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From Dr. M. Piep's Files

T-458

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High Pressure Experiments
Leads

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NR/ls

THE EFFECT OF HIGH PRESSURE ON THE CATALYTIC ACTIVITY OF THE
RUBBER WALLS IN THE FUEL PROCESS (MICROORGANISM SYNTHESIS)

It has already been stated in previous reports *
when in the course of high pressure experiments with
and hydrocarbons using the form process, a peculiar phenomenon
is observed which may be called the "leakage"
of the catalyst from the liquid phase. There are some
of the solid deposit is found on the reactor walls
consisting principally of catalyst, and the thickness
grows from below where it is slight towards the top.
The deposit has reached the thickness of 3/16 in. in the
rubber part of the reactor after three months operation
in a tube 3/4 in. in diam. A similar phenomenon has
been observed in the laboratory reactor. It is suggested
possibly is prevents some of the catalyst from performing
the reaction by reducing the available reaction
area.

* See reports of 11-22-42 (T-451) and 1-18-43 (T-452)

A remedy stirrer structure was built which scrapes the surfaces on which deposits may form. These are the top and the cylinder walls in the reactor and the cylinder wall and the walls of the inner settling pot of the degasifier vessel (see figure 1). The outlet tube of the degasifying top was no longer placed to a side but as far as possible centrally and lower down to permit scraping the wall of the degasifier. The walls of the settling pot were also scraped (figure 2).

The stirrer shafts of the reactor and degasifier were driven by a motor with conical drives which were kept at a slow revolution. A continuous operation of the stirrer is, however, unnecessary merely to prevent the formation of the deposit. For that reason it was occasionally used at first. The minute deposit formed in the course of a few hours can be scraped off without using up much power. It has been found, however, that after the occasional stirring the yield was invariably somewhat increased, as manifested in the increase by several percent in the carbon dioxide content, and this was the reason for changing over to continuous stirring in spite of its resulting in a great strain on the stuffing boxes.

These phenomena leads one to assume that loose catalyst was gradually collected in the lower part of the reactor, and this loose catalyst was again dispersed by the action of the stirrer.

The trouble was not entirely overcome by having the stirrer keep the reacting surfaces clean. The stirrer structure in itself offers a chance for deposition of the catalyst, even though in much smaller amounts than on the reactor walls. An additional precaution was required to maintain this stirrer clean. It was found that a fine deposit would form on the shaft and installation, which would probably be in itself not appreciable and would not cause any loss of mass. To tests of it have, however, been made showing the apparatus was becoming much less efficient.

The deposit found on the stirrer actually caused disturbance in operation after three months from the start. The stirrer began to stop and the liquid phase circuit was disturbed with. Dismantling of the reactor showed that a lot of deposit pieces was formed in the reactor in a weight of 50 gm. and they interfere with the flow of the circuit and caused deterioration of the installation of the gas.

through the foam plate. The outward appearance of these pieces showed distinctly their origin from the stirrer support. They have grown chiefly on the upper part of the stirrer, broke up after reaching a certain thickness and then fell down upon the foam plate. The broken pieces showed a layer structure. Figures 3 and 5 are photographs of a mixer withdrawn from the reactor. One may clearly see that the thickness of deposits increases towards the top.

The degasifier mixer operated only six weeks and showed no deposits whatsoever. A certain thickness of deposit was to be expected. We cannot as yet say whether conditions existing in the degasifier are less favorable for the deposition on the stirrer support.

The catalyst deposit showed a distinct layer formation and was sufficiently strong not to be destroyed by the liquid currents inside the reactor. The principal constituents were different forms of iron, such as the carbonate, oxide, carbide and metallic iron. The total iron amounted to 43 - 49 percent of the deposit, calculated as metallic iron. The deposit could not be fused to a paste, while the liquid phase with new catalysts with an equally high proportion of iron become rather thin-flowing at 120°C in the liquid phase.

The catalyst used in the present gas was obtained by reduction at 450°C of red iron oxide obtained from iron carbonyl, pasting with 2 percent dissolved borax followed by grinding under middle oil. A particle size of 2 μ has been obtained, and could not be further reduced by additional grinding. The reduction (determined by the method of Villner and Merk) of the catalyst reduced in large furnaces amount to 50 - 60 percent, while in the small laboratory furnace, where operations could be conducted with a large excess of hydrogen a reduction of 85 - 90 percent could be obtained. The iron was suspended in the middle oil obtained by synthesis and forced into the liquid phase which consisted principally of high melting paraffins. If the liquid phase is not stirred it settles out as a result of its gravity, but no deposits are formed on the vertical surfaces. It was therefore surprising that these catalyst deposits were formed under conditions of synthesis and were not caused by gravity.

It has already been stated that the upper part of the reactor has the greatest deposition of the catalyst. The liquid is being continuously circulated at a rate of once every three months, and its composition is practically the same at the top and in the bottom of the reactor. Gas, however, behaves differently.

It enters from below as the fresh gas and contains only about 2 percent H_2 in addition to CO and N_2 . As it rises, up to 80 percent of the fresh gas disappears, depending on the method of operation, and is replaced by the reaction products, including several percent of hydrocarbons, steam, and carbon dioxide as the principal product by volume. Composition of gas with 71-percent conversion:

	Inlet Gas	End Gas (as it leaves the reaction)
CO	55	25
H_2	2	25
Hydrocarbon	-	7
H_2O	-	6
CO_2	-	33
N_2	2	4

If the liquid phase does not lose all of its gas in the degasifier, some of the end gas is returned to the bottom of the reactor with the returning liquid phase, and in that case certain amounts of CO, H_2O , and hydrocarbon vapors are present even at the bottom instead of the pure fresh gas, but their concentration must be strongly increased on the way up. This means that the reducing properties of the gas are greatly reduced on the way up.

Oxygen of carbon monoxide and hydrogen from the carbon monoxide-hydrogen mixture react with the

formation of water or also carbon dioxide by interaction with a second molecule of carbon monoxide. This reaction proceeds catalytically, and evidently with the formation of an iron oxide as an intermediate stage, i.e. carbon monoxide will react with iron carbide with its carbon and an iron oxide with its oxygen. The latter is reduced by hydrogen with the formation of water, and the water can further interact with carbon monoxide according to the water gas reaction with formation of carbon dioxide and hydrogen. When iron catalysis was used this second reaction is the principal one, so that in general more CO_2 than H_2O is formed.

The reduction of the iron oxide formed proceeds less readily with less favorable proportion of hydrogen : steam. When the latter becomes less than a certain value, probably around 4 - 6, no more iron oxide will be reduced but conversely metallic iron will be oxidized by steam.

Analyses of the catalyst used and the reactor deposits are given in the table. In the deposits one is struck with a high content of iron carbonate (columns 2 and 3), in comparison with the circulating catalysts column 1. Moreover the proportion of metallic iron, which alone is catalytically active, is greatly reduced. The next question is whether iron oxide

and iron carbonates, which both form the principal constituents of the deposit have a particularly strong tendency for deposition and are therefore preferentially deposited on the walls, or whether the circulating catalyst adheres so to say unselectively regardless of the form the iron is in.

It is first of all striking, that the deposit formation is retarded in the reactor the lower down one looks. It might be assumed that there is more motion in the liquid phase below as a result of its circulation, and that the higher velocities hinder the formation of deposits, for no deposits could actually be proven in the actual circulation tube in which the liquid phase velocity is approximately ten times higher than in the reactor.

Experiments in glass models have been made. They consisted of a tube 5 m high and 8 cm wide, filled with oil, with the gas forced in at the bottom through foam plates. The bubbles have been found to move with very different velocities and strong liquid flow disturbances formed, with one of the currents rising upward while another one was moving downward and compensating the former. There was formed a sort of liquid turbulence.

We may understand it by considering a system with quiescent liquid containing uniformly distributed rising

gas bubbles as being unstable, because as soon as a slight motion of liquid over the foaming stone is produced, the oil becomes non-uniformly loaded with gas bubbles, and the rate of rise of the particles differing in gravity will be different, and the heavier ones will sink.

One cannot peak into the pressure reactor but there are no grounds to assume that conditions in them are any different. This causes us to draw the conclusion that the motion of liquids throughout the reactor are as strong as could be seen in the model and the added velocities resulting from the circulating liquid entering from below are of no importance.*

The formation of deposits in the upper part of the reactor can be explained only by the increasing concentration of carbon dioxide and steam. The question arises whether the catalysts in the upper part of the reactor has throughout a different composition depending on changes in the composition in the gas mixture, and whether it contains more of iron oxide and iron carbonate. This question must be answered in the negative as — proven by simple consideration. The liquid phase is

* This motion is superimposed upon the velocity caused by the liquid phase circuit. In the reactor a high the liquid phase velocity equal 5 cm/sec and is directed upward. The turbulence velocity should exceed on the average 5 cm/sec.

changed over some 500 times during a day. The catalyst in it produces about the same weight of products during the day and carries therefore about the same amounts of oxygen from CO to H_2 or to another CO.

Even if we are to assume that the FeO formed as an intermediate has a longer life, which contradicts all the facts, the proportion of the FeO could not be increased even by 1 percent during the movement up from below. As a result the composition of the catalyst in the reactor is practically uniform and the causes for the disturbances may be found in the amounts of carbon dioxide and steam which increase during the passage through the reactor, without our being able to decide whether both of them are equally active.

The disappearance of the catalyst from the sump is nevertheless surprising in many cases.* If it settles non-selectively, it will then have sufficient time to become strongly oxidized with the existing steam pressure and to form carbonates. One might assume in this case that the catalyst is uniformly deposited in the lower and in the upper reaches, but that the iron oxide and carbonates near the top is more resistant to the loosening effect of the liquid, while

* One may bear in mind the well known fact that rust can be loosened with oil.

the deposit is at least partially adhered in the bottom part.

The sticking together of the different catalyst particles remains unexplained. Even if one were to deal with crystallites, a certain amount of only in the presence of some adhesive substance, as shown by examples in nature. The deposit contains several percent of organic matter, which organic substance can be extracted with hot xylol, and the remaining solid treated with HCl to dissolve the iron. Definite traces of asphalt like material will be found, and they shall like fatty acids. These fatty acids were probably in combination with iron. Dr. Eberhard has worked up 1 kg of the reactor deposits. He has failed to find any adhesive material in it. His failure to prove, however, that no adhesive is present, because minute amounts are sufficient to cause sticking.

If the reactor deposit is ground or let off it will again exhibit catalytic properties. Each product is shown in column 4. It is the product from the column 2 which was used in a laboratory reactor after being ground in oil. The last product is similarly broken down after the same way as the first. The high conversion value of the reactor is in agreement with the other values obtained in laboratory reactors. The production value is similar to that obtained with

new catalysts of average quality.

We must conclude therefore the changes in the catalysts are reversible. It is to be noted that in the reactivation of the catalyst the gas remains unchanged as long as the catalyst is still inactive, and the reducing power of the gas remains high.

We must qualify this statement, however, for our laboratory tests, in that they are carried out for another reason with a large gas throughput, which will naturally prevent conversion of the gas to the same extent as in the large reactor. This explains also the high reduction value of 60 percent.

Deposits of catalysts has not been observed in laboratory experiments. Operations could not, however, be conducted as trouble-free as on a large scale. The principal trouble probably was in that the gas was not sufficiently converted in one pass.

Similar conditions can be also created on a large scale when the gas is returned through a carbon dioxide wash. Steam then is also eliminated, and the return gas is to a certain extent similar to the original gas and may also be used on a large reactor through the reactor without being so deficient in insufficient conversion of the gas. This was also at present being conducted. This was found reducing the deposition to a practically negligible part.

/s/ Michael
Stenmark

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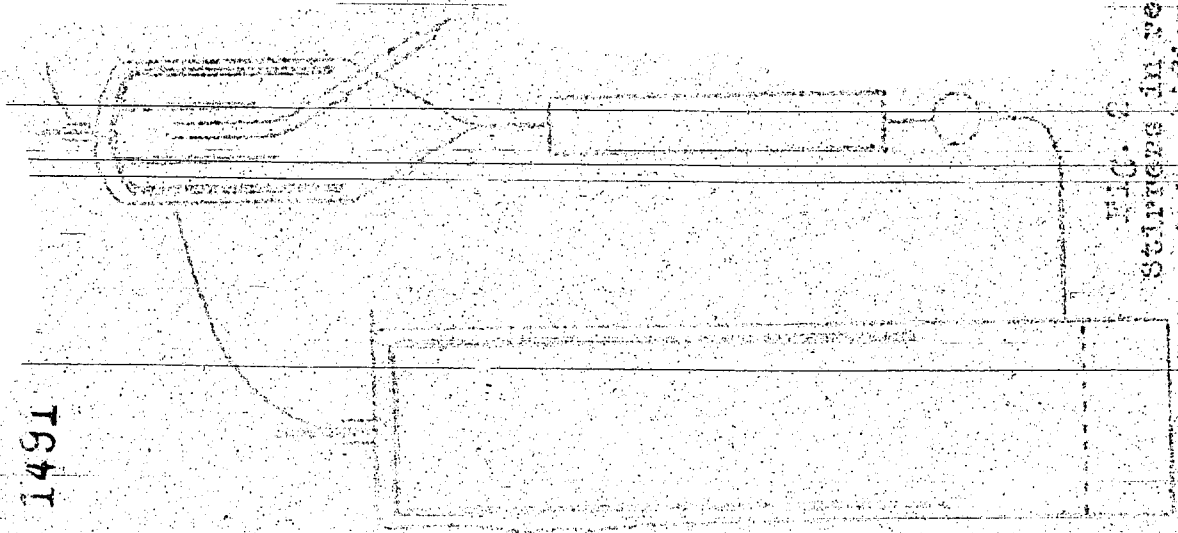
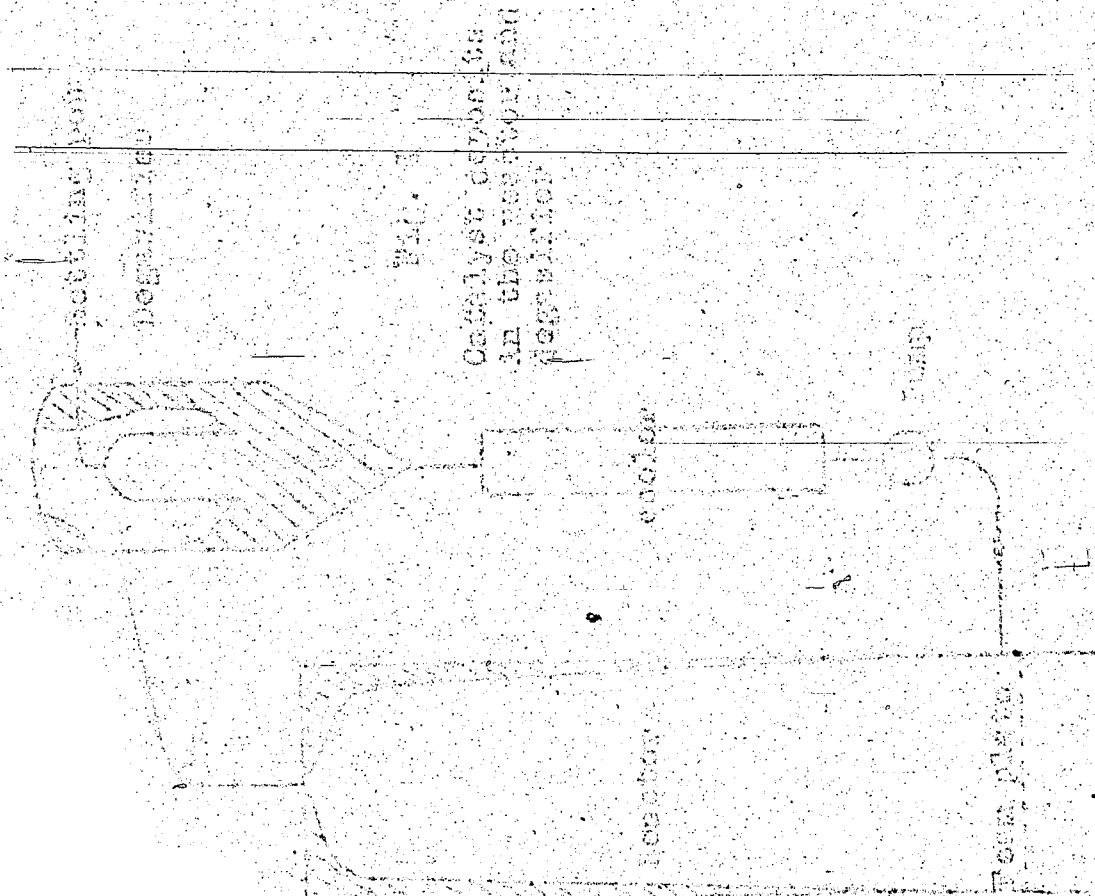
The Composition of the Catalysts and the Reactor Deposits

	Catalyst from the liquid phase after two months	The extracted deposit (the 3 mm layer adhering to the converter wall)	Extracted deposit (the outer 30 mm layer)	Deposit (the same as in column 3) together for two days in the reactor
Total iron content	77%	65.1%	65.3%	80.0%
Metallic iron	25%	10.1%	2.4%	45.0%
Metallic FeO	33%	16.1%	5.7%	68.0%
Fe ₂ O ₃ (calculated)	2.4%	11.7%	17.0%	2.0%
Fe ₂ O ₃ (total)	2.4%	11.7%	17.0%	5.0%
C (as Fe ₂ O ₃)	0.1%	1.1%	1.0%	2.8%

1) The 3 mm layer adhering to the reactor wall is thicker than the other further away from the wall.

2) According to more hours of work the catalyst may be present as Fe₂O₃. Here this introduced into the table and taking into consideration the total content, amounting to about 1 percent, the FeO value would be 20 - 65. No free carbon has been found. Only traces of sulfate have been found.

1491

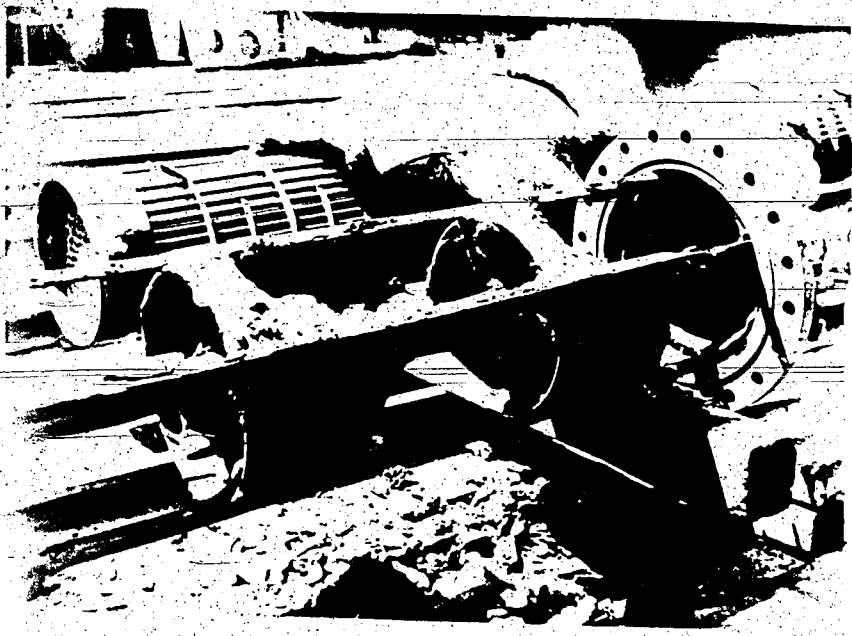


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Field 7.
Reactor Mixer
(upper end at left)

Fig. 3
Reactor Mixer
(upper end at left)



Reactor Mixer

Fig. 4
Upper end of
Mixer



Fig. 5
Upper end of
Mixer