

LATEST GERMAN DEVELOPMENTS ON THE GAS PHASE
GASOLINE SYNTHESIS AT MIDDLE PRESSURES, 1942 - 1945

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Summary of Results

In the middle pressure synthesis with iron catalysts of different origin, using CO-rich gas,

1) either the Leuta or the Lux gas purification masses are suitable for use as catalysts in the synthesis after some preliminary treatment. The temperature required is higher than with actual catalysts, but appears to be capable of being lowered by a suitable reduction (forming methods) of the catalyst.

As an example, the preliminary gas purification Lux mass prepared by washing, drying and alkalization, operated for 3,000 hours with a CO-rich synthesis gas at 10 atm pressure and 248° with a normal load, producing 180 g hydrocarbons, of which 154 gram were the higher hydrocarbon (propane and up).

2) The effect of alkali content on the life, olefin, paraffin and alcohol formation of the carrier-free catalysts was reinvestigated.

A liquid phase synthesis catalyst, 2500 hours old and containing 2% K_2CO_3 produced an 87% CO conversion with 175 gr higher hydrocarbons, with no methane production.

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The proportion of oxygenated compounds is only about 1/2 of that produced in the liquid phase.

A comparison of precipitated ferric nitrate catalysts with 0.25 to 10% K_2CO_3 showed that 1% K_2CO_3 produced the best results. The methane production is reduced from 18 to 3 g/nbcm $CO + H_2$ in comparison with the usual alkalization of 0.25% K_2CO_3 . The proportion of paraffin formed has not been determined. Higher alkalization than 1% yields products richer in paraffin, but the life of the catalyst is proportionately reduced. The effect of alkalization on the production of oxygenated products is but slight in comparison to the effect in the liquid phase.

- 3) Efforts to apply the process of reduction under pressure, which has been found successful in the liquid phase, to operations in the gas phase was not successful.
- 4) Powdered iron, activated with copper and alkalies, can be used for gas phase hydrogenation. Activity is not satisfactory (80% conversion of CO at $260^\circ C.$). Surprisingly, no methane was formed with a high thruput.
- 5) The substitution of potassium silicate for potassium carbonate in catalysts deposited upon carriers and in carrier-free catalyst, as protected by a patent, has not been found to affect the direction of the $CO:H_2$ consumption, nor the paraffin production. It is possible to introduce a larger amount of K_2SiO_3 than of K_2CO_3 into

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the catalyst without harming the catalyst, but no effect upon the proportion of the CO:H₂ consumption nor on the paraffin production could be observed. Blue water gas has been used in these tests.

II. Middle pressure synthesis experiments with circulation of the tail gas with a low proportion of make-up gas to circulation gas and using either a CO-rich synthesis gas or an H₂-rich synthesis gas showed that:

1) with CO-rich gas (and a carrier-free catalyst) the proportion of circulation gas (between 0.6 and 3 p./l part of make-up gas) did not affect the consumption proportion of CO to H₂, as could have been expected. The effect was great on the conversion, increase in yield from 170 to 190 g/nbcm CO + H₂ and the olefin proportion increased from 65% to 78%.

2) No solution of the problems was found in the circulation tests with dolomite carrier catalysts and a 2 H₂:1 CO with a circulation proportion of 1:1 because of deposition on the catalysts.

III. Circulation experiments at middle pressure with catalysts reduced by the manufacturer with either water gas or with hydrogen-rich synthesis gas for the increase of the CO conversion, and through that to increase the yield and the proportion of olefines, produced the following information:

1) The H₂:CO consumption proportion was increased from 0.63 with direct pass of the gas to 0.84 with a 1:1 circulation

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and a dolomite catalyst using water gas with 1.05 H₂:1 CO. This is the first indication that iron catalyst can convert even a high-hydrogen gas with optimum gas utilization and yields.

2) The H₂ + CO consumption increases from 80% with 1.20 H₂:1 CO water gas, in a single pass and a dolomite catalyst to 85% in a two stage process and to 0.96% with a 1:1 and 1:1.02 gas in the first stage and 1:2 in the second stage. The methane formation still remains very high, forming 11 to 17% of the products formed, depending on the method of operation. The proportion of olefines is slightly increased by circulation, from 43.5 to 48.5%.

III b. Circulation tests with water gas or hydrogen-rich gas on dolomite catalysts reduced with CO at 0.1 atm resulted in satisfactory gas utilization under suitable operating conditions.

1) Preliminary tests under a great variety of operating conditions permitted us to select operating conditions suitable to any H₂:CO ratio.

2) The following circulation proportion (vol. circulating gas:volumes make-up gas) with a normal load of make-up gas (100 n.li. make-up gas/h, 11 catalyst volumes) were adapted to properly utilize the make-up gas used:

Synthesis gas H ₂ :CO	Circulation ratio about
1.18	6
1.37	7
1.56	8
1.84	10
1.90	11
1.93	13

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In this way 180 g hydrocarbons, (and over/nobm CO + H₂ were obtained by using the above method of synthesis, which has never been produced heretofore by others, as far as we know.

These circulation proportions appear, however, undesirably high for industrial operations. Experimental runs with water gas and a circulation proportion down to 3:1 produced acceptable yields of 160 - 165 g with 86% CO conversion.

The effectiveness of the process even at atmospheric pressure has been discovered at a lower excess pressure with circulation, by showing that the H₂ + CO consumption at 2 atm gauge was but slightly less than at 10 atm.

3) When the middle pressure circulation synthesis with water gas is used immediately after reduction of the catalysts, without first operating with no circulation of the gas, the synthesis temperature can be reduced by about 5° to 210-212°C. With water gas of the composition of 1.28 H₂:1 CO and a circulation proportion of 5, 175 g of hydrocarbons are obtained on the average, although the H₂:CO consumption is not entirely in the same proportion as in the water gas.

4) Even with a circulation proportion of 1:2.5, 167 g hydrocarbons are obtained from water gas with an 88% CO conversion. The formation of methane is greater with higher circulation proportion, than with lower, and with a circulation of 1:2.5 it still equals 19-21 g.

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5) The effect of higher (210°C.) or lower (190°C.) starting temperatures cannot be definitely stated when starting the circulation operations after reduction with CO under reduced pressure. Higher starting temperatures seem to require slower temperature increases.

6) Special tests were performed to lower the methane formation during circulation water gas synthesis on dolomite carrier catalysts, after having definitely established the satisfactory yield of total CH₄:

With very low starting temperatures and very slight temperature increases, with a very low CO conversion of below 70%, the CH₄ formation is reduced from the normal 14% to 5% of the liquid products.

Increased alkalization has also a favorable effect, but not as much as expected.

It appears that the tendency for methane production is a peculiar property of the dolomite carrier catalyst used. The methane formation could not be kept below 10% in long time operations with a 90% CO conversion even with strong alkalization.

III c. Middle pressure circulation synthesis with kiselguhr-magnesia catalyst using water gas indicated that this catalyst behaved exactly like the dolomite catalyst with respect to H₂:CO consumption, permissible load, CO conversion, synthesis temperature and methane formation.

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IV. Testing the applicability of the various processes for the reduction of the catalysts for the middle pressure synthesis gave the following results:

- 1) A synthesis temperature lowering by 10° was brought about by the carbon monoxide + hydrogen reduction of carrier-free catalysts for the middle pressure synthesis with CO-rich synthesis gas, in comparison to the usual reduction process.
- 2) A 10° lowering of the temperature results also with the reduced pressure CO-reduction of carrier-free catalysts for middle pressure synthesis with water gas. Similar synthesis temperatures seem to be well suited for the same space velocities as in the carrier catalysts. For equally high CO conversion the $H_2:CO$ consumption is equally high, i.e. 0.9 with water gas. Appreciably more methane was formed (17 g) with low alkalinity catalysts (0.25% K_2CO_3).
- 3) Only negative results were obtained in the experiments for the direct pressure reduction of the dolomite catalysts with hydrogen-rich CO-free synthesis gas.
- 4) A repeated reduction of a dolomite catalyst reduced with hydrogen, for synthesis with water gas at 250° , has been found to have no effect upon the activity in the middle pressure synthesis.

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5) When testing the reduction method used by Lurgi, in which the reduction was done for a short while at 250° and later at 225°, a less active catalyst was produced than in our original simple reduction.

V. "Taifun Reduction".

Reduction at very high space velocities with hydrogen-rich synthesis gas at atmospheric pressure in the temperatures of 280-320°C. has produced the most favorable results so far. The simplest process to be carried out industrially produces especially high activity state for the middle pressure synthesis, which manifests itself in lower synthesis temperature and greatly reduced tendency of methane formation.

Special tests have shown that:

1. Dolomite catalysts with 1% K_2CO_3 .

Re-reduction by the Taifun Process of the catalyst already reduced with hydrogen was successful.

Still better results are obtained when green corn is reduced by the Taifun Process.

The carbon dioxide which used to be removed from reduction gases for the sake of safety, can be left in it.

The effect of space velocity is slight, as long as kept above 2000.

No preheating of the reduction gas is necessary.

The reduction temperature should mostly be kept between 300 and 350°C. with thick layers of catalyst.

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The considerable heating up of the catalyst must be watched.

The methane formation with a 90% CO conversion amounts to 4-5% of the liquid products.

- 2) Use of more strongly alkalized dolomite catalyst did not lower any more the formation of methane during the middle pressure synthesis with a direct gas throughput. One might possibly detect disadvantages of the increased alkalization in a lower catalyst life and a reduced consumption ratio of $H_2:CO$.
- 3) Taifun-reduced lime catalysts excelled by a complete absence of methane formation. Their life was not, however, satisfactory.
- 4) Carrier-free catalysts showed the same advantages for water gas middle pressure synthesis after Taifun reduction as do catalysts upon carriers. The methane formation is again reduced to a minimum.
- 5) A cobalt catalyst reduced by the Taifun process for experimental reasons was almost inactive.
- 6) The connection has been investigated between carbide formation and free carbon.

VI. Experimental atmospheric pressure reduction under special operating conditions.

- 1) The carrier-free catalyst can also be used with satisfactory CO conversion at temperatures below $225^\circ C.$, if operated at space velocities commonly used in large scale

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operations. With an 85% CO conversion, 105 g. CH₄ was formed during the first 1000 hours.

2) The recirculation of the tail gas permitted operating with a proper H₂:CO consumption with iron catalysts at atmospheric pressure with yields similar to the cobalt catalysts.

For a proper consumption proportion H₂:CO, the circulation proportion of H₂-rich gas must be very high, about 12-14. The H₂:CO consumption is less satisfactory with a lower circulation proportion, but economical conversions are still obtainable with it.

Harmful effects of the water gas reaction are reduced by having the synthesis gas as dry as possible during synthesis. The synthesis temperature is between 205 and 225°C.

3) Brief preliminary experiments at increased space velocities (excessive loads). The catalyst life and the H₂:CO consumption appeared less promising with a straight pass than the recirculation process.