4.4 Catalyst Testing Plant and Procedure

4.4.1 Fixed-Bed Reactor System

The process flow diagram for the existing fixed-bed pilot plant is in Figure 4-4. A premixed blend of CO, H_2, and Ar contained in an aluminum cylinder is compressed to about 205 atm and then flows through a capillary restriction where flow is controlled by regulating the pressure drop across the restriction. The feed gas then passes through a fixed bed of γ-Al_2O_3 particles at about 208°C where iron carbonyl contaminant decomposes. The feed then flows downflow through the fixed-bed reactor situated in an electric furnace. Three different reactors were used. Tests with C-73-1-101 reference iron catalyst and ruthenium catalysts early in the program used reactors with 1/2 inch ID stainless steel catalyst section. One type of reactor had a 12-inch long catalyst zone and the other a 20-inch long zone. Later in the program, ruthenium catalysts were tested in a 7/8-inch ID glass-lined fixed-bed reactor. The glass lining was used in order to prevent iron carbonyl formation from reactor walls. The pilot plant also has H_2 addition capability at the inlet of the reactor. The flow out of the reactor passes through a series of product collectors and is then metered by a wet test meter.

4.4.2 Product Collection and Overview of Analytical Procedures

The wide range of Fischer-Tropsch synthesis products requires a multi-step collection and analysis system. This system is described in detail in Figure 4-5. The first separation is done in two identical, alternating vessels at reactor pressure and 115°C. The vessels are located in an insulated box where uniform separation temperature is maintained by circulating heated air. Here, an aqueous and an organic phase are collected. The products include water and some of the C_{20} and heavier hydrocarbons and oxygenates. These products were

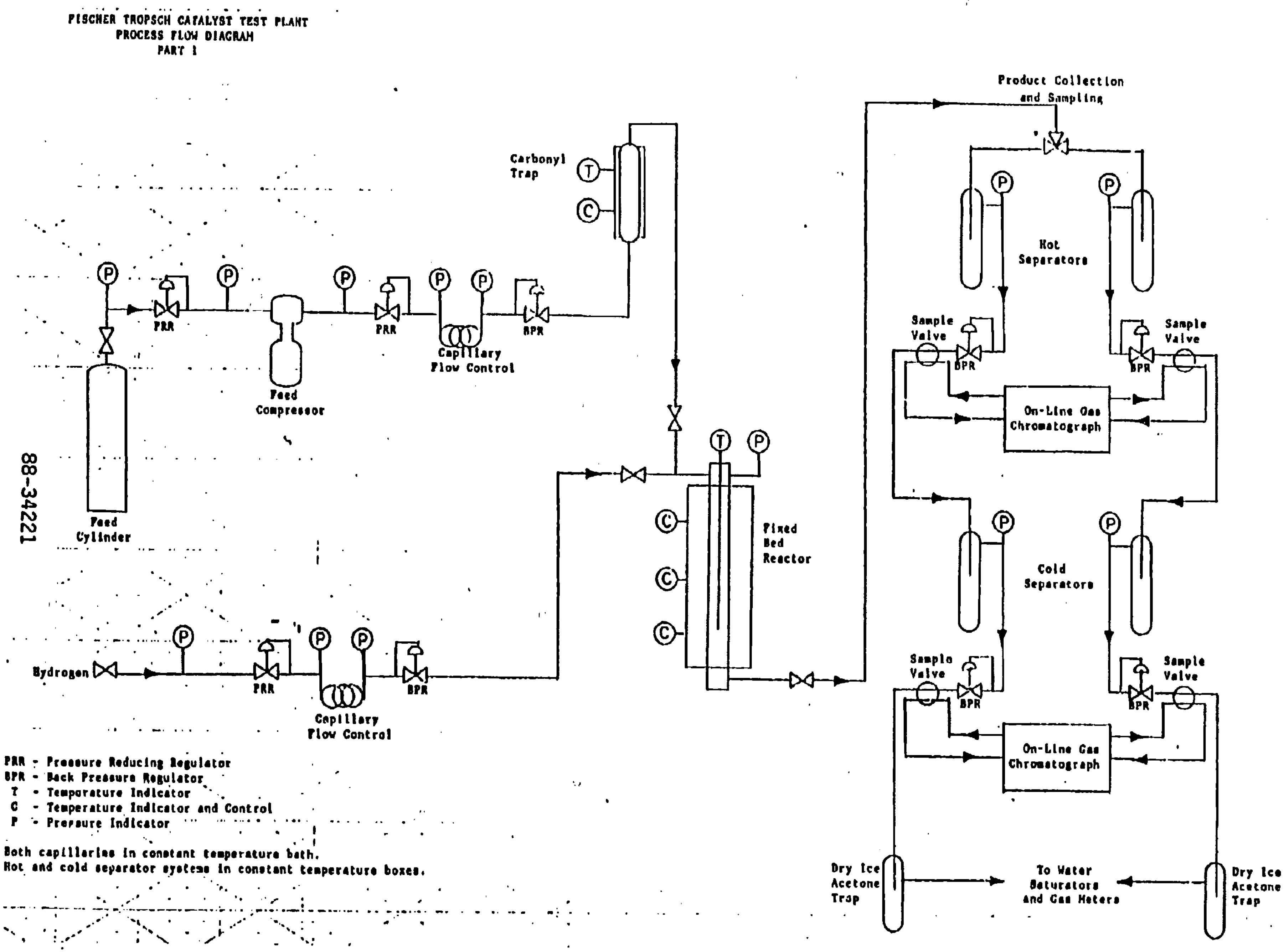


Figure 4-4 Integrated Fischer-Tropsch Pilot Plant

88-34221

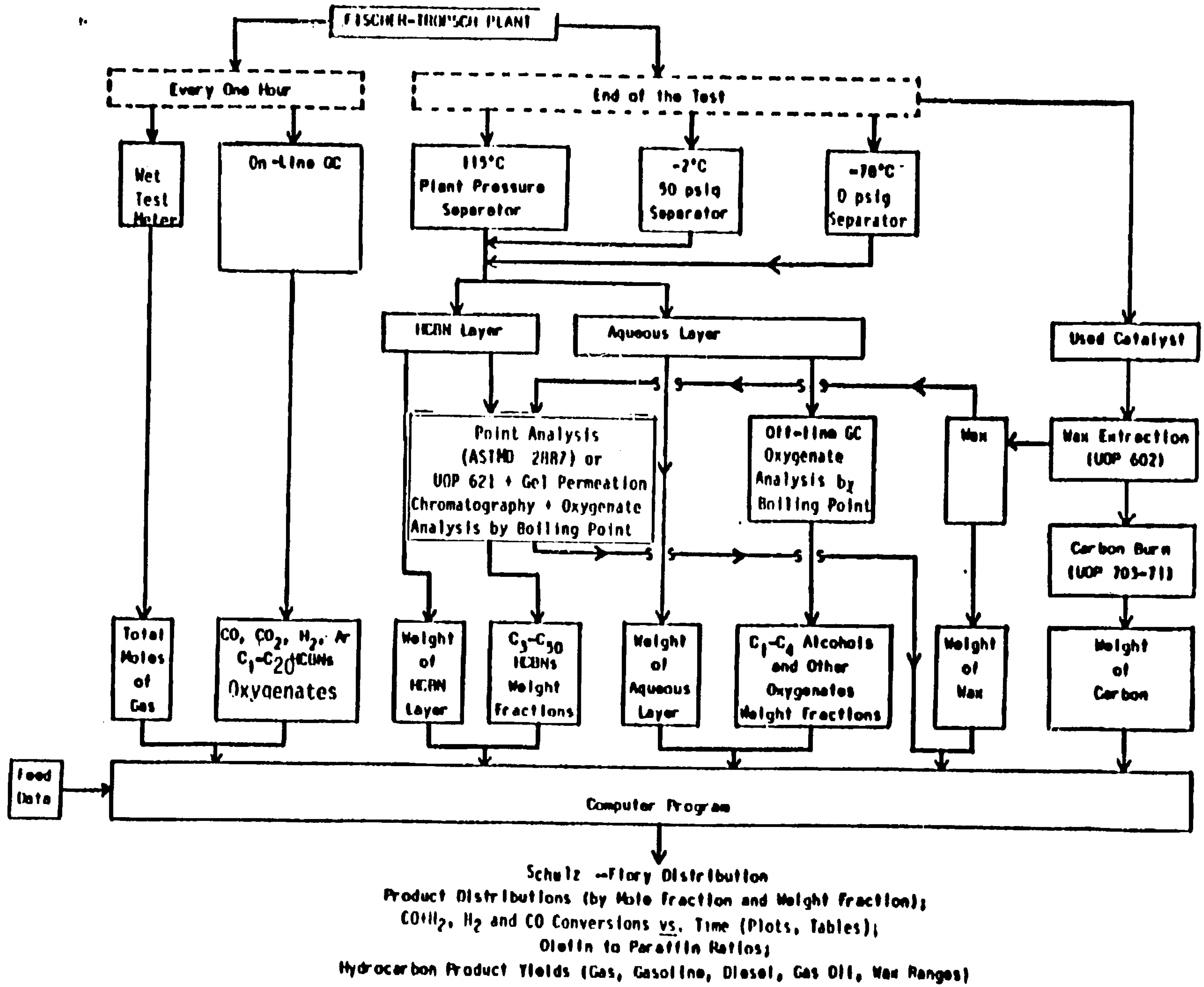


Figure 4-5 **Fischer-Tropsch Run Analysis Procedure**

weighed in the separators' removable glass liners and later analyzed separately by gas chromatography (GC) and gel permeation chromatography (GPC).

Regulators on the gas lines leaving these separators control the reactor pressure. The first on-line gas chromatograph (GC) analyzes the gas leaving these hot separators for hydrocarbons and oxygenates in the range of C_1 to C_{20}. A detailed description of both on-line instruments is given in the next section.

The second separation is also done in two alternating vessels in an insulated box with forced air circulation to maintain a uniform temperature. Here, glass vessels are maintained at 0°C and 4.4 atm for the collection of some of the remainder of the aqueous phase, and of the organic phase containing hydrocarbons and oxygenates in the range of C_5 to C_{20}. These products are analyzed by gas chromatography at the end of the run to verify the results of on-line analysis.

The pressure in the cold separator is controlled by regulators on the exiting gas lines. The second on-line GC analyzes the gas leaving the cold separator for total gas composition including CO, CO_2, H_2, Ar and hydrocarbons in the range of C_1 to C_5. The results of the hydrocarbon analyses are also used to verify the first on-line analyzer.

The second on-line GC was not installed on the plant during Runs 1-14. For these runs the gas leaving the 0°C separator was analyzed off-line by GC. Results from this GC were utilized beginning with Run 43.

Finally, the remaining gas product is sent to traps operating at atmospheric pressure in dry ice and acetone baths for the collection of mostly C_5 to C_{10} hydrocarbons.

4.4.3 Pilot Plant On-Line Analytical Equipment

The on-line analyses of the gas products from the Fischer-Tropsch catalyst test plant provide immediate feedback on the catalyst performance. This section gives a detailed description of the on-line analytical systems.

The first on-line analysis is done on the gas stream leaving the heated separator. The sample is taken with a heated switching valve, after the pressure is reduced, to ensure that a representative gas phase sample is sent to the gas chromatograph (GC). The stream is analyzed once every hour; the analysis takes 57 minutes. The instrument is calibrated once a week, and at the beginning and end of each run.

The instrument used for the analysis is a Hewlett Packard 5880A GC. The components currently quantified are C_1 through C_{20} hydrocarbons in the range of 1 to 2000+ mole ppm. The analysis is done with a hydrocarbon carrier gas on a cross-linked methyl silicone capillary column, HP PONA, coupled with an HP single flame ionization detector.

The analytical results obtained with the first on-line GC were used for monitoring the catalytic performance during the run and were not used for calculating the overall product distributions at the end of the run.

The second on-line analysis is done on the gas stream leaving the cooled separator at 0°C. The sample is taken with a heated switching valve, after the pressure is reduced, to ensure that a representative gas-phase sample is sent to the GC. The stream is analyzed once an hour; the analysis takes 55 minutes. A reference calibration blend is analyzed every day to check the reliability of the GC instrument. The instrument is calibrated at least once a week and at the beginning and end of each run.

The instrument used for this second analysis is another Hewlett Packard 5880A GC. The following components are quantified in the analysis:

Hydrogen	Propylene
Helium	Propane
Composite Oxygen and Argon	Composite 1-Butene and Isobutene
Nitrogen	Isobutane
Carbon Monoxide	Normal-Butane
Carbon Dioxide	Trans-2-Butene
Methane	Cis-2-Butene
Ethylene	Isopentane
Ethane	Normal-Pentane

The detection range is 0.1 to 100 mole %. The analysis is done in four parts, then the data are integrated for the reported results. In all cases an HP Dual Thermal Conductivity Detector is used. The first part of the analysis is for hydrogen and uses a 13X molecular sieve packed column with helium carrier gas. The second part of the analysis is for the O_2, Ar, N_2, C_1, CO, and the separation is done with a 13X molecular sieve packed column with hydrogen carrier gas. The third part of the analysis is for CO_2, C_2, and C_2= and the separation is done with a Poropak Q column with hydrogen carrier gas. Finally, the C_3 through C_5 hydrocarbons are separated by a combination of a Squaline column and a BEEA column with hydrogen carrier gas.

The analytical results with the second on-line GC were used for calculating the overall product distributions at the end of Runs 15-47. In Runs 1-14 the effluent from the cooled separator at 0°C was analyzed off-line.

4.4.4 Off-Line Analytical Procedures

4.4.4.1 Analysis of Gas Leaving the 0°C Separator

A proprietary UOP method was used for off-line analysis of gas leaving the 0°C separator.

At low $CO+H_2$ conversion, the amounts of ethane, ethylene, propane, propylene, butane, and butylene were each less than 0.1% in the effluent gas. Since these are very close to the detectability limits in the UOP method, desired accuracy for the C_2-C_4 hydrocarbon was not obtained. For other runs, an improved GC analysis technique was used for detecting the hydrocarbons in the effluent gas, with significantly higher precision.

4.4.4.2 Analysis of Oxygenates

Another UOP method developed for water and C_1-C_4 alcohols was used for the GC analysis of the aqueous layer samples in Runs 3, 6, 7, and 8. Some experimental difficulties were, however, encountered during several of these measurements, i.e., baseline shift, very long elution times, unknown peaks. An alternate GC technique was used in subsequent runs to analyze the aqueous products. This analysis is performed with a boiling point column using dioxane as an external standard and an FID detector. Retention times and response factors were determined for C_1-C_9 alcohols and aldehydes by using calibration blends. The fraction of the sample that was not detected by the FID detector was taken to be water. The amounts of water calculated in this manner were later found to be in agreement (within 2%) with independent quantitative determination of water via Karl Fischer analysis.

Most of the oxygenates were in the organic phase. C_2-C_{20} alcohols and aldehydes were present in the organic phases collected in the two cooled separators (at 0°C and at -78°C). These oxygenates were detected along with the hydrocarbons present using the same PONA column that was used in the first on-line GC.

Oxygenates were also present in the organic phase collected in the heated separator. However, the GC method used for analyzing this phase identified the compounds that are present by boiling point ranges and assigned carbon numbers based on the boiling points of the n-paraffins. Accordingly, the oxygenates were typically lumped together with the n-paraffin having 2 higher carbon number.

Measurement of oxygenates in the organic phase from the heated separator would have required separating the heavy hydrocarbons with higher than 30-40 carbon numbers, i.e. by distillation prior to GC analysis. This kind of approach was not taken in order to reduce analytical costs.

4.4.4.3 Analysis of Organic Phase by GC

Products in the carbon number range C_3-C_{55} were analyzed by the ASTM D2887 chromatographic boiling point method.

4.4.4.4 Analysis of Organic Phase by Gel Permeation Chromatography

Size separation of the hydrocarbons by gel permeation chromatography was done with a Waters ALC/GPC Model 150C Chromatograph, equipped with a differential refractometer as the detector.

A 50 µl sample of a 0.25% solution of Fischer-Tropsch wax in ortho-dichlorobenzene (ODCB) was separated on a set of ASI Ultragel 0.2-5.0 nm, 0.2-10 nm, 30 cm x 7.8 mm columns. The injector and detector were maintained at 100°C. ODCB flow rate was 4.8-5.0 mL/min. A Waters Model 730 Data Module was used to monitor the detector response. The charge speed was set at 1 cm/min. The separation columns were calibrated by analyzing C_6 through C_{60} n-paraffin standards and a polyethylene polymer with an average carbon number of 144. Retention time was related to carbon number, and a third order calibration curve was established. The results reported, for hydrocarbons C_{144} through C_{250} were calculated by extrapolating the third order plot beyond the calibrated carbon number range. The instrument was calibrated to generate a third order plot before each set of GPC measurements. Also, the correlation between responsefactor and carbon number was established by analyzing known blends of C_{12}-C_{60} n-paraffins. This correlation was also used for determining the response factor for hydrocarbons with carbon numbers greater than 60.

GPC results indicate that the products collected in the high temperature-high pressure separator and the wax recovered from the used catalyst contain a significant fraction of hydrocarbons with carbon numbers greater than 55. These hydrocarbons are not detected by GC (most stay in the capillary column). Beginning with Run 11, the weight of the samples analyzed by GC was corrected by omitting the fraction of the sample not detected by GC according to the GPC analysis.

4.4.5 Conversion and Selectivity Calculations

The results of GC and GPC analyses of hydrocarbons, other products and unreacted gases were fed to a computer program for calculation and graphical presentation of:

1. CO, H_2 and CO+H_2 conversions
2. H_2:CO usage ratios
3. CO selectivities of CO_2 to CH_4, and to C_2-C_4 olefins and paraffins
4. Olefin to paraffin ratios
5. Overall hydrocarbon product distributions by GC (with and without oxygenates)
6. Overall hydrocarbon distributions by GC and GPC
7. Hydrocarbon distributions and selectivities to different carbon number ranges

8. Chain growth probabilities

9. Total amount of hydrocarbons, oxygenates and water made

10. Amount of wax extracted from the used catalyst

11. Amount of coke on the used catalyst

12. Weight recoveries (total, argon and elemental for C, H, O)

13. Catalyst maximum temperatures

Argon was present in the feed at the 5 to 6% level (by mole) and was used as an internal standard to determine the conversion of the feed gas, i.e.:

$$\%\ CO\ Conversion = \frac{\left(\frac{CO}{Ar}\right)_{feed} - \left(\frac{CO}{Ar}\right)_{product}}{\left(\frac{CO}{Ar}\right)_{feed}} \times 100$$

H_2 and $CO+H_2$ conversions were calculated similarly. Selectivity calculations were done in the following manner:

$$\%\ CO\ Selectivity\ to\ CO_2 = \frac{\left(\frac{CO_2}{Ar}\right)_{product}}{\left(\frac{CO}{Ar}\right)_{feed} - \left(\frac{CO}{Ar}\right)_{product}} \times 100$$

$$C_n\ Selectivity,\ \% = \frac{\left(\frac{C_n}{Ar}\right)_{product} \times n}{\left(\frac{CO}{Ar}\right)_{feed} - \left(\frac{CO}{Ar}\right)_{product}} \times 100$$

where n is the number of carbon atoms in one molecule of hydrocarbon C_n. The calculation of selectivity of CO to CO_2 is similar to the calculation of selectivity to methane for which n=1.

H_2:CO usage ratio was equal to the moles of H_2 converted divided by the moles of CO converted. It was calculated in the following manner:

$$H_2\text{:CO Usage Ratio} = \frac{H_2 \text{ Conversion, \%}}{\text{CO Conversion, \%}} \times H_2\text{:CO Feed Ratio}$$

4.4.6 Catalyst Testing Procedure

Ground catalysts were loaded into the fixed-bed reactor in reduced form under N_2.

In Runs 1-33 the temperature was then raised under H_2 flow at 1 atm to reaction temperature. The reactor was then pressurized with He to 14 atm above the reaction pressure for a 1 hour pressure test. Then, the pressure was lowered to reaction pressure and synthesis gas was introduced. The start-up procedure for Runs 34-40 was similar to that of Runs 1-33 except for the pressure test, which was conducted with H_2 at 14 atm above the reaction pressure and at reaction temperature. In Run 41 the reactor was first pressure tested with H_2 at 14 atm above the reaction pressure at room temperature. Then, H_2 was depressured, synthesis gas was introduced and the pressure raised to reaction pressure. Then, the temperature was raised to reaction temperature in 53 hours. The start-up in Runs 42-47 was similar to that in Run 41 except the temperature was raised to reaction temperature in about 2 hours.

The catalyst temperature control point was 2-4 inches above the catalyst inlet. Inlet temperatures in the range 200-250°C, pressures in the range 14-103 atm, H_2:CO feed ratios in the range 0.9-3.0, and testing times from 1/2 day to 70 days were used. The catalysts were diluted with alumina powder or quartz sand for most runs to prevent the occurrence of excessively high temperatures due to reaction heat. Accordingly, the temperatures in the catalyst bed typically did not exceed the inlet temperature by more than about 10°C.

4.4.7 Catalyst Testing Conditions

The testing conditions for all the runs conducted in this work are described in Table 5-1.

It is important to point out that the demonstration of the new modified ruthenium catalyst was conducted at 62 atm, which is higher than that used in current commercial Fischer-Tropsch processes. A systematic study of the effect of total pressure on the catalytic performance of the new modified ruthenium catalyst has not been made because of the limitations of research funds. Also, it is not presently clear whether the use of very high pressures is detrimental to the overall process economics.

5.0 RESULTS AND DISCUSSION

The results in this work are presented in three groups.

The first group of results describes the work done for establishing the experimental procedures.

Under the first group, the application of gel permeation chromatography for determining the carbon number distribution in Fischer-Tropsch wax is described.

Included in the first group is a description of the work done with the reference C-73-1-101 iron catalyst. This section includes STEM and XRD examination results with the iron reference catalyst. These results demonstrate that the catalyst characterization techniques used in the program give expected results for the iron reference catalyst, i.e., relatively large iron particles with wide size distribution. This section also includes fixed-bed pilot plant testing of the iron reference catalyst under four different sets of operating conditions. These results establish the catalyst testing and the analytical procedures for the rest of the program, and also establish reference performance in the pilot plant at relatively low α's (chain growth probability).

The first group of results also includes the application of the proprietary reverse micelle technique to the preparation of supported ruthenium catalysts of controlled particle size. First, characterization of the reverse micelle solutions by SAXS is described. Also included in this section are the descriptions of highly dispersed ruthenium catalysts prepared by conventional aqueous impregnation techniques. Various techniques have been investigated to identify techniques most suitable for characterizing particle size in ruthenium catalysts. These results indicate that STEM, EXAFS, and gas adsorption are suitable.

The second group of results describes the work done for selection of the most promising catalyst development approach. These approaches include a non-Anderson-Schulz-Flory catalyst approach which would result in a hydrocarbon cutoff at a carbon number of about 20 and an Anderson-Schulz-Flory catalyst approach with minimal selectivity to light ends. The second approach was selected for further work.

Under this second group of results, first, control of ruthenium metal agglomeration in supported ruthenium catalysts is described. Suppression of ruthenium agglomeration during Fischer-Tropsch synthesis is essential for investigating the validity of hydrocarbon cutoff hypothesis with small ruthenium particles. This group of results also describes the investigation of the hydrocarbon cutoff hypothesis. These results indicate that hydrocarbon cutoff did not occur. Then, ruthenium metal particle size effects and support effects on activity and selectivity in Fischer-Tropsch synthesis are described. Also, the effect of operational conditions with catalysts having ~5 nm ruthenium particles is described. These sets of results establish that ~5 nm size ruthenium particles were suitable for achieving low light ends selectivity. Finally, under the second set of results, the work done for determining the developmental needs with catalyst systems with low light ends selectivity is described. This set of results established that stability improvement was needed.

The third set of results describes modification of the catalytic composition for improving stability. Performance of the best ruthenium catalyst in a 1650-hour-stability test is then described in detail. Finally, the coke on used ruthenium catalysts used in Runs 39, 46 and 47 are characterized.

Forty-seven runs were conducted with the reference iron catalyst and with various experimental ruthenium catalysts. The catalyst descriptions, operating conditions, some of the key results and percent weight recoveries for these runs are summarized in Table 5-1.

The list of ruthenium catalysts evaluated in this work and their properties are summarized in Table 5-2.

Table 5-1

Run Summary Data for Plant 700

Run	Catalyst Wt. (g)	Catalyst Vol. (cc)	Catalyst Ru (%, wt.)	Catalyst Number	α-Al_2O_3 wt. (g)	Reactor	Bed Length (in.)	Inlet Temp. (°C)	Max. Catalyst Temp. (°C) (During Hours)	Outlet Press. (atm)	Feed H_2:CO (Molar)	Feed Rate (scc/min)	Feed GHSV (hr^{-1})	Hours	Outlet H_2:CO Ratio (Molar)	Outlet Olefin/Paraffin Ratio (Molar) C_2	C_3	C_4	H_2:CO Usage Ratio
1	21.40	10.0	No	4966-2	0	1 (stainless steel)	4 1/2	250	320 (46)	35	1.5	401	2400	30-78					
2*	6.42	3.0	No	4966-4	25.47	"		250		35	1.5	120	2400						
3	6.42	3.0	No	4966-5	25.47	"	7	250	262 (18)	35	1.5	120	2400	28-55	2.2	1.3	3.3	3.0	1.0
4*	19.26	9.0	No	4966-6	76.41	"	6	250	536 (1.5)	35	0.9	708	4710						
5*	14.27	6.7	No	4966-7	56.60	2 (stainless steel)	16 1/4	250	269 (19)	35	0.9	566+ 94	5080+ 850						
6	6.42	3.0	No	4966-8	45.00	"	12	250	367 (1)	35	0.88	283	4650	14-38	0.79	2.7	3.0	1.9	1.1
6	6.42	3.0	No	4966-8	45.00	"	12	250		35	0.88	189	3800	38-60	0.82	1.2	3.0		1.1
7	6.42	3.0	No	4966-12	42.00	"	13 1/8	208	223 (16)	35	0.88	47	950	38-116	0.80	2.6	2.9	1.0	1.1
8	6.42	3.0	No	4966-13	42.00	"	9	208	213 (3)	103	0.88	24	475	32-108	0.00	1.1	1.1	3.4	1.4
9	20.00	75.0	1.19	4966-21	0	"	17 1/2	207	218 (2)	103	0.88	94	75	0-81	0.80	0.5	0.4	0.4	
10	6.42	3.0	C-73-101 Iron cat.	4966-34	0	"	11 3/4	208	210 (28-212)	35	0.88	57	1140	0-252	0.80	2.4	2.2	1.7	1.4
11	22.0	81.3	0.988	4956-27	0	"	16	208	218 (4)	35	0.5	99	73	0-56					
12	21.5	79.4	1.3	4956-30	0	"	18 1/4	208	217 (1)	35	0.9	94	71	0-142					
13	10.93	40.4	1.1	4956-22	0	2 (glass lined)	4	208	214 (2)	35	1.3	57	84	0-56					
14	13.8	51.0	1.1	4956-56	0	"	5	208+ 230+ 265	212 (8)	35	4.0	66	78	0-94					
15	15.71	58.0	0.926	4956-76	0	"	5 1/2	208	229 (1 1/2)	35	0.91	61	66	0-248	0.3+0.8	2.1	1.3	1.11	1.96
16	15.80	58.4	1.09	4956-86	0	"	5 1/2	208	210	35	0.83	61+ 29	65+ 30	0-152	0.84	2.0	0.37	0.54	0.76
17	15.71	58.0	0.861	4956-101	0	"	5 1/2	208	212 (7)	35	0.90	66	68	0-220	0.78	2.0	1.2	[illegible]	[illegible]

Table 5-1 continued

Run	Catalyst Wt. (g)	Catalyst Vol. (cc)	Catalyst Ru (%, wt.)	Catalyst Number	γ-Al_2O_3 wt. (g)	Reactor	Bed Length (in.)	Inlet Temp. (°C)	Max. Catalyst Temp. (°C) (During Hours)	Outlet Press. (atm)	Feed H_2:CO (Molar)	Feed Rate (scc/min)	Feed GHSV (hr^{-1})	Hours
18	15.57	58	1.05	4966-72		2 (glass-lined)	5 3/8	208	211 (1)	35	2.9	61	69	152
19	15.70	58	0.93	4966-76		"	6 7/8	208	210 (8)	103	2.9	61	70	100
20	15.90	58	0.93	4966-76		"	6 7/8	200	200	14	1.5	42	50	12
21	15.70	58	1.05	4966-72		"	6 1/8	208	217 (3)	35	2.9	61	70	12
22*	15.7	58	1.12	4966-96-1		"	6	208		35	2.0	61	70	
23	3.85	11	1.12	4966-96-1	31	"	16 1/4	208-250	250	35-103	2.0		180-500	76
24	7.85	29	1.12	4966-96-1		"	3	208-225	234 (75)	35-52	2.0	330-127	63-250	135
25	16.37	61	1.05	4966-72		"	5 7/8	208	211 (12)	35	2.0	118	140	12
26	14.96	62	~1	4966-108		"	7 3/4	208-225		35	2.0	31-123	30-125	32
27	6.81	18	6.3	4966-114		"	2	200	260 (1)	14	1.5	151	500	1
28	1.01	2.7	6.3	4966-114	8 (quartz)	"	7/8	200	202 (1)	14	1.5	190→ 56→ 42	4240→ 1248→ 936	28
29*	15.01	17	0.93	5345-61		"	2 1/4	208	237 (1)	35	2.0	123	120	1
30	14.18	16.1	0.93	5345-61	11.18	"	6 1/2	208	226 (1)	35	2.0	123	460	12
31	15.7		~1	4966-106	11.38	"	6 1/8	208	209 (5)	35	2.0	136→ 50	460→ 170	12
32	10.79	30	1.05	4966-72		"	3 3/4	225	233 (23)	35	2.0	50-212	100-425	43
33	7.13	25	1.12	4966-96-1		"	2 13/16	225	328 (1)	35	2.0	30-217	70-510	47

*Run shut [illegible] because of plant problems.

Table 5-1 continued

Run	Catalyst Wt. (g)	Catalyst Vol. (cc)	Catalyst Ru (%, wt.)	Catalyst Number	γ-Al_2O_3 wt. (g)	Reactor	Bed Length (In.)	Inlet Temp. (°C)	Max. Catalyst Temp. (°C) (During Hours)	Outlet Press. (atm)	Feed H_2:CO (Molar)	Feed Rate (scc/min)	Feed GHSV (hr^{-1})	Hours
34	7.13	25	1.5	4966-119	12.99	2 (glass-lined)	9 1/4	225	243 (4)	35	1.9	71↓ 47	170↓ 113	175
35	3.57	12.5	1.5	4966-119	16.24	"	9 1/4	225	233 (1)	25-49	2.0	71↓ 24	340↓ 113	250
36	3.57	12.5	1.5	4966-119	16.24	"	9	225	237 (1)	35	2.0	104↓ 27	500↓ 130	260
37	3.53	12.5	1.5	4966-119	16.24	"	8	210	217 (1)	60-89	2.0	104↓ 24	500↓ 114	366
38	5.50	19.3	~1	4966-118	25.0	"	12	210		62	2.0	241	750	12
39	5.50	6.4	~1	4966-124	25.0	"	10 1/2	210	215 (2)	62	2.0	160↓ 33	1518↓ 311	273
40*				4966-124										
41	5.5	6.4	~1	4966-124	24.7	"	10 1/2	210	215 (56)	62	2.0	160↓ 22	1520↓ 205	160
42	5.5	6.4	~1	4966-124	24.7	"	10 1/2	210	216 (4)	62	2.0	52↓ 39	490↓ 360	126
43	5.05	5.9	~1	4966-124	24.5	"	10	210	216 (5)	62	2.0	146↓ 30	1518↓ 310	116
44	6.5	22.8	~1	4966-102	29.6	"	12 1/2	210	219 (2)	35	2.0	189↓ 28	500↓ 75	46
45	6.5	22.8	2.8	4966-174	29.6	"	12 1/2	210	211 (4)	62	2.0	189↓ 28	500↓ 75	18
46	6.5	22.8	2.8	4966-180	29.6	"	12 3/8	208↓ 210	216 (675)	62	2.0	189↓ 47↓ 56	500↓ 125↓ 150	0-814
46	6.5	22.8	2.8	4966-180	29.6	"	12 3/8	210↓ 224	232 (940)	62	2.0	63↓ 77	168↓ 205	814-1701
47	6.5	22.8	2.8	4966-198	29.6	"	16 9/16	208	220 (35)	62	2.0	189↓ 55	500↓ 147	825

Table 5-1 continued

Run Summary Data for Plant 700

Run	Hydrocarbons Made (g)	Oxygenates Made (g)	H_2O Made (g)	Used Catalyst: Wax (g)	Used Catalyst: Carbon (g)	Used Catalyst (Includes α-Al_2O_3): % Wax (by wt.)	Used Catalyst (Includes α-Al_2O_3): % C (by wt.)	Iron Carbonyl Scrubber	Ru in Liquid Product (g)	Argon Recovered (%)	Total Weight Recovered (%)**	Total Weight Recovered / Argon Weight Recovered (%)
1								No		98.0	100.2	102.2
2*								No				
3	24.3	1.9	10.7	4.6	0.5	12.0	1.4	No		107.1	103.1	96.3
4*								No				
5*								No				
6	19.5	0.7	13.8					No		105.4	100.7	95.5
6	22.9	0.9	9.4					No		104.1	102.6	98.6
7	14.2	1.5	11.6	4.3	0.9	8.0	1.9	No		117.4	115.2	98.1
8	9.4	0.3	5.9	1.8	1.0	2.1	1.6	No		126.1	131.0	103.9
9	13.4	1.0	13.9	2.6	4.9	20.3	4.9	No	0.0068	95.0	94.2	99.2
10	47.4	3.5	25.7	4.6	2.1	9.2	2.1	No		93.2	92.7	99.5
11				6.6-7.6	1.6	25.1	6.8	Yes (208°C)	0.0018			
12				3.4	1.3	16.0	5.9	Yes (260°C)	0.0083			
13				8.0	0.7	9.0	6.2	Yes (260°C)	0.0004			
14				0.54	0.2	4.0	1.6	Yes (260°C)	0.00015			
15	41.5	0.25	58.7	21.4	2.8	56.0	15.3	Yes (208°C)		85.7	85.2	99.4
16	11.1	0.32	1.9	2.8	0.8	14.4	4.6	Yes (208°C)		98.4	93.2	94.7
17	22.8	?	?	17.8	1.9	50.2	10.8	Yes (208°C)		101.2	95.0	94.1

*Run shut down because of plant problems.
**Doesn't include wax retained on catalyst.
***Wax co[illegible]t be recovered properly; exact weight unknown.

Table 5-1 continued

Run	Hydrocarbons Made (g)	Oxygenates Made (g)	H_2O Made (g)	Used Catalyst: Wax (g)	Used Catalyst: Carbon (g)	Used Catalyst (Excludes Diluent): % Wax (by wt.)	Used Catalyst (Excludes Diluent): % C (by wt.)	Iron Carbonyl Scrubber	Argon Recovered (%)	Total Weight Recovered (%)**	Total Weight Recovered / Argon Weight Recovered (%)
18	15.66	0.59	15.14	5.40	1.07	24.5	6.4	Yes	89.96	89.68	99.69
19	6.62	0.02	8.30	3.61	1.82	17.1	10.4		108.85	108.52	99.70
20	0.53		0.53	0.49	0.18	3.0	1.1		79.19	80.49	101.65
21	4.07	0.03	6.28	1.70	0.43	9.5	2.4		74.05	77.95	105.26
22											
23											
24			29.60	15.3	0.39	65	4.7				
25			0.70	0.43	0.18	2.5	1.1				
26											
27											
28	2.86	0.07	5.80	0.78	0.08	42	7.3		86.56	86.95	100.46
29											
30	2.28	0.09	5.15	1.09	0.40	7.1	2.8		90.57	91.94	101.51
31											
32											
33											
34											
35											
36											
37	67.48	0.31	47.7	22.89		86.6			108.09	96.75	89.50
38											
39	56.90	0.47	68.94	31.25	2.49	79.6	31.1		82.77	85.46	103.25
40											

Table 5-1 continued

Run	Hydrocarbons Made (g)	Oxygenates Made (g)	H_2O Made (g)	Used Catalyst: Wax (g)	Used Catalyst: Carbon (g)	Used Catalyst (Excludes Diluent): % Wax (by wt.)	Used Catalyst (Excludes Diluent): % C (by wt.)	Iron Carbonyl Scrubber	Total Argon Recovered (%)	Weight Recovered (%)**	Total Weight Recovered / Argon Weight Recovered (%)
41								Yes ↓			
42											
43											
44											
45											
46	320	4.94	330	38.81		84.9			97.45	83.27	85.45
46	467	10.17	613						89.95	87.63	97.42
47	480	9.70	503	30.75	1.64	79.1	20.2	↓	98.76	85.95	87.03

Table 5-2

List of Ruthenium Catalysts

Catalyst Number	Run Number Tested	% Ru (by wt.) Fresh	% Ru (by wt.) Used	Support	Preparation Technique (Micelle Solution)	Size of Prep. (g)	STEM Examination	H_2:Ru	O:Ru	Ru Particle Size from EXAFS (nm)
4956-19		1.7		Al_2O_3	Micelle (4956-24-1)	2	4-6 nm ruthenium particles			
4956-21		1.1		Al_2O_3	Micelle (4956-24-1)	2	4-6 nm ruthenium particles			
4956-23	9	0.98	0.98	Al_2O_3	Micelle (4956-24-1)	30	Broad size distribution (most 4-25 nm, many >100 nm particles)			
4956-27	11	0.99		Al_2O_3	Micelle (4956-24-1)	30	Broad size distribution (most 3-7 nm, many 100 nm particles			
4956-30	12		0.95	Al_2O_3	Micelle (4956-24-1)	30	Broad size distribution			
4956-22	13	1		Al_2O_3	Micelle (4956-24-1)	30	Broad size distribution 4-500 nm			
4956-56	14	1		Al_2O_3	Micelle (4956-24-1)	30	Broad size distribution 4-500 nm			
4966-118	38	1		Al_2O_3	Micelle (4956-24-1)	30	Broad size distribution $\leq$10 nm			
4956-76	15	0.93	0.95	Al_2O_3	Micelle (4956-24-1)	30	4-6 nm ruthenium particles	0.29	0.31	
4966-96-1	22-24, 33	1.12		Al_2O_3	Micelle (4956-24-1)	30	45% of ruthenium 3-4 nm 45% 5-7.5 nm 10% 8-20 nm			
4966-108	26	f1		Al_2O_3	Micelle (4956-24-1)	30	95% of ruthenium 4-6 nm 5% 10-15 nm			

Table 5-2 (continued)

List of Ruthenium Catalysts

Catalyst Number	Run Number Tested	% Ru (by wt.) Fresh	% Ru (by wt.) Used	Support	Preparation Technique (Micelle Solution)	Size of Prep. (g)	STEM Examination	H_2:Ru	O:Ru	Ru Particle Size from EXAFS (nm)
4966-119	34-37	1.5		Al_2O_3	Micelle (4956-24-1)	30	1/3 of ruthenium >100 nm, the rest: 80% 4-6 nm, 20% 8-10 nm			
4966-198	47	3		Al_2O_3	Micelle (4956-24-1)		95% of ruthenium 4-6 nm 15% 3-4 nm or 6-20 nm			
4966-102		1.07 (+0.5% Fe)		Al_2O_3	Micelle		4 nm ruthenium particles	0.52		4
4966-96-2		f1 (+0.7% K)		Al_2O_3	Micelle	30	2-4 nm ruthenium particles	0.27		1-3
4956-101	17	0.86	0.37	Al_2O_3	Micelle (4956-50)	30	Some 2-4 nm ruthenium particles (most particles may be invisible and <2 nm)	0.59	0.54	
4966-76	25,32, 19	0.84	-	Al_2O_3	Micelle (4956-50)	75	Some 2-3 nm ruthenium particles (most particles may be invisible and <2 nm)	0.50	0.55	1.5
4966-106	31	f1		TiO_2 (anatase)	Micelle (4956-24-1)	30	3-10 nm ruthenium particles (mostly 3-7 nm)			2-3
4956-86	16	1.09	0.62	Al_2O_3	Conventional	30	No observed ruthenium particles	0.85	0.87	
4966-72	18	1.05	1.0	Al_2O_3	Conventional	75	No observed ruthenium particles	1.1	1.1	0.8
5345-61	30	0.934		TiO_2 (anatase)	Conventional		No observed ruthenium particles	0.13	0.48	

5.1 Establishment of Experimental Procedures

5.1.1 Application of Gel Permeation Chromatography to Analysis of Fischer-Tropsch Wax

A blend of C_6-C_{60} normal paraffins was prepared and analyzed by gel permeation chromatography in order to determine the retention time and response factors for the individual hydrocarbons.

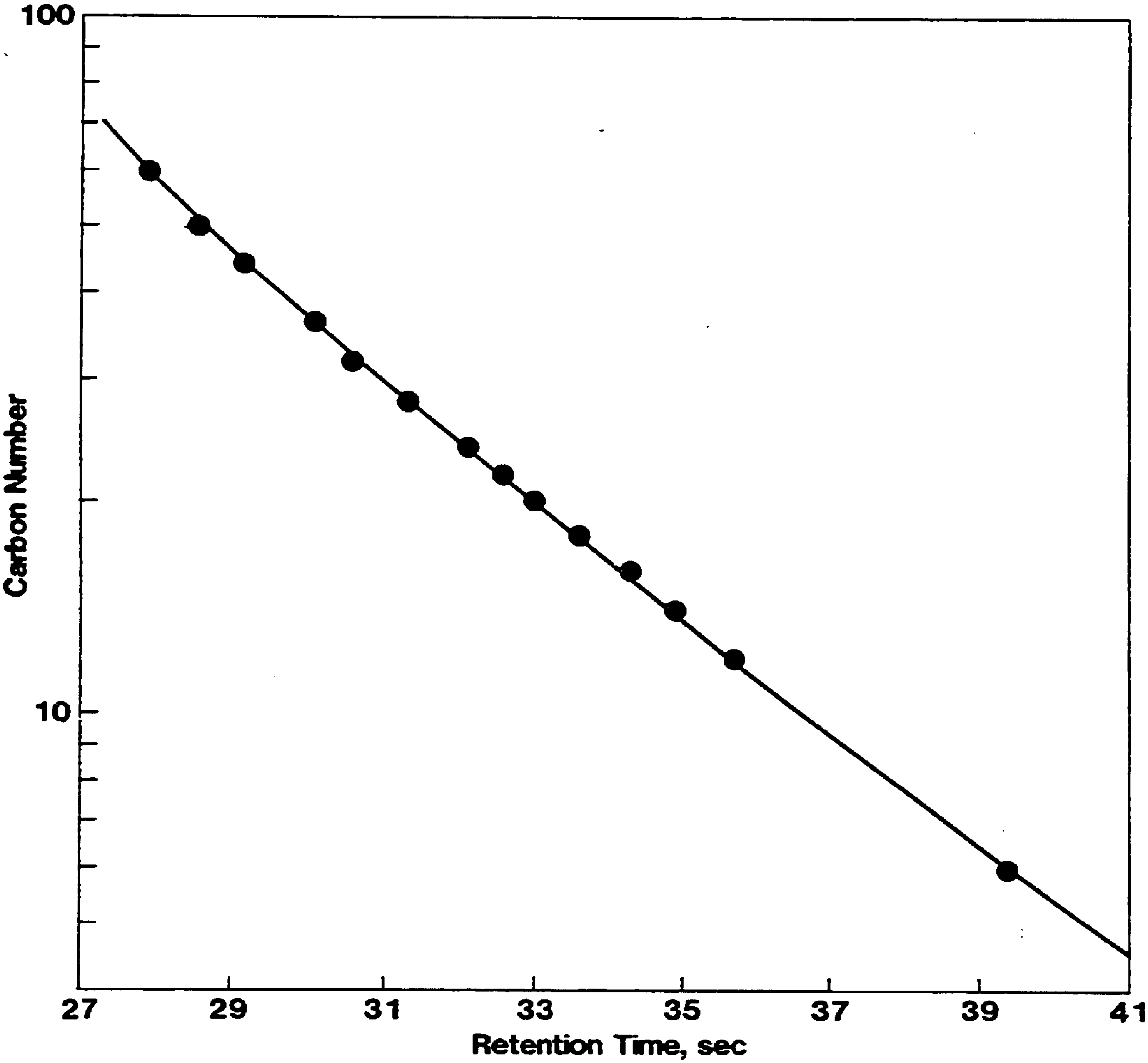
The relation between carbon number and retention time for this calibration blend is in Figure 5-1. A third order relation was evaluated for fitting the data:

$$\log CN \times 1000 = D_0 + D_1 (RT) + D_2 (RT)^2 + D_3 (RT)^3$$

Here CN is the carbon number, RT is the retention time and D's are the coefficients:

$$D_0 = 1.39 \times 10^{1}$$
$$D_1 = -6.72 \times 10^{-1}$$
$$D_2 = 1.68 \times 10^{-2}$$
$$D_3 = -1.58 \times 10^{-4}$$

Figure 5-1. Relation Between Carbon Number and Retention Time in GPC Analysis



The carbon numbers in the calibration blend were calculated using the experimentally observed retention times for the individual hydrocarbons. The results summarized in Table 5-3 illustrate that the carbon numbers calculated from the third order relation are within 1.5% of the actual carbon numbers.

In an attempt to extend the range of the carbon number calibration, Apolane-87, a branched hydrocarbon with a carbon number of 87, and polyethylene with an average molecular weight of 2015 and a calculated carbon number of 144 were added to the calibration blend and analyzed. The results summarized in Figure 5-2 indicate that the branched C_{87} hydrocarbon apparently had a higher retention time than the linear paraffin with the same carbon number. The polyethylene molecule with a calculated carbon number of 144, on the other hand, had a retention time which was in fair agreement with that calculated by extrapolating the carbon number vs. retention time relation beyond the calibrated range. Accordingly, the polyethylene standard was then included routinely in each calibration blend.

The relation between carbon number and response factor in gel permeation chromatography experiments for n-paraffins in C_{12}-C_{60} range are summarized in Table 5-4. This relation is also illustrated in Figure 5-3. A sharp increase of the response factor in picogram per unit area is observed in the C_{12}-C_{40} carbon number range, whereas the relation levels off at higher carbon numbers. The relation between weight percent and area percent at different carbon numbers in gel permeation chromatography experiments is then correlated in the following manner.

$$W\% = A\% \times \frac{CN}{0.314 + (0.0198 \times CN)}$$

Here W% is weight percent and A% is area percent for individual hydrocarbons.

Table 5-3

Comparison of the Calculated Carbon Number from the 3rd Order Fit vs. the Actual Carbon Number for Gel Permeation Chromatography Measurements

RT Min	Actual CN	Calculated CN
27.9	60	59.50
28.6	50	50.30
29.2	44	43.85
30.1	36	35.99
30.6	32	32.38
31.3	28	28.00
32.1	24	23.90
32.6	22	21.70
33.0	20	20.10
33.6	18	17.90
34.3	16	15.75
34.9	14	14.09
35.7	12	12.16
39.4	6	5.99

Figure 5-2. Extrapolated Relation Between Carbon Number and Retention Time in GPC Analysis

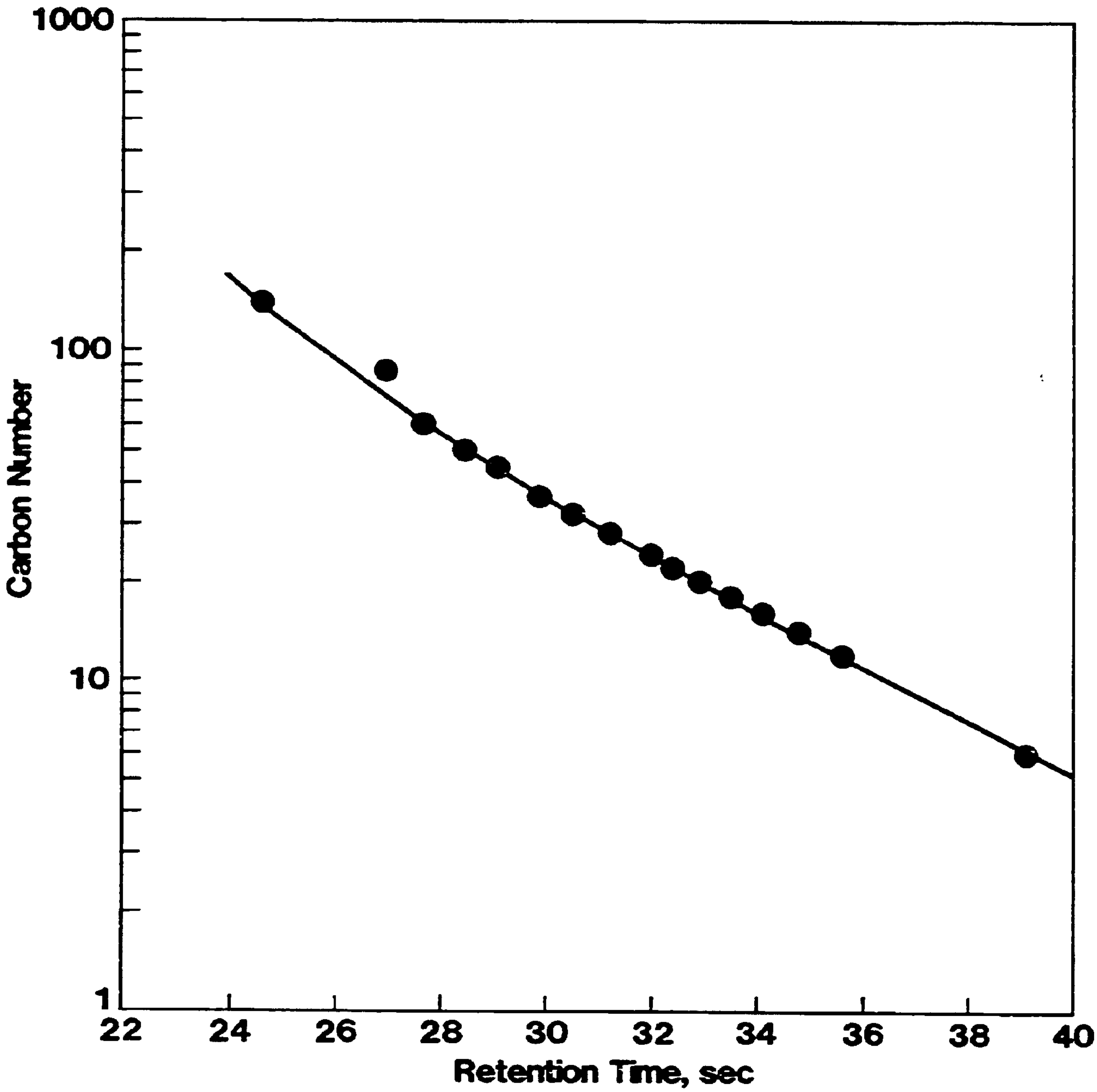
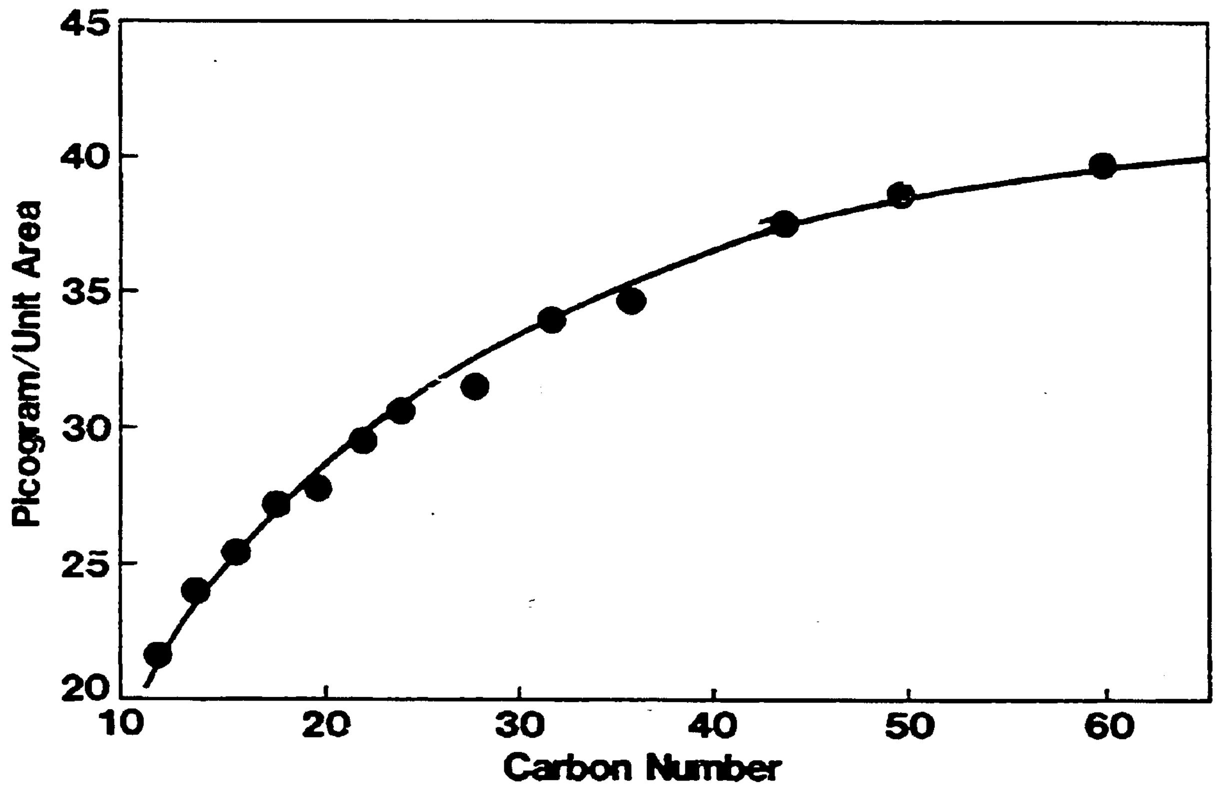


Table 5-4

The Relation Between Carbon Number and Response Factor in Gel Permeation Chromatography Measurements

C_N	Picogram/A
60	39.8
50	38.8
44	37.7
36	34.9
32	34.2
28	31.5
24	30.4
22	29.4
20	27.3
18	26.7
16	25.4
14	23.8
12	21.9

Figure 5-3. Response Factors at Different Carbon Numbers in GPC Analysis



The results obtained with the calibration blend were then applied for analysis of a Fischer-Tropsch wax sample from Run 15. The chromatogram of this sample is shown in Figure 5-4. Gel permeation chromatography analysis gives the area percents of a Fischer-Tropsch wax sample at various retention time ranges, each 0.3 to 0.5 seconds apart. The high end of each retention time range was related to a carbon number based on the third order relation discussed above. Using this carbon number, the corresponding response factor was used for calculating weight percents for every retention time range for the wax sample (Table 5-5). This weight percent was then divided by the number of carbon atoms in each range to calculate the weight percent at the mid-point carbon number. A spline smoothed curve was then fitted between the weight percents and the mid-point carbon numbers to calculate the weight percents at individual carbon numbers.

It was later determined that a more correct interpretation of GPC data would have been to assign the weight percent for every retention time range divided by the number of carbon atoms in each range to the carbon number at the high end of each retention time range. Figure 5-5 shows that with this latter method of data interpretation, the Anderson-Schulz-Flory distribution for Run 20 data which uses GPC at $>C_{44}$ leads to a slightly higher chain growth probability at higher than 100 carbon numbers. The hydrocarbon distribution results for the modified method and the method used here are summarized in Tables 5-6 and 5-29, respectively. Since the differences were not large, the former data interpretation method was used for all tests.

Figure 5-4. Gel Permeation Chromatogram of a Fischer-Tropsch Wax Sample from Run 15

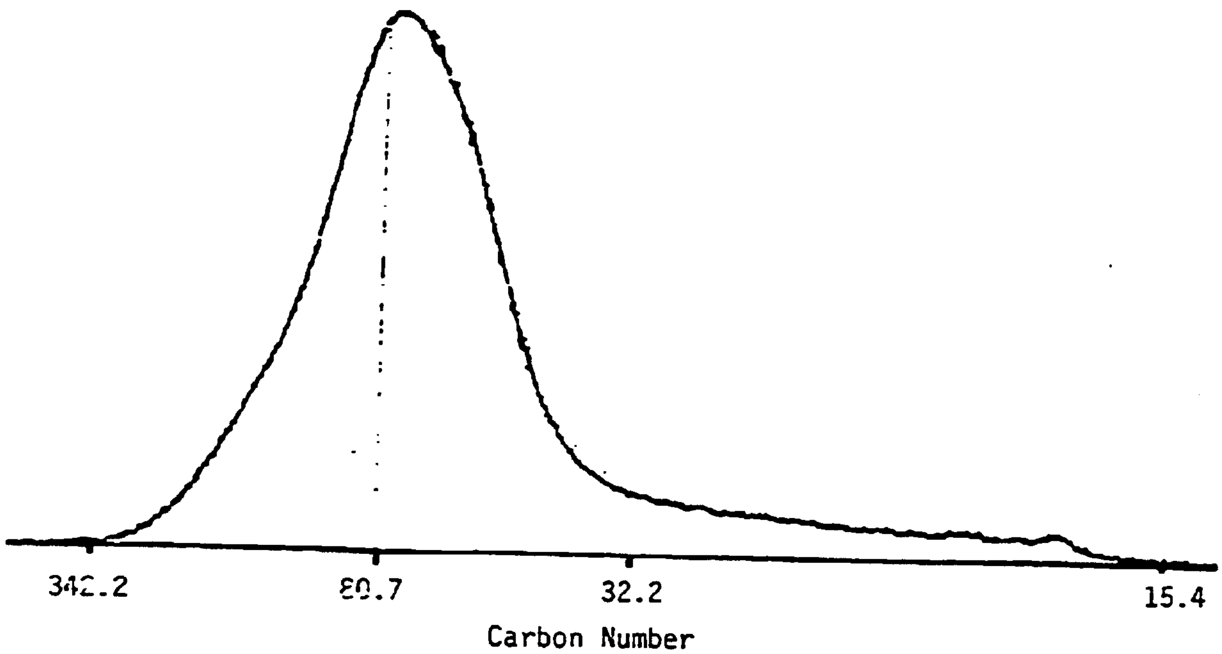


Table 5-5

Analysis of a Fischer-Tropsch Wax Sample by Gel Permeation Chromatography

CN	A%	Wt.%
342.2	0.66	0.7
283.3	1.42	1.6
236.4	2.65	2.9
198.7	4.42	4.8
168.2	6.19	6.7
143.4	8.89	9.5
123.1	12.33	12.9
106.3	14.27	14.5
92.4	13.76	13.9
80.7	11.56	11.4
70.9	7.97	7.7
62.5	4.31	4.1
55.5	2.24	2.1
49.4	1.47	1.3
44.2	1.25	1.1
39.6	0.97	0.8
35.7	0.75	0.6
32.2	0.60	0.5
29.2	0.62	0.5
26.5	0.53	0.4
24.1	0.69	0.5
22.0	0.79	0.5
20.1	0.30	0.2
18.4	0.28	0.2
16.8	0.60	0.4
15.4	0.32	0.2

Table 5-6. Weight Percent at Individual Carbon Numbers of Run 20 Data by the Modified GPC Interpretation Method (> C_{44} Analyzed by GPC)

C1	1.5657	C51	0.9533	C101	0.5010	C151	0.2268	C201	0.0909
C2	0.3123	C52	0.9436	C102	0.4942	C152	0.2226	C202	0.0891
C3	0.8933	C53	0.9291	C103	0.4875	C153	0.2184	C203	0.0874
C4	1.4493	C54	0.9196	C104	0.4807	C154	0.2143	C204	0.0856
C5	0.8433	C55	0.9103	C105	0.4740	C155	0.2102	C205	0.0839
C6	0.7419	C56	0.9011	C106	0.4674	C156	0.2062	C206	0.0822
C7	0.5536	C57	0.8920	C107	0.4663	C157	0.2023	C207	0.0806
C8	0.4322	C58	0.8830	C108	0.4597	C158	0.1984	C208	0.0789
C9	0.2952	C59	0.8628	C109	0.4531	C159	0.1946	C209	0.0773
C10	0.0975	C60	0.8540	C110	0.4465	C160	0.1966	C210	0.0758
C11	0.0758	C61	0.8453	C111	0.4399	C161	0.1929	C211	0.0742
C12	0.0254	C62	0.8367	C112	0.4334	C162	0.1893	C212	0.0727
C13	0.0016	C63	0.8281	C113	0.4270	C163	0.1857	C213	0.0737
C14	0.0000	C64	0.8196	C114	0.4206	C164	0.1821	C214	0.0723
C15	0.0000	C65	0.8112	C115	0.4142	C165	0.1786	C215	0.0708
C16	0.0000	C66	0.7942	C116	0.4078	C166	0.1752	C216	0.0694
C17	0.2485	C67	0.7859	C117	0.4015	C167	0.1718	C217	0.0679
C18	0.4888	C68	0.7776	C118	0.3953	C168	0.1684	C218	0.0665
C19	1.6151	C69	0.7694	C119	0.3891	C169	0.1652	C219	0.0652
C20	1.3245	C70	0.7612	C120	0.3830	C170	0.1619	C220	0.0638
C21	1.1174	C71	0.7531	C121	0.3769	C171	0.1587	C221	0.0625
C22	1.4499	C72	0.7450	C122	0.3704	C172	0.1556	C222	0.0612
C23	1.2262	C73	0.7370	C123	0.3644	C173	0.1525	C223	0.0599
C24	1.7718	C74	0.7158	C124	0.3585	C174	0.1495	C224	0.0586
C25	0.9386	C75	0.7079	C125	0.3527	C175	0.1466	C225	0.0573
C26	0.7570	C76	0.7001	C126	0.3469	C176	0.1436	C226	0.0561
C27	0.7591	C77	0.6923	C127	0.3412	C177	0.1408	C227	0.0549
C28	0.7686	C78	0.6845	C128	0.3355	C178	0.1379	C228	0.0537
C29	0.8062	C79	0.6768	C129	0.3299	C179	0.1352	C229	0.0525
C30	1.1548	C80	0.6691	C130	0.3243	C180	0.1324	C230	0.0514
C31	0.8295	C81	0.6614	C131	0.3189	C181	0.1298	C231	0.0502
C32	0.7012	C82	0.6538	C132	0.3134	C182	0.1271	C232	0.0491
C33	0.6456	C83	0.6401	C133	0.3081	C183	0.1246	C233	0.0480
C34	0.6273	C84	0.6325	C134	0.3028	C184	0.1273	C234	0.0470
C35	0.6699	C85	0.6250	C135	0.2975	C185	0.1248	C235	0.0459
C36	0.6940	C86	0.6174	C136	0.2924	C186	0.1224	C236	0.0449
C37	0.6685	C87	0.6099	C137	0.2872	C187	0.1200	C237	0.0439
C38	0.5514	C88	0.6024	C138	0.2822	C188	0.1177	C238	0.0429
C39	0.5003	C89	0.5950	C139	0.2820	C189	0.1154	C239	0.0419
C40	0.4875	C90	0.5876	C140	0.2771	C190	0.1131	C240	0.0409
C41	0.4915	C91	0.5802	C141	0.2722	C191	0.1109	C241	0.0400
C42	0.5036	C92	0.5729	C142	0.2674	C192	0.1087	C242	0.0391
C43	0.4664	C93	0.5657	C143	0.2627	C193	0.1066	C243	0.0382
C44	0.4434	C94	0.5499	C144	0.2580	C194	0.1045	C244	0.0373
C45	1.0072	C95	0.5428	C145	0.2533	C195	0.1025	C245	0.0364
C46	0.9970	C96	0.5357	C146	0.2488	C196	0.1005	C246	0.0356
C47	0.9931	C97	0.5287	C147	0.2442	C197	0.0985	C247	0.0348
C48	0.9831	C98	0.5217	C148	0.2398	C198	0.0965	C248	0.0347
C49	0.9731	C99	0.5148	C149	0.2354	C199	0.0946	C249	0.0339
C50	0.9631	C100	0.5079	C150	0.2311	C200	0.0928	C250	0.0332

Figure 5-5 Anderson-Schulz-Flory Distributions of Run 20 Data Based on Two Different Interpretations of GPC Data

Δ method used here

□ modified method