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High Pressure Experiments
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THE DEPOSITION OF THE FINELY DIVIDED CATALYSTS ON THE REACTOR WALLS IN THE FOAM PROCESS (HYDROCARBON SYNTHESIS)

It has already been stated in previous reports *
when hydrocarbons are synthesized from carbon monoxide
and hydrogen using the foam process, a peculiar phenomenon
is observed which may be called the disappearance
of the catalyst from the liquid phase. More and more
of the solid deposit is formed on the reactor walls
consisting principally of catalysts, and its thickness
grows from below where it is slight towards the top.
The deposit has reached the thickness of 5 cm in the
upper part of the reactor after three months operation
in a tube 50 cm in width. A similar phenomenon has
been observed in the degasifier vessel. It is undesired
because it prevents some of the catalysts from performing
its function and by reducing the available reaction
space.

* See reports of 11-28-42 (T-431) and 2-18-43 (T-432)

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 scraping 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 arrangement was required to maintain this
stirrer clean. However, in this case some deposit
would form on the additional installation, which
would probably be in this case inconsiderable and
would not cause any disturbances. No tests of it
have, however, been made because the apparatus was
becoming much too complicated.

The deposit formed on the stirrer actually
caused disturbances in operation after three months
from the start. The yield began to drop and the
liquid phase circuit was interfered with. Dismantling
of the reactor showed that a mess of deposit pieces
was formed in the reactor to a height of 50 cm, and
they interfered with the liquid phase circuit and
caused deterioration of the distribution 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 N_2 in addition to CO and H_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 reactor)
CO	55	25
H_2	43	25
Hydrocarbon	-	7
H_2O	-	6
CO_2	-	33
N_2	2	4

If the liquid phase does not loose 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_2, 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 else 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 first form 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 catalysts are 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 carbonate, which both form the principal
constituents of the deposit have a particularily
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 3 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 peek 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

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* This motion is superimposed upon the velocity caused
by the liquid phase circuit. In the reactor 8 m 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 its 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 stronger 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 carbonate near the top is more
resistant to the loosening affect of the liquid, while

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

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

The sticking together of the different catalyst
particles remains unexplained. Even if one were to
deal with crystallites, a sediment should form only
in the presence of some adhesive substance, as shown
by examples in nature. The deposit contains several
percent of organic substances. This organic substance
can be extracted with hot xylol, and the remaining
solid treated with HCl to dissolve the iron. Definite
traces of an oily liquid will be freed, and they smell
like fatty acids. These fatty acids were probably
in combination with iron. Dr. Bueren has worked up
1 kg of the reactor deposits. He has failed to find
any adhesive material in it. This fails to prove,
however, that no adhesive is present, because minute
amounts are sufficient to cause sticking.

If the reactor deposit is ground under oil it will
again exhibit catalytic properties. Such a 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 iron carbonate is largely
broken down after two days and reduced to iron. The
high reduction value of 60 percent is an 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 un-
changed 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 lab-
oratory tests, in that they are carried out for another
reason with a large gas thruput, which will naturally
prevent conversion of the gas to the same extent as
in the large reactors. 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 one may operate with a large thruput through
the reactors without having to consider an insufficient
conversion of the gases. This test is at present
being conducted. This may permit reducing the deposition
to a practically irreducible part.

/s/ Michael
Mehrmann

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)[1]	Extracted deposit (the outer 30 mm layer)	Deposit (the same as in column 2) treated for two days in the laboratory
Total iron content	77%	65.4%	63.3%	80.0%
Metallic iron	26%	10.6%	3.6%	48.0%
Reduction	33%	16.0%	5.7%	60.0%
CO_2 liberated	2.4%	11.0%	13.0%	2.0%
$FeCO_3$	6.3%	29.0%	34.2%	5.3%
C as carbide 2)	0.1%	1.1%	0.25%	2.8%

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

2) According to more hours of work the carbide may be present as Fe_2C. Were this introduced into the table and taking into consideration the borax content, amounting to about 1 percent, the FeO value would be 20 - 65. No free carbon has been found. Only traces of sulfide have been found.
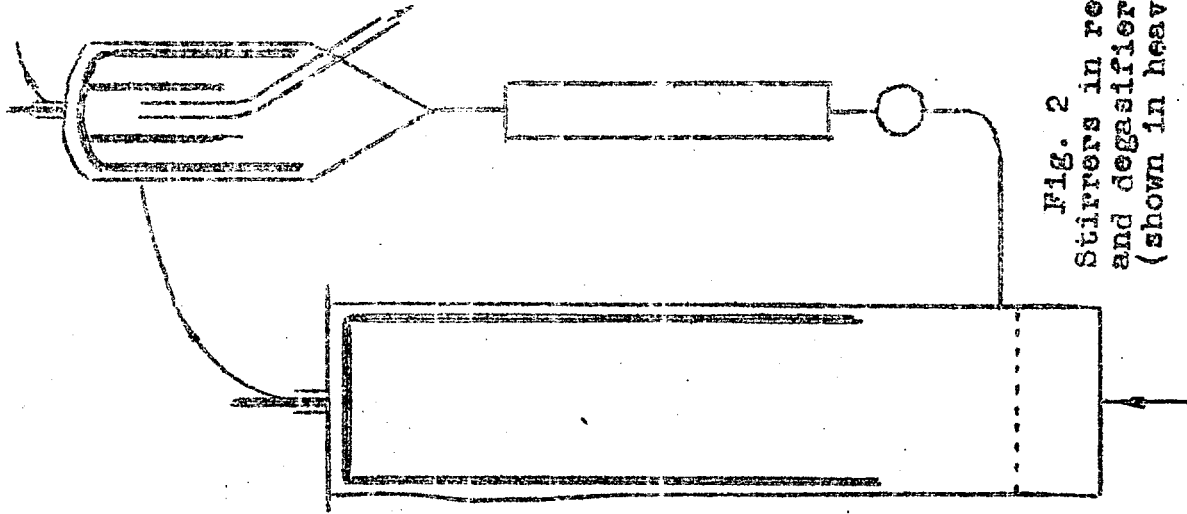
Fig. 2
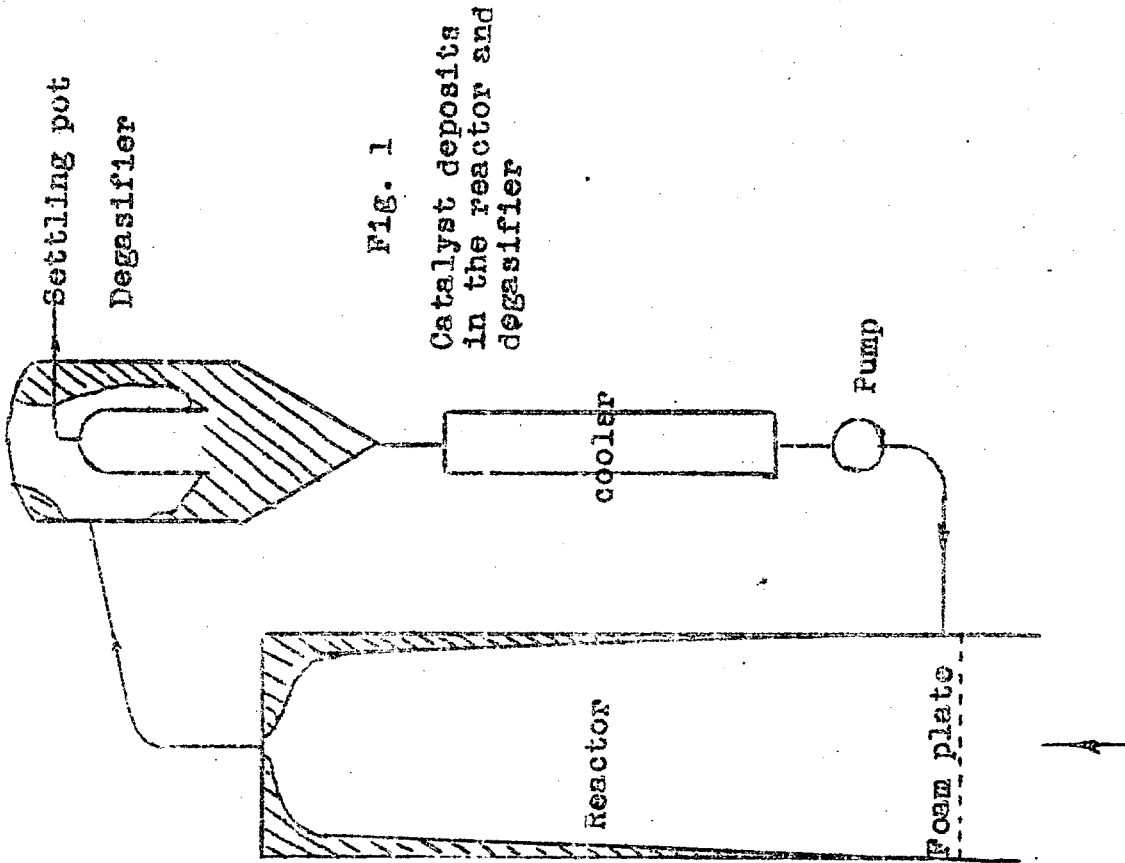Stirrers in reactor
and degasifier
(shown in heavy lines)

Fig. 1
Catalyst deposits
in the reactor and
degasifier

Bild 3.
Rührer aus dem Ofen
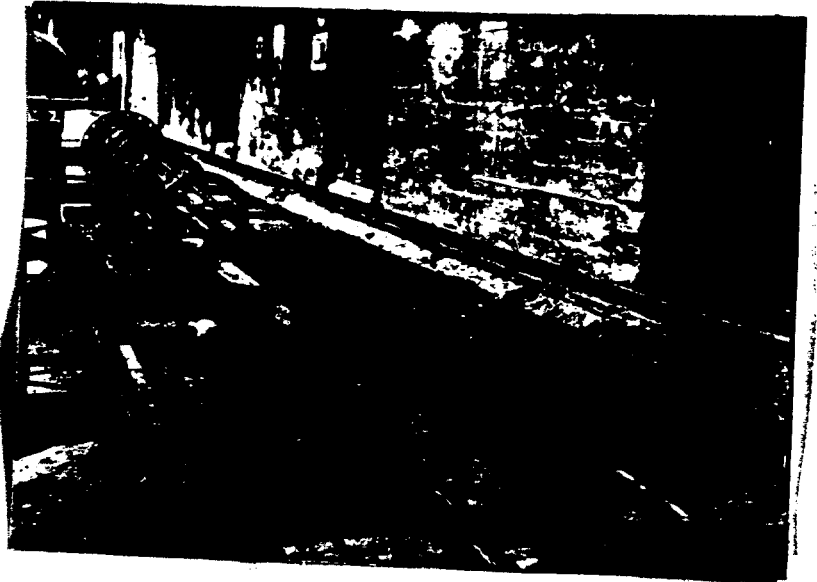(links oberes Ende)

Fig. 3
Reactor Mixer
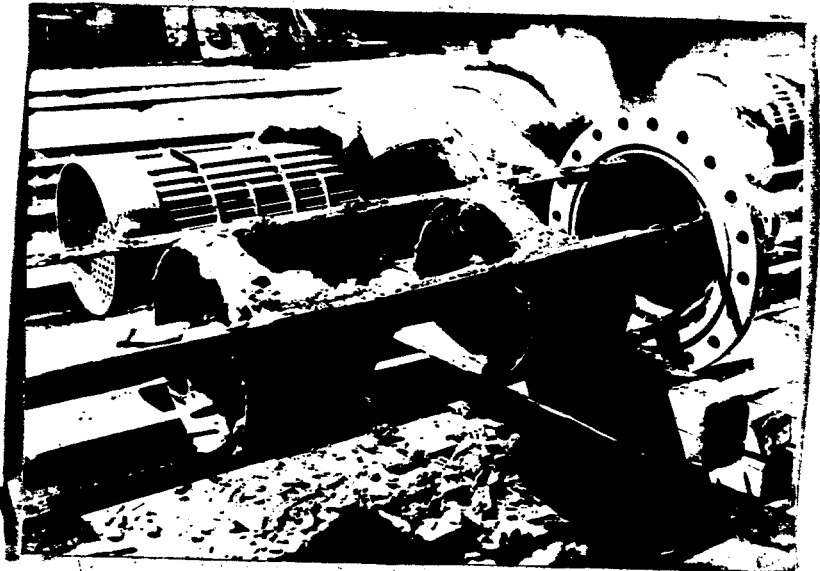(upper end at left)

Bild 4.
Oberer Rührerteil.

Fig. 4
Upper end of
Mixer

Bild 5.
Oberer Rührerteil.

Fig. 5
Upper end of
Mixer