PATENT SPECIFICATION

776,781

Date of Application and filing Complete Specification Nov. 25, 1953.
No. 32681/53.
Application made in Germany on Dec. 27, 1952.
Complete Specification Published June 12, 1957.

Index at acceptance:—**Class 2(3), B1G.**
International Classification: **—C07c.**

COMPLETE SPECIFICATION

Process for the Hydrogenation of Carbon Monoxide in a Liquid Medium

We, RHEINPREUSSEN AKTIENGESELLSCHAFT FUER BERGBAU UND CHEMIE, of Homberg, Niederrhein, Germany, a German Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The process relates to a process for the hydrogenation of carbon monoxide in the liquid phase.

In the reaction of gases with liquids it is important that the gas should be introduced into the liquids in as finely a divided form as possible so that intimate contact between the two reactants is obtained. This applies particularly to the hydrogenation of carbon monoxide in the liquid phase, in which the catalyst is suspended in a liquid medium, and the synthesis gas is passed through the suspension. Conforming to the known principle of passing the synthesis gas in a finely divided state through the catalyst suspension, the synthesis gas has hitherto been forced or pumped through finely porous frits of metal, glass or ceramic material into the catalyst suspension. Jets having a diameter of up to 3 mm. have also been used. However, the frits as well as the jets of a diameter of up to 3 mm. involve the great disadvantage that they are readily clogged.

Surprisingly, it has now been found, according, to the invention, that the hydrogenation of carbon monoxide in a liquid medium, for example a heavy hydrocarbon fraction such as one obtained by the catalytic hydrogenation of carbon monoxide, proceeds under advantageous conditions when the synthesis gas is passed into the catalyst suspension through jets or openings having an inner diameter of from 7 mm. up to 50% of the inner diameter of the reactor or reaction tube. The inner diameter of the jets or openings is preferably not greater than 15 mm. The synthesis conditions are more advantageous in so far that substantially no interruption of operation is caused by the clogging of the jets or frits and that less carbon is deposited on the catalyst, so that the performance of the catalyst is substantially improved. Moreover, the methane formation is reduced to the extent of, or up to, approximately 30% which implies a corresponding increase in the yield of valuable or utilisable hydrocarbons.

It is not readily possibile to provide an explanation of the effect obtained by means of the measures taken according to the invention. It appears that in view of the larger gas bubbles that are formed when the jets or openings referred to are used, an excessively intimate contact between the synthesis gases and the surface of the catalyst is avoided so that the reaction heat is prevented from being released too suddenly.

The invention is illustrated in greater detail in the following example:—

Two synthesis reactors having a height of 5 metres and an inner diameter of 50 mm. were charged with 4.5 kilograms of a catalyst suspension which contained 10% Fe, the suspending medium being a liquid hydrocarbon fraction. The catalyst contained 0.05% Cu and 0.5% K_2CO_3 in addition to the iron, the iron and the copper in the catalyst having been precipitated from a common, aqueous solution of their nitrates by bubbling NH_3 through the solution. The catalyst was decidedly a benzine former in view of the fact that 80% to 85% of utilisable products (C_{3+}) boiled below 200° C.

In reactor I, the synthesis gas rich in carbon monoxide was passed through three jets having an inner diameter of 1.5 mm., and in reactor II through a tube having an inner diameter of 12.7 mm. After four hours, both reactors had a CO conversion of above 90% with the same catalyst load (2.2 normal litres $CO+H_2$ contacted with the catalyst per hour per gram of iron in the catalyst) and the same synthesis temperature (275° C.) The tem-

[*Price 3s. 6d.*]

peratures could be continuously reduced. After 120 hours of operation and at 252° C. the values given in the following tables were established:—

Gas analyses vol %	CO_2	C_{3+4}	C_2	CO	H_2	Hydro-carbons	N_2
Synthesis gas	3.5	0.0	0.0	56.2	36.3	0.2	3.8
End gas reactor I	57.4	3.0	0.8	10.8	14.2	6.4	7.4
End gas reactor II	63.1	3.2	0.7	7.4	13.2	4.3	8.1

	CO conversion %	CH_4/normal cubic meter $CO+H_2$, grams	C_{3+}/normal cubic metre $CO+H_2$, grams
Reactor I	90.7	23.2	156.3
Reactor II	93.8	13.2	170.3

It may be seen that the yield in reactor II was higher as a result of an increased CO conversion and a reduced formation of methane.

When the run was continued, it was found that the performance of the catalyst in reactor II was raised from 400 kilograms to approximately 500 kilograms of hydrocarbons per kilogram Fe as compared with the catalyst in reactor I.

What we claim is:—

1. A process for the catalytic hydrogenation of carbon monoxide carried out with the catalyst suspended in a liquid medium, in which the synthesis gas is passed into the catalyst suspension through openings the diameter of which is not less than 7 mm. and not greater than 50% of the diameter of the reaction tube containing the suspension.

2. A process according to Claim 1, in which the inner diameter of each opening is not greater than 15 mm.

3. A process according to Claim 1 or Claim 2, in which the catalyst is an iron catalyst.

4. A process according to any one of the preceding claims, in which the catalyst is a precipitated catalyst.

5. A process according to any one of the preceding claims, in which the liquid medium is a hydrocarbon fraction.

6. A process according to Claim 5, in which the hydrocarbon fraction is one produced by the catalytic hydrogenation of carbon monoxide.

7. A pocerss for the catalytic hydrogenation of carbon monoxide, substantially as described in the example with respect to reactor II.

8. Hydrocarbons and oxygen-containing organic compounds whenever obtained by the process claimed in any preceding claim.

EDWARD EVANS & CO.,
Agents for the Applicants.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press,—1957
Published at the Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.