COAL LIQUEFACTION SUPPORT STUDIES

Annual Report

October 1975—September 1976

by

J. Fischer, R. Lo, S. Nandi,
D. Fredrickson, T. Cannon,
T. Bump, T. Mulcahey,
H. Huang, and A. Jonke

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ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

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Chemical Engineering Division

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**Chemistry Division

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ABSTRACT

This work is in support of the development of processes, such as the SYNTHOIL process, for converting coal to a liquid fuel that has a low sulfur content and is suitable for use in power production.

In the SYNTHOIL process for converting coal to a low-sulfur fuel oil, coal is liquefied and hydrodesulfurized in a turbulent-flow, catalytic packed-bed reactor. In this process, a slurry of coal in recycled oil is reacted with hydrogen at 450°C and 2,000-4,000 psi in the presence of Co-Mo/SiO₂-Al₂O₃ catalyst. Turbulent flow of fluid prevents the coal's mineral matter from settling and plugging the reactor. In a 1/2 ton per day pilot plant at PERC, the gross liquid product is centrifuged to remove unreacted solids, producing a low-sulfur, low-ash liquid fuel.

The work for this program includes tasks I-IV, started in September 1975.

Task I, Heat of Reaction of Hydrogen with Coal Slurries

The heat of reaction of coal-oil slurries with hydrogen will be determined in the presence and absence of catalysts, at 2,000-4,000 psi and 400-475°C, using a calorimeter. The design of the calorimeter and the principles of operation are presented in this report.

Task II, Heat Transfer Coefficient

The coefficients of heat transfer from SYNTHOIL reactor fluids to heat exchangers will be determined in the following ranges of conditions: pressure, 2,000-4,000 psi, and temperature, to 465°C. The test unit is being installed, and initial testing will be started in October 1976.

Task III, Additives to Facilitate Separation of Solids from Liquids

Additives to facilitate the removal of solids from oil produced in coal-liquefaction processes have been investigated. Additives considered were those which alter the physical properties of the mixture, improving separation in subsequent steps. We have tested a variety of additives and have also performed experiments on the settling of solids in SYNTHOIL gross product. The work on this task has been completed.

Task IV, Catalyst Testing

New catalysts were to be tested in 300-hr runs in a continuous high-pressure coal-liquefaction unit to operate at 2,000-4,000 psi and 450°C. This task has been terminated; however, the test unit which is being built by a contractor will be completed. The unit will be delivered in October 1976. Installation and final testing of the test unit will be completed by the end of November 1976.

SUMMARY

Heat of Reaction of Hydrogen with Coal Slurries

(D. Fredrickson and S. Nandi)

Heat of reaction data will be obtained for the hydrogenation of coal slurries typical of those used in the SYNTHOIL process. To obtain the information needed, a calorimetric system has been designed and is currently being built. A detailed description of the calorimetric system is given in this report.

The basic components of the system are a drop tube to suspend the bagged sample prior to start of the experiment, a heated pressure vessel (containing hydrogen) in which the reaction takes place, and a calorimeter surrounding the pressure vessel to measure the energy change occurring in the vessel.

Heat Transfer Coefficient

(T. P. Mulcahey and T. R. Bump)

The objective of this task is to provide measured coefficients of heat transfer from SYNTHOIL process feed and effluent products to container walls, for use in the future design of heat transfer equipment for the process.

Preliminary unit configuration and component sizing of the test unit were completed, based on the slurry and hydrogen flow rates being comparable to those in a plant designed for 1/2 ton/day capacity. A SYNTHOIL process development unit of this capacity operates with 25 lb/hr of slurry feed and 1,300-scfh hydrogen flow. Fabrication and installation of the test unit is proceeding and initial testing will be started in October 1976.

Additives to Facilitate Separation of Solids from Liquids

(H. Huang)

The objective of this task was to investigate the effect of additives in facilitating the removal of solids from oil produced in coal-liquefaction processes. Additives considered were those which would alter the physical properties of the mixture, improving separation in subsequent steps.

We received from the Pittsburgh Energy Research Center (PERC) two one-gallon samples of SYNTHOIL centrifuged product oil and two one-gallon samples of SYNTHOIL uncentrifuged product for this study. The viscosity of the centrifuged oil has been measured between 50 and 200°C, using a Brookfield Model LVT viscometer along with a Brookfield Thermosel System. We observed changes in viscosity of the oil upon exposure to air, as well as non-Newtonian viscosity behavior.

We tested a variety of surfactants which have been used in the petroleum industry as pour depressants and flow improvers. None of these had a significant effect on the viscosity of SYNTHOIL product. The largest decrease in viscosity was obtained when ~1% Emsorb 2503 (sorbitan trioleate) was added to SYNTHOIL product. The viscosity reduction at 80-200°C was 5%.

A screening study of commercial additives that may improve the precipitation or coprecipitation of suspended solid residues in SYNTHOIL gross product was made. The study was done by determining the extent of settling of solid particles in a copper settling tube in a prescribed time. Of the precipitation solvents evaluated by settling tests, kerosene was found to be an effective precipitation solvent for SYNTHOIL gross product.

Work on this task has been completed.

Catalyst Testing

(R. Lo and T. Cannon)

The objective of this task was to evaluate new commercially available catalysts for use in the SYNTHOIL process. A continuous high-pressure coal liquefaction unit (Catalyst Test Unit) is being constructed to operate at SYNTHOIL process conditions--450°C and 2,000 to 4,000 psi.

Construction of the Catalyst Test Unit is progressing at the contractor's plant. Work on this task will be suspended upon completion and testing of the Catalyst Test Unit. The unit will be delivered to us in October 1976. Final testing will be completed by the end of November 1976.

I. HEAT OF REACTION OF HYDROGEN WITH COAL SLURRIES (D. Fredrickson and S. Nandi)

Heat of reaction data will be obtained for the hydrogenation of coal slurries typical of those used in coal liquefaction processes such as the SYNTHOIL process. In order to obtain the information needed, a calorimetric system has been designed and is being built.

The energy evolved will be measured while the hydrogenation reaction takes place in a constant-volume system. The calorimeter will operate in such a manner that there will be a constant heat flow between the calorimeter and the jacket. The primary energy quantity to be measured in this calorimeter is power. (A more detailed explanation of this calculation is found in a following Calculations section.) The primary information obtained will be joules per mole of hydrogen consumed in the reaction. The hydrogen consumption will be determined from the difference between (1) the hydrogen content of coal and slurry added to the calorimeter and (2) the assayed bound hydrogen in the gas, solid, and liquid contents of the calorimeter after reaction.

A schematic diagram of the heat of reaction calorimeter is shown in Fig. 1. The basic components are a drop tube to suspend the bagged sample prior to the start of an experiment, a heated pressure vessel (containing hydrogen) in which the reaction takes place, and a calorimeter surrounding the vessel to measure the energy change occurring in the vessel.

A. Apparatus

A pressure vessel is bolted to a heavy aluminum calorimeter ring, to which are welded aluminum cylinders (calorimeter attenuation cylinders). These cylinders attenuate the temperature gradient on the vessel so that the gradient on the outer calorimeter cylinder and the corresponding heat flow are affected to a negligible extent by temperature differences along the pressure vessel length. A lid on the calorimeter prevents direct heat exchange between the vessel and the temperature-controlled jacket. This jacket also consists of a heavy aluminum ring with cylinders welded to its bottom surface and a similarly constructed lid. Thin aluminum nested cylinders spaced 1/2 in. apart surround the jacket for thermal insulation. These serve to reduce both convection and radiation. An aluminum outer cover serves as mechanical protection and directs the argon flow upward through the apparatus. Argon has a lower thermal conductivity than air and thus reduces the heat transfer from the calorimeter to the room. Argon also reduces the rate of oxidation of the aluminum shields. The lids, insulating cylinders, and cover are fabricated as half-cylinders above the rings so that they can be assembled while the tubes connected to the pressure vessel are in place.

Fig. 1. Heat-of-Reaction Calorimeter

Extending from the pressure vessel are four small tubes; one is connected to the pressure gauge, another to the pressure relief valve, another to the hydrogen supply, and the other (gas outlet) to the gas analysis train. A large drop tube extends upward from the center of the vessel closure. Cold slurry samples are dropped through this tube into the hot pressure vessel. Before a drop, the sample is held in a constant-temperature region at about 35°C. Three small stainless steel cylinders (shields) are placed in the drop tube to control heat transfer. The lower shield forces any gas leaving or entering the vessel to pass close to the tube wall and thus to acquire a temperature approaching that of the wall. When a sample is dropped, this shield falls into the pressure vessel and its function is taken over by the upper shield. The middle shield serves to prevent radiation to the sample from the hot zone. It, too, falls into the pressure vessel before the sample does.

The sample and shields are suspended on a drop wire consisting of a stainless steel chain connected to a polyethylene fiber; the chain is in the hot zone. The fiber is looped over a Nichrome V wire, which when heated electrically melts through the fiber, releasing the sample and shields.

Mixing is accomplished by alternately lifting and dropping a perforated stainless steel stirrer plate shaped to fit the bottom of the vessel. The stirrer is attached to a thin-walled stainless steel tube which fits closely inside the drop tube and extends upward to the magnetic stirrer drive. The stirrer can be driven at any of several frequencies selected by the operator.

The calorimetric system is being built by Calorimetrix, Inc. of Boulder, Colorado. A recent trip to Calorimetrix Inc. indicated a very nearly complete calorimetric system. We observed mechanical assembly of the calorimeter for a typical experimental run and also observed nominal temperature control of the calorimeter at 100°C. Assembly of the calorimeter has progressed very well, and electrical calibrations and testing with a standard substance (sapphire) will commence shortly.

Laboratory space is being provided for the calorimeter. A two-liter floor model Magnedash autoclave has been ordered for use in preliminary studies of oil-coal slurries prior to completion of the heat of reaction calorimeter. Table 1 summarizes the status of the project.

B. Operating Procedure

In a typical experiment, the sample and shields are drawn up into the drop tube. The closure is then bolted to the pressure vessel, and air is removed. Hydrogen is added, and the system is checked for

Table 1. Schedule for Heat of Reaction Calorimeter.

leaks. The lids, insulating cylinders, and cover are installed and the power is fed to a heatup heater and a jacket heater (both located in the jacket) and to the heater in the calorimeter ring. During an experiment, this temperature-maintenance heater keeps the temperature of the calorimeter ring a few degrees above the jacket temperature.

The desired operating temperature for an experiment is selected by adjusting one arm of a resistance bridge; the sensitive platinum arm of the bridge is located on the jacket ring. About ten degrees below this selected temperature, the heatup heater is shut off to avoid overshoot and the other two heaters bring the apparatus to operating condition. When the temperature is observed to be stable, the logic switch "Start Experiment" is closed. The logic (i.e., the operations controlled by electronic instrumentation) then determines the steady-state power to the temperature-maintenance heater as a base level and then drops the sample. The cold sample removes heat from the calorimeter, and the power to the temperature-maintenance heater increases accordingly. As the sample comes to temperature and the reaction begins to give off heat, this power decreases. The logic computes the power throughout an experiment and integrates the difference between this power and the steady-state power computed before the drop. The integral represents the total energy of the drop and reaction.

The operator may choose to record this power difference, as well as the temperature and pressure, on a paper-tape printer. He may choose to end the experiment at any time. Integration would then be stopped and the integral displayed. The upper shielding may be removed to speed up cooling. For product removal, the calorimeter may be cooled to and held at $\sim 150^{\circ}\text{C}$.

C. Calculations

The theory on which the computation is based is simple: A constant power, P_o , is required to maintain the temperature difference between the calorimeter and the jacket. Using a heat transfer constant k ,

$$P_o = k(T_c - T_j) \quad (1)$$

The sample requires or supplies a power P , which we take to be positive if it is supplied by the reaction. The power P_h to the temperature-maintenance heater will be varied to maintain the controlled temperature difference. After the drop of the bagged sample,

$$P_h + P = k(T_c - T_j) \quad (2)$$

Eliminating $k(T_c - T_j)$ from (1) and (2) and rearranging, we get

$$P = P_o - P_h \quad (3)$$

We obtain by integration the power P associated with the sample or the total energy ΔU

$$\begin{aligned}\Delta U &= \int P \, dt \\ &= P_o \Delta t - \int P_h \, dt.\end{aligned}\tag{4}$$

This computation is performed automatically by the built-in electronic system.

D. Conclusions

It was concluded at the end of this reporting period that a suitable design has been devised for a calorimeter to determine the heat of reaction of hydrogen with coal slurries. The fabrication, delivery, installation, and acceptance testing will be completed late November 1976.

II. HEAT TRANSFER COEFFICIENT

(T. P. Mulcahey,* R. Lo, T. Cannon, and T. R. Bump*)

The objectives of this task are to determine heat transfer coefficients suitable for the design of feed heat exchangers and effluent heat exchangers used in coal liquefaction processes and to identify mechanisms for the heat transfer process. Heat transfer film coefficients for mixtures of gas, liquids, and solids in a turbulent flow will be measured for (a) reactor effluent cooled by a stainless steel surface and (b) feed heated by a stainless steel surface. The experimental work will be carried out in a test module in a nominal 1/2-ton-per-day Heat Transfer Test Unit, which will include a slurry makeup system; slurry feed system; heaters; coolers; letdown tanks; and power, flowrate, and temperature instrumentation.

The following ranges of conditions will be covered:

Pressure	2,000-4,000 psig (14-28 MPa)
Temperature	200-465°C
Flow of Fluids:	turbulent

Three different coals suitable for liquefaction will be studied in the investigation. Slurries will be used having the compositions of SYNTHOIL gross product (unfiltered oil) and SYNTHOIL feed containing 30% by weight of finely ground coal.

There will be significant changes in the slurry parameters. The size of finely ground coal particles may increase by a factor as large as 6 during liquefaction, and the viscosity of the liquid may vary from 17 to 700 cp. Chemical changes may occur which liberate or absorb energy--the heats of reaction, the reactants, the products, and the energy changes for the reactions are ill-defined. Evaporation and condensation of reactant and product components provide still another complicating factor, which will be considered later.

Theoretical modeling of the heat transfer process will be attempted, correlating primary interaction of the gas, liquid, particles, and walls. The resulting model should be capable of describing the heat transfer rates, as well as the temperature history, of the particles in the slurry.

A flow diagram of the Heat Transfer Test Unit is contained in Fig. 2. It is similar to a SYNTHOIL process flow diagram except that the preheater and reactor elements have been replaced with a heating and cooling test module designed to measure the heat transfer coefficients of the fluids processed. Figure 3 is a flow diagram of a representative test module showing five heaters (HS-0 through HS-4) and four coolers (CS-1 through CS-4). Additional information on the heaters and coolers is contained in a following section (Test Module) of this report.

*Components Technology Division

 

Fig. 3. Heat Transfer Coefficient Measurement Test Module

The basic operation of the unit is as follows: A coal slurry consisting of an oil with physical properties similar to those of SYNTHOIL and a 200-mesh coal is mixed and heated in the 140-gal slurry make-up tank. A mixer and a rotating cavity recirculation pump maintain the slurry in suspension; the pump also provides the pressure to transfer the slurry to the 10-gal slurry feed tank. A mixer and recirculation pump connected to the slurry feed tank maintain slurry suspension, and the pump provides slurry at pressure to the suction side of the piston-type high-pressure pump. The high-pressure pump supplies the slurry to the entrance of the test module at 4,000 psi.

Hydrogen supplied to the unit at 500 to 1,000 psi, is compressed to 4,000 psi and merged with a recirculating hydrogen stream. The recirculating hydrogen is merged with the slurry before it enters the test section. The gas/slurry mixture passes into the heaters where a heat transfer coefficient is measured; the mixture then passes into the coolers where another heat transfer coefficient is measured.

The gas and liquid solid phases are separated in the high-pressure receiver. The gas stream is washed and cooled and returned via another gas compressor as the recirculating hydrogen stream. The liquid SYNTHOIL type effluent and water wash are collected in low-pressure receivers and periodically sampled and removed from the system.

A. Heat Transfer Test Unit

A commercial firm is fabricating the Heat Transfer Coefficient Test Unit. The test module heater and cooler sections are being fabricated in the ANL machine shop. Table 2 shows the schedule for construction and testing of the unit.

The commercial firm is constructing the test unit components exclusive of the test section in six modular frames. Four of these frames have been assembled with their major components and delivered; they have the following dimensions:

1. Hydrogen Recycle 26x34x66 in. (see Figs. 4 & 5)
2. Downstream 34x34x66 in. (see Figs. 6 & 7)
3. High-pressure
water and
slurry delivery 52x52x66 in. (see Figs. 8 & 9)
4. High-pressure
receiver and
scrubber tank 34x37x156 in.

Table 2. Schedule for Construction, Shakedown, and Testing of the Heat Transfer Coefficient Measurement Unit

Activity	1975								
	Mar	Apr	May	June	July	Aug	Sept	Oct	Nov
Contract Awarded	▼								
System Design and Engineering	■	■	■	■	■				
Procurement of Materials		■	■	■	■				
Technical Program Review Meeting			▼						
Assembly of System Modules						■	■		
Delivery of System Modules							■	■	
System Integration and Installation								□	□
System Debugging and Shakedown									□
System Performance Tests									□
Complete Installation									▼

Fig. 4. Hydrogen Recycle Module--Front and Side View

Fig. 5. Hydrogen Recycle Module--Rear View

Fig. 6. Downstream Module--Front View

Fig. 7. Downstream Module--Rear View

Fig. 8. High Pressure Water and Slurry Delivery Module--Front View

Fig. 9. High Pressure Water and Slurry Delivery Module--Rear View

The two remaining frames, consisting of the low-pressure slurry makeup module and the low-pressure slurry delivery module, are being assembled at ANL. The frame to hold the high-pressure receivers was shipped empty so that the safety liner and tanks can be assembled in place at Argonne. Figure 10 shows the planned layout of the unit in the experimental area.

To protect other equipment and personnel in the building during operation of this unit, it is planned to put a steel wall structure around all apparatus containing high-pressure gas. Currently planned wall thicknesses and heights are as follows:

- a. High-pressure compressor and hydrogen recycle room, 1/2-in.-thick steel plate, 10 ft high.
- b. Test module room, 1/8-in.-thick steel plate, 13 ft high.
- c. 5-gal high-pressure receiver, 3/4-in.-thick steel plate, 6 ft high.

Construction of the wall around the high-pressure compressors has been initiated.

The concrete floor serves as the base for the compressor and test module rooms, and a platform located 8 ft above the floor serves as the base for the high-pressure receivers. A 3/4-in.-thick plate will also be located below the high-pressure receivers. The building outside walls (W) are of blowout construction, and a 1-ft-thick steel-reinforced concrete wall (X) separates the units.

B. Test Module

The test module consists of heating, cooling, and mixing elements principally constructed of and connected by 0.25-in.-ID, 0.375-in.-OD tubing within which the process mixture will flow. The heating elements are vertically oriented, with the process mixture inside the tubing flowing in alternating directions (up in the first element and down in the second element, etc.). The heat is supplied by passing electric current directly through the wall of a 6-ft length of tubing between attached electrodes.

The cooling elements are of two different types, both of which use air to remove heat from the outside surface of a tube containing the process mixtures. The first type is a 6-ft vertical straight-tube arrangement similar to the heating elements but with a shell around the tube to contain the air flow. The second type consists of approximately 22 ft of tubing coiled within an air-cooling shell and has an overall length of about 2 ft. The process mixture will flow from the heating elements to the single straight-tube cooling element and then in series through three coiled cooling elements. Process mixture will enter two of the coiled cooling elements at the bottom and exit at the top and will flow in the opposite direction in the coiled cooling element in between.

Fig. 10. Layout of Heat Transfer Coefficient Unit

Temperature test results will be obtained from thermocouples attached to: the walls of the heating and cooling elements, electrode connections, cooling element shells, cooling air inlet and outlet ducts, and thermocouples built into the mixer elements. Tube wall temperatures will be measured at approximately 1-ft intervals along the heating elements and the straight-tube cooling elements and at approximately 3-ft intervals along the tubing of the coiled cooling elements. The locations at which temperatures of cooling element shells will be measured will be approximately the same as those at which the tube wall temperatures within the shells are measured. The electric current in each heating element will be monitored, as well as the voltage applied at the electrodes and at each heater wall thermocouple location.

Manufacture of the test module components, which is being done in the ANL shops as mentioned in section A, is continuing and is almost complete. The fluid mixers, straight-tube cooler, SYNTHOIL heaters, and cooling air mixers are complete. The nonavailability of some parts required some substitutions, as well as minor changes in the design specifications for the helical coolers. The helical coolers are being assembled; test module assembly will be completed in early October. Thermocouples and thermocouple wire for instrumentation of the test module components has been delivered. The layout design for the test module components, including the six heaters, has been completed except for the detailed electrical supply to the heaters and the detailed compressed-air supply to the coolers. Six heaters are being included to allow balanced electrical voltage operation of pairs of heaters. Balanced voltage operation is desirable to ensure zero voltage across the test section under all normal and abnormal conditions.

An automatic data acquisition system has been ordered; it will be used to collect data from approximately 170 thermocouples and 70 voltage references representing pressure, flow, current, and voltage, then to digitize and record the data on punch paper tape and in printer format. The information collected will be processed on a large computer to obtain the heat transfer coefficients.

An air compressor (with water-cooled aftercooler) capable of supplying 300 scfm at 13 psi was procured and installed on a concrete pad in a metal building next to the experimental area. The compressed air will be used to remove heat from the liquefaction effluent in the test module coolers.

C. Procurement of Substitute Oils for SYNTHOIL

Because of a shortage of SYNTHOIL, the Midwest's largest distributor of coke tar products was contacted for information on possible materials to substitute for SYNTHOIL in the heat transfer tests. Three 5-gal samples of their standard products were received. Tests will be run at ANL to determine the applicability to heat transfer coefficient determination of the pure product or appropriate blends of these products.

D. Design of Test Module for Measurement of Heat Transfer Coefficients

1. Experiment Design Philosophy

Determination of the number of heating, cooling, and mixer elements to use in the test module has to be a compromise resulting from evaluation of minimum data required, fabrication costs, desired measurement accuracies, expected changes in significant process parameters, and operational reliability and convenience. On the basis of these factors, the test module was designed to provide four or five heating elements, four cooling elements, and nine or ten mixing elements in the slurry flow path. The basic heating design is based on the use of four heating elements with the option of including a fifth one. Mixer elements will be located upstream and downstream from each heating and cooling element to provide bulk fluid temperature so that gross heat transfer coefficients can be obtained for the temperature range across each heating and cooling element. Also, each element is to be divided into six contiguous regions, and appropriate interpolation and correction factors are to be used based on measured parameter values. It is expected that a consistent set of six heat transfer coefficients can be obtained over each element. The heat transfer data developed can be used to obtain detailed engineering information for plant and process designers for use in the construction of preheaters, coolers, and economizers for large coal liquefaction plants.

2. Unit Design Parameters

The temperature of the slurry feed mixture in the test module should increase from approximately 100°C to 260°C in the first heating element, to 360°C in the second heating element, to 420°C in the third heating element, and to 460°C in the fourth heating element. A maximum tube wall temperature of 460°C has been selected to prevent charring of the mixture. Installation of the fifth heating element is also being considered to allow the temperature rise in the heating elements to be shifted to a heater whose flow is in the opposite direction (e.g., upward vs downward) to obtain any differences in heat transfer coefficient that might be associated with a particular direction of flow.

The corresponding design temperatures associated with fluid leaving the cooling elements are 420°C from the first, 330°C from the second, 240°C from the third, and 150°C from the fourth. The anticipated design current and voltage requirements of the four basic heating elements, rounded off to convenient whole numbers, are:

	<u>I(amp)</u>	<u>E(volt)</u>
1st heating element	360	18
2nd heating element	280	14
3rd heating element	220	11
4th heating element	170	9

A constraint placed on the operation of the heating elements which has not been taken into consideration in calculating the heat rates in the heating elements in the above table is the requirement that a zero voltage drop be maintained across the test module containing all heating elements so as to prevent current flow and voltage drops in the test unit outside the heating elements zone. It is expected that this can be accomplished by connection of voltage/current sources in series with the proper polarity sequence and values. Design factor allowances used in the calculations are expected to accommodate variations from the above tabulations.

3. Calculations

The desired heat transfer information will be obtained from the experimental information discussed below.

The heat transfer coefficient, h , between a metal surface and a fluid is expressed as:

$$h = \frac{q}{A(T_w - T_b)} \quad (1)$$

where q = heating rate

A = area of the metal surface

T_w = temperature of the metal inside surface (wall)

T_b = temperature of the bulk fluid

A, Area. The area A of metal surface to be used in the calculations is the surface area of the inside of the heating or cooling element tubing containing the process mixture; it will be the surface area per unit length of the 1/4-in.-ID tubing, multiplied by the active length of heat transfer. In English units, the area will be expressed in square feet; in metric units, it will be expressed in square meters.

q, Heating Rate of Heating Elements. The heating element design provides for direct electrical (resistance) heating of the tube wall. It is assumed that in an ideal experiment, the resistivity of the stainless steel would be constant, the wall would have a uniform cross section, and the heat generation rate in the wall would be uniform. If the transfer of heat were also restricted only to the direction of fluid flow and there were no heat losses along the outside surface of the tubing or at the electrode, the heat generation rate in the wall multiplied by the length of tubing in a heat transfer element or segment would be equal to the value of q for that heating element or segment.

Under these ideal conditions, there would be several ways of monitoring the rate of heat generation in the wall of a heating element. If the resistance of a heating element or segment of tubing could be measured or accurately calculated, Equation 2 could be used to measure the heat generation rate by monitoring the current.

$$q = I^2 R \quad (2)$$

where I = the measured electrical current in the heating element
 R = the resistance of the heating element or segment of the element.

Also, if direct current is applied to a heating element, Equation 3 will represent the heat generation rate.

$$q = V I \quad (3)$$

where V = the voltage drop across the heating element or segment. The values of q obtained from Equations 2 and 3 should be identical.

For the experiment, the resistivity of stainless steel is a nonlinear function of temperature, ranging from $72 \mu\Omega \text{ cm}$ at 20°C to about $104 \mu\Omega \text{ cm}$ at 450°C . Also, heat losses or heat gains may not be negligible in regions around the electrodes, and the total of voltage measurements on heating elements (or segments of a heating element) may not equal the overall voltage measurement on an element across the electrodes. To determine the effects of the above nonideal conditions and to provide compensating values, additional thermocouples will be attached to one of the two electrodes of each heating element. The heat losses and voltage drops associated with the other electrode attachments on each heating element should be similar to those measured because they are of identical designs. Therefore, compensation for the losses will be possible.

The heat generation rate, q , to be used in Equation 1* for a single heating element is then calculated on the basis of measured heat rate values, q_{E1} and q_{E2} , at the electrode attachments, the heat loss from the outside tube surface, q_s , and the total heat input between the electrodes.

$$\begin{aligned} q &= IV_{E1 - E2} + q_{E1} + q_{E2} - q_c \\ &= \sum_{i=1}^6 I^2 R_i + q_{E1} + q_{E2} - q_s \end{aligned}$$

*The right-hand expression assumes the heating element to be subdivided into six elements.

$V_{E_1 - E_2}$ is the voltage drop across the heating element excluding the electrodes and I is the current in the element. For high q values, the value of q_s may usually be neglected. Measurements will be made to confirm this.

The method of calculating the individual heat generation rates, q_i , for the six segments of each heater will depend on the detailed design of the heating elements and the exact location of the voltage and temperature sensor attachments, but to make this presentation complete, a possible simplified method will be assumed. In this method, each heating element will be divided into six 1-ft segments, numbered consecutively from inlet to outlet. The calculations will proceed as follows:

1. Readings of the surface thermocouples on the test section segments will be corrected for voltage errors based on the measured voltage drops across the corresponding segments to which the thermocouples are attached. The resulting temperatures will then be plotted against the distance along the test section, and a smoothing function will be applied to obtain a rough temperature distribution along the test section.

2. The voltage drop across each segment, V_i , will then be determined by using

$$\begin{aligned} V_i &= IR_i \\ &= I \frac{\rho L_i}{A_s} \end{aligned}$$

where ρ is the stainless steel resistivity corresponding to the segment surface temperature, L_i is the segment length, and A_s is the transverse cross-sectional area of the tube wall.

No allowances will be made for thermal expansion of the tube, temperature gradient through the tube wall, current leakage through or from the loop external to the heating element being considered, or current leakage through the fluid in the heating element; calculations show that errors from neglect of these factors should be insignificant. The calculated and measured voltage drops will be compared.

On the basis of past experience in the measurement of heat transfer to the tube and heat losses from the electrodes, as well as problems in measuring voltages and heat losses in the area of the electrodes, it is expected that the sum of the voltage drops across the segments will differ from (probably be less than) the total voltage drop across the entire test section. Temperatures and other electrical measurements from thermocouples attached to the electrodes will be used to estimate and correct the voltage and the heat input rates.

A typical correction factor, q_{E1} , to be used includes the heat gained as the fluid passes an electrode junction

$$q_{E1} = I^2 R - 2kA_r \frac{\Delta T}{\Delta X}$$

k = thermal conductivity of type 316 stainless steel

$\frac{\Delta T}{\Delta X}$ = thermal gradient along electrode.

where A_r is the cross-sectional area of the electrode. The first term in the above equation gives the heat generated in the electrode junction and tube wall. The second term gives the heat loss (or gain) at the electrode due to heat conduction along the electrode. Both electrodes on the same element will be treated the same except the resistivity of the lower-temperature electrode will be less and hence the heat rate will be less.

3. Once the voltage and heat input rate have been corrected, any required changes to the indicated temperatures of the six segments due to a revised voltage correction factor will be made. The process will be repeated until a consistent set of wall temperatures and voltage values are obtained.

4. After a consistent set of voltages and temperatures is obtained, the heat rate for each segment will be calculated with the equation, $q_i = V_i I_i$.

q , Cooling Rates of Cooling Elements. The value of the cooling rate, q , for each cooling element or segment will be based on the temperature rise of the cooling air as it passes through the cooling segment being considered.

$$q_i = MC_{pA} (T_{i+1} - T_i)$$

where q_i = cooling rate of the i^{th} segment

M = mass flow rate of the cooling air

C_{pA} = heat capacity of the cooling air

T_i = temperature of the air going into the cooling segment

T_{i+1} = temperature of the air exiting from the cooling segment

The mass flow rate and/or the heat capacity of the air for each cooler will be based on measured parameters as corrected, if necessary, for temperature, pressure, and humidity. The temperature rise of the air will be based on the inlet and outlet temperatures for the i^{th} segment, as interpreted from the measured cooling element air mixed mean inlet and outlet temperatures and from the measured temperature profile along

the shell of each cooler. A correction of the shell temperature profile will be made to accommodate the temperature mixing/diffusion distance necessary to transport heat from the pipe containing the SYNTHOIL to the shell. As with the heating element, temperatures will be monitored within the insulation surrounding the cooling element to determine the heat losses; appropriate corrections will be made if significant heat losses are found.

T_w , Temperature of the Metal Inside Surface, Wall Temperature of Heating Elements. The inner wall tube temperature for each heating element or segment of an element is related to the temperature of the outside surface by the expression:

$$T_w = T_{out} - \frac{q_i}{4k \text{ Vol.}} \left[r_w^2 - r_{out}^2 \left(1 - 2 \log_e \frac{r_{out}}{r_w} \right) \right]$$

which describes the temperature distribution in a tube with uniform heat generation, no losses from the outside surface, and heat flow in the radial direction only. Calculations and measurements will be made to establish whether these assumptions are as valid as has been indicated in other heat transfer experiments.

T_w = average inside wall temperature over a unit area

T_{out} = average outside tube temperature over a unit area

q_i = heat rate of the i^{th} segment

k = thermal conductivity of stainless steel

Vol. = volume of the segment tube

r_w = inside radius of tube

r_{out} = outside radius of tube

The average outside wall temperature will be calculated for each heating element and each segment of an element as indicated below.

For this experiment, the initial calculations will use the linear average of the element or segment temperatures for calculating the outside wall temperature; however, this averaging technique

$$T_{out} = \frac{T_j + T_{j+1}}{2}$$

where T_j = wall temperature at one end of an element or segment.

T_{j+1} = wall temperature at the other end of an element or segment.

is valid only for nicely behaved fluids. Since SYNTHOIL feed material is not a nicely behaved fluid over a wide temperature range, averages obtained in other ways may have to be used. The corrected temperature distributions, as arrived at in calculating the values of the heat rate, will provide information indicating whether or not linear averages are acceptable or what type of average might be better.

T_w , Temperature of the Metal Surface of the Cooling Elements.

For a first approximation of the inside wall temperature, T_w , the equation given in the previous section for heating elements will be used. This equation relates the measured outside tube wall temperature, the heat rate (cooling rate), and a log of the mean radius, to the inside wall temperature. The justification of its use for the six individual subsections of each cooler is that the cooling rate value, q_i , should be constant within each subsection. The validity of this assumption will be determined as one goal of the experiment. If the value of the cooling rate is not sufficiently uniform to be considered constant, equations based on other assumptions will be used to relate the measured parameters to the inside wall temperature of the tube (see section E, Further Comments).

T_b , Average Bulk Temperature of the Fluid in the Heating Elements.

Direct measurement of the average bulk temperature of the fluid is possible only in mixer elements located upstream and downstream from each heating and cooling element. Since there are currently no models or correlations that relate (1) the input and output bulk temperatures, (2) the properties of the SYNTHOIL three-phase fluids, and (3) the heat transfer coefficients relevant to metal-to-fluid heat transfer, no test method has been devised to average the bulk temperature of the fluid. However, one obvious temperature average for use in calculation would be the arithmetic average

$$T_b = \frac{T_j + T_{j+1}}{2}$$

where

T_j = the bulk temperature at one end of a heating element or segment and

T_{j+1} = the bulk temperature at the other end of the heating element

If used over an entire heating element or cooling element, this would provide a representative heat transfer coefficient that could be used in the design of their heat transfer equipment operating at the same flow and temperature conditions. Such an average would neglect the heats of reaction and vaporization resulting from reactions or vaporization occurring within the bulk fluid. Methods of determining average bulk

temperatures that include corrections for heats of reaction and vaporization require models that correlate the temperatures, amounts of material, and heat values. Estimates of some of these values may become available from results of experiments currently planned.

T_b , Average Bulk Temperature of the Fluid in the Cooling Elements.
Although the fluid in the cooling elements is expected to behave in a more normal fashion than the fluid in the heating elements, the comments in the discussion of calculating the average bulk temperature of fluid in the heating elements are relevant, i.e., process modeling is necessary to select more appropriate definitions of average bulk temperature or to make other appropriate corrections for condensation or chemical heat of reaction.

E. Further Comments

1. Heater Analysis

It is planned to infer fluid behavior by use of a technique based on changes in the heat transfer coefficient in individual segments. This technique involves weighting the heat transfer coefficient of the fluid as a function of the measured outside wall temperature. The rationale for taking a weighted average can be seen by considering what would happen under some ideal conditions. Assume that:

1. The heat generation rate (q) and the area (A) are constant.
2. The heat capacity (C_p), the mass flow rate (M), and the inlet temperature of the heating element (or segment) are constant.

From the first assumption and Equation 1, the difference between bulk temperature and inside wall temperature ($T_w - T_b$) is inversely proportional to the heat transfer coefficient, h ,

$$\text{i. e., } (T_w - T_b) = \frac{q}{A} \frac{1}{h}$$

Given the second assumption, it can be shown that the temperature rise of the fluid along the heating channel would be linearly related to distance from the inlet. Therefore, the inside wall temperature must vary to accommodate any changes in the heat transfer coefficient. Likewise, the outside wall temperature must vary since it is related to the inside wall temperature by constants.

2. Cooler Analysis

As in the case for heaters, it is expected that the conformity of measured temperatures to calculated values will be used to determine the validity of assumptions or to provide insight into the mechanisms of SYNTHOIL heat transfer. For example, if the assumption is made that the

cooling rate is constant, the rate of enthalpy rise in the air will also be constant; therefore, a comparison of corrected shell temperatures to calculated air temperatures should provide a means of assessing the validity of this assumption. Likewise, the deviation of the value of the air heating rate can be reflected across the tube wall boundary to deviations in the heat transfer coefficient of the SYNTHOIL fluid. This is possible because of the wealth of data on air heat transfer coefficients and knowledge of the rate of heat conduction in the tubing material containing the SYNTHOIL. The errors involved in determining the SYNTHOIL heat transfer coefficient in the coolers will be estimated; it is expected that the errors will be significantly greater than those obtained from using the electrical heaters.

F. Conclusions

Two conclusions arrived at in this reporting period are:

1. On the basis of current delivery schedules, the unit will be available in October for initiation of calibration procedures and in November for the performance of preliminary heat transfer coefficient measurements using gases only. Measurements of heat transfer coefficients of liquids other than SYNTHOIL will be initiated in December. SYNTHOIL and slurry testing will be initiated in January 1977.

2. From the analysis of data that will be obtained from the heating and cooling units, sufficient information on heat transfer coefficients should be obtained for heat exchanger design; the data will also be useful in verifying models of the liquefaction processes.

III. ADDITIVES FOR SEPARATION OF SOLIDS FROM LIQUIDS^{*} (H. Huang)

The objective of this task is to investigate the use of additives to facilitate the removal of solids from oil produced in coal-liquefaction processes. These additives should be able to alter the physical properties of the mixtures so as to improve separation in subsequent steps.

This study is limited to the evaluation of candidate additives which act as surface-active agents, wetting agents, and settling agents. The evaluation is based on the additives' effect in reducing the viscosity of the mixture and/or inducing settling. Viscosity measurements have been performed with a Brookfield Thermosel System to heat the sample. Also, settling tests have been conducted by determining the extent of settling of suspended solid particles in 3/4-in. copper tubes for prescribed times.

A. Viscosity Reduction

We observed that small amounts of two DuPont surfactants, Petrowet R and Alkanol WXN, are capable of reducing the viscosities of SYNTHOIL gross product and SYNTHOIL (centrifuged) product, when added to these products. At 82°C, the viscosities of the gross product and centrifuged product are reduced by 11% and 12%, respectively, with the addition of 1 wt % Petrowet R, and the viscosity of the gross product is reduced by 14%, with the addition of 1 wt % Alkanol WXN. However, the magnitude of reduction in viscosity decreases as the temperature increases. Also, cost figures do not justify them as potential additives.

We next tested eight sorbitan-ester surfactants, which have been used as effective pour depressants and flow improvers in the petroleum industry.² The surfactants were provided by Emery Industries Inc., and are: Emsorb 2500, 2503, 2505, 2515, 6903, and 6915 and Emrest 2400 and 2410. All of these except Emsorb 2503 (sorbitan trioleate) had practically no effect on the viscosity of the SYNTHOIL product. With the addition of about 1 wt % Emsorb 2503, the viscosities of the SYNTHOIL gross and centrifuged products were reduced by about 5%. The complete results for Emsorb 2503 are tabulated as Table 3. In contrast to our previous results for Petrowet R and Alkanol WXN, the reduction in viscosity by the addition of Emsorb 2503 appears to remain steady from 80 to 200°C. Nevertheless, its lesser effect on viscosity does not recommend Emsorb 2503 as a suitable additive for viscosity reduction.

In view of the success of Oak Ridge researchers in their settling tests,³ we evaluated the effectiveness of six flocculants used by them for viscosity reduction. The flocculants were obtained from the Tretolite Division of Petrolite Corporation. Unfortunately, none of them had a significant effect (>5% reduction) on the viscosity of SYNTHOIL product.

^{*}The work on this task has been completed. The details of this work have been published in a separate report.¹

Table 3. Percentage Reduction of Viscosity for SYNTHOIL Products Upon the Addition of 1 wt % Emsorb 2503.

SYNTHOIL Product	82°C	100°C	150°C	200°C
Centrifuged	4.7	4.6	4.0	4.5
Gross	5.8	4.9	6.4	3.5

B. Precipitation/Settling Test

A screening study of commercially available additives that may improve the precipitation or coprecipitation of suspended solid residues was completed. This study was concerned with two types of solids removal. We tested additives that would induce flocculation and/or coagulation, when only a small amount is added to the SYNTHOIL gross product, so as to simplify subsequent separation steps, such as solids concentration, filtration, or centrifugation. We also assessed the potentials of high-temperature settling and solvent-precipitation deashing⁴⁻⁶ as alternative separation methods for the SYNTHOIL process.

The background information, experimental details, and detailed results of this work have been published as part II of ref. 1.

Settling studies on additive-induced agglomeration were performed at 200°C for three Nalco flocculants (81C09, 8861, and 8863) and two DuPont surfactants (Petrowet R and Alkanol WXN) which are capable of reducing the viscosity of SYNTHOIL gross product. Comparison of the results for these five additives with the results for blank tests showed no additional settling. Settling runs also have been conducted at 250°C, with the addition of 3,000 ppm of two Tretolite additives that Oak Ridge researchers found to be very effective agglomerating agents for SRC product. No significant additional settling for SYNTHOIL product was found.

Table 4 presents settling results at 200°C for SYNTHOIL gross product, mixed with various amounts and types of precipitation solvents. These results indicate that of the additives we have tried, kerosene is the most effective precipitation solvent for SYNTHOIL gross product. The kerosene used by us was obtained commercially; it had a wide boiling range (from 160 to 300°C). Special-cut kerosene as suggested by Sze and Snell^{5,6} should give better results. Results should also be improved by settling the SYNTHOIL-kerosene mixtures at higher temperatures.

The settling run with 30 wt % kerosene gave particularly good results; the top three fractions in the column were ash-free oil. the settling time required for obtaining three top fractions of ash-free oil was 6 hr at a settling temperature of 200°C and only 4 hr at a settling temperature of 250°C. The viscosity of each settling fraction at 200°C has been determined.¹ The viscosity results suggest that most of the heavy asphaltenes and pre-asphaltenes had been precipitated to the bottom fraction during the course of settling.

Table 4. Analyses of 200° C Settling Fractions of Mixtures of SYNTHOIL Gross Product and Solvents

Additive	Settling Time (hr)	Fraction No.	wt%		
			Ash	Iron	Sulfur
10 wt % Toluene	4	1	3.6	0.68	1.0
		2	3.6	0.69	1.0
		3	3.6	0.69	1.0
		4	3.7	0.69	1.0
		5	3.6	0.69	1.1
		6	4.8	0.88	1.3
20 wt % Toluene	4	1	2.1	0.39	0.91
		2	2.5	0.46	0.94
		3	2.6	0.49	0.96
		4	2.7	0.51	0.95
		5	2.5	0.47	0.98
		6	4.6	0.83	1.3
25 wt % Octane	4	1	1.5	0.27	0.76
		2	2.1	0.38	0.70
		3	2.5	0.44	0.64
		4	2.7	0.49	0.78
		5	2.8	0.32	0.85
		6	7.8	1.4	1.4
12 wt % Kerosene	3	1	1.6	0.30	0.72
		2	3.6	0.64	0.89
		3	5.8	1.0	1.1
		4	7.9	1.3	1.4
25 wt % Kerosene	3	1	0.91	0.16	0.44
		2	1.0	0.18	0.56
		3	0.77	0.14	0.55
		4	1.7	0.29	0.67
		5	5.5	0.95	1.1
		6	8.7	1.5	1.4
30 wt % Kerosene	6	1	0.03		
		2	0.02		
		3	0.03		
		4	1.5		
		5	6.7		
		6	11.8		
30 wt % Fuel Oil No. 2	6	1	0.45	0.08	
		2	0.47	0.09	
		3	0.46	0.08	
		4	1.1	0.20	
		5	6.3	1.1	
		6	10.	1.7	
30 wt % Fuel Oil No. 2	4	1	1.7	0.30	
		2	1.9	0.34	
		3	1.8	0.31	
		4	1.4	0.25	
		5	4.8	0.81	
		6	8.4	1.4	

C. Conclusion

Tests of more than two dozen additives indicate that the use of additives to reduce the viscosity of coal-liquefaction process streams is not productive. The biggest reduction in viscosity observed so far is 14% at low temperature; however, the magnitude of further reductions in viscosity decreases as the temperature increases, and this relatively small decrease in viscosity could be realized with a small increase in temperature without an additive. Also, cost figures do not support the use of additives as a potential pretreatment step.

Solvent precipitation de-ashing appears to be a promising solid separation method for the SYNTHOIL process. Of six different hydrocarbon liquids tested, kerosene was found to be an effective precipitation solvent for SYNTHOIL gross product.

IV. CATALYST TESTING (R. Lo and T. Cannon)

The objective of this task was to evaluate new commercially available catalysts for use in the SYNTHOIL process. Testing was to be carried out in a continuous unit at the operating conditions of SYNTHOIL, and the results were to be used to identify the better catalysts. Subsequent screening of these selected catalysts would then be made on the long-life test unit at PERC to optimize catalyst selection for use in a 10-ton-per-day (TPD) SYNTHOIL process development unit currently under design.

Phase I. Design, Construction, and Shakedown on Test Unit

We have designed (in consultation with PERC) and have subcontracted the construction of a continuous high-pressure coal liquefaction unit wherein catalysts may be tested under SYNTHOIL process conditions, 450°C and 2000-4000 psi. The unit will have the capacity to process at least 1.1 kg/hr of coal slurry containing 35-50 percent coal in recycle oil. The design will include sufficient instrumentation and will be automated so that it can be operated continuously with minimal attention for periods of no less than 12 days. A schematic flow diagram of the Catalyst Test Unit is shown in Fig. 11. Due to budget problems and reevaluation of the program with PERC and ERDA, Fossil Energy Division, work on this task will be unfunded after completion of phase I.

Phase II, Tests of Catalysts

It was planned to select, with PERC's agreement, four or more commercially available hydrodesulfurization catalysts and to test them on the Catalyst Test Unit in 300-hr continuous runs to determine the intermediate life and product variability at 2000 psi and 4000 psi for each catalyst. Product samples would be collected at least once every 24 hr during a run and would be analyzed to determine: coal conversion; sulfur, nitrogen, and oxygen removal; hydrogen consumption; viscosity; and specific gravity of the product oil.

A. Fabrication of Catalyst Test Unit

A commercial firm is constructing the test unit in a modular format. All frames for the various modules have been erected. Instrument panels have been laid out, punched out, and silver screened. Assembly of the modules began in August. Delivery of the modules and installation are scheduled for early November.

SYMBOL	SCHEDULE LISTING
	FORGED CONTROL VALVE
	ON-OFF BALL VALVE
	HIGH PRESSURE BONNET VALVE
	REGULATING/SHUTOFF VALVE
	NEEDLE VALVE
	THROTTLING VALVE
	THREE WAY BALL VALVE
	CHECK VALVE
	SOLENOID VALVE
	RELIEF VALVE
	BACK PRESSURE REGULATOR
	PRESSURE GAUGE
	PRESSURE SWITCH
	HIGH PRESSURE ALARM
	LOW PRESSURE ALARM
	LIQUID LEVEL CONTROL
	PRESSURE TRANSDUCER
	DIAPHRAGM SEAL
	FILTER
	RUPTURE DISC
	DRY TEST METER
	GAS SNUBBER
	PRESSURE REGULATOR
	DELTA-P TRANSDUCER
	PUMP
	GAS COMPRESSOR
	PRESSURE VESSEL

Fig. 11. Schematic Flow Diagram of the Catalyst Test Unit

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