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WET SYNTHESIS

After completing a few tests with cobalt catalysts
(Tests 1 - 10 and Test 12), the first wet synthesis test with
an iron catalyst (100 Fe - 5 Cu - 10 Mn - 100 Kieselguhr)
was started on December 28, 1939 (Test 11). This test, as well
as the preceding ones with cobalt catalysts were run in a
vertical tubular reactor with 6 m thickness of the layer and
with a double oil circuit (the first for fuel oil, and the
second for the catalyst-oil suspension). This type of reactor
has not been found satisfactory because of the gradual deposition
of catalysts in the return pipe of the inner circuit leading to
a gradual plugging up. In later experiments the catalyst-oil
circuit was therefore omitted and a simple tube of 100 mm internal
diameter and 6 m high was used as a reactor. The top was connected
to a side piece in which the catalyst suspension and a thorough
stirring were caused by the reaction gases. A fine distribution
of the gas was obtained by a porous plate of the filter stone
material. The reactor was provided with a fuel oil jacket (with
circulation oil). The top construction was practically the same
as in the past reactor tops.

In the next experiments (Tests 13 - 17) the catalysts (100 Fe - 5 Cu - 10 CaO - 100 Kieselguhr) were used in a direct path. The load had to be selected four to six times greater than had been normally used in order to produce a uniform distribution of the catalysts. With smaller loads some of the catalysts would settle on the bottom after a short operating time, and this resulted in an increased gasification and a reduced conversion. Naturally such a large overload on the catalyst resulted in a relatively low conversion. Under such conditions the CO conversion amounted to only 25 - 35% and was found to reach 40% in some occasional measurements. The gasification was low, only 2.0 - 2.5%. The proportion of catalysts to oil in the first experiment was 1 : 10. Doubling the proportion of the catalyst (1:5) and leaving the gas intake the same lowered the gas thruput by 2 - 3 times of the normal values, with a corresponding increase in conversion of the CO to 40 - 45% (Test 17).

Further increase in the amount of catalysts to 2:5 gave no further increase in the conversion with a direct path, because it required a further increase in the gas thruput (to produce a uniform suspension of the catalyst) and in the load.

A uniform distribution of the catalyst was obtained by substituting recirculation for the direct thruput. It became in this case possible to bring the load upon the catalyst in relationship to the amount of the catalyst and to produce a proper suspension of the catalyst by using a smaller or larger proportion of the recirculation gas. The very first test run in a circuit

(Test 18) showed a much better utilization. A 72% CO conversion
was obtained with a single stage, with a gasification of 4%.
The consumption proportion CO : H_2 was altered in comparison with
a direct path by a displacement towards greater hydrogen consump-
tion and was in part in proportion of 1 : 1.30. The circuit
consisted in 1 synthesis gas + 2.5 recirculation gas to 1 + 3.0.
Operation in a circuit improved the life of the catalyst as well
as the conversion. With a direct thruput the conversion fell off
after a short time (mostly as early as after 100 hours of operation
because of a partial deposition of the catalyst) while in the
circuit experiments the conversion was kept constant for over
600 hours of operation.

The effect of the length of the reactor was studied by
conducting some experiments in reactors of 12 m in height. The
absence of suitable compressors prevented the use of these
reactors in the circuit, and they were only used for a direct
thruput. However, these tests showed no appreciably difference
in thruput, gasification and formation of products, than the
corresponding tests in the 6 m reactors (Tests 21 and 22).

Later tests (25) in the 6 m reactor were run with a much
higher proportion of recirculation (1 + 33). The CO conversion
amounted to 70% in this case, but the gasification was around
20%. The consumption proportion was very greatly displaced _
towards the H_2 side (1 : 1.55). The high proportion of the
recirculation gas resulted in carrying considerable amounts of

oil out of the reactor, so that the level of the oil in the reactor was dropping continuously. The lowering of the oil level was later prevented by a corresponding return of the oil.

These first experiments were strongly affected by the frequent interruptions. It was found here that a test in which the catalysts had settled out because of a stop in operations could no longer be resumed.

The wet synthesis experiments were resumed on September 12, 1941, after the installation of the required compressors and reactors. The present wet synthesis operations are run as follows:

Reactors: two reactors (vertical tubular reactors with a 6 m filling level and with an oil circuit for fuel oil) were available for the tests. The first reactor held 55 li of the catalyst-oil mixture; the second reactor held a larger amount of the catalyst-oil mixture, namely 85 li. The volume in the second reactor was made larger in order to reduce the amount of entrained oil with a higher gas thruput (gas circulation). Much oil was carried out from the liquid phase even with a normal or low gas thruput and then separated in the coolers. The oil level in the reactors as a result sank continuously. To overcome that a return of the oil was provided, which permitted the return of the total condensate in the cooler back to the reactor. This arrangement resulted in only gasoline and gasol being removed away with the tail gas, and which were then adsorbed in the activated charcoal.

The oil level was observed in an oil level glass and was maintained by a periodical draining of the synthesis reactors through a filter located behind the liquid phase. The oil level reacts to small variations in the pressure with resulting variations in production, which will therefore affect the computation of the yield, and the synthesis pressure has therefore to be maintained st rigorously. It is therefore recommended to calculate the yield as an average of several days or a weeks operation. The reaction water was periodically drained from behind the first catchpot. Care must be taken in the starting or stopping to have the pressure rise or fall very gradually to prevent the carrying over of the catalysts into the cooler and the catchpot.

The synthesis gas was originally finely distributed through a ceramic porous plate. During disturbances or stoppages the catalyst would settle out more or less upon the plate which caused a great loss in pressure (up to 6 atm) between the compressor and the reactor when re-starting the reactors. The porous plate was therefore replaced by a simple bent copper capillary tube. The pressure loss became there practically equal to 0 and in spite of the poorer gas distribution the gas consumption remained practically the same as when a porous plate was used.

When reactors were temporarily stopped for repairs the whole reactor contents were drained through a bottom valve. It is recommended to lead gas through the reactor during draining in order to prevent the settling out of the catalysts. The mixture

of catalysts and paraffins solidified (with a partial settling
out), and could be returned to the reactor after melting, and the
reactors started again without any effect upon the activity.
Repeated filling and emptying would cause no difficulties as
corresponding tests have shown. The wet synthesis is very
trouble-proof in that respect.

When the test is to be ended, the catalyst is filtered off
from the reactor paraffin through a let-down valve connected
with the filter press. The filtered reactor paraffin can well
be used in the next experiment because it requires from two to
four weeks to become saturated with the diesel oil, depending
on the nature of the paraffin.

One reactor was provided with an arrangement permitting
the addition of catalysts or other materials through the reactor
during the test.

The temperature of the wet synthesis test was the same
as in the dry synthesis. The average operating temperature
varied between 230 and 250°C. A higher temperature was in
general required only during the starting period; later the
temperature needed not be changed for weeks. The temperature
should be uniform throughout the whole length of the reactor for
uniform operations which was obtained in all reactors by using
reactor jackets.

The synthesis pressure was 15 atm on the average. No
special tests were made to determine the effect of pressure

during wet synthesis. It can not, however, be assumed that
any differences could be found in comparison with dry synthesis
operations, and that the most favorable synthesis pressure was
as formerly in the neighborhood of 10 - 20 atm.

The CO conversion during operations with intermediate circuit
(1 + 1 to 1 + 3) was 70 - 75% in a single stage. Occasionally
80 - 82% could be converted in one stage. Numerous experiments
have shown, however, that there is no advantage in a great in-
crease in the conversion in the first stage because that results
in an increased gasification and reduces the catalyst life. The
most favorable conversion of CO in the wet synthesis is probably
around 65 - 75% in the first stage.

The gas from the first stage can be readily worked up in
a second reactor in series with it, again with a 70 - 75% conversion.
In a two stage test (Test 27) a total of 93 - 94% CO conversion
has been obtained.

Gasification (formation of CH_4) was throughout lower than
in the corresponding dry synthesis test.

The gasification was particularily low during the first part
of the test (1.5 - 2.0%, even often below 1%). When catalysts are
used which produce paraffin preferentially and have a low tendency
for producing methane, one may count on an average of 3 - 4%
gasification with a total conversion of 70 - 90%. The gasification
in the wet synthesis increases with increased length of the
test as well.

<u>The consumption proportion of CO : H_2 was shifted towards</u>
the H_2 side in the wet synthesis in comparison with the dry
synthesis (even with otherwise identical experimental conditions).
In the first stage the consumption proportion was mostly greater
than 1 : 1.30 (e. g. 1 : 1.40 - 1 : 1.50, experiments 25 - 27).

It is remarkable that the proportion is very little affected
by the amount of recirculation (1.0 + 1.7 to 1 + 7, Test 25).
Even with a direct thruput the consumption proportion is above
1 : 1.30. (During normal operations with water gas, more H_2
than CO is used in the first stage, with a very small amount of
simultaneous methane formation, so that the liquid products are
more greatly saturated than in the corresponding dry synthesis
tests, in which the consumption proportion is mostly displaced
towards the CO side).

The CO content of the tail gas of the first stage (or the
intake gas of the second stage) was fairly high because of the
large H_2 consumption. As a result more CO than H_2 was consumed
in the second stage, corresponding to the composition of the
reacting gas. The consumption proportion is therefore the
reverse of that in the first stage and equal to about CO : H_2
= 1.0 : 0.90 (Test 27).

The total consumption proportion in the first and the second
stages corresponds to the proportion in the water gas and varies
between 1 : 124 and 1 : 126. Attention must be paid in subsequent
experiments to have not merely the total consumption proportion
but also the consumptions in the first and second stages

always correspond to that of the water gas, because any deviations towards greater hydrogen or CO consumption will result in a reduction of the yield

The gas load and the amount of catalyst per reactor. A conversion of 73 - 75% of the CO was obtained with a catalyst content of 10 li per reactor (1 part by volume of the dry granulated catalyst: 5 parts by volume of oil), with normal gas load (100 fold gas volume per hour, circulation 1 ÷ 3). Increasing the catalyst load by 30% reduced the CO conversion to 62 - 64%; a 100% overload resulted in a further reduction to 48 - 52%. These tests were repeated many times and showed conclusively that no important increase in the catalyst load is possible.

The amount of catalysts in the reactors could, on the other hand, be appreciably increased and a conversion of 73 - 75% could be obtained with a 20 li catalyst content per reactor and with a normal gas load. With 30 li catalyst content and corresponding gas load, the CO conversion amounted to 70 - 75% (in a single stage). It appears therefore entirely possible to still further increase the amount of catalysts. The table below shows the comparative results obtained.

Amount of Catalysts	Gas Load	Absolute amount of gas (intake)	CO conversion, %
10 li	Normal	1 cbm	73 - 75
10 li	50% increase in load	1.5 cbm	62 - 64
10 li	Double gas load	2.0 cbm	48 - 52
20 li	Normal	2. cbm	73 - 75
20 li	50% increase in load	3 cbm	62 - 64
20 li	Double load	4 cbm	48 - 53
30 li	Normal	3 cbm	70 - 75

Yield: The theoretical yield of 170 g has been reached in a two stage test with a total conversion of $CO + H_2$ = 90 - 93%. The detailed study of the products formed was not complete because of the difficulties in metering the gas. Tests intended for that purpose will be run after the installation of suitable equipment (gas holders etc.).

The composition of the products depended primarily on the nature of the catalysts as in the dry synthesis, and secondarily on experimental conditions (high temperature, high circulation etc.). With a paraffin-producing catalyst, paraffin again was the principal products of the wet synthesis (up to 60%). Whenever there was a gradual cracking of the hard paraffin with the production of diesel oils and soft paraffins in the wet synthesis, the paraffin had to be hardened subsequently. The products are always somewhat more saturated than in the dry synthesis.

Life. The longest wet synthesis tests have been run so far for 7 1/2 weeks without much reduction in activity. The gasification

was somewhat increased (from 2 - 2.5% to 6 - 8%). The present experiments permit us to assume that the life of the catalyst in the wet synthesis is no less than in the dry synthesis.

Later additions of catalysts. On the strength of the fact that more H_2 than CO is consumed in the first stage of the wet synthesis, experiments were run (Test 27) to displace the consumption proportion towards the CO side by the addition of alkaline materials. This was done by adding 750 g of soda (finely ground in diesel oil) to the reactor contents (10% of the iron present), and the consumption proportion changed from 1 : 1.30 before the addition to 1 : 1.08 - 1: 096. Conversion and gasification underwent no change; but the reactor paraffin underwent in a few days (about 6 days) a sudden remarkable change. It turned brown and finally a black-brown, became jelled and semi solid. No analytical investigation of this substance has yet been made.

In another test 5 li of fatty acids (C_{10} - C_{18}) were added . The proportion rose immediately after the addition from 1 : 1.15 to 1 : 1.81. The consumption proportion dropped again to 1 : 130 in a short while, and finally in the course of a few days to 1 : 1.05, i.e. to lower final values than before the addition of the fatty acid. The effect of the addition of the fatty acid was therefore of but short duration. One must assume therefore that the fatty acid was quickly consumed. A test of the filtrate from the reactor showed zero saponification number and neutralization

numbers, which showed that no more fatty acid was present. The

gasification rose somewhat after the addition of the fatty acid

(8 - 10%) and the conversion dropped off.

We will give in conclusion a general survey of the course of

the synthesis in a two stage process.

	1st stage	2nd stage	1st + 2nd stage
Hours of operation	833	732	
Temperature °C	250	252	
Pressure, atm. gauge	15.0	15.0	
Amount of gas, cbm/h	3.1	1.33	
Circulation	1 + 2	1 + 3	
Contraction, %	50.2	35.6	67.3
CO conversion, %	64.0	75.0	91.0
CO as CO_2, %	25.0	31.3	27.6
CO as CH_4, %	3.3	6.3	4.3
% liquefaction of CO	71.7	62.4	68.1
H_2 conversion, %	69.3	73.0	91.6
CO + H_2 conversion, %	69.4	74.0	91.2
Yield, g/n cbm	126	93.0	170
Boiling range:			
-200°C	18.4	50.3	24.9
200 - 320°C	21.9	30.1	29.8
320 - 460°C	26.6	}18.3	21.6
>460°	32.1		23.6
Olefins:			
-200°C	63.0	78.0	65.0
200-320°C	21.0	5.0	17.0
Analysis of tail gas, %:			
CO_2	24.7	48.3	
C_mH_n	1.6	1.8	
O_2	0.1	0.1	
CO	27.8	10.8	
H_2	30.0	12.6	
CH_4	2.1	5.6	
N_2	13.7	21.2	
Consumption proportion CO : H_2	1 : 1.36	1 : 1.05	1 : 1.28

/S/ Schenk