

UNITED STATES
DEPARTMENT OF THE INTERIOR
BUREAU OF MINES
OFFICE OF SYNTHETIC LIQUID FUEL
LOUISIANA, MISSOURI

From Dr. Pier's File

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High Pressure Experiments
Ludwigshafen, 558

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SYNTHESIS IN THE LIQUID PHASE

by Miss Goring (?)

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Go/Py

The basic patents for CO/H₂ synthesis in the liquid phase were issued to Dr. Pier in 1928 (DRP 630,829)

Dr. Duftschmidt in Oppau has developed a special form of operations by this method, where a synthesis product was used as a liquid medium. It was obtained primarily from the evaporated products obtained under the conditions of the reaction. The application was first denied at the objections of the Ruhrchemie, because in the methanol synthesis the reaction take place in a liquid medium with evaporation under the existing reaction synthesis, and it is moreover customary in the hydrocarbon synthesis to circulate the synthesis products. The I. G. at present argues this interference.

The catalyst used in the process consists of metallic iron obtained by reduction of a fused ferro-ferric oxide, containing Ti and/or Si, as well as other activators, such as alkalies, uranium, tungsten, barium, magnesium etc. Other iron catalysts as well have been developed in Oppau, which are characterized by treating iron or iron oxide with hydrogen and steam at above 600° C, followed by reduction, or by the addition of As, Sb or Cu.

While the Oppau method of operations requires a fixed bed catalyst, Dr. Michael prefers working with a finely divided catalyst. A patent has been applied for a method of synthesis in a liquid medium with a catalyst suspended in it, and with very rapid stirring.

Dr. Michael has developed four groups of catalysts for catalysis in the liquid phase, and applied for patents on the use of:

- 1). sintered iron
- 2). oxidized and reduced compact iron
- 3). iron from iron carbonyl, by way of the oxide
- 4). a new catalyst is at present being claimed

by Dr. Michael with additions of barium or tungsten. Iron or iron oxide is here treated in a not reducing atmosphere at high temperatures, while in the Oppau applications I. G. #, 11,123 and 12,169, which describes

similar catalysts, iron or iron oxide heated in presence of steam, containing hydrogen.

Synthesis in the Liquid Phase

Oppau (Duftschmidt, Linckh)

High pressure (Michael)

Method of Operations:

Fixed bed catalyst

Products of the reaction evaporating under the operating conditions

Principally sintered iron, Finely subdivided catalyst. Synthesis in a liquid medium with a finely subdivided catalyst and with very violent stirring. Burning of iron carbonyl, reduction and grinding of iron oxide.

Principles of the catalysts:

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| <ul style="list-style-type: none"> 1). iron from ferro-ferric oxide with Ti and/or Si + activator 2). Preformed iron oxide or iron + activator, treated with steam at 600°C, then reduced 3). Iron with additions of As, Sb, Cu | <ul style="list-style-type: none"> 1). Sintered iron 2). Oxidation, followed by reduction of compact iron 3). Iron from iron carbonyl by way of the oxide. 4). Iron with additions of barium and tungsten |
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Synthesis in the Liquid Phase with an Iron Catalyst.

- 1). Oppau (Dr. Duftschmidt, Dr. Linckh)
 - a). Method of Operations

I. G. No. 9104, 11/18/35 (Duftschmidt, Linckh, Winkler)
Synthesis in the liquid phase, with the products of the synthesis used as the liquid medium, appreciable amounts of which evaporate under the conditions of the

synthesis and the products of the synthesis recovered by condensation of the gases and vapors. Interferences cited by Ruhrchemie 1st claim disallowed (F.P. 788,266, recirculation of the synthesis products. DRP. 484,166, F.P. 639,058; Methanol synthesis in the presence of a medium evaporating under the conditions of the synthesis).

I. G. No. 9,635, 11/4/36 (Being examined)

Supplement to No. 9104

Use of a mixture of CO and H₂ containing over 50%, and preferably 55-70% vol. % of CO.

I.G. No. 11,661, 3/31/39 (Duftschmidt, Linckh, Winkler)

Synthesis for the preferential production of paraffin, conducted in refluxing circuit of a liquid partially evaporating medium, characterized by having the mixture of circulating oil synthesis products and the residual gases, leaving the catalyst space, continuously deposit high boiling constituents by condensation at the withdrawal temperature (paraffin), and then recovering the residual products by fractional condensation with a recovery of the circulating oil.

I.G. No. 10,479, Standard Oil Co., 1/21/37 (Application made out by us) (Examination satisfactory)

Synthesis in a steadily maintained liquid phase, with the medium principally or entirely consisting of oxygenated derivatives of hydrocarbons obtained in the liquid state under the conversion conditions (products of oxidation of paraffins).

b). Catalysts:

I.G. No. 9099 (DRP 708,512), 11/15/39 (Linckh)

Fused ferro-ferric oxide with Ti and/or Si or their compounds and other activating substances (such as U, Mn, Cr, W, K, Ca, Mg, Ba), treated with hydrogen above 300° C.

I.G. No. 11,123, 11/12/38 (to be published 3/27/40) (Klemm, Linckh)

Shaped iron oxides, mixed with activating substances, treated with hydrogen-containing steam at high temperature, preferably above 600°C, and finally reduced (spinel structure).

I.G. No. 11,964, 1/19/40 (being published) Supplement to No. 11,123

The use of iron instead of iron oxide, otherwise like No. 11,123

I.G. No. 11,841, 10/23/39, publication agreed upon. (Klemm)

Iron, cobalt or nickel coated with a thin adhering coating of copper, silver or gold by the action of their diluted salts.

I.G. No. 12,415, 10/23/40, publication agreed upon. (Linckh, Weiler)

Fusing iron with alkalies in a stream of oxygen, reduction of the ferro-ferric oxide with the addition of arsenic or antimony or their compounds.

I.G. No. 14,034, 3/2/43 (Duftschmidt)

Iron ores, primarily of oxidic nature, or iron ores converted into oxides by heating or roasting, treated with reducing gases.

I.G. No. 11,450, 3/25/39. Published, at present suspended because of earlier applications (Scheuermann, Marecek)

Iron or nickel produced by dropping a solution of iron or nickel salts into an alkaline precipitating solution, in the course of over 3 hours, except of the case of simultaneously cobalt-containing catalysts which are produced under a pressure in excess of 2 atm.

I. G. No. 12,937, 8/9/41 (suspended) (Scheuermann)

Reduction of precipitated iron compounds with a thruput of at least 500 li/li/hr.

I.G. No. 12,534 (Scheuermann)

A catalyst for the production of paraffin at about 5 atm, composed of iron, with alkaline compounds, kieselguhr and magnesium oxide, in amounts of 10% or over.

2. High Pressure Experiments :

a). Methods of Operation:
DRP 630,823, 9/18/28 (Pier)

Synthesis in the presence of larger amounts of hydrocarbons stable and liquid under the operating conditions, in a way to have the reaction always take place in the above mentioned liquid materials.

I.G. No. 10,189, 8/26/37 (Michael) (being published)

Synthesis with sintered iron in the liquid phase.

I.G. No. 13,042, 10/14/41

Synthesis in the liquid phase with a finely divided catalyst, obtained by combustion of iron carbonyl, reduction and grinding.

I.G. No. 12,591, 2/22/41 (in publication)

Synthesis in a liquid medium with a suspended catalyst with stirring by a vertical stirrer on a vertical shaft, with sufficiently large vane or vanes at right angle to the motion, with the stirring sufficiently rapid to have the liquid level drop on the shaft or its elongation to the lower or the middle part of the liquid layer at rest, and intersecting the surfaces of the stirrer.

b). Catalysts:

I.G. No. 12,169, 11/30/39 Sintered catalyst (iron). in publication.

I.G. No. 9,261 (DRP 729,290) 2/25/36. Addition of difficultly reducible oxides before sintering.

I.G. No. 9,919, 4/14/37. Catalyst sintered at different temperature stages.

I.G. No. 9,960, 5/5/37. Sintered catalyst from iron carbonyl.

I.G. No. 11,217, 12/22/38. Compact iron oxidized, then reduced.

I.G. No. 13,105, 10/2/40. Compacted iron oxidized, the iron oxide ground, tabletted, reduced.

I.D. No. 13,106, 10/3/40. Iron oxidized in the presence of steam, then treated as in No. 13,105.

Summary

Dr. Michael carries out the synthesis in the sump phase with a finely divided catalyst. This method of operation is independent of Dr. Dufts Schmidt's. Dr. Michael requires a high boiling practically non-volatile liquid phase to keep the finely divided catalyst in motion in the liquid during the reaction. A good distribution of CO, H₂, and the catalyst in the liquid is obtained by having the gases either enter through a filter plate, or by a rapid stirring of the liquid. The first method of operation was not patentable, but the rapid stirring was claimed in the patent application. Dr. Michael has not applied for a patent for a fixed bed catalyst.

The catalyst claims of Dr. Michael are also independent of the Oppau patent rights.