FISCHER TROPSCH SYNTHESIS IN SUPERCRITICAL FLUIDS

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QUARTERLY TECHNICAL PROGRESS REPORT

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I. Objectives for the Second Quarter, Year 1:

Our objective during the second quarter of the project was to complete the procurement of necessary parts for our reactor set-up, complete equipment modification, start safety and shake-down tests and complete preliminary calculations that are needed before starting experimentation.

II. Accomplishments, Second Quarter, Year 1:

A. Fischer Tropsch Reactor Assembly

The experimental set-up was completed. Different pieces of equipment such as the reactor, the mass flow controller, steady state low pressure glass trap, etc. were installed in the system. The system was then pressure tested for safety purposes. There were many aspects of the safety tests like the cold pressure tests, the hot pressure tests, the flow through tests, etc. All these tests were successfully completed. various safety devices in the set-up such as relief valves, temperature interlocks, solenoid valves and the emergency shut-down system were also tested successfully.

A schematic of the experimental is given in Figure 1. A list of valves, pressure gauges, mass flow controllers, etc. used in the set-up was made along with their temperature and pressure ratings. Information on the sensitivity of the catalyst to sulfur was obtained from various sources in the literature. Information on the availability and prices of propane was also obtained form various sources.

a.Experimental Set-Up

The reactor was received from Autoclave engineers and was installed. In addition, the following items were ordered and received. They were first tested and then installed in the experimental set-up.

1) Mass flow controller (0-500 SCCM).

2) Steady state low pressure glass trap.

3) Pressure gauge in the propane line.

The following items in the experimental set-up were found to be defective. They were repaired and re-installed in the set-up.

1) Solenoid valve in the purge line

2) Helium pressure regulator.

3) Back pressure regulator.

4) Pressure gauge in the syn-gas line.

5) Check valve after the pre-heater.

A profile thermocouple was designed and has been ordered from Omega. The thermocouple can measure temperatures at six points along the length of the reactor. Various factors such as the length of the reactor, the catalyst loading and dilution, and the position of the cylindrical heaters were considered for designing the thermocouple.

The experimental set-up has been completed and is ready for carrying out experiments.

b. Pressure tests

After the experimental set-up was completed, a series of tests were carried out. These tests insured that the set-up was safe to operate at pressures upto 1200 psig and reactor temperatures of upto 250° C. These tests are listed below.

1) The equipment set-up was pressurized to a pressure of 1200 psig. The gas flow was shut off and different sections of the reactor were isolated from each other by shutting off appropriate valves. The pressures in the different sections of the apparatus were noted. The pressures were then monitored as a function of time. Any drop in pressure suggested a leak for that section. The leak was found using soap solution, and was fixed. The system was re-pressurized and was tested again for leaks. This process was repeated until all the sections in

the set-up were leak-free (pressure drop < 10 psig in 24 hrs). After this, the appropriate valves were opened and the pressure tests were repeated for the entire system. These tests were carried by using nitrogen and helium gases.

2) Heating tape was wound on the system along with insulation tape. Thermocouples were then installed at various points in the set-up. The set-up was then heated to the desired temperature. The temperatures were monitored by thermocouples which were connected to a read-out. The system was then pressurized to 1200 psig and the gas flow was shut off. The pressures in various parts of the set-up were monitored as a function of time. These tests were successful as indicated by negligible pressure drop over time.

3) A Flow through test was then carried out by using nitrogen. The system was heated and pressurized to 1200 pig. Nitrogen was then made to flow through the reactor at a flow rate of 100 Ncc/min. The pressure and temperature of nitrogen were controlled by using the back pressure regulator and the mass flow controller respectively. The temperatures and pressures in various parts of the reactor were monitored over a period of time along with the nitrogen flow rate. The test was performed for 21 hours. The temperatures, pressures and the nitrogen flow rates remained during the entire period, indicating the success of the flow through test.

4) The three relief valves used in the set-up were tested at pressure of 1000 psig. The tests were successful.

5) The solenoid valves were sucessfully tested at 1000 psig.

6) The temperature interlocks were tested at a temperature of 250° C. They were then reset to a temperature of 350° C.

7) The liquid line for propane was first pressure tested with nitrogen at 1200 psig. The tests were successful, as there was a pressure drop of only 30 psig after 56 hrs. The liquid line was

then plugged and acetone was pumped in till the pressure reached 1200 psig.

8) The emergency shut-down system located in room # 325A was tested.

c. List of Equipment Used in the Set-Up

The schematic of the experimental set-up was drawn using the drawing software Macpaint (Figure 1). Various valves in the set-up have been labeled for easy identification. A list of valves, pressure gauges, mass flow controllers etc. used in the set-up was made along their temperature and pressure ratings. (Tables I to IX). This list is necessary for writing the safety report.

d. Information on Catalyst Sensitivity to Sulfur

It is known that the Ruhrchmie catalyst is sensitive to Sulfur. Sulfur can enter the system as an impurity with syn-gas or propane. Various references were reviewed and it was concluded that in order to maintain catalyst activity, sulfur levels has to be less than 0.05 ppm

e. Information on Propane

Information was collected from various sources for purchasing propane. Factors such as price, shipping costs, overall purity, sulfur, oxygen and water content were considered for choosing the best possible supplier. It was found that IWECO company of Houston was the best supplier. The following are the specifications of the propane supplied by IWECO:

Grade : Instrument

Purity :99.5%

Cost :100 lbs of propane for $533.

Rental Cost : $3.00/month

Sulfur :<1 ppm

Impurities : Ethane, butane, iso-butane < 0.5%.

f. Catalyst for Sulfur Removal

Various potential sources were contacted for finding a catalyst which could remove S from the propane stream. It was found that a catalyst supplied by Carasorb company could remove S in the form of sulfur dioxide, hydrogen sulfide, marcaptans and other sulfur containing compounds. The catalyst consists of potassium permanganate impregnated on activated carbon. This catalyst is capable of removing 0.022 lbmass of hydrogen sulfide per lbmass of the catalyst pellet.

g. Gas Cylinder Consumption

The syn-gas and propane cylinders consumption per run was determined. A syn-gas flow rate of 100 Ncc/min and a run time of 300 hrs were used as basis for calculations. It was found that one cylinder of syn-gas along with one cylinder of propane would be required for carrying out a run. Based on the prices available, it was determined that the total gas cost per run would be approximately $750.

h. Effect of Impurities on Product Composition

The effect of impurities present in propane on product distribution was determined. Calculations were done on a per hour basis. Data from run FB-1588-7 was used in these calculations. This run was carried out in this laboratory using Ruhrchemie catalyst, but in the absence of propane. The results from this comparison are shown in Table X.

On the basis of this Table, it was concluded that amount of propane and iso-butane produced in the reaction cannot be determined beause of their large presence in the feed.

B. Taylor Dispersion Apparatus for Diffusion Measurements

We have successfully measured diffusion coefficients of various organics in supercritical CO_2 using the Taylor dispersion technique along three different isotherms, 35, 45 and 55 °C, in the density range from 0.40 to .90 g/ml and pressures in excess of 3600 psia. Figure 2 is a representation of the data for diffusion coefficients in supercritical carbon dioxide. Calculation of the leak rates at high pressures indicate that the system should have minimal leaks at the operating conditions we will encounter.

We have located and begun to install parts for the conversion of the system for use of solvents such as propane, butane, and hexane. Preliminary calculations of the necessary criteria for using the Taylor dispersion technique show that run-time tests will be necessary to determine the final configuration of the apparatus when using any of the above solvents.

III. Plans for the Third Quarter, Year 1.

A. Fischer Tropsch Reactor Assembly

Propane, butane and hexane can potentially be used as solvents for carrying out the Fischer-Tropsch synthesis. These solvents have different critical temperatures and pressures. Thus, the supercritical properties of the reaction mixture will depend on the type of solvent used for carrying the reaction.

The reaction will be carried out at a temperature of 250° C and pressures from 800-1500 psig. It is essential that the critical properties of the solvent in the reaction mixture are close to the reaction conditions. That ensures that the solvent is indeed in supercritical state and it retains its beneficial properties.

There are various empirical and semi-empirical formulas in the literature for calculating supercritical temperatures, pressures and densities of the reaction mixtures. These properties will depend on the composition of the reaction mixture and the type of solvent used. The Schultz-Flory formula will be used to determine the product distribution of the Fischer-Tropsch reaction. Based on this product distribution, the supercritical properties of the reaction mixture will be calculated for various solvents. Different expressions will be used to determine the best equation for the given system. Because of the complexity of the reaction products, a FORTRAN program will be written to make the calculations faster.

The results form this program will be compared to data available in the literature for hydrocarbon-carbon monoxide and hydrocarbon-hydrogen systems. Based on these comparisons, a correction factor might be incorporated in the original program to overcome possible discrepancies between the actual and the predicted results. The choice of an appropriate solvent will then be made based on these results.

B. Taylor Dispersion Apparatus for Diffusion Measurements

We will begin conducting the experiments to determine if the apparatus can be used in the recently modified configuration or if further changes will be necessary. The experiments will be conducted at supercritical pressures. UV wavelengths for the diffusing compounds will be determined experimentally as UV data are not readily available in the literature for the olefins of our interest.

We will write computer programs to determine densities of a hexane reaction mixture and to check the viability of hexane as a supercritical solvent; we have begun a literature search in regard to this problem.

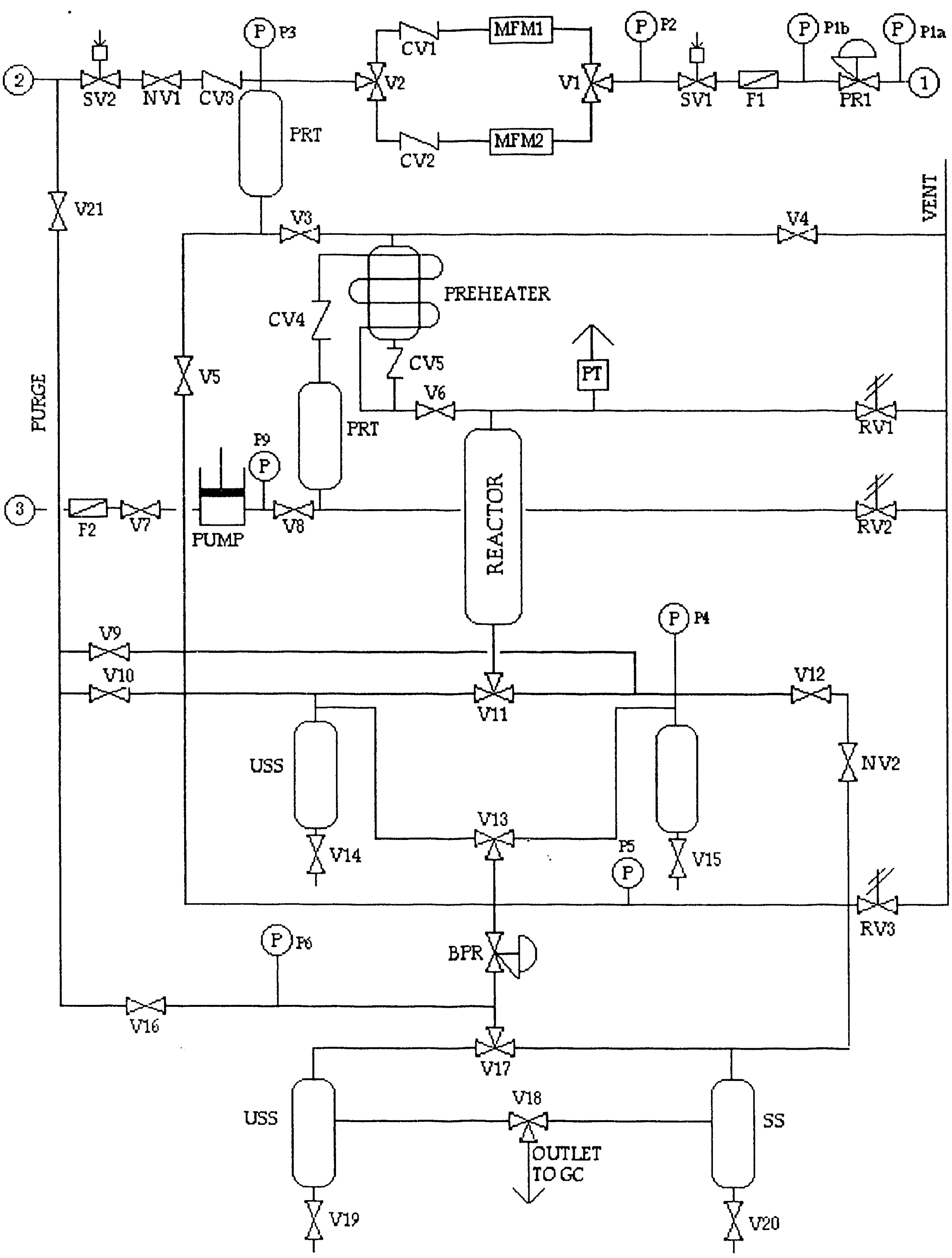
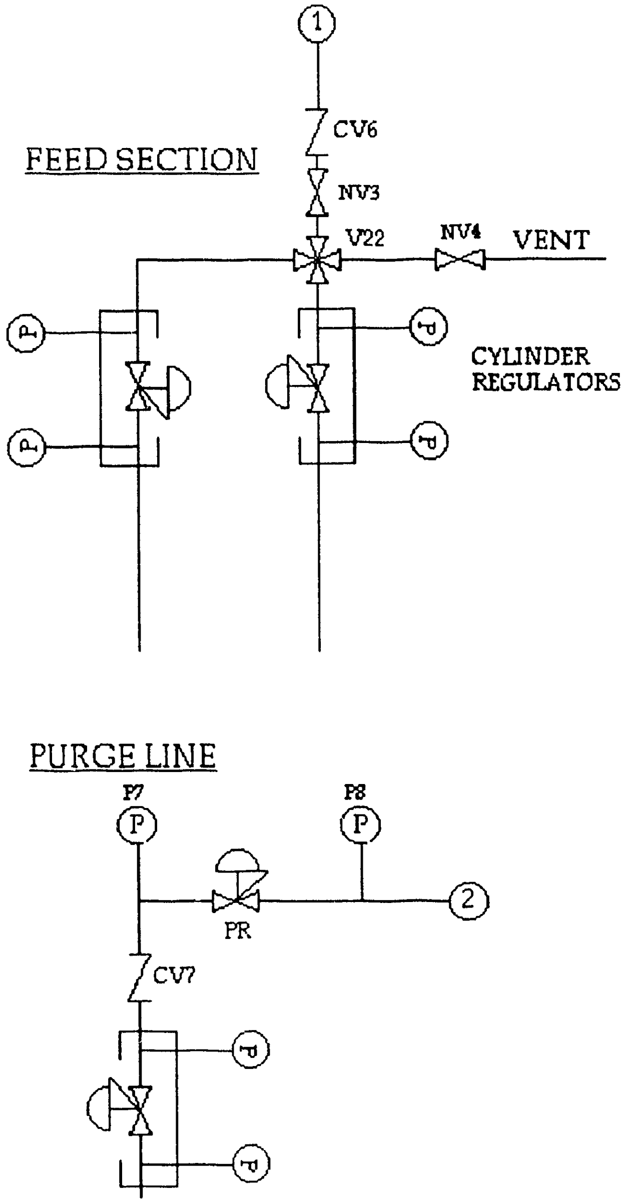
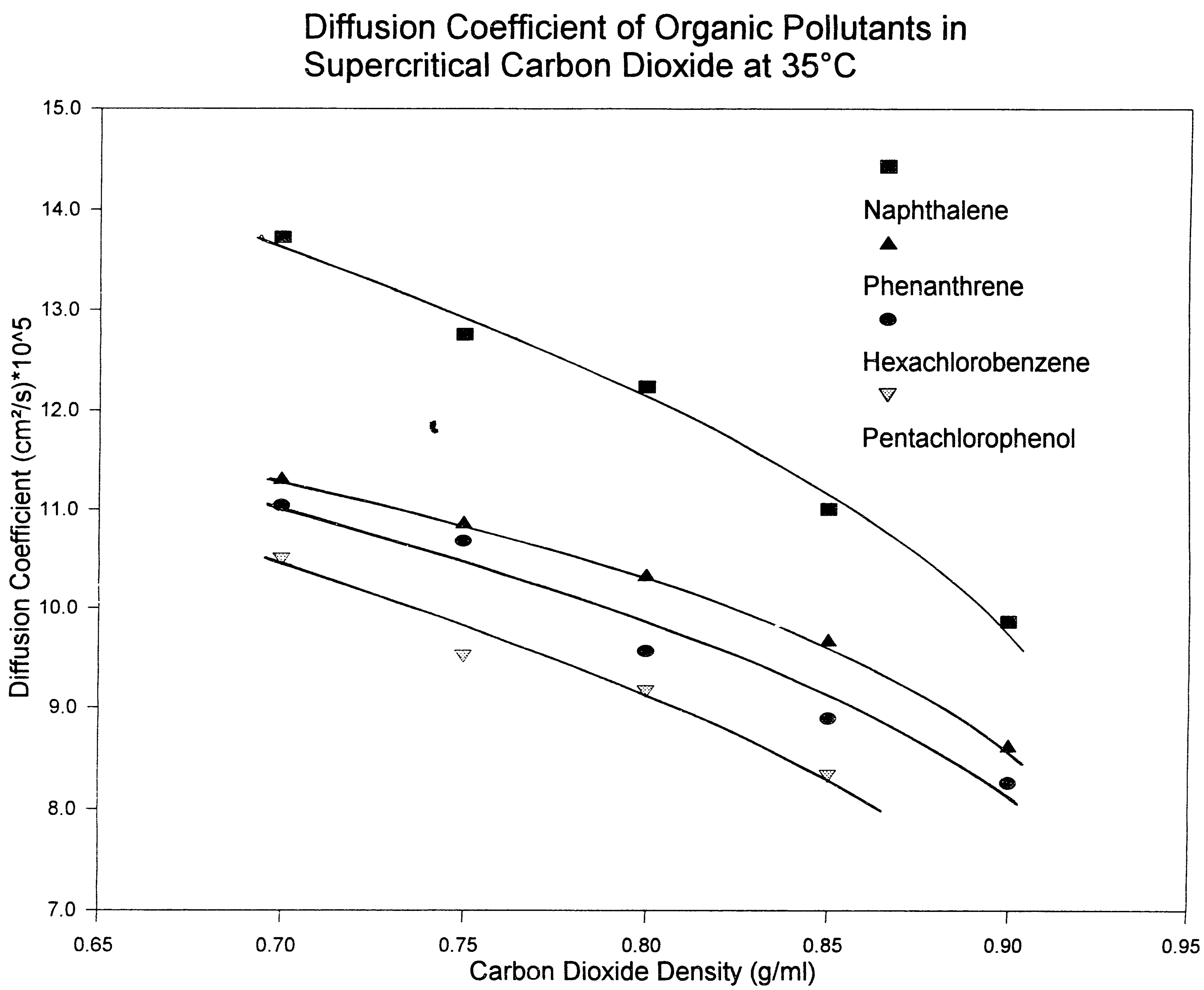


FIGURE 1. EXPERIMENTAL SETUP



LEGEND

BPR - Back Pressure Regulator	PRT - Purification Trap
CV - Check Valve	PT - Pressure Transducer
F - Filter	RV - Relief Valve
MFM - Mass Flow Meter	S - Solenoid Valve
NV - Needle Valve	SS - Steady State Trap
PR - Pressure Reducer	USS - Unsteady StateTrap



Diffusion Coefficient of Organic Pollutants in
Supercritical Carbon Dioxide at 35°C
Diffusion Coefficient (cm²/s)*10^5
15.0
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
0.65
0.70
0.75
0.80
0.85
0.90
0.95
Carbon Dioxide Density (g/ml)
Naphthalene
Phenanthrene
Hexachlorobenzene
Pentachlorophenol

Table I

		VALVES			
#	MANUFAC TURER	PART #	DESCRIPTI ON	MAXIMUM PRESSURE (PSI)	MAXIMU M TEMP C
1	Whitey	SS-43YF2	3-Way	3000	65
2	Whitey	SS-43YF2	3-Way	3000	65
3	Autoclave	SW-4081-TG	2 Way	11,500	316
4	Autoclave	SW-4081-TG	2 Way	11,500	316
5	Autoclave	SW-4081-TG	2 Way	11,500	316
6	Autoclave	SW-4081-TG	2 Way	11,500	316
7	Autoclave	10V-4081	2 Way	11,500	236
8	Autoclave	10V-2082	2 Way	11,500	236
9	Autoclave	10V-2082	2 Way	11,500	236
10	Autoclave	10V-2082	2 Way	11,500	236
11	Autoclave	10V-4075-TG	3 Way	11,500	316
12	Autoclave	10V-4081	2 Way	11,500	236
13	Autoclave	10V-4075-TG	3 Way	11,500	316
14	Autoclave	SW-4081-TG	2 Way	11,500	316
15	Autoclave	SW-4081-TG	2 Way	11,500	316
16	Autoclave	10V-2082	2 Way	11,500	236
17	Whitey	SS-41XS2	3 Way	2500	65
18	Whitey	SS-41XS2	3 Way	2500	65
19	Nupro	SS-4P-4T1	2 Way	3000	204
20			Stop Cock	15	300
21	Autoclave	10V-2082	2 Way	11,500	236
22	Whitey		4 Way		

Table II

		FILTERS			
#	MANUFACTURER	PART #	DESCRIPTION	MAXIMUM PRESSURE (PSI)	MAXIMUM TEMP C
1	Nupro	SS-4F-2	2 Microns	6000	480
2	Nupro	SS-4F-2	7 Microns	6000	480

Table III

		PRESSURE GAUGES			
#	MANUFAC TURER	PART #	DESCRIPTI ON	MAXIMUM PRESSURE (PSI)	MAXIMU M TEMP C
1a	USG	PV844U	Liquid Filled	0-3000	65
1b	USG	PV844U	Liquid Filled	0-3000	65
2	USG	SER 1900 4 1/2"	General Mount Gauge	0-1500	65
3	USG	SER 1900 4 1/2"	General Mount Gauge	0-1500	65
4	USG	551L	Liquid Filled	0-2000	65
5	USG	PV844U	General Mount Gauge	0-3000	65
6	USG	PV844U	General Mount Gauge	0-3000	65
7	USG	PV844U	General Mount Gauge	0-3000	65
8	USG	PV844U	General Mount Gauge	0-3000	65
9	USG	551L	Liquid Filled	0-2000	65

Table IV

		MASS FLOW CONTROLLERS			
#	MANUFACTURER	PART #	DESCRIPTION	MAXIMUM PRESSURE (PSI)	MAXIMUM TEMP C
1	Brooks	51242578AAA	0-500 SCCM	1500	65
2	Brooks	5816 A1A31	0-10000 SCCM	1500	65

Table V

		NEEDLE VALVES			
#	MANUFAC TURER	PART #	DESCRIPTI ON	MAXIMUM PRESSURE (PSI)	Maximum Temp C
1	Whitey	SS-31RS4	Metering Valve	5000	232
2	Nupro	SS-SS4	Metering Valve	2000	204
3	Whitey	SS-31RS4	Metering Valve	5000	232
4	Whitey	SS-31RS4	Metering Valve	5000	232

Table VI

		PRESSURE REGULATORS			
#	MANUFACTURER	PART #	DESCRIPTION	MAXIMUM PRESSURE (PSI)	MAXIMUM TEMP C
1	Tescom	26-1025-24-280	Pressure Regulator	1500	74
2	Tescom	26-1025-24-280	Pressure Regulator	1500	74
3	Tescom	26-1725-24	Back Pressure Regulator	1500	74

Table VII

		SOLENOID VALVES			
#	MANUFAC TURER	PART #	DESCRIPTI ON	MAXIMUM PRESSURE (PSI)	MAXIMU M TEMP C
1	Asco	8262C98	Normally Closed	1900	140
2	Tescom	8262G260	Normally Open	750	140

Table VIII

			CHECK VALVES		
#	MANUFAC TURER	PART #	DESCRIPTI ON	MAXIMUM PRESSURE (PSI)	MAXIMU M TEMP C
1	Parker	4Z-4CL	CPI	5000	205
2	Nupro	SS-4C-10	C Series	3000	190
3	Nupro	SS-4C-10	C Series	3000	190
4	Nupro	SS-4C-10	C Series	3000	190
5	Nupro	SS-4C-10	C Series	3000	190
6	Nupro	SS-4C-10	C Series	3000	190
7	Parker	4Z-4CL	CPI	5000	205

Table IX

			RELIEF VALVES		
#	MANUFACTURER	PART #	DESCRIPTION	MAXIMUM PRESSURE (PSI)	MAXIMUM TEMP C
1	Nupro	SS-4R3A5	Orange Spring R3A-D	6000	121
2	Nupro	SS-4R3A5	Orange Spring R3A-D	6000	121
3	Nupro	SS-4R3A5	Orange Spring R3A-C	6000	121

Table X

#	Component	Moles Produced in Reaction	Moles Fed In With Propane	Moles Fed in/moles produced
1	Propane	0.00025	1.25	5000
2	Oxygen	0	0.000125	Infinity
3	Methane	0.00363	0.000125	0.0344
4	Isobutane	0.0000164	0.0025	152
5	Ethane	0.000771	0.000875	1.13