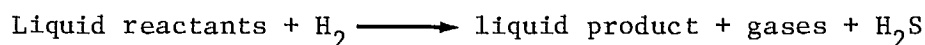
HEAT OF REACTION AND VAPORIZATION OF
FEED AND PRODUCT IN THE THERMAL HYDROCRACKING
OF ATHABASCA BITUMEN

by

B.B. Pruden* and J.M. Denis**

ABSTRACT

The heat of reaction for thermal hydrocracking of topped (to 260°C) Athabasca bitumen was measured as a function of pitch conversion, hydrogen consumption and sulphur removal. A pilot plant reactor 3.8 cm ID by a length of 3.95 m was used as calorimeter. Results are reported on the basis of liquid reactants converted to liquid products plus gases:



and on the basis of heat removed from the reactor to maintain isothermal conditions.

Results for the equilibrium flash vaporization of products in the presence of hydrogen are compared with computed predictions of product flash vaporization. Predictions are given for feed flash vaporization in the presence of hydrogen.

Results are given for the ranges of reactor temperatures and pressures from 450 to 485°C and 2000 to 3500 psi (13.9 to 24.23 MPa) respectively, for liquid hourly space velocities (LHSV) of 1 and 2 and for a hydrogen-hydrocarbon gas (85:15 volume ratio) recycle flow of 1.5 ft³/h (0.042 m³/h) at room temperature and reactor pressure. This recycle gas flow would correspond to industrial conditions of recycle gas of 3350 SCF/bbl at 2000 psi and LHSV = 2, or 6700 SCF/bbl at 2000 psi and LHSV = 1.

*Research Scientist, **Head, Process Engineering Section, Energy Research Laboratories, Canada Centre for Mineral and Energy Technology, Department of Energy, Mines and Resources, Ottawa, Canada.

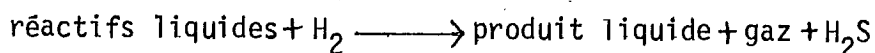
LA CHALEUR DE REACTION ET L'EVAPORATION DE LA CHARGE
D'ALIMENTATION ET DU PRODUIT LORS DE L'HYDROCRAQUAGE THERMIQUE DE BITUME
DE L'ATHABASCA

par

B.B. Pruden* et J.M. Denis**

SOMMAIRE

La chaleur de réaction lors de l'hydrocraquage thermique de bitume décanté (à 260°C) de l'Athabasca a été calculée en fonction de la conversion du brai, la consommation d'hydrogène et l'élimination de soufre. Un réacteur d'une installation pilote dont le diamètre intérieur est de 3.8 cm et la longueur de 3.95 m a été utilisé comme calorimètre. Les résultats obtenus en se basant sur des réactifs liquides convertis en produits liquides plus des gaz:



et sur la chaleur retirée du réacteur pour maintenir les conditions isothermiques sont donnés.

Les auteurs comparent les résultats obtenus des expériences d'équilibre de la vaporisation par détente isenthalpique des produits en présence d'hydrogène avec les calculs empiriques de la vaporisation différentielle du produit. Ils formulent aussi des prévisions concernant la vaporisation différentielle de la charge d'alimentation en présence d'hydrogène.

Les paramètres ont été calculés à des températures et pressions variant entre 450 et 485°C et entre 2000 et 3500 lb/po² (13.9 à 24.23 MPa) respectivement, à des vitesses spatiales liquides horaires (VSLH) de 1 et 2 et à un débit de recyclage d'un gaz, d'hydrogène et d'hydrocarbone (taux de 85:15 par volume) de 1.5 pi³/h (0.042 m³/h) à la température ambiante et pression du réacteur. Ce débit de gaz de recyclage devrait correspondre aux conditions industrielles de gaz de recyclage, de l'ordre de 3350 pi³/baril à 2000 lb/po² et à une VSLH de 2, ou de 6700 pi³/baril à 2000 lb/po² et à une VSLH de 1.

* Chercheur scientifique, ** Chef de la section de la Technique de combustion, Laboratoires de recherche sur l'énergie, Centre canadien de la technologie des minéraux et de l'énergie, Ministère de l'Énergie, des Mines et des Ressources, Ottawa, Canada.

INTRODUCTION

Pilot plant studies on thermal hydrocracking, described in this report, form an integral part of the Energy Research Program of the Department of Energy, Mines and Resources to ensure an adequate future supply of energy for Canada. The aims and objectives of this program have been documented in earlier reports (1,2). The bench scale and pilot scale studies described in those reports must be supported by work in other related areas in order that larger scale units may be designed and operated. One requirement is in the determination of reactor heat balance, for which the heat of reaction and the extent of vaporization of feed and product in the presence of hydrogen are required. Both items are necessary because, despite the heavy feed and high pressure, the thermal hydrocracker is a boiling reactor with a large percentage (as high as 90%) of the product in the vapour phase at the reactor outlet.

The heat of reaction and its sensitivity to operating conditions is important not only in design of new systems, but also in simulation to ensure that safe operating limits can be set, and that adaptation to new conditions can be made without further experimentation.

Feed and product vaporization data is necessary to develop an understanding of what is happening inside the reactor, and to eventually understand and control the factors responsible for coke formation. It is also important in scale-up, since the true liquid residence time can be found only through knowledge of gas hold-up, and feed and product vaporization.

In this work, the heat of reaction was determined by heat balances on a reactor 3.8-cm inside diameter and 3.95-m inside length. Details concerning the reactor and other equipment may be found in Reference 2. The product vaporization data were obtained on the same apparatus by mass balance on the hot receiver (HCP). Feed vaporization and the computed product vaporization data were computed from "K" constants based on the Grayson-Streed modifications of the Chao-Seader equation of state (3,4).

PREVIOUS WORK

In their discussion of residual petroleum stocks, Galbreath and Van Driesen (5) estimated that the heat of hydrocracking was -59 Btu/ft^3 of hydrogen consumed ($-11.8 \text{ kcal/mol H}_2$) for hydrocracking and -67 Btu/ft^3 of H_2 consumed ($-13.4 \text{ kcal/mol H}_2$) for desulphurization. These were combined values which apparently neglected the amount of cracking (endothermic) versus hydrogenation (exothermic).

Jaffe (6) discussed heat release in hydrogenation of pure petroleum compounds, from which generalizations can be made concerning petroleum types and various carbon-bond types. For example, olefin saturation yields -27 to -30 kcal/mol of H_2 , aromatic saturation -14.5 to -16.5 kcal/mol of H_2 and saturate cracking -7 to -10 kcal/mol of H_2 . Ueda et al. (7) presented data on the heat of hydrodesulphurization of heavy oil and found values of -6 to -67 kcal/kg of heavy oil for 0.6 to 2.9 mol of H_2/kg oil. They found a linear relationship between heat of reaction and hydrogen consumption. Their data, which was for catalytic hydrodesulphurization, is compared in more detail with this work in a later section.

Edmister (8) presented an alignment chart for the endothermic heat of cracking based on the molecular weight of feed and products. This chart was based on the equation:

$$\text{Heat of reaction} = \frac{53,600 (M_F - M_p)}{M_F M_p} \text{ Btu/lb feed} \quad (\text{Eq. 1})$$

where M_F and M_p are the molecular weight of feed and product respectively. One of the problems with this equation is the determination of feed and product molecular weights. The feed molecular weight for topped Athabasca bitumen has been calculated as 542 g/g mol based on distillation data (4) and 722 g/g mol based on viscosity data (9). Speight (10) measured the molecular weights of separated components of virgin bitumen which, together, yield a molecular weight of 578 g/g mol . Camp (11) gave a range of 600 to 800 g/g mol for virgin bitumen. It follows that feed molecular weight varies with the feed source and with the methods of measurement. Until extensive effort is expended to correlate bitumen molecular weight with other measurable quantities, or until Equation 1 is actually tested with measured variables, it should be used only as a rough guide since the constant in this

equation will vary with the feed type (aliphatic, aromatic, asphaltic, etc.). In this work, neither feed nor product molecular weights were measured, but were computed from distillation data.

Schuman (12) in his report on hydrodesulphurization, has pointed out that 50 to 100 Btu per standard cubic foot of hydrogen may be released depending on the degree of hydrocracking. A better model for the heat release would include hydrogen consumption, desulphurization and the degree of thermal cracking.

APPARATUS

A detailed description of the apparatus is given in Reference 2. A schematic diagram of the reactor and preheaters is given in Fig. 1. Feed bitumen or heavy oil and recycle gas (85% H_2) entered the preheaters together. The three preheaters were regulated with individual controllers to maintain preset outside-surface (skin) temperatures. The temperatures T_{PI} to T_{P4} and the reactor temperatures T_{RI} to T_{R5} were measured with sheathed thermocouples installed in the flowing stream. The reactor heaters were controlled in a similar manner to the preheaters. Power input to the preheaters and reactor was measured with wattmeters. Heat losses from the preheaters and reactor to the atmosphere were measured in experiments in which gas alone flowed through the reactor.

RESULTS AND DISCUSSION

This section is divided into three parts. First the data for reactor and preheater heat losses to the atmosphere are given and discussed. Next the results on vaporization and heat of vaporization of product and feed are discussed. Finally the heat of reaction results are given and compared with published results.

Reactor and Preheater Heat Losses

The reactor and preheater heat losses are shown as a function of reactor temperature in Fig. 2. This graph was used to calculate heat losses for all computations in this report. Reactor temperature is a suitable parameter on which to base reactor heat losses, but inappropriate for pre-

heater heat losses. In this study preheater heat balances were used as a check only in the temperature range of 440-470°C. The variation as shown in Fig. 2 is not large. A better correlation of heat losses is shown in Fig. 3, where heat losses are plotted as a function of the average temperature difference (ΔT_{AV}) between the external reactor or preheater surface and ambient temperature. This figure is for data with no flow and the numbers are not comparable with Fig. 2. This type of correlation will be developed in future with gas flow and used in future measurements of heat of reaction. It was not used in this work because a reliable skin temperature measurement was not available until recently (January 1976).

Feed and Reactor Product Vaporization and Heat of Vaporization

During a run, the feed and gas are heated and partially vaporized in the preheaters, and enter the reactor at about 70°C below the reaction temperature. Energy required to heat the feed and gas, and to vaporize a portion of the feed and product, is necessary to compute the heat of reaction and to determine the heat duty for process exchangers, etc.

Feed Vaporization

Feed flash vaporization data is given in Table 1, with "f" the weight per cent of the feed vaporized at the stated temperature, pressure and initial gas-to-liquid ratio, G/L. These are computed values (4) assuming 10 liquid pseudo-components as shown in Table 2. The values of G/L were calculated for all runs, to correspond to a gas recycle to the reactor of 1.5 ft³/hr (0.042 m³/h) at reactor pressure and 25°C and the stated liquid space velocity. The pilot plant was always operated at this gas recycle rate. Figure 4, a semi-logarithmic plot of f versus temperature, shows a straight line relationship for data sets 2 and 3. Data set 5 shows a similar relationship but of different slope. If the liquid and gas had one ideal component each, the data from sets 2, 3 and 5 for a space velocity of 2.0 would fall on one straight line, and the data from sets 1 and 4 for a space velocity of 1.0 would fall on another. Proof of this is given in Appendix A. This system is complex and because of interactions, more feed is vaporized at the lower pressure for a given space velocity. For example, about twice as much feed is vaporized at 1500 psi (10.44 MPa) as at 3500 psi (24.22 MPa) for the same space velocity. This indicates that the liquid residence time will be in-

creased at the lower pressure for the same LHSV since there is less liquid flowing through the reactor. This is unique to this system in which a constant volumetric gas flow at pressure and 25°C has been maintained to keep mass transfer and gas hold-up roughly constant for all runs. Because of an abrupt change in the component properties used in the computer program, curve 1 on Fig. 4 approaches a value f of 50% asymptotically. The same relationship exists for all curves since the component which simulates pitch (component 10 in Table 2) will vaporize very little and it makes up 51% by weight of the mixture. Typical feed and gas properties are shown in Table 3. The discrepancy of 0.5% between the distillation result and the pitch determination is due to experimental error and to errors inherent in the two methods.

Assuming that the portion of the feed which is vaporized passes through the reactor quickly, it will be changed slightly and therefore the product distribution for the same pitch conversion should be different at other pressures for the reason described above. This will be an interesting subject for further work.

Earlier work was performed on bitumen coker distillate to determine the percentage vaporized (14). In this reference, calculations based on the critical temperature of components and on Raoult's law were made. It was shown that the governing factor in the calculations was critical temperature. The methods were the same as those reported by Maxwell (15).

Reactor Product Vaporization

Results for vaporization of the reactor product are given in Fig. 5. The upper solid lines are computer predictions (4) using pseudo components based on a distillation of the product, and shown in Table 2. The triangles represent data obtained in this work with pitch conversion shown beside the triangle. In the pilot plant, the gas and liquid from the reactor enter a hot separator through a dip tube equipped with a distributor. Gas and liquid product enter the separator below the liquid level, thereby mixing the contents; also the hot separator is temperature-controlled and behaves almost like an equilibrium flash still. The amounts of liquid from the hot separator and the cold separator downstream are measured on a routine basis, so that the value of f can be found as a function of the hot separator temperature for all runs. The triangles represent data at 2000 psi (17.3 MPa) a gas recycle rate of 1.5 ft³/h, and a LHSV of 2.0, i.e., for the same gas/liquid

ratio and pressure. The single cross is for a run at a LHSV of 1.0 at the same gas recycle rate and pressure as above.

The lower curve for LHSV = 2.0, computer prediction, gives high values of f above 375°C. The upper curve (LHSV = 1.0) predicts high values of f for all temperatures. The dotted line approximates measured values from this work at 87% pitch conversion. Obviously, further work is necessary to establish a comparison of f values above 420°C, the limit of the data, since the useful reactor operating temperatures lie above this value.

From Figs. 4 and 5, the true liquid residence time can be established as, for example, 460°C, a LHSV of 2.0, a pressure of 2000 psi (17.33 MPa) and a gas holdup of 21%⁽¹⁷⁾. With no feed or product liquid vaporization and with 90% weight yield of liquid product, the liquid residence time is 0.41 hours.

With corrections for vaporization based on the computed curves in Figs. 4 and 5, the liquid residence time is as follows:

Feed, f = 28%

Product, f = 80.5%

Gas hold-up = 21%, (reactor total volume 4.5 ℓ)

Feed input = 9000 g/h

Liquid at reactor bottom = $9000 \times 0.72 = 6480$ g/h or $6480 \text{ cm}^3/\text{h}^*$

Liquid at reactor top = $9000 \times 0.9 \times 0.195 = 1580$ g/h or $1580 \text{ cm}^3/\text{h}^*$

Average liquid flow = $4030 \text{ cm}^3/\text{h}$

Average liquid residence time = $4500 \times 0.79/4030 = \underline{0.88 \text{ h}}$

This is the average residence time. It is more than double the value of 0.41 h computed with no vaporization. Actually the residence time will lie between $4500 \times 0.79/6480$ and $4500 \times 0.79/1580$, or between 0.55 and 2.25 hours, depending on where the reaction takes place and on how fast the feed and product are vaporized. Difficulty in determining the actual residence time is the reason that industry always reports reciprocal LHSV as a measure of liquid velocity, and not the actual value. The actual value is very important in the analysis of reactor performance, especially where solid material may be present in the feed which has to be fluidized in the reactor.

* Liquid density in reactor is based on reactor samples of a density of 1.23 g/cm^3 at 20°C extrapolated to 460°C.

Heat of Vaporization

Heat of vaporization was computed for the distillate portion of the feed and product using methods reported by Maxwell (15) and Nelson (16). In the calculation, the distillation data for that portion of the feed and product boiling below 524°C at atmospheric pressure was used.

Example:

Distillate (-975°F) from Run 79-1-1, 87% pitch conversion, 26° API

Volume average boiling point = 548°F, measured

Mean average boiling point = 486°F, Reference 15, p 72

Molal average boiling point = 438°F, Reference 15, p 72

Pseudo-critical temperature = 820°F, Reference 15, p 72

At 470°C, reduced temperature $T_R = 878/820 = 1.07$

Therefore heat of vaporization = 0 p 174, Nelson (16)

Maxwell's method (15) produced similar results.

The critical temperatures of the lighter components in the distillate are lower than the critical temperature of the whole distillate. It follows that the reduced temperature, T_R , will be greater than one for the lighter components and hence the heat of vaporization will be zero even if only a portion of the distillate is vaporized. Similar calculations were made with the 975°F (524°C) distillate from the feed. Nelson's method (16) gave 76 Btu/lb, and Maxwell's method (15) gave 64 Btu/lb for an average of 70 Btu/lb. Because the feed was topped and contained only a small amount of lighter material (see Table 3) this value of 70 Btu/lb was used in computation of the heat of vaporization for the feed.

Heat of Reaction

Heat of reaction results are given in Table 4. The duration of all runs was at least 4 hours, up to a maximum of 21 days. This data is shown in Table 5.

Pitch is defined in this work as that portion of the material boiling above 975°F equivalent atmospheric boiling point as measured by a Model 500 Podbielniak equilibrium flash still (13). The feed material contained 51.5% pitch, so that the per cent pitch conversion multiplied by the factor 0.00515 gives the pitch conversion in kg of pitch removed per kg of

feed.

The hydrogen consumption value is the chemical consumption only, and does not include losses. This was determined by measurement of hydrogen gas flows and mass balance. The "H₂S formed" was determined by sulphur analysis of liquid feed and products, assuming that all sulphur was converted to H₂S. The heat of reaction was determined by heat balance. Details of this calculation, with an example, are given in Appendix B.

As discussed earlier, a model which includes hydrogen consumption, sulphur removal and degree of hydrocracking would be desirable. Pitch conversion in kg/kg feed was chosen as a measure of the degree of hydrocracking. As shown in Figure 6, there is a correlation between pitch conversion in the range of operation and the moles of product per mole of feed. The calculation for product and feed was based on molecular weights from ASTM distillations of feed and product (14) assuming that the molecular weight of pitch was 1500 for feed, 643 for 80% pitch conversion (4) and linear with pitch conversion, which yielded a pitch molecular weight of 960 at 50% pitch conversion. The feed molecular weight used was 528. The straight line in Figure 6 is a linear regression (least squares) line.

The model for heat of reaction tested was:

$$\Delta H_R = A.H. + B.P. + C.S \quad \text{kcal/kg feed} \quad (\text{Eq. 2})$$

where ΔH_R is the heat of reaction in kcal per kg of feed, H is the hydrogen consumption in gmol/kg feed, P is the pitch conversion in kg pitch/kg feed, S is the sulphur removed in gmol/kg feed, and A, B and C are constants.

A multiple regression analysis with the constraint that A and C were less than zero gave the equation:

$$\Delta H_R = -10.2 H + 70 P \quad \text{kcal/kg feed} \quad (\text{Eq. 3})$$

with A = -10.2, B = 70 and C = 0. The value of D in Table 4 was found from the following equation:

$$D = 10.2 H - 70 P + \Delta H_R \quad (\text{Eq. 4})$$

where H, P and ΔH_R were measured quantities. The multiple regression minimized the summation of D². The correlation could be improved by rejecting run data with large deviations. When runs 77-1-1, 84-2-1 (a) and 84-1-1

were deleted, constants $A = 10.7$, $B = 75$ and $C = 0$. This type of selection could not be justified in this work since some deviations were expected due to the method of computing the heat of reaction. For example, in run 84-1-1, the total heat input was 2142 kcal/h. The heat output of 2376 kcal/h gave a heat of reaction, by difference, of -234 kcal/h. Since both numbers are large relative to the difference, an error of 10% in either number could cause an error of 100% in the result for heat of reaction.

The value of A in Equation 4 is -10.2 kcal/g mol of H_2 , comparable to -11.8 kcal/g mol of H_2 reported by previous workers. The value of B is 70 kcal/kg pitch converted. For 80% pitch conversion the endothermic heat of reaction is $70 \times 0.41 = 28.7$ kcal/kg feed. By comparison, for 80% pitch conversion, the molecular weights of feed and product are 528 and 162 respectively. Substitution of these values in Equation 1 gave an endothermic heat of reaction of 229 Btu/lb (128 kcal/kg) feed. Based on Edmister's constant, the heat of reaction for the destructive hydrogenation of heavy gas oil is 56.4 kcal/kg of feed. This approximates the value 28.7 kcal/kg of feed computed using the determined value of "B", and represents a proper comparison. For comparison with Edmister's equation (8) the conversion must be known. The constant B is analogous to Edmister's constant, with pitch conversion replacing the function $E = (M_F - M_P)/M_F M_P$. The correlation of pitch conversion with this function is shown in Figure 7. The curve has a shape similar to the curve in Figure 6. It is preferred to report the data in terms of pitch conversion for this work until the problem with molecular weights is solved. The correlation for 70% or greater pitch conversion shown in Figures 6 and 7 indicate that an Edmister-type constant for thermal hydrocracking could ultimately be reported. The data also show the consistency with other published work. The value of C was zero because the ratio of hydrogen chemical consumption to sulphur removal was constant, and less than one-tenth of the total hydrogen was used to convert sulphur to hydrogen sulphide. Attempts to improve the correlation using the net hydrogen consumption (total chemical consumption - hydrogen to make H_2S) rather than total hydrogen consumption were not successful.

The reported heat of reaction is based on the following equation:



and does not take into account the heat of solution of gases. The computed heat of vaporization of the products was zero for the temperatures in this study. The heat of reaction for thermal hydrocracking was found to be low, about -26 kcal/kg feed or -235 kcal/h for run 84-1-1. The reactor heat losses were 1.69 kW (1434 kcal/h), more than six times the heat of reaction for a well-insulated vessel wrapped with 0.32 cm thick asbestos tape and insulated with 3.8 cm "Newtherm 73" insulation. The complete conditions for run 84-1-1 are given in Table 4 and in Figures B-1 and B-2. The highest heat of reaction was in run 81-4-1, where the hydrogen consumption was high. However, the heat of reaction of -849 kcal/h was below the reactor heat loss of 1540 kcal/h. Table 5 is a summary of the conditions in the runs in Table 4, giving pressure, temperature, space velocity, hydrocarbon gas make and liquid yield.

It is obvious from the above results why few attempts were made in the literature to separate the effects of hydrogenation and cracking. The exothermic heat of hydrogenation is the dominant term, and the endothermic heat of cracking is a correction in the equation.

CONCLUSIONS

The results of computation of feed flash vaporization have been presented. They show a larger percentage of feed vaporized at the lower pressures for the same liquid space velocity, temperature, and volumetric flow of gas at the conditions in the reactor. They also show that about 40% of the feed can be vaporized at conditions typical of the pilot-plant reactor.

Actual product vaporization results have been compared with computed data based on product distillations, and show that a large portion of the product leaves the reactor as vapour. This information considered for a LHSV of 2.0 demonstrates the actual liquid residence time can be between 0.55 and 2.25 hours or a mean of 0.88 hours when based on average liquid flow. This value is more than double the 0.41 hour residence time based on the space velocity and gas holdup with no vaporization. Furthermore, the liquid velocity at the top of the reactor can be less than 20% of the liquid velocity at the bottom of the reactor - an important consideration if solid particles are to

be removed.

The heat of reaction has been correlated with hydrogen consumption and pitch conversion by the equation:

$$\Delta H_R = A.H + B.P \quad (\text{Eq. 5})$$

were $A = -10.2$ kcal/mol H_2 and $B = 70$ kcal/kg pitch converted. The value for constant A compares favourably with the literature value for A of -11.8 kcal/g mol H_2 . However, the value for B is less by a factor of four when compared with a constant for thermal cracking of heavy oil (8). The value of B is about 30% lower than the constant for destructive hydrogenation of gas-oil (8) which is a fair comparison. Pitch conversion as a parameter is consistent with Edmister's parameter (8).

It has been shown that the heat of reaction is mainly a function of hydrogen consumption and for thermal hydrocracking, where hydrogen consumption is small, the heat of reaction is less than the heat losses for the small insulated reactor even for pitch conversions over 98%. For large reactors, however, with higher volume/surface ratios, provision will have to be made to remove the heat from the reaction.

REFERENCES

1. The Staff of the Fuels Research Centre. Objectives and projects of the Fuels Research Centre; Fuels Research Centre (now Energy Research Laboratories, CANMET), Divisional report FRC 72/74-ADM; 67 pp; Sept. 1972.
2. Merrill, W.H., Logie, R.B. and Denis, J.M. A pilot scale investigation of thermal hydrocracking of Athabasca bitumen; Mines Branch (now CANMET), Research report R-281; 25 pp; Dec. 1973.
3. Grayson, H.G. and Streed, C.W. Vapor-liquid equilibria for high temperature, high pressure hydrogen-hydrocarbon systems; 6th World Pet. Congr. v. 7, pp 233-245; 1963.
4. Vandenhengle, W. Report on consulting contract GPS NAG001, Saturn Engineering Co., Calgary, Alberta, March 1976.
5. Galbreath, R.B. and Van Driesen, R.P. Hydrocracking of residual petroleum stocks; 8th World Pet. Congr., v. 4, pp 129-137; 1967.
6. Jaffe, S.B. Kinetics of heat release in petroleum hydrogenation; Ind. Eng. Chem., Process Des. Dev.; v. 13, no. 1, pp 34-39; 1974.
7. Ueda, S., Yokoyama, S., Ishii, T., Makino, K. and Takeya, G. The heat of hydrodesulfurization reaction of heavy oil; Ind. Eng. Chem., Process Des. Dev.; v. 14, no. 4, pp 493-499; 1975.
8. Edmister, W. Applied hydrocarbon thermodynamics, part 51 - heats of chemical reaction; Hydrocarbon Processing; pp 123-129; July 1973.
9. McColgan, E., Soutar, P.S., Denis, J.M. and Parsons, B.I. The hydrocracking of residual oils and tars, part 4: catalyst de-activation with bitumens from Athabasca, Cold Lake and Lloydminster; Mines Branch (now CANMET) Research report R 261; 12 pp; Feb. 1973.
10. Speight, J.G. A structural investigation of the constituents of Athabasca bitumen by proton resonance spectroscopy; Fuel; v. 49, no. 1, pp 76-90; 1970.
11. Camp, F.W. The tar sands of Alberta, Canada, 2nd Edition; Cameron Engineers Inc.; Denver, Colorado 80210; 1974.

12. Schuman, S.C. The desulfurization of petroleum stocks; Joint symposium on pollution problems due to sulfur in petroleum, Am. Chem. Soc. meeting Atlantic City; Sept. 1968.
13. DuBois, J.J., Glover, J.A. and Buehler, R.J. Laboratory-scale flash still for petroleum oil fractions; U.S. Patent no. 3,399,116; Jan. 1966.
14. Aitken, A.R., Merrill, W.H., Pleet, M.P., Fulford, G.N. and Parsons, B.I. Characteristics of the high pressure hydrogenating characteristics of cobalt molybdate catalysts with different pore volume distributions; Mines Branch (now CANMET) Internal report FMP 62/40-HPC; 66 pp; March 1962.
15. Maxwell, J.B. Data book on hydrocarbons; Van Nostrand Reinhold, Princeton, N.J.; 1950.
16. Nelson, W.L. Petroleum Refinery Engineering, 4th edition; McGraw Hill, New York; 1969.
17. Shah, A. and Denis, J.M. Correlation of reactor voidage in vertical two-phase flow for the thermal hydrocracking of Athabasca bitumen. CANMET report; in preparation.

TABLE 1

FEED FLASH VAPORIZATION (GCOS BITUMEN)

Data Set	Temperature °C	Pressure MPa	LHSV	G/L* g mol/kg	f** %
1	430	10.44	1	51.1	42.9
	450	10.44	1	51.1	46.1
	470	10.44	1	51.1	47.7
2	430	10.44	2	25.55	27.6
	450	10.44	2	25.55	38.4
	470	10.44	2	25.55	44.0
3	93	17.33	2	42.4	0
	204	17.33	2	42.4	1.0
	316	17.33	2	42.4	4.5
	371	17.33	2	42.4	10.0
	427	17.33	2	42.4	20
	482	17.33	2	42.4	37
4	430	24.22	1	118.5	22.5
	450	24.22	1	118.5	26.3
	470	24.22	1	118.5	30.1
5	430	24.22	2	59.3	14.6
	450	24.22	2	59.3	17.3
	470	24.22	2	59.3	20.1

*G/L - gas/liquid ratio, g mol gas/kg of total liquid

**f = kg of liquid feed vaporized per kg fed

10.44 MPa = 1500 psi

17.33 MPa = 2000 psi

24.22 Mpa = 3500 psi

TABLE 2

INPUT DATA TO COMPUTER PROGRAM
FOR LIQUID FEED

Component Number	Wt %	API No.*	Mean Avg Boiling Point, °R	Molecular Wt
<u>FEED</u>				
1	0.2	67.00	609.7	82.00
2	0.1	54.00	709.7	109.00
3	0.4	37.00	809.7	140.00
4	0.4	31.70	909.7	180.00
5	3.1	27.00	1009.7	222.00
6	11.0	22.00	1109.7	275.00
7	11.2	17.60	1209.7	334.00
8	11.2	13.30	1309.7	392.00
9	11.4	9.30	1409.7	450.00
10	51.0	0.30	1659.7	1508.00
<u>PRODUCT</u>				
1	2.9	67.00	609.7	82.00
2	7.3	54.00	709.7	109.00
3	10.8	43.00	809.7	139.00
4	13.3	34.00	909.7	173.00
5	18.1	25.00	1009.7	211.00
6	22.9	20.00	1109.7	260.00
7	11.3	15.00	1209.7	314.00
8	3.2	13.00	1309.7	387.00
9	2.3	9.00	1409.7	457.00
10	7.8	0.60	1659.7	643.00

* Specific gravity in °API

TABLE 3

FEED AND GAS PROPERTIES

Feed - G.C.O.S. Topped (260°C) Bitumen, Lot 109

Pitch - 51.5% by wt, 47.7% by volume

Distillation of Feed at 1 Atm

IBP - 200°C	2.1% by wt
200 - 250°C	1.5 "
250 - 333°C	10.7 "
333 - 418°C	18.7 "
418 - 524°C	16.0 "
524 +	51.0 "

Feed - Specific Gravity 60/60 °F 1.010

Nitrogen	wt %	0.38
Sulphur	wt %	4.73
Vanadium, as V	ppm	211
Nickel, as Ni	wt %	0.56
Pentane insol	wt %	15.6
Benzene insol	wt %	0.57
CCR	wt %	13.7

Viscosity @ 100°C, centistokes, 176
@ 54°C, centistokes, 2000

Gas Composition

H ₂	74.1	mol %
H ₂ S	2.1	"
CH ₄	16.0	"
C ₂ H ₆	4.4	"
C ₃ H ₈	2.2	"
C ₄ H ₁₀	0.9	"
C ₅ H ₁₂	0.3	"

TABLE 4

HEAT OF REACTION RESULTS

Run No.	Pitch Conv. %	Pitch Conv. kg/kg Feed	H ₂ Consumed g mol/kg Feed	H ₂ S Formed g mol/kg Feed	Heat of Reaction kcal/kg Feed	D kcal/kg Feed
71-1-2	76.0	0.391	5.66	0.479	- 30.9	- 0.5
71-1-3	79.0	0.407	5.66	0.48	- 37.0	- 7.8
77-1-1	74.3	0.382	5.15	0.54	- 39.4	- 13.6
79-1-1	84.5	0.435	7.13	0.72	- 39.2	3.1
81-2-1	88.7	0.457	9.63	0.83	- 72.1	- 5.9
81-3-1	93.2	0.480	10.67	0.90	- 76.0	- 0.8
81-4-1	98.8	0.509	12.06	0.96	- 96.1	- 8.7
82-3-1	81.6	0.420	6.70	0.72	- 40.2	- 1.3
82-4-1	82.7	0.426	7.18	0.72	- 42.0	1.4
84-1-1	81.9	0.422	6.59	0.66	- 25.7	12.1
84-2-1(a)	88.9	0.458	8.96	0.79	- 43.2	16.0
84-2-1(b)	89.4	0.460	8.96	0.80	- 54.7	4.5

TABLE 5

SUPPLEMENTARY RUN DATA

Run No.	Temp °C	Press MPa	LHSV	Run Length h	Liquid Yield wt %	Gas Make g mol/kg feed
71-1-2	460	13.9	2	480	93	1.72
71-1-3	460	13.9	2	308	90	-
77-1-1	450	13.9	2	384	92	1.74
79-1-1	470	17.3	2	497	90.4	2.20
81-2-1	475	20.8	2	4	87.5	2.77
81-3-1	480	20.8	2	4	84.2	2.86
81-4-1	485	20.8	2	4	85.3	3.38
82-3-1	450	17.3	1	4	93.3	2.00
82-4-1	450	17.3	1	4	94.8	2.25
84-1-1	460	24.2	2	493	89.5	2.04
84-2-1(a)	470	24.2	2	34	89.4	2.43
84-2-1(b)	470	24.2	2	440	89.4	2.43

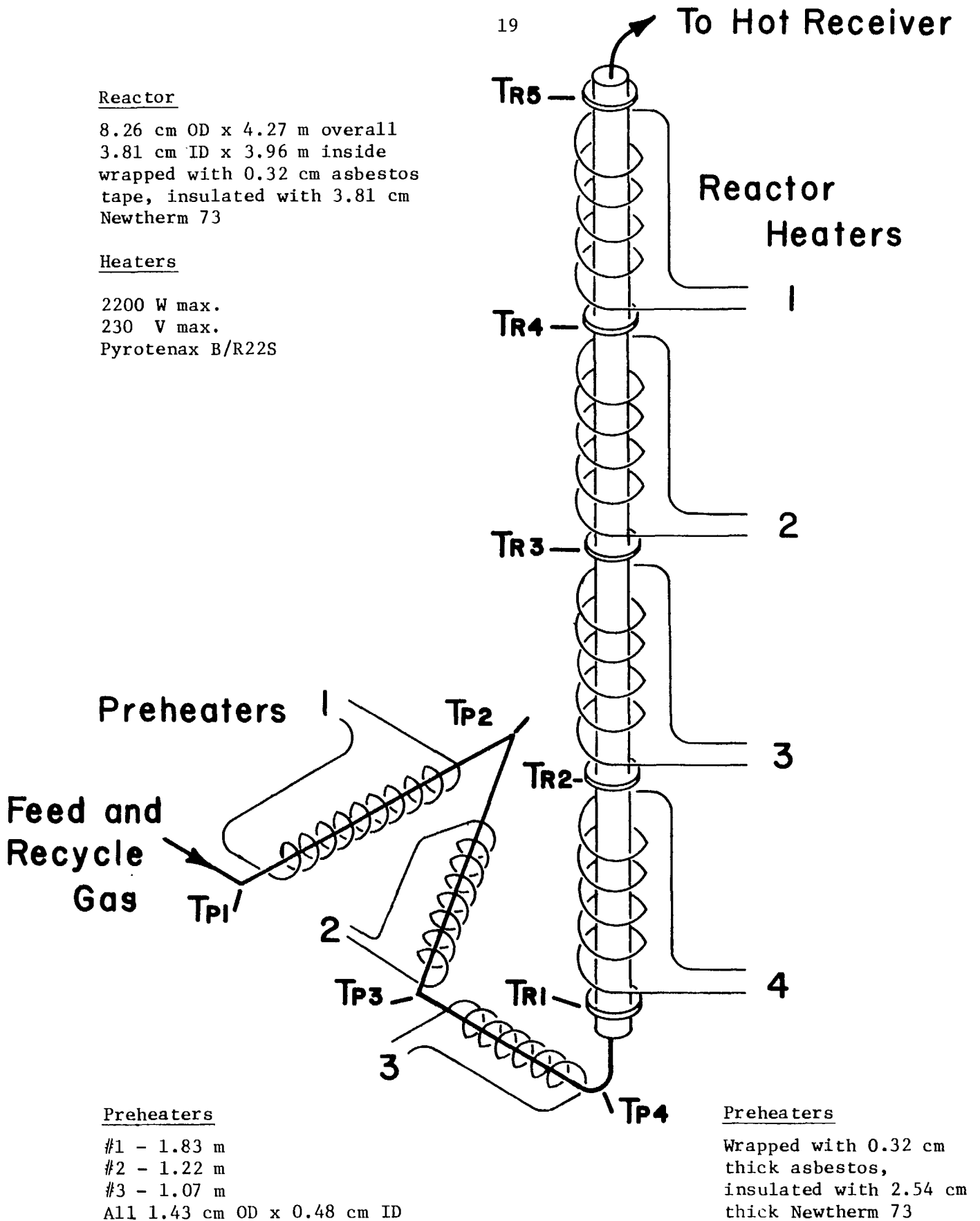
To Hot Receiver

Reactor

8.26 cm OD x 4.27 m overall
 3.81 cm ID x 3.96 m inside
 wrapped with 0.32 cm asbestos
 tape, insulated with 3.81 cm
 Newtherm 73

Heaters

2200 W max.
 230 V max.
 Pyrotenax B/R22S

Preheaters

#1 - 1.83 m
 #2 - 1.22 m
 #3 - 1.07 m
 All 1.43 cm OD x 0.48 cm ID

Preheaters

Wrapped with 0.32 cm
 thick asbestos,
 insulated with 2.54 cm
 thick Newtherm 73

FIGURE 1 - REACTOR AND PREHEATER DETAILS

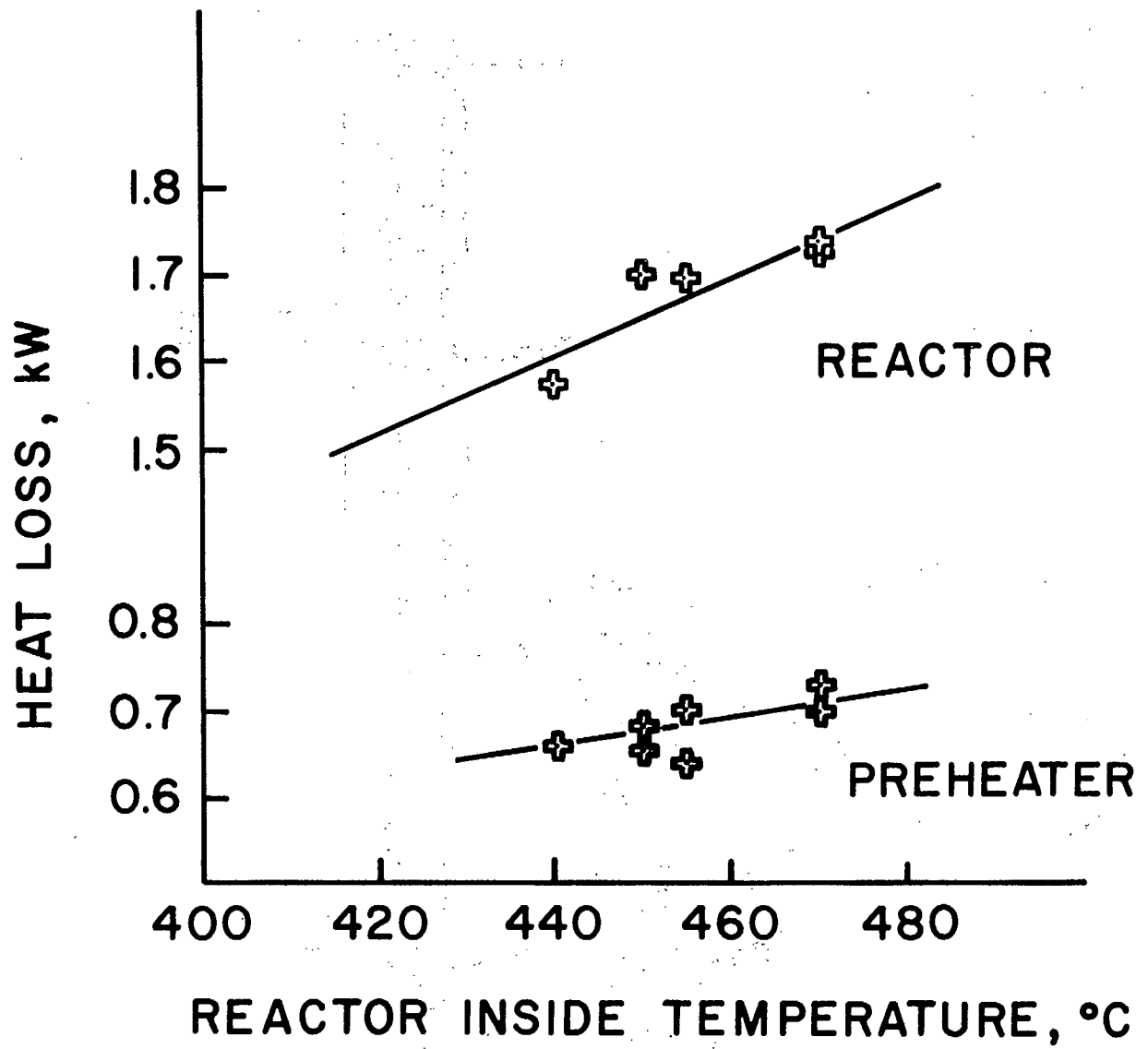


FIGURE 2 - HEAT LOSSES FROM REACTOR AND PREHEATER
AS A FUNCTION OF THE REACTOR INSIDE TEMPERATURE

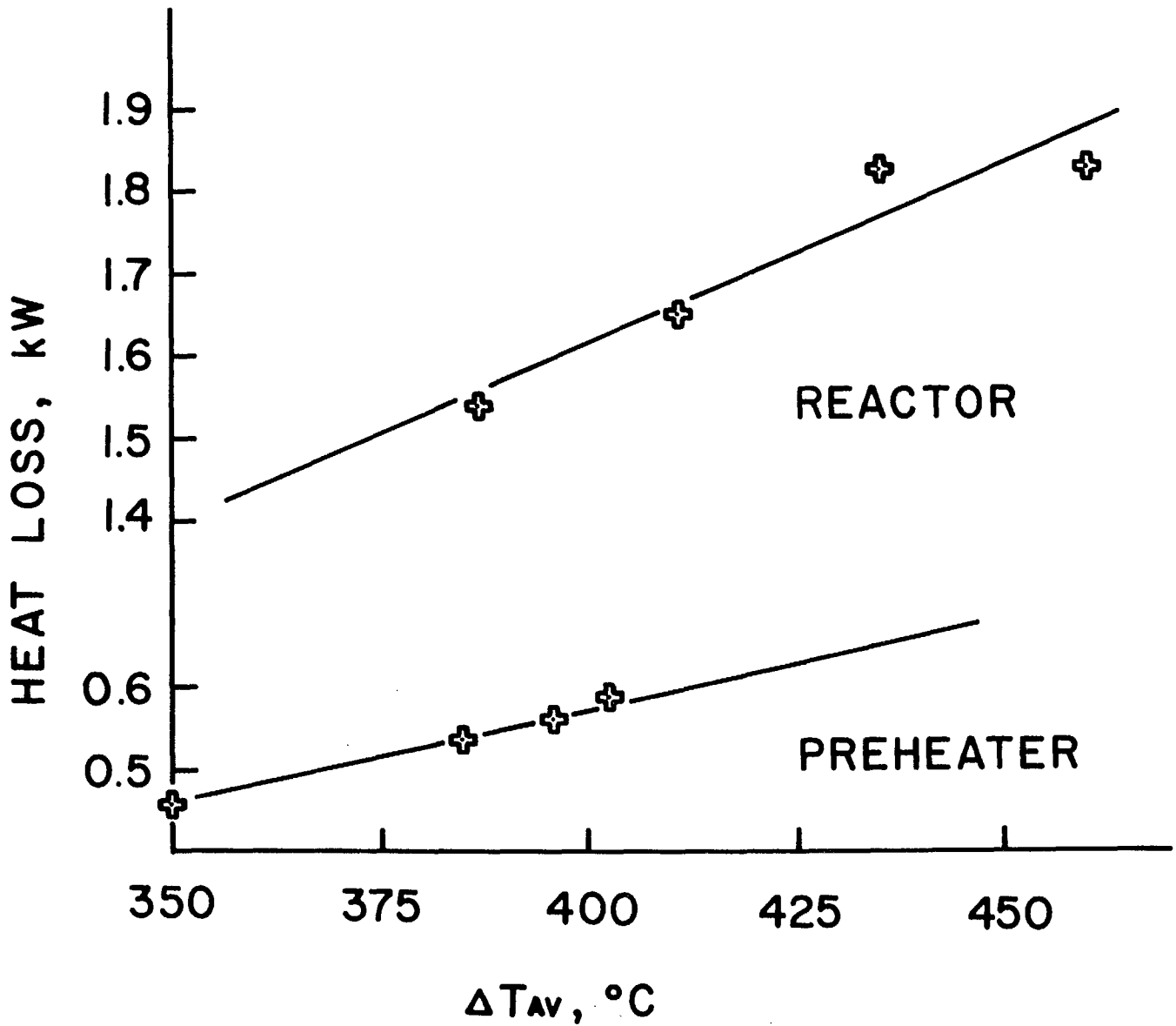


FIGURE 3 - HEAT LOSSES BASED ON DIFFERENCE (ΔT_{AV}) BETWEEN OUTSIDE SKIN AND AMBIENT TEMPERATURE

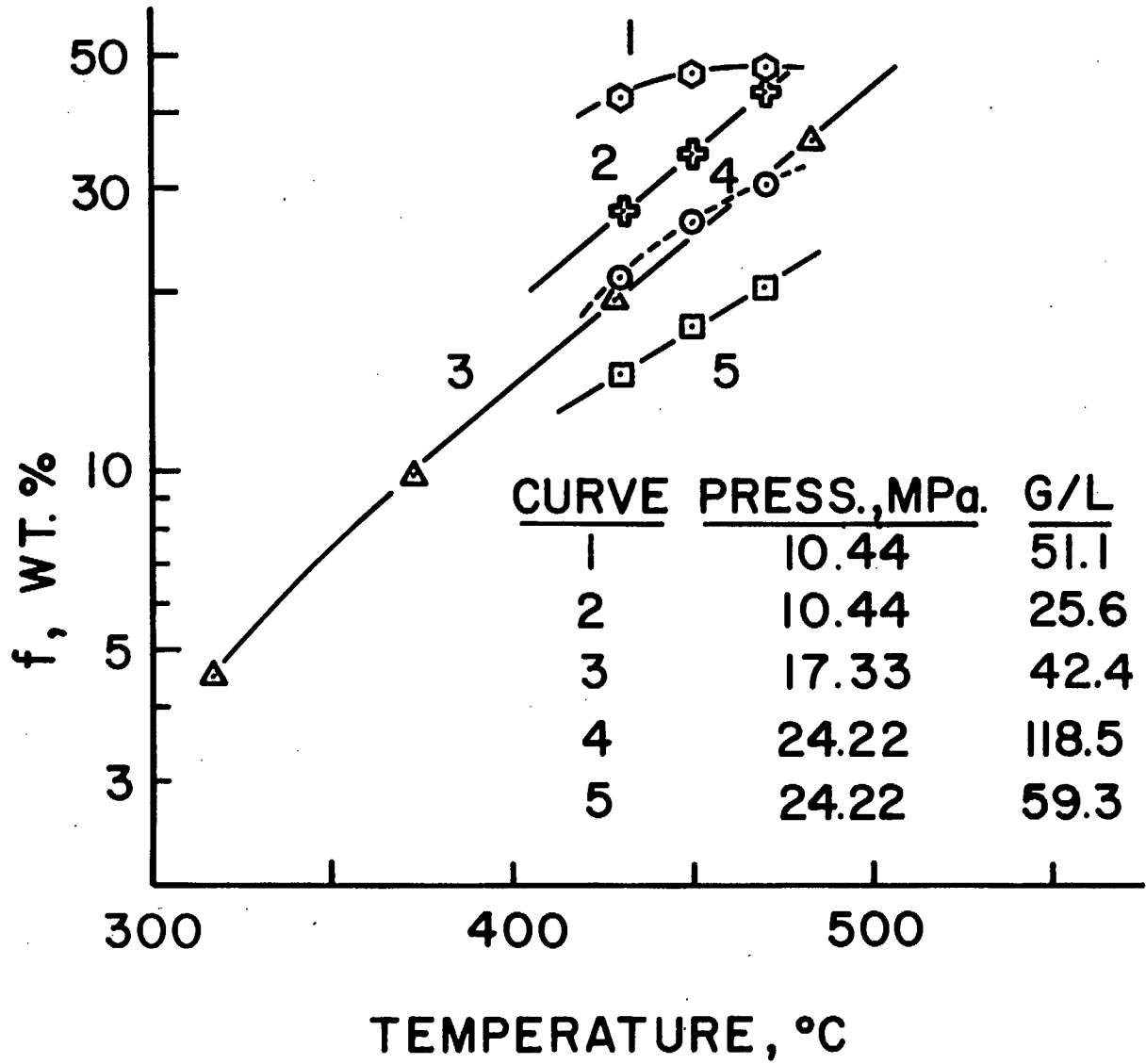


FIGURE 4 - FEED EQUILIBRIUM FLASH VAPORIZATION

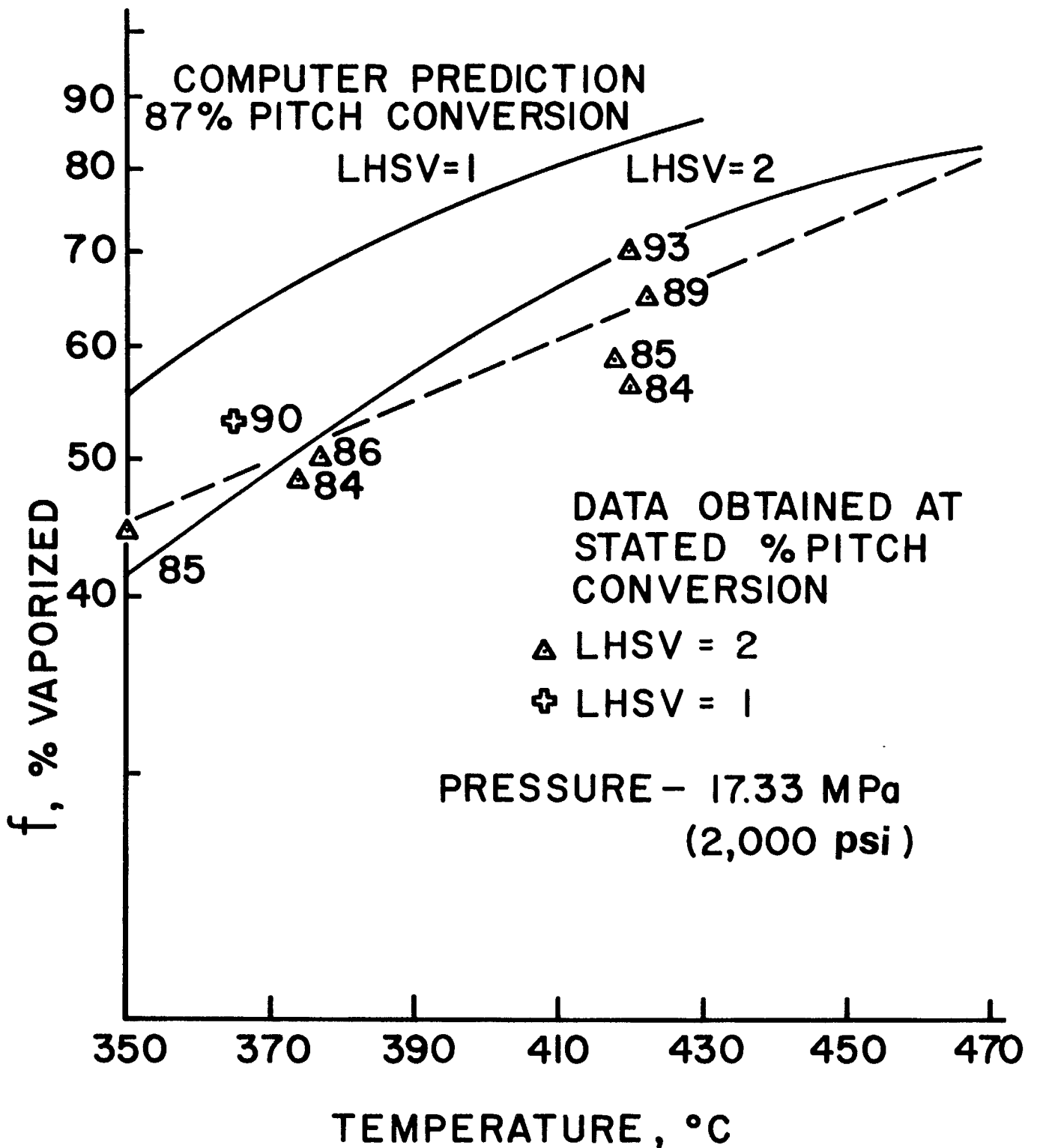


FIGURE 5 - PRODUCT EQUILIBRIUM FLASH VAPORIZATION

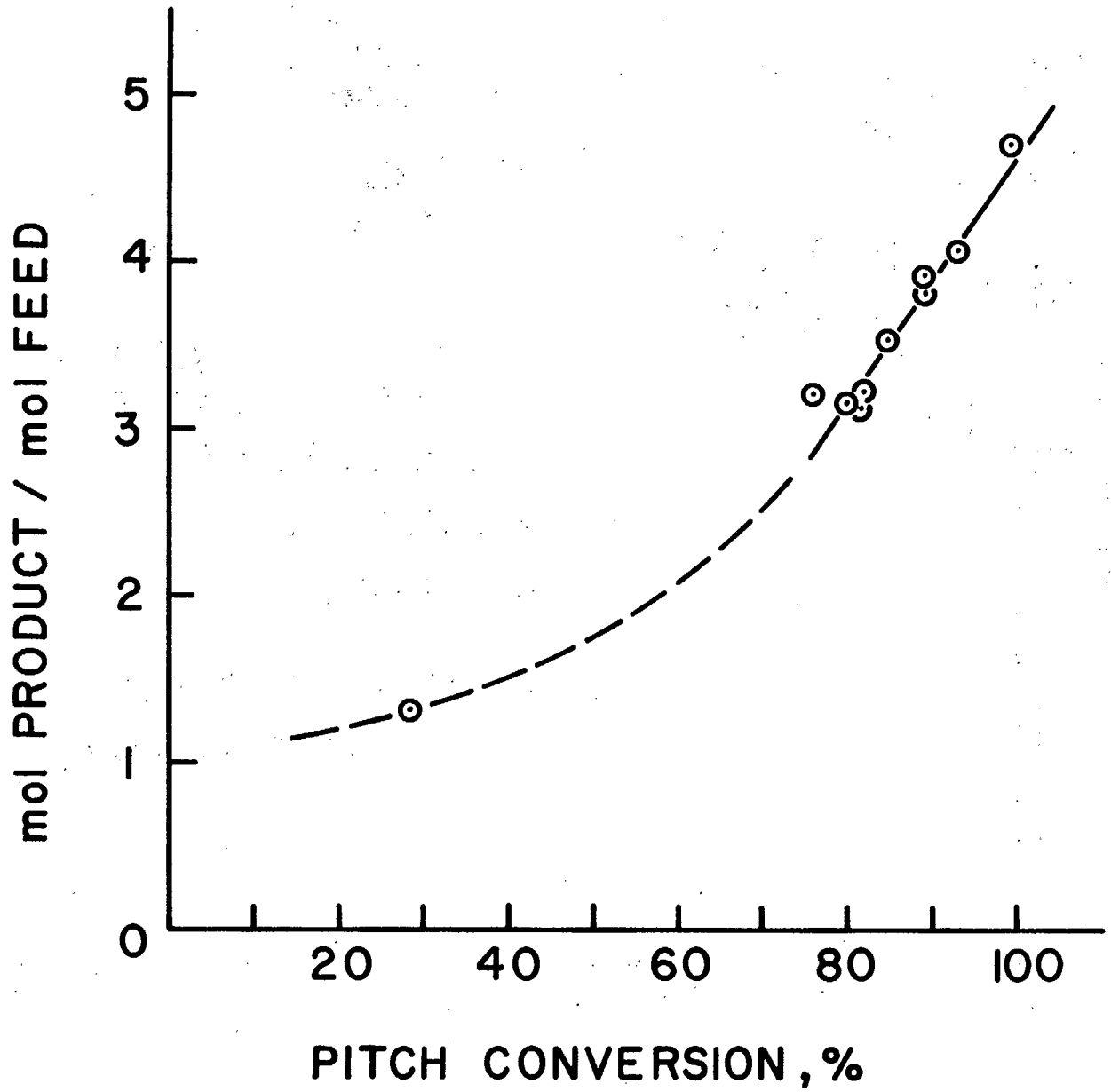


FIGURE 6 - MOLAR CONVERSION VERSUS PITCH CONVERSION

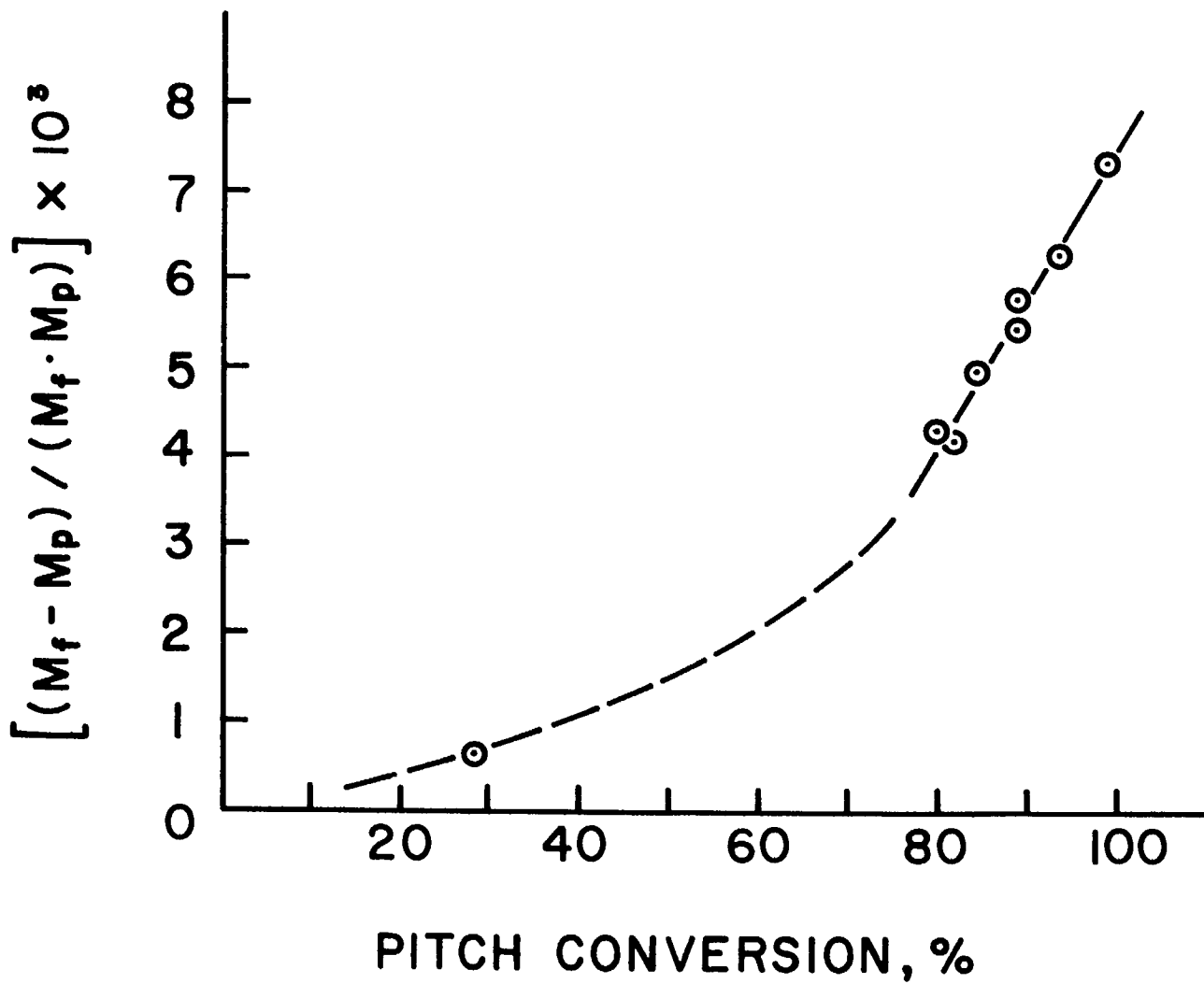


FIGURE 7 - EDMISTER'S PARAMETER VERSUS PITCH CONVERSION

APPENDIX A

A DERIVATION TO SHOW FOR A SINGLE LIQUID AND GAS, THE NUMBER OF MOLES OF LIQUID VAPORIZED IS A CONSTANT FOR A FIXED VOLUMETRIC GAS FLOW AT DIFFERENT PRESSURES

If a single liquid and a gas, i.e., water and nitrogen are considered in a flowing system and the system follows Raoult's law, then at equilibrium,

$$\frac{N_g}{N_l} = \frac{P_g}{P_l}$$

in the gas phase, where N_g and N_l are the number of moles of gas and liquid in the gas phase respectively, and P_g and P_l are the partial pressures of gas and liquid respectively. Also,

$$\text{Total pressure, } P_t = P_g + P_l$$

Hence, for a small P_l

$$\frac{N_g}{N_l} = \frac{P_t - P_l}{P_l} \approx \frac{P_t}{P_l}$$

or

$$N_l = N_g \frac{P_l}{P_t}$$

For this reactor system, the volumetric flow rate of gas is kept constant at a particular pressure and according to the ideal gas law:

$$N_{g1} = N_{g2} \times \frac{P_1}{P_2} \quad (1)$$

where N_{g1} is the molar flow at pressure P_1 and N_{g2} is the molar flow at pressure P_2 . For a pure liquid, P_l is a function of temperature only, and

$$P_l = P_{l1} = P_{l2}$$

considering N_{ℓ} at P_1 :

$$N_{\ell 1} = N_{g1} \times \frac{P_{\ell}}{P_1}$$

Similarly for N_{ℓ} at P_2 :

$$N_{\ell 2} = N_{g2} \times \frac{P_{\ell}}{P_2} = N_{g1} \frac{P_2}{P_1} \times \frac{P_{\ell}}{P_2} = N_{\ell 1}$$

Therefore, the number of moles of liquid vaporized remains unchanged, provided that the same volume of gas at conditions is maintained. In the derivation of this relationship it is assumed there is negligible gas dissolved in the liquid, the temperature is unchanged, and $P_t - P_{\ell} \approx P_t$.

It has been proven that the number of moles of liquid vaporized is constant provided that a fixed volumetric gas flow is maintained at all pressures. Hence, for a fixed space velocity (fixed liquid flow rate), the fraction of feed vaporized will be constant. However, this condition is not valid at different space velocities.

APPENDIX B

SAMPLE DATA AND CALCULATIONS

A typical heat of reaction data sheet and a typical heat of reaction calculation sheet are given in Figures B-1 and B-2 respectively. These were prepared for each run from data obtained during the run.

The "Liquid Flow Rate" is the liquid feed rate measured using weigh tanks. The "Gas Flow Rate" is the recycle gas flow rate through the reactor in ft^3/h ($1 \text{ ft}^3/\text{h} = 0.0283 \text{ M}^3/\text{h}$). The LHSV is the liquid feed rate in ℓ/h divided by the total reactor volume (4.5 ℓ). The duration of the run is the number of hours on stream at the stated conditions. This does not include start-up and shut-down times which (normally) vary from 7 hours to a few minutes respectively.

The "Overall Mass Balance" is the sum of light ends (LE) and heavy ends (HE) from the cold and hot receivers respectively, divided by the liquid feed, expressed as a percentage. It is a balance on liquid product only, equivalent to liquid yield. If the gas-make plus H_2S is included, the true balance for this run is 98% on a weight basis.

The heat input was measured using wattmeters as described earlier. The net heat input was obtained by deducting the heat losses shown in Figure 2 from the total measured inputs.

The gas flow was computed from the gas recycle flow given as 1.5 cfh (ft^3/h) at 3500 psi (24.2 MPa) and 25°C . This is based on the ideal gas law and a gas molecular weight of 4.2. It may be in error by $\pm 5\%$ due to variation in the gas analysis which was not taken into account for the different runs.

The preheater balance is a verification of the gas and liquid flows. The liquid (W_L) and gas (W_G) flows and the fraction of feed vaporized in the preheater (f_p) are shown in Figure B-2. To heat the feed, the computation involves multiplication of the weight flow (lb/h) by the temperature difference ($^\circ\text{F}$) and the heat capacity of $0.69 \text{ Btu}/\text{lb}/^\circ\text{F}$ ($.69 \text{ cal}/\text{g}/^\circ\text{C}$). The factor 1.8 converts the temperature difference to degrees Fahrenheit.

Calculation for the gas is similar, using a gas heat capacity of 1.84 Btu/lb/^oF. The heat to vaporize the feed was computed using a heat of vaporization of 70 Btu/lb (39 cal/g). The sum of the above heat requirements was then compared to the net electrical input in Btu/hr. If the balance exceeded an absolute value of 10% the run was not used in the study.

The heat of reaction was computed in a manner similar to that shown above. The value of heat capacity (C_p) for the recycle gases was computed using the gas analysis. The value for bitumen was based on preheater studies over many runs, and was the most reliable value available. The computed C_p value, based on a feed volume-average-boiling-point of 975^oF (485^oC), was found to be 0.72 at 860^oF (460^oC) and 0.66 at 716^oF (360^oC) for an average of 0.69 Btu/lb/^oF or 0.69 cal/g/^oC over the range normally encountered in the reactor (15). For the preheater, the same value was used, although the computed average value was 0.57 Btu/lb/^oF.

The reactor balance was independent of the preheater balance. In other words, it was assumed that the reactor feed was liquid at the inlet temperature. This simplified the calculation and was permissible since the vapour heat capacity was close to the liquid heat capacity in this range.

FIGURE B-1

TYPICAL HEAT OF REACTION DATA SHEET (RUN 84-1-1)

Run No.	85-1-1		
Feed - Athabasca bitumen	lot No. 109		
Temperature	460°C		
Pressure	3500 psi		
Feed flow rate	9073 g/h		
Gas flow rate	9300 l/h at stp		
Gas composition %	85.5 H ₂ , 0.05 H ₂ S, 13.7 CH ₄ , 0.33 C ₂ H ₆ and 0.29 C ₃ H ₈		
Length of run	493 h		
Pitch conversion	81.9%		
Product molecular weight from distillation	223		
Hydrogen usage	1660 l/h at stp		
Hydrogen in vent gases	324 l/h at stp		
Hydrogen consumed	1336 l/h at stp		
HE	5185 g/h		
LE	2938 g/h		
Gas make	411 l/h at stp		
H ₂ S make	134 l/h at stp		
Heat input, electrical, kw		Temperatures, °C	
Preheater total	3.32	Preheater inlet	135
Preheater net	2.63	Preheater outlet	370
Reactor total	2.49	Reactor 1	430
Reactor net	0.8	2	460
		3	460
		4	460
		5	460
		Hot receiver	376

FIGURE B-2
TYPICAL HEAT OF REACTION CALCULATION
RUN 84-1-1

1. Preheater Balance

$$\begin{array}{rcl}
 T_i & = & 135^{\circ}\text{C} \\
 T_o & = & 370^{\circ}\text{C} \\
 T_R & = & 460^{\circ}\text{C} \\
 W_L & = & 20 \text{ lb/h} \\
 W_G & = & 3.86 \text{ lb/h} \\
 f_p & = & 0.096 \\
 f_p & = & 0.29
 \end{array}$$

$$\begin{array}{rcl}
 \text{To heat feed, } W_L \times 0.69 \times (T_o - T_i) \times 1.8 & = & 5837 \text{ Btu/h} \\
 \text{To heat gases, } W_G \times 1.84 \times (T_o - T_i) \times 1.8 & = & 3004 \text{ Btu/h} \\
 \text{To vaporize part of feed, } W_L \times f_p \times 70 & = & \underline{134 \text{ Btu/h}} \\
 \text{Total} & = & \underline{8975 \text{ Btu/h}} \\
 \text{Net electrical input, } 2.63 \times 3414 & = & 8979 \text{ Btu/h} \\
 \text{Difference} & = & -4 \text{ Btu/h}
 \end{array}$$

2. Reactor Balance

$$\begin{array}{rcl}
 \text{To heat feed, } W_L \times 0.69 \times (T_R - T_o) \times 1.8 & = & 2235 \text{ Btu/h} \\
 \text{To heat gases, } W_G \times 1.84 \times (T_R - T_o) \times 1.8 & = & 1151 \text{ Btu/h} \\
 \text{To vaporize portion of feed, } W_2 \times (f_R - f_p) \times 70 & = & 272 \text{ Btu/h} \\
 \text{Total} & = & 3658 \text{ Btu/h} = \text{A} \\
 \text{Net electrical input, } 0.8 \times 3414 & = & 2730 \text{ Btu/h} = \text{B} \\
 \text{Heat of reaction} = \text{B} - \text{A} & = & -927 \text{ Btu/h (minus sign indicates exothermic} \\
 & & \text{reaction)}
 \end{array}$$

CANMET REPORTS

Recent CANMET reports presently available or soon to be released through Printing and Publishing, Supply and Services, Canada (addresses on inside front cover), or from CANMET Publication Office, 555 Booth Street, Ottawa, Ontario, K1A 0G1.

Les récents rapports de CANMET, qui sont présentement disponibles ou qui ce seront bientôt, peuvent être obtenus de la direction de l'Imprimerie et de l'Édition, Approvisionnement et Services, Canada (adresses au verso de la page couverture), ou du Bureau de Vente et distribution de CANMET, 555 rue Booth, Ottawa, Ontario, K1A 0G1.

- 76-7 Catalogue and Index of CANMET Scientific and Technical Papers Published in or Submitted to Periodicals and Presentations, 1967-1973; Technology Information Division;
Cat. #M38-13/76-7; Price: \$2.00 Canada, \$2.40 other countries.
- 76-8 Comparison of Pull-Out Strength of Concrete with Compressive Strength of Cylinders and Cores, Pulse Velocity and Rebound Number; V.M. Malhotra and G. Carette;
Cat. #M38-13/76-8; Price: \$1.00 Canada, \$1.20 other countries.
- 76-9 Catalysts for Hydrocracking and Refining Heavy Oils and Tars Part 3: The Effect of Presulphiding Conditions on Catalyst Performance; M. Ternan and M.J. Whalley;
Cat. #M38-13/76-9; Price: \$1.00 Canada, \$1.20 other countries.
- 76-10 Recent Advances in Copper Electrowinning; O.J. MacKinnon and V.I. Lakshmanan;
Cat. #M38-13/76-10; Price: \$1.00 Canada, \$1.20 other countries.
- 76-11 The Determination of Radium 226 in Uranium Ores and Mill Products by Alpha Energy Spectrometry; J.B. Zimmerman and V.C. Armstrong;
Cat. #M38-13/76-11; Price: \$1.00 Canada, \$1.20 other countries.
- 76-12 Lightweight Aggregates for Structural Concrete; H.S. Wilson;
Cat. #M38-13/76-12; Price: \$3.75 Canada, \$4.50 other countries.
- 76-13 Development of a Zirconia Electrolyte for Use in a Steel-Making Oxygen Probe; T.A. Wheat;
Cat. #M38-13/76-13; Price: \$5.00 Canada, \$6.00 other countries.
- 76-14 Estimation of Upper Bounds to Rock Slopes by Analysis of Existing Slope Data - Wall Stability in the South Roberts Pit - An example of the use of previous slopes;
Cat. #M38-13/76-14; Price: \$2.00 Canada, \$2.40 other countries, ISBN 0-660-00521-2.
- 76-15 Competing Reactions in Hydrotreating Coker Distillates from Athabasca Bitumen on Unpromoted and Promoted Catalysts; R. Ranganathan, M. Ternan and B.I. Parsons;
Cat. #M38-13/76-15; Price: \$0.50 Canada, \$0.60 other countries.
- 76-16 A Digest of Environmental Regulations Pertinent to Open Pit Mining in Canada (Current at April 1975); Oames and Moore, Toronto;
Cat. #M38-13/76-16; Price: \$1.75 Canada, \$2.10 other countries.
- 76-17 The Floatability of Eleven Non-Metallic Minerals and Three Metallic Oxides (Sequel to TB 108 and TB 186); R.A. Wyman;
Cat. #M38-13/76-17; Price: \$1.50 Canada, \$1.80 other countries, ISBN 0-660-00586-7.
- 76-18 Use of Recycled Concrete as a New Aggregate; V.M. Malhotra;
Cat. #M38-13/76-18; Price: \$1.50 Canada, \$1.80 other countries, ISBN 0-660-00522-0.
- 76-22 Pit Slope Manual - Chapter 1, Summary; R. Sage, Editor;
Cat. #M38-14/1-1976; Price: \$2.50 Canada, \$3.00 other countries, ISBN 0-660-00505-0.
- 76-23 Catalysts for Hydrocracking and Refining Heavy Oils and Tars Part 2: The Effects of Molybdenum Concentration and of Zinc to Molybdenum Ratio on Desulphurization and Denitrogenation; R.J. Williams, M. Ternan and B.I. Parsons;
Cat. #M38-13/76-23; Price: \$1.25 Canada, \$1.50 other countries, ISBN 0-660-00504-2.