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

QUARTERLY TECHNICAL PROGRESS REPORT

DOE/PC/90053--T3

for the period

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1.0 SUMMARY

This is the third Quarterly Report for this program. It covers the period April 1, 1991 through June 30, 1991. 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 was devoted to experimental design and fabrication tasks. A brief description of the progress made and program issues that arose during this quarter are given below.

During this reporting period detailed machine drawings for the particle collection, coal material impregnation section were finalized. These drawings were sent out for fabrication and orders were placed for required miscellaneous pieces, such as optical windows, o-rings, etc. The final design for this section is based on a spouted bed reactor configuration. This approach allows the expansion jet to issue upward into a volume containing pulverized coal or coal-derived liquid. Since ultra-fine particle coagulation time scales are small, immediate and intimate mixing of ultra-fine catalyst particles and coal materials must be achieved in order to impregnate the coal materials with the smallest possible catalyst particle sizes.

The spouted bed concept achieves the required immediate and intimate mixing, which is why it was selected for this section.

The particle collection, coal material impregnation section has provisions for inserting a particle collection probe. This probe will deliver the particle laden gas to a cryogenic particle sampler. The design of this sampler was developed in the second quarter of this program. It was assembled and tested during this quarter, i.e., the third quarter. The cryogenic sampler contains a collection surface that is maintained at liquid nitrogen (LN₂) temperatures during collection. Thus, it freezes out all material that contacts the collection surface. By warming the surface to the sublimation temperature of the supercritical solvent species, and pumping on the surface by a second LN₂ trap, it is possible to leave the catalyst particles on the cryogenic sampler collection surface and collect the supercritical solvent species in the second LN₂ trap. Simple techniques will be used to acquire the mass of collected catalyst particles and of the supercritical solvent individually. By simulating the conditions the particle probe will experience during ultra-fine catalyst particle generation, it was possible to test the performance of the cryogenic sampler. The performance of this device was found to behave as expected and should provide a more than adequate means for determining supercritical solution composition and for acquiring SEM particle samples.

A pumping system is needed for varying the pressure in the particle collection, coal material impregnation section when

generating ultra-fine catalyst particles. Varying background pressure in this section will be used to optimize particle characteristics by altering jet expansion characteristics and particle coagulation time scales. During the third quarter a 80 cfm Kinney vacuum pump was installed in the exhaust stage of the particle generation system. By installing a blank flange at the interface between the particle collection, coal material impregnation section and the manifold to the exhaust system, it was possible to test the exhaust pumping system to verify that back-pressures in the range of interest could be achieved. The back-pressure range is 0.01 to 1.0 atm. By simulating the exhaust flow rates anticipated when generating ultra-fine catalyst particles, it was possible to check whether the lower pressure bound of 0.01 atm could be achieved. The tests performed confirmed that 0.01 atm should be achievable.

At this point in the program all major components of the system have been designed and are being, or have been fabricated. Based on the attention given to each of these components, each component should exceed baseline performance specifications. As noted in prior Monthly Status and Quarterly Technical Reports, however, the cost of the experimental apparatus has significantly exceeded proposal phase expectations. This has been driven by the exotic materials needed to withstand the severe conditions posed by the process being implemented, and by safety and environmental issues that were not foreseen. In an attempt to minimize cost over-runs, personnel key to this program became

involved in other programs in progress at Textron Defense Systems (TDS). This is natural, especially during the procurement phase of system hardware, where lead times hinder progress. Given the high activity level needed to resolve final designs during the first three quarters of this program, and the escalating demands on this program's key personnel by other programs, the Program Manager for this program fell behind in Quarterly Reporting responsibilities. In order to bring Quarterly Reporting back in line with the original milestone schedule, technical effort on all technical tasks, except for the Management and Reporting task, will be reduced to a maintenance level of effort. This will provide time for key personnel to reduce their activity level in other TDS programs and the time needed to rectify the Quarterly Reporting situation. This mode of operation will continue until Quarterly Reporting is brought back in line with the original milestone schedule, which should be November 1, 1991. This mode of operation should not be detrimental to achieving the goals of this program within the period of performance of this contract.

2.0 TECHNICAL PROGRESS

2.1 TASK 1. PROJECT WORK PLAN

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

2.2 TASK 2. EXPERIMENT DESIGN AND FABRICATION

APRIL 1991. The design of the ultra-fine catalyst generator was completed this month, and the fabrication/assembly phase commenced. This transition is defined as the point in time where designs for all elements have been established, most importantly the point where a final design for the particle collection, coal material impregnation section was achieved. The fabrication of the cryogenic sampler was completed this month also and its basic behavior will be examined during May 1991.

The major effort during this reporting period was devoted to finalizing the design of the catalyst particle, coal material impregnation section. As noted in our last Quarterly Report, a spouted bed configuration has been selected. The nozzle assembly part of this section is the most critical for the successful performance of the particle generator system. This assembly experiences the most severe conditions associated with the particle generation process (i.e., high pressures and temperatures, vacuum integrity, thermal isolation of the hot nozzle from the coal material, and electrical isolation, which is necessary to allow Ohmic heating of the upstream supercritical

transfer line.

The spouted bed, particle collection, coal material impregnation section is shown in Figure 2.1. This section will consist of an expansion nozzle discharging vertically against gravity into a circular tube. More specifically, a 45 degree cone, with the nozzle located at its apex, will form the bottom end of the mixing section tube. The 45 degree cone allows transition from the small nozzle orifice opening to the inside diameter of the mixing section tube. Since the nozzle element will be supported by a stainless steel flange, which will have a high temperature vacuum seal, the 45 degree cone allows a diameter transition from 0.25 to 4.0 inches. It should be noted that the transition from the nozzle orifice diameter (0.002 inches) to 0.25 inches occurs below the cone and inside the stainless steel flange. The 45 degree cone will be 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 will be an insert and the mixing section tube will be welded directly to the nozzle support flange. The ceramic cone and stainless steel retainer cone are shown in Figures 2.2 and 2.3, respectively.

Heat transfer from the hot nozzle support flange will be 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

Figure 2.1 Spouted Bed, Particle Collection, Coal Material Impregnation Section Final design.

NOTES:

- 1 - MATERIAL: COTRONICS 914 HT MACHINABLE CERAMIC

Figure 2.2 Particle Collection, Coal Material Impregnation Section Ceramic Transition Cone.

Figure 2.3 Particle Collection, Coal Material Impregnation
Section Stainless Steel Retainer Cone.

section tube. When the nozzle is maintained at 600 C, only 30 W of power will be lost to the mixing section tube by heat conduction from the hot nozzle support flange.

A 1 KW flat ring heater by Watlow will be 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 will be 15.5 inches, its inside diameter 4.0 inches, and will have a wall thickness of 0.25 inches. Two optical access windows, 180 degrees apart, will be 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 degree 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 will contain a 1.0 inch OD open-ended, hollow tube, center-body. This center-body tube, as shown in Figure 2.4, will be plugged at the end farthest from the nozzle. The end of the centerbody nearest the nozzle

Figure 2.4 Particle Collection, Coal Material Impregnation Section Centerbody.

assembly will lie in the plane where the 45 degree cone intersects the wall of the 4.0 inch mixing chamber tube. The center-body will provide a stagnant gas region which will slow 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 will also set up a recirculation pattern that will assist in drawing coal particles back into the cone section, which will then guide them into the discharge of the jet. Lastly, the center-body will 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 will be bored smooth to minimize coal particle attachment. Pairs of Swadgelock 0.25 inch ID tube fittings, 180 degrees apart, will be located at 2 and 10 inches from the nozzle exit in the walls of the 4 inch mixing section tube. These will be 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 downstream exhaust manifolding will be electrically isolated. The flanges at this union will be separated by a double o-ring, linen phenolic disk and the bolts will be isolated using ceramic washers. The isolation disk is shown in Figure 2.5.

The throttle valve, cross for pressure gauge and

Figure 2.5 Particle Collection, Coal Material Impregnation Section Isolation Disk.

thermocouple probe diagnostics, and inline filter will be close coupled to the nozzle component to minimize heat losses. These items will be housed in a sand-bath heater. This arrangement is shown in Figure 2.6. A 2.5 KW flat plate heater will form the bottom of the sand-bath heater, the remaining walls will be made of 1 inch thick Fiberfrax insulation board. A thermocouple will monitor the temperature of the sand-bath heater, which will service the temperature control unit supplying power to the plate heater. All tubing in this section will be thick-walled, 0.25 inch OD Hastelloy tubing, which will transition in the upstream direction to 1/16 inch, thick-walled Hastelloy tubing that will run nominally 8 feet back to the autoclave. Electric Power for heating the 1/16 inch line will be applied between the mixing section and the autoclave, which will be supplied by an existing Lindberg electric furnace power supply and controller.

Progress was also made in finalizing the methodology for constructing the orifice nozzles. We will be using high pressure tubing caps as the platform for our nozzles. This will require 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 Hastelloy-cap/nozzle is shown in Figure 2.7. It has been confirmed that this machining can be accomplished by EDM for the 0.02 inch counterbore and laser drilling for the nozzle orifice bore. The laser drilling for the nozzle orifice will be accomplished by drilling from the outside free surface to the

Figure 2.6 Pre-Expansion Sandbox Heater Assembly and Diagnostics Arrangement.

Figure 2.7 Laser Drilled Orifice Nozzle Final Design.

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 have been performed on the nozzle component in order to see if the required drilling will detrimentally effect the structural integrity of this part. The results indicate that a factor of two safety exists after the drilling described above has been performed. Based on our discussions with laser capable machine shops, the minimum orifice diameter that can be drilled is 0.002 inch ID. This is completely compatible with our overall design. These parts will be sent out for machining during the next reporting period.

MAY 1991. The assembly/fabrication of the ultra-fine catalyst generator continued this month. Emphasis was given to finalizing machine drawings for the coal impregnation section, defining final specifications for the expansion nozzles, installing the vacuum pump system for the coal impregnation section, and testing the basic behavior of the cryogenic particle sampler. Progress in these areas follows.

A complete set of machine drawings for the particle collection, coal material impregnation section was produced during this reporting period. At the present time they are being reviewed for accuracy and will be sent out for bids during the early part of June 1991.

TDS has made available an 80 cfm Kinney vacuum pump for this

program. This pump will be used to provide particle collection, coal material impregnation section pressures down to nominally 0.01 atm during supercritical fluid expansion. This capability will be used to optimize particle size through expansion chamber pressure control. This pump was installed during this reporting period, together with vacuum plumbing that will mate to the mixing section of the experiment. The pump has an inline ball valve that can be used to adjust particle collection, coal material impregnation section pressure. A second ball valve has been installed on the particle collection, coal material impregnation side of the pump, which will be used to by-pass the pump and allow the flow to discharge to atmospheric pressure. A thermocouple vacuum pressure gauge and a Wallace-Tiernan pressure gauge will be used to monitor pump inlet pressure.

During this reporting period the cryogenic particle sampler was tested to assess its basic behavior. This was done by supplying CO₂ from a high pressure bottle through a regulator, which provided CO₂ gas at standard conditions, then through a flow meter and a needle valve, and finally to the inlet of the sampler. With the sampler cooled to LN₂ temperature, a flow of CO₂ of 1.5 scfh was achieved with the sampler operating at 0.5 atm. This flow was maintained for approximately 2.5 minutes. After the sampling flow was stopped, the copper block that supports the aluminum collection foil was raised to approximately 5 degrees Kelvin below the sublimation temperature of CO₂. Then the second LN₂ cold trap was allowed to pump on the cryogenic

sampler chamber. We had hoped to be able to see a 1 torr pressure in the cryogenic sampler when the second cold trap was allowed to pump, but this was not observed and the cryogenic sampler chamber remained in the sub-torr pressure range, i.e., no increase in cryogenic sampler chamber pressure was detectable. The second LN₂ cold trap was allowed to pump on the cryogenic sampler chamber for nominally 0.5 hours. The temperature of the collection foil was then allowed to increase slowly over the next 0.5 hour to room temperature, and still no increase in cryogenic sampler pressure was detected. The valve on the second LN₂ trap was then closed and the trap was allowed to warm to room temperature. Once at ambient temperature, the second LN₂ trap pressure reached 120 psig. Based on the volume of the second LN₂ trap, the measured temperature and pressure, it was possible to get a value for the mass of CO₂ collected by the cryogenic sampler, which was nominally 3 grams. This quick check on the performance of the cryogenic sampler indicates that it is working as hoped and should be more than satisfactory for collecting particles during up-coming experiments. It was also found that the second LN₂ cold trap has a very high pumping speed, so care will have to be exercised when processing samples not to sublime the carrier gas from samples too quickly. It should be noted that the 0.001 inch thick aluminum collection foil did not fail when its temperature was reduced to the LN₂ level. Polyethylene foil was also tested for its compatibility with LN₂ temperatures in the cryogenic sampler, and it performed without

problems. This demonstrates that plastic foils, which may be useful for sample collection for SEM analysis, can be used.

JUNE 1991. The assembly/fabrication of the ultra-fine catalyst generator continued this month at a significantly reduced level. There are several reasons for this which are discussed under Section 1.0. Emphasis was given to sending the mixing section drawings out for fabrication and completing the vacuum pumping system for the mixing section. Progress in these areas follows below.

A complete set of machine drawings for the coal/coal-liquid impregnation section was produced during the May reporting period. These drawings have been reviewed for completeness and accuracy, and have been sent out for fabrication. Miscellaneous parts, such as optical access windows, o-rings, etc., have been ordered also. The completed mixing section and other ordered materials should be received by the first week of August 1991. The nozzle assemblies will be sent out for laser drilling during the next reporting period, i.e., during July 1991.

The vacuum manifold that connects the 80 CFM kinney vacuum pump to the mixing section of the ultra fine particle generation system was installed during this reporting period. This assembly consists of a section of 2.5 inch SS pipe that penetrates one end of the enclosure for the experiment and an upper chamber to which the mixing section mates. The upper chamber being used is a baffled water vapor trap from a previous experiment. The baffling provided by this unit is appropriate for hindering the

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progress of coal particles or coal-liquids from escaping the mixing section. It also serves as a 90 degree elbow so that mating can be achieved between the horizontal vacuum pipe penetrating the enclosure and the vertically aligned mixing section.

Cooling water plumbing for the vacuum pump was installed this month, as well as required 3-phase, 220 VAC electrical power. The system was operated and checked for vacuum leaks. No leaks were detected. A blank flange was installed on the flange where the mixing section will mate to the upper chamber for performing the leak checks. Air was bled into the upper chamber through a port installed in the blank flange. Using a flow meter, the bleed air was adjusted to simulate conditions that will exist when flowing supercritical mixtures into the mixing chamber. The results of these tests indicate that the vacuum pump should be able to maintain a chamber pressure of nominally 0.01 atm when performing particle generation studies. A back-pressure of 0.01 atm was the design goal we were striving to achieve.

The Lexgard (bullet resistant transparent plastic) panels that will form one of the vertical sides of the enclosure will be delivered in early July 1991. Installation of the ventilation systems for the enclosure and fume hood will take place beginning July 15, 1991. At that time, required shop air, water, and electrical power service will be installed also.

2.3 TASK 3. SOLUTE/SOLVENT OPTIMIZATION

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

2.4 TASK 4. CATALYST PREPARATION AND EVALUATION

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

2.5 TASK 5. REPORTING AND DOCUMENTATION

APRIL 1991. By the end of April, TDS has submitted status, milestone, and cost management reports for the first seven reporting periods (October 1990 through April 1991). The last five months of this program have been very busy and, consequently, timely preparation of the first two quarterly reports has suffered. It was difficult to focus on finishing these reports during this reporting period because of the need to finalize the mixing section design so that system assembly would be delayed no further. This done, an earnest attempt will be made to bring reporting back in line in the next reporting period.

MAY 1991. By the end of May 1991, TDS has submitted status, milestone, and cost management reports for the first eight reporting periods (October 1990 through May 1991). The last six months of this program have been very busy and, consequently, timely preparation of the first two quarterly reports has suffered. An earnest attempt will be made to bring reporting back in line as soon as possible.

JUNE 1991. By the end of June 1991, TDS has submitted

status, milestone, and cost management reports for the first nine reporting periods (October 1990 through June 1991). The last seven months of this program, as well as other programs key personnel are involved in, have been very busy and, consequently, timely preparation of quarterly reports has suffered. An earnest attempt will be made to bring reporting back in line as soon as possible.

3.0 CONCLUSIONS AND FUTURE WORK

3.1 CONCLUSIONS

The performance of the cryogenic particle sampler was tested during May 1991. This device will be used for determining the composition of the supercritical solution and for acquiring catalyst particle samples for SEM analysis. These tests have shown that this device is operating as desired. The pumping speed of the second LN₂ trap is enormous. A throttle valve will be installed between the cryogenic sampler and this second trap so that the pumping speed of the second trap can be reduced to the point where a pressure rise in the cryogenic sampler can be detected when the temperature of the cryogenic sampler collection surface is raised just below the sublimation temperature of the supercritical solvent species. This pressure rise will be used to monitor the sublimation process and, therefore, is important to be able to detect.

The pumping speed of the system to be used for reducing the pressure of the particle collection, coal material impregnation section was tested during June 1991. Conditions representing those expected during catalyst particle generation were simulated by bleeding air into the exhaust manifold downstream of the particle collection, coal material impregnation section. Pressures of nominally 0.01 atm were measured during these tests, which demonstrate that the exhaust pumping system should be

adequate for upcoming catalyst particle optimization tests.

3.2 FUTURE WORK

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

- * Continue Task 2 work at a reduced level (Experiment Design and Fabrication) until Quarterly Reporting is brought back in line with the original milestone schedule.
- * Bring Quarterly Reporting back in line with the original milestone schedule.

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