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PATENT SPECIFICATION

Application Date: July 15, 1938. No. 21463/39.

519,613

(Divided out of Application No. 21086/38).

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Complete Specification Accepted: April 1, 1940.

PROVISIONAL SPECIFICATION

Improvements in the Manufacture and Production of Liquid Hydrocarbons

I, George William Johnson, a British Subject, of 47, Lincoln's Inn Fields, in the County of London, Gentleman, do hereby declare the nature of this invention (which has been communicated to me from abroad by I. G. Farbenindustrie Aktiengesellschaft, of Frankfort-on-Main, Germany, a Joint Stock Company, organized under the Laws of Germany) to be as follows:—

In the preparation of liquid hydrocarbons by the conversion of products obtained by the reduction of carbon monoxide with hydrogen, as for example by cracking or destructive hydrogenation or dehydrogenation, a marked formation of undesirable low molecular, in particular gaseous, hydrocarbons takes place when working in the gaseous or vaporous phase and when using very active catalysts. This formation of gas reduces the yield of the desired products and is therefore undesirable in most cases.

My foreign correspondents have now found that in the treatment of liquid carbon monoxide reduction products by said reactions in the gas or vapour phase the formation of undesirable low molecular hydrocarbons can be reduced considerably by adding cyclic hydrocarbons boiling within the boiling point range of middle oils, which under the reaction conditions are at least partly vaporous.

Both aromatic hydrocarbons and naphthenes may be used. The most suitable cyclic hydrocarbons are naphthalene or its homologues or mineral coal tar middle oil or middle oil from the destructive hydrogenation of mineral coal.

The said cyclic hydrocarbons are generally speaking added in amounts of between 10 and 60 per cent. by weight with reference to the initial products. The amount to be added in individual cases depends in particular on the nature of the reaction, on the activity of the catalyst and on the nature of the additional substance. The amounts added are greater in the case of catalysts which tend strongly to form gas than in the case of catalysts having this tendency to a lesser degree.

The cyclic hydrocarbons may be added continuously or at intervals. In the latter case the addition is preferably made when the formation of undesirable low molecular hydrocarbons begins to exceed the allowable degree, which may become evident by the occurrence of great evolution of heat. The additions may also be made at equal intervals of time. When adding the additional substances continuously, the amount added may be constant or variable. The cyclic hydrocarbons may also be added at several places in the reaction chamber. The catalyst may also be laden with cyclic hydrocarbons before use.

The conversion to which the above-mentioned products obtained by the interaction of carbon monoxide and hydrogen may be subjected according to the present invention are in particular the destructive hydrogenation, the cracking and the dehydrogenation, preferably in the presence of added hydrogen. The process is of great advantage in the destructive hydrogenation in the presence of catalysts having a strong splitting action. Among such catalysts there may be mentioned, for example, oxides and sulphides of the metals of the 5th to the 7th groups of the periodic system and the iron group as well as mixtures containing the same. In the cracking process advantageously activated hydrosilicates, such as bleaching earths or also alumina, magnesia, active carbon, lignite small coke, or oxides of chromium, molybdenum, tungsten, manganese, iron, nickel, cobalt or titanium or mixtures of these substances are employed.

In the dehydrogenation of the said carbon monoxide reduction products in the presence of hydrogen, the process has the advantage that the partial splitting into low molecular hydrocarbons which is unavoidable in most cases is considerably reduced.

The said reactions are carried out under known conditions, the destructive hydro-

[*Price* 1/-]

genation at temperatures between 250° and 600° Centigrade and under increased pressures, advantageously of more than 20 atmospheres, the cracking at temperatures between 300° and 700°, advantageously between 300° and 550° Centigrade and at atmospheric or preferably at increased pressure (as for example 20 to 200 atmospheres or more), and the dehydrogenation at temperatures between 400° and 600° Centigrade.

The other conditions, such as time of treatment, relative proportions of the reactants and the like are also as usual. The cracking may be carried out in the presence of gases, such as hydrogen, carbon monoxide, carbon dioxide, methane, ethane, propane or ethylene, propylene or butylene, which have preferably been previously heated to the temperatures used in the cracking or to still higher temperatures.

Dated this 22nd day of July, 1939.

J. Y. & G. W. JOHNSON,
47, Lincoln's Inn Fields, London, W.C.2,
Agents.

COMPLETE SPECIFICATION

Improvements in the Manufacture and Production of Liquid Hydrocarbons

I, GEORGE WILLIAM JOHNSON, a British Subject, of 47, Lincoln's Inn Fields, in the County of London, Gentleman, do hereby declare the nature of this invention (which has been communicated to me from abroad by I. G. Farbenindustrie Aktiengesellschaft, of Frankfort-on-Main, Germany, a Joint Stock Company, organized under the Laws of Germany), and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

In the preparation of liquid hydrocarbons by the conversion of products obtained by the reduction of carbon monoxide with hydrogen, as for example by cracking or destructive hydrogenation or dehydrogenation, a marked formation of undesirable low molecular, in particular gaseous, hydrocarbons takes place when working in the gaseous or vaporous phase and when using very active catalysts. This formation of gas reduces the yield of the desired products and is therefore undesirable in most cases.

My foreign correspondents have now found that in the treatment of liquid carbon monoxide reduction products by said reactions in the gas or vapour phase the formation of undesirable low molecular hydrocarbons can be reduced considerably by adding cyclic hydrocarbons boiling within the boiling point range of middle oils, which under the reaction conditions are at least partly vaporous.

Both aromatic hydrocarbons and naphthenes may be used. The most suitable cyclic hydrocarbons are naphthalene or its homologues or mineral coal tar middle oil or middle oil from the destructive hydrogenation of mineral coal.

The said cyclic hydrocarbons are generally speaking added in amounts of between 10 and 60 per cent. by weight with reference to the initial products. The amount to be added in individual cases depends in particular on the nature of the reaction, on the activity of the catalyst and on the nature of the additional substance. The amounts added are greater in the case of catalysts which tend strongly to form gas than in the case of catalysts having this tendency to a lesser degree.

The cyclic hydrocarbons may be added continuously or at intervals. In the latter case the addition is preferably made when the formation of undesirable low molecular hydrocarbons begins to exceed the allowable degree, which may become evident by the occurrence of great evolution of heat. The additions may also be made at equal intervals of time. When adding the additional substances continuously, the amount added may be constant or variable. The cyclic hydrocarbons may also be added at several places in the reaction chamber. The catalyst may also be laden with cyclic hydrocarbons before use.

The conversion to which the above-mentioned products obtained by the interaction of carbon monoxide and hydrogen may be subjected according to the present invention are in particular the destructive hydrogenation, the cracking and the dehydrogenation, preferably in the presence of added hydrogen. The process is of great advantage in the destructive hydrogenation in the presence of catalysts having a strong splitting action. Among such catalysts there may be mentioned, for example, oxides and sulphides of the metals of the 5th to the 7th groups of the periodic system and the iron group as well as mixtures containing the same. In the cracking process advantageously activated hydrosilicates, such as bleaching earths or also alumina, magnesia, active carbon, lignite small coke, or oxides of chromium, molybdenum, tungsten, manganese, iron, nickel, cobalt or titanium or mixtures of these substances are employed.

In the dehydrogenation of the said carbon monoxide reduction products in the presence of hydrogen, the process has the advantage that the partial splitting into low molecular hydrocarbons which is unavoidable in most cases is considerably reduced.

The said reactions are carried out under known conditions, the destructive hydrogenation at temperatures between 250° and 600° Centigrade and under increased pressures, advantageously of more than 20 atmospheres, the cracking at temperatures between 300° and 700°, advantageously between 300° and 550° Centigrade and at atmospheric or preferably at increased pressure (as for example 20 to 200 atmospheres or more), and the dehydrogenation at temperatures between 400° and 600° Centigrade.

The other conditions, such as time of treatment, relative proportions of the reactants and the like are also as usual. The cracking may be carried out in the presence of gases, such as hydrogen, carbon monoxide, carbon dioxide, methane, ethane, propane or ethylene, propylene or butylene, which have preferably been previously heated to the temperatures used in the cracking or to still higher temperatures.

I am aware of Specification No. 505,953, in which a process has been described and claimed for the manufacture and production of high quality benzine and Diesel motor fuels by hydrogenation from tars which have been prepared by carbonisation which consists in separating the tar constituents by mixing with middle oils obtained by the reduction of carbon monoxide with hydrogen into two components of different specific gravity, the lighter component being subjected to hydrogenation in the gas phase, together with at least a part of the said middle oils, and the heavier component subjected to hydrogenation in the liquid phase, and I do not claim anything claimed in the said specification.

Having now particularly described and ascertained the nature of my said invention, and in what manner the same is to be performed, I declare that what I claim is:—

1. A process for the production of valuable liquid hydrocarbons from liquid carbon monoxide reduction products by catalytic treatment in the vaporous phase, preferably in the presence of hydrogen, in particular by destructive hydrogenation, cracking or dehydrogenation of the said products, which comprises working with an addition of cyclic hydrocarbons boiling within the boiling point range of middle oils, which under the reaction conditions are at least partly vaporous.

2. In the process as claimed in claim 1, adding the cyclic hydrocarbons after intervals, particularly at moments when the formation of low boiling hydrocarbons becomes undesirably large.

3. In the process claimed in claim 1, adding the cyclic hydrocarbons continuously.

4. In the process as claimed in claims 1 to 3, adding the cyclic hydrocarbons while varying the amount of the additions.

5. In the process as claimed in any of claims 1 to 4, adding the cyclic hydrocarbons at several points of the reaction space.

6. Liquid hydrocarbons when prepared by the process particularly described and ascertained.

Dated this 22nd day of July, 1939.
J. Y. & G. W. JOHNSON,
47, Lincoln's Inn Fields, London, W.C.2,
Agents.

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