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**CONVERSION OF HIGH CARBON
REFINERY BY-PRODUCTS**

Annual Technical Report

**Fiscal Year 1995
(Oct 1994 - Sep 1995)**

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For

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Pittsburgh Energy Technology Center
Bartlesville Project Office
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Job 7519**

By

**The M.W. Kellogg Company
Houston, Texas**

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1.0 PROJECT OBJECTIVE

The overall objective of the project is to demonstrate that a partial oxidation system, which utilizes a transport reactor, is a viable means of converting refinery wastes, byproducts, and other low-value materials into valuable products. The primary product would be a high quality fuel gas, which could also be used as a source of hydrogen.

The concept involves subjecting the hydrocarbon feed material to pyrolysis and steam gasification in a circulating bed of solids. Carbon residue formed during pyrolysis, as well as metals in the feed, are captured by the circulating solids, which are returned to the bottom of the transport reactor. Air or oxygen is introduced in this lower zone and sufficient carbon is burned, sub-stoichiometrically, to provide the necessary heat for the endothermic pyrolysis and gasification reactions. The hot solids and gases leaving this zone pass upward to contact the feed material and continue the partial oxidation process.

2.0 BACKGROUND

In order to accomplish the project objective, the major effort planned was the testing of selected feeds in the Transport Reactor Test Unit, a pilot plant facility located at Kellogg's Technology Development Center. At the end of FY94, a limited number of pyrolysis runs were made in this unit, using an oil in water emulsion of Hondo crude as the feed material. It was intended to conduct these tests in the fully integrated partial oxidation mode. However, severe problems were encountered with sustaining the liquid feed to the reactor due to coking in the feed tube, not only preventing integrated operation, but also limiting the pyrolysis runs to very short periods.

At the completion of the tests, it was concluded that the reactor configuration was not suitable for handling highly coking liquid hydrocarbon feeds. The decision was made to design and build, at Kellogg's expense, a new reactor which, in addition to a better feed injection system, includes other design features that improve the performance and reliability of the unit. The new design is also more suitable for integrated partial oxidation testing.

3.0 SUMMARY OF TECHNICAL PROGRESS

FY95 was spent in design, construction, and start-up of the new Transport Reactor Test Unit (TRTU-II). Problems with the heating system during start-up resulted in a re-design of the system. The new heating system design was successfully tested and will be installed when the unit comes down for repairs in November.

3.1 Basis For Design

The re-designed unit incorporates the following new equipment items:

1. Two-stage reactor (including feed injection nozzles)
2. High efficiency cyclone
3. Standpipe
4. Solids return leg (from standpipe to riser)

The new reactor is designed to accept vapor, liquid, mixed (v/l), and solids (dry or slurry) feeds. Several of these are planned for the PETC program.

The design bases for the new unit are summarized in Table 1. The reactor itself will have a lower mixing zone below the riser. This arrangement is useful for staging reactions. For example, in partial oxidation, carbon on the solids returning to the mixing zone can be burned with air or oxygen in the mixing zone prior to admitting hydrocarbon feed to the bottom of the riser.

The reactor is designed to operate at high temperatures and low to moderate pressures. At the highest planned operating temperature of nominally 1800°F, the carbon gasification reactions will proceed at significant rates, thus maximizing the conversion of feed carbon to gaseous products. Additionally, any higher molecular weight products which might tend to form from feed pyrolysis should crack at this temperature. This simplifies downstream product recovery as well as eliminating the potential for plugging of equipment.

A high efficiency cyclone has been incorporated into the design to conserve solids inventory in the system. In addition, the standpipe has been designed for minimum solids holdup, resulting in rapid solids turnover and a more homogeneous system. This combination should permit a rapid approach to steady-state conditions.

3.2 Description of Unit

Figure 1 is a simplified sketch of the new unit. It consists of a mixing zone, a riser, a cyclone, and a standpipe (downcomer).

The hydrocarbon feed is usually injected into the upper part of the mixing zone where it mixes with hot solids, returning to the zone from the standpipe, and oxidant/steam/N₂ fed to the bottom of the reactor. The solids/vapor mixture flows upward through the riser and the hydrocarbon undergoes pyrolysis, with laydown of carbon on the solids. The mixture enters the cyclone, which separates virtually all of the solids and returns them to the standpipe. Product gas is sent to the cooling, conditioning, and recovery system. Solids flow from the standpipe back to the mixing zone is controlled by a plug valve at the bottom of the standpipe.

During pyrolysis runs, steam and nitrogen are injected into the bottom of the mixing zone. At the higher riser temperatures, the steam will gasify some of the carbon on the solids, but basically the carbon is allowed to accumulate on the circulating solids. During partial oxidation runs, air is injected at the bottom, either with or without steam, to burn off the net carbon make from pyrolysis of the feed in the riser. This produces an "equilibrium" loading of carbon on the solids.

3.2.1 Reactor

The reactor is comprised of two sections, a lower mixing zone and an upper riser. The mixing zone is fabricated from 1½" schedule 160 Incoloy 800HT pipe, and is 10 feet high. The riser is 1" schedule 160 pipe, approximately 30 feet high, and is made from the same material. Details of the reactor are shown in Figure 2.

TABLE 1

Design Bases for New Transport Reactor

REACTOR

Operating environment	reducing or oxidizing
Operating temperature, °F	1800 (max)
Operating pressure, psia	100 (max)
Hydrocarbon feed rate, lbs/hr	5 (max)

Mixing Zone

Operating regime	turbulent fluid bed
Gas velocity, fps	1-3
Bed density, lb/ft ³	20 (typical)

Riser

Operating regime	entrained bed
Gas velocity, fps	20-30
Bed density, lb/ft ³	4-6 (typical)
	1-10 (range)

CYCLONE

Mean particle size, μ	70 (typical)
Efficiency, %	99.99
Inlet gas velocity, fps	40-50

STANDPIPE

Operating regime	moving bed
Gas velocity, fps	0.1-0.3
Bed density, lb/ft ³	40-50
Solids flux, lbs/ft·sec	50 (typical)
Solids circulation, lbs/hr	1600 (max)

FIGURE 1
TRANSPORT REACTOR UNIT

FIGURE 2
REACTOR DETAILS

The mixing section is designed to operate as a dense phase turbulent fluidized bed. Oxidant (air) and/or steam, or N_2 , enters the zone through the bottom flange and flows through a specially designed gas distributor. Solids returning from the standpipe enter this section 1½ feet above the flange and are thoroughly mixed with the gas in the turbulent bed. During partial oxidation runs, this will ensure that the oxygen is fully consumed before the gas reaches the top of the mixing section.

Hydrocarbon feed, either liquid or vapor, is injected well up in the mixing section, at a point 9 feet above the bottom flange, and is injected upward at a 30° angle to the vertical. This arrangement should provide very good dispersion of the feed in the upper portion of the turbulent bed just prior to the vapor/solids mixture entering the riser.

A nitrogen feed nozzle is also located at the top of the mixing zone, at a level 6" above the hydrocarbon feed nozzle. This nozzle provides the flexibility to independently adjust the riser gas velocity, if desired, in order to limit the contact time in the riser.

For increased flexibility, two additional feed nozzles are located in the riser section. One is located at the very bottom of the riser and is basically an alternate feed point to the feed nozzle in the mixing zone. The other feed nozzle is located halfway up the riser. This nozzle will permit testing to be done under very short contact time conditions (~0.5 sec).

Solids can be drained from the reactor through a connection provided 3 feet above the bottom flange. Since the solids drain into a bomb, sized to handle the entire inventory, the unit can be emptied while at pressure. This simplifies change-out of the solids inventory.

As shown in Figure 2, junction blocks have been used at the three hydrocarbon injection points as well as the solids drain and the point of solids return to the reactor from the standpipe. These blocks are bored out solid blocks of Incoloy 800HT and are generally used where it is impractical to weld the branch line (nozzle) to the header (reactor body). They add structural stability and strength to the design.

3.2.2 Cyclone

The cyclone has a 3.0" ID and is also made from Incoloy 800HT. It has been designed for a very high collection efficiency. The normal inlet gas velocity will be about 40 ft/sec when the riser velocity is 30 fps.

Since the system has been designed for minimum solids inventory, to permit faster solids turnover and more rapid equilibration, a very high efficiency is an absolute requirement, in order to conserve solids. For example, with the maximum expected solids circulation rate of 1600 lb/hr, a cyclone efficiency of 99.99% corresponds to a solids inventory loss of almost 1%/hr.

The inlet pipe from the riser to the cyclone consists of a long-radius elbow. This design serves two functions. First, it provides a smooth flow entry into the cyclone, which should facilitate good cyclone performance. Second, it accommodates differential thermal expansion between the riser and the standpipe. As designed, the system is capable of withstanding a 200°F difference in average temperatures between the reactor section and the standpipe section.

3.2.3 Standpipe

The standpipe contains the bulk of the solids inventory in the system and provides the head needed to circulate solids back to the mixing zone of the reactor. It is fabricated from 1½" schedule 160 Incoloy 800HT pipe. Figure 3 shows some of the standpipe details.

The normal solids level in the standpipe is about 23 feet above the solids entry point into the mixing zone. To provide positive control of solids flow, a plug valve, located at the base of the standpipe, is used. An aeration port is provided at the valve location to aid in keeping the valve clear and freely moving,

Additional aeration ports are also provided in the standpipe assembly, three along the standpipe itself, and one in the lateral which connects the standpipe to the mixing zone. These keep the solids fluidized and assist in maintaining solids flow.

3.2.4 Heating and Insulation

Instead of using clamshell furnaces, as on the old reactor system, it was decided to use Kanthal windings for heating the new unit. This results in a much simpler, cleaner design and permits much easier installation of thermocouples, dP connections, etc.

There are seven independent heating zones, with two on the riser, three on the standpipe, and one each on the cyclone and the reactor mixing section. Most zones have multiple windings in parallel, with a total of 25 windings on the unit. Maximum total heat input to the unit is 83,000 BTU/hr.

The entire system is insulated with 6" of ceramic fiber and 2" of rigid calcium silicate, covered with banded aluminum sheeting. The aluminum is painted (blue) to reduce emissivity. Insulation supports have been included for the upper section(s) of both the riser and standpipe.

3.2.5 Structural Support System

The reactor/cyclone/standpipe system is supported (anchored) at the bottom and allowed to "grow" upward as it heats up to its normal operating range of 1600-1800°F. A counterweight system is used at the top and in the middle of the unit to maintain directional stability during heatup. Four-way guides are also provided near the middle and top of both the riser and standpipe to limit lateral movement.

This type of design for the support system minimizes vertical movement of the bottom sections of the unit (mixing zone, lateral, plug valve assembly), where most of the process connections are. It has been successfully used in several other pilot plants built at the Kellogg Technology Development Center.

FIGURE 3
STANDPIPE DETAILS

3.2.6 Instrumentation and Analytical

A process and instrumentation drawing, which shows all of the instrumentation in the mixing zone, riser, cyclone, and standpipe, is attached (DWG No. 1500C). The unit is not as heavily instrumented as the previous unit, but there are sufficient thermocouples, pressure and dP measurements, and flow meters to adequately monitor the unit and determine densities, solids levels, solids flows, etc. All of the thermocouple readings and dP measurements are continuously recorded by a computer data logging system or on chart recorders.

Much of the instrumentation for the upstream (feeds) and downstream (gas processing) sections of the pilot plant remain from the previous unit. These sections are shown on the attached drawings (DWG No. 1500A, 1500B). Important temperature, pressure, and dP measurements for these systems are also continuously recorded by the data logger.

The unit has several gas analyzers, and measurements of CO, CO₂, SO₂, and O₂ can be continuously recorded by the data logger. There is also a gas chromatograph which can be periodically used for determining gas compositions. Additionally, gas sampling stations are provided for obtaining grab samples for complete gas analysis.

3.3 Construction and Start-up

Construction of the new reactor was completed in mid-May, with the installation of the electrical heater windings and insulation. The unit was successfully erected and the counterweight support system was adjusted after dry-out of the insulation. The unit was then turned over to operations for commissioning.

Commissioning of the system was routine. All rotameters were calibrated or re-calibrated. Gas lines were checked to ensure that connections were properly made. Instruments were checked for proper operation. Minor modifications were made to the data logging system to provide better and more complete output. No significant problems were encountered, and by late May the unit was ready for initial heat-up.

3.3.1 Start-up

Plans were developed, reviewed, and finalized for using a simulated naphtha feed during the initial start-up. This feed can be fully vaporized before being injected into the reactor and has a low coking tendency. Not only does this facilitate the start-up, but it also permits the acquisition of some basic information under relatively mild conditions. It was planned to evaluate the effects of steam, temperature, and alkali addition (to the solids) on the gasification and combustion reactions taking place during partial oxidation. A reactor temperature of 1800°F was selected for the test.

The initial heat-up was done slowly and carefully to make sure that all heating elements and controllers were functioning normally. During this period, the reactor temperatures were limited to approximately 1000°F. With solids (FCC catalyst) circulation established, temperature control was excellent. Temperatures throughout the entire reactor/standpipe system were typically within a range of 20-30°F.

System temperatures were gradually raised to 1800°F without incident, and the heaters appeared to be easily capable of maintaining the system at this temperature. Some problems were experienced in maintaining stable solids circulation and there appeared to be bridging occurring in the standpipe. Solids circulation rates were well below the maximum design rate of 1600 lb/hr, and solids losses from the system were, at times, high.

Before naphtha feed could be started, several of the windings burned out. Some of the heating elements experienced large temperature excursions, with temperatures well in excess of 2000°F being recorded. These excursions may have been related to the solids circulation problems. As a result, the unit was shut down and cooled to ambient temperature. Inspection of the burned out windings revealed that there were serious problems with the ceramic tape and beads as well as the heating element wire.

The ceramic tape is used as a pipe wrap between the metal surfaces and the heating elements. The tape was torn in numerous places, exposing the metal surface underneath, and had lost most of its structural integrity. Sections around the reactor mixing zone were brittle and easily crumbled to dust.

The ceramic beads are used as insulators around the heating element wire. In numerous places the beads, which are silica base, appeared to be partially "melted", exposing the wire underneath.

The heating element wire, Kanthal AF, also failed in several places. Failures were of two types: tensile failure and shorting out of the wire due to contact with exposed metal surfaces.

Almost half of the windings experienced a failure, all due to limitations on materials of construction.

3.3.2 Analysis of Heating System Problems

Discussions were held with representatives of the manufacturers of the ceramic tape, wire, and ceramic beads. These discussions revealed information that was not known prior to construction of the unit.

The ceramic tape has a maximum recommended continuous operating temperature of 1800°F, rather than the 2600°F temperature originally quoted. Additionally, it loses all structural integrity above 2000°F and shrinks almost 10% upon heating to 1800°F. Thus, as the TRTU was heated, the tape tore apart. An improved tape, Nextel 440, which has better structural and heat resistant properties, will be used in the new design.

The beads used to insulate the wire are reported to have a softening point as low as 2000°F to as high as 2550°F. Temperatures well in excess of 2000°F were recorded during start-up. The beads are high in silica, which can react with the aluminum oxide coating that forms on the wire surface. This will produce a lower melting point complex. Both of these conditions could have been responsible for the "melting" observed. For the new design, a high alumina bead, containing less than 0.1% silica, has been selected.

The Kanthal AF wire forms a protective coating of aluminum oxide when heated to elevated temperatures. Disruptions to this layer, through reaction with silica, for example, causes further migration of aluminum to the surface and eventually can result in failure. Cycles of heating and cooling can also produce shedding of this layer. Additionally, several sections of the wire could have been at temperatures above 2300°F, which is above the recommended maximum temperature for the wire diameter used. Kanthal APM has been selected for the new design and a larger diameter has been specified. This material is less susceptible to shedding of the aluminum oxide layer.

3.3.3 Test Piece

To compare and evaluate the performance of the original heating system design with the proposed new design, a 9-foot long test piece was built. The test piece has two sections, one representing the original design and the other incorporating the new design. To simulate the actual unit, each section was fitted with pipe nipples and thermocouples.

Over a two-week period, the test piece operated at temperatures between 1400°F and 2200°F. During the first week, the piece was slowly heated to a pipe wall temperature of 1850°F and held there for several days. It was then subjected to stress tests, with intermittent heating and cooling, abrupt temperature changes, etc. Temperatures as high as 2200°F were achieved.

Neither section failed during the test. However, inspection of both sections revealed significant deterioration of the old design, whereas the new design looked like new.

Based on this test, the new design should perform satisfactorily and will be installed on the TRTU when it comes down for repairs. New operating procedures and alarms should provide further protection against the possibility of high temperature failure.

4.0 PLANS FOR NEXT YEAR

The major effort planned for FY96 is the testing of the following four feeds in the TRTU:

- simulated naphtha
- ROSE bottoms
- petroleum coke
- aqueous waste (sludge)

Each feed will be run for 4 weeks, including assumed downtime for system upsets and equipment/instrument malfunctions.

The unit is now scheduled for repairs (installation of the new heating system) in late November and will be unavailable until the first of the year. However, the existing unit is capable of achieving at least 1600°F, and perhaps 1800°F. Consequently, it is planned to run at least some of the naphtha tests prior to repair of the unit.

Since there are currently no facilities for handling a solid feed, a feed system will have to be designed, installed, and tested before the work with petroleum coke can be started. It is anticipated that a slurry system will be used.

Modifications will be made to the solids plug valve which is used to control solids circulation in the TRTU. This is intended to get more accurate, consistent, and reproduceable control of solids flow.

In addition to the experimental work, a conceptual flowsheet will be developed to illustrate the commercial application of the partial oxidation concept. The flowsheet will be based on data collected during one of the test campaigns, most probably the ROSE bottoms data. Economics will be developed for the flowsheet application.

3	REVISED PLOYSHEET	EAO		18	AUG	78
4	REVISED PLOYSHEET	JC	EAO	3	FEB	91
5	GENERAL REVISIONS	WPK		FEB	92	
6	REMOVED F-348 AND F-418, ADDED F-338.	OPM		2	FEB	93
7	ADDED F-798 AND NUMEROUS MISSING PT & VALVE NUMBERS. GENERAL REVISIONS.	OPM		15	MAR	95
8	REVISION DESCRIPTION	BY	CHK.	APPR.	DATE	
ENGINEERED	CHKD	EAO	SCALE			
DESIGNED	CHKD	EAO	ISSUED FOR			
DATE	13 MAY 78		ISSUED FOR			
THE M. W. KELLOGG COMPANY						
TATU PROCESS & INSTRUMENTATION						
DRAWING						
REACTOR DOWNSTREAM SECTION						
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CL. NO.	AREA	JOB NO.	DRAWING NO.	REV		

NOTES:

- RISER IS 1 INCH SCH 160 800HT PIPE.
- STANDPIPE IS 1.5 INCH SCH 160 800HT PIPE.
- MIXING SECTION IS 1.5 INCH SCH 160 800HT PIPE.
- CYCLONE IS 4.5 INCH O.D. 800HT B-564 PIPE.
- JUNCTION BLOCKS WILL BE CONSTRUCTED OF 800HT B-564.
- FEED NOZZLES WILL BE DESIGNED TO BE REMOVABLE.
- PRESSURE & DP TRANSMITTER TAPS ARE TO BE INSTALLED DOWNFLOW AT A 45 DEGREE ANGLE FROM HORIZONTAL.
- AERATION/FLUIDIZATION TAPS ARE TO BE INSTALLED DOWNFLOW AT A 45 DEGREE ANGLE TO HORIZONTAL.
- THE SOLIDS SAMPLING DEVICE WILL SERVE AS A DRAIN DURING COAL/COKE COMBUSTION/GASIFICATION/PYROLYSIS OPERATIONS.
- THE SOLIDS DRAIN ON D-200 WILL SERVE AS A FEED NOZZLE DURING COMBUSTION MODE OPERATIONS.
- PRESSURE, DP TRANSMITTER & FLUIDIZATION TAPS WILL BE 1/2 INCH SCH 80 800HT PIPE NIPPLES.

NO.	REVISION DESCRIPTION	BY	DATE
1	REVISED PER PROCESS DESIGN REVIEW MEETING ON 1 FEB 70.	DM	
2	REVISED PER DESIGN HAZARD ANALYSIS.	DM	
3	REVISED RISEN ELBOW RADIUS AND COLLECTED TAPING 312.	DM	
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