PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION

A Process for Improving the Products of the Synthesis of Hydrocarbon Oils from Carbon Monoxide and Hydrogen

We, SYNTHETIC OILS LIMITED, a British Company, of 31, East Street, Epsom, in the county of Surrey, and WILLIAM WHALLEY MYDDLETON, a British subject, of 3, Woodlands Avenue, New Malden, in the county of Surrey, do hereby declare the nature of this invention to be as follows:—

This invention relates to the synthesis of hydrocarbons from carbon monoxide and hydrogen and has for its object to improve the fraction of the synthetic product useful as Diesel oil.

It is known that various devices can be employed to improve the anti-detonatory properties of the motor spirit fraction of the hydrocarbon oils synthesised from gaseous mixtures containing carbon monoxide and hydrogen.

Amongst the methods employed to this end may be the use of a gaseous mixture containing carbon monoxide and hydrogen in a ratio between 1:1 and 1:1.5 by volume.

Blue water gas is a suitable industrial gas for the purpose.

It has been found however that although the octane number of the motor spirit fraction is in this case better than is obtained from an initial gas containing carbon monoxide and hydrogen in the ratio 1:2 by volume the Diesel oil fraction of the product is not so good with reference to cetene number, although the cetene number is higher than Diesel oils prepared from natural hydrocarbon oils.

It is the specific object of this invention to improve the cetene number of the Diesel oil fraction of the synthetic hydrocarbon oil produced by synthesis from an industrial gas containing a ratio of carbon monoxide and hydrogen between 1:1 and 1:1.5.

The invention is carried out by taking that fraction of the synthetic product which distils between 180° and 330° C. or other limits which are near these points, the limits being actually defined by the limits imposed from time to time by the volatility requirements of the Diesel engine.

This fraction is then re-admitted to the catalyst chamber in which it was synthesised or passed into a separate vessel charged with the catalyst employed in synthesising hydrocarbon oils. The catalyst chamber is maintained either at the synthesising temperature or at a temperature not higher than 20° C. above that point.

A gas containing hydrogen which may be blue water gas, coke oven gas or hydrogen is admitted along with the oil.

A convenient oil flow is found to be four litres per litre of catalyst space per hour and a suitable gas flow is one hundred litres per litre of catalyst space per hour.

It has been found that the oil which leaves the catalyst chamber after this treatment may contain further products of synthesis from carbon monoxide and hydrogen present in the gas admitted with it. In such a case the improved Diesel oil must be separated by fractionally distilling the liquid products recovered.

Dated this 31st day of August, 1938.

A. A. THORNTON,
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COMPLETE SPECIFICATION

A Process for Improving the Products of the Synthesis of Hydrocarbon Oils from Carbon Monoxide and Hydrogen

We, SYNTHETIC OILS LIMITED, a British Company, of 31, East Street, Epsom, in the county of Surrey, and WILLIAM WHALLEY MYDDLETON, a British subject, of 3, Woodlands Avenue, New Malden, in the county of Surrey, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the synthesis of hydrocarbon oils from carbon monoxide

and hydrogen and has for its object to improve the properties of certain fractions of the synthetic product.

It is known that various expedients may be employed to improve the anti-detonatory properties of the motor spirit fraction of hydrocarbon oils synthesised from gaseous mixtures containing carbon monoxide and hydrogen.

To this end it has been proposed to use a gaseous mixture containing carbon monoxide and hydrogen in a ratio of between 1:1 and 1:1.5 by volume.

Blue water gas is a suitable industrial gas for this purpose.

It has been found however that although the octane value of the motor spirit fraction is in this case better than that of the corresponding fraction obtained from an initial gas mixture containing carbon monoxide and hydrogen in the ratio of 1:2 by volume, the fractions of the product heavier than those useful as motor spirit, and up to those in which the lubricating oils predominate, and particularly the fractions useful as Diesel oils and passing over between about 180° C. and 330° C., are inferior with reference to cetene value and other properties, although the cetene number of these Diesel oils is higher than that of Diesel oils prepared from natural hydrocarbon oils.

It has been proposed to exert a refining and improving action upon saturated or weakly unsaturated hydrocarbon oils of mineral origin by subjecting them to a treatment with hydrogen in the presence of a carrier-catalyser, the improvement achieved being attributed to the use of this particular kind of catalyser and being chiefly in the direction of eliminating colour and odour.

It has also been proposed to subject hydrocarbon oil products obtained from tars and the like, from which aromatic constituents have first been removed by selective extraction, to a refining treatment by the action of reducing gas such as hydrogen, carbon monoxide or mixtures thereof, preferably in the presence of a catalyst, for the purpose of eliminating non-hydrocarbon impurities and improving the physical properties generally of the products.

It has further been proposed to convert unsaturated constituents or crude hydrocarbon oil mixtures of mineral origin into saturated, without separation of the constituents, by hydrogenation treatment in the presence of hydrogenating catalysts generally, at a temperature not in excess of 200° C.

In these and other proposed methods of treating or refining hydrocarbon oils and mixtures thereof, it has also variously been proposed to divide a hydrocarbon product into high and lower boiling fractions, treating only one of such fractions with hydrogen and then combining the fractions. This applies more particularly to motor fuel oils, and the fraction to be treated has generally been a higher boiling fraction.

We are aware of these prior proposals, and we make no claim to any of these methods or to the application of hydrogenation treatment of hydrocarbon oils in general.

It is the specific object of this invention to improve the properties of those fractions of composite hydrocarbon oil produced by synthesis from a gas mixture containing carbon monoxide and hydrogen in a volumetric ratio of between 1:1 and 1:1.5, which are useful as Diesel oils, so as to make up for the unequal gain otherwise achieved over the range of products obtainable from catalyzed synthesis of hydrocarbon oils in the gas phase by adjusting the ratio of $CO:H_2$ in the reacted gaseous mixture to between 1:1 and 1:1.5.

With this object in view, the invention consists in an improved process for the production of hydrocarbon oils from carbon monoxide and hydrogen of the kind in which a gaseous mixture containing carbon monoxide and hydrogen in a ratio of between 1:1 and 1:1.5 by volume is subjected to a catalyzed synthesizing reaction in conventional working conditions, wherein of the product of said reaction a fraction which boils predominantly between the limits of 180° and 330° C., useful as a Diesel oil, is segregated and treated by reaction, in the presence of a hydrogenating catalyst, with further hydrogen or gas containing hydrogen, in conditions similar to those employed in said first synthesizing reaction.

The working conditions and the catalysts used are those employed in any known process for the synthetic production of hydrocarbons from a gaseous starting mixture containing carbon monoxide and hydrogen in a volumetric ratio of between 1:1 and 1:1.5, such as for instance that described in British Patent No. 491,778.

The described improving treatment, which is presumed to be due, at least in part, to the addition of hydrogen to unsaturated constituents (such as olefines) of the fractions treated, has the incidental advantage, when carried out in the synthesizing plant, of serving to dislodge waxy constituents deposited on the catalyst in a preceding synthesizing run.

Generally speaking, the results ob-

tained, as regards improvement of cetene value, are less pronounced with higher than with lower boiling fractions, and for this reason it is preferable to subject only a lower boiling sub-fraction of a Diesel oil covering a boiling point range having a high upper limit, and then to add this treated sub-fraction to the untreated portion of the original fraction, in order to obtain the desired improvement as economically as possible.

The actual limits of the fractions useful as Diesel oils, and especially the upper limit, will normally depend on the volatility and other requirements of the engines in which they are to be used, but will not exceed appreciably the relatively extreme values specified.

The invention may for instance be carried out by taking the whole fraction of the product of a synthesizing reaction of the kind indicated which distils between 180° and 330° C., and re-admitting this fraction to the reaction chamber containing a hydrogenation catalyst in which it was originally synthesized or passing the same into a separate vessel charged with a hydrogenating catalyst of a kind employed in such synthesizing reaction. The said chamber or vessel is maintained substantially at the temperature normally employed in the synthetic production of hydrocarbon oils from gaseous mixtures containing carbon monoxide and hydrogen in a volumetric ratio of between 1:1 and 1:1.5 or at a temperature not higher than 20° C. above that point.

Hydrogen or a gas containing hydrogen, which may be blue water gas or coke oven gas, is admitted to the reaction chamber along with the oil.

As a further example of the operation of the invention, assuming it is desired to improve a Diesel oil distilling between 200° C. and 330° C. or thereabouts, the oil is first separated into two sub-fractions a lower distilling between 200° C. and, say, 250° C. and a higher distilling between, say, 250° C. and 330° C. or thereabouts. The lower boiling sub-fraction is re-admitted to the catalyst chamber together with hydrogen or gas containing hydrogen. After re-distillation the recovered oil is added to the higher boiling sub-fraction, which results in the production of a Diesel oil having a more satisfactory cetene number.

A convenient oil flow is found to be four litres per litre of catalyst space per hour and a suitable gas flow is one hundred litres per litre of catalyst space per hour.

It has been found that the oil which leaves the catalyst chamber after this treatment may contain further products of synthesis from carbon monoxide and hydrogen present in the gas admitted with it. In this case the treated fraction is separated from such concomitant products by fractionally distilling the liquid recovered.

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

1. An improved process for the production of hydrocarbon oils from carbon monoxide and hydrogen of the kind in which a gaseous mixture containing carbon monoxide and hydrogen in a ratio of between 1:1 and 1:1.5 by volume is subjected to a catalysed synthesizing reaction in conventional working conditions, wherein of the product of said reaction a fraction which boils predominantly between the limits of 180° and 330° C., useful as a Diesel oil, is segregated and treated by reaction, in the presence of a hydrogenating catalyst, with further hydrogen or gas containing hydrogen, in conditions similar to those employed in said first synthesizing reaction.

2. A process according to claim 1, wherein only a lower boiling sub-fraction of said fraction is re-subjected to the synthesizing hydrogenation reaction after which the product of this second reaction is mixed with the higher boiling sub-fraction, to yield a hydrocarbon oil of improved properties.

3. A process according to claim 1 or 2, wherein the temperature maintained during the re-hydrogenation treatment is higher but not more than 20° C. higher than that at which the original synthesizing reaction proceeds.

4. A process according to claim 2, wherein said fraction is a Diesel fuel oil with a high boiling point upper limit, and said lower boiling sub-fraction thereof is a fraction distilling over at or below 250° C.

5. A process according to claim 1, 2, 3 or 4, wherein the treated fraction or sub-fraction is re-fractionated after treatment, to effect separation from concomitant products of the reaction involved in this treatment.

6. Hydrocarbon oils when produced according to the process hereinbefore specified.

Dated this 19th day of August, 1939.

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For the Applicants.

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