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 26, East Street, Ipswich, in the County of Suffolk, William Whately Myddelton, a British Subject, of 3, 5 Woodlands Avenue, New Malden, in the County of Surrey, and Alfred August Axen, a British Subject, of 23, Holland Avenue, Wimbledon, in the County of Surrey, do hereby declare the nature of this invention to be as follows:

10 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.

15 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.

20 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.

25 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.

30 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.

35 It will be appreciated that within the 65 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.

40 At a yield, for example, of 0.75 gallon per 1,000 cubic feet of blue water gas (calculated as inert free gas), which comes 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 per 1,000 cubic feet 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 space, was considerably extended.
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 other carbonaceous hydrocarbons. 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. 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 rate of increase 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 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 wafer 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 between 70 and 100 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 water gas. 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.

A. A. THORNTON,
Chartered Patent Agent,
For the Applicants.
COMPLETE SPECIFICATION

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

We, SYNTHESIZING OILS LIMITED, a British
Company, of 31, East Street, Ripon, in the
County of Yorkshire, and William Wharton
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County of Surrey, and Alfred August
Acher, a British Subject, of 32, 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
15 synthesising reactions for the production of
hydrocarbon oils from gaseous mixtures of
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 oil 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
throughput of the gas being treated for a given composition of the initial gas mix-
ture and volume of catalyst space so as to obtain theoretical yield of liquid hydro-
carbons 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 olefins 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% olefins. By
reducing the gas flow the proportion of olefins would be reduced and might fall
as low as 10%. At the same rate of gas flow and at slightly higher temperature
the proportion of olefins would be higher.
The yield of liquid hydrocarbons that
65 can be obtained from a unit volume of a
gas of definite composition will depend
upon the proportion of olefins in the pro-
60 duct. The theoretical yield should there-
65fore be related to the composition of the
product it is desired to obtain. In the
present case the theoretical yield is based
70 to be the quantity of liquid product ob-
tained 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 sur-
plus 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,
each condition cannot be maintained for
a sufficiently long period for economic
efficiency. In the second place, quanti-
ties of fog are formed in the gaseous pro-
duct and are found in the gas emerging
from the coolers after treatment. And in
the third place, the active life of the cata-
lyst 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 100
yield, that is to say by adjusting the
working conditions in the reaction cham-
ber or chambers and particularly the tem-
perature and velocity of gas flow so that
they fall short of the condition for maxi-
mum efficiency.

The present invention consists therefore
of a method of producing hydrocarbon
oils by catalytic synthesis from gaseous
mixtures of hydrogen and carbon mono-
oxide according to which the rate of flow
of the gas through the reaction appar-
tus and the reaction temperature or tem-
peratures 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 of waste gases containing the unreacted carbon monoxide and hydrogen may, of course, be subjected to further treatment if desired.

10 The temperature limits for carrying out the synthesis by means of a cata-

lytic catalyst are roughly 175° C. to 230° 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.

20 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 25 unit volume of catalyst space per hour—instead of the usual 100 volumes—in the case of blue water gas containing 12% inert. In other words the rate of gas flow is adjusted so that between 16.5 and 30.8 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 47/3 = 15.5%.

When the gas flow has been adjusted, 40 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 amount 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 is desired.

50 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 80%.

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 utilized 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% inert. If the gas volumes were maintained at the usual 100 volumes per unit volume of catalyst space per hour and the tempera-

ture was so adjusted by raising it to the point that the percentage in the gas mixture were completely converted into liquid hydrocarbons, that is, if the theoretical yield were obtained, the yield 75 of liquid hydrocarbons would be 30.5 litres per cubic metre of catalyst space per hour, or 38.9 litres calculated on inert free gas.

By reducing the flow to 75 gas volumes 80 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 15.8 litres per cubic metre of 85 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 90 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 cubic 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 product is produced. That is to say the contemplated restriction is from 20% to 50%. 105 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 110 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 120 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 con. 125 visible 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 120
performs a much greater amount of work volume for volume than catalyst in some 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.

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 for volume which it is not desirable to allow the temperature to rise. During the life of the catalyst, the intervals between successive flushing 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 not forth are secured by admitting water gas suitably purified to the catalyst chamber heated to a temperature at which very little reaction between carbon 85 maximum and hydrogen occurs, setting the flow of the gas (including the inertes which probably amount to some 12%) to between 75 and 80 normal volumes per unit volume of catalyst space per hour 90 and then slowly adjusting the temperature, until a yield of approximately 0.155 to 0.160 litres of liquid hydrocarbon per cubic metre of inert-free gas is obtained, or against a yield of 0.238 per litre which is theoretically economical.

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 100 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 was partially treated in the first part 105 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 vapors produced by evaporation of the cooling liquid was passed from the upper end of the system to a condenser and re-heated before admission at the lower end of the system and 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.P.T. per unit volume of catalyst space per hour per.

The temperature of the cooling liquid was slowly raised until after from eight to ten days the yield in the final hydrocarbons in the combined operation of the two stages was approximately the desired 0.125 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.

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 last flow of water gas had been admitted, and the cycle was repeated.

Successively, fractions 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 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 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 50% or less than 30% of the theoretical yield—these 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 coal gasing 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 meters per cubic meter of catalyst space was regarded as necessary, when working according to the method of the present invention, satisfactory cooling was attained with the cooling area reduced to 1.58 square meters per cubic meter of catalyst space.

It is to be noted that this invention is solely concerned with the production of hydrocarbon oils from gaseous mixtures of hydrogen and carbon monoxide according to the rate of 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 reaching 90° C. 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 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 oil by catalytic synthesis 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 Claim 1, from blue water gas containing not more than 15% inert gases 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 and 80 volumes per unit volume of catalyst space per hour and the temperature of the reaction is maintained between 777° C. and 827° C.

4. A method of producing hydrocarbon 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
per unit volume of catalyst space per hour.

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

Dated this 14th day of January, 1942,
A. A. THORNTON,
Chartered Patent Agents,
7, Essex Street, Strand, London, W.C.2,
For the Applicants.

Reference has been directed, in pursu-  
ance of Section 7, sub-section (4), of the  
Patents and Designs Acts, 1907 to 1942,
Specifications No. 318,373 and 507,366.

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