[Third Edition.]

PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION

An Improved Process for the Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen.

We, SYNTHETIC OILS LIMITED, formerly known as Robinson Bindley Processes Limited, a British Company of 31, East Street, Epsom, Surrey, and WILLIAM WHALLEY MYDDLETON, a British Subject, of Warrendale, Combe Lane, Kingston-on-Thames, Surrey, do hereby declare the nature of this invention to be as follows :—

This invention relates to the production of anti-detonatory motor spirit, kerosene lubricating oil, Diesel oil, paraffin wax and the like from hydrocarbon oils which have been produced by catalytic synthesis from carbon monoxide and hydrogen.

According to our invention the high anti-detonating motor spirit and at the same time the valuable solvent oils, kerosene and lubricating oils are produced by the following process.

A gas is employed containing a carbon monoxide-hydrogen ratio between 1 : 2 and 1 : 1. The catalyst used contains preferably cobalt, but may contain nickel, provided that the synthesis is conducted in two or more stages, the liquid products being removed by cooling or otherwise between the stages. The whole of the oil formed or any desired fraction thereof is subjected to further treatment.

The further treatment referred to is a process of vapour phase hydrogenation. The hydrogenation vessel which forms a part of the complete plant contains a catalyst containing nickel or other hydrogenation catalyst. The hydrogenation is effected by vapourising the desired fraction of the total oil and passing the vapour together with hydrogen or gas containing hydrogen through a bed of the catalyst at a temperature in excess of 120° C. and under suitable pressures varying from atmospheric to several atmospheres.

The oil is thus readily hydrogenated, and is ready for physical separation into solvents or kerosenes of any desired range of volatility.

Dated this 8th day of December, 1936.

A. A. THORNTON,
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For the Applicants.

COMPLETE SPECIFICATION.

An Improved Process for the Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen.

We, SYNTHETIC OILS LIMITED, a British Company, of 31, East Street, Epsom, Surrey, and WILLIAM WHALLEY MYDDLETON, a British Subject, of Warrendale, Combe Lane, Kingston-on-Thames, 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 :—

Our invention relates to processes in which gases or vapours containing hydrogen and the oxides of carbon are reacted by catalytic means to produce gasoline, kerosene, Diesel oil, solvent oils, waxes and other hydrocarbons.

In processes for the production of hydrocarbons by the reaction, in the presence of a catalyst, of gaseous mixtures containing hydrogen and the oxides of carbon, the principal products of the reaction are normally liquid hydrocarbons. Gaseous and solid hydrocarbons are also usually produced simultaneously with the liquid. The gaseous and liquid hydrocarbons, at least, consist of both saturated paraffinic and olefinic compounds. The value of each of these products is dependent on its physical properties and chemical composition.

While the exact mechanism of such synthesis is not known, the general reaction is written as follows :—

$$(CO + 2H_2)_n = (CH_2)_n + {}^n(H_2O + 48 \text{ K. cal.})$$

Under the physical conditions which govern such synthesis reactions the normally liquid product is of the nature of a synthetic crude oil having specific properties determined by the major variables of the process which distinguish it from

[*Price* 1*s.*]

other synthetic or naturally occurring crude oils. Such products or fractions thereof may be processed subsequently to produce the desired products of greatest value. The usual subsequent treatment has consisted of distillation and fractionation of the crude product according to the boiling point of the compounds present into motor fuels, burning oils such as kerosene, light fuel oils, gas oils and Diesel oils, lubricating oils base stocks and waxes.

It has been suggested to increase the yield of synthetically produced aliphatic hydrocarbons having more than one carbon atom in the molecule, more particularly liquid hydrocarbons, from the oxides of carbon and hydrogen by the use of catalysts at ordinary or slightly increased or reduced pressure and at temperatures within the range of 180° C. to 200° C. by taking gaseous mixtures of carbon monoxide and hydrogen, which contain not less hydrogen than carbon monoxide and, in the first instance, only partly converting and then, after removing the condensible reaction products, subjecting the unconverted gases to further conversion, additional gas capable of reacting being added if required to effect this second conversion.

It has also been suggested to subject the whole of the hydrocarbons obtained from a mixture of $CO + H_2$ such as water gas, by a synthesis reaction to hydrogenation.

The present invention involves processing by two treatments the first of which is a synthesis treatment, which may be carried out in one or more stages, and the second a hydrogenation of the higher boiling point fractions of the synthesis product. The characteristics of the process are the use of gaseous carbon monoxide and hydrogen mixtures in which the carbon monoxide-hydrogen ratio is between 1 : 2 and 1 : 1 by volume the preferred ratio being, in fact, 1 : 1.17, separating out the motor fuel—the products boiling below 150° C.—from the liquid products of the synthesis from the products boiling above the motor fuel range, and then submitting the higher boiling point fraction to hydrogenation in the presence of a suitable catalyst and separating this second product into solvents, kerosenes, Diesel and lubricating oils as desired.

The invention therefore consists of a process for simultaneously producing by catalytic synthesis an anti-knock motor fuel and hydrocarbon oils boiling above the motor fuel range and adapted to be used as solvents, kerosenes, Diesel oils and lubricants, according to which a gaseous mixture of carbon monoxide and hydrogen in a ratio between 1 : 2 and 1 : 1 by volume is passed in contact with a catalyst containing cobalt or nickel under pressure not exceeding 3 atmospheres and at a temperature in the region of 200° C. and from the liquid products thereby produced the motor fuel is separated from the product boiling above the motor fuel range and the higher boiling point fraction—that is the fraction boiling above 150° C.—is then submitted to hydrogenation treatment at atmospheric or increased pressure in the presence of a hydrogenation catalyst at a temperature above 120° C. and this hydrogenation product is then subjected to fractionation and the parts thereof suitable for use as solvents, kerosenes, Diesel oils and the like separated for use.

The invention further comprises the use in the first conversion or synthesis process of a gaseous mixture having a carbon monoxide-hydrogen ratio of 1 : 1.17 and the invention further comprises the vaporisation of that part of the reaction product of this first conversion or synthesis boiling above 150° C. and the hydrogenation of this higher boiling point fraction in vapour phase.

In carrying out the invention a gas is employed containing a carbon monoxide-hydrogen ratio between 1 : 2 and 1 : 1, as before indicated. The catalysts used for the first conversion or synthesis process contain nickel or cobalt and the synthesis is conducted in one, two or more stages, the liquid products being removed by cooling or otherwise between the stages where this first conversion is effected in more than one stage. For example, experiment has shown that a gaseous mixture composed of 48% hydrogen; 41% carbon monoxide, and 11% other gases, such as carbon dioxide, nitrogen and water vapour, all on a volume basis, passed at 202° C. and substantially atmospheric pressure, over a catalyst composed of nickel and the oxides of manganese and aluminium with Kieselguhr yields 109 grams of total product per cubic meter of inlet gases when the process is carried out in one stage.

The second treatment—that is the treatment of the product derived from the first or synthesis treatment—is a process of hydrogenation over a suitable catalyst in the presence of hydrogen or hydrogen containing gases, and this hydrogenation treatment may be effected in the vapour phase any suitable hydrogenating catalyst being employed, but preferably one, for example, containing nickel, manganese and aluminium together with silica, obtained by treating the oxides with a silicon ester, which may be hydro-

lysed readily, and hydrolysing and reducing the product substantially in accordance with the method disclosed in the Specification of Patent No. 397,295. The hydrogenation is effected in known manner by vaporising the oil fraction to be treated, and passing the vapour, together with hydrogen, or gas containing hydrogen, through a bed of the catalyst at a temperature in excess of 120° C. under a suitable pressure which may vary from atmospheric to several atmospheres. The oil is thus readily hydrogenated and is thereafter separated into solvents, kerosene or Diesel oils, or other fraction possessing desirable properties.

According to one specific operation, which we have carried out successfully, blue water gas, having a carbon monoxide-hydrogen ratio of 1 : 1.17, from which organic sulphur compounds had been substantially completely removed, was passed over a catalyst consisting of cobalt and thorium oxide on kieselguhr. The catalyst was maintained at 200° C. and the gas was passed at the rate of 100 volumes per unit volume of catalyst space per hour.

Hydrocarbon oil was recovered at the rate of 147 cc. per cubic metre of blue water gas treated.

The oil was fractionated by distillation into three fractions :—

A. Initial boiling point to 150° C. (motor spirit).

B. 150°—200° C.

C. 200°—320° C.

The motor spirit had an octane number of 62.5. The fractions B and C were separately volatilised in a current of hydrogen and led at atmospheric pressure over a hydrogenating catalyst, which in this case was the catalyst which had been employed for the synthesis from CO and H_2.

The temperature of the catalyst was maintained at 180—200° C.

The liquid hydrocarbon fractions were vaporised at the rate of one liquid volume per volume of catalyst space per hour.

The total hydrogenated oil was fractionally distilled to yield solvent oils, kerosenes and Diesel oils and the characteristics of the products, with reference to the purpose to which they were put, were found to be improved by the treatment.

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. A process for simultaneously producing by catalytic synthesis an anti-knock motor fuel and hydrocarbons boiling above the motor fuel range and adapted to be used as solvents, kerosenes, Diesel oils and lubricants, according to which a gaseous mixture of carbon monoxide and hydrogen in a ratio between 1 : 2 and 1 : 1 by volume is first passed in contact with a catalyst containing cobalt or nickel under pressure not exceeding 3 atmospheres and at a temperature in the region of 200° C., and from the liquid products thereby produced the motor fuel, i.e. the product boiling below 150° C., is separated from the product boiling above the motor fuel range and this higher boiling point fraction is then submitted to hydrogenation at atmospheric or increased pressure in the presence of a hydrogenation catalyst at a temperature above 120° C. and this further product is then subjected to fractionation and the parts thereof suitable for use as solvents, kerosenes, Diesel oils and lubricants thereby separated for use.

2. A process according to claim 1 characterised in that the carbon monoxide-hydrogen ratio of the gaseous mixture employed is 1 : 1.17.

3. A process according to claims 1 or 2 characterised in that the fraction of the liquid product obtained by the first synthesis treatment boiling above 150° C. is vaporised and hydrogenated by passing the vapour together with hydrogen or a gas containing hydrogen in contact with the hydrogenation catalyst.

4. The improved process for the production of hydrocarbons substantially as described.

Dated this 10th day of January, 1938.

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