substantially more than that of the molecules in the hump area, i.e., 1,400-1,600 MW. The above speculation is partly supported by the fact that the intensity increase of low mass (56, 57, and 71) peaks was substantially higher at about 380-400°C.

We have, thus, improved our understanding of the sample fragmentation during FIMS analyses. However, we still do not understand the mechanism of fragmentation.

Based on our evaluation of FIMS technique, the following limitations have been identified:

- The extent of fragmentation of the heavy reactor-waxes is not completely understood.
- The response factors of different hydrocarbon types are unknown.
- High-resolution data can be obtained only up to molecular weight of 1300.

D. Analyses of Oxygenates in Fischer-Tropsch Reactor-Waxes

D.1. Low Temperature Liquid Chromatography

For light waxes, a low temperature Liquid Chromatography (LC) method was initially developed and used. An extraction is performed prior to LC to remove as much as possible the components with a carbon number greater than C40. This is necessary to prevent the high carbon number hydrocarbons from eluting with the oxygenated hydrocarbons.

Approximately 1 g of the wax was weighed into a 15 cm³ centrifuge tube. Ten cm³ of pentane was added. The wax was dispersed with a mini-spatula, after which an additional 4 cm³ of pentane was added. The centrifuge tube was capped and carefully shaken prior to centrifuging it for 15 minutes. The supernatant pentane was removed and the extraction was repeated two additional times. The pentane soluble consists mostly of C40-hydrocarbons and oxygenates. The amount of pentane soluble material was obtained by difference after drying and weighing the insoluble fraction.

The combined pentane soluble fractions were further fractionated on a 30 cm x 1.1 cm (ID) Michel-Miller glass column (Ace Glass, Vineland, NJ) packed with 25 cm of 20-44 micron Bio-Sil A silica gel (Bio-Rad, Richmond, CA). Prior to use, the silica gel was activated overnight at 150°C. The column was eluted sequentially with 250 cm³ pentane to remove the

hydrocarbons, 250 cm³ methylene chloride to elute esters and ketones and 150 cm³ methanol to elute alcohols. A Kuderna-Danish concentrator was used to remove the bulk of the solvents. The cuts were then brought to dryness in preweighed inverted rim beakers with a slight nitrogen purge.

D.2. High Temperature Liquid Chromatography

Reactor-waxes containing greater than 5 wt % C60⁺ hydrocarbons were difficult to extract with pentane. In addition, these waxes may contain higher molecular weight oxygenates which may not be completely extracted into pentane. As a result, a general high temperature liquid chromatographic method applicable to most F-T waxes was developed.

Approximately 2.5 g of finely dispersed F-T waxes was loaded on a Michel-Miller column as described above. The column was packed with 40-63 micron Woelm silica gel. The sample was mixed with silica gel on top of the bed to prevent plugging of the column. The temperature was controlled with heating tape and a powerstat. The column was initially eluted with 100 cm³ of n-nonane at 80°C to elute the hydrocarbons and then 75 cm³ of n-propanol to elute the oxygenates. The temperature of the eluting solvents was monitored with a thermometer immediately at the column exit. After an initial run, the temperature settings were readily reproduced for a given column system. The hydrocarbon and oxygenates were brought to dryness as indicated above. Total percent hydrocarbons, oxygenates and loss and/or residue remaining on the column was reported. Table VI-5 summarizes oxygenates results by the high temperature method for two F-T waxes.

E. Routine Product Analyses

Routine product analyses to support other tasks were carried out. Results are reported with the operating results of each tasks.

Table VI-5

Total Uxygenates by High

Temperature Liquid Chromatography Method

(Wt %)

Reactor-Waxes	Run <u>CT-256-3</u> (83 DOS)	Run <u>CT-256-4</u> (Blended)
Hydrocarbons	84	72
Oxygenates	13	22
Residue/Loss	3	6_
	100	100

VII. Task 4 - Slurry Fischer-Tropsch Reactor Hydrodynamic Studies

A. Literature Review

Literature data for slurry bubble-columns were analyzed to determine the effect of gas distributor design, column drameter, static liquid height, gas and liquid physicochemical properties, and experimental conditions on gas holdup and bubble size. The results of this work were used as guidelines for hydrodynamic studies in hot-flow columns.

The literature data are divided into three main areas: studies using F-T derived wax (relatively few); studies using other liquid media; and design criteria for gas distributor design. The data from actual F-T reactor-wax were non-existent. The major F-T derived waxes are FT-200 and FT-300 Vestowaxes from SASOL. These waxes are produced from the Arge tubular F-T reactor with further hydrotreating and fractionation. They contain essentially 100% paraffins. The literature data emphasize the need of:

- Stidies with F-T wax in tall hot-flow columns.
- Studies in large diameter columns operating in the high gas velocity regime.

A.1. Fischer-Tropsch Derived Waxes

The major highlights from literature studies with F-T derived waxes are:

- The data on large-size reactors at high gas velocity are essentially nonexistent.
- Gas holdup is significantly larger and bubble size significantly smaller with F-T derived waxes than with other liquid media.
- The gas holdup and bubble size depend on the type of gas distributor.
 - Sintered-metal plate (SMP) distributors give significantly higher gas holdups than single orifice distributors (Koelbel et al., 1968; and Calderbank, 1963).

- Contrary to the above, Quicker and Deckwer (1981a and 1981b) observed that a single orifice distributor gives higher gas holdups (also somewhat smaller bubbles) than either a multi-hole perforated plate or a SMP distributor.
- The gas holdup is independent of column diameter in the range 4.1-10 cm for columns equipped with SMF distributors (Deckwer et al., 1980).
- Increased static liquid height significantly reduces the gas holdup (Calderbank et al., 1963). Deckwer et al. (1979, 1980) claim no such effect for short bubble-columns (static liquid heights in the range 60-95 cm).
- The gas holdup increases with: decreasing catalyst loading (Deckwer et al., 1979, 1980; Zaidi et al., 1979; and Farley and Ray, 1964); sometimes decreasing temperature (Deckwer et al., 1980), and is independent of type of gas (Koelbel and Ralek, 1980). Koelbel et al. (1968) observed, however, that hydrogen produced somewhat lower gas holdup than nitrogen.
- Transition from homogeneous bubbly to slug flow regime initiates in a 3.8 cm diameter column equipped with a SMP distributor at superficial gas velocities of 2-4 cm/s (Koelbel et al., 1968).
- Foaming occurs at superficial gas velocities >4 cm/s in columns equipped with SMP distributors (Deckwer et al., 1979 and 1980).

Bubble-column hydrodynamic studies with F-T waxes were performed by three groups: in the Sixties in Germany, Koelbel and co-workers (1968); also in the Sixties in Great Britian, Calderbank, and Farley and Ray (Calderbank et al., 1963; and Farley and Ray, 1964). Recently in Germany, Deckwer and co-workers (Deckwer et al., 1979, 1980, 1981; Zaidi et al., 1979; Quicker and Deckwer, 1981).

A summary of the experimental conditions in these studies is given in Table VII-1. Most of the work was done in small diameter columns -- up to 10 cm ID (except Calderbank et al., 1963; and Farley and Ray, 1964 -- up to 25 cm ID), at low gas superficial velocities -- up to 4.5 cm/s (except Farley and Ray, 1964 -- 7 cm/s, and Koelbel et al., 1968 -- up to 23 cm/s).

Table VII-1

		Summe	Summary of Aubble-Column Mydrodynamic Studies	Colum	n Bydro	dynamic !	Studies						:	
ij	8	Column	Distributor	5		ı		Comditions	8		(2)	3		Course 11ty
	Ð		ð	اع	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	51	30	۳	٠	(4)		ł		
(1979, 1980)	4 - 10	001-09	.0075	•	ŝ		91-0	~	143-270	11-4	ŧ	<u>.</u> ~	•	, b
1979;	٠	•	•	1	•	. 7- 3. A	2-14		250-390	•		CO/N3		•
Quicker and Deckwer (1981 asb)	9.5	561	.9, 1.1	67 '7	ŧ	+ .		٠.	330-170	¥	7.T 300	* ×		
Koelbel et al.		ğ	12700.	ı		1-23	01- c	2-60	310-318	- - - - -	• 4	H 2 . H 2	. E.	. <u>°</u>
Calderbenk et el.	5.3	230-460	4	~	2	6-4.5	4	£	365	~	2	1, co	Ę	
Pariey and Ray (1964)	25.4	920	1.9	~		7. 3	2	1-3	365			•		
Eso (1962:	3,2-5.3	46-100	46-100 .00160060	•	ş	6-3.5	9-15	ž	200-230	•	77200		a	
•	•		.3250	-	2					.,	Z.	•		•
•	5.1		305-762 .001003		15	Ţ	2-14		260-267	11.2.25	e Li	N2/CO	Ę	
	S I I	(1) SP - Sintered Plate PP - Perforated Plate SN - Single Norsle	Flate od Plate szło			28£		Molten Pareffin Krupp Wax Product wax	E	(S)	Slag	Acyeneous Bubbly	V (7)	Atm.

The majority of the data was obtained in the homogeneous bubbly (laminar) flow regime, except for Koelbel et al. (1968), who measured gas holdup in the slug and transition from homogeneous bubbly to slug flow regimes as well. It is not clear what flow regimes were covered in the 25 cm diameter column operated by Calderbank et al. (1963) and Farley and Ray (1964).

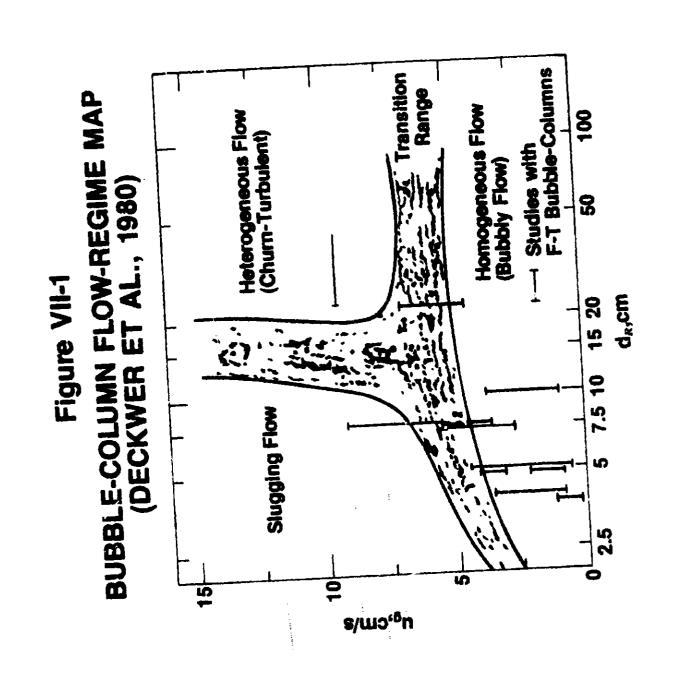
The three flow regimes mentioned above are determined mainly by the column diameter and the superficial gas velocity. Deckwer et al. (1980) plotted a flow regime map (Figure VII-1) which attempts to qualitatively characterize this dependence. At low gas velocities, the gas flow is characterized by bubbles rising rather undisturbed. The bubble size distribution is narrow, and the interaction between bubbles is small. This is the homogeneous bubbly (laminar) flow regime. At high gas velocities, bubble coalescence and disintegration occur and large bubbles may appear. Although the number of large bubbles may be small, they may contribute considerably to the gas flow as they rise fast. This is the heterogeneous or turbulent flow regime. In small diameter columns (<10 cm), the large bubbles may bridge across the column, forming slugs; this is the slug flow regime. In Figure VII-1, the large gray areas represent the transition between the various flow regimes. The boundaries shown in Figure VII-1 are used only for qualitative illustration. The exact boundaries may depend on gas distributor design, static liquid height, operating conditions and gas and liquid media. It is expected that commercial F-T reactors will probably operate in the turbulent regime.

Quicker and Deckwer (1981a and 1981b) obtained higher gas holdups with a single orifice distributor than with a nineteen-hole perforated plate distributor, probably because the orifice Weber number for the former was ~7000 at 4 cm/s superficial gas velocity, while that of the latter was only ~10. The orifice Weber number is defined as the ratio of the gas kinetic energy to the surface energy:

$$We_{o} = u_{o}^{2} d_{o} \rho_{g} / \sigma \qquad (VII-1)$$

It is reasonable to expect that the higher the orifice Weber number, the better the gas distribution, as shown by the data of Quicker and Deckwer.

An orifice Weber number cannot be defined for a SMP distributor, and the higher gas holdup with the single orifice distributor versus that with a SMP distributor cannot be similarly rationalized. It also contradicts other available data (Koelbel et al., 1968; and Calderbank et al., 1963) and Mobil's data described in Section VII.C.



Deckwer et al. (1979, 1980) showed that the gas holdup is independent of column diameter in the range 4.1-10 cm. This is in agreement with the criterion derived from data with liquids other than F-T waxes that wall effects are only important for column-diameter/bubble-diameter less than 40-100. If this criterion is translated to bubble sizes in F-T waxes (0.5-0.7 mm; Quicker and Deckwer, 1981a and 1981b; Deckwer et al., 1980), then wall effects, i.e., column diameter, are not important for dg>5 cm.

The effect of static liquid height can be explained by postulating the existence of a gas holdup profile composed of three zones (Langemann and Koelbel, 1967): a bottom dynamic zone in which bubbles form and eventually attain an equilibrium size distribution; a middle stable equilibrium zone, where the gas holdup may decrease slightly due to the static pressure drop; and a zone with very high gas holdup at the top, in which the bubbles disengage from the liquid within a finite time. Langemann and Koelbel (1967) showed that in a given column the top and bottom zones are independent of the static liquid height, while the middle stable equilibrum zone is longer for taller columns and may completely disappear for short columns. Hence for short columns the zone of high gas holdup occupies a large fraction of the column, leading to high overall gas holdups. The opposite is true for tall columns.

Increased catalyst loading results in increased slurry viscosity, which in turn results in larger bubbles and smaller gas holdup. This explains the results of Deckwer et al. (1979, 1980), Zaidi et al. (1979), Calderbank et al. (1963) and Farley and Ray (1964) on the effect of catalyst loading and viscosity. It contradicts, however, the results of Deckwer et al. (1980) on the effect of temperature: higher temperature results in decreased viscosity and should, therefore, result in higher gas holdup; Deckwer et al. (1980) obtained low gas holdup at higher temperatures in a 4.1 cm diameter column, and no change with temperatures in a 10 cm diameter column. This behavior cannot be satisfactorily rationalized and further study is required.

The contradictory results on the effect of type of gas (Koelbel and Ralek, 1980; and Koelbel et al., 1968) are not understood at this time.

From the above results, it is apparent that the few studies on hydrodynamics with F-T waxes results in many contradictions. Also, these studies deal almost exclusively with the homogeneous bubble-flow regime, and neglect the commercially important turbulent-flow regime.

A.2. Liquids Other Than F-T Derived Waxes

The major highlights from literature studies with liquids other than F-T waxes are:

- Gas holdup is significantly smaller and bubble size significantly larger than those with F-T waxes (Deckwer et al., 1980). Exceptions may be hydrocarbon mixtures (Langemann and Koelbel, 1967).
- The gas distributor design affects gas holdup and bubble size only in the homogeneous bubble-flow regime: single nozzles produce lower gas holdups than perforated and SMP distributors (Ostergaard, 1980).
- Increased static liquid height decreases the gas holdup (Langemann and Koelbel, 1967).
- Column diameter affects gas holdup up to a column/bubble diameter ratio of 40-100 (Shah et al., 1982; Ostergaard, 1980).
- Increased solids loading decreases the gas holdup, while pressure has no effect (Shah et al., 1982).
- Transition from homogeneous bubble to slug or turbulent flow occurs at higher gas velocities with SMP distributors than with perforated plate distributors. When perforated plates with large holes are used, no homogeneous bubble flow can be observed at all (Shah et al., 1982).

There is a vast amount of bubble-column hydrodynamic studies with liquids that are not F-T derived waxes (e.g. see reviews by Shah et al., 1982; Ostergaard, 1980; Van Landeghem, 1980; and Mashelkar, 1970). The common denominator in the bubble size and gas holdup studies is that most were done in air-water systems. Some use other gases and liquids, but the liquids are either pure hydrocarbons or aqueous solutions of alcohols.

The bubble size and gas holdup correlations developed from these studies account for the liquid and gas properties, gas superficial velocity, and column diameter. Some of the major correlations for gas holdup and bubble size are summarized in Table VII-2. When applied to F-T wax conditions, however, these correlations fail, predicting significantly larger bubble size (Quicker and Deckwer, 1981a and 1981b) and smaller gas holdup (Deckwer et al., 1980) than observed. Thus, pure hydrocarbons with the same viscosity, density and surface tension of F-T wax

TABLE VII-2

CONSELATIONS FOR CAS HOLDUP AND BURGLE SIZE (Shah et al. 1982)

Hughmark (1967)	Akite and Yoshide (1973)	Gestrich and Debos (1975)	Bach and Pilhofor (1978)
$c_g = \frac{2 + (0.35/4_g)(g_L/72)}{1/3} 1/3$	$\frac{c_g}{(1-c_g)^2} = \frac{\varphi d^2 \rho_{\perp}}{\sigma}^{1/2} = \frac{\omega_g}{\sqrt{L}}$ $\frac{(1-c_g)^2}{\sigma} = \frac{\varphi d^2 \rho_{\perp}}{\sigma}^{1/2} = \frac{\omega_g}{\sqrt{L}}$ $C=0.2 \text{ for pure liquids and non-electolytes}$ $C=0.25 \text{ for eletrolytes}$	$\frac{d_{B}}{d_{R}} = \frac{d_{R}^{2} g_{A}}{\sigma_{R}} - \frac{10.35}{\sqrt{\frac{2}{4}}} \cdot \frac{g_{A}^{2}}{(\frac{9d_{1}}{4})^{2})^{-9.12}} \cdot \frac{d_{B}}{(\frac{9d_{1}}{4})^{2})^{-9.12}} \cdot \frac{d_{B}}{(\frac{9d_{1}}{4})^{2}} \cdot \frac{1}{\sigma_{B}} $	K = PL ¹³ /µL ⁴ 9 dB = .3 cm EE = 0.115 (
Mange of Parameters Wg, Cm/8:,4-45 dg, cm: >18	ug, cm/m:0.3-40 ul, cm/m:0-4.4 dg, cm:15.2-60 L, cm:126-350	u g, cm/s:1-8 dg, cm:7.56-61 L, cm:2-350	Mg, CM/B: 0-10 48; CM:>10 1. CM:>120
System Air-Mater Air-Karcsene Air-Ka ₂ 80 ₃ eq. soln.	Air-Glycerol Air-Light Oil Air-InCl ₂ ag. solm. Air-Water Air-Methanol O ₂ -Water CO ₂ -Water	Air-Different Liquida	Air-Alcohole Air-Helogeneted Mydrodens

produce 2-3 times larger bubbles and about one-half the gas holdup produced in F-T wax. It may be postulated that mixtures of hydrocarbons behave differently from pure hydrocarbons. This is supported by the very high gas holdups obtained by Langemann and Koelbel (1967) using a hydrocarbon mixture they called mineral oil. It follows that results obtained using liquids other than F-T waxes may only be used as qualitative guidelines.

A.3. Criteria for Orifice-Type Feed-Gas Distributor Design

General criteria for gas distributor design are given by Mersmann (1977) and Pilhofer et al. (1978). For perforated plates or tubes with small diameter orifices, the design criterion is:

We_o > 2;
$$d_o < d_o^* = 2.32(\sigma/\rho_g) \cdot \frac{5(\rho_g/(\rho_L - \rho_g))}{5}$$
 (VII-2)

Physically, Equation (VII-2) implies that good gas distribution is obtained if the gas kinetic energy at the orifice exceeds the surface energy due to surface tension. For larger orifice diameter, good distribution and "rain" through the holes is prevented if:

$$Fr_o^2 (\rho_{\rm g}/(\rho_{\rm L}-\rho_{\rm g}))^{5/4} > .37; d_o > d_o^*,$$
 (VII-3)

where From the Eroude number. The Froude number is a ratio of the kinetic energy to the potential energy.

An additional consideration for gas distributor design is the allowed maximum pressure drop across the distributor. The pressure drop across a perforated plate may be estimated by the conventional orifice equation (Fair, 1987).

$$\Delta P = (\rho_g/2g) (u_O/C_V)^2 \qquad (VII-4)$$

Equation (VII-4) neglects the velocity of approach to the orifice. According to Fair, a good approximation for $C_{\rm v}$ is 0.8. A more detailed discussion of this subject is given in the next Section.

Literature data on gas distributors used in F-T bubble-column reactors were analyzed and compared with criteria (VII-2) and (VII-3). The results are shown in Table VII-3. It is apparent that the designs are very conservative compared to

Table VII-3

Gas Distributor

Designs in F-T Bubble-Columns

		Quick Deckwer (1	er and 981a and b)	Farley and Ray (1964)
Column	d _R , cm	9.5	9.5	24.8
Orifice	no, mm do*,mm do, mm uo, cu	1 0.9 2 4	19 1.1 2 4	1 19.1 2 7.2
Conditions	T, [°] C P, MPa ΔP, MPa We _O Fr _O	130-170 0.1 1.0 0.007 7,720	130 170 0.1 1 0 0.007 11.4	275 1.14 0.014 550 1.05

criterion (VII-2). For example, Quicker and Deckwer (1981a and 1981b) used a single orifice with Weo = 7220 at 4 cm/s superficial gas velocity. Even Quicker and Deckwer's perforated plate had Weo = 11.4, which is 5 times larger than that required by Equation (VII-2). Data by Farley and Ray (1964) indicate that the Froude number satisfies criterion (VII-3), although this design appears considerably less conservative than that of the smaller orifices used in the other works. Note that Quicker and Deckwer obtained significantly higher gas holdups with a single orifice than with a nineteen-hole perforated plate. This is consistent with the higher Weo for the single orifice. In general, it would appear that for small orifices, the higher Weo, the better the gas distribution.

The importance of the distributor design depends on the flow regime, the physical properties of the liquid medium, and even the height of the column. Thus, literature results indicate that distributor design may not be important in the turbulent-flow regime, or for liquid media which favor bubble coalescence and disintegration, or for very tall columns (e.g., Shah et al., 1982; Mashelkar, 1970). In addition, other criteria may replace criteria (VII-2) and (VII-3) (e.g., Kastanek et al., 1980; Bhavaraju et al., 1978; Kurten and Zhner, 1979; Shah et al., 1982). These shall be further examined.

B. Pressure Drop Across Orifice-Type Feed-Gas Distributors

The pressure drop across gas distributors is an important consideration for both pilot-plant studies and evaluations of commercial designs. For this reason, a correlation from the literature was used to predict the pressure drops across orifice-type distributors used in our hydrodynamic studies. While the predicted values nearly always underestimate the experimental results obtained in our studies, the use of the correlation enabled us to avoid potential problems with either excessive or too low a pressure drop.

The working equation for weight rate of discharge through an orifice, adopted by the ASME Research Committee on Fluid Meters is (Perry, 1973):

$$w = C_0 Y A_f [2x10^7 (\Delta P) \rho_g u/(1-\beta^4)]^{1/2}$$
 (VII-5)

In our studies with small orifices, the value of β can be assured negligible, and the value of C_0 is held constant at 0.61. Equations for the expansion factor (Y) as a function of the downstream to upstream pressure ratio (r) can be theoretically derived for either adiabatic or isothermal flow. However,

neither gives satisfactory results as the flow becomes supercritical (r less than about 0.53 for most gases). For this reason, a correlation by Cunningham (1951) was used.

In his paper, Cunningham experimentally measured the value of the gas expansion factor through various orifices for both sub- and super-critical flows. All the data was taken with air at room temperature, which differs from our case of hot (>204°C) gases expanding into a somewhat hotter liquid medium. Pipe-taps were used for the DP-measurements. The author recommended that for high pressure ratios (r>0.77) the expansion factor is represented well by an ASME-proposed relation:

$$Y = 1 - [0.333 + 1.145(\beta^2 + 0.7\beta^5 + 12\beta^{13})](1-r)/\gamma$$
 (VII-6)

At low pressure ratios (r<0.77) however, the author presents the following:

$$Y = Y_{0.77} - .364 (.77-r)$$
 (VII-7)

where $Y_{0.77}$ is the value of Y from Equation (VII-6) at r = 0.77.

Comparison of the correlation with actual data from our bubble-columns is shown in Table VII-4. The pressure drop reported here is the difference between the feed-gas pressure and the downstream pressure. It is seen that the equation over-predicts the pressure drops from the hot-flow bubble-column, and under-predicts the values from the small bubble-column reactor (Unit CT-225). However, this is the best agreement we were able to obtain, and use of the equation prevented unusually high or low pressure drops.

Using this correlation, we have prepared a graph (Figure VII-2) showing enjected pressure drops across various orifices in the BSU bubble-column reactor. The values were calculated for reactor conditions of 2.51 MPa, 260°C, and 0.7 H2/CO ratio feed-gas. The plot helped us select orifice-type distributors for both the BSU bubble-column and the new hot-flow columns.

When the 1 mm orifice distributor was repaired after 76 days on-stream during Run CT-256-7, pressure drops across it were measured using nitrogen and synthesis gas at various pressures and temperatures. The results were then compared with the calculated values, as shown in Figure VII-3. The agreement is excellent, and the wide range of pressure drops indicate that the correlation may be used with confidence.

Comparison of Calculated and Experimental Pressure Drops Through Orifices

Unit CT-225; 0.10 MPa, 25°C, 0.37 mm Orifice

Superficial Gas Velocity, cm/s	Measured ΔP	Calculated
3 5	8	4.4
5	17	10.6
7	26	17.9
10	45	30.0
Unit CT-225; 2.17 MPa, 25	O*C, 0.37 mm Orifice	_
1	8	3.4
1.4	15	7,2
1.8	20	11.2
5.1 cm ID Hot-Flow Bubble 0.25 MPa, 260°C, 1 mm Ori:	-Column (Unit CT-284);	<u>L</u>
1	0.5	0.2
3	1.3	1.8
5	3	4.7
8	7	11.1
	•	44.4

