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

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QUARTERLY TECHNICAL PROGRESS REPORT
for the period
January 1, 1992 through March 31, 1992

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TABLE OF CONTENTS

	<u>Page</u>
1.0 SUMMARY	1
2.0 TECHNICAL PROGRESS	3
2.0 FUTURE WORK	21

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1.0 SUMMARY

This is the sixth Quarterly Report for this program. It covers the period January 1, 1992 through March 31, 1992. The purpose of this program is to design and fabricate an experimental ultra-fine particle generation system; use this system to generate ultra-fine, iron compound, catalyst particles; and to assess the ability of these ultra-fine catalyst particles to improve the performance of the solubilization stage of two-stage, catalytic-catalytic liquefaction processes. The effort applied to this program during this reporting period focused on assembling the supercritical particle generation/collection system. Effort was applied to constructing a shakedown testing plan also.

Regrading system assembly, good progress was made despite the fact that assembly efforts did not begin until the last week of January 1992. Although the system is somewhat more complex than initially planned, most of the supercritical flow system was assembled during this reporting quarter. The remainder of the supercritical plumbing will be installed during the next quarter.

The supercritical particle generation system can be divided into three categories, namely: supercritical flow system components, heating system components, and diagnostics and instrumentation. The strategy applied in assembling the system was to assemble supercritical flow system components first. Next, the electric heating systems were to be installed.

Finally, diagnostics and data acquisition systems were to be installed. Although the electric circuits for the heating systems and diagnostics and data acquisition systems were not installed during this reporting quarter, they will be installed easily by the end of the next quarter.

During this quarter, a plan was constructed for system shakedown testing. This plan involves calibrating system thermocouples, pressure transducers, and flow meters. It also includes systematic startup procedures that leak test the system from ambient temperature, low pressure conditions to maximum temperature and pressure conditions. The shakedown tests will be carried out first using carbon dioxide as the supercritical solvent. This is because the first particle generation tests will be conducted using carbon dioxide. After completing the carbon dioxide particle generation tests, system shakedown tests using water as the supercritical solvent will be conducted before beginning supercritical water particle generation tests.

We hope that we will be conducting Task 3 tests (Solute/Solvent Optimization Tests) before the close of the next quarter and hope to be conducting Task 4 tests (Catalyst Preparation and Evaluation Tests) during the last quarter of this program.

2.0 TECHNICAL PROGRESS

This program consists of five tasks that cover technical effort and management details. These tasks are listed below and their status is discussed in the remainder of this section.

- Task 1 Project Work Plan
- Task 2 Experiment Design and Fabrication
- Task 3 Solute/Solvent Optimization
- Task 4 Catalyst Preparation and Evaluation
- Task 5 Reporting and Documentation

Task 1: Project Work Plan

This is a completed task and the work plan report was submitted during November 1990.

Task 2: Experiment Design and Fabrication

The technical effort applied during the sixth quarter of this effort focussed on assembling the supercritical particle generation/collection system. Some effort was applied to defining system shakedown tests that will be conducted once system assembly has been completed. An account of the progress made in these areas follows.

System Assembly

The plan for this reporting quarter was to completely assemble the supercritical particle generation/collection system. This included plumbing the entire supercritical flow system,

fabricating and installing the sandbox heater which maintains the correct pre-expansion temperature of the awkward plumbing fixtures just upstream of the expansion nozzle, installing all diagnostic instruments, and completing the mixing chamber vacuum pump system by connecting the pump exhaust to the exhaust stack installed for this program at TDS' expense. Although good progress was made in many of these areas, not all were completed. Shakedown and particle generation tests will take place, therefore, during the next quarter. The progress made during this quarter, however, is conveyed in what follows.

Before beginning assembly of the core of the supercritical particle generator, work began by completing the particle generator exhaust system. The exhaust of the vacuum pump, which allows variable coal-material/catalyst-particle section pressure, was connected to the exhaust stack installed for this program. Hereafter the coal-material/catalyst-particle mixing section will be referred to as the mixing section or mixing chamber. The vacuum pump requires water cooling also, so a supply and return manifold connected to our facilities 90 psig, 100 gpm, closed circuit cooling water supply system was installed. Subsequently, the vacuum pump was connected to these manifolds. These manifolds will also be used to supply water cooling to the upper half of the mixing chamber. The nozzle end, or base of this section, will be maintained at temperatures as high as 600 C, so some cooling of the upper half of this section must be implemented to minimize heat damage. To effect this, one loop of

0.25" OD copper tubing was wound around and brazed to the outside of the mixing chamber, nominally 2.5" from the nozzle end of this section. Water cooling lines from the supply/return manifolds were installed to supply water to the copper cooling loop installed on the mixing section.

Following installation of water cooling systems and completion of the vacuum pump exhaust system, the mixing section was installed. Some assembly of the mixing section was required prior to bolting it to the already installed vacuum pump manifold. The mixing chamber was cleaned and the ceramic and stainless steel conical sections that seat against the nozzle end of this section were installed. Difficulties were encountered when an attempt was made to slide the conical sections in place, i.e., they would not slide from the open end of the cylindrical mixing section to the closed, nozzle end. It was determined that the machine shop that had bored the inside diameter of the mixing section had tool bit difficulties and lost control of the bore diameter. Thus, the mixing section was sent back to the machine shop to have the inside diameter brought back into specification. This exercise took one week and did not delay assembly progress significantly.

After the mixing section was returned to TDS, final assembly went smoothly and this section bolted nicely into place with the vacuum pump manifolding. While waiting for the mixing section to be returned from the machine shop, several other tasks were completed, one of which was cleaning many of the supercritical

flow system parts. The explosion resistant Lexgard panels that cover the open face of the explosion proof enclosure were installed also while waiting for the mixing section to be returned.

During March 1992 Hastelloy tubing caps were sent out to a laser drilling machine shop to have the nozzle passages drilled. Figure 1 shows the Hastelloy cap modifications required. The machining consists of boring a 0.031" ID counterbore, nominally 5/16" deep from the inside surface to within 0.03" of the outside blank surface. The counterbore will be drilled using EDM. A 0.002" ID bore will be laser drilled in such a way as to bridge the 0.03" section of material that lies between the blank outside surface and the bottom of the 0.031 ID counterbore. The laser drilled 0.002" ID bore forms the nozzle. Finite element calculations were performed on this configuration to ensure that it would not fail under the severe conditions of supercritical water. We expect these parts to be finished early in the next reporting quarter. The absence of these parts will not delay system assembly, since blank Hastelloy caps can be used in place of laser machined ones for sizing and fitting adjacent supercritical flow system elements. When the Hastelloy nozzle caps are available, they can be installed quickly.

After the mixing section was bolted to the vacuum pump exhaust manifolding, work began on fabricating the sandbox heater that maintains the proper pre-expansion temperature of the awkward plumbing parts that reside just upstream of the expansion

Figure 1. Hastelloy Tubing Cap Modifications for Nozzle Fabrication.

nozzle. These parts include: a fritted 2 μ m inline filter and housing, a pre-expansion throttle valve, and a cross for monitoring pre-expansion temperature (via thermocouple) and pressure (via 20,000 psig Bourdon-tube gauge). These parts will reside in a shallow Fiberfrax box, where the bottom of the box is a 3 KW heater plate. This box will be filled with sand to ensure that the enclosed parts will be heated uniformly. A K type thermocouple will be inserted into the sand in the sandbox heater, which will monitor temperature and provide the feedback control signal to an on/off temperature controller. The fabrication of the sandbox heater system was completed during this reporting quarter.

As noted above, a fritted filter, contained in an appropriate housing, is located in the supercritical flow system in the sandbox heater just upstream of the expansion nozzle. This is a 2 μ m filter used for removing particles that may plug the nozzle. The fritted filter housing was purchased from High Pressure, Inc. When we ordered the housing, which was made of Hastelloy C-276, High Pressure told us that they could not provide the Hastelloy fritted filters. High Pressure said that we would need filters that were 0.75" diameter with a thickness of 0.125". Three at a time would be needed. It was found that Mott Metallurgical Corp. could supply the fritted Hastelloy filters, so the dimensions called-out by High Pressure were passed on to Mott, who fabricated the required filters. When we attempted to install the Mott fritted filters into the High

Pressure filter housing, they would not fit. The bore in the filter housing was 0.375" ID versus the 0.75" ID conveyed to us initially by High Pressure. After discussions with High Pressure regarding the bore discrepancy, they kindly agreed to turn the 0.75" OD fritted filters to 0.375" OD. High Pressure performed the required machining of nominally 25 filters in less than one week. After receipt of the remachined filters, assembly of the filter system proceeded smoothly.

The next element that was to be installed in the system was the 0.0625" OD, 8' long Hastelloy tube, supercritical transfer line. This line delivers the supercritical solution from the autoclave to the flow system components in the sandbox heater. This line is electrically heated so that pre-expansion temperature can be controlled independent of autoclave settings. The Hastelloy tubing was received during February 1992, but was damaged during shipping. This tubing is very difficult to find in small quantities and is very expensive (nominally \$40/ft). EG&G Chandler, who makes high pressure gas chromatography instruments, was kind enough to sell us the amount we required. They shipped two 12' lengths of the Hastelloy tubing in a 1.5' coil between two pieces of cardboard. The cardboard was folded during shipping, which left small radii bends in the tubing every 2.5'. Since straightening these bends would leave the tubing work hardened, which could cause failures when used under the severe conditions anticipated, EG&G Chandler was contacted and they were kind enough to replace the damaged tube with new

tubing.

The supercritical transfer line will be installed during the next reporting quarter. Ceramic beads will be strung on the 0.0625" OD Hastelloy tube to reduce heat losses. Two K type 0.031" OD thermocouple probes will be attached to the 0.0625" OD Hastelloy tube, one 6" before the sandbox heater, the other at the mid point of the tube. These thermocouples will be attached by lashing them to the tube using ceramic thread. While applying the coils of ceramic thread, a coat of ceramic cement will be applied. This approach makes the thermocouple probe region heat losses appear similar to the ceramic beads covering the tubing elsewhere, and eliminates the need for spot welding the thermocouple probes to the electrically heated Hastelloy tube. It should be noted that ungrounded thermocouple probes will be used.

Final preparation of the autoclave took place next. The inlet flow to the autoclave will enter from the top, and the exit flow will be out through the bottom. This was chosen to take advantage of gravity to hold in place fritted filter disks that will be placed in the autoclave. Nearest the exit of the autoclave, a 2 μ m fritted Hastelloy filter, which is 1.5" in diameter and 0.125" thick, will be located nearest the bottom of the autoclave. Next furthest away from the exit will be a 100 μ m fritted Hastelloy filter, having the same dimensions. These filters serve two purposes. First, they support the packing in the autoclave that helps disperse the solid solute materials.

Second, they prevent particles larger than 2 μm from leaving the autoclave. The ID of the autoclave is nominally 1.5". The OD of these filters was adjusted so that they fit snugly into the autoclave bore.

The packing to be used in the autoclave is +60/-30 mesh (250-600 μm) nickel powder. This material was selected because it is very difficult to dissolve. A one inch layer of the nickel powder will be placed on top of the fritted filters in the autoclave, followed by a two inch layer of a mixture of nickel powder and solute material. This type of packing should give very good dispersion of the solute powder and should provide good heat transfer from the autoclave walls to the supercritical solution.

The removable top of the autoclave was fitted with an inconel thermocouple probe that will penetrate that nickel packing in the autoclave. This should give a very good indicator of autoclave interior temperature.

After the autoclave modifications were completed, it was installed in the sandbath fluidized bed heater. A 10" diameter collar was added to the top of the sandbath heater so that support pins could be installed that would hold the autoclave suspended in the sandbath. Pins extend from the collar, each located 180 degrees apart, and insert into 0.375" ID holes that exist in the removable top of the autoclave. After these modifications were made, support blocks were fabricated from wood, which the sandbath-heater/autoclave assembly will set on.

Once the autoclave was positioned, work began on plumbing the low pressure side of the supercritical pumping system. This included:

- Installing heat exchangers that will sub-cool the supercritical solvent before passage through the capillary flow meter, and in the recirculation path from high pressure pump outlet, through the back-pressure regulator, to the inlet of the high pressure pump. The supercritical solvent CO_2 , prior to the high pressure pump, is a saturated liquid at ambient temperature. Since a pressure drop of nominally 5 psi is expected across the capillary tube flow meter, the saturated CO_2 liquid should be sub-cooled so that vaporization does not take place in the flow meter. Likewise, as liquid CO_2 circulates through the high pressure pump, back-pressure regulator, and back to the high pressure pump inlet, it will be heated. This heat will be removed by a heat exchanger to prevent vaporization. The heat exchangers are cooled by glycerin, which is cooled by an external chiller. The high pressure pump will not operate effectively if the inlet fluid contains vapor.
- The high pressure pump was installed. The shop air needed to drive the Haskel high pressure pump was installed.
- The capillary tube flow meter was installed. This flow

meter is made up of a 20 cm length of 0.0625" OD tubing from which the pressure drop over its length due to fluid flow is measured by a 5 psid differential electronic pressure transducer.

- A 1000 psig dial type pressure gauge and a 1000 psig electronic pressure transducer were installed on the inlet side of the high pressure pump so that this pressure could be read visually and logged using the data acquisition computer. A J type thermocouple was mounted on the inlet side of the high pressure pump so that this temperature could be logged also.
- A pair of metering pumps, with associated plumbing and check valves were installed also. These metering pumps will inject iron pentacarbonyl and carbon disulfide into the inlet side of the high pressure pump.
- A circuit for charging the system with gaseous CO₂ was installed also. This will be needed achieve a well behaved liquid CO₂ flow when the high pressure pump is first started.
- All plumbing needed to complete the low pressure side was installed.

It should be noted that we planned initially to use a rotameter for monitoring the flow rate of iron pentacarbonyl into the supercritical flow system. This flow meter is capable of measuring 0.0005 ml/min. After inspecting this flow meter carefully it was concluded that the least bit of particulate

contamination would seize the motion of the ruby ball float. It was decided that an alternate approach was needed. A metering pump was purchased initially to supply the iron pentacarbonyl to the high pressure pump. This pump has a minimum flow rate of 0.5 ml/min. This pump was to be fitted with a needle valve based bypass circuit that would allow one to achieve flow rates of iron pentacarbonyl into the supercritical flow system of 0.001 ml/min. Based on the solvent flow rates anticipated, this would give low limit iron pentacarbonyl concentrations of nominally 100 ppmw, which is what is desired. Upon inspecting the manual for this metering pump, it was found that the manufacturer makes pumps that will deliver flows as low as 0.002 ml/min. Since this would yield minimum iron pentacarbonyl concentrations only a factor of two greater than desired (which is acceptable), our metering pump was returned for the model that gives the lowest flow rate possible. Since metering pumps can control flow rates accurately without the need for a flow meter, the very delicate rotameter is no longer needed. Since this same approach would work well for injecting carbon disulfide into the inlet side of the high pressure pump, a second metering pump was purchased and installed.

There are several things that need to be done to complete the low pressure side of the supercritical pumping system. The burettes that will hold the iron pentacarbonyl and carbon disulfide need to be installed. The gaseous and liquid carbon dioxide cylinders need to be plumbed in.

Some of the high pressure side plumbing between the high pressure pump and autoclave was installed during this reporting quarter. The back-pressure regulator was installed, the high pressure relief valve was installed, and the high pressure dial type pressure gauge was installed. The remainder of this plumbing will be installed next quarter.

The systems for the supercritical particle generator can be broken into three main categories, namely: flow components, electric heating components, and diagnostics and instrumentation. The strategy for assembling the system has been to assemble the flow components of the system first, which entails assembling all hardware. The next step will be to install all electrical heating and control circuits. The last step will be to connect all diagnostics to a data acquisition system. All these steps will be completed during the next reporting quarter.

Regarding data acquisition, a Masscomp 5500 computer/data-acquisition system (TDS property) became available for this program during this reporting quarter. A service technician from Masscomp was brought in to check out this system and correct problems under a TDS blanket service plan. It is now ready for use. This data acquisition system consists 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 type of data acquisition system has been used by TDS extensively over the last 12 years and is well understood. It will be used during this program to

monitor all thermocouple and pressure signals that have DC voltage or current outputs. This will be very useful for keeping a record of operating conditions during the anticipated long runs, and for providing on-screen results of temperatures around the system, solvent flow rates, and critical pressures.

Shakedown Test Plan

Discussions with Dean Matson of Battelle Pacific Northwest Laboratories took place during January 1992 in order to determine what success he has had dissolving iron pyrite and hematite with supercritical water. He informed us that negligible concentrations of these materials were observed in supercritical water. In view of this a revised test matrix was defined, which is given in Table 1. Since iron pentacarbonyl is highly soluble in carbon dioxide (liquid), as well as numerous organic solvents, this catalyst precursor material will receive highest testing priority. Chemical equilibrium calculations were performed that suggest iron sulfides may result if carbon disulfide is introduced into the autoclave when processing iron pentacarbonyl in supercritical carbon dioxide. This is important since it may be possible to produce pre-sulfided iron catalyst particles of uniform size using the supercritical expansion process. Since Matson has informed us that iron pyrite and hematite have low solubilities in water, they will be given lower testing priority. Basically, we plan to confirm Matson's iron pyrite and hematite results, and if we obtain the same results we plan to explore the solubility of iron hydroxides.

Table 1. Updated Test Matrix.

Priority	1st	2nd	3rd
Solute	Fe(CO) ₅	FeS ₂	Fe ₂ O ₃
Supercritical Solvent	CO ₂	H ₂ O	H ₂ O
Solubilizing or Coprecipitant Additive	CS ₂	CS ₂ or H ₂ S	CS ₂ or H ₂ S
Supercritical Fluid Mixture	Fe(CO) ₅ /CS ₂ /CO ₂	FeS ₂ /CS ₂ /H ₂ O FeS ₂ /H ₂ S/H ₂ O	Fe ₂ O ₃ /CS ₂ /H ₂ O Fe ₂ O ₃ /H ₂ S/H ₂ O
Solute/Additive Concentration (ppm)	Fe(CO) ₅ /CS ₂ 50-50K/0-50K	CS ₂ or H ₂ S 0-50K	CS ₂ or H ₂ S 0-50K
Pre-Expansion Pressure (atm)	200-350	<600	<600
Pre-Expansion Temperature (C)	50-100	<600	<600

Note

If FeS₂ and Fe₂O₃ prove to have negligible solubility in supercritical water, iron hydroxides will be tested.

Since testing involving iron pentacarbonyl will be conducted first, system shakedown tests using carbon dioxide as the supercritical solvent will take place as soon as system assembly has been completed. After particle generation tests using iron pentacarbonyl have been completed, shakedown tests using water as the supercritical solvent will be conducted, followed by particle generation tests using supercritical water.

Prior to shakedown testing, system calibrations will be made. All thermocouples and pressure transducers will be calibrated using standard techniques. The metering pumps that inject iron pentacarbonyl and carbon disulfide will be calibrated in such a way as to map flow rate with micrometer setting. Water will be used as the working fluid. Each pump will be allowed to pump water until a measurable change in burette column height has taken place. The time required to achieve the column height change will be recorded and the process will be repeated for several micrometer settings over the range of interest. This information will be used to correlate pumping flow rate with micrometer setting.

The capillary flow meter will have to be calibrated also. Water will be passed through this flow meter at several rates spanning the range of interest. From this information the constant C , in $\text{flow rate} = C (\Delta p)^{1/2}$, can be determined. Based on viscosity and density differences between water and carbon dioxide, the coefficient C for carbon dioxide will be determined.

Whether using carbon dioxide or water as the supercritical

solvent, the shakedown testing format is the same. The shakedown tests will be performed without introducing solute material into the system. First, with the nozzle throttle valve closed to prevent flow out of the system, the system will be charged with the supercritical solvent at standard temperature and corresponding saturation pressure (i.e., 0 psig for water and 860 psig for carbon dioxide). A check will be made for leaks. Next, the high pressure pump will be started and the system will be brought up slowly to maximum pressure (i.e., 8700 psig for water and 5100 psig for carbon dioxide). Then another check will be made for leaks. If leaks are detected, their location will be noted and the system will be shutdown so that the problem can be fixed.

With the system at maximum pressure, the sandbath autoclave heater will be turned on and the autoclave temperature will be gradually increased. As the autoclave temperature climbs, the nozzle throttle valve will be opened gradually to permit flow out of the system so that system pressure can be held constant. The autoclave will be checked for leaks during this test.

Once the autoclave has been brought up to maximum temperature (i.e., 500 C for water and 177 C for carbon dioxide), electric power will be applied to heat the supercritical transfer line. The transfer line will be brought up to maximum temperature gradually (i.e., 600 C for water and 177 C for carbon dioxide). The temperature controller for the transfer line will be tuned to give correct response and a visual inspection for

leaks will be made. If leaks are detected, the system will be shutdown, vented, and the problem corrected.

Once the autoclave and transfer line behave satisfactory at maximum temperature and pressure, the sandbox heater just upstream of the nozzle assembly will be brought up to maximum temperature gradually (i.e., 600 C for water and 177 C for carbon dioxide). Once this heating system behaves correctly, the ring heater system on the base of the mixing chamber will be brought up to temperature and checks for leaks will be made.

Once these shakedown tests have been completed, the system will be ready for particle generation tests, i.e., Task 3 can be started.

Task 3: Solute/Solvent Optimization

No effort has been applied to this task yet.

Task 4: Catalyst Preparation and Evaluation

No effort has been applied to this task yet.

Task 5: Reporting and Documentation

All monthly and quarterly reports have been submitted.

3.0 FUTURE WORK

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

- * Complete system assembly.
- Perform calibrations and shakedown tests.
- Begin Task 3 Solute/Solvent Optimization Tests.

**DATE
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8/11/92