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

FINAL TECHNICAL REPORT

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**U.S. DEPARTMENT OF ENERGY
Office of Fossil Energy
Pittsburgh Energy Technology Center
Pittsburgh, PA 15236**

by

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1.0 EXECUTIVE SUMMARY

The research conducted by Textron Defense Systems (TDS) represents a potential new and innovative concept for dispersed coal liquefaction. The technical approach is generation of ultra-fine catalyst particles from supercritical solutions by rapid expansion of either catalyst only, or mixtures of catalyst and coal material in supersaturated solvents. The process of rapid expansion of supercritical fluid solutions was developed at Battelle's Pacific Northwest Laboratories for the intended purpose of providing a new analytical technique for characterizing supercritical fluids.

The concept forming the basis of this research is that ultra-fine particles can be generated from supercritical solutions by rapid expansion of either catalyst or catalyst/coal-material mixtures in supersaturated solvents, such as carbon dioxide or water. The focal point of this technique is the rapid transfer of low vapor pressure solute (i.e., catalyst), dissolved in the supercritical fluid solvent, to the gas phase as the solution is expanded through an orifice. The expansion process is characterized by highly nonequilibrium conditions which cause the solute to undergo extremely rapid supersaturation with respect to the solvent, leading to nucleation and particle growth resulting in nanometer size catalyst particles.

A supercritical expansion system was designed and built by TDS at their Haverhill facility. A schematic diagram of the basic supercritical expansion system is shown in Figure 1.0-1.

This system has five principal components, namely: 1) a pump capable of producing pressures several times higher than the supercritical fluid of interest; 2) an optional heated autoclave for use in those cases where the solute material has a very low solubility in the liquid solvent at ambient conditions, and which needs elevated temperatures to achieve the required solubility; 3) a heated region wherein the supercritical mixture is heated to temperatures above the critical point; 4) a nozzle through which the solution can be expanded; and 5) a chamber for collecting the ultra-fine catalyst particles and where impregnation of coal materials (coal particles or coal liquids) with ultra-fine catalyst particles can be performed.

Figure 1.0-1 Diagram of Basic Supercritical Expansion System for Ultra-fine Particle Generation

Based on results reported by Dean Matson on the negligible solubility of FeS_2 and Fe_2O_3 in supercritical water, TDS focused their work on particle generation involving $\text{Fe}(\text{CO})_5$ in supercritical CO_2 . The final catalyst is known to be pyrrhotite.

TDS testing indicated that supercritical CO_2 also was not very effective in dissolving iron/sulfur compounds. SEM photographs showed no signs of particles being generated during the nozzle expansion process. However FeS particles were formed in the autoclave. SEM photographs of these particles showed them to be spherical in shape and ranging from 20-50 nm in size.

A 2 g sample of the autoclave material was collected for activity testing at Sandia Laboratory. This sample has been stored waiting DOE's instruction to ship it to Sandia.

Since the program goal was to achieve particle sizes in the 2-20 nm range, it can be said that TDS was not successful in reaching these goals.

2.0 INTRODUCTION

2.1 BACKGROUND

Coal constitutes greater than 75% of the world's proven nonrenewable energy resources. Oil and natural gas, however, account for about 70% of total fossil fuel utilization, and coal for 30%. This disproportionate usage of energy resources is due to fuel resource form (solid versus liquid) and is aggravated by geographical factors, primarily the location of the fuel relative to the customer. Conversion of coal to liquid form is a potentially sound approach for circumventing these obstacles. While both direct and indirect liquefaction have been used to commercially produce liquids from coals, it is acknowledged that new technological processes based on fundamental research are required for the effective, economic, and environmentally acceptable conversion and utilization of coal.

The overall goal of U.S. coal liquefaction R&D has been defined to be the development of technologies capable of producing marketable liquids economically and, consequently, to be competitive with crude oil prices (\$25/bbl by 1995). The development and application of effective catalysts will be central to the economic viability and operability of processes to convert coals to useful liquid products. The potential impact on process economics by progress in catalyst technology is significant, for example: increased rate of conversion; increased selectivity to desirable products; and reduced severity for liquefaction conditions. In the absence of significant developments in new catalyst materials, it is generally agreed that major improvements will be achieved through utilization of once-through, dispersed catalysts with emphasis placed on optimizing the effects of catalyst particle size, uniformity, and dispersion. Most importantly, catalyst activity is known to increase significantly with decreasing particle size. Experimental evidence suggests it is reasonable to expect significant improvements in coal solubilization by using catalyst particles with good size uniformity and mean size less than 400 Å. The current program, undertaken by the Energy Technology Office of TDS responds to this need.

2.2 PROGRAM CONCEPT

The research being conducted by TDS represents a new and innovative concept for dispersed coal liquefaction. The technical approach is generation of ultra-fine catalyst particles from supercritical solutions by rapid expansion of either catalyst only, or mixtures of catalyst and coal material in supersaturated solvents. The process of rapid expansion of supercritical fluid solutions was developed at Battelle's Pacific Northwest Laboratories for the intended purpose of providing a new analytical technique for characterizing supercritical fluids.⁽¹⁾ The precipitation of a number of monomers and polymers following rapid expansion of supercritical solutions and extraction and precipitation of pharmaceutical products has been reported recently.⁽²⁾ The effects of pre- and post-expansion conditions on the formation of naphthalene and lovastatin from supercritical solutions have also been studied.⁽³⁾ From these works, it became apparent that this technique could be suitably modified and exploited for material processing, especially for generation of ultra-fine catalyst particles for coal liquefaction processes.

The concept forming the basis of this research is that ultra-fine particles can be generated from supercritical solutions by rapid expansion of either catalyst or catalyst/coal-material mixtures in supersaturated solvents, such as carbon dioxide or water. The focal point of this technique is the rapid transfer of low vapor pressure solute (i.e., catalyst), dissolved in the supercritical fluid solvent, to the gas phase as the solution is expanded through an orifice. The expansion process is characterized by highly nonequilibrium conditions which cause the solute to undergo extremely rapid supersaturation with respect to the solvent, leading to nucleation and particle growth. It is estimated that particle nucleation and growth in the expansion jet occur on a time scale of microseconds or less. A detailed understanding of the expansion phenomenon and nucleation processes relevant to particle formation does not currently exist. Qualitatively, Battelle Northwest describes the process in terms of the nucleation and condensation of nonvolatile monomolecular species which are initially present in the supercritical solution.⁽⁴⁾ When the expansion conditions favor nucleation and condensation of the solute, the product is small particles of nonvolatile solute. Although the precise mechanisms are not known, the

technique of rapid expansion of supercritical fluids has been demonstrated to give product characteristics which are reproducible for a given material and expansion conditions.

A schematic diagram of the basic supercritical expansion system is shown in Figure 2.2-1. This system has five principal components, namely: 1) a pump capable of producing pressures several times higher than the supercritical fluid of interest; 2) an optional heated autoclave for use in those cases where the solute material has a very low solubility in the liquid solvent at ambient conditions, and which needs elevated temperatures to achieve the required solubility; 3) a heated region wherein the supercritical mixture is heated to temperatures above the critical point; 4) a nozzle through which the solution can be expanded; and 5) a chamber for collecting the ultra-fine catalyst particles and where impregnation of coal materials (coal particles or coal liquids) with ultra-fine catalyst particles can be performed.

Process parameters strongly affect the characteristics of the expansion process and the nature of the catalyst product. Two classes of process parameters can be identified. The chemical and physical properties of the solute and its concentration in the supercritical fluid prior to expansion constitute the first class of parameters, which directly affect product characteristics. The properties of the supercritical fluid constitute the second class of parameters, which directly affect the expansion process. A judicious combination of these two classes of parameters provides the capability to produce ultra-fine particles from a variety of materials having mean sizes in the range 10-10,000 nm with narrow particle size distributions. In order to identify parameter values producing optimum product characteristics, the experimental apparatus to be assembled during this program will be designed to provide independent control of all relevant process variables, such as pre-expansion composition and pre- and post-expansion pressure and temperature.

The procedure for generating ultra-fine dispersed catalyst particles by means of the present approach can be described as follows. The supercritical fluid solvent is pressurized using a high pressure hydraulic piston pump operated to maintain a system pressure between 200 and 600 atm. The supercritical fluid is delivered at constant flow rates which are slow enough to

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Figure 2.2-1 Diagram of Basic Supercritical Expansion System for Ultra-fine Particle Generation

provide sufficient time for equilibration between the solvent (i.e., supercritical fluid) and solute (e.g., iron-based catalyst compounds) as the supercritical solution flows through the system. Typical equilibrium flow rates in the range 5-50 cc/min (i.e., at ambient temperature and pressure) are anticipated.

When the solute has significant solubility in the solvent at ambient conditions, premixed solutions are prepared and pumped under pressure directly into the heated region prior to expansion. For materials having low solubilities at ambient conditions (e.g., solid catalyst stock), a preheat region is used to facilitate dissolution. This preheat region consists of a two-port autoclave unit. Typical solute concentrations in the range 50-50,000 ppm were anticipated.

The solute/solvent solution exits the preheat region and passes through a supercritical transfer line, and on to an expansion nozzle. At this stage, pre-expansion temperatures of typically 50-500°C are required. The residence time of the supercritical fluid in the supercritical temperature region depends on the solvent flow rate, but will be typically less than 30 seconds.

The expansion nozzle can be one of two designs, namely: a short capillary restrictor or a "pin-hole" orifice. For the conditions needed for ultra-fine catalyst particle generation for direct coal liquefaction, stainless steel hypodermic tubing 50-60 microns in diameter and 2-5 mm in length can be used to construct the restrictor nozzle and laser-drilled 0.25-0.75 mm stainless steel disks can be used to construct "pin-hole" orifice nozzles. Other durable, stable, and inert (i.e., inert at process temperatures and pressures) materials that can be used to fabricate nozzles are sapphire and diamond.

In scale-up or process development units, catalyst production rate will be an important factor. Given the range of expansion nozzle orifice sizes required for generation of ultra-fine particles, process development units will utilize nozzle arrays.

Impregnation of coal particles with ultra-fine catalyst particles or their suspension in coal liquids can be achieved in two general ways. The most effective approach, which would guarantee the best dispersion, would be to inject coal particles or liquids into the supercritical

solution prior to expansion. Although this approach provides the most intimate contact between catalyst and coal material, the severity of the supercritical solution conditions may lead to thermal decomposition of the coal, which may be detrimental to liquefaction processes. Dilution effects due to addition of coal material may make the process energy intensive. This approach may also lead to unacceptable nozzle erosion rates. Even though these issues could have a detrimental effect, their impact is uncertain, and due consideration was given to this approach. The second approach is to entrain coal particulates in the expansion jet in order to achieve impregnation of coal particles with catalyst particles. In a similar way, suspending catalyst particles in coal liquids could be achieved by impingement of the expansion jet with a fine droplet spray of coal liquid. These impregnation/suspension processes take place in the expansion chamber.

In the application of this concept for generation of ultra-fine particle catalysts for direct coal liquefaction, iron-based compounds are preferred as the solute material with carbon dioxide and water as the supercritical solvent. This permits reasonable operating parameters based on solubility data for these iron-based compounds, relatively low materials costs which make these compounds suitable as disposable catalysts, and, if desired, offers recovery and recycling ease from coal ash using ferromagnetic separation techniques. Suitable solute materials for ultra-fine catalyst generation for coal liquefaction include, but are not limited to, the following: iron pentacarbonyl [$\text{Fe}(\text{CO})_5$], iron pyrite [FeS_2], and iron oxide (Fe_3O_4). During the course of the present program, two of these catalyst solutes will be investigated. Carbon dioxide will be the primary solvent, but others, such as H_2O , H_2S , or CS_2 , will be considered if the solutes are not sufficiently soluble in CO_2 . Carbon dioxide and water are preferred from an environmental point of view.

In summary, the present program attempts to verify, optimize, and assess the potential of the supercritical expansion concept for generating ultra-fine, unsupported catalyst particles for the solubilization stage of two-stage catalytic-catalytic coal liquefaction processes. This novel concept shows promise for producing catalyst particles with narrow size distributions in the

range 10-10,000 nm. These features are projected to significantly improve the cost performance and product quality of current liquefaction processes.

2.3 PROGRAM OBJECTIVES

The overall objective of this research program was to evaluate the potential toward enhancing the performance of the solubilization stage of two-stage catalytic-catalytic coal liquefaction processes by use of ultra-fine, unsupported catalyst particles generated in situ (in coal or coal liquids) by means of the supercritical nucleation/growth concept. To achieve this goal, a twelve-month experimental program supported by analytical efforts was planned. Specific objectives included: 1) verifying the supercritical nucleation/growth concept for generating ultra-fine catalyst particles; 2) optimizing catalyst particle characteristics by systematically varying process parameters; 3) impregnating coal or coal liquid samples with ultra-fine catalyst particles; and 4) performing liquefaction tests on impregnated coal material samples to assess the activity of the ultra-fine catalyst particles generated by means of the supercritical nucleation/growth concept. The analytical efforts applied during this program were mainly related to test rig design and correlation of experimental data.

The first phase of the program was to design and fabricate a flexible test rig that can be used for investigating generation of ultra-fine catalyst particles by means of the supercritical nucleation/growth concept. The design allows independent control of process parameters and utilization of solid and liquid phase catalyst feedstock. It has an expansion chamber in which catalyst particles can be collected. It provides apparatus for dispersing catalyst particles into coal materials. Temperature, pressure, and flow rates at critical points in the system were monitored by suitable diagnostic instruments. During the design phase, an experimental test plan was defined for the remainder of the program.

The experimental tests to be conducted during the remaining phases of the program can be divided into three main areas: 1) solute/solvent optimization; 2) particle generation and optimization; and 3) catalyst performance evaluation. The purpose of the solute/solvent

optimization studies was to determine process parameters (i.e., supercritical solvent type and pre-expansion temperature and pressure) which yield the greatest solubility for a given catalyst compound. The purpose of the particle generation and optimization studies was to systematically vary process parameters around those values defined during the solute/solvent optimization effort in order to achieve the desired catalyst particle characteristics, namely: mean sizes in the range 2 to 40 nm, with particle size distributions $\pm 20\%$ of the mean value. The purpose of the catalyst performance evaluation studies was to impregnate a coal and a coal liquid with ultra-fine catalyst particles, determine their activity via liquefaction testing, and compare their performance to uncatalyzed coal liquefaction results and with current catalytic methods. The sequencing and substance of the testing described above constitutes a well-planned approach for achieving the goals of this research program.

3.0 SUPERCRITICAL EXTRACTION APPARATUS PLAN AND METHOD

3.1 SUPERCRITICAL FLUID CATALYST GENERATOR

The key elements of the ultra-fine catalyst generator are shown in block diagram format in Figure 3.1-1. 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.

The temperature/pressure specifications presented in Figure 3.1-1 were derived based on the work performed at Battelle Northwest Laboratories by Dean Matson.⁽⁵⁾ He 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 500°C in the autoclave, with the option to raise the temperature of the supercritical solution exiting the autoclave to 600°C. 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 3.1-2 and 3.1-3 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 3.1.

Figure 3.1-1 Block Diagram of Catalyst Particle Generator

Figure 3.1-2 Solvent/Solute Supercritical Flow System

Figure 3.1-3 Autoclave/Nozzle Supercritical Flow System

TABLE 3.1
LIST OF CONSTRUCTION MATERIALS FOR 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
S0-1	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	JOIN-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	55.55	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 3.1 (continued)

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-PAARMER	N-07143-90	TO 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	RSHER	14-831-312A		1	58.00	58.00	3-4 wks
MICRO ROTAMETER	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	

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
PP-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-PAARMER	N-01189-50	TO 600 C	1	3810.00	3810.00	4-5 wks
AUTOCLAVE	HIGH PRESSURE	GC-5 (HAS C278)	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	6	29.09	174.54	5-6 wks
SUBTOTAL						12300.54	

AUTOCLAVE TO NOZZLE LEG

Part	Vendor	Catalog No.	Spec.	No. 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	KOIN-116(G)-12	1000 C	1	27.00	27.00	2-3 wks
CAPS (HASTELLOY)	HIGH PRESSURE	60-21 HF4-C	60 KPSI	4	71.25	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	

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	

The design pressure and temperature for the flow system between the liquid solvents reservoir and check valve CV-1 (see Figure 3.1-2) is 1500 psig and 20°C, respectively. The pressure specification was based on the saturation pressure for liquid CO₂ at 20°C. 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 20°C, respectively. The design specifications for the flow section between the metering pump PM-2 and check valve CV-2 are 5000 psig and 20°C. 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 3.1-2, 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 20°C. 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 (20°C). Thus, the outlet side of the pump is rated for an operating pressure of 30,000 psig at 20°C.

The second main element of the supercritical fluid catalyst particle generator is the autoclave/nozzle flow system, which is shown in Figure 3.1-3. 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 was used to vent the high pressure side of the flow system after system shutdown. Autoclave inlet pressure and temperature was 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 ensured that an adequate pressure safety factor is maintained at temperatures up to 600°C at 10,000 psig. Figure 3.1-4 shows the strength of 316 stainless steel relative to Hastelloy C-276. As can be seen, the Hastelloy superalloy has a significantly higher tensile strength, which was needed to ensure the structural integrity of the high temperature/pressure section of the autoclave/nozzle flow system. For this reason, as well as Hastelloy's low iron content, Hastelloy C-276 was 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 were being processed in this supercritical flow system, it is desirable to minimize iron introduction by other sources.

The autoclave was made by High Pressure, Inc. from Hastelloy C-276, with a volume of 300 cm³, and an operating pressure of 600 atm at 500°C. The autoclave is 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 can be monitored by a thermocouple (see Figure 3.1-3, TC-5) in a thermowell integrated into the top of the autoclave. The 0.0625" OD solvent feed line helixed around the autoclave before entering it at its bottom in order to preheat the liquid solvents. A Hastelloy 100 µm fritted board filter was 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 µm 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.

Figure 3.1-4 Strength Dependence of Construction Materials on Temperature

The flow path branches immediately at the exit of the autoclave. One path leads to a bypass 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 bypass circuit was 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 was a 2 μm fritted filter (IF-2) made of Hastelloy C-276. This filter removed particulate matter escaping from the autoclave, which could plug the small diameter expansion nozzle. A 0.0625" OD x 0.020" ID x 8' Hastelloy C-276 tube transfers the supercritical solution exiting the autoclave to the nozzle assembly. This line was heated by passing a DC current through the Hastelloy tube. A 100 volt DC, 60 amp power supply regulated by a temperature controller was used to drive current through the transfer tube, which responded 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 600°C. Heat transfer analysis applied to the transfer line indicates that an 8' length of tubing should be adequate to raise the temperature of the supercritical fluid leaving the autoclave to 600°C 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 3.1-3, MV-1), pressure gauge (PG-3), and thermocouple gauge (TC-3) was installed at the downstream end of the supercritical solution transfer line. The metering valve was used to adjust the pre-expansion pressure, and the pressure and thermocouple gauges were used to obtain the thermodynamic state of the supercritical solution prior to expansion.

The nozzle shown in Figure 3.1-3 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 Matson⁽⁵⁾ 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 should 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 3.1-5 and 3.1-6 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 seen physically in the sketch of the laser drilled Hastelloy cap nozzle shown in Figure 3.1-7. State 3 represents the conditions just upstream of the Mach disk shock shown in Figure 3.1-8. The barrel shock and Mach disk structure shown in Figure 3.1-8 is for a pre-expansion/post-expansion pressure ratio of $\text{NPR} = 6.44$. The Mach number contours shown in Figure 3.1-8 were computed by Childs and Caruso,⁽⁶⁾ which agree well with the shadowgraph data acquired by Petrie and Walker.⁽⁷⁾ 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 is variable between 0.01 and 1 atm).

The pre-expansion thermodynamic conditions (state 1, Figures 3.1-5 and 3.1-6) are derived from several factors. First, to achieve good solvent dissolution power, the pressure should be 3-5⁵ times the critical pressure of the supercritical solvent and the temperature should

Figure 3.1-5 Supercritical CO₂ Expansion Process

Figure 3.1-6 Supercritical H₂O Expansion Process

Figure 3.1-7 Laser Drilled Orifice Nozzles

Figure 3.1-8 Characteristics of an Extremely Underexpanded Jet

be above the critical temperature. To ensure that supercritical fluid condensation does not occur during the expansion process, a rule of thumb⁽⁵⁾ dictates that the pre-expansion temperature should be greater than 1.3 times the critical temperature. Referring to Figures 3.1-5 and 3.1-6, 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 CO₂ were determined to be 450°C, 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 570°C, 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 used in this study. As noted earlier, 3 g/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, it can still achieve reasonable impregnation times.

In the previous discussion, it was mentioned that a laser drilled Hastelloy cap will be used as the expansion nozzle. Figure 3.1-7 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 3.1-7. 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 3.1-7. 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 3.1-8 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 was fabricated from a Hastelloy C-276 fitting, tube cap. It was counterbored from the threaded side of the fitting and the expansion nozzle was laser machined from the blank side of the cap. Finite element stress analysis was performed on this part to derive counterbore and nozzle bore dimensions that can

give a reasonable safety factor at the maximum operating conditions, namely 600 atm and 600°C. The minimum area point in the nozzle can have a diameter of 0.002".

High pressure tubing caps were used as the platform for our nozzles. Fabrication involved an 0.02 inch ID counterbore, 0.335 inches deep, followed by an 0.001 to 0.003 ID orifice bore, nominally 0.040 inches deep, which will break through to the closed end of the fitting. A sketch of the final design of the Hastelloy-cap/nozzle is shown in Figure 3.1-9. The required machining was accomplished by EDM for the 0.02 inch counterbore and laser drilling for the nozzle orifice bore. The laser drilling for the nozzle orifice was accomplished by drilling from the outside free surface to the inside counterbore. A taper of 0.0005 inches is expected over the 0.040 inch drill length. This will lead to some expansion of the supercritical fluid in the nozzle, which is not expected to be detrimental to the particle evolution process. Finite element stress calculations were performed on the nozzle component in order to see if the required drilling would detrimentally effect the structural integrity of this part. The results indicate that a factor of two safety exists after the drilling described above. Based on discussions with laser capable machine shops, the minimum orifice diameter that can be drilled is 0.002 inch ID. This was completely compatible with our overall design.

3.2 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 3.1-1, 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

Figure 3.1-9 Laser Drilled Orifice Nozzle Final Design

mentioned above. These will be discussed in that which follows, as well as possible configurations and the final configuration.

Matson⁽⁵⁾ 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 was 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 was 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 3.2-1 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

Figure 3.2-1 Preliminary Concept for Expansion/Particle-Collection Section

have a circular cross-section and would mate to the downstream coal material impregnation section. The purpose of 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 Love⁽⁸⁾ for nozzle/Mach-disk separation distance as a function of pre- and post-expansion pressures, the jet spreading angle (18 degrees) given by Abramovich,⁽⁹⁾ 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 represents the preliminary design details for the first concept for the expansion/particle-collection section.

Figures 3.2-2 and 3.2-3 give the 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 effective for depositing most of the catalyst particles in the flow onto the pulverized coal 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 Friedlander,⁽¹⁰⁾ particle coagulation time scales ranging from 0.3 to 30 milliseconds are

Figure 3.2-2 Preliminary Concept for Pulverized Coal Impregnation Section

Figure 3.2-3 Preliminary Concept for Coal-Liquid Impregnation Section

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 3.2-1 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 leads 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 3.2-4. 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 can 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 can 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.

As shown in Figure 3.2-4, 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-

Figure 3.2-4 Final Concept for Particle Collection, Coal Material Impregnation Section

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 3.1, 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 3.2-4 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 3.2-4 was 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 can 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 is such that the back-pressure can be smoothly adjusted from 0.01 to 1 atm.

The manifolding just upstream of the expansion nozzle are housed in a sandbox heater. The components 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 is constructed using a 3 KW 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 is filled with sand to provide good thermal contact between the plumbing fixtures and the flat board heater.

The final design for the spouted bed, particle collection, coal material impregnation section is shown in Figure 3.2-5. This section consists of an expansion nozzle discharging vertically against gravity into a circular tube. More specifically, a 45° cone, with the nozzle located at its apex, forms the bottom end of the mixing section tube. The 45° cone allows

Figure 3.2-5 Spouted Bed, Particle Collection, Coal Material Impregnation Section Final Design

transition from the small nozzle orifice opening to the inside diameter of the mixing section tube. Since the nozzle element is supported by a stainless steel flange, which has a high temperature vacuum seal, the 45° cone allows a diameter transition from 0.25 to 4.0 inches. The cone was fabricated from machinable ceramic, which has low thermal conductivity, in order to thermally isolate the hot nozzle and its support flange from the coal-material during impregnation studies. This ceramic cone is an insert and the mixing section tube was welded directly to the nozzle support flange. The ceramic cone and stainless steel retainer cone are shown in Figures 3.2-6 and 3.2-7, respectively.

Heat transfer from the hot nozzle support flange was minimized by reducing the wall thickness of the mixing section tube from 0.25 inches to 0.1 inches for one inch starting at the weld junction between the nozzle support flange and mixing section tube. When the nozzle is maintained at 600°C, only 30 W of power is lost to the mixing section tube by heat conduction from the hot nozzle support flange.

A 1 KW flat ring heater by Watlow was used to heat the nozzle support flange, and thus the nozzle itself. Since nozzle plugging may be a problem with this type of process, ease of nozzle removal was seen as a key design feature. As stated above, the nozzle is supported by a flange. More precisely, the nozzle support flange has a counterbore in which the nozzle component is seated. The mixing section face of the nozzle component seats against a metal o-ring. This seal serves as a high temperature vacuum seal. The force needed to make the seal between the nozzle component and the metal o-ring is applied by a smaller retainer flange that bolts to the nozzle support flange.

The overall length of the mixing section tube is 15.5 inches, its inside diameter 4.0 inches, and has a wall thickness of 0.25 inches. Two optical access windows, 180 degrees apart, were located in the walls of the mixing section tube at the nozzle end of the mixing section tube, such that their lowest point lies just above the intersection of the 45° cone and the mixing section tube wall. These windows are needed to detect if condensation is appearing in the expansion jet. The 4.0 inch ID mixing section tube contains a 1.0 inch OD open-ended, hollow tube, center-

NOTES:

- 1 - MATERIAL: COTRONICS 914 HT MACHINABLE CERAMIC

Figure 3.2-6 Particle Collection, Coal Material Impregnation Section Ceramic Transition Cone

Figure 3.2-7 Particle Collection, Coal Material Impregnation Section Stainless Steel Retainer Cone

body. This center-body tube, as shown in Figure 3.2-8, will be plugged at the end farthest from the nozzle. The end of the centerbody nearest the nozzle assembly lies in the plane where the 45° cone intersects the wall of the 4.0 inch mixing chamber tube. The center-body provides a stagnant gas region that slows coal particles, which have been accelerated by the expansion jet, to speeds which will not cause fracture when they collide with the plugged end of the center-body tube. The center-body also sets up a recirculation pattern that assists in drawing coal particles back into the cone section, which guides them into the discharge of the jet. Lastly, the center-body can deflect coal particles or droplets into the wall of the mixing chamber tube, thereby minimizing the possibility of their escaping from the mixing chamber and entering further downstream exhaust sections. The inside bore of the mixing chamber tube was bored smooth to minimize coal particle attachment. Pairs of Swadgelock 0.25 inch ID tube fittings, 180 degrees apart, were located at 2 and 10 inches from the nozzle exit in the walls of the 4 inch mixing section tube. These were used for inserting the particle sampling probe, measuring chamber pressure, and for injecting coal and coal liquid samples. The flange on the 4.0 inch mixing section tube that couples this section to the downstream exhaust manifolding was electrically isolated. The flanges at this union are separated by a double o-ring/ phenolic disk and the bolts are isolated using ceramic washers. The isolation disk is shown in Figure 3.2-9.

The throttle valve, cross for pressure gauge and thermocouple probe diagnostics, and in-line filter were closed coupled to the nozzle component to minimize heat losses. These items are housed in a sand-bath heater. This arrangement is shown in Figure 3.2-10. A 2.5 KW flat plate heater forms the bottom of the sand-bath heater, the remaining walls are made of 1 inch thick Fiberfrax insulation board. A thermocouple monitored the temperature of the sand-bath heater, which services the temperature control unit supplying power to the plate heater. All tubing in this section is thick-walled, 0.25 inch OD Hastelloy tubing, which transitions in the upstream direction to 1/16 inch, thick-walled Hastelloy tubing that runs nominally 8 feet back to the autoclave. Electric Power for heating the 1/16 inch line was applied between the mixing section and the autoclave, which was supplied by an existing power supply and controller.

Figure 3.2-9 Particle Collection, Coal Material Impregnation Section Isolation Disk

Figure 3.2-10 Pre-expansion Sandbox Heater Assembly and Diagnostics Arrangement

3.3 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.

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 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 is 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 3.3-1 and 3.3-2 show a schematic representation of the cryogenic particle sampling system that was 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 was straight forward. With the LN₂ trap in Figure 3.3-1 empty, the cryogenic sampler was pumped to a vacuum of nominally 10 millitorr. This was achieved 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 was 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 3.3-1 was then closed and the valve to the sampling probe was 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 CO₂ was 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.

Figure 3.3-1 Particle Sampler and Concentration Analyzer

Figure 3.3-2 Cryogenic Sampler Details

After the frozen sample has collected in the cryogenic sampler, the sampling probe valve was closed, the valve to the inlet of the LN₂ trap in Figure 3.3-1 was opened, and the outlet valve from the LN₂ trap to the pump was closed. LN₂ was added to the LN₂ trap shown in Figure 3.3-1, and the collection surface in the cryogenic sampler was raised to within a few degrees of the sublimation temperature of the supercritical solvent species. The LN₂ trap collects the supercritical solvent sublimated from the collection surface in the cryogenic sampler. The sublimation process was monitored via the pressure gauge attached to the LN₂ trap shown in Figure 3.3-1. When sublimation begins, the pressure in the system rose. The pressure fell when all supercritical species material had been removed from the collection surface in the cryogenic sampler.

When the supercritical solvent species was CO₂, the amount of CO₂ collected in the LN₂ trap in Figure 3.3-1 was determined by removing the LN₂ in the trap, allowing its temperature to achieve ambient temperature, measuring the LN₂ trap pressure, and knowing the volume of the LN₂ trap. If the supercritical solvent species was H₂O, the LN₂ trap would be allowed to achieve ambient pressure and the mass of H₂O 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 was measured. Thus, the concentration of catalyst species in the supercritical solution was determined.

Figure 3.3-2 shows the details of the cryogenic sampler. The lower chamber of the sampler contains a LN₂ cooled copper rod, nominally 2 in. in diameter and 6 in. long. The copper rod contains 110 volt AC electric heaters and a thermocouple gauge that was used to elevate and monitor the temperature from LN₂ temperatures to a few degrees below the sublimation temperature of the supercritical solvent species. The bottom of the copper rod was insulated from the chamber via a 3 in. long, 2 in. OD thin wall stainless steel tube. The upper

chamber has an internal ID of 3.5 in. and a cavity height of 0.5 in. The collection surface, as noted, is 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 would 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 3.3-2 was not needed, which is good since the copper disk would provide a very good heat loss path from the copper rod to the chamber flanges. The thin aluminum foil collection surface was used for determining the mass of catalyst contained in the supercritical solution. The thin aluminum foil was also used for collecting samples for SEM particle size distribution analysis. It was felt that a very versatile design was developed for the particle collection and analysis required for this program.

3.4 SUPPORT SYSTEMS

A number of support systems and utilities were required for this experimental effort. The main support system required was 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 3.4-1 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 was fitted with 3/4 in. thick Lexguard plastic sheet. Lexguard is a bullet resistant material and is light weight. The Lexguard side was fabricated in four panels, providing optical and physical access to the components inside the

Figure 3.4-1 Experimental Explosion-Proof Enclosure and Ventilation System

enclosure. TDS provided the chamber, Lexguard side panels, and a ventilation system for the enclosure. The ventilation system has a capacity of 600 CFM. The inlet ventilation duct can 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 of the inlet duct can 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.

Two other safety support systems were installed in the laboratory containing the experimental apparatus. A fumehood with a ventilation system was installed by TDS. This was needed for loading supply reservoirs with $\text{Fe}(\text{CO})_5$ for the supercritical flow system. The vapors from this liquid 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 installed an emergency eyewash/shower next to the fumehood when the fumehood was installed. TDS installed the ventilation system and water and electrical services needed for these systems.

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

3.5 DATA ACQUISITION SYSTEM

A TDS owned Masscomp 5500 computer/data acquisition system was used for this program. The system consisted of an Analog Devices signal conditioner (16 channels), an A/D

16 channel converter, a Masscomp 5500 (Unix) computer, and TDS proprietary data acquisition/reduction software. This system was used to monitor all thermocouple and pressure signals. This was useful for recording operating conditions during runs, and for providing on-screen results of temperatures around the system, solvent flow rates and critical pressures.

4.0 TEST RESULTS AND DISCUSSION

4.1 TEST MATRIX

The original test matrix prepared for the Program Plan (see Table 4.1-1) contained well over 32 elements, which would have required extensive test rig operation and costly catalyst characterization analyses. The original test matrix included two (2) supercritical solvents (CO_2 and H_2O), two (2) catalyst precursors (two of the following: $\text{Fe}(\text{CO})_5$, FeS_2 , or Fe_2O_3), two (2) solubilizing or coprecipitant additives (CS_2 and H_2S), two (2) sets of pre-expansion temperature and pressure conditions for each supercritical solution, and variations on solute, solvent, and additive concentrations.

Based on results presented by Dean Matson at the 1991 Pittsburgh Coal Conference and program budget constraints, it was possible and necessary to construct a new test matrix with better focus and scope.

Matson found that both FeS_2 and Fe_2O_3 have negligible solubilities in supercritical water. Also TDS concluded that safety and environmental regulations will make testing using CS_2 and H_2S as supercritical solvents for FeS_2 and Fe_2O_3 too costly to be undertaken. Based on these factors, particle generation studies based on FeS_2 and Fe_2O_3 were given low priority and would be undertaken as program resources allow. The main thrust will be to explore particle generation involving the catalyst precursor $\text{Fe}(\text{CO})_5$ and the supercritical solvent CO_2 . Although $\text{Fe}(\text{CO})_5$ is known to be an effective catalyst precursor for hydroliquefaction of coal, it is apparent that the final form, thus the active catalyst, is pyrrhotite. Therefore, in order to produce catalyst particles with high activity, a sulfur compound must be introduced during the particle generation process.

Gas/liquid phase chemical equilibrium calculations at 1 atm indicate that a mixture of 99% CO_2 , 1% $\text{Fe}(\text{CO})_5$, and 1% CS_2 (molar basis) produces FeS_2 from 300-600K and FeS above 600K. Although the kinetic rates are not known, especially under supercritical conditions, these results suggest that it may be possible to produce highly active, ultra-fine, iron sulfide

TABLE 4.1-1

**TEST MATRIX FOR ULTRA-FINE PARTICLE, UNSUPPORTED
CATALYST GENERATION**

<u>Solute</u>	<u>Solubilizing Additive</u>	<u>Solvent</u>	<u>Supercritical Fluid Mixture</u>	<u>Solute/Additive Concentration (PPM)</u>	<u>Pre-Expansion</u>	
					<u>T (°C)</u>	<u>P (atm)</u>
Fe(CO) ₅	CS ₂	CO ₂ , (CS ₂)	Fe(CO) ₅ //CO ₂	50-50K	50, 100	200, 350
			Fe(CO) ₅ /CS ₂ //CO ₂	(50-50K)/(10K-50K)	50, 100	200, 350
			Fe(CO) ₅ /CS ₂ (Optional)			
FeS ₂ (PYRITE)	H ₂ O, H ₂ S, CS ₂	CO ₂ , (CS ₂ , H ₂ O, H ₂ S)	FeS ₂ /H ₂ O//CO ₂	(25-25K)/(10K-50K)	100, 150	200, 350
			FeS ₂ /H ₂ S//CO ₂	(25-25K)/(10K-50K)	50, 100	200, 350
			FeS ₂ /CS ₂ //CO ₂	(25-25K)/(10K-50K)	50, 100	200, 350
			FeS ₂ //CS ₂ (Optional)			
			FeS ₂ //H ₂ O (Optional)			
			FeS ₂ //H ₂ S (Optional)			
FeS (TROILITE)	H ₂ O, H ₂ S, CS ₂	CO ₂ , (CS ₂ , H ₂ O, H ₂ S)	FeS/H ₂ O//CO ₂	(20-20K)/(10K-50K)	100, 150	200, 350
			FeS/H ₂ S//CO ₂	(20-20K)/(10K-50K)	50, 100	200, 350
			FeS/CS ₂ //CO ₂	(20-20K)/(10K-50K)	50, 100	200, 350
			FeS//CS ₂ (Optional)			
			FeS//H ₂ O (Optional)			
			FeS//H ₂ S (Optional)			
Fe ₂ O ₃ (HEMATITE)	H ₂ O, H ₂ S, CS ₂	CO ₂ , H ₂ O, H ₂ S, (CS ₂)	Fe ₂ O ₃ /H ₂ O//CO ₂	(20-20K)/(10K-50K)	100, 150	200, 350
			Fe ₂ O ₃ /H ₂ S//CO ₂	(20-20K)/(10K-50K)	50, 100	200, 350
			Fe ₂ O ₃ //H ₂ O (Optional)			
			Fe ₂ O ₃ //H ₂ S (Optional)			
			Fe ₂ O ₃ //CS ₂ (Optional)			

catalyst particles using supercritical CO₂. The refined test matrix (see Table 4.1-2 includes studies that will explore the effect of introducing the additive CS₂.

If the chemistry just described does not take place, particles will be generated consisting of coprecipitated metallic iron and CS₂. Under the severe conditions of the solubilization stages of liquefaction processes, these coprecipitants will probably react to form activated pyrrhotite. In either case, suitable catalyst particles are obtained.

4.2 SYSTEM SHAKEDOWN TESTING

After completing system calibrations, system shakedown tests commenced. These tests included: heating systems checkouts, achievement of supercritical CO₂ conditions and steady flow, and liquid solute (Fe(CO)₅) and liquid additive (CS₂) metering systems checkout. With the system pressurized with CO₂ to 3000 psig, the autoclave easily reached an internal temperature of 400°C, which is the maximum anticipated for the CO₂/Fe(CO)₅/CS₂ system. It is clear that an autoclave temperature of 500°C, which is a structural maximum for the autoclave, could be reached easily. The electrically heated 1/16" OD Hastelloy supercritical transfer line could be heated to 375°C using the DC power supply initially installed for heating this line. This temperature is a little low (400°C would be appropriate for the CO₂/Fe(CO)₅/CS₂ system) and was limited by the current the power supply can deliver (15 amps). A 40 amp, 50 volt DC power supply was available for use in this circuit and should provide temperatures up to 600°C easily.

The sandbox heater, which heats the awkward plumbing components just upstream of the expansion nozzle, easily achieved 600°C. The ring heater that heats the base of the mixing chamber, which maintains the desired pre-expansion temperature, easily achieved 400°C. However, the Variac controlling this heater had to be set to 70% power to reach 400°C. Additional insulation around the base of the mixing chamber was necessary to achieve 600°C. All heating systems are well behaved in that temperature control within ± 5°C is readily achieved.

TABLE 4.1-2
UPDATED TEST MATRIX

Priority	Primary	Optional	Optional
Solute	Fe(CO)₅	FeS₂	Fe₂O₃
Supercritical Solvent	CO₂	H₂O	H₂O
Solubilizing or Coprecipitant Additive	CS₂	CS₂ or H₂S	CS₂ or H₂S
Supercritical Fluid Mixture	Fe(CO)₅/CS₂/CO₂	FeS₂/CS₂/H₂O FeS₂/H₂S/H₂O	Fe₂O₃/CS₂/H₂O Fe₂O₃/H₂S/H₂O
Solute/Additive Concentration (ppm)	Fe(CO)₅/CS₂ 50-50K/0-50K	CS₂ or H₂S 0-50K	CS₂ or H₂S 0-50K
Pre-Expansion Pressure (atm)	200-350	<600	<600
Pre-Expansion Temperature (C)	50-100	<600	<600

Since the system was pressurized with CO₂ during heating system shakedown tests, an attempt was made to achieve the nominal operating conditions for the CO₂/Fe(CO)₅/CS₂ system. Indeed these conditions were achieved, i.e., autoclave temperature = 400°C, transfer line temperature = 400°C, pre-expansion temperature = 400°C, system pressure = 5000 psig, and a CO₂ mass flow of nominally 10 g/min. Two problems occurred under these conditions. First, steady flow could only be maintained for about 1 hour. Second, nozzle plugging occurred several times.

The inability to maintain steady flow indefinitely was traced to the fact that the CO₂ syphon bottles, which supply liquid CO₂ to the system, drop in pressure as CO₂ is removed from these bottles. When this happens the bottle pressure drops below the liquid saturation pressure and cavitation occurs easily at the inlet of the high pressure pump. Pump inlet cavitation occurs because the Haskel pump has a fast suction stroke driven by the nominally 850 psig inlet head and a rather strong return spring. To minimize pump inlet cavitation, the return spring was removed from the pump and a restricting orifice plate was installed on the vent for the air side of the driving piston. These changes slow the suction stroke action and minimize the inlet cavitation.

Changes to the high pressure pump alone would not cure the cavitation problem completely. We must deliver to the high pressure pump liquid CO₂ which has a pressure above the liquid saturation pressure at local ambient temperatures. We tried back filling the CO₂ syphon bottles with nitrogen to 1400 psig. This seemed to reduced the cavitation problem, but did not eliminate it completely. We assume that some nitrogen is dissolving in the liquid CO₂, which raises its liquid saturation pressure. We also tried heating the CO₂ syphon bottles with heating lamps to increase the saturation pressure. This also helped to reduce the cavitation problem, but did not eliminate it completely. In the process of trying these changes, it was observed that the flow meter was making the problem worse. The pressure drop across the flow meter, which is used to monitor supercritical solvent flow rate, is enough to cause cavitation. This flow meter was removed from the high pressure pump supply circuit. Instead of using the

supply side flow meter to measure CO₂ flow rates, a gas flow meter was installed on the mixing chamber. The exhaust from the mixing chamber could be valved off and the exhaust flow was forced through a Dywer float-type flow meter.

By trial and error we have found that the cavitation problem can be remedied by sub-cooling the liquid CO₂ to 0°C, removing the supply side flow meter, reducing the suction stroke rate on the Haskel high pressure pump, and using 0.5" diameter supply side tubing rather than the 0.25" tubing originally installed.

Steady flow of the supercritical solvent was interrupted also by nozzle plugging. Two nozzles plugged during the first 3 hours of operation. As a result, an order was placed with the vendor (Lenox Lasers) that drilled the orifice hole nozzles for clearing plugged nozzles. The two nozzles that plugged were easily cleared by Lenox Lasers. The contact person at Lenox said the blockage was formed from carbonaceous material. We have concluded that the carbonaceous material is residue from cutting oils used during component machining. To clean the system of residual oils, the nozzle was replaced with a needle valve, all heaters were turned on to provide 300°C temperatures, and CO₂ was flowed through the system at 3000 psig for approximately 10 hours. This cleared up the plugging problem. We expected this to occur and recognize that under certain solute/additive concentrations plugging will occur. This is the only risk area that could inhibit achieving particle generation, at least beyond the physics of the process.

The last system check to be performed was testing the behavior of the metering pumps that feed Fe(CO)₅ and CS₂ into the inlet of the high pressure pump. Two 10 ml burets act as the liquid reservoirs for these pumps. The fill end (top) of these burets are open and 7 µm in-line filters appear between the burets and the metering pumps. With the burets at atmospheric pressure, the metering pumps would not pump. In conversations with the metering pump vendor, it was found that these pumps need an inlet pressure of nominally 20 psig to get consistent operation. As a result, a pressurized buret system will be constructed. The 20 psig inlet head specification was overlooked when setting up the metering pump circuits. This oversight, however, forced a close look at these systems. As a result, flow circuits were defined that

provided correct pump inlet conditions as well as an overall system that makes filling and emptying $\text{Fe}(\text{CO})_5$ and CS_2 from the burets more convenient and, therefore, more safe.

Based on the preceding discussion the following system changes were made:

1. Modified inlet plumbing to high pressure pump to eliminate cavitation. A 4' long coaxial heat exchanger was installed. It had an outer tube OD of 0.5" and an inner tube OD of 0.25". Nitrogen gas from the vent of a 240 liter liquid nitrogen dewar was used to cool the inner tube. Liquid CO_2 flows in the annular region between the inner and outer tubes.
2. Fabricated a pressurized buret feed systems for each metering pump circuit. The design for each allows safe and easy removal of the harmful $\text{Fe}(\text{CO})_5$ and CS_2 liquids.
3. Replaced supercritical transfer line DC power supply with a higher power unit, i.e., one that can deliver 60 amps and 100 volt DC.

4.3 PARTICLE GENERATION TESTING

4.3.1 First Test

After system shakedown tests were completed, TDS commenced work on Task 3, Solute/Solvent Optimization tests. The purpose of this task is to experimentally derive system operating conditions that produce optimum catalyst particle characteristics, which include particle size, size distribution, and chemical composition. Due to budgetary constraints, TDS focused on the $\text{Fe}(\text{CO})_5/\text{CS}_2/\text{CO}_2$ system. The free system parameters are: S/Fe molar ratio, solute ($\text{Fe}(\text{CO})_5$) flow rate, supercritical fluid (CO_2) flow rate, autoclave temperature, autoclave pressure, pre-expansion pressure, pre-expansion temperature, and post expansion pressure.

Iron pyrrhotite exhibits effective catalytic characteristics for the hydroliquefaction of coal. The Fe/S molar ratio for pyrrhotite is between 1 and 2. For the first test, therefore, CS_2 and $\text{Fe}(\text{CO})_5$ were metered into the autoclave with a molar ratio of $\text{CS}_2/\text{Fe}(\text{CO})_5 = 2$. In order to ensure that the flow in the mixing section contained a detectable concentration of iron sulfide,

the flow rate of $\text{Fe}(\text{CO})_5$ was set assuming a supercritical solution flow rate of 10 g/m containing 0.5 wt% FeS. Based on these constraints, the volumetric flow rates for $\text{Fe}(\text{CO})_5$ and CS_2 were found to be 0.076 and 0.017 cc/min, respectively. The $\text{Fe}(\text{CO})_5$ and CS_2 metering pumps were adjusted to deliver these flow rates, and during the first test these rates were measured to be 0.052 and 0.013 cc/min, giving a S/Fe molar ratio of 1.8. The actual concentration of FeS in the mixing chamber should have been 0.45 %wt.

To simplify parameter variations, the pre-expansion and supercritical fluid transfer line pressures were set equal to the autoclave temperature. Likewise, the pre-expansion and supercritical transfer line temperatures were set equal to the autoclave temperature. The post-expansion pressure was set to local atmospheric pressure. The autoclave pressure was set to five times the critical pressure of CO_2 (5400 psig). Gas phase chemical equilibrium calculations, based on the NASA Chemical Equilibrium Code (CET-85),⁽¹¹⁾ were used to guide selection of the autoclave temperature. These calculations suggest that the dominant iron-sulfur compound will be FeS at temperatures above 400°C. Thus, the autoclave temperature was set to 400°C.

The first test took nominally 4.75 hours. It took about 1.5 hours to bring the system up to the desired temperature (400°C). During the warm-up period CO_2 was pumped through the system at 5400 psig. The CO_2 flow rate through the system was measured to be 10.2 g/m, which is extremely close to the design specification (10 g/min). During the preheat time, an aluminum diaphragm was installed in the cryogenic sampler, and the mixing section particle sampler was readied for use. At 1.5 hours into the test the $\text{Fe}(\text{CO})_5$ and CS_2 metering pumps were turned on. Based on the wetted volume of the system and the CO_2 flow rate, the plug flow time through the system was estimated to be nominally 20 minutes. The plug flow time is important to know since this is the time it will take for the catalyst product to appear in the mixing chamber after making changes to the inlet flow conditions to the autoclave.

Twenty minutes after solute injection initiation, the flow rate through the system decreased from 10.2 g/min to 5.1 g/min, indicating the presence of catalyst product at the expansion nozzle. Unfortunately, it also indicated nozzle plugging. Nominally 30 minutes after

solute injection initiation, the first particle sample was taken using the cryogenic sampler. The cryogenic sampler was allowed to draw mixing chamber gas for 2.5 minutes. During this time the sampler collected 2.8 g of gas. If particles were generated, the aluminum diaphragm, after sublimation of gas upon heat up, should have retained at most 24 mg of particle matter. Post-run high resolution SEM photographs showed that no catalyst particles were present on the aluminum diaphragm. Although it took only 2.5 minutes to collect the first particle sample, sample processing and preparation of the cryogenic sampler for the next sample took nominally one hour. By the time the sampler was ready for acquiring a second sample, 1.5 hours had passed and the system flow rate was down to 1.3 g/min, indicating that the expansion nozzle was nearly plugged. Shortly after this, the system was shut down. A second particle sample from the mixing section was not taken.

Teardown and inspection of the system after the first run revealed that there was a tremendous amount of black-brownish material in the autoclave. This observation suggests that the CS_2 and $\text{Fe}(\text{CO})_5$ were reacting in the autoclave and immediately precipitating to a solid form in the autoclave. High resolution SEM/EDS analyses of the autoclave material, Figure 4.3-1, revealed that the S/Fe molar ratio of the autoclave particles was 0.75. This is a reasonable value for iron pyrrhotite, but since this is a bulk S/Fe value it is not clear what phase these particles are. High resolution SEM photographs, Figure 4.3-2, show that the small particles, which aggregate into larger structures, have a size between 20 and 50 nm. If autoclave formation of particles is an acceptable approach for catalyst particle generation, we are not too far off the mark of reaching the 10 nm size range goal.

SEM photographs of particle samples taken from the post-expansion region (mixing section), Figure 4.3-3, revealed that no particles were being generated with the system in standard configuration.

The concept behind the first test was to form FeS molecules in the autoclave and see if the high solvation nature of supercritical CO_2 would prevent precipitation and coagulation of the molecular form into large particles in the autoclave. If this were to occur, the molecular form

SAMPLE #4 9-24-92 TEST 1 AUTOCLAVE MAT.
2013 1

100 secs
68 secs

Figure 4.3-1 SEM/EDS Analysis of Autoclave Samples on Test 1

P7470

Figure 4.3-2 SEM Photographs of Autoclave Samples on Test 1

P7471

Figure 4.3-3 SEM Photographs of Post-expansion Samples on Test 1

would persist until the expansion process where nucleation and particle growth could take place for a brief instant, forming particles in the 2-10 nm size range. The first test clearly demonstrated that precipitation readily occurs in the autoclave and that essentially no catalyst product is staying in solution. The nozzle plugging that was observed is more than likely due to particles passing through the in-line filters, which eventually build up in the throat region of the orifice nozzle.

4.3.2 Tests 2 and 3

Tests 2 and 3 were designed to reconfigure the system so that heat was not applied to the $\text{Fe}(\text{CO})_5/\text{CS}_2/\text{CO}_2$ solution until it reaches the nozzle. In hopes that if the residence time in the heated region of the nozzle is short enough, there is the possibility that ultra-fine particles may be generated in the expansion process.

To achieve the desired system configuration for Tests 2 and 3, the pressure control plumbing just upstream of the nozzle was removed, as was the sandbox heater which maintains the temperature of these parts. The supercritical solution transfer line was plumbed directly into a standard 0.002" orifice nozzle. The system parameter settings for Tests 2 and 3 were: autoclave temperature = ambient temperature, autoclave pressure = 5400 psig (five times the critical pressure of CO_2), supercritical solution transfer line temperature = ambient temperature, and post-expansion pressure = 1 atm absolute.

The experimental procedure for Tests 2 and 3 was to increase the nozzle temperature from 100 to 400°C, in increments of 50°C, taking particle samples from the mixing chamber at each temperature. This procedure is based on the desire to obtain a correlation between particle characteristics versus pre-expansion temperature when trying to force the reaction $\text{CS}_2 + 2 \text{Fe}(\text{CO})_5 + \text{CO}_2 \rightarrow 2 \text{FeS} + 12 \text{CO}$ to occur in the expansion nozzle.

Three particle samples were taken during Test 2 and one sample was taken during Test 3. Test 2 sample 1 was taken under the following conditions: supercritical solution flow rate = 17.3 g/min, S/Fe molar ratio = 1.48, solute loading = 0.26 wt% based on FeS as the catalyst product, and a pre-expansion nozzle temperature of 101°C.

Test 2 sample 2 was taken under the following conditions: supercritical solution flow rate = 12.8 g/min, S/Fe molar ratio = 1.80, solute loading = 0.39 wt% based on FeS as the catalyst product, and a pre-expansion nozzle temperature of 157°C.

Test 2 sample 3 was taken under the following conditions: supercritical solution flow rate = 5.6 g/min, S/Fe molar ratio = 1.90, solute loading = 0.93 wt% based on FeS as the catalyst product, and a pre-expansion nozzle temperature of 210°C. An attempt was made to acquire a fourth sample at a pre-expansion nozzle temperature of 250°C during Test 2, but the expansion nozzle finally plugged. During acquisition of Test 2 samples 1-3 the supercritical solution flow rate dropped from 17.3 to 5.6 g/min, indicating nozzle plugging was in progress.

Test 3 sample 1 was taken under the following conditions: supercritical solution flow rate = 5.8 g/min, S/Fe molar ratio = 1.84, solute loading = 0.85 wt% based on FeS as the catalyst product, and a pre-expansion nozzle temperature of 250°C.

SEM photographs taken of Test 2 sample 3 and Test 3 sample 1 revealed that no catalyst particles were collected, and it is assumed that the cryogenic sampler would have collected catalyst particles if they were present in the post-expansion mixing chamber. The fact that the nozzles in Tests 2 and 3 showed signs of plugging when the nozzle temperature reached 200-250°C suggests that the solute material was precipitating in the nozzles causing plugging, and that none of the catalyst product stayed in solution.

Tests 2 and 3 clearly demonstrate that the precipitation process is fast once the catalyst precursors have reacted (i.e., $\text{Fe}(\text{CO})_5$ and CS_2). Precipitation leads to nozzle plugging either by deposits in the throat of the nozzle or by large particle (agglomerates) blockage. Tests 1 through 3 suggest that no catalyst particles are being generated, which can be interpreted to mean that very little catalyst material is staying in solution. This is probably the case, yet the uncertainty introduced by nozzle plugging must be eliminated before a definitive conclusion can be formed.

4.3.3 Tests 4 and 5

Tests 4 and 5 were designed to verify the premise that little catalyst material is staying in solution in the supercritical solvent (CO_2). For Tests 4 and 5 the 0.002" orifice nozzle was

replaced with a large bore orifice nozzle (7/64" throat diameter). The idea was to remove small passages down stream of the autoclave so that plugging can be minimized. The flow through the system will be controlled by the ID (0.021") of the supercritical solution transfer line and by making use of the phenomena known as the Rayleigh Line effect. The Rayleigh Line effect describes, for compressible fluids, the effect heat addition has on the Mach number of a fluid flowing through a constant area passage. It can be shown that the flow in the supercritical transfer line chokes (reaches Mach 1) at some point in the line. It is the conditions at this point that determine the mass flow rate through the system. The higher the heating rate of the supercritical transfer line, the lower the system flow rate will be. This effect will be used to reduce the system flow rate as much as possible, since large flow rates are expected due to the large throat of the expansion nozzle.

The system parameters for Test 4 were: autoclave temperature = 400°C, supercritical solution transfer line = 400°C, expansion nozzle temperature = 400°C, autoclave pressure = 5400 psig, supercritical solution flow rate = 72 g/min, S/Fe = 1.24, and a solute loading = 0.27 wt% based on FeS as the catalyst product. One particle sample was taken during Test 4, and is designated Test 4 sample 1.

The system parameters for Test 5 were: autoclave temperature = 400°C, supercritical solution transfer line = 600°C, expansion nozzle temperature = 600°C, autoclave pressure = 5400 psig, supercritical solution flow rate = 27 g/min, S/Fe = 0.69, and a solute loading = 0.97 wt% based on FeS as the catalyst product. One particle sample was taken during Test 5, and is designated Test 5 sample 1.

The drop in supercritical flow rate from Test 4 to Test 5 is not due to Rayleigh Line effects due to an increase from 400 to 600°C on the supercritical transfer line and nozzle temperatures. It was due to an operational error that occurred early in Test 5. Early in Test 5, before the autoclave heaters were on, but after the supercritical transfer line and nozzle were up to operating temperature (600°C), Fe(CO)₅ was metered into the system inadvertently while setting up the Fe(CO)₅ and CS₂ metering pumps. When the Fe(CO)₅ reached the transfer line, it

precipitated and partially plugged the transfer line. Difficulties were experienced also during Test 5 in achieving the proper flow rate of $\text{Fe}(\text{CO})_5$, which lead to a S/Fe ratio lower than desired (i.e., we wanted $1 < \text{S/Fe} < 2$, but obtained $\text{S/Fe} = 0.69$).

To illustrate the Rayleigh Line effect, we would, without this effect, expect the flow rate through the system to vary with the orifice nozzle throat area, which says that the 7/64" ID nozzle flow should be limited by the ID of the supercritical solution transfer line ID, which is 0.020". The area ratio between the 0.002" throat nozzle and the 0.02" ID transfer line is 100. Since the 0.002" ID nozzle gives a flow rate of nominally 10 g/min, the 7/64" ID nozzle configuration should give a flow rate of 1000 g/min. But the flow rate achieved during Test 4 is only 72 g/min. The lower flow rate is due to Rayleigh Line effects and to frictional effects in the supercritical solution transfer line. When the system is configured for the 7/64" expansion nozzle, the system supercritical flow rate increased by a factor of 7 and the velocities in the transfer line are even higher than the factor of 7 due to expansion of the fluid in the transfer line. This, in turn, leads to shorter transfer line residence times and higher viscous shear forces, both of which should reduce precipitation of solute material on the walls of the transfer line, thereby decreasing the possibility of transfer line plugging.

It was disappointing to see that the SEM photographs, Figure 4.3-4, of the particle samples from Tests 4 and 5 showed no sign of particles. These results clearly demonstrate that very little solute material is staying in solution in the supercritical solvent (CO_2).

4.3.4 Test Conclusions

The five solute/solvent optimization tests clearly show that very little solute material is staying in solution in the supercritical solvent (CO_2), and that supercritical CO_2 is not a very effective solvent for iron/sulfur compounds. One might consider repeating the tests conducted so far using supercritical water as the solvent, but Matson's results at Battelle Northwest Laboratories indicated that supercritical water yields very similar results to those obtained in Tests 1 through 5. As a result, TDS ceased solute/solvent optimization testing and proceeded to Task 4, Catalyst Preparation and Evaluation.

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Figure 4.3-4 SEM Photographs of Post-expansion Samples on Tests 4 and 5

4.4 CATALYST PREPARATION

TDS abandoned attempts to generate catalyst particles by rapid expansion of a $\text{Fe}(\text{CO})_5/\text{CS}_2/\text{CO}_2$ supercritical solution, and instead, focused on making FeS particles by precipitation in the autoclave of the supercritical flow system.

The goal of the last test, Test 6, was to generate a sufficient amount of FeS particles in the autoclave so that activity testing could be conducted by Sandia Laboratory, if approved by DOE/PETC.

Conversations with Sandia Laboratory revealed that they would need nominally 5 g of catalyst material in order to perform the activity testing. For Test 6, the $\text{Fe}(\text{CO})_5$ and CS_2 buret reservoirs were filled with amounts sufficient to generate 7.5 g of FeS particles.

The system parameters for Test 6 were: autoclave temperature = 400°C , supercritical solution transfer line = 300°C , expansion nozzle temperature = ambient temperature, autoclave pressure = 6600 psig, supercritical solution flow rate = 13 g/min, S/Fe = 1.06, and a solute loading = 0.81 wt% based on FeS as the catalyst product. No post-expansion particle samples were taken during Test 6. The expansion nozzle had a throat ID of 7/64". The system flow rate was controlled by a needle valve inserted just upstream of the 7/64" ID expansion nozzle.

The particle generation part of Test 6 lasted for 60 minutes. During this time, 14.6 g of $\text{Fe}(\text{CO})_5$ and 2.9 g of CS_2 were injected into the system. As noted above, this yields a S/Fe molar ratio of 1.06. These values imply that 6.7 g of FeS should have been deposited in the autoclave. The amount of material removed was only 2.4 g, or that only 36 wt% of the expected material deposited in the autoclave. This discrepancy can be explained by the thick layer of powder that deposited on the inside walls of the autoclave. TDS suspects that this material acted as insulation, which prevented the $\text{Fe}(\text{CO})_5$ and CS_2 from achieving decomposition/reaction temperatures later in the test after the product material deposited to a sufficient depth on the walls of the autoclave.

Immediately after Test 6, 2 g of the autoclave material was placed in a stainless steel vessel, which was evacuated and back-filled with dry argon. This sample is ready for shipment to Sandia Laboratory for activity testing. It should be noted that the autoclave material was exposed to the atmosphere for nominally 10-15 minutes while being transferred to the stainless steel vessel. This could not be avoided because the system autoclave would not fit in the glove box at the TDS Haverhill facility. The remaining 0.4 g of material was sent out for SEM and SEM/EDS analyses. The SEM/EDS analysis revealed, Figure 4.4-1, that the S/Fe molar ratio of the particles is 1.07, which is very close to the injection S/Fe molar ratio. The SEM photographs of the autoclave material, Figure 4.4-2, showed particles that are spherical in shape, ranging in size from 20-50 nm. These small particles had agglomerated forming larger structures. These photographs also showed crystal structures, probably iron crystals, having a characteristic size of nominally 100 nm.

Since the program goal was to achieve particle sizes in the 2-20 nm range, it can be said that we have not reached the program goal. It is not clear whether Sandia Laboratory should pursue activity testing on this sample. It may be worthwhile, however, due to the extraordinary conditions under which these particles were generated (400°C, 6600 psig). TDS will await a verdict by DoE/PETC regarding this issue. Test 6 completed the entire suite of tests planned for this program.

11-8-92 AUTOCLAVE MATERIAL
Vert= 2003 counts Disp= 1

Preset= 100 secs
Elapsed= 50 secs

Figure 4.4-1 SEM/EDS Analysis of Autoclave Samples on Test 6

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Figure 4.4-2 SEM Photographs of Autoclave Samples on Test 6

5.0 DISCUSSION OF RESULTS

During experimental testing, TDS conducted 5 tests under Task 3, Solute/Solvent Optimization, for a total of 6 solute/solvent optimization tests overall, and conducted one test under Task 4, Catalyst Preparation and Evaluation. These tests complete the entire suite of tests planned for this program.

A number of system configurations and system parameter variations were examined under Task 3, Solute/Solvent Optimization. These tests revealed that supercritical CO₂ is not a very effective solvent for iron/sulfur compounds. Particle samples taken from the mixing section down stream of the expansion nozzle revealed that this approach, when applied to the Fe(CO)₅/CS₂/CO₂ system, does not produce any ultra-fine iron compound catalyst particles. This implies that supercritical CO₂ is not very effective towards dissolution of iron/sulfur compounds.

There is, however, an abundance of catalyst material that precipitates into a powder in the autoclave component of the system. SEM/EDS analysis shows that the S/Fe molar ratio of the autoclave powder ranges between 0.77 and 1.06, which may be representative of some form of pyrrhotite, which is known to be fairly active toward coal solubilization for hydroliquefaction processes. The size distribution of the autoclave material lies in the 20-50 nm range. SEM microphotographs showed that the particles were mostly spherical in shape, but under some conditions (higher pressures) crystal structures were observed that have characteristic sizes of nominally 100 nm. Under Task 4, Catalyst Preparation and Evaluation, a 2 g sample of the autoclave material was generated for activity testing by Sandia Laboratory. Since the size characteristics of this sample of autoclave material (20-50 nm, with some 100 nm crystal structures) does not meet program goals (2-20 nm size range), it is unclear whether this sample is worth performing activity testing on. It may be worthwhile, however, due to the conditions under which these particles were generated (i.e., 400°C and 6600 psig). TDS has awaited a response from DOE/PETC regarding whether activity testing should be performed on this sample.

Albeit, TDS has completed all testing so far as program budgetary constraints permit. The goal of generating ultra-fine catalyst particles in the 2-20 nm range has not been achieved using the $\text{Fe}(\text{CO})_5/\text{CS}_2/\text{CO}_2$ system. One is tempted to explore the performance of supercritical water, but Matson at Battelle Northwest Laboratories has demonstrated that iron/sulfur compounds have little solubility in supercritical water. Based on this, supercritical water testing did not appear encouraging, and would not be pursued even if program resources permitted.

6.0 REFERENCES

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