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NATURAL GAS CONVERSION PROCESS

PROJECT: Build a Laboratory Apparatus and Operate it to Provide Data
for a Large-Scale Gas Conversion Process

Contract: DE-FG01-90CE15459

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FIRST QUARTERLY REPORT

ABSTRACT:

Task No.1 is nearing completion.

Prior to starting this project, a review of the patent situation was made. Since the issuance of our basic US patent No. 4,705,908 on 11/1987, three subsequent patents have cited it as a reference. Two of them, assigned respectively to Electricite de France (EDF) and to the Standard Oil Company of Ohio (now BP America) have been evaluated. They confirm our findings and re-inforce our Claims. Contact has been made with Pr. J. Amouroux, one of the inventors named in the EDF patent towards doing research jointly on our process.

This may provide an opportunity to greatly extend the use of the Laboratory Apparatus which will be built under the present contract.

Results of Task No.1.:

The main difficulties in achieving a continuous flow of catalyst and gases within the proposed apparatus have been identified. Fortunately industrial experience gained recently with Circulating Fluidized Bed (CFB) combustion systems is now available (Ref.3). This was used to design a catalyst flow control system for our laboratory apparatus,

which has no moving part. This is a very desirable feature in view of the high temperature range in this apparatus.

Start-up procedures have been outlined.

The apparatus is designed to provide a complete mass balance of the process, over a relatively wide range of operating conditions.

Full-scale industrial facilities may be designed on the basis of the data provided by the laboratory apparatus, since both use the same catalyst flow system. The main difference is that, in industrial scale facilities a cluster of cyclone reactors is used, instead of a single one in the laboratory apparatus. Except for the use of a furnace to heat the feed and of heat exchangers to recover waste heat, all the components of the process facilities are similar, regardless of scale.

1. EVALUATION OF SUBSEQUENT PATENTS:

Other than in our own patent, No. 4,761,515, issued on 8/2/88, our basic US patent No. 4,705,908 issued 11/10/87 was cited as a reference in US patent No. 4,941,965, issued 7/17/90 and assigned to EDF, in US patent No. 4,929,789, issued on 5/29/90 and assigned to the Standard Oil Co. (Ohio). These two are listed as Ref. 1 and 2 respectively.

In Ref. 2, V.R. Gupta describes on Fig. 1 a continuous process for handling an oxidation catalyst used in the posterior half 58 of the vessel 12 to provide heat to a natural gas feed (C1, C2) which is pyrolyzed at a temperature of 1,000 to 1,600 C with a residence time of 5 to 100 milliseconds. This reaction is known to produce large amounts of coke and heavy hydrocarbons on the catalyst particles. These are transferred into the frontal part 56 of the reactor for regeneration in an air or Oxygen stream, with additional heat provided by a semi-circular gas ramp. The toroidal rotating bed of catalyst

crosses the vertical separating wall 36 through two windows 42 and 44. This, of course, provides an opportunity for mixing the reducing atmosphere of the back compartment with the oxidative atmosphere of the front compartment, with a corresponding loss of product, even if the hazards of an explosion can be avoided. This problem, inherent in any continuous conversion/regeneration system is addressed in a more conventional way in our catalyst circulation process. This will be illustrated in Task No.1.

In Ref.1, J. Amouroux et al. show that heavy hydrocarbons (C₂₀) are easily converted into light hydrocarbons by a Hydrogen plasma, in the presence of a known hydrocracking catalyst in a spouting bed. This is a confirmation of our observations that coking and heavy hydrocarbons content were considerably decreased by the Hydrogen plasma. Conversion efficiency of C₂₀ to C₇- reported by J. Amouroux et al. (Fig.2) is nearly 100% in the temperature range of 700-750 C for a C₂₀ feed residence time of about 7 minutes in the spouting bed and reactor tube of Fig.3.

In Fig.3, the spouting bed of catalyst fluidized by a mixture of Argon, Hydrogen and vaporized heavy hydrocarbon feed plays the same part as that of the fluidized catalyst accumulating in the conical part of our cyclone reactor. In such a reactor, the residence time of the C₁, C₂ feed is very short, comparable to that of Ref.2, but the residence time of our catalyst particles, which adsorb most of the heavy hydrocarbons produced by unwanted pyrolysis reactions, is much longer and comparable to that of the C₂₀ feed in Ref.1. This provides a confirmation of the advantages of the cyclone reactor over those of more conventional reactors. In view of the similarity of the results presented in Fig.2 with our own, it might be of mutual advantage to work jointly with Pr. Amouroux on this process. (Pr. Amouroux is a well

known expert of Plasma Chemistry).

2.TASK No.1:DESIGN AND SPECIFICATIONS OF THE CLOSED-LOOP FLOW SYSTEM

As previously mentioned,one major problem in the design of a closed-loop flow system is to reduce the risk of accidental mixing of the oxidizing atmosphere in one part of the loop with the reducing atmosphere in another part of the loop.This usually is accomplished by inserting suitable buffer gases between these two atmospheres.In the schematic flow sheet presented in our proposal (see Fig.4),the spent catalyst leaving the reducing atmosphere of the cyclone reactor is delivered through a sliding valve to a steam stripper before entering the oxidizing atmosphere of the riser/regenerator.Conversely,the feed gas is prevented from backflowing into the auxiliary cyclone by a small fluidizing flow of Hydrogen.These features are expected to be sufficient to insure safe operations and to avoid contamination of the Syngas by-product with lost feed.

Reliable operation of sliding valves in fluidized catalyst flow loops,such as in the FCC process,becomes more difficult at high temperature.For this reason a catalyst flow control system requiring no mechanical moving part is preferred.This same difficulty was encountered in the design of Continuous Fluidized Bed (CFB) combustion process loops,which operate at temperatures comparable with those in our process.It was solved very elegantly by the use of "L" valves in which the flow of solid particles is controlled only by a fluidizing gas stream.Such a valve is shown on Fig.5,taken from Ref.3.These valves have shown to be very reliable for handling solids which have a low tendency to agglomerate in the vertical flow tubes.In our case,if the catalyst particles become heavily coked,they may exhibit

sufficient stickiness to agglomerate in the horizontal, defluidized branch of the "L" valve. For this reason a "V" valve (Fig.6) was chosen. It effectively operates as a check valve protecting against any possibility of back flow of the solids in the event of any excess pressure in the riser. This is a slight modification of the "loop seal" valve (Fig.7) which has proven to be very reliable in industrial CFB combustion systems. The fluidizing gas in this valve is a slip-stream of the feed. This cold C1, C2 stream ends up partly in the cyclone reactor and partly in the steam stripper, where it mixes with the vaporized heavy hydrocarbons product. A separate outlet at the top of the stripper section in the riser permits to send a portion of this mixture to the chromatograph for analysis. Depending upon its relative richness, this stream may have to be recovered in an industrial process loop. In the laboratory apparatus, however, it is oxidized and ultimately contributes to the Syngas by-product stream.

2.1-MASS BALANCE IN THE LOOP:

The mass flow rate of total feed and its composition are measured. (see Fig.8). The mass flow rate and composition of Syngas and of products from the cyclone reactor are also measured. The only other components in the gas flow loop are the small fluidizing H₂ stream in the "L" valve controlling the flow of fresh catalyst and that in the plasma torch, that of Argon in the torch and of the internal standard for the chromatography analyses (N₂) and finally that of water, for which mass balances are also derived from the other flowmeters.

2.3-ADJUSTMENT OF THE RISER PRESSURE:

The riser inlet pressure determines that of the fluidizing feed gas in the "V" valve controlling the flow of spent catalyst out of the cyclone reactor. It is equal to the boiler pressure, which can be measured directly from the boiler feed water pressure. That water pressure is used as a reference from which the fluidizing feed gas is adjusted. A mercury tube or any other differential pressure controller may be used for that purpose.

2.4-ADJUSTMENT OF THE CYCLONE REACTOR PRESSURE:

The cyclone reactor inlet pressure is equal to the pressure at the top of the riser, minus the pressure drops in the auxiliary cyclone and in the "L" valve. The riser pressure drop from bottom to top is directly related to the solids inventory in the riser. To adjust the density of solids in the riser, at any given boiler pressure, it is sufficient to control the back pressure of the auxiliary cyclone. This in turn determines the fluidizing Hydrogen pressure in the "L" valve and that of the main feed stream at the inlet of the cyclone reactor. By applying a suitable back pressure on the product stream at the outlet of the cyclone reactor, the velocity of the spent catalyst in the vertical stand pipe is also adjusted to minimize the flow rate of the fluidizing feed gas in the "V" valve. This flow rate is measured with a separate mass flow controller to facilitate the adjustment of the back pressure on the product stream. The use of back pressures on both effluent streams also prevents any accidental air entry into the apparatus, an important safety consideration. To make sure that none of the unreacted Oxygen (if any) in the riser can reach the cyclone reactor, the back pressure of the product stream is significantly greater than that of the Syngas stream, which is therefore the lowest

pressure in the flow apparatus, while that of the boiler is the maximum pressure in the system.

For any value of the solids content flowing as a lean suspension in the riser, the steam pressure and that of the Syngas back pressure are determined. They in turn determine all the other fluid pressures in the loop. The stability of the solids flowrate at constant pressure drop between the boiler and the outlet of the auxiliary cyclone is enhanced by the fact that while the pressure drop in the riser (Ref.4) increases with increasing solids content W , as $W \exp. 0.7$, that of the auxiliary cyclone decreases, as $1/(1 + aW)$, where a is a geometry dependent constant (Ref.5).

For the same solids flowrate, the difference between the feed pressure and the back pressure of the product stream is also fixed by the geometry of the cyclone reactor, as $1/(1 + bW)$. If that pressure drop is too low, the catalyst tends to accumulate in the cyclone reactor to the detriment of the auxiliary cyclone. The solids level in that auxiliary cyclone must be observed visually when setting the feed pressure and the product stream back pressure, relative to the boiler pressure. To facilitate this adjustment of the cyclone reactor flow, it is desirable that the storage capacity of the auxiliary cyclone be greater than that of the cyclone reactor. The feed pressure is linked to that of the boiler by using a mercury tube or any other differential pressure controller.

The fluidizing Hydrogen stream controlling the "L" valve outlet pressure must be slightly greater than the feed pressure. It is determined by a mercury tube or any other differential pressure controller. Conversely the back pressure of the product stream is also determined from the feed pressure by means of a differential pressure

controller.

The complexity of this solids flow loop is comparable with that of a Lurgi CFB system, in which a fluidized bed external heat exchanger with its own aeration has requirements comparable with those of our cyclone reactor. Considering that 16 Lurgi CFB boilers are currently in operation, with capacities reaching 150 MW per unit, the pressure control of the present process loop does not seem to present unsurmountable difficulties.

2.5-START-UP PROCEDURE:

The fresh catalyst inventory is loaded into the auxiliary cyclone. Without any Hydrogen flow, the "L" valve is effectively closed. The flows of steam, feed gas, Oxygen are also closed.

1) The apparatus is pressurized with an inert gas (Argon) to eliminate any air from the system. The Argon inlet is through a T connection on the steam stripper outlet (see Fig.9), which is normally closed, except for analysis of the effluent. The back pressure regulators are adjusted to their approximate value, for a flowrate of Argon equal to the total gas flowrate required in the experiment.

2) The plasma torch is lighted up, and adjusted for minimum Argon concentration in the torch feed.

3) All electric heaters are brought to their specified temperatures.

4) The boiler temperature is raised and the steam flowrate is gradually increased while decreasing the Argon flowrate of the same amount.

5) The fluidizing Hydrogen flow is started, gradually opening the "L" valve to the flow of catalyst out of the auxiliary cyclone.

Concurrently, the flow of feed gas is started, while decreasing the

Argon flowrate by the same amount. The Argon content of the torch gas may have to be increased to maintain the torch lighted.

The fluidizing feed stream controlling the "V" valve is started on.

6) The main feed gas stream is gradually adjusted to its required flowrate value, while the Argon flowrate is decreased by the same amount.

7) The Oxygen flowrate is gradually increased until CO₂ is detected in the Syngas stream. It is then adjusted at a somewhat lower value, and the Argon flow is stopped. The flow loop is then in full operation. Minor adjustments of the respective gas pressures relative to the boiler pressure are made to adjust the solids level in the auxiliary cyclone at a stable value when the temperature equilibrium has been reached.

2.6-COMPARISON OF THE LABORATORY LOOP WITH AN INDUSTRIAL FACILITY:

The flow diagram of Fig. 9 is easily applied to an industrial facility shown schematically on Fig. 10. It consists of a cluster of cyclone reactors, each of them equipped with a plasma torch, discharging the spent catalyst into a common hopper and the product gas into a water-cooled plenum chamber above the cyclones. The catalyst is sent to the steam stripper and from there to the riser/regenerator which discharges into a single auxiliary cyclone. Depending on the size of the unit, a cluster of several auxiliary cyclones of smaller diameter may be used instead to separate the regenerated catalyst from the Syngas by-product. In that case, the diplegs of each cyclone will again discharge into a common hopper, controlled by a single "L" valve. The steam stripper may be part of the heat recovery system rather than part of the riser/regenerator if the stripped heavy hydrocarbons are

worth recovering as an additional liquid product stream, otherwise the stripper is incorporated in the riser. In either case, the riser flow is controlled by a single "V" valve. A furnace is used to provide heat in place of the electric heaters of the laboratory loop. Waste heat from the furnace also generates the required steam. This comparison shows that the data obtained on the laboratory loop can be readily used for scaling-up to commercial size.

2.7-CONCLUSIONS OF TASK No.1:

The detailed drawings of the flow loop and specifications of the torch are inter-related. Due to budget constraints, leasing of the torch (a Secheron micro-plasma torch) was initially considered but other alternatives are now considered. The final drawings will not be issued until the actual dimensions of the torch are firmed-up.

The present analysis has shown the importance of using a differential pressure controller on each stream, all of them linked to the boiler pressure. Alternatives to the use of mercury tubes will be evaluated from the point of view of reliability versus cost.

Control of the catalyst flow is by means of a "L" valve on the fresh catalyst and of a "V" valve on the spent catalyst. These valves have no moving part and their reliability at high temperature has been demonstrated in CFB systems of large capacity.

The feasibility of the project has been shown and its timeliness has been confirmed by the review of subsequent patents. The EDF patent is of special interest in providing useful information for planning the experiments to extend the range of catalyst residence time and Hydrogen concentration to those used by Pr. Amouroux and his team. Joint research with them on our process might be considered in

the future.

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- 4) Fluidization and fluid-particle systems, by F. Zenz, D. F. Othmer, 1960 Reinhold Chem. Eng. Series, P. 320
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FIG. 1 - STANDARD OIL PATENT

FIG. 2

100% Conversion

700-750°C

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FIG. 4 - SCHEMATIC OF
FLOW SYSTEM
(NOT TO SCALE)

FC = Mass Flow Controller

TC = Thermocouple

Oven = Electric Furnace

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Figure 5. L valve.

Figure 6. V valve.

Figure 7 . Loop seal.

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FIG. 8 BLOCK DIAGRAM OF FLOW SYSTEM, ANALYTICAL AND CONTROL SYSTEMS

FIG. 9 - QUARTZ FLOW APPARATUS (SOLID LINES)

FIG. 10
 SCHEMATIC
 CROSS SECTION
 OF INDUSTRIAL
 FACILITY —
 SIMILAR TO
 FIG. 9)

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