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PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION
No. 21679 A.D. 1938.

Improvements in the Catalytic Cracking of 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 organised under the Laws of Germany) to be as follows:—

My foreign correspondents have found that in the cracking of hydrocarbons by leading the same in the vapour phase over rigidly arranged catalysts, the yield of non-knocking motor fuels can be increased and the nature of the products improved by increasing the pressure in the reaction zone in such a manner that the pressure increase is at least 10 atmospheres and preferably 20 atmospheres or more. By working in this way motor fuels are obtained having a high non-knocking value, high sensitivity to lead and which generally speaking require no subsequent refining.

As initial materials there may be mentioned in particular hydrocarbons rich in hydrogen, in particular heavy benzines or middle oils. The hydrocarbon mixtures obtained by the reduction of carbon monoxide may be used with advantage. Hydrocarbons rich in hydrogen may also be worked up in admixture with hydrocarbons poorer in hydrogen, in particular aromatic hydrocarbons.

The process, for which generally speaking temperatures of from 400° to 700° Centigrade are used, may be carried out for example by increasing the pressure in the whole reaction chamber during the reaction, for example during from about 1 to 5 hours by the amount specified above, the initial pressure being for example within the range of 1 to 100 atmospheres, 200 or even 500 atmospheres. Generally speaking the pressure is always increased when the activity of the catalyst commences to subside or short before this point of time. If no satisfactory activity of the catalyst can be obtained by a further increase in pressure, the catalyst must be replaced or regenerated and working at the lower pressure recommenced. The intervals of time at which the catalyst is replaced or regenerated may, however, be chosen shorter.

As catalysts there may be mentioned substances promoting cracking, as for example natural or synthetic aluminium silicates, which if desired may be pretreated with acids, or alumina, active carbons, if desired together with the oxides of chromium, molybdenum, tungsten or manganese, or the oxides of magnesium, zinc, manganese or mixtures of these oxides, as for example the oxides of aluminium and chromium. The said metal oxides may also be used alone. Catalysts containing silicic acid and magnesia are especially suitable.

The reaction zone may be provided with catalysts of different cracking action. The used catalysts are preferably regenerated first with hydrogen and then with gases containing oxygen, for example with gradually increasing oxygen content, at increasing temperature and then used again, if desired in admixture with fresh catalyst.

The following Example will further illustrate the nature of this invention but the invention is not restricted to this Example.

EXAMPLE.

Paraffinic middle oil (boiling limits 210° to 340° Centigrade) is led at 460° Centigrade through a reaction chamber filled with pieces of bleaching earth, a throughput of 0.5 litre of oil per litre of catalyst per hour being chosen. The pressure in the reaction chamber is increased gradually to 30 atmospheres during the course of 90 minutes. The reaction product is cooled, first with water and then with solid carbon dioxide. The non-condensed portion (permanent gases) is collected in a gas holder. The condensate

[*Price* 1/-]

separated by water cooling contains 35 per cent. by weight of benzine (boiling up to 200° Centigrade). This is colourless, has an iodine value of 37, an aniline point of 62°, an octane number of 64 and, after the addition of 0.09 per cent. by volume of lead tetra-ethyl, an octane number of 82.

By working under otherwise identical reaction conditions but without increasing the pressure gradually, the operation must be interrupted after about an hour by reason of the strong falling off of the activity of the catalyst. A condensate is obtained containing only 24 per cent. by weight of benzine. This is yellow, has an iodine value of 136, an aniline point of 52°, an octane number of 64 which, after the addition of 0.09 per cent. by volume of lead tetra-ethyl, rises to 76.

Dated this 21st day of July, 1938.

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

PROVISIONAL SPECIFICATION

No. 23365 A.D. 1938.

Improvements in the Production of Non-knocking Fuels by Cracking Hydrocarbon Oils

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 organised under the Laws of Germany) to be as follows:—

My foreign correspondents have found that in the cracking of hydrocarbon oils, the initial materials flowing through the reaction zone, as for example being led in the vapour phase over rigidly arranged catalysts, the yield of non-knocking fuels is increased and the nature of the products can be improved by increasing both the pressure and the temperature in the reaction zone in such manner that the pressure difference is at least 5 atmospheres, preferably 10 atmospheres or more, and the temperature difference is at least 10° Centigrade. By working in this manner fuels are obtained having a high non-knocking value, high sensitiveness to lead and which generally speaking do not require subsequent refining.

As initial materials there may be mentioned in particular hydrocarbons rich in hydrogen and capable of being vaporised under the reaction conditions from petroleums, destructive hydrogenation products and the like, in particular heavy benzines or middle oils. The hydrocarbon mixtures obtained by the reduction of carbon monoxide may be used with advantage. Hydrocarbons rich in hydrogen may also be worked up in admixture with hydrocarbons poorer in hydrogen, in particular aromatic hydrocarbons.

The process is carried out for example by increasing the pressure in the reaction chamber during the reaction, for example during from about 1 to 5 hours, by the amount specified above, the initial pressure being for example within the range of 1 to 100 atmospheres or more, as for example from 200 to 300 atmospheres. Generally speaking the pressure is always increased when the activity of the catalyst begins to subside or shortly before this time. When a sufficient activity of the catalyst can no longer be obtained by a further increase in pressure, the catalyst is renewed or regenerated and working at lower pressure again commenced. Temperatures between 400° and 700° Centigrade may be used. The increase in temperature usually amounts to from 10° to 100° Centigrade, preferably from 15° to 50° Centigrade. The temperature may be raised either continuously or at intervals within the whole cracking zone up to the point in time at which the catalyst is renewed or regenerated.

As catalysts, which are preferably rigidly arranged in the reaction chamber, there may be mentioned substances promoting the cracking reaction, as for example natural or synthetic aluminium silicates, which if desired may be pretreated with acids, and also aluminas or active carbons, if desired together with oxides of chromium, molybdenum, tungsten, manganese, magnesium and zinc, as for example alumina together with chromium oxide, or mixtures of the said oxides. The said metal oxides may also be used alone.

The reaction zones may be provided with catalysts having different cracking action. The used catalysts are preferably regenerated first with hydrogen and then with gases containing oxygen, as for example with gradually increasing oxygen content, at increasing temperature and then used again, if desired in admixture with fresh catalyst.

The following Example will further illustrate the nature of this invention but the invention is not restricted to this Example.

EXAMPLE.

Paraffinic middle oil (boiling range 210° to 340° Centigrade) is led at an initial temperature of 460° Centigrade through a reaction chamber filled with pieces of bleaching earth, the throughput being 0.5 litre of oil per litre of catalyst per hour. The pressure in the reaction chamber is increased gradually during the course of 1½ hours to 30 atmospheres and the temperature to 480° Centigrade. The reaction product is cooled first with water and then with solid carbon dioxide. The uncondensed portion (permanent gases) are collected in a gasometer. The condensate separated by water cooling contains 40 per cent. by weight of benzine (boiling up to 200° Centigrade). This is colourless, has an iodine value of 37, an aniline point of 62° Centigrade, an octane number of 64 and, after the addition of 0.09 per cent. by volume of lead tetraethyl, an octane number of 82.

Dated this 8th day of August, 1938.

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

COMPLETE SPECIFICATION

Improvements in the Catalytic Cracking of 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:—

My foreign correspondents have found that in the cracking of hydrocarbon oils, the initial materials flowing at a cracking temperature through the reaction zone containing a cracking catalyst, as for example being led in the vapour phase over rigidly arranged catalysts, the yield of non-knocking fuels is increased and the nature of the products can be improved by increasing the pressure and if desired also the temperature in the reaction zone in such a manner that the pressure increase is at least 5 atmospheres, preferably 10 atmospheres or more, while the cracking catalyst is acting on the initial material. The temperature difference may be at least 10° Centigrade. The pressure and the temperature may be raised continuously or stepwise. The pressure in the reaction zone may be regulated by means of appropriate valves. By working in this manner fuels are obtained having a high non-knocking value, high sensitiveness to lead and which generally speaking do not require subsequent refining.

A convenient method of producing a stepwise increase in pressure in the reaction chamber is to increase from time to time the pressure at which the feed is introduced into the reaction vessel. Stepwise increase in temperature may be effected by the provision of heating elements within the reaction chamber which can be supplied from time to time with heating medium to raise the temperature to any desired degree.

As initial materials there may be mentioned in particular hydrocarbons rich in hydrogen and capable of being vaporised under the reaction conditions from petroleums, destructive hydrogenation products and the like, in particular heavy benzines or middle oils. The hydrocarbon mixtures obtained by the reduction of carbon monoxide may be used with advantage. Hydrocarbons rich in hydrogen may also be worked up in admixture with hydrocarbons poorer in hydrogen, in particular aromatic hydrocarbons.

The process is carried out for example by increasing the pressure in the whole reaction chamber during the reaction, for example during from about 1 to 5 hours, by the amount specified above, the initial pressure being for example within the range of 1 to 100 atmospheres or more, as for example from 200 to 500 atmospheres. Generally speaking the pressure is always increased when the activity of the catalyst begins to subside or shortly before this time. When a sufficient activity of the catalyst can no longer be obtained by a further increase in pressure, the catalyst is renewed or regenerated and working at lower pressure again commenced. Temperatures between 400° and 700° Centigrade may be used. The increase in temperature, if desired at all, usually amounts to from 10° to 100° Centigrade, preferably from 15° to 50° Centigrade. The temperature may be raised either continuously or at intervals within the whole cracking zone up to the point in time at which the catalyst is renewed or regenerated.

As catalysts, which are preferably rigidly arranged in the reaction chamber, there may be mentioned substances promoting the cracking, as for example natural or synthetic aluminium silicates, which if desired may be pretreated with acids, and also aluminas or active carbons, if desired together with the oxides of chromium, molybdenum, tungsten, manganese, magnesium and zinc, as for example alumina together with chromium oxide, or mixtures of the said oxides. The said metal oxides may also be used alone.

The reaction zone may be provided with catalysts having different cracking action. The used catalysts are preferably regenerated first with hydrogen and then with gases containing oxygen, as for example with gradually increasing oxygen content, at increasing temperature and then used again, if desired in admixture with fresh catalyst.

The following Examples will further illustrate how the said invention may be carried out in practice but the invention is not restricted to these Examples.

EXAMPLE 1.

Paraffinic middle oil (boiling limits 210° to 340° Centigrade) is fed at 460° Centigrade and at an initial pressure of 1 atmosphere into a reaction chamber filled with pieces of bleaching earth, a throughput of 0.5 litre of oil per litre of catalyst per hour being chosen. The pressure in the reaction chamber is increased gradually to 30 atmospheres during the course of 90 minutes. The reaction product is cooled, first with water and then with solid carbon dioxide. The non-condensed portion (permanent gases) is collected in a gas holder. The condensate separated by water cooling contains 35 per cent. by weight of benzine (boiling up to 200° Centigrade). This is colourless, has an iodine value of 37, an aniline point of 62°, an octane number of 64 and, after the addition of 0.09 per cent. by volume of lead tetra-ethyl, an octane number of 82.

By working under otherwise identical reaction conditions but without increasing the pressure gradually, the operation must be interrupted after about an hour by reason of the strong falling off of the activity of the catalyst. A condensate is obtained containing only 24 per cent. by weight of benzine. This is yellow, has an iodine value of 136, an aniline point of 52°, an octane number of 64 which, after the addition of 0.09 per cent. by volume of lead tetra-ethyl, rises to 76.

EXAMPLE 2.

Paraffinic middle oil (boiling range 210° to 340° Centigrade) is fed at an initial temperature of 460° Centigrade and at an initial pressure of 1 atmosphere into a reaction chamber filled with pieces of bleaching earth, the throughput being 0.5 litre of oil per litre of catalyst per hour. The pressure in the reaction chamber is increased gradually during the course of 1½ hours to 30 atmospheres and the temperature to 480° Centigrade. The reaction product is cooled first with water and then with solid carbon dioxide. The uncondensed portions (permanent gases) are collected in a gasometer. The condensate separated by water cooling contains 40 per cent. by weight of benzine (boiling up to 200° Centigrade). This is colourless, has an iodine value of 37, an aniline point of 62° Centigrade, an octane number of 64 and, after the addition of 0.09 per cent. by volume of lead tetra-ethyl, an octane number of 82.

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 a non-knocking motor fuel by cracking a hydrocarbon oil, especially a heavy benzine or middle oil which may be obtained by the reduction of carbon monoxide, which comprises passing the hydrocarbon oil in the liquid or vapour phase at a cracking temperature and at an initial pressure of 1 to 100 atmospheres through a reaction zone containing a cracking catalyst and increasing the pressure in the reaction zone continuously or stepwise by at least 5 atmospheres, preferably 10 atmospheres or more, while the catalyst is acting on the hydrocarbon oil without interruption of the process.

2. In the process as claimed in claim 1, also increasing the temperature in the reaction zone by at least 10° Centigrade, while the catalyst is acting on the hydrocarbon oil.

3. The process for the production of valuable non-knocking motor fuels substantially as described in each of the foregoing Examples.

4. Valuable non-knocking motor fuels when prepared by the process particularly described and ascertained.

Dated this 3rd day of July, 1939.

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

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