LIQUEFACTION OF COALS USING ULTRA-FINE PARTICLE,
UNSUPPORTED CATALYSTS: IN SITU GENERATION BY
RAPID EXPANSION OF SUPERCRITICAL FLUID SOLUTIONS

QUARTERLY TECHNICAL PROGRESS REPORT

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1.0 SUMMARY

The program objective is to generate ultra-fine catalyst particles (20 to 400 Å in size) and quantify their potential for improving coal dissolution in the solubilization stage of two-stage catalytic-catalytic liquefaction systems. In the first quarterly report for this program the concept behind our approach was detailed, the structure of the program was presented, key technical issues were identified, preliminary designs were outlined, and technical progress was discussed. All progress made during the second quarter of this program related to experiment design of the proposed supercritical expansion technique for generating ultra-fine, iron compound, catalyst particles. This second quarterly report, therefore, presents descriptions of the final designs for most system components; diagnostic approaches and designs for determining particles size and size distributions, and the composition of the pre-expansion supercritical solution; and the overall technical progress made during this reporting period.

The supercritical flow, ultra-fine catalyst particle generator can be divided into two distinct elements, namely: 1) A supercritical fluid catalyst particle generator, and 2) A particle collection, coal material impregnation section. A detailed design was developed during this quarter for the supercritical fluid catalyst particle generator element of the system. The design will provide very severe conditions for

catalyst feed stock dissolution (i.e., the most severe being supercritical H₂O at 600 atm and 500 C). These conditions, coupled with residence times as long as 100 minutes at these severe conditions, should optimize the probability of achieving dissolution of most catalyst materials identified for consideration. Expansion nozzle characteristics have been defined that will yield supercritical solution flow rates with an upper bound of 20 cm³/min, which should give catalyst particle generation rates that will produce reasonable coal material impregnation times.

A concrete, cost effective, preliminary design for the particle collection, coal material impregnation section, which follows downstream of the supercritical fluid catalyst particle generator, has been developed. The first approach considered for impregnating coal materials with catalyst particles was based on a two-stage process. The first stage was an expansion region which provided sufficient length for the supersonic expansion jet to diffuse to a low momentum flow. The diffuser section would then be followed by either a fluidized bed containing pulverized coal, or a chamber containing a fine spray of coal derived liquid. Since Brownian coagulation theory indicated that particle coagulation time scales are short relative to the time scale for diffusing the supersonic expansion jet, this approach was abandoned.

Brownian motion coagulation theory dictates that immediate and intimate contact between the expansion jet and coal materials

must be achieved in order to impregnate the coal material with the smallest possible catalyst particles. Based on this thinking a final design concept was defined. The final design will be a spouted bed reactor. The expansion nozzle will be located at the base of a cylindrical tube. The bottom of the cylindrical tube will have a conical shape. The nozzle will discharge vertically upward from the apex of the cone. The cone can be filled with either pulverize coal or coal derived liquid. This design will provide the immediate and intimate contact required between the expansion jet and coal material.

The spouted bed reactor will contain ports where a particle sampling probe can be inserted. A cryogenic technique will be used to freeze out the material collected by the sampling probe. By sublimating the supercritical solvent species from the collection surface in the cryogenic sampler, collecting it in a second cryogenic trap, and determining the mass collected on both cryogenic surfaces via appropriate gravimetric techniques, the catalyst loading in the supercritical solution can be determined. The cryogenic sampler can also be used to acquire STEM samples of the generated catalyst particles for size distribution analysis.

Critical support systems were defined this quarter, along with electrical, pneumatic, and water utility services. Plans have been defined for installation of an explosion proof enclosure for the experiment. This enclosure will have a dedicated ventilation system also. A Fumehood and an emergency eyewash/shower will be installed near the experiment so that

substances posing health risks can be handled safely. These systems should be installed in the next quarter of this program.

At this point in the program actual progress is lagging original plans by nominally four months. A one year no-cost extension has been requested. Due to unforeseen costs for components of the supercritical flow system and planning and design efforts for support systems, there will be a cost over-run on the experiment design and fabrication task. Careful budgeting, however, should help achieve program goals within budget.

2.0 TECHNICAL APPROACH

The technical work performed to date falls under Task 2 Experiment Design and Fabrication, and has consisted entirely of experiment design activities. As noted in prior reports, the ultra-fine catalyst particle generator consists of two main elements, namely: 1) a supercritical fluid catalyst particle generator and 2) a particle collection and coal material impregnation section. The designs for these elements plus particle sampling approaches and support systems will be presented in that which follows.

2.1 SUPERCRITICAL FLUID CATALYST PARTICLE GENERATOR

The key elements of the ultra-fine catalyst generator are shown in block diagram format in Figure 2.1. The elements between the solute/solvent reservoirs and the expansion nozzle constitute the first major element of the particle generator system, which will be referred to as the "supercritical fluid catalyst particle generator. The elements downstream of the expansion nozzle constitute the second major element of the particle generator system, which will be referred to as the "particle collection and coal material impregnation section." The remainder of this subsection will focus on the supercritical fluid catalyst particle generator and the next subsection will deal with the particle collection and coal material impregnation section.

Figure 2.1 Block Diagram of Catalyst Particle Generator.

The temperature/pressure specifications presented in Figure 2.1 were derived based on the work performed at Battelle Northwest Laboratories by Dean Matson¹. Matson and co-workers achieved significant dissolution of quartz in supercritical water and, via rapid expansion through a capillary tube nozzle, produced quartz particles in the submicron range. Since the dissolution characteristics of the iron compound catalysts of interest ($\text{Fe}(\text{CO})_5$, FeS_2 , and Fe_2O_3) in supercritical solvents are not known, the conditions employed by Matson to achieve dissolution of quartz in supercritical water were adopted to make certain dissolution will be achieved during this program. The supercritical water conditions produced in Matson's studies had an upper bound of 600 atm and 500C in the autoclave, with the option to raise the temperature of the supercritical solution exiting the autoclave to 600C. These are very severe conditions and are upper limits based on strength limitations of materials of construction.

The supercritical fluid catalyst particle generator element can be conveniently divided into two components, namely: 1) solvent/solute flow system and 2) autoclave/nozzle flow system. Figures 2.2 and 2.3 give detailed flow schematics for the solvent/solute and autoclave/nozzle flow systems, respectively. A detailed parts list for all elements in these two flow systems is given in Table 2.1.

The design pressure and temperature for the flow system

Figure 2.2 Solvent/Solute Supercritical Flow System.

Figure 2.3 Autoclave/Nozzle Supercritical Flow System.

SOLVENT SUPPLY LEG

Part	Vendor	Catalog No.	Spec.	No. or Length (ft)	Cost/Part	Total Cost	Delivery
ES-1	ASCO		1 KPSI	1	40.00	40.00	2-3 wks
SO-1	NUPRO	SS-4P4T	1KPSI	1	37.40	37.40	2-3 wks
CV-1	NUPRO	SS-4C-1	1KPSI	1	30.00	30.00	2-3 wks
CV-2	NUPRO	SS-4C-1	1KPSI	1	30.00	30.00	2-3 wks
PR-1	NUPRO	SS-4R3A-C	1KPSI	1	90.00	90.00	2-3 wks
F	NUPRO	SS-4FW-0.5	0.5 MICRON	1	39.60	39.60	2-3 wks
V-1	NUPRO	SS-4P4T	1 KPSI	1	37.40	37.40	2-3 wks
FM-1	KENTROL	10A2147AXX2	1.5 KPSI	1	1925.00	1925.00	10 wks
PM-1	HASKELL	MS-110	10 KPSI	2	400.00	800.00	5-6 wks
BP-1	TESCOM	54-2161W24	10 KPSI	1	700.00	700.00	7-8 wks
PG-1	OMEGA	PGS-25L[1500]	1.5 KPSI	1	50.00	50.00	2-3 wks
TC1	OMEGA	JQIN-116(G)-12	400 C	2	27.40	54.80	2-3 wks
ADAPTER T/C	OMEGA	SS-100-1-4	1 KPSI	3	11.00	33.00	2-3 wks
TEE-FEMALE	OMEGA	SS-400-3-4TTF	1 KPSI	3	18.55	55.65	2-3 wks
UNION CROSS	OMEGA	SS-400-4	1 KPSI	2	27.25	54.50	2-3 wks
FEMALE CON.	OMEGA	SS-400-7-4	1 KPSI	2	7.55	15.10	2-3 wks
UNION TEE	OMEGA	SS-400-3	1 KPSI	2	15.05	30.10	2-3 wks
MALE NPT	OMEGA	SS-400-1-4	1 KPSI	4	4.75	19.00	2-3 wks
S.S. TUBE		1/4 OD X 0.180 ID	316 S.S.	15	5.65	84.75	
					SUBTOTAL	4126.30	

Table 2.1 List of Construction Materials for Supercritical Flow System.

SOLUTE SUPPLY LEG

Part	Vendor	Catalog No.	Spec.	No. or Length (ft)	Cost/Part	Total Cost	Delivery
ES-2	ASCO			1	40.00	40.00	
PM-2	COLE-PAWMER	N-07143-90	T0 10 KPSI	1	1911.00	1911.00	4-5 wks
WATER	ALFA RESEARCH	19391	ULTRAPURE	12 LITERS	28.00/4L	112.00	2-3 wks
TANK	FSHER	14-831-312A		1	58.00	58.00	3-4 wks
MICROFLOMETER	OMEGA	FL-310		1	60.00	60.00	3-4 wks
TEFLON O-RINGS	OMEGA	FL-11		1	20.00	20.00	3-4 wks
SO-2	NUPRO	SS-4P4T	1 KPSI	1	37.40	37.40	2-3 wks
MALE NPT	OMEGA	SS-400-1-4	1 KPSI	4	4.75	19.00	2-3 wks
S.S. TUBE	TUBE SALES	1/4 OD X 0.180 ID	316 S.S.	5	5.65	28.25	
					SUBTOTAL	2285.65	

Table 2.1 Continued.

PUMP TO AUTOCLAVE LEG

Part	Vendor	Catalog No.	Spec.	No. or Length (ft)	Cost/Part	Total Cost	Delivery
V-2	HIGH-PRESSURE	10-11AF4	10 KPSI	1	53.00	53.00	3-4 wks
PR-2	HIGH-PRESSURE	4-1177	SET 10 KPSI	1	320.00	320.00	3-4 wks
TC-2	OMEGA	JOIN-116(G)-12	400 C	1	27.40	27.40	2-3 wks
TC-4.5	OMEGA	KOIN-116(G)-12	1000 C	2	27.00	54.00	2-3 wks
PG-2	HIGH-PRESSURE	6PG-20	20 KPSI	1	398.00	398.00	3-4 wks
SAND BATH	COLE-PAWNER	N-01189-50	TO 600 C	1	3810.00	3810.00	4-5 wks
AUTOCLAVE	HIGH-PRESSURE	GC-5 (HAS C276)	600 A,500 C	1	6740.00	6740.00	5-6 wks
FITTING T-HM	HIGH-PRESSURE	10-21AF4HM9	10 KPSI	1	27.00	27.00	3-4 wks
CROSS	HIGH-PRESSURE	10-24AF4	10 KPSI	2	32.70	65.40	3-4 wks
TEE	HIGH-PRESSURE	10-23AF4	10 KPSI	2	26.90	53.80	3-4 wks
ELBOW	HIGH-PRESSURE	10-22AF4	10 KPSI	2	32.00	64.00	3-4 wks
ADAPTER TC	HIGH-PRESSURE	10-21AF1AM4T	10 KPSI	2	27.00	54.00	3-4 wks
ADAPTER PG	HIGH-PRESSURE	10-21AF4HM4	10 KPSI	1	15.65	15.65	3-4 wks
STRAIGHT	HIGH-PRESSURE	10-21AF4	10 KPSI	1	69.40	69.40	3-4 wks
ELBOW (HAS)	HIGH-PRESSURE	60-22HF4	60 KPSI	1	126.00	126.00	5-6 wks
TUBE	HIGH-PRESSURE	10-9AF4-316	316 S.S	20	7.01	140.20	3-4 wks
ADAPTER HM (HAS)	HIGH-PRESSURE	60-21HM4HM4	60 KPSI	1	108.15	108.15	5-6 wks
TUBE HASTELLOY	HIGH-PRESSURE	1/4 OD X 0.083 ID HASTELLOY	HASTELLOY	6	29.09	174.54	5-6 wks
SUBTOTAL						12300.54	

Table 2.1 Continued.

AUTOClave TO NOZZLE LEG

Part	Vendor	Catalog No.	Spec.	Q. or Length (ft)	Cost/Part	Total Cost	Delivery
IF-2 (HASTELLOY)	HIGH-PRESSURE	60-51HF4	60 KPSI	1	353.00	353.00	5-6 wks
MV-1 (HASTELLOY)	HIGH-PRESSURE	60-11HF4V	60 KPSI	1	614.00	614.00	5-6 wks
PG-3	HIGH-PRESSURE	6PG-20	TO 20 KPSI	1	398.00	398.00	3-4 wks
T/C-3	OMEGA	KQIN-116(G)-12	1000 C	1	27.00	27.00	2-3 wks
CAPS (HASTELLOY)	HIGH-PRESSURE	60-21 HF4-C	60 KPSI	4	71.35	285.40	5-6 wks
CROSS (HASTELLOY)	HIGH-PRESSURE	60-24 HF4	60 KPSI	1	230.00	230.00	5-6 wks
ELBOW (HAS)	HIGH-PRESSURE	60-22HF4	60 KPSI	1	126.00	126.00	5-6 wks
ADAPTER HM (HAS)	HIGH-PRESSURE	60-21HM4HM4	60 KPSI	2	108.15	216.30	5-6 wks
ADAPTER TC (HAS)	HIGH-PRESSURE	10-21AF4HM-T	10 KPSI	1	71.00	71.00	5-6 wks
TUBE HASTELLOY	HIGH-PRESSURE	1/4 OD X 0.083 ID	60 KPSI	4	29.09	116.36	5-6 wks
					SUBTOTAL	2437.06	
					TOTAL	21149.55	

Table 2.1 Continued.

MISCELLANEOUS AND CONSUMABLE ITEMS

Part	Vendor	Catalog No.	Spec.	No. or Length (ft)	Cost/Part	Total Cost	Delivery
L CARBONDIOXIDE	LIQUID CARBONICS	13202	99.90%	2	40.00	80.00	2 wks
	LIQUID CARBONICS	13102	99.99%	2	70.00	140.00	2 wks
IRON(IV) SULFIDE	ALFA RESEARCH	12842	99.90%	100	187/50	374.00	2-3 wks
IRON(III) OXIDE	ALFA RESEARCH	14680	99.99%	100	15.90/50	31.80	2-3 wks
PENTACARBONYLIRON	ALFA RESEARCH	31113	99.50%	1000	83.00	83.00	2-3 wks
SUBTOTAL						708.80	

Table 2.1 Continued.

between the liquid solvents reservoir and check valve CV-1 (see Figure 2.2) is 1500 psig and 20C, respectively. The pressure specification was based on the saturation pressure for liquid CO₂ at 20C. A shutoff valve (SO-1) and an electric solenoid valve (ES-1) appear in this section also. The electric valve is for automatic shutoff of the solvent flow should a failure be sensed elsewhere in the system. An armored flow meter (FM-1) will be used in this leg for measuring solvent flow rate, which will operate safely at the design pressure. The capacity of the armored flow meter is 20 cc/min and the resolution is 0.2 cc/min. Check valve CV-1 was placed in this section to prevent high pressures from reaching this section should a downstream failure occur.

The design pressure and temperature for the flow section between the liquid solutes reservoir and metering pump PM-2 are 0 psig and 20C, respectively. The design specifications for the flow section between the metering pump PM-2 and check valve CV-2 are 5000 psig and 20C. All liquid solutes or solubilizing additives that may be introduced into the flow system via this section will be at ambient pressure. A shutoff valve (SO-2) and an electric solenoid valve (ES-2) appear in this section also. The electric valve is for automatic shutoff of solute flow should a failure be sensed elsewhere in the system. The flow meter for the solute feed section (FM-2) will have a capacity of 0.12 cc/min (H₂O) with a resolution of 0.0001 cc/min. A metering pump (PM-2) appears in this section so that pressure matching with the

solvent flow section can be achieved. This pump will be capable of producing 5000 psig and 10 cc/min (H₂O). Check valve CV-2 was placed in this section to prevent high pressures from reaching this section should a downstream failure occur.

The next major element of the solvent/solute flow system contains the high pressure pump (see Figure 2.2, PM-1). The high pressure pumping element has been designed to generate a pressure of 10,000 psig at a flow rate of 160 cc/min. Based on analysis applied to the expansion nozzle, which will be discussed later, a maximum flow rate of 11 cc/min (liquid solvent) is anticipated. The high pressure pumping system, therefore, is more than adequate for this application. Autoclave pressure will be controlled through a back-pressure regulator (BP-1). The flow system between both the high pressure pump inlet and the back-pressure regulator points and the points defined by check valves CV-1 and CV-2 will be made of stainless steel and designed for a working pressure of 10,000 psig at 20C. A 1000 psig set point pressure relief valve (PR-1) is located near the inlet of the high pressure pump in case the pump or back-pressure regulator fail. A heat exchanger (HX-1) is located between the back-pressure regulator and pump inlet to remove heat added by the pump to recirculated fluid. This will be important when using CO₂ as a solvent to ensure that bubbles do not form upstream of the high pressure pump inlet. A 2 µm in-line filter is located upstream of the high pressure pump inlet to remove solid contaminants prior to passage through the pump. High pressure

pump inlet conditions will be monitored via pressure gauge PG-1 and thermocouple gauge TC-1. Valve V-1 will be used to vent the system after system shutdown. Stainless steel tubing (0.25" OD X 0.180" ID, SS316) will be used on the high pressure side of the pump where the temperature is nominally ambient (20C). Thus, the outlet side of the pump is rated for an operating pressure of 30,000 psig at 20C.

The second main element of the supercritical fluid catalyst particle generator is the autoclave/nozzle flow system, which is shown in Figure 2.3. The main elements of this flow system are: 1) an autoclave and autoclave heater for solid catalyst dissolution; 2) a heated transfer line that allows the option to raise the temperature of the supercritical solution prior to expansion through the nozzle; and 3) a nozzle assembly that allows rapid expansion of the supercritical solution.

Upstream of the autoclave, valve V-2 will be used to vent the high pressure side of the flow system after system shutdown. Autoclave inlet pressure and temperature will be monitored via pressure gauge PG-2 and thermocouple gauge TC-2, respectively. Pressure relief valve PR-2 on the upstream side of the autoclave is present to ensure that the pressure does not exceed the maximum operating pressure of the autoclave, namely 10,000 psig.

The 0.25" OD stainless steel tubing extends from the high pressure pump to the cross containing pressure gauge PG-2 and pressure relief valve PR-2. The tubing then transitions to 0.0625" OD X 0.020 ID Hastelloy C-276 tubing, which is a low

iron, high strength superalloy, which will ensure that an adequate pressure safety factor is maintained at temperatures up to 600C at 10,000 psig. Figure 2.4 shows the strength of 316 stainless steel relative to Hastalloy C-276. As can be seen, the Hastalloy superalloy has a significantly higher tensile strength, which will be needed to ensure the structural integrity of the high temperature/pressure section of the autoclave/nozzle flow system. For this reason, as well as Hastalloy's low iron content, Hastalloy C-276 will be used as the material of construction from the cross at pressure relief valve PR-2 to and including the expansion nozzle. In private communications with Dean Matson at Battelle Northwest Laboratories, it was learned that it is important to use low iron content alloys in components on the high temperature and pressure side of the supercritical flow system, since these severe conditions can leach iron from the materials of construction. Since iron based catalyst compounds are being processed in this supercritical flow system, it is desirable to minimize iron introduction by other sources.

The autoclave will be made by High Pressure, Inc. from Hastalloy C-276, have a volume of 300 cm³, and an operating pressure of 600 atm at 500C. The autoclave will be heated by a Cole-Parmer, 4 KW sand bath heater. The sand bath heater has a temperature controller that responds to a thermocouple gauge located in the fluidized sand in the sand bath. The temperature within the autoclave will be monitored by a thermocouple (see Figure 2.3, TC-5) in a thermowell integrated into the top of the

Figure 2.4 Strength Dependence of Construction Materials On Temperature.

autoclave. The 0.0625" OD solvent feed line will helix around the autoclave before entering it at its bottom in order to preheat the liquid solvents. A Hastalloy 100 μ m fritted board filter will be placed at the bottom of the autoclave, then a mixture of solid powder catalyst and 100 mesh pure nickel powder (the nickel powder acting as packing), which is followed on top by a 2 μ m fritted board filter. This arrangement was chosen to minimize particle migration out of the autoclave and to maximize solubilization. Nickel powder packing was selected due to its inert behavior under the severe thermodynamic conditions anticipated in the autoclave. Based on the volume of the autoclave and the solvent flow rates allowed by the expansion nozzle, autoclave residence times between 10 and 110 minutes are expected, which should be adequate to allow dissolution of the solid powder catalyst materials.

The flow path branches immediately at the exit of the autoclave. One path leads to a by-pass metering valve and on to a discharge vent. The other path leads to the supercritical solution transfer line, which delivers the supercritical solution to the expansion nozzle. The by-pass circuit will be used to reduce the concentration of solute in the supercritical solution by increasing the solvent flow rate through the autoclave, thereby reducing residence time.

The first element in the circuit leading to the expansion nozzle is a 2 μ m fritted filter (IF-2) made of Hastalloy C-276. This filter will remove particulate matter escaping from the

autoclave, which could plug the small diameter expansion nozzle. A 0.0625" OD X 0.020" ID X 8' Hastalloy C-276 tube transfers the supercritical solution exiting the autoclave to the nozzle assembly. This line will be heated by passing a DC current through the Hastalloy tube. A Lindberg oven power supply/controller will be used to drive current through the transfer tube, which will respond to a thermocouple gauge monitoring the temperature of the transfer tube at the end nearest the nozzle assembly. This transfer line can be safely operated at 10,000 psig for transfer line temperatures less than or equal to 600C. Heat transfer analysis applied to the transfer line indicates that an 8' length of tubing should be adequate to raise the of the supercritical fluid leaving the autoclave to 600C for the range of flow rates allowed by the expansion nozzle and for the anticipated range of fluid temperatures leaving the autoclave.

A metering valve (see Figure 2.3, MV-1), pressure gauge (PG-3), and thermocouple gauge (TC-3) will be installed at the downstream end of the supercritical solution transfer line. The metering valve will be used to adjust the pre-expansion pressure, and the pressure and thermocouple gauges will be used to obtain the thermodynamic state of the supercritical solution prior to expansion.

The nozzle shown in Figure 2.3 is the most critical component of the supercritical fluid catalyst particle generator system. The reason being that it controls the overall flow rate

through the system. If it is assumed that a catalyst molar concentration of 1000 ppm can be achieved in the supercritical fluid, which appears possible based on the results obtained by Matson¹ for the quartz/supercritical water system, and that we wish to load a 100 gm coal material sample with catalysts material to 1000 ppm by weight, it will take, based on the supercritical fluids (CO_2 and H_2O) and catalyst species ($\text{Fe}(\text{Co})_5$, FeS_2 , and Fe_2O_3) of interest, at most 10 minutes to achieve this loading if the supercritical fluid mass flow rate is nominally 3 gm/min. This is also based on the assumption that all catalyst material is deposited onto the coal material sample. In general it is not expected that the deposition efficiency of catalyst particles onto the coal material will be 100 percent. It will more likely be of order 10 percent and will be heavily dependent of the performance of the coal material impregnation section. Albeit, if supercritical fluid flow rates in the 2-5 gm/min range can be achieved, impregnation times in the range 1-5 hours can be expected, which are satisfactory. Thus, the nozzle should be designed to allow supercritical fluid flow rates in the range 2-5 gm/min.

Figures 2.5 and 2.6 show a T-S diagram for the process that takes place in the expansion nozzle for the supercritical solvents CO_2 and H_2O , respectively. State 1 represents the pre-expansion thermodynamic state. State 2 represents the choked condition (sonic point) at the minimum cross-sectional area station in the expansion nozzle. The minimum area station can be

Figure 2.5 Supercritical CO₂ Expansion Process.

Figure 2.6 Supercritical H₂O Expansion Process.

seen physically in the sketch of the laser drilled Hastalloy cap nozzle shown in Figure 2.7. State 3 represents the conditions just upstream of the Mach disk shock shown in Figure 2.8. The barrel shock and Mach disk structure shown in Figure 2.8 is for a pre-expansion/post-expansion pressure ratio of $NPR = 6.44$. The Mach number contours shown in Figure 2.8 were computed by Childs and Caruso², which agree well with the shadowgraph data acquired by Petrie and Walker³. Finally, state 4 represents the conditions that prevail after the hypersonic jet has diffused to negligible momentum and is in equilibrium with the discharge plenum chamber pressure (i.e., the particle collection, coal material mixing section pressure, which will be variable between 0.01 and 1 atm).

The pre-expansion thermodynamic conditions (state 1, Figures 2.5 and 2.6) are derived from several factors. First, to achieve good solvent dissolution power, the pressure should be $3-5^1$ times the critical pressure of the supercritical solvent and the temperature should be above the critical temperature. To ensure that supercritical fluid condensation does not occur during the expansion process, a rule of thumb¹ dictates that the pre-expansion temperature should be greater than 1.3 times the critical temperature. Referring to Figures 2.5 and 2.6, condensation will occur if path 2-3 intersects the saturated vapor line (i.e., the curve labeled "saturation line").

Based on the guidelines stated above regarding the pre-expansion thermodynamic state, the upper bounds for supercritical

Figure 2.7 Laser Drilled Orifice Nozzles.

Figure 2.8 Characteristics of an Extremely Underexpanded Jet.

CO₂ were determined to be 450C, which is 1.5 times the critical temperature, and 350 atm, which is nominally 5 times the critical pressure. The upper bounds for H₂O were determined to be 570C, which is 1.3 times the critical temperature, and 600 atm, which is nominally 3 times the critical pressure. Assuming supersonic flow after the minimum area point in the nozzle (i.e., after state 2) and isentropic expansion between the pre-expansion thermodynamic state (state 1) and the minimum cross-sectional area point in the expansion nozzle (state 2, where sonic conditions prevail), it is possible to calculate the maximum mass flux possible. If a minimum diameter of 0.002" is assumed for the minimum cross-sectional area point in the expansion nozzle, the maximum flow rate for CO₂ and H₂O will be 11.3 and 10.0 gm/min, respectively. These are the design conditions for the nozzle to be used in this study. As noted earlier, 3 gm/min was considered satisfactory based on reasonable impregnation times, but since it may not be necessary to use the most extreme pre-expansion conditions to obtain good solute concentrations in the supercritical fluid, a nozzle diameter which gives significantly higher flow rates (i.e., by a factor of three) is in order so that if and when less severe conditions are used, which means reduced supercritical flow rates, we will still achieve reasonable impregnation times.

In the previous discussion, it was mentioned that a laser drilled Hastalloy cap will be used as the expansion nozzle. Figure 2.7 presented a sketch of this part. There are two ways

to fabricate such a nozzle. The first is shown in the top sketch of Figure 2.7. Here a counterbore of modestly large diameter is drilled from the existing truncated cone at the bottom of the threaded bore. If the laser beam is brought through from the threaded side of the cap, a converging nozzle profile will be obtained, which will have its minimum cross-sectional area where the laser drilled hole breaks through the blank side of the cap. This converging profile follows naturally from laser drilling due to the converging nature of the light rays as they reach the focus of the lens delivering the laser beam to the work-piece surface. This is the most desirable profile since negligible fluid expansion will take place, which is a result of the contracting passage. Given the overall geometry of the part, however, it is unlikely that this machine process can be done. The second approach is to counterbore from the threaded side and laser drill from the blank side of the cap. This approach is shown in the lower sketch in Figure 2.7. Although a diverging profile will exist between the minimum area point and the blank face of the cap, which will act as a supersonic nozzle, the effects of fluid expansion can be minimized here by making the laser drilled hole as short as possible, thereby minimizing the divergence of the laser bore downstream of the minimum area point. For a 0.002" diameter laser drilled hole, a laser drilling shop has stated that the divergence (i.e., increase in bore diameter) can be kept below 0.0005" for a bore length of 0.040".

It may be advantageous, however, to allow some divergence in the nozzle bore, since this may cause more uniform properties over the cross-section during the early stages of expansion. The barrel shock and Mach disk shock structure shown in Figure 2.8 leads to highly nonuniform properties over most of the cross-sections through the free expansion region. This suggests that different fluid elements will experience different thermodynamic conditions for different times, which may lead to expansion process limitations on the particle size distribution width of the resulting catalyst particles. By constraining the expanding flow in a short diverging section, more uniform conditions can be forced to occur, which may lead to more narrow particle size distribution widths.

Based on the discussion given above, the expansion nozzle will be fabricated from a Hastalloy C-276 fitting, tube cap. It will be counterbored from the threaded side of the fitting and the expansion nozzle will be laser machined from the blank side of the cap. Finite element stress analysis will be performed on this part to derive counterbore and nozzle bore dimensions that will give a reasonable safety factor at the maximum operating conditions, namely 600 atm and 600C. The minimum area point in the nozzle will have a diameter of 0.002".

2.2 PARTICLE COLLECTION AND COAL MATERIAL IMPREGNATION SECTION

The second major element of the ultra-fine catalyst particle generator system is the particle collection and coal impregnation

section. Referring to Figure 2.1, this element includes all components downstream of the expansion nozzle, namely: catalyst collection/mixing section and exhaust system. The main purposes of this element are to provide variable post-expansion conditions (i.e., pressure and temperature), access for acquiring catalyst particles samples, and a means for impregnating coal materials (e.g., pulverized coal or coal derived liquids) with the catalyst particles produced by the supercritical fluid catalyst particle generator. The final design for this section must satisfy the constraints posed by each of the purposes mentioned above. These will be discussed in that which follows, as well as possible configurations and the final configuration.

Matson¹ has observed that decreasing expansion section back-pressure (i.e., background pressure in the particle collection and coal material impregnation section) changes the particle characteristics. There are two possible explanations for this. First, for otherwise fixed conditions, decreasing expansion section back-pressure causes more rapid expansion of the supercritical solution, which produces lower densities and collision rates during the expansion process, thus altering the duration of conditions appropriate for nucleation and particle growth. Second, in regions downstream of the Mach disk shock, decreasing expansion section back-pressure produces lower collision rates among product particles, which provide a mechanism for particle growth after initial particle formation, thereby reducing particle coagulation rates. It is necessary,

therefore, to provide a means for varying mixing chamber back-pressure so that this effect can be used to minimize particle size and particle size distribution.

The upper bound on mixing chamber back-pressure will be atmospheric pressure. The lower bound will be dictated by the pumping speed of the vacuum pump dedicated to this system. TDS has made available an 80 CFM Kinney vacuum pump for this program. Given the pumping speed of the available vacuum pump and the maximum supercritical solvent flow rates discussed under Section 2.1, back-pressures of nominally 0.01 atm should be obtainable. This range of back-pressures (0.01 to 1.0 atm) should provide a range broad enough to allow investigation of back-pressure effects on catalyst particle size and size distribution.

In order to minimize hardware costs, it is desirable to design and fabricate an expansion section that can be used for particle collection and impregnation of coal material with catalyst particles. The first iteration on concepts for a particle collection and coal material impregnation section resulted in a design having an expansion/particle-collection section followed by a coal material impregnation section. Figure 2.9 gives a conceptual sketch of the expansion/particle-collection section. This section contains the nozzle, optical access windows for visual detection of condensation if present in the expansion jet, and particle collection probe. This section would have a circular cross-section and would mate to the downstream coal material impregnation section. The purpose of

Figure 2.9 Preliminary Concept for Expansion/Particle-Collection Section.

this section is to diffuse the high momentum expansion jet so that a low speed, particle laden flow is delivered to the coal material impregnation section.

Based on the empirical relationship given by Love⁴ for nozzle/Mach-disk separation distance as a function of pre- and post-expansion pressures, the jet spreading angle (18 degrees) given by Abramovich⁵, the most severe pre-expansion conditions expected (H_2O , 600 atm and 600 C), and a nozzle orifice diameter of 0.003 in., the diameter of the mixing section should be $D = 2$ in. and the length of the expansion section should be at least $L = 15$ in. in order to achieve a well diffused, low momentum jet before particle sampling or discharge into the coal material impregnation section. This diameter, length, and configuration represent the preliminary design details for the first concept for the expansion/particle-collection section.

Figures 2.10 and 2.11 give the first iteration concept sketches for sections that would follow downstream of the expansion section for mixing pulverized coal and coal liquids, respectively, with product catalyst particles. To impregnate pulverized coal with product catalyst particles, the low momentum, catalyst particle laden flow could be delivered to a bed of pulverized coal supported by a screen mesh. At high gas flow rates, the bed would operate as a fluidized bed. At lower gas flow rates, the bed would operate as a fixed bed. In general, this approach would be very effected for depositing most of the catalyst particles in the flow onto the pulverized coal

Figure 2.10 Preliminary Concept For Pulverized Coal Impregnation Section.

Figure 2.11 Preliminary Concept For Coal-Liquid Impregnation Section.

particles. To impregnate coal derived liquids with product catalyst particles, the low momentum, catalyst particle laden flow would enter a section containing a fine spray of coal derived liquid. The fine spray could be generated by a fuel-oil spray nozzle and liquid could be recirculated in order to achieve exposure times needed to achieve the desired loading of catalyst particles in the coal liquid.

As can be seen, the two section concept (i.e., an expansion section followed by a coal material impregnation section) has the potential for performing the tasks desired. This approach, however, has one major problem, which prevents its use. Based on the analytical approach given by Friedlander⁶, particle coagulation time scales ranging from 0.3 to 30 milliseconds are estimated as the mixing section backpressure is varied from 1 to 0.01 atm. The convective time scale produced by the expansion section shown in Figure 2.9 is nominally two to three orders of magnitude greater than the coagulation time scales. Thus, the two section concept would result in significant particle coagulation, probably producing catalyst particle sizes outside the range of interest for this application.

This last result indicates that immediate and intimate mixing between the expansion jet and coal material is needed in order to minimize the particle size distribution of the catalyst particles impregnated into the coal material. This reasoning lead immediately to the final design concept for the particle collection, coal material impregnation section, namely a spouted

bed mixing chamber, which is shown in the sketch given in Figure 2.12. The design shown in this figure utilizes an upward discharging nozzle. The nozzle is anchored in a stainless steel disk, which is heated electrically so that the desired pre-expansion temperatures are maintained right to the exit of the expansion nozzle. The disk in which the nozzle is anchored is thermally isolated from the expansion chamber via a thick ceramic disk. This disk severely limits heat loss from the heated SS nozzle assembly to the circular cross-sectional mixing chamber tube. The lower end of the mixing chamber tube and ceramic disk form a cone with the nozzle orifice located at the apex of the cone. When pulverized coal or coal liquid are introduced into the mixing section, the jet will lift these materials vertically. A hollow tube centerbody, with the end nearest the jet open and the opposite end closed, provides a dead volume of gas in which the lifted particles or droplets can decelerate before fracturing due to impact with the closed end of the centerbody tube. When the coal particles or coal liquids return to the base of the mixing section through the action of gravity, the conically shaped bottom of the mixing section will direct these materials back into the expansion jet. This design is expected to give the immediate and intimate contact needed to minimize the particle size distribution of the product catalyst particles impregnated into the coal materials.

The final design of this section will be completed by the end of the next quarter. The final design must resolve issues

Figure 2.12 Final Concept for Particle Collection, Coal Material Impregnation Section.

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relating to the very extreme conditions that prevail at the nozzle/mixing-chamber interface. At this interface extreme temperatures and pressures (600 atm and 600 C) exist; heat losses to the mixing chamber must be minimized; surfaces in which the coal materials come into contact with must be insulated from the high temperature nozzle assembly; and mixing chamber vacuum integrity must be maintained. The design of this section will present an interesting challenge.

As shown in Figure 2.12, the mixing section will be fitted with optical access windows so that the presence of condensation in the expansion jet can be detected. The pre- and post-expansion conditions should be adjusted so that condensation does not form. The characteristics of the product catalyst particles will be greatly changed if condensation is allowed to occur. As noted in Section 2.1, the supercritical transfer line between the nozzle and the autoclave is heated by passing a DC current through it. The ceramic insulator shown in Figure 2.12 between the SS nozzle assembly and mixing section also serves as an electrical insulator to provide a current path only through the transfer line.

The upper chamber shown in Figure 2.12 is actually a condensation trap from a previous, completed experiment. This part serves two purposes. First, it acts as a 90 degree elbow so that the flow path can be directed horizontally after leaving the mixing chamber. Space limitations in the enclosure necessitate this. Second, this part has a baffle structure inside which will

help prevent coal particles from leaving the mixing chamber should they lift to its exit plane. The 80 CFM Kinney vacuum pump will be plumbed so that it can pump on the exhaust of the mixing chamber assembly or, optionally, the pump can be by-passed to allow discharge to atmospheric pressure. The valving for accomplishing this will be such that the back-pressure can be smoothly adjusted from 0.01 to 1 atm.

The manifolding just upstream of the expansion nozzle will be housed in a sandbox heater. The components to be housed in this heater are: 1) A cross containing a tap for a pressure gauge for monitoring pre-expansion pressure, a tap for a thermocouple for monitoring pre-expansion temperature, and Hastelloy tube for delivering the supercritical solution to the nozzle, and 2) A metering valve for adjusting the pre-expansion pressure. The sandbox heater will be constructed using a 3kW flat board electric heater as the floor of the sandbox, and the remaining sides made of 1.5 in. thick Fibrefax insulation board. The box will be filled with sand to provide good thermal contact between the plumbing fixtures and the flat board heater.

2.3 CRYOGENIC PARTICLE SAMPLER

In order to understand the effects of supercritical solution composition on product catalyst particle characteristics, methods are needed to determine the concentration of catalyst solute in the supercritical solvent. In order to quantify the size distribution, porosity, and chemical composition of the product

catalyst particles, methods are needed also for acquiring particulate samples. A significant amount of attention has been given to identifying methods for measuring the composition of the supercritical solution just prior to the expansion process. Optical absorption methods are not appropriate, since the absorption cross-sections are temperature and pressure sensitive. Supercritical fluid liquid chromatography techniques, which are relatively new, are not compatible with the very severe conditions expected in the pre-expansion region of our experimental apparatus (i.e., H_2O , 600 atm, 600 C). We have abandoned, therefore, trying to obtain a direct measurement of supercritical solution concentration and have focused on deriving this information from analysis of post-expansion gas/particulate samples.

There are a number of ways to acquire gas/particle samples from a particle laden gas stream with pressures < 1 atm and at moderate temperatures (i.e., $T < 350$ C). Particulate membrane filters with pore sizes in the 10 nm range are available. These filters, when coupled with a gas flow meter, could provide, in principle, the mass ratio between particulates and solvent. This combined with a chemical analysis of the particulates would provide the information needed to determine the composition of the supercritical fluid. This approach is not practical because the flow rate of gas through the membrane filter is extremely small, leading to prohibitively long sampling times. In principle an electrostatic precipitator could be used for

removing particles from a gas stream. This coupled with a measurement of gas stream flow rate would provide the results needed to derive the composition of the supercritical solution. The particle collection efficiency of electrostatic precipitators, however, decreases to prohibitive levels below particle sizes less than 10 nm. The variation of electrostatic precipitator efficiency with particle size would lead to size biased particle collection also. Thus, electrostatic techniques do not provide an adequate approach.

Based on private communications with Professor Sidney Self, Mechanical Engineering Department, Stanford University, it was learned that unbiased, efficient, ultra-fine particle (i.e., particles < 100 nm) collection can be achieved via cryogenic methods. If a very low temperature surface is exposed to a gas stream containing ultra-fine particles, the gas and particulates can be condensed/frozen onto the collection surface in proportion to their respective concentrations in the gas stream, provided the temperature of the surface can be maintained at a temperature below the freezing point of the carrier gas, or for the present application, the freezing temperature of the supercritical solvent. The carrier gas can be removed from the collected/frozen sample by raising the temperature of the surface to within a few degrees below the sublimation temperature of the carrier gas, and then pumping on the sample with a suitable vacuum pump. After the carrier gas has been removed via sublimation from the sample, all that remains is the ultra-fine

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particulates. By collecting the gas removed from the sample by collecting it on a second cold surface, and determining its weight by an appropriate technique, and then applying an appropriate gravimetric analysis to the particulate sample, the ratio of catalyst material to solvent material can be determined. Through careful design of a cryogenic sampler based on the ideas presented above, it will be possible to determine the concentration of catalyst in the supercritical solution and determine the porosity, size distribution, and chemical composition of the catalyst particles.

Figures 2.13 and 2.14 show a schematic representation of the cryogenic particle sampling system that will be fabricated for this program. A particle probe, having an orifice sampling port small enough so that the flow is choked at the orifice during sampling, is inserted into the mixing section a few inches from the expansion nozzle. This sampling probe delivers the particle laden gas to the cryogenic sampler through a heated transfer line. The sampling orifice is operated choked so that a low pressure can be maintained in the transfer line and cryogenic sampler. The low pressure and heated transfer line allow rapid transfer of the particle laden gas from the sampling probe to the cryogenic sampler, with minimal particle coagulation and wall condensation.

The procedure for sample collection is straight forward. With the LN_2 trap in Figure 2.13 empty, the cryogenic sampler is pumped to a vacuum of nominally 10 millitorr. This is achieved

Figure 2.13 Particle Sampler and Concentration Analyzer.

Figure 2.14 Cryogenic Sampler Details.

by opening all valves between the vacuum pump and cryogenic sampler, and by closing the valve to the sample probe. The collection surface in the cryogenic sampler is then cooled to LN₂ temperatures by flowing LN₂ through the collection surface in the cryogenic sampler. The valve to the inlet of the LN₂ trap in Figure 2.13 is then closed and the valve to the sampling probe is opened. For a particle collection, coal material impregnation section back-pressure of 1 atm and a sampling probe orifice diameter of nominally 0.01 in., a 2-3 gram frozen sample of particle laden gas can be collected in less than 5 minutes when either H₂O or CO₂ is used as the supercritical solvent. If a 1000 ppm molar concentration of catalyst material in the supercritical solvent can be assumed to be achievable, the frozen sample should contain more than 10 milligrams of catalyst particles.

After the frozen sample has been collected in the cryogenic sampler, the sampling probe valve is closed, the valve to the inlet of the LN₂ trap in Figure 2.13 is opened, and the outlet valve from the LN₂ trap to the pump is closed. LN₂ is added to the LN₂ trap shown in Figure 2.13, and the collection surface in the cryogenic sampler is raised to within a few degrees of the sublimation temperature of the supercritical solvent species. The LN₂ trap collects the supercritical solvent sublimed from the collection surface in the cryogenic sampler. The sublimation process will be monitored via the pressure gauge attached to the LN₂ trap shown in Figure 2.13. When sublimation begins, the

pressure in the system should rise. The pressure will fall when all supercritical species material has been removed from the collection surface in the cryogenic sampler.

When the supercritical solvent species is CO_2 , the amount of CO_2 collected in the LN_2 trap in Figure 2.13 can be determined by removing the LN_2 in the trap, allowing its temperature to achieve ambient temperature, measuring the LN_2 trap pressure, and knowing the volume of the LN_2 trap. When the supercritical solvent species is H_2O , the LN_2 trap is allowed to achieve ambient pressure and the mass of H_2O is obtained by making a volume measurement of the liquid contained in the trap. Since the collection surface in the cryogenic trap is thin aluminum foil and can be easily removed (the details of the cryogenic sampler follow soon), the mass of catalyst material collected can be obtained by applying gravimetric analysis to the aluminum foil. Based on the procedure just outlined above, the mass of catalyst material collected and mass of supercritical fluid carrying the catalyst material collected can be measured. Thus, the concentration of catalyst species in the supercritical solution can be determined.

Figure 2.14 shows the details of the cryogenic sampler. The lower chamber of the sampler contains a LN_2 cooled copper rod, nominally 2 in. in diameter and 6 in. long. The copper rod contains 110 VAC electric heaters and thermocouple gauges used to elevate its temperature from LN_2 temperatures to a few degrees below the sublimation temperature of the supercritical solvent

species of relevance. The bottom of the copper rod is insulated from the chamber via a 3 in. long, 2 in. OD thin wall stainless steel tube. The upper chamber will have internal ID of 3.5 in. and a cavity height of 0.5 in. The collection surface will be a thin aluminum foil that rests on the top surface of the LN₂ cooled copper rod and which is sandwiched between the double o-ringed flanges joining the upper and lower chambers of the cryogenic sample. Since the lower chamber will be maintained at a pressure less than 20 millitorr, it was originally thought that the aluminum foil would need extra support because the upper chamber could have a pressure as high as atmospheric pressure. Stress calculations, however, have shown that the thin aluminum foil should not fail at the edges of the annular region between the copper rod and chamber flanges when a 1 atm differential pressure is applied across the aluminum foil. Thus, the thin copper support disk shown in Figure 2.14 will not be needed, which is good since the copper disk would provide a very good heat loss path from the copper rod to the chamber flanges. A thin aluminum foil collection surface will be used for determining the mass of catalyst contained in the supercritical solution. A thin plastic foil will be used for collecting samples for STEM particle size distribution analysis. It is felt that a very versatile design has been developed for the particle collection and analysis required for this program.

2.4 SUPPORT SYSTEMS

A number of support systems and utilities are required for this experimental effort. The main support system required is an explosion proof enclosure. The TDS Safety Department was consulted regarding safety guidelines for systems operating at design pressures and temperatures of nominally 9000 psig and 600 C. The enclosure shown in Figure 2.15 was concluded to provide adequate safety for personnel in the vicinity of the present experiment. This chamber was a laser cavity for a previous, completed program. It is made of 6161 aluminum. The walls are 2 in. thick. The dimensions are nominally 4 ft. X 4 ft. X 13 ft. One of the 13 ft. long vertical sides is open. This wall will be fitted with 3/4 in. thick Lexguard plastic sheet. Lexguard is a bullet resistant material and is light weight. The lexguard side will be fabricated in four panels, providing optical and physical access to the components inside the enclosure. TDS will be providing the chamber, Lexguard side panels, and a ventilation system for the enclosure. The ventilation system will have a capacity of 600 CFM. The inlet ventilation duct will draw air from the room. The length of the inlet duct was chosen so that if the autoclave decompresses, the resulting flow of gas out the inlet duct will not reach the inlet of the inlet duct. By the time such an incident ceases, the ventilation system should be drawing room air back through the inlet duct. Thus it was designed to prevent back-flow into the room if the autoclave fails.

Figure 2.15 Experiment Explosion-Proof Enclosure and Ventilation System.

Two other safety support systems will be installed in the laboratory containing the experimental apparatus. A fumehood with ventilation system will be installed by TDS. This will be needed for loading supply reservoirs with $\text{Fe}(\text{CO})_5$ or CS_2 for the supercritical flow system. The vapors from these liquids present health safety risks and must be handled in well ventilated spaces. OSHA regulations dictate that an emergency eyewash/shower be located close to fumehoods. TDS will install an emergency eyewash/shower next to the fumehood when the fumehood is installed. TDS will install the ventilation system and water and electrical services needed for these systems.

When the enclosure, fumehood, emergency eyewash/shower, and required ventilation systems are installed, water, shop air, and additional electrical services will be installed also. Nominally 100 psig shop air at 5-50 SCFM will be needed to drive the supercritical flow system high pressure pump. A 3-phase, 208 VAC, 30 Amp electric service will be needed to supply power to the 80 CFM Kinney vacuum pump that will be used to reduce the back-pressure of the particle collection, coal material mixing chamber section. A 1-phase, 208, 30 Amp electric service will be needed to power the sand bath heater for the autoclave. Several 1-phase, 110 VAC, 30 Amp services will be needed for other electric heaters and for powering diagnostic equipment. All these services will be provided by TDS.

3.0 TECHNICAL PROGRESS

3.1 TASK 1. PROJECT WORK PLAN

This task was completed during November 1990. The Project Work Plan was submitted to DOE/PETC on November 30, 1990.

3.2 TASK 2. EXPERIMENT DESIGN AND FABRICATION

JANUARY 1991. Design of the Ultra-Fine Particle Generator continued this month. As noted in prior reports, the apparatus consists of two main elements, namely: 1) a supercritical flow system for generating catalyst particles and 2) a post-expansion flow system for collecting catalyst particles and for impregnating coal or coal-liquids with catalyst particles. The design for the supercritical flow system has been completed and all necessary parts for this element have been ordered. Based on preliminary reports from vendors, delivery times in the range from five to eight weeks are anticipated. Thus, flow system assembly is expected to commence near the end of March 1991.

Between now and the end of March, facility support systems will be installed, namely: a flow system enclosure, a ventilation system for the enclosure, a fume hood for handling hazardous substances, and an exhaust system. Meetings with facility personnel are taking place now to define specifications for these systems. Based on delivery times and lead times associated with facility systems, the program is lagging the original schedule by nominally two to three months. A request for a no cost extension

is being prepared at this time.

During January 1991, preliminary design concepts were generated for the second element of the Ultra-Fine Particle Generator, i.e., the particle collection and impregnation flow systems. This flow system element must address a critical issue, which is that particles of submicron size are difficult to collect. A highly efficient means for collecting these particles is necessary for two distinct reasons. First, a suitable approach for determining the concentration of the catalyst solute in the supercritical solution has not been identified. This data is important for determining the influence of solute concentration on particle characteristics. The only option remaining is to deduce solute concentration by gravimetric analysis of collected particles, which will require an efficient collection method. Second, the mass flow rate of catalyst species is expected to be small (of order milligrams per minute), so particle collection for particle characterization and for coal material impregnation must be efficient in order to achieve reasonable run times.

Particle collection for characterization analysis can be performed efficiently and conveniently by thermophoresis. This approach will involve placing a sub-cooled collection surface near the expansion jet, which will attract and collect particles via thermal-molecular action. Although this approach will work well for obtaining particle samples, it does not provide information useful for determining catalyst flow rate. Thus,

catalyst solute concentration in the supercritical solution cannot be deduced by this method. As a result, our attention has turned to other effects that show promise for efficiently collecting all particles in the post expansion flow.

The most promising is electrostatic precipitation (ESP). This approach uses a corona discharge to charge particles in a gas stream, which then can be removed and deposited onto a collection electrode by means of an applied electric field. This approach is being considered as a means for collecting catalyst particles for gravimetric analysis to determine catalyst mass flow rate, collecting particles onto electron microscope slides for particle characterization, and for providing an efficient attachment vehicle for impregnating coal material with catalyst particles. Design analysis for integration of ESP has just begun and will be the focus of attention in the coming month.

FEBRUARY 1991. Design of the ultra-fine catalyst generator continued this month. The design and ordering of parts for the supercritical flow system element of the generator have been completed and ordered parts are being received by TDS.

Further analysis has been applied to the catalyst impregnation sections that follow downstream of the expansion nozzle. The preliminary design for the coal impregnation section was a fluidized coal bed that would operate in the fluidized mode when it experienced the highest expansion nozzle flow rates, and would operate as a fixed bed at the lower flow rates. The preliminary design for the coal liquid impregnation section

utilized a fuel-oil burner type spray nozzle that would atomize the coal liquid and deliver it into the oncoming expanded catalyst/solvent flow. Brownian particle coagulation analysis indicated that these designs would be very effective for impregnating coal materials with catalyst particles, i.e., particle attachment to the coal materials should be acceptable. These designs will be abandoned because they require an upstream section which is long enough to diffuse the high momentum expansion jet (nominally 15 inches). Brownian particle coagulation analysis applied to catalyst particles in the 10 nm size range indicates that the time scale for coagulation of likesize 10 nm particles ranges from 0.3 to 30 ms as the expansion backpressure is decreased from 1 to 0.01 atm. The flow time in the 15 inch diffuser section will be of order seconds, which means significant coagulation of catalyst particles will occur before entering the impregnation sections described above. Preliminary designs which provide close proximity between the expansion nozzle and the coal material are being formulated.

Determining the composition of the supercritical solution prior to expansion is necessary for optimizing catalyst particle size. Several approaches have been reviewed and only one has been identified as applicable. Particle collection via electrostatic effects was thought to be the best candidate, but its efficiency in the 1-10nm size range is uncertain. This approach has been abandoned in favor of a more promising one. The selected method will use a choked orifice sampling probe located

downstream of the expansion nozzle, which will be connected to a cryogenic sampler. The cryogenic sampler is a small chamber containing a thin aluminum foil collection surface maintained at liquid nitrogen temperature. This surface will freeze out all material that is drawn into the cryogenic sampler. By pumping on the collection surface by a second cryogenic trap, and raising the collection surface to a few degrees below the sublimation temperature of the solvent material, the solvent material can be sublimed off the collection surface leaving just the catalyst material. After isolating the second cryogenic trap and raising its temperature above the vapor pressure of the solvent, pressure and temperature measurements of the gas phase in the trap, together with knowing the volume of the trap, will allow calculation of the mass of solvent extracted from the aluminum foil collection surface in the cryogenic sampler. Application of gravimetric analysis to the aluminum foil containing just catalyst material will give the mass of catalyst collected. This method, therefore, gives both the mass of the catalyst and the mass of the solvent collected by the cryogenic sampler, hence the composition of the supercritical solution prior to expansion. This device can also be used for acquiring STEM slides coated with catalyst particles by placing an electron microscope slide on the aluminum collection foil. This approach should minimize particle coagulation since the orifice probe can be located close to the expansion jet and the pressure in the cryogenic sampler after the orifice should be low. The design of this device is

being finalized and its fabrication will commence while waiting for the system enclosure to be installed, along with enclosure support systems (i.e., shop air, ventilation, fume hood, and emergency shower).

The enclosure for the supercritical experiment must be explosion proof and reasonably air tight. TDS will be moving an unused laser cavity from a previous government program from its Everett site to its Haverhill site for this purpose. This chamber is made of two inch thick aluminum and measures 4' X 4' X 13.3' and will provide the strength and air seal needed. The one open face of this chamber will be fitted with Lexgard, which is a bullet resistant material that will provide optical access, strength, and air seal. TDS will also be providing a pedestal to set this chamber on, a ventilation system for the chamber, a fume hood for handling associated hazardous chemicals, and an emergency eyewash/shower station. Plans for moving, installing, and identification of miscellaneous parts to be supplied by TDS have been defined during this reporting period.

MARCH 1991. Design of the ultra-fine catalyst generator continued this month, and fabrication of the cryogenic sampler, which will be used for collecting catalyst particles and for determining the concentration of catalyst species in the supercritical solution, commenced. Time was dedicated to coordinating the transfer of the system enclosure and pedestal, fumehood, emergency eyewash/shower, high CFM vacuum pump, and flammable liquid storage cabinet from our Everett to Haverhill,

MA facilities. The transfer of this equipment took place on March 17, 1991. The chamber was put in place on its pedestal at that time. Final specifications and designs were established for the enclosure and fumehood ventilation systems, and for water, shop air, and electrical power for the experiment. A completion date for installation of ventilation systems and utilities of May 17, 1991 has been delivered to our Industrial Resources Department.

Design activities focused on refining a design for the mixing section of the system. A spouted bed configuration has been selected as the final concept for the mixing section. The expansion nozzle will be located at the bottom of a circular tube with the jet issuing up against gravity. A 45 degree cone, with the nozzle located at its apex, will form the bottom end of the tube, with the cone extending so that it merges with the inner surface of the tube. Particles returning to the bottom end of the tube via gravitational effects will be directed into the jet by the cone. A center-body will be installed in the main tube, which will consist of a plugged tube, with its open end facing the nozzle. The center-body will establish a recirculation pattern that will return coal particles or coal liquid droplets to the nozzle, and impede the progress of high momentum particles from reaching the exit of the spouted bed chamber by deflecting them to the wall. The center-body will be open-ended and hollow so that high momentum particles will enter a stagnant gas region sufficiently long so that they will slow by viscous drag to a

speed where particle fracture will be minimized when they collide with the plugged end of the center-body tube. This chamber will serve as an expansion chamber for optimization studies and as a mixing chamber for impregnation studies. This design should work very well for impregnating coal particles. Since the jet will be submerged in a liquid when attempting to impregnate the coal liquid, the performance of this configuration will depend on how the jet interacts with the coal liquid.

The spouted bed configuration has been adopted because it gives immediate and intimate contact between the jet and the coal material to be impregnated, thereby overcoming the catalyst particle coagulation problems inherent in the fixed or fluidized bed configurations discussed in prior reports. The nozzle assembly mating to the expansion tube will require innovative design concepts. This is because extreme conditions prevail in this assembly, namely: high temperatures and pressures, vacuum integrity, thermal isolation of the coal materials from the hot nozzle, and electrical isolation, which is needed to allow Ohmic heating of the supercritical transfer line. The engineering and fabrication costs for the nozzle assembly are expected to be greater than initially anticipated due to the extreme conditions this assembly experiences. A final design with drawings for the spouted bed mixing chamber will be produced during the next reporting period.

During this reporting period fabrication of the cryogenic sampler began. This device will be used to collect catalyst

particles for gravimetric and electron microscopy analysis. Sample collection times of a few minutes and sublimation times of an hour have been estimated for the operation of this device. The fabrication of this unit will be completed during the next reporting period.

3.3 TASK 3. SOLUTE/SOLVENT OPTIMIZATION

No work has been performed under this task as of yet.

3.4 TASK 4. CATALYST PREPARATION AND EVALUATION

No work has been performed under this task as of yet.

3.5 TASK 5. REPORTING AND DOCUMENTATION

JANUARY 1991. By the end of January 1991, TDS had submitted status, milestone, and cost management reports for the first four reporting periods of this contract (October, 1990 through January, 1991). Based on a recent telephone discussion with DOE's Project Manager, Dr. Udaya Rao, the date March 11, 1991 has been confirmed for the DOE/TDS kickoff meeting. The first Quarterly Progress Report has been delayed slightly due to rapid developments in experiment design, but should be delivered to DOE/PETC soon.

FEBRUARY 1991. By the end of February 1991, TDS had submitted status, milestone, and cost management reports for the first five reporting periods (October 1990 through February 1991). The first two quarterly reports are near completion and

will be submitted soon. The program kickoff meeting was held on March 11, 1991. TDS gave a program progress report and DOE/PETC personnel informed TDS of the overall scope of the ultra-fine catalyst effort, including other participating groups and their approaches. Discussions that took place during the kickoff meeting lead to resolution of choice of the coal and mesh size to use for impregnation and the coal liquid to be used for impregnation. Based on progress to date, this program is approximately four months behind schedule. The reasons for this have been given in earlier status reports. For this reason TDS submitted a request for a no-cost extension. A one year extension has been requested. TDS has received the contract amendment forms from DOE/PETC to formalize this request. These are being processed by TDS and will be returned to DOE/PETC very soon.

MARCH 1991. By the end of March 1991, TDS has submitted status, milestone, and cost management reports for the first six reporting periods (October 1990 through March 1991). The last four months of this program have been extremely busy and, consequently, timely preparation of the first two quarterly reports has suffered. Almost all of the design and facility issues have been resolved. With these demands lessening, a devoted effort will be applied to bring program reporting back in line. The formal contract amendment notification for the no-cost extension was received by TDS during this reporting period. Included in this amendment was a new reporting element titled

Property Reports. This information has been passed on to our property personnel for report preparation. TDS does not anticipate submitting one for February 1991, since the amendment was received after this date. However, TDS will adhere to the August 1991 Property Reports milestone.

4.0 CONCLUSIONS AND FUTURE WORK

4.1 CONCLUSIONS

Based on the designs presented in this report for the supercritical flow system and particle collection, coal material impregnation sections, several conclusions can be stated. The cost of the system will be significantly higher than originally anticipated. There are several reasons for this. Hastelloy, which is a low iron superalloy, must be used for the high pressure, high temperature components of the system in order to reduce contamination of the product catalyst particles from iron that would have been leached from these components if they had been fabricated from stainless steel. Safety and environmental issues have required more attention to resolve than originally envisioned. Although TDS will be providing the support systems needed to ensure personnel safety and compliance with environmental regulations, a considerable amount of time has been devoted to defining support systems and procedures.

During the process of identifying methods for obtaining the composition of the supercritical solution prior to expansion, an indirect method was devised that allows measurement of the supercritical solution prior to expansion and a means for acquiring STEM samples for determining the particle size distributions of product catalyst particles. The method is based on a cryogenic sampling technique and should provide a simple and

well behaved diagnostic for this experimental effort.

4.2 FUTURE WORK

The scope of the work that will be performed in the next quarter is listed below.

- * Continue Task 2 effort (Experiment Design and Fabrication).
- * Finish 1st and 2nd Quarterly Reports.

5.0 REFERENCES

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- 5 Abramovich, G.N., The Theory of Turbulent Jets, MIT Press, 1963.
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