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**CLINTON ENGINEER WORKS
TENNESSEE EASTMAN CORPORATION**

MODIFIED LIQUID PHASE REACTOR

AECD-4183
(CD-RETA-3-517)

Photostat Price \$ 1.80

Microfilm Price \$ 1.00

Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

June 23, 1944.

A modified Kraus type reactor has been constructed for use in beta chemical conversion operations. The reactor consists of a shell of 4" seamless stainless steel pipe, 17" long, with a steam heating jacket of 6" steel pipe 13" long, welded on the outside. The shell holds the liner made from 4" O.D. seamless stainless steel tubing 12" long. The agitation is provided by 3 bladed squirrel cage stirrer on which the blades are 4" long. The shell is closed by a stainless steel flange which has a tongue and groove joint holding a lead gasket. The top flange includes a stuffing box for the stirring shaft, a thermocouple well, and a dry air inlet tube. The stirrer drive shaft that goes through the head and stuffing box connects to the stirring mechanism inside the liner by means of a pin and slot arrangement. The stirrer is driven by a 1/12 H.P. motor geared down to 32 1/2 R.P.M. The motor is coupled to the stirrer shaft by a removable pinned coupling so that the motor can be slid out of the way on a track when the top flange is to be removed. The vent line take-off or header is welded onto the side of the shell, rather than coming off through the top flange as in older models. The steam jacket is piped so that it can be supplied with 175 pounds steam or cold water.

The attached perspective drawing shows the general piping layout as the reactor is now being operated. All joints on the high pressure side of the vent line header are now either welded or the screwed fittings have been tinned with tin-lead solder. The first header came directly out of the side of the reactor and consisted of nipples and tees all threaded together with ordinary pipe dope. The tees provided for a gauge line, a vacuum line take-off, and a relief valve take-off. It was immediately apparent that these ordinary screwed fittings do not work and a straight welded header was made, eliminating the close nipples and tees, but still depending upon threaded fittings to accommodate the gauge vacuum line, etc. This was somewhat of an improvement but did not work very well until we began using solder to tin the joints. Acetic acid was used as a flux when tinning the joints. The header was finally altered into its present form by putting in a small up-right condenser where the header joins into the reactor and moving the vacuum valve onto the low-pressure side of the bleed valve. This eliminated one valve that had to hold the total pressure. The final improvement was to double-valve the bleed line, the first valve being a floating tip globe valve made by substituting a lead disc holder for the floating stainless steel tip of a 3/4" needle valve. This gives in effect a lead disc globe valve which has proven extremely satisfactory. Up until the point that we used this valve, we were continually having trouble with needle valves leaking during the course of a run, so we tried a number of models, including some Stellite tipped Chapman needle valves, none of which proved satisfactory. This lead disc valve has

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the extreme advantage that if dirt gets into it in the course of venting so that it doesn't close tightly by hand, a wrench can be applied to close it since you are only squeezing down the lead disc instead of getting a hard metal to metal contact. This valve was backed up by a 3/4" Stellite tip needle valve since the lead disc cannot be used very well for throttling or slow bleeding. We have now had some 1/2" and 3/4" valves of various makes re-built to lead disc globe valves in our shop and they perform very satisfactorily.

The vent line was run into a CCl₄ trap which had a water cooled condenser on both the inlet and the outlet sides. The lid of the trap had a baffle plate on it so that the vapor could not short-cut through the trap. From the CCl₄ trap the vent line was run into the bottom of an entrainment trap which was partially filled with dilute ammonia. A perforated stainless steel plate was put in the trap to diffuse the gas through the liquid. We have now eliminated the use of ammonia in this trap since we have a circulating ammonia scrubbing tower. However, we use glass wool in it to catch any material which might be entrained in the gas being vented.

The vacuum line runs to a CCl₄ dry ice trap which condenses any CCl₄ that comes off during the evacuation. The relief line runs to an expansion tank of approximately 8 gallons capacity and then to the scrubbing tower. The expansion tank is to act as an entrainment trap in the event of the relief valve opening to let off excess pressure. Due to a lack of sufficient number of relief valves, we have also used blow-out patches in the relief line.

The method of operating the reactor is as follows:

A charge of TO_3 is placed in the liner with the correct amount of CCl₄. The ratio was 250 grams of TO_3 to one liter of CCl₄. The liner was then placed in the shell and the head fastened in place, the stirrer mechanism connected and the stirrer started.

Steam was then let into the jacket at 170 pounds pressure. This steam pressure was maintained until the pressure in the reactor was 100 p.s.i. The temperature was generally around 125-135° at this point. At a reactor pressure of 100 p.s.i., the steam was shut off and the steam pressure bled out of the jacket through the water outlet. Water was let into the header condenser. When the reactor pressure reached 200 p.s.i., water was run into the reactor jacket. If the pressure continued to rise to 300 p.s.i., the excess pressure above 300 p.s.i. was carefully bled off through the bleed line. As soon as the maximum pressure had been reached and pressure began to fall off, the water was shut off and drained from the reactor jacket and the water was shut off in the header condenser. Steam pressure was then applied and the reactor heated for 15 minutes at 150-175° C. If the pressure began to rise during this heating period to 300 p.s.i., steam was shut off and water let into the condenser and reactor jacket, if necessary.

At the end of the 15 minute heating period, steam was shut off and water run into the jacket. When the temperature reached 130°, the pressure was vented out of the reactor through the vent line, taking 15-20 minutes of careful bleeding to reach 0 p.s.i. The reactor temperature was now usually 65°. At this point, starting from a temperature of 65-70° with the steam on

in the jacket, we began blowing in dry air through a $\frac{1}{8}$ " orifice under a pressure of about 10 p.s.i. Dry air blowing was continued until the temperature of the reactor rose to 90°. The reactor was then cooled down again to about 65° by running water into the jacket. Dry air was shut off and vacuum applied. The steam was turned on again and evacuation carried on with heating until the reactor temperature again rose to about 90° C. The vacuum was then broken by letting in a little dry air and the reactor cooled with water at about 65°.

The stirrer was stopped and the stirrer motor pushed out of the way; the thermocouple removed from the wall and then the top flange was removed. The liner was immediately pulled out, the stirrer removed from the liner with considerable shaking and some scraping to remove caked material and the contents of the liner poured into a glass test tube 45mm. in diameter x 15" long. The reactor was then immediately recharged for another run. The average reaction time is 2 3/4 hours.

The product of the reaction under these conditions is mostly TCI_5 . It is decomposed to TCI_4 by placing this glass test tube inside a 55 cm. tube 43" long supporting it with a disc welded at right angles to the end of a rod. The outer tube is closed at both ends with stoppers, the bottom one having an inlet for CO_2 and a place for the supporting rod and the top one having an outlet for CO_2 and chlorine. The tube containing the product has a plug of glass wool placed in the top of it and the outer jacket also has a plug of glass wool placed just under the top stopper. The outer tube is supported in an upright position by 2 ordinary laboratory clamps. A 3" split tube furnace is hung by counterweights so that it can be raised and lowered over the length of the outer tube. At the start of the decomposition the furnace is at the bottom of the tube so that the entire test tube holding the product is outside the range of the furnace. The furnace is then raised 1" in 10 minutes for 30 minutes and then alternated 1" in 5 minutes and 1" in 10 minutes until the product is entirely inside the furnace. The furnace is then left in this position for 15 minutes to insure complete decomposition. A temperature of 500° C. $\pm 10^\circ$ C is maintained. The furnace is then lowered and when the tube is cool enough to handle, it is removed from the apparatus and the material poured into the product bottle in a dry box. The average running time of the decomposition is 1 1/2 hours.

Two series of experimental runs according to this method using TO_3 were made as part of an over-all cycle with the department supplying us with oxide. In the first 23 runs, the total of 6524.3 grams of T as TO_3 were placed in the reactors and 6046.4 grams of T as TCI_4 were removed as usable product. 372.1 grams were recovered as salvage from washing the various parts of the system giving a recovery of 98.4% with a loss of 105.4 grams of T. It should be noted at this point that the department supplying us with oxide in the cycle showed a gain of approximately the same amount which indicated probably error in the solid sampling of the oxide. The salvage in these 23 runs was distributed as follows:

In the ammonia absorber	34.2 grams
In the reactor wash	307 grams
Handling box	26.7 grams
In the glass wool plug from the decomposer	1 gram
Miscellaneous	3.2 grams

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All of these figures are as T. In an additional 7 runs in this same cycle 1695.6 grams of T as TO_3 were charged into the reactor and 1580 grams of T as chlorides were removed as usable product. The salvage was 86 grams, leaving a loss of 29.6 grams and a total recovery of 98.25%. In this cycle the department supplying us with oxide showed a gain of approximately the same magnitude as our loss which again indicated an error in solid sampling. The salvage in the second series was distributed as follows:

Reactor wash	61.3 grams
Ammonia absorber	3.4 grams

In this case the miscellaneous salvage is included in this reactor wash. In the course of this cycle, it was determined that a charge of 250 grams of TO_3 is the optimum charge for this size reactor. However, we were able to handle up to 350 grams charges of TO_3 but there is considerable danger of having to vent excess pressure during the course of the reaction with resultant entrainment losses.

Some experimental runs were made with T_3O_8 made from oxalate. The material produced from 2 batches analysed 62.6% T, 37.4% chlorine, the ratio being 1/4.01 and another batch analysed 62.9% T, 37.7% chlorine with a ratio of 1/4.03.

The reaction of this T_3O_8 goes more smoothly than the reaction with TO_3 . However, the product of the reactor contains considerable TOl_4 and the final product after decomposing is lumpy and coated as considerable light green dusty powder.

We attempted to make TOl_4 in this reactor but the results were rather discouraging. The material is dusty and lumpy and the analyses indicated about 2% insoluble material in the product and a high non-volatile.

This reactor seems to be very well suited for running small charges of either TO_3 or T_3O_8 in the beta chemical conversion, except that as noted the product made from T_3O_8 is not nearly as satisfactory in appearance and crystal structure as that from TO_3 .

The steam heated reactor is much easier to control than the previously used oil heated reactor though the over-all time cycle is about the same. The use of the lead disc globe valve in the vent line and the tinning of the joints using solder contributed in great measure to the success with this reactor.

J. W. Zuidema
J. W. Zuidema

A. E. Ballard
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- 1 Water Outlet
- 2 Steam Inlet
- 3 Steam Outlet
- 4 Water Inlet
- 5 Dry Air Inlet
- 6 Pressure Gage
- 7 Main Lead Seat
- 8 Throttle Bleed Valve
- 9 Vacuum Line
- 10 Vacuum Check
- 11 Header Condenser
- 12 Dry Air Control
- 13 Vacuum Control
- 14 15 Absorber Drains
- 16 Pyrometer

STEAM REACTOR

VALVE DIAGRAM

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DRAWN BY JAC

END