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T.J.W. de Bruijn, J.D. Chase and W.H. Dawson

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T.J.W. de Bruijn, J.D. Chase and W.H. Dawson

Synthetic Fuels Research Laboratory, Energy Research Laboratories,

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

ABSTRACT

Gas holdup in a tubular reactor was measured at pressures from 5 to 14 MPa and temperatures of 300, 350 and 400°C using a differential pressure cell. The effects on gas holdup of gas density, temperature, liquid superficial velocity and gas superficial velocity were studied using vacuum tower bottoms from a Venezuelan feedstock with 95.1 wt % +525°C material. Hydrogen was used at superficial gas velocities from 0.7 to 2.3 cm/s.

The feed density at 300°C (5.57 MPa) and 400°C (13.9 MPa) was found to be 852 and 782 kg/m^3. Increased gas density at a constant temperature of 300°C increased the gas holdup at all superficial gas velocities. Increasing the temperature from 300°C to 400°C did not affect the gas holdup for gas velocities up to 2.3 cm/s. Only at the highest gas rate of 2 cm/s at 300°C was a higher gas holdup value obtained. An increase in the liquid flow rate from about 0.04 to 0.1 cm/s did not affect the gas holdup.

RÉTENSION DE GAZ DANS UN RÉACTEUR TUBULAIRE À HAUTE PRESSION

par

T.J.W. de Bruijn, J.D. Chase et W.H. Dawson

Laboratoire de recherche sur les combustibles synthétiques,
Laboratoire de recherche sur l'énergie,
CANMET, Énergie, Mines et Ressources Canada, Ottawa, K1A 0G1

Résumé

Une rétention de gaz dans un réacteur tubulaire a été mesurée à des pressions allant de 5 à 14 MPa et des températures de 300, 350 et 400°C, grâce à une cellule de pression différentielle. Les effets de cette rétention de gaz sur la densité du gaz, la température, la vitesse superficeille du liquide et la vitesse superficielle du gaz, ont été étudiés un utilisant des résidus de tour sous vide, provenant de matières premières vénézuiliennes se caractérisant par un pourcentage en poids de 95,1 et une température de +525°C. De l'hydrogène a été utiliseé à des vitesses superficielles du gaz allant de 0,7 à 2,3 cm/s.

La densité d'alimentation à 300°C (5,57 MPa) et à 400°C (13,9 MPa) fut respectivement de 852 Kg/m^3 et de 782 kg/m^3. L'augmentation de la densité du gaz, à une température constante de 300°C, faisait augmenter la rétention de gaz, et cela pour toutes les vitesses superficielles du gaz. L'augmentation de la température, passant de 300°C à 400°C, n'a pas affecté la rétention de gaz pour des vitesses de gaz au dessus de 2,3 cm/s. C'est seulement au plus haut taux de gaz de 2 cm/s à 300°C que feet obtenue la plus haute valeur de rétention de gaz. Enfin, une augmentation du débit du liquide, allant de 0,04 à 0,1 cm/s, n'affecte pas la rétention de gaz.

INTRODUCTION

Bubble columns are applied in a number of industrial processes such as gas absorption, oxidation of organics, hydrogenation, coal liquefaction, bioprocesses and hydrocracking. Consequently, extensive literature is available on this subject (Shah et al. 1982, Heijnen and van't Riet, 1984, Reilly et al. 1986a). Many correlations describing gas holdup as a function of liquid and gas properties and process variables have been published. Most correlations were derived from measurements on water and air, or some other gas at atmospheric conditions. Some investigators used alcohols or electrolyte solutions to a limited extent and some used a hydrocarbon oil such as kerosene (see review by Shah et al., 1982). Although most measurements were done in laboratory equipment and at the same (atmospheric) conditions, many of these correlations predict quite different gas holdup values for a given system (Reilly et al., 1986a).

Commercially sized reactors are usually designed using kinetic data obtained in small pilot plants. The (apparent) reaction rate constants and (apparent) activation energies calculated from pilot plant data are, however, dependent on the actual gas holdup in the pilot plant reactors. Because of the inadequacy of existing data and correlations, even for small scale equipment, it is important to measure the gas holdup at actual conditions to minimize extrapolation errors.

Additional errors arise because many industrial applications operate at high temperature and pressure. In particular, for hydrogen-hydrocarbon oil systems under high temperature and high pressure virtually no data are available.

In this study, a set of screening experiments was performed with hydrogen in a very heavy hydrocarbon oil. Gas flow rate, pressure and temperature were varied to obtain estimates for the effect of gas superficial velocity, gas density and temperature on gas holdup. The effect of increasing the liquid flow rate was also investigated.

EXPERIMENTAL

EQUIPMENT

A schematic of the pilot plant used to perform the measurements is given in Fig. 1. The reactor is 2.40 m long and 5.08 cm in diameter. A differential pressure (d/p) cell was employed to obtain gas holdup (Taylor Instruments differential pressure transmitter, model 307T, range 0-100 in. of water). The d/p cell was connected to reactor ports 1 and 5 as shown in Fig. 2. The lines to the d/p cell were filled with a heavy gas oil (Zerice-46, with an IBP/FBP of 246 and 573°C) to prevent reactor liquid from entering and coking up the line. The d/p cell measures the difference in hydrostatic head for the reactor and the Zerice filled line. Depending on the density difference between Zerice and reactor liquid, and the gas holdup, either the side connected to port 1 or port 5 could be the high side of the d/p cell. With the reactor liquid and under the conditions employed in this study the side connected to port 5 was always the high side.

GAS FLOW

The gas volumetric flow was measured by a calibrated orifice. Calibration curves were available for 3.55, 6.99, 10.44 and 13.89 MPa (500, 1000, 1500 and 2000 psig) for 100% hydrogen and 13.89 MPa for 85% hydrogen and 15% methane. Gas flow at intermediate pressures was obtained by interpolation. The orifice was calibrated by letting the pressure down and measuring the off-gas with a wet gas meter calibrated by the National Research Council of Canada and making the appropriate temperature and pressure corrections.

At 300 and 350°C virtually no cracking of the liquid feed occurs and virtually no gases are formed. However, at 400°C some hydrocracking of the feed does occur with the formation of hydrocarbon gases. Even though the reactor recycle gas stream was scrubbed, not all hydrocarbon gases were removed resulting in a higher gas density affecting the orifice readings. A set of three recycle gas analyses taken at 400°C and three different gas rates showed an average of about 97 vol % hydrogen with the remainder consisting mainly of methane and smaller amounts of hydrogen sulphide and higher hydrocarbons. The gas composition changed very little with gas rate for the range of gas rates investigated. A composition of 97 vol % hydrogen and 3 vol %

methane was used to calculate the gas density at 400°C. The superficial gas velocity at 400°C, was calculated from the volumetric flow which was estimated by interpolation from the available calibration curves for pure hydrogen and hydrogen with 15 vol % methane.

MATERIALS

The specific gravity and viscosity of Zerice 46 are given in Table 1. The experiments were performed using Blend 24 vacuum bottoms originally consisting of a blend of Venezuelan heavy oils from the Tia Juana region. An analysis of Blend 24 is given in Table 2. The density of this feed at 300 and 400°C was measured with the d/p cell to allow calculation of the gas holdup according to Eq 2 (see below).

D/P CELL CALIBRATION

The d/p cell had an adjustable range from 0-20 in. of water to 0-250 in. of water. A range of 0-100 in. of water was used. The d/p cell was calibrated at atmospheric pressure against a Portable Pneumatic Calibrator, Series 65-120 (Wallace and Tiernan, PennWalt Corp., Belleville, New Jersey).

The setup was tested over the whole cell range by adding and withdrawing known amounts of Zerice from the reactor at atmospheric pressure. The d/p cell readings were compared with hydrostatic pressures calculated from the weight of Zerice in the reactor and the reactor cross-sectional area. The results of the calibration are given in Table 3. With one exception, at low d/p cell readings, all readings were within 3% (relative) of the calculated reading.

PROCEDURES

The gas holdup (ϵ) can be obtained in two ways:

1. By measuring the d/p cell reading for an empty reactor (dp_e), a reactor completely filled with liquid (dp_{full}) and a reactor when gas and liquid are flowing ($dp_{g,l}$). The gas holdup is then given by:

$$\epsilon = \frac{dp_{g,l} - dp_{full}}{dp_e - dp_{full}} \tag{1}$$

2. By measuring the pressure drop across the reactor when completely filled with liquid (dp_{full}) and when gas and liquid are flowing ($dp_{g,l}$). If the reactor length (Z) and liquid density (ρ_l) are known then the gas holdup can be calculated as:

$$\varepsilon = (dp_{g,l} - dp_{full}) * 0.0254 * 1000/(Z * \rho_l) \qquad (2)$$

(Note: the d/p cell readings are expressed in inches of water).

Initially, gas holdups were calculated from both Eq 1 and 2. Values were always in very close agreement. Furthermore, dumping the reactor contents to obtain dp_e was quite time consuming, so after the initial experiments procedure 1 was abandoned.

For all experiments except those at 400°C, the results were checked by measuring the gas holdup directly by stopping the gas flow and measuring the amount of feed needed to fill the reactor completely. The two sets of gas holdup values agreed well. All d/p cell experiments were done at least twice.

The effect of pressure (gas density) was investigated at 300°C and hydrogen pressures of 5.57, 8.30, 11.03 and 13.89 MPa. Additional experiments were performed at 13.89 MPa and 350 and 400°C to estimate the effect of temperature. At all conditions, the hydrogen gas flow was varied to investigate a range of superficial gas velocities (0.7-2.3 cm/s). Finally, the effect of liquid superficial velocity was checked at 300°C and 5.57 MPa by increasing it from 0.04 to 0.1 cm/s.

RESULTS AND DISCUSSION

FEED DENSITY MEASUREMENTS

To allow calculation of the gas holdup according to Eq 2, the feed density was measured using the d/p cell at 300°C (5.57 MPa) and 400°C (13.89 MPa) and by pycnometer at 15°C (atmospheric pressure). The densities at 300 and 400°C were calculated from duplicate d/p cell measurements for an empty and full reactor and the known reactor length of 217.8 cm between the d/p cell hookups. The average feed densities were 852 kg/m^3 (300°C) and 782 kg/m^3 (400°C). The results are plotted in Fig. 3. The density at 400°C

may have been affected slightly by a small amount of hydrocracking although this was minimized by filling the reactor as quickly as possible.

EFFECT OF PRESSURE

Table 4 lists the conditions and results for runs 83-VD-247 to 265. In Fig. 4 gas holdup is plotted versus superficial gas velocity for pressures of 5.57, 8.30, 11.03 and 13.89 MPa. At very low gas rates (≤ 1 cm/s) the gas holdup values for all pressures converge towards zero gas holdup at zero gas velocity. At higher gas rates there is a significant effect of pressure; a higher pressure (gas density) results in a higher gas holdup, particularly at somewhat higher gas velocities. It appears that at low gas velocities the incremental increase in gas holdup with gas density becomes smaller at higher gas densities. The hydrogen densities given in the figure were calculated taking into account compressibility factors, interpolated from values given elsewhere (Perry, 1973).

The curves at all pressures are concave upwards indicating the non-linear behaviour of the gas holdup with increasing gas velocity. The increasing slope of these plots is an indication of bubbly flow. It is only observed if there is no interaction between the individual bubbles (Bach and Pilhofer, 1978, Molerus and Kurtin, 1985). In general, such an upward trend is rare and occurs only at low gas rates where the number of bubbles is small. At higher gas rates the bubbles interact and coalesce and the increase in gas holdup with superficial gas velocity is reduced. At this stage the relation between gas holdup and superficial gas velocity is usually close to linear. A further gas flow increase causes the flow regime to change from bubbly to churn-turbulent, resulting in a further decrease in the slope of the gas holdup versus gas superficial velocity plot.

Why gas density and pressure effect gas holdup is not well understood. However, experiments performed at the University of Waterloo at pressures up to 1100 kPa indicate that higher gas densities cause the change from bubbly to churn-turbulent flow to occur at higher gas rates (Reilly et al., 1986b). If this trend continues towards higher pressures, such as used in this study, very high gas holdup values are possible, even at relatively low superficial gas velocities. Tarmy et al. 1984 reported a gas holdup of more than 50% at 17.0 MPa at a superficial gas velocity of about 7 cm/s. Typical

gas holdup in an air-water system at atmospheric pressure would be approximately 15% at this gas rate. Tarmy et al. 1984 attributed the effect of pressure to smaller bubbles being formed due to increased contribution of gas momentum to the bubble formation process.

EFFECT OF LIQUID FLOW RATE

Increasing the liquid flow rate from 0.038 to 0.097 cm/s at 300°C and 5.57 MPa did not change the gas holdup. However, the liquid flow rates were very small and more than an order of magnitude smaller than the superficial gas velocities. Under these conditions no effect of liquid flow rate is expected.

EFFECT OF TEMPERATURE

The conditions and results (all at 13.89 MPa) are given in Tables 4 and 5. The gas densities at all three temperatures were similar. The gas holdup at the three temperatures is plotted versus superficial gas velocity in Fig. 5. One curve can describe all data except for one gas holdup value at the highest gas rate of 2 cm/s and the lowest temperature of 300°C. This one point, however, is the calculated average of 3 d/p cell experiments and was also checked by stopping the gas flow and filling the reactor with liquid. Both methods gave almost the same gas holdup value, 0.347 and 0.346, respectively. However, this value does not follow the trend of the other experiments and even though this point follows the trend with gas density very nicely, as shown in Fig. 4, further investigations are needed to substantiate whether the gas holdup depends on temperature below 350°C and gas velocities above 1.5 cm/s.

CONCLUSIONS

Gas holdup measurements on a hydrogen/vacuum tower bottoms system in a tubular reactor at high pressure and temperature showed interesting trends. For this particular feedstock the gas holdup depends on pressure: increasing the (hydrogen) pressure from 5.5 to 13.9 MPa resulted in higher gas holdups for gas rates above approximately 1.5 cm/s. Gas holdup appeared independent of temperature at all gas rates. However, one exception was obtained at the lowest temperature of 300°C and high gas rate of 2 cm/s. Here a substantially

higher gas holdup value was obtained than at higher temperatures. More work is needed to explain this observation. Increasing the liquid superficial velocity by a factor of 2.5 did not affect the gas holdup.

The density of the vacuum tower bottoms was 852 kg/m^3 at 300°C and 5.57 MPa and 782 kg/m^3 and 400°C and 13.9 MPa.

No thorough explanation is available yet for the observed behaviour. Further research is needed at high pressures to understand which physical phenomena are responsible.

NOMENCLATURE

dp   = dp cell reading, inches of water

Z   = reactor length, m

ε = gas holdup, fraction

ρ = density, kg/m^3

subscripts

e   = empty reactor

full = reactor filled with liquid

g,l = reactor with gas and liquid flowing

l   = liquid

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Table 1 – Specific gravity and viscosity of Zerice oil at
different temperatures

Temperature °C	Specific gravity	Viscosity cSt
21	0.893	–
40	–	42.46
100	0.845	5.87
156	0.815	2.39

Table 2 – Analysis of feed B24 (29-B24-83)

Gravity	°API	6.95
Specific gravity	15/15°C	1.022
Ash	wt %	0.120
Sulphur	wt %	3.34
Carbon	wt %	85.3
Hydrogen	wt %	9.36
Nitrogen	wt %	0.72
R.C.R.	wt %	18.6
Pentane insolubles	wt %	21.5
Toluene insolubles	wt %	trace (<0.1%)
Pour point	°C	–
Softening point	°C	49.5
Chloride	ppm	–
Viscosity at 100°C	cp	2212
Viscosity at 130°C	cp	351.0
Heat of combustion	kJ/kg	42.1
Vanadium	ppm	649
Nickel	ppm	89
Iron	ppm	291
Titanium	ppm	2
Aluminum	ppm	38
Silicon	ppm	20
Sodium	ppm	40
Potassium	ppm	18
Calcium	ppm	14
Pitch (+524°C)	wt %	95.1

Table 3 — D/p cell calibration by draining and
filling reactor

Weight withdrawn /added g	Measured d/p cell reading (in. H_2O)	Calculated reading (in. H_2O)	Error: measured vs. calculated %
Draining reactor:			
-	12.0		
326.0	18.4	18.33	+0.38
796.0	27.6	27.46	+0.51
1256.1	36.6	36.40	+0.55
1853.5	48.1	48.00	+0.21
2397.5	59.0	58.57	+0.73
2980.8	70.8	69.90	+1.29

Total drained: 2980.8 g Zerice
d/p cell reading increased from 12.0 to 70.8, i.e., 58.8
in. of H_2O, which corresponds to 3027.1 g of Zerice;
error 1.55%.

Filling reactor:			
-	70.8	-	-
369.9	64.0	62.715	+2.05
1507.5	41.8	40.615	+2.92
3529.5	1.0	1.235	-19.0

Total filled: 3529.5 g Zerice
d/p cell reading decreased from 70.8 to 1.0, i.e., 69.8
in. of H_2O. This corresponds to 3593.4 g of Zerice;
error 1.81%.

Table 4 – Conditions and gas holdup for runs 83-VD-247 to 265
with hydrogen, and B24 at 300°C,[1]

| Run | Pressure | | Gas flow | Liquid flow | | Gas holdup |
	MPa	psig	cm/s[2]	kg/h	cm/s[2]	ε
247	5.57	793	1.0	3.5	0.056	0.040
248	5.57	793	0.66	2.1	0.034	0.028
249	5.57	793	1.5	2.1	0.034	0.091
250	5.57	793	2.0	2.35	0.038	0.135
251	5.57	793	2.0	6.0	0.097	0.147
252	5.57	793	2.0	2.5	0.040	0.155
253	5.57	793	1.0	2.5	0.040	0.061
254	8.30	1190	1.0	2.0	0.032	0.066
255	8.30	1190	1.47	2.4	0.039	0.099
256	8.30	1190	2.0	2.5	0.040	0.224
257	11.03	1585	1.0	2.7	0.043	0.073
258	11.03	1585	1.5	2.23	0.036	0.181
259	11.03	1585	1.23	2.5	0.040	0.100
260	11.03	1585	2.03	2.4	0.039	0.264
261	11.03	1585	1.75	2.45	0.039	0.187
262	11.03	1585	0.75	2.53	0.041	0.049
263	13.89	2000	1.0	2.58	0.042	0.067
264	13.89	2000	2.0	2.48	0.040	0.347
265	13.89	2000	1.5	2.35	0.038	0.125

[1] Density of B24 = 852 kg/m^3.

[2] At reactor conditions.

Table 5 – Conditions and gas holdup for runs 83-VD-266 to 279
with hydrogen at 13.89 MPa (2000 psig) and B24 at
350°C and 400°C[1]

Run	Temperature °C	Gas flow cm/s[2]	Liquid flow kg/h	cm/s[3]	Gas holdup ε
266	350	1.05	2.65	0.044	0.080
267	350	2.0	2.40	0.040	0.196
268	350	1.43	2.35	0.039	0.128
269	400	0.93	2.5	0.044	0.07
270	400	1.18	2.48	0.043	0.087
271	400	0.71	2.5	0.044	0.045
272	400	1.42	2.5	0.044	0.118
273	400	1.66	2.5	0.044	0.137
274	400	1.89	2.5	0.044	0.179
275	400	2.13	2.5	0.044	0.209
276	400	2.34	2.5	0.044	0.243
277	400	1.89	2.5	0.044	0.177
278	400	1.42	2.5	0.044	0.113
279	400	0.93	2.5	0.044	0.061

[1] density of B4 at 350°C = 817 kg/m^3.

density of B4 at 400°C = 782 kg/m^3.

[2] at reactor conditions; the gas flows at 400°C were calculated assuming 3 vol % methane.
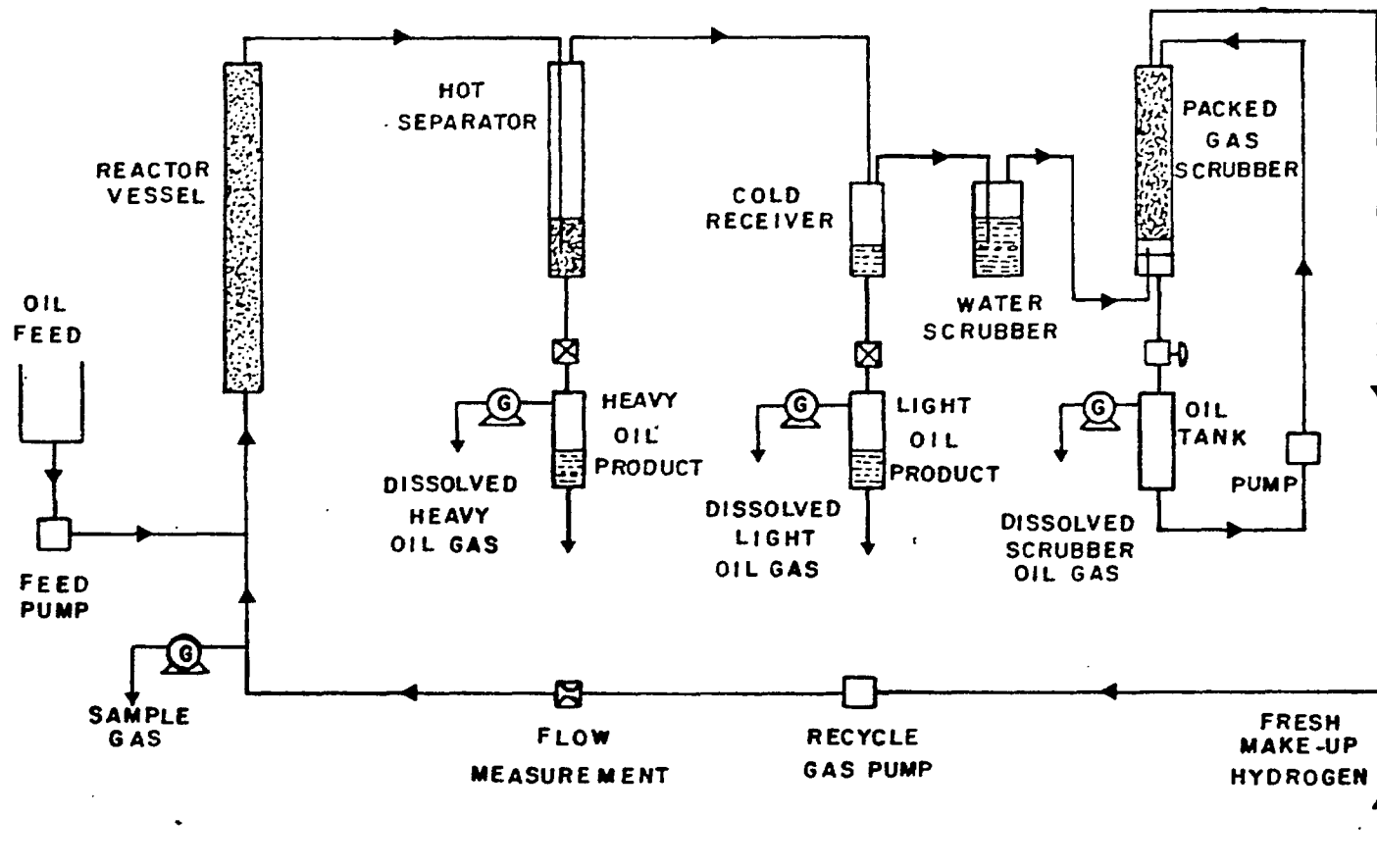
[3] at reactor conditions.
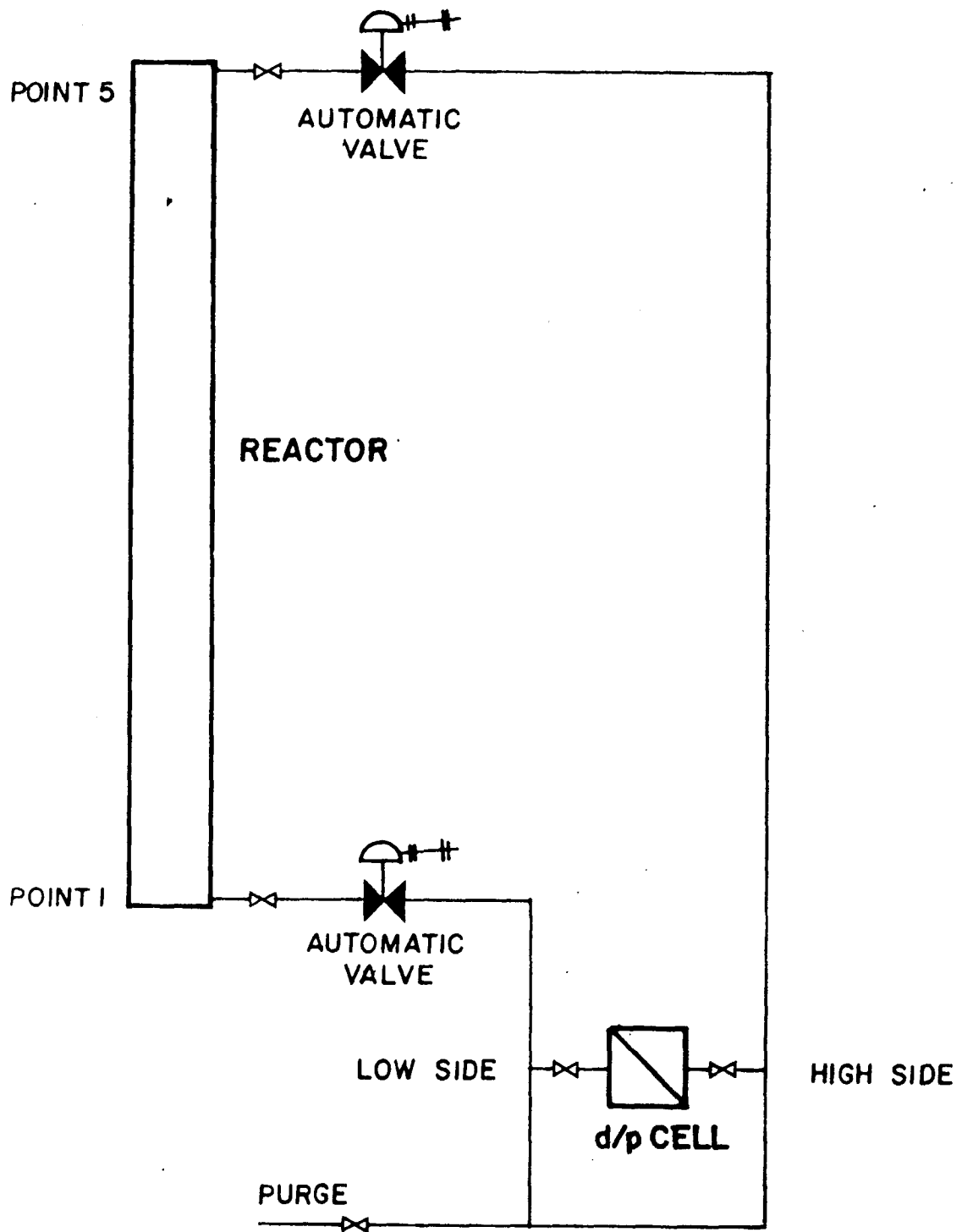
Fig. 1 - Schematic of CANMET hydrocracking pilot plant

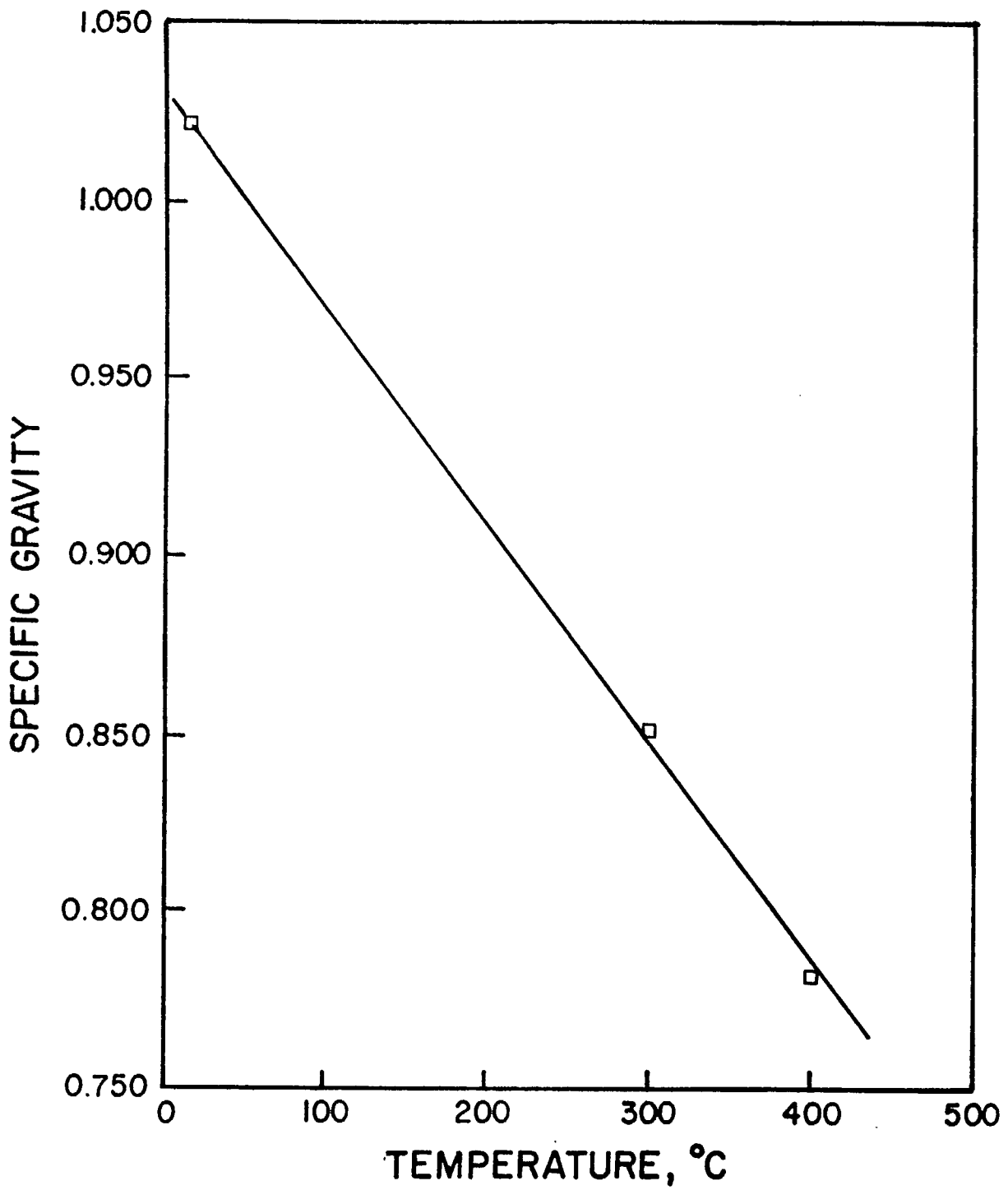Fig. 2 — Schematic of dp cell arrangement

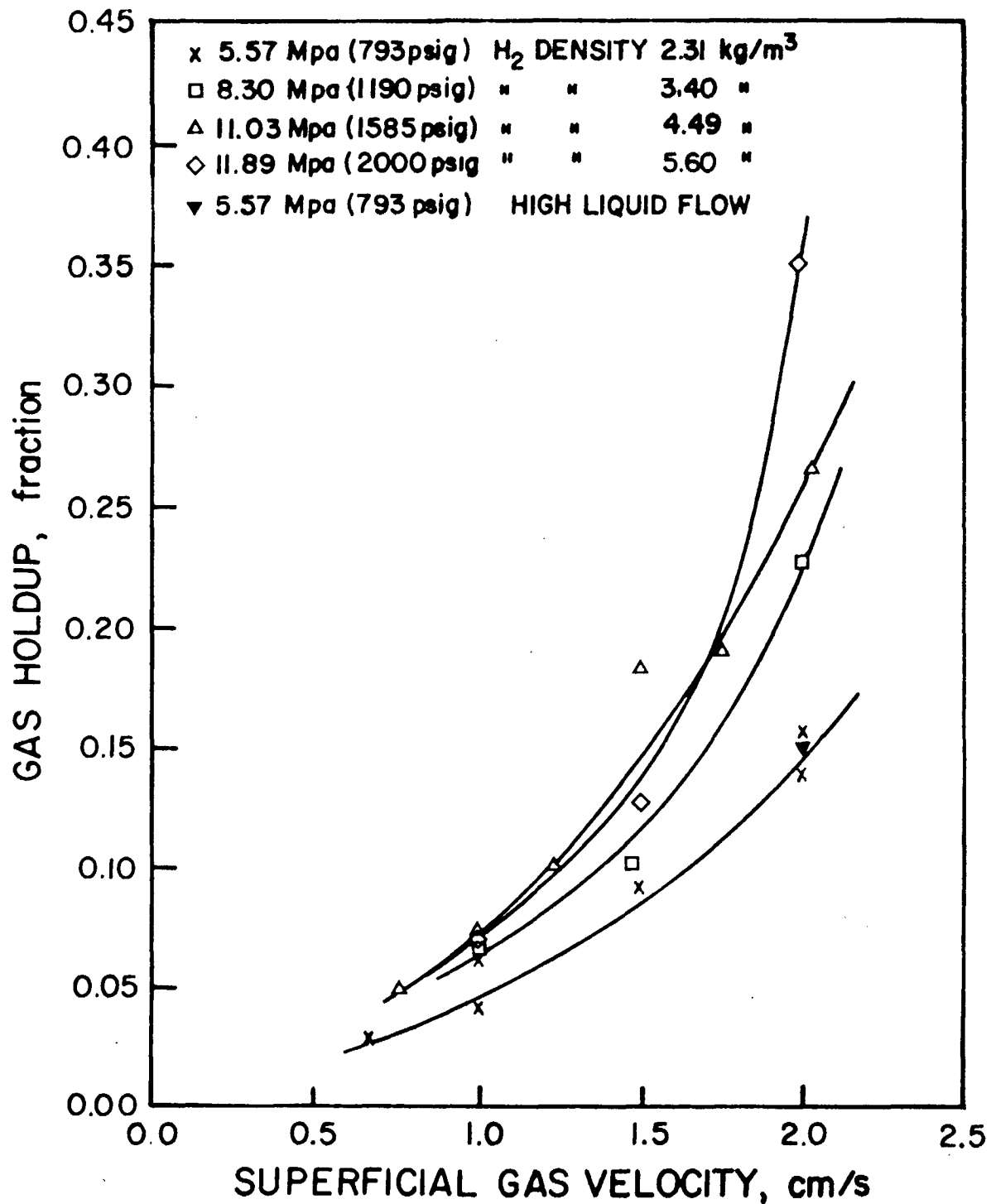Fig. 3 – Specific gravity of feed B24 vs temperature

Fig. 4 – Gas holdup at 300°C at different pressures
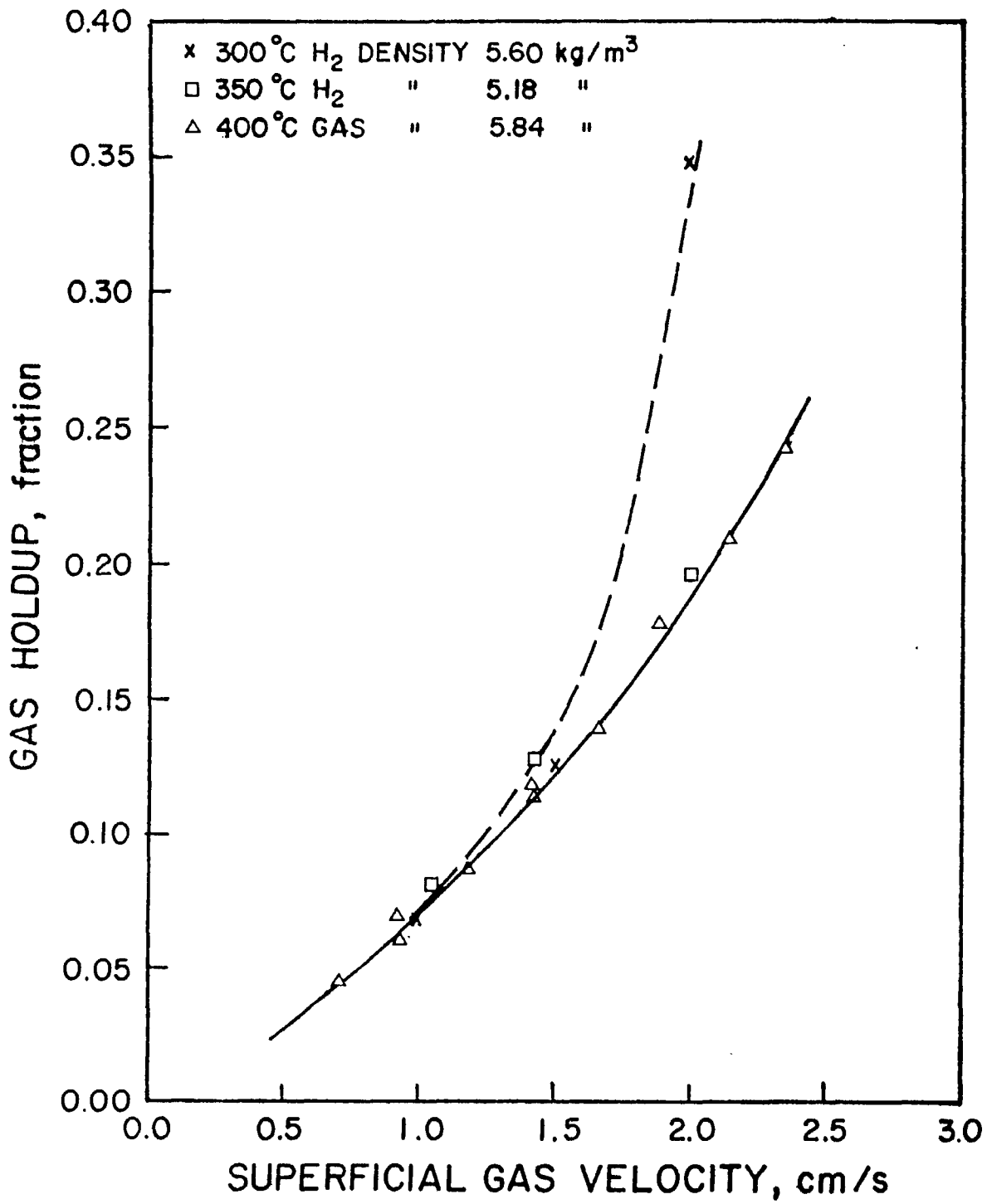vs superficial gas velocity

Fig. 5 — Gas holdup at 13.89 MPa and different temperatures
vs superficial gas velocity