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PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION

Improvements relating to the Catalytic Synthesis of Hydrocarbon Oils from Gaseous Mixtures of Carbon Monoxide and Hydrogen.

I, WILLIAM WHALLEY MYDDLETON, a British Subject, of 3, Woodlands Avenue, New Malden, Surrey, do hereby declare the nature of this invention to be as follows:—

This invention relates to the catalytic synthesis of hydrocarbon oils from gaseous mixtures of carbon monoxide and hydrogen and has among its objects to provide an economic process by which spirit particularly useful as motor spirit by reason of an enhanced octane rating can be produced.

The catalytic synthesis of hydrocarbon oils from gas mixtures containing carbon monoxide and hydrogen is known to produce olefines and paraffins in proportions dependent upon the nature of the catalyst and upon the ratio of carbon monoxide and hydrogen in the gas mixture employed. Catalysts containing cobalt as the basic substance produce larger proportions of olefines than those in which cobalt is replaced by nickel.

Gases containing higher proportions of carbon monoxide are converted into hydrocarbon products richer in olefines than those gases containing a lower proportion of carbon monoxide to hydrogen. Thus it is known that blue water gas gives products richer in olefines than a gas mixture containing carbon monoxide and hydrogen in the ratio 1:2.

I have found that the primary product of synthesis is composed of mono-olefines and that this product, which can be designated as "primary oil", is subject to further chemical action, as it passes in vapour form through further layers of catalyst, provided that some hydrogen still remain in the gas passing onwards with it. This secondary reaction is catalytic hydrogenation.

I have found moreover that although cobalt is a feebler hydrogenation catalyst than nickel, it is nevertheless impossible to recover the "primary oil" without hydrogenation occurring to some extent, even when blue water gas is submitted to the synthesis reaction.

It is desirable to preserve as far as possible the nature of the "primary oil", because the presence of mono-olefines in the motor spirit fraction enhances the octane rating of the spirit and furthermore the higher proportion of olefines provides higher yields of alcohols, lubricating oils and other products, which are commonly derived from olefines by hydration, polymerisation or other means.

The underlying principle of my invention is the preservation of the nature of the "primary oil" by the use of an oil forming catalyst to which an alkali metal carbonate has been added and by limiting the hydrogenating action of the catalyst, while retaining its power to form oil from carbon monoxide and hydrogen, by the introduction with the gas of an ingredient which will act as a catalyst poison which affects the olefine hydrogenating power of the catalyst.

A suitable poison which is invariably available is sulphur, whether present as sulphuretted hydrogen or in organic combination as thiophen, carbon disulphide or carbon oxysulphide, and in carrying my invention into practice according to one method, instead of freeing the gas being treated from sulphur to the greatest extent possible, as is the present practice, I deliberately allow the sulphur compounds in appreciable quantity to pass through the catalyst containing an alkali metal carbonate with the gas. That is to say I have proved by experiment that if an alkali metal carbonate, such for example as potassium carbonate, be added to an oil-forming catalyst with a cobalt base beneficial results accrue in that not only is it unnecessary to free the gas from its sulphur compounds with meticulous care in order to effect the oil formation but that the presence of the sulphur has beneficial results in certain directions.

For example, when blue water gas which has been purified only by removal of sulphuretted hydrogen, is passed directly over such a catalyst at atmospheric pressure and at a temperature between 180° and 210° C., primary oil is formed and is thereafter hydrogenated to a lesser extent than when pure gas is used for the synthesis in the normal manner.

The effect observed is that the proportion of olefines in the synthetic product is increased. At the same time the poisoning action of the sulphur compounds upon the oil forming activity of the treated catalyst is substantially delayed and for some time an increase in the oil forming capacity of the catalytic mass is observed.

I have found it advantageous to interrupt the flow of gas at intervals and then to pass hydrogen through the catalytic mass for a short period before resuming the synthesis.

In one example of the invention, which I have successfully carried out, the synthesis is effected by passing, for example, blue water gas preferably freed from sulphuretted hydrogen but still containing some of the organically combined sulphur. In one experiment the gas used for the synthesis contained 25 grains organically combined sulphur per 100 cubic feet. The temperature of synthesis lies between 180° and 210° C. The velocity of the gas treated depends upon whether the reaction is to be completed in one or two stages. A convenient velocity for the case where two stages are to be operated lies between 150 and 200 gas volumes, per unit volume of catalyst space per hour. The oil produced by an alkaline catalyst under these circumstances in one example contained 50 per cent. olefines and the fraction of the product boiling between 33° and 150° C. contained 73 per cent. olefines.

The alkaline catalyst is prepared by dissolving 996 grammes cobalt nitrate and 72 grammes thorium nitrate in a quantity of water which may be varied. The hot solution is added to 378 grammes of kieselguhr. The mass which may be in the form of a damp powder or a thin paste according to the amount of water used, is added to a hot solution of up to 900 grammes potassium carbonate in approximately 4.5 litres water.

The precipitated catalyst is filtered, washed and dried. Catalysts prepared from some forms of kieselguhr require to be washed at this stage until an aqueous extract of the press cake is neutral to phenol phthalein.

The dried press cake is then either granulated and screened into granules of convenient size or powdered and pelleted. The granules or pellets are now impregnated with a solution of potassium or sodium carbonate either in water or a mixture of water and alcohol and then dried. A convenient strength of solution to use contains 10 grammes of anhydrous potassium carbonate in a mixture of 100 cc. ethyl alcohol and 125 cc. water.

The dried granules or pellets used in successful experiments contained in one case 1.7 per cent. by weight potassium carbonate and in another case 10 per cent.

The dried alkaline granules or pellets must be reduced in a known manner as for example by heating to a temperature between 350° C. and 400° C. in a current of hydrogen.

Dated this 22nd day of January, 1938.

A. A. THORNTON,
Chartered Patent Agent,
7, Essex Street, Strand, London, W.C. 2,
For the Applicant.

COMPLETE SPECIFICATION.

Improvements relating to the Catalytic Synthesis of Hydrocarbon Oils from Gaseous Mixtures of Carbon Monoxide and Hydrogen.

I, WILLIAM WHALLEY MYDDLETON, a British Subject, of 3, Woodlands Avenue, New Malden, 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 catalytic synthesis of hydrocarbon oils from gaseous mixtures of carbon monoxide and hydrogen and has among its objects to provide an economic process by which spirit particularly useful as motor spirit by reason of an enhanced octane rating can be produced.

The catalytic synthesis of hydrocarbon oils from gas mixtures containing carbon monoxide and hydrogen is known to produce olefines and paraffins in proportions dependent upon the nature of the catalyst and upon the ratio of carbon monoxide and hydrogen in the gas mixture employed. Catalysts containing cobalt as the basic substance product larger proportions of olefines than those in which cobalt is replaced by nickel.

Gases containing higher proportions of carbon monoxide are converted into hydrocarbon products richer in olefines than those from gases containing a lower proportion of carbon monoxide to hydrogen. Thus it is known that blue water gas gives products richer in olefines than a gas mixture containing carbon monoxide and hydrogen in the ratio 1:2.

I have found that the primary product of synthesis is composed of mono-olefines and that this product, which can be designated as "primary oil", is subject to further chemical action, as it passes in vapour form through further layers of catalyst provided that some hydrogen still remains in the gas passing onwards with it. This secondary reaction is catalytic hydrogenation.

I have found moreover that although cobalt is a feebler hydrogenation catalyst than nickel, it is nevertheless impossible to recover the "primary oil" without hydrogenation occurring to some extent, even when blue water gas is submitted to the synthesis reaction.

It is desirable to preserve as far as possible the nature of the "primary oil", because the presence of mono-olefines in the motor spirit fraction enhances the octane rating of the spirit and furthermore the higher proportion of olefines provides higher yields of alcohols, lubricating oils and other products, which are commonly derived from olefines by hydration, polymerisation or other means.

In Specification No. 332,284 it was suggested that when using catalysts such as I employ containing metals of the eighth group of the periodic system to which alkali metal compounds such as hydroxides, carbonates and acetates have been added, an addition to the catalyst of small quantities of sulphur in free or combined state is advantageous in that it lengthens the life of the catalyst, reduces the proportion of hydrocarbons of high boiling point and strongly promotes the formation of liquid unsaturated hydrocarbons from gaseous mixtures of oxides of carbon and hydrogen. Such catalysts may be prepared by treating a catalyst free from sulphur with gases containing sulphuretted hydrogen.

The underlying principle of my invention is the taking advantage of the fact that sulphur is invariably present in the gas being treated and utilising the sulphur in the gas being treated as a catalyst poison which limits the hydrogenating power of the catalyst and affects its olefine hydrogenating power whereby the nature of the "primary oil" is preserved. This method has the two-fold advantage that it is unnecessary to add the sulphur to the catalyst during its preparation and it is unnecessary to free the gas being treated from sulphur to the greatest extent possible, which is the present practice.

According to my invention I deliberately allow the sulphur compounds in the gas being treated to pass through the catalyst.

The present invention consists therefore of a process for the production of hydrocarbon oils from gaseous mixtures of carbon monoxide and hydrogen by catalytic synthesis according to which a catalyst to which an alkali metal carbonate has been added is used and sulphur which acts as a catalyst poison affecting the olefine hydrogenating power of the catalyst while leaving substantially unchanged the power of the catalyst to form oil from the gaseous mixture is introduced together with the gaseous mixture into the reaction chamber.

In the operation of the invention I have found potassium carbonate a suitable alkali metal carbonate with which to treat the catalyst. That is to say if potassium carbonate be added to an oil-forming catalyst with a cobalt base beneficial results accrue in that not only is it unnecessary to free the gas from its sulphur compounds with meticulous care in order to effect the oil formation but that the presence of the sulphur has beneficial results in certain directions.

For example, when blue water gas which has been purified only by removal of sulphuretted hydrogen is passed directly over such a catalyst at atmospheric pressure and at a temperature between 180° and 210° C., primary oil is formed and is thereafter hydrogenated to a lesser extent than when sulphur free gas is used for the synthesis in the normal manner.

The effect observed is that the proportion of olefines in the synthetic product is increased. At the same time the poisoning action of the sulphur compounds upon the oil forming activity of the treated catalyst is substantially delayed and for some time an increase in the oil forming capacity of the catalytic mass is observed.

I have found it advantageous to interrupt the flow of gas at intervals and then to pass hydrogen through the catalytic mass for a short period before resuming the synthesis.

In one example of the invention, which I have successfully carried out, the synthesis is effected by passing, for example, blue water gas preferably freed from sulphuretted hydrogen but still containing some of the organically combined sulphur. In one experiment the gas used for the synthesis contained 25 grains organically combined sulphur per 100 cubic feet. The temperature of synthesis lies between 180° C. and 210° C. and is usually carried out at substantially atmospheric pressure and never above about 5 atmospheres. A convenient gas velocity lies between 75 and 100 gas volumes per unit volume of catalyst space per hour. The oil produced by an alkaline catalyst under these circumstances in one example contained 50 per cent. olefines and the fraction of the product boiling between 33° and 150° C. contained 73 per cent. olefines.

The motor spirit fraction with a final boiling point of 150° C. had an octane number of 68 C.F.R. (M.M.) The actual gum present as determined by the glass dish method was 2.0 m.g. per 100 cc. Potential gum determined after incubation at 35° C. was 1.0 m.g. per 100 cc.

The lead susceptibility of the motor spirit was such as 2 cc. of tetra ethyl lead added to one gallon of the spirit raised the octane number to 77.

The addition of 20% by volume of benzol to the undoped spirit raised the octane number from 68 to 72. The addition of 3 cc. tetra ethyl lead to one gallon of the blended mixture raised the octane number to 81.5.

The fraction of the synthetic product distilling between 150° and 200° C. contained 52.6 per cent. by volume of olefines, which were converted into lubricating oils by polymerisation with aluminium chloride.

The polymerised product can be separated, for example, by fractional distillation into oils of different viscosity suitable for different purposes. The products are characterised by their low rate of change of viscosity with temperature change.

The synthetic product liquid at ordinary temperature produced by the method of this invention is clearly suitable for the direct production of motor spirit. Diesel oil and lubricating oil fulfilling the modern requirements without the necessity for the installation of a cracking process to improve their properties.

The yield of olefines for the production of lubricating oils by polymerisation is increased by the operation of the method.

At the same time, the uncondensed hydrocarbons contain higher percentages of olefines than when highly purified gas is employed for synthesis.

In the experiment described, the uncondensed gases contained over 60 per cent. C_3 and C_4 olefines by volume. Thus by the operation of the method of the invention, the yield of gaseous olefines suitable for further treatment for production of high octane number motor spirit or alcohols or other substances usually produced from olefines is increased.

Furthermore, the products described have been formed in one stage of reaction, that is, by passing the gas containing organic compounds of sulphur once only through the catalyst vessel.

Hitherto, it has been found necessary to pass highly purified gas at least twice through a catalyst chamber, condensing out some of the products formed after the first passage before admitting the residual gas to the second contact stage.

The latter procedure involved heating the original highly purified gas to the temperature of reaction, cooling after the first contact to condense out the products, and heating the residual gas again to the temperature of reaction.

Economy is therefore brought about not only during the synthesis but also by eliminating the necessity for rigid purification of the gas.

The alkaline catalyst may be prepared by dissolving 996 grammes, cobalt nitrate and 72 grammes thorium nitrate in a quantity of water which may be varied. The hot solution is added to 378 grammes of kieselguhr. The mass which may be in the form of a damp powder or a thin paste according to the amount of water used, is added to a hot solution of up to 900 grammes potassium carbonate in approximately 4.5 litres water.

The precipitated catalyst is filtered washed and dried, catalysts prepared from some forms of kieselguhr require to be washed at this stage until an aqueous extract of the press cake is neutral to phenol phthalein.

The dried press cake is then either granulated and screened into granules of convenient size or powdered and pelleted. The granules or pellets are then impregnated with a solution of potassium or sodium carbonate either in water or a mixture of water and alcohol and then dried. A convenient strength of solution to use contains 10 grammes of anhydrous potassium carbonate in a mixture of 100 cc. ethyl alcohol and 125 cc. water.

A convenient procedure is to spray the granules or pellets of catalyst with the solution of the alkali metal carbonate.

The dried granules or pellets used in successful experiments contained in one case 1.7 per cent. by weight potassium carbonate and in another case 10 per cent.

The dried alkaline granules or pellets must be reduced in a known manner as for example by heating to a temperature between 350° C. and 400° C. in a current of hydrogen.

The importance of the invention will be understood when it is stated that, apart altogether from the obvious advantage consequent upon the elimination of the necessity to purify the gas, advantageous characteristics of the product obtained are enhanced.

This has been proved as before mentioned by actual experiments on gas, in the one instance, purified to the extent that not more than 0.1 m.g. of organically combined sulphur per 100 c.f. of gas remained in the gas after purification and before treatment, while in the other instance blue water gas treated in accordance with this invention contained as much as 25 m.g. of organically combined sulphur per 100 c.f.

Using catalysts with cobalt as the base both the olefine content and octane number of the product were increased when the treatment was according to this invention.

As one specific example it can be stated that with gas containing carbon monoxide and hydrogen in the ratio of 1 to 1.17 the percentage by volume of olefines in the total liquid product was, in the case of the gas which has been freed from organic sulphur 48% and in the case where the organic sulphur had not been removed 50%. In the motor spirit fraction of the gas, that is the fraction cut at 150° C., the olefine percentage by volume was, in the one case, 69%, in the other 73%, while the octane number rose from 65 to 68.

It should be mentioned that the quantity of the product obtained proved to be substantially the same in the two cases and amounted to 0.9 gallon for every 1000 cubic feet of the gas treated.

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 hydrocarbon oils from gaseous mixtures of carbon monoxide and hydrogen by catalytic synthesis according to which a catalyst to which an alkali metal carbonate has been added is used and sulphur which acts as a catalyst poison affecting the olefine hydrogenating power of the catalyst while leaving substantially unchanged its power to form oil from the gaseous mixture is introduced together with the gaseous mixture into the reaction chamber.

2. A process according to claim 1, wherein the catalyst is impregnated before use with a solution of potassium carbonate.

3. A process according to claim 1, wherein the catalyst employed comprises cobalt.

4. A process for the production of hydrocarbon oils from gaseous mixtures of carbon monoxide and hydrogen by catalytic synthesis according to claim 1 according to which blue water gas containing appreciable quantities of sulphur is passed at an appropriate low pressure not exceeding five atmospheres, through or in contact with a catalyst having a cobalt base the temperature of the synthesis reaction being maintained between 180° C. and 210° C.

5. The improved process for the production of hydrocarbon oils from gaseous mixtures containing carbon monoxide and hydrogen substantially as specified.

6. Hydrocarbon oils when produced by the process according to the preceding claims.

Dated this 12th day of May, 1938.

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