

ENCLOSURE (B)ig

PART III

STUDIES ON LIQUID PHASE SYNTHESIS
WITH IRON CATALYST

by

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Research Period: 1942-1943

SUMMARY

Experiments were made to investigate the activity of iron catalysts in liquid phase synthesis of oil from water gas.

Significant results were as follows:

1. Fe-Cu catalysts, containing small amounts of alkali, had a strong oil synthesis activity, at temperatures under 250°C.
2. A similar catalyst, but containing no alkali, showed weaker activity for oil synthesis, but strong hydrogenating power at 250-270°C.
3. The catalysts, Fe-Cu-CaO, were prepared by precipitation from nitrate mixtures with an excess of sodium hydroxide. The catalysts Fe-CaO (100:100-150) and Fe-CaO-Cu (100:100-150:25) could be made into very hard tablets, and were suitable for liquid phase synthesis at 260-270°C, and pressure 10 kg/cm². The catalysts Fe-CaO(100:10) and Fe-CaO-Cu(100:10:25) had better activity than the afore-mentioned, but binders were required to make satisfactory tablets.

I. INTRODUCTION

Research on the synthesis of hydrocarbons from water gas was made chiefly for vapor-phase reaction conditions, which resulted in some difficulties in removing reaction heat in a large-scale apparatus. Reaction chambers of tubular design were used for controlling reaction temperature, but these chambers were expensive to construct and difficult to maintain.

A new, simpler method for removing reaction heat was proposed by the I. G. Co. in Germany, which was based on the circulation of synthetic oil through the reaction system.

F. Fischer and H. Pichler experimented with liquid phase synthesis using an iron catalyst suspended in water under 10-40 atmospheres of pressure and 200-250°C., but their results were unsuccessful.

The following experiments were made to determine a more suitable catalyst for the liquid phase synthesis.

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II. DETAILED DESCRIPTION

The catalyst, containing 4 gm of iron, was mixed in a two-liter rotary autoclave with 200cc of Fischer-Tropsch synthetic oil, (iodine number of 8.83). Water gas was charged into the autoclave, to an initial pressure of 10 atmospheres at 15°C. The autoclave was heated electrically to the required reaction temperatures, held for the desired time, and then cooled to room temperature. The pressure drop was measured and the residual gas and oil analyzed.

III. EXPERIMENTAL RESULTS

A. Experiments with Fe-Cu-K₂CO₃ Catalyst

Catalysts were prepared by precipitating from iron and copper nitrate solutions with an excess (about 20% of theoretical) of sodium carbonate solution. This procedure was similar to that used for an iron catalyst, described in Part II of this enclosure.

Experimental data on these catalysts, summarized in Table I(B)19 show that, (1) the catalyst Fe-Cu-K₂CO₃ showed activity for oil synthesis at temperatures under 250°C, but variation of K₂CO₃ content had little influence on this activity, (2) the catalyst Fe-Cu (containing no alkali), showed lower synthesis activity than the former, but possessed hydrogenating power at 250-270°C.

B. Experiments with Fe-CaO and Fe-CaO-Cu Catalyst.

These catalysts were prepared by precipitating from nitrate mixtures with a large excess (about 100% of the theoretical amount) of sodium hydroxide solution, and the precipitate was washed with 1/20 N sodium hydroxide.

Data on these catalysts, given in Tables VII(B)19, and VIII(B)19, show that, (1) the catalyst Fe-CaO was active at a reaction temperature of 260-270°C., and its activity was better with lower CaO content, (2) the catalyst Fe-CaO-Cu was more reactive than the former at lower temperatures and the CaO content had less influence on the synthesis activity, (3) the catalyst with high CaO content was very hard and made excellent tablets.

IV. CONCLUSIONS

The best catalyst for the liquid phase reaction appeared to be Fe:CaO:Cu (100:150:25). The amount and quality of oil formed in these experiments was not determined, and it would be necessary to perform experiments on a larger continuous-pilot plant scale to establish the economic attractiveness of this process.

All work on Fischer-Tropsch synthesis was stopped in 1943. The work covered in these three sections of "Studies on the Fischer-Tropsch Synthesis" represents all of the work done by the Naval Research Department on development of the process.

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Table VI(B)19
EXPERIMENTS WITH Fe-Cu AND Fe-Cu K₂CO₃ CATALYSTS

Catalyst	Final* Press. kg/cm ²	Synthesis (Temp. °C)	Synthesis (Time, hr)	Contraction (Vol. %)	Iodine Value, After Reaction
No Catalyst Used	10	230-285	5.5	0	54.11**
Fe-Cu Catalyst Ratios 100:25	4.2	248-270	5.5	58	8.83#
100:25	6.8	220-250	4	32	48.56
Fe-Cu-K ₂ CO ₃ Catalyst Ratio 100:25:2	6.0	220-250	4	40	42.80
100:25:4	6.1	220-250	4.5	39	44.14
100:25:6	6.1	220-250	4	39	45.43
100:25:6	6.1	240-270	4	39	45.98
100:25:8	6.1	220-263	4	39	47.87
100:25:25	6.2	218-252	4	38	48.65
100:25:25	6.0	240-270	4	40	49.07
100:25:50	8.3	223-254	4	17	48.61

*In all cases initial pressure was 10 kg/cm²

**Partial cracking occurred

#Synthesis and hydrogenation occurred

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Table VII(B)19
EXPERIMENTS WITH Fe-CaO CATALYST

Catalyst (Fe-CaO)	Final* Press. kg/cm ²	Synthesis Temp. (°C)	Synthesis Time (hr)	Contraction (Vol. %)
100:5	4.5	270	2	55
100:10	4.8	260	2	52
100:20	4.2	270	2	58
100:100	5.0	270	2	50
100:100	7.2	260	2	28
100:150	6.0	270	2	40
100:150	7.0	260	2	30
100:200	6.0	270	2	40
100:200	7.0	260	2	30

*In all cases initial pressure was 10 kg/cm²

Table VIII(B)19
EXPERIMENTS WITH Fe-CaO-Cu CATALYST

Catalyst (Fe-CaO-Cu)	Final* Press. kg/cm ²	Synthesis Temp. (°C)	Synthesis Time (hr)	Contraction (Vol. %)
100:10:5	4.3	260	2	57
100:10:10	4.0	260	2	60
100:10:25	3.7	260	2	63
100:100:25	4.8	260	2	52
100:150:25	4.0	260	2	60
100:200:25	4.2	260	2	58

*In all cases initial pressure was 10 kg/cm²