

PATENT SPECIFICATION



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PROVISIONAL SPECIFICATION

Improvements in or relating to Methods of Producing
Hydrocarbon Oils from Gaseous Mixtures of Hydrogen
and Carbon Monoxide

We, SYNTHETIC OILS LIMITED, a British Company, of 31, East Street, Epsom, in the County of Surrey, WILLIAM WHALLEY MYDDLETON, a British Subject, of 3, 5 Woodlands Avenue, New Malden, in the County of Surrey, and ALFRED AUGUST ARCHER, a British Subject, of 22, Holland Avenue, Wimbledon, in the County of Surrey, do hereby declare the nature of this invention to be as follows:—

This invention relates to the conduct of synthesizing reactions for the production of hydrocarbon oils from gaseous mixtures containing hydrogen and carbon monoxide in the presence of a catalyst, and has for its object to effect improvements in methods involving such reactions, and in particular to increase the length of the run during which a given yield of hydrocarbon oils can be maintained at a substantially constant level, to reduce or eliminate fog formation in the products of reaction and to prolong the life of the catalyst.

The normal procedure in establishing the conditions is to adjust the throughput, for a given composition of the initial gas mixture and volume of catalyst space so as to obtain maximum yield within the desired temperature range which in its turn depends largely on the desired nature of the synthetic product. This condition might be termed maximum efficiency of the reaction.

Now we have found that working at or near conditions of maximum efficiency has serious drawbacks. In the first place, such conditions cannot be maintained for a sufficiently long period for economic efficiency. In the second place, quantities of fog are formed in the gaseous product and are found in the gas emerging from the coolers after treatment. This fog has hitherto necessitated special treatment of the fog-bearing gas for its removal, as for example by the use of an electrical precipitator. And in the third place, the active life of the catalyst is strictly limited.

We have found, and this forms the

basis of the present invention, that all these drawbacks can be substantially mitigated by intentionally restricting the rate of yield, that is to say by adjusting the working conditions, and particularly the temperature so as to fall short of the condition of maximum efficiency.

According to the invention, in a method of the kind referred to, the rate of yield of liquid hydrocarbons is restricted to such a degree that for each cubic metre of catalyst space there is produced, per hour, between seven and twelve litres of liquid hydrocarbons.

It will be appreciated that within the terms of the above definition of the restriction in the rate of yield, the yield, when expressed in terms of the gas input may vary within fairly wide limits, according to the composition of the initial gas mixture, the velocity of the gas flow and the working temperature. Broadly speaking, the velocity of gas flow can not be increased beyond a certain optimum value without loss of efficiency, for a given plant, and, as already mentioned, the temperature range is also determined by external considerations and particularly by the desired nature of the synthetic product. To all intents and purposes, therefore, it is by suitably adjusting the rate of input of the initial gas mixture and the temperature of the reaction space within the given limits that the rate of yield of the liquid hydrocarbons is restricted to conform to the terms of the above definition.

At a yield, for example of 0.75 gallon per 1,000 cubic feet of blue water gas (calculated as inert free gas), which came within the specified limits of the yield: catalyst space relationship, the period during which this yield was maintained was more than three times as long as the period for which a yield of 0.85 gallon could be maintained, while fog was present in negligible amounts requiring no special treatment for fog removal, and the observed life of the catalyst, with periodical flushing of the catalyst cham-

[Price 1/-]

ber with hydrogen at intervals of approximately ten days to remove wax deposit, was at least six months.

As is well known in the art, the catalyst suffers a gradual reduction in activity, which becomes appreciable after several days continuous working, and it has been proposed to periodically reactivate the catalyst by flushing the catalyst chamber with hydrogen or a gas mixture rich in hydrogen and containing no more than traces of oxides of carbon.

This replacement of the gas stream by hydrogen or a hydrogen-bearing gas is normally necessary at very short intervals if high yields are to be achieved, for example at daily intervals in some cases. Moreover, after longer periods, flushing with hydrogen no longer serves to restore activity completely, and recourse has been had to extraction of wax from the catalyst by means of a solvent. The intervals between the hydrogen flushes are determined by the rise in temperature of the reaction which accompanies the reduction in the activity of the catalyst and the fact that the working temperature range has an upper limit beyond which it is not desirable to allow the temperature to rise. During the life of the catalyst, the intervals between successive flushes tend to become shorter, while the duration of the flushes for effective reactivation increases and the recovery temperature rises, until eventually reactivation by hydrogen flushing ceases to be economical. The expedient of restricting the rate of yield of the hydrocarbon product according to the present invention has the great advantage that it enables an improvement to be achieved in all these respects.

Thus, for example, a prolonged active life of catalyst and the other advantages set forth are secured by admitting water gas suitably purified to the catalyst chamber heated to a temperature at which very little reaction between carbon monoxide and hydrogen occurs, setting the gas flow to between 70 and 80 normal volumes per unit volume of catalyst space per hour and then slowly adjusting the temperature, until a yield of approximately 0.75 gallon of liquid hydrocarbon per 1,000 cubic feet of inert free gas is obtained.

In a preferred mode of carrying out the invention, the catalyst vessel was an annular space, the outer wall of which was surrounded by a cooling surface kept at a uniform temperature by circulation of

vigorously boiling water under pressure. The catalyst vessel was divided into two parts, so that gas partially treated in the first part or stage was cooled to condense heavy oil and wax before it was passed into the second part or stage. The cooling system designed to carry away the heat of the exothermic reaction of synthesis was such that vapour produced by evaporation of the cooling liquid was passed from the upper end of the system to a condenser and re-heated before readmission at the lower end at practically the temperature of the boiling liquid in the cooling jacket. The temperature of the boiling liquid was regulated by adjusting the pressure under which it was maintained in a boiling condition.

The gas was admitted to the first stage at a rate of approximately 73 volumes measured at N.T.P. per unit volume of catalyst space per hour.

The temperature of the cooling liquid was slowly raised until after from eight to ten days the yields of liquid hydrocarbons in the combined operation of the two stages was approximately 0.75 gallon per 1,000 cubic feet of inert free water gas. The temperature was further slowly raised during the following week or ten days to maintain this yield.

At the end of this period the gas flow was replaced by a current of hydrogen flowing at approximately the same rate as the water gas.

The temperature of the cooling liquid was raised by from ten to twenty-five degrees centigrade during the passage of hydrogen for six or seven hours.

Thereafter the temperature of the cooling liquid was lowered to a point about which the first flow of water gas had been admitted, and the cycle was repeated.

Succeeding flushes with hydrogen were lengthened until finally a period of from two to three days was reached.

Considerable amounts of wax were removed from the catalyst by the hydrogen stream.

The observed life of the catalyst under the conditions described was at the minimum six months.

Dated this 14th day of January, 1941.

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For the Applicants.

COMPLETE SPECIFICATION

Improvements in or relating to Methods of Producing
Hydrocarbon Oils from Gaseous Mixtures of Hydrogen
and Carbon Monoxide

We, SYNTHETIC OILS LIMITED, a British Company, of 31, East Street, Epsom, in the County of Surrey, WILLIAM WILLEY MYDDLETON, a British Subject, of 3, Woodlands Avenue, New Malden, in the County of Surrey, and ALFRED AUGUST AICHER, a British Subject, of 22, Holland Avenue, Wimbledon, 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 conduct of synthesising reactions for the production of hydrocarbon oils from gaseous mixtures containing hydrogen and carbon monoxide in the presence of a catalyst, and has for its object to effect improvements in methods involving such reactions, and in particular to increase the length of the run during which a given yield of hydrocarbon oils can be maintained at a substantially constant level with consequent prolongation of the life of the catalyst and to reduce or eliminate fog formation in the products of reaction.

The obvious and natural procedure in establishing the conditions for reactions of the kind with which this invention is concerned is, of course, to adjust the through-put of the gas being treated for a given composition of the initial gas mixture and volume of catalyst space so as to obtain theoretical yield of liquid hydrocarbons per unit volume of gas treated, within the desired temperature range which in its turn depends largely on the desired nature of the liquid hydrocarbon product. This condition might be termed maximum efficiency of the reaction.

It is to be borne in mind that by varying the conditions of operation synthesis can be made to yield products which are substantially gaseous, substantially liquid or substantially solid. Each of these groups will contain a relatively large number of different hydrocarbons some saturated or paraffin hydrocarbons and some unsaturated or olefine hydrocarbons. The proportion of olefines will depend upon such conditions as gas flow and temperature. For example in the case with which our invention is concerned where liquid hydrocarbons are being formed the temperature and gas flow may be such that the product contains 50% olefines. By

reducing the gas flow the proportion of olefines would be reduced and might fall as low as 10%. At the same rates of gas flow and at slightly higher temperature the proportion of olefines would be higher.

The yield of liquid hydrocarbons that can be obtained from a unit volume of a gas of definite composition will depend upon the proportion of olefines in the product. The theoretical yield should therefore be related to the composition of the product it is desired to obtain. In the present case the theoretical yield is taken to be the quantity of liquid product obtained if reaction was carried out under conditions of maximum efficiency and the gas mixture were converted as completely as possible.

Thus by the expression "theoretical yield" we mean the yield which would be obtained if the reaction be carried out under conditions of maximum efficiency and all the carbon monoxide or all the hydrogen in the gaseous mixture was converted into liquid hydrocarbons and the inert constituents together with the surplus hydrogen or carbon monoxide passed away as gas.

Now we have found that working at or near conditions of maximum efficiency has serious drawbacks. In the first place, such conditions cannot be maintained for a sufficiently long period for economic efficiency. In the second place, quantities of fog are formed in the gaseous product and are found in the gas emerging from the coolers after treatment. And in the third place, the active life of the catalyst is strictly limited.

We have found, and this forms the basis of the present invention, that all these drawbacks can be substantially mitigated by intentionally restricting the rate of yield, that is to say by adjusting the working conditions in the reaction chamber or chambers and particularly the temperature and velocity of gas flow so that they fall short of the condition for maximum efficiency.

The present invention consists therefore of a method of producing hydrocarbon oils by catalytic synthesis from gaseous mixtures of hydrogen and carbon monoxide according to which the rate of flow of the gas through the reaction apparatus and the reaction temperature or temperatures are so adjusted that the yield

of liquid hydrocarbon products resulting from the treatment of a given volume of gas is substantially below the theoretical yield, the unreacted carbon monoxide and hydrogen passing away.

The exhaust or waste gases containing the unreacted carbon monoxide and hydrogen may, of course, be subjected to further treatment if desired.

The temperature limits for carrying out the synthesis by means of a cobalt-thoria catalyst are roughly 175° C. to 220° C.

Early in the life of the catalyst a working temperature at the lower end of the range will be effective, but as the catalyst ages then the working temperature will require to be raised in the direction of the upper limit.

In the process as defined by this invention reaction is started at as low a temperature as possible within the limits stated. The rate of gas flow is then adjusted to between 70 and 80 volumes per unit volume of catalyst space per hour—instead of the usual 100 volumes—in the case of blue water gas containing 12% inerts. In other words the rate of gas flow is adjusted so that between 16.5 and

18.8 volumes of available carbon monoxide are admitted per unit volume of catalyst space per hour. The volume of available carbon monoxide may be defined as the volume of carbon monoxide associated with twice its volume of hydrogen. Thus if the gas contains CO 41% and H₂ 47%, the available carbon monoxide is $47/2 = 23.5\%$.

When the gas flow has been adjusted in this way the yield of liquid hydrocarbons is measured over a period of several hours.

The temperature may then be slowly raised until the yield amounts to not more than 80% of the theoretical yield per unit volume of gas admitted, the carbon monoxide and hydrogen which has not reacted passing away for further treatment if desired.

The yield may be reduced to a total of 50% of the theoretical yield with advantage in so far as the operative life of the catalyst is concerned but the cost of the gas may make it desirable to sacrifice some proportion of the active working period by approaching the higher limit of yield.

Thereafter the temperature is adjusted from time to time to maintain the yield at the selected value.

As before indicated we have found that the advantages of our invention are attained if the rate of gas flow through the catalyst space be restricted to between 70 and 80 gas volumes per unit volume of

catalyst space per hour when the gas mixture is blue water gas containing 12% inerts. If the gas volume were maintained at the usual 100 volumes per unit volume of catalyst space per hour and the temperature was so adjusted by raising it to the point that the reactants in the gas mixture were completely converted into liquid hydrocarbons, that is if the theoretical yield were obtained, the yield of liquid hydrocarbons would be 20.5 litres per cubic metre of catalyst space per hour, or 23.3 litres calculated on inert free gas.

By reducing the flow to 75 gas volumes and by lowering the temperature so that the theoretical yield of liquid hydrocarbons is obtained from a given volume of gas, the theoretical yield would be expressible as 15.4 litres per cubic metre of catalyst space per hour. According to our invention the yield is restricted below this theoretical yield.

It may be mentioned in passing that were the gas inert free the ratio of gas flow would be restricted to between 60 and 70 volumes per unit volume of catalyst space per hour.

The order of restriction contemplated is from 30% to 50% or thereabout. That is to say, to take the one particular example, where the theoretical yield of hydrocarbon products is 15.4 litres for each metre of catalyst space in the reaction chamber, satisfactory results will be obtained if the yield is deliberately restricted to such a degree that only some 7 to 12 litres of hydrocarbon liquid products are produced. That is to say the contemplated restriction is from 20% to 50%. In other words, the yield aimed at should be from 80% to 50% of the theoretical yield.

The production of the theoretical or near theoretical yield per unit volume of gas is found to result in an appreciable temperature gradient in the catalyst; under these conditions the catalyst which comes into contact with fresh gas entering the vessel tends to attain a high temperature and there is a tendency for a hot spot or zone to develop. In order that the highest temperature reached in the hot spot shall not lead to undesirable reactions in which the yield of liquid hydrocarbons would be reduced by the formation of methane and carbon dioxide it is necessary while maintaining the theoretical yield to limit the general temperature and rate of gas flow so that a considerable quantity of catalyst below the hot zone is at a temperature below that at which efficient reaction takes place.

There is thus brought about a condition in which the catalyst near the gas inlet

performs a much greater amount of work volume for volume than catalyst in zones more remote from the gas inlet. As a consequence of this the efficiency of the process is rapidly reduced because of the reduced yield per unit volume of catalyst per hour and because of the relatively rapid breakdown in the activity of the overloaded catalyst in the gas inlet zone.

10 The procedure we have found to lead to a prolonged period of efficient activity of the catalyst is so to adjust the temperature and gas flow that the work performed by the catalyst volume for volume is fairly uniformly distributed throughout the mass of the catalyst.

It will be appreciated from the foregoing that in substance the invention has the effect of deliberately restricting the work load imposed on the catalyst, and at the same time the yield per unit volume of gas treated is below theoretical.

In multi-stage processes of the character to which this invention relates it has already been suggested to avoid maximum conversion in the first or earlier stages of treatment but to operate under maximum output conditions in the final stage so as to give complete conversion of the reactants as the final result. It is characteristic of the present invention that the rate of yield is restricted substantially in the final stage also in cases where conversion is effected in stages.

35 That is to say, in the practice of the present invention, the process may be carried out in more than one stage but only in such manner that in the final result substantially less than the complete conversion of the reactants is achieved.

As is well known in the art, the catalyst suffers a gradual reduction in activity, which becomes appreciable after several days continuous working, and it has been proposed periodically to reactivate the catalyst by flushing the catalyst chamber with hydrogen or a gas mixture rich in hydrogen and containing no more than traces of oxides of carbon.

50 This replacement of the gas stream by hydrogen or a hydrogen-bearing gas is normally necessary at very short intervals if high yields are to be achieved, for example at daily intervals in some cases.

55 Moreover, after longer periods, flushing with hydrogen no longer serves to restore activity completely, and recourse has been had to extraction of wax from the catalyst by means of a solvent. The intervals between the hydrogen flushes are determined by the rise in temperature of the reaction which always accompanies the reduction in the activity of the catalyst and the fact that the working temperature range has an upper limit beyond

which it is not desirable to allow the temperature to rise. During the life of the catalyst, the intervals between successive flushes tend to become shorter, while the duration of the flushes for effective reactivation increases and the recovery temperature rises, until eventually reactivation by hydrogen flushing ceases to be economical. The expedient of restricting the rate of yield of the hydrocarbon product according to the present invention has the great advantage that it enables an improvement to be achieved in all these respects.

Thus, for example, a prolonged active life of catalyst and the other advantages set forth are secured by admitting water gas suitably purified to the catalyst chamber heated to a temperature at which very little reaction between carbon monoxide and hydrogen occurs, setting the flow of the gas (including the inerts which probably amount to some 13%) to between 70 and 80 normal volumes per unit volume of catalyst space per hour and then slowly adjusting the temperature, until a yield of approximately 0.135 to 0.140 litres of liquid hydrocarbon per cubic metre of inert free gas is obtained, as against a yield of 0.233 per litre which is theoretically obtainable.

In one successful experiment carried out according to the invention, the catalyst vessel was an annular space, the outer wall of which was surrounded by a cooling surface kept at a uniform temperature by circulation of vigorously boiling water under pressure. The catalyst vessel was divided into two parts, so that gas partially treated in the first part or stage was cooled to condense heavy oil and wax before it was passed into the second part or stage. The cooling system designed to carry away the heat of the exothermic reaction of synthesis was such that vapour produced by evaporation of the cooling liquid was passed from the upper end of the system to a condenser and re-heated before readmission at the lower end at practically the temperature of the boiling liquid in the cooling jacket. The temperature of the boiling liquid was regulated by adjusting the pressure under which it was maintained in a boiling condition.

The gas was admitted to a two-stage apparatus at a rate of approximately 73 volume measured at N.T.P. per unit volume of catalyst space per hour.

The temperature of the cooling liquid was slowly raised until after from eight to ten days the yield of liquid hydrocarbons in the combined operation of the two stages was approximately the desired 0.135 to 0.140 litres per cubic metre of

inert free water gas. The temperature was further slowly raised during the following week or ten days to maintain this yield.

5 At the end of this period the gas flow was replaced by a current of hydrogen flowing at approximately the same rate as the water gas.

10 The temperature of the cooling liquid was raised by from ten to twenty-five degrees centigrade during the passage of hydrogen for six or seven hours.

Thereafter the temperature of the cooling liquid was lowered to a point about 15 which the first flow of water gas had been admitted, and the cycle was repeated.

Succeeding flushes with hydrogen were lengthened until finally a period of from two to three days was reached.

20 Considerable amounts of wax were removed from the catalyst by the hydrogen stream.

The observed working life of the catalyst under the conditions described was 25 nine months.

Although it has been mentioned above that a limitation of yield per unit volume of catalyst space per hour of the order of 30 from 20% to 50% of the theoretical yield is contemplated for practical operation—that is to say the yield should not ordinarily be more than 80% or less than 50% of the theoretical yield—these 35 figures are not to be taken as of limiting effect as a somewhat lower rate of yield restriction may be to some extent effective.

An important advantage of the invention is that it enables the amount of cooling 40 surface in relation to catalyst space to be substantially reduced. For example, whereas, with the normal method of operation, a cooling area of 187 square metres per cubic metre of catalyst space 45 was regarded as necessary, when working according to the method of the present invention, satisfactory cooling was attained with the cooling area reduced to 113 square metres per cubic metre of catalyst space.

It is to be noted that this invention is solely concerned with the production of hydrocarbon oils from gaseous mixtures in direct contact with the catalyst and is 55 therefore not concerned with reactions where the reaction takes place in an oil medium or with reactions for the production of solid hydrocarbons.

Nor is it suggested that there have not 60 been cases in the past with reactions of this general type, where analyses have shown that the conversion of the gas has been incomplete.

Doubtless there have been many such 65 cases, but the restrictions of yield in

these cases have been purely fortuitous and did not lead to the advantages derived from the present invention, since other conditions such as high gas flow and high yield per volume of catalyst space 70 per hour were such as to render the advantages of the present invention unattainable.

We are, of course, aware that in the specification of our prior Patent No. 75 509,325 it was mentioned that a convenient gas velocity for that reaction was between 75 and 100 gas volumes per volume of catalyst space per hour. There was, however, in that case no suggestion of 80 restricting yield and, moreover, it is essential to the present invention that the velocity of gas flow must be at the lower end of the foregoing range and would never exceed 80 volumes per volume of 85 catalyst space per hour.

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 90 claim is:—

1. A method of producing liquid hydrocarbon oils by catalytic synthesis from gaseous mixtures of hydrogen and carbon monoxide according to which the rate of 95 flow of the gas through the reaction apparatus in direct contact with the catalyst, and the reaction temperature or temperatures are so adjusted that the yield of liquid hydrocarbon products resulting 100 from the treatment of a given volume of gas is substantially below the theoretical yield, the unreacted hydrogen and carbon monoxide passing away; whereby the length of the run of the reaction during 105 which a given yield of the hydrocarbon oil can be maintained at a substantially constant level is increased and the life of the catalyst prolonged.

2. A method of producing hydrocarbon 110 oils according to Claim 1, wherein the yield is so restricted that it falls below the theoretical yield by from 20% to 50%.

3. A method of producing hydrocarbon oils by catalytic synthesis according to 115 Claim 1, from blue water gas containing not more than 12% inerts and using a cobalt-thoria catalyst, according to which the rate of flow of the gas through the catalyst space is restricted to between 70 120 and 80 volumes per unit volume of catalyst space per hour and the temperature of the reaction is maintained between 175° C. and 220° C.

4. A method of producing hydrocarbon 125 oils by catalytic synthesis according to Claim 1 from blue water gas regarded as inert gas, according to which the rate of flow of the gas through the catalyst space is restricted to between 60 to 70 volumes 130

per unit volume of catalyst space per hour.

5. The improved method of producing hydrocarbon oils from gaseous mixtures of hydrogen and carbon monoxide substantially as specified.

Dated this 14th day of January, 1942.
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Reference has been directed, in pursuance of Section 7, sub-section (4), of the Patents and Designs Acts, 1907 to 1942, to Specifications No. 518,372 and 507,366.

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