PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION

Improvements relating to the Synthesis of Hydrocarbons and Other Compounds from Mixtures of Carbon Monoxide and Hydrogen

We, ANGLO-IRANIAN OIL COMPANY LIMITED, of Britannic House, Finsbury Circus, London, E.C.2, a British joint-stock Corporation, and STANLEY FRANCIS BIRCH and JOHN HABESHAW, both of the Research Station of Anglo-Iranian Oil Company Limited, Chertsey Road, Sunbury-on-Thames, and both of British Nationality, do hereby declare the nature of this invention to be as follows:—

The invention relates to the synthesis of hydrocarbons and other compounds from mixtures or carbon monoxide and hydrogen, and has among its objects to increase the production of olefins in the operation and to render practicable the utilisation of natural gas and petroleum fractions that are otherwise of little value.

The Fischer-Tropsch synthesis of hydrocarbons from carbon monoxide hydrogen mixtures is well known. Many modifications of this synthesis to produce high yields of olefins have been proposed. These methods involve the use of gases containing a high proportion of carbon monoxide, for example water gas having a $CO:H_2$ ratio of about 1:1, or in some cases of gases containing even more CO than this. The use of such gas mixtures has some disadvantages. For example, with gases of such a high carbon monoxide content the tendency to deposit carbon on the catalyst with a consequent loss of catalyst activity is much increased. Proposals have therefore been made to overcome this by dilution of the feed gas, and this is most usually done by recycling relatively large amounts of exit gas, to the process containing principally methane, nitrogen unconverted carbon monoxide and hydrogen, but only small amounts of other compounds. Such processes to operate successfully require an initial feed gas of high CO content. The production of such gas mixtures from methane or other hydrocarbons presents difficulty.

In refining petroleum relatively large amounts of hydrocarbons of little value are produced, for example ethane, propane and some of the residual fractions of petroleum. Also, the light gases from cracking plants contain large amounts of the lower paraffins and olefins (C_2 and C_3) which are not generally utilised. Again the partial combustion with oxygen of methane and other hydrocarbons, including heavier fractions, using a deficiency of oxygen, leads to the production of carbon monoxide, hydrogen and cracked hydrocarbon mixtures of high olefin content. The $CO:H_2$ ratio of the gas so produced is however considerably below 1:1 and is generally close to 1:2. Thus in processing petroleum and natural gas it is easy to produce a gaseous product comprising carbon monoxide and hydrogen in the ratio of approximiately 1:2.

The value of the hydrocarbons produced normally by Fischer-Tropsch synthesis from gas mixtures of $CO:H_2$ ratio of 1:2 or more is low, since the products are almost entirely straight chain and of relatively low olefin content (about 25 per cent. olefins.)

We have now found, that the synthesis may be carried out in the presence of olefins with the following advantageous results:—

(1) The olefin content of the oil produced is much increased.

(2) With gas mixtures of $CO:H_2$ ratio below about 1:3 the amount of hydrogen consumed relative to CO is much increased, so that the $CO:H_2$ ratio of the exit gas is very much greater than that of the feed gas.

(3) The oil produced has a high olefin content, and contains appreciable quantities of branched chain hydrocarbons, and is thus of greater value both for use as motor or aviation fuel and for the production of chemicals.

(4) The quantity of valuable oxygen

[*Price 2/-*]

containing compounds (alcohols, aldehydes etc.) produced is considerably increased, and may be very considerable.

(5) The synthesis temperature in the presence of olefins becomes much less critical than is the case without their addition, and the design of full scale convertors for the purpose is therefore simplified.

The invention consists in reacting mixtures of carbon monoxide, hydrogen and olefins in the presence of catalysts and under conditions capable of yielding hydrocarbons other than methane from carbon monoxide and hydrogen alone. As catalysts, iron and cobalt are generally preferred, and may be used either alone or on porous supports and with or without the addition of promoters. Nickel catalysts are less suitable on account of the excessive methane production occurring with these catalysts and also because of the ready formation of nickel carbonyl under the reaction conditions.

Generally also we prefer to operate the process at temperatures a few degrees higher than those usual in hydrocarbon synthesis with a given catalyst. We have however found that with our method the temperature is considerably less critical than in normal synthesis. Thus with a cobalt catalyst at 10° C. rise in temperature had very little effect, although the effect of such a temperature rise in normal synthesis would have been appreciable.

The optimum temperature of operation is governed by a number of factors, such as $CO:H_2$ ratio of the feed gas, the proportion of added olefin, pressure, and the nature and age of the catalyst.

The synthesis should be carried out at pressures below about 50 atmospheres, pressures below 20 atmospheres being generally suitable, and good results being obtained even at atmospheric pressure.

The olefins added are those which are normally gaseous or boiling in the gasoline range. They may be added alone, or as is generally more convenient in practice, in admixture with inert gases or paraffin hydrocarbons with which they usually occur.

It will be understood that olefins and other materials passed to the synthesis must be first freed from sulphur compounds.

The process may advantageously be carried out in stages, since the addition of olefin in the first stage produces an effluent gas having an increased $CO:H_2$ ratio which is therefore advantageous in the production of highly olefinic products in the later stages of the process irrespective of whether olefin is added in the later stages.

According to the invention, a gas mixture obtained by reacting methane with oxygen and having a $CO:H_2$ ratio of 1:2 is passed with the added olefin to the first synthesis stage. About 50% of the input CO is converted in this stage and after separation of the C_4+ products, the gas is passed to a second synthesis stage together with sufficient of the initial gas mixture to make up the $CO:H_2$ ratio of the feed gas to 1.25:1. With such a feed gas a highly olefinic product is obtained in the second stage.

The following examples show the effect of adding olefins in the process:—

Example 1.

The operation was carried out using an ordinary cobalt synthesis catalyst of composition 100 $Co:6ThO_2:12MgO:200$ Keiselguhr (parts by weight). The feed gas used had a $CO:H_2$ ratio of 1:2. Diisobutylene was added at the rate of 0.2g. per litre of gas processed. Other conditions of the operation are as follows:—

Mean gas rate = 0.94 litres/g. cobalt/hour.
Pressure = Atmospheric.
Temperature = 190—195° C.
Gas contraction = 83 per cent.
Total running time = 270 hours.

85 per cent of the input CO reacted. The yield of all hydrocarbons was 179g./standard cubic metre, made up as follows:—

Methane - - -	12 per cent
C_2-C_4 - - -	20 per cent
Over C_4 - - -	68 per cent

The weight of added diisobutylene being deducted from these yields. The yield of synthesised oil (C_4 and over) was 142g. per standard cubic metre. The composition of the product over C_4, excluding unchanged diisobutylene, was as follows:—

Gasoline to 165° C. - - -	55 per cent by weight
- - - -	(35 per cent. olefins)
Oil 165—260° C. - - - -	19 per cent.
- - - -	(15 per cent. olefins)
Oil 260—310° C. - - - -	13 per cent.
- - - -	(10 per cent. olefins)
Over 310° C. - - - - -	13 per cent.

The olefin content of the corresponding gasoline fraction in normal synthesis was 30 per cent.

The CO : H_2 ratio of the exit gas was 1 : 1. 25 per cent of the added diisobutylene reacted, an appreciable part to isobutylene.

The operation was carried out under the same conditions as the foregoing, but with a synthesis temperature of 250° C. Under these conditions practically no condensible oil is formed in normal synthesis, but a yield of synthesised oil over C_4 (excluding added diisobutylene) of 110g./standard cubic metre was obtained, the gasoline fraction containig 45 per cent of olefins. In addition 83g. per cubic metre of C_2-C_4 hydrocarbons were obtained, having an olefin content of 60 per cent.

EXAMPLE 2.

The operation was carried out with the added ethylene, the total gas composition being (moles per cent.):—

N_2 - - - -	13
H_2 - - - -	44
CO - - - -	22
Ethylene - -	21

The same catalyst as in Example 1 was used, and the conditions were as follows:—

Synthesis temperature	193—210° C.
Pressure	Atmospheric.
Mean gas rate (total)	0.8 litres/g. cobalt/hr.
Total running time	400 hours.

51 per cent. of the input CO reacted. The yields of total hydrocarbons over C_2 obtained was 185g. per standard cubic metre of gas. The product had the following composition (weight per cent.):—

C_3	14	(65 per cent. propylene)
C_4	17	(65 per cent. olefins)
Oil over C_4	69	

The composition of the oil over C_4 was (weight per cent):—

Up to 120° C.	51 per cent.	(55 per cent. olefins)
120—200° C.	23 ,, ,,	(45 per cent. olefins)
200—266° C.	8 ,, ,,	(30 per cent. olefins)
266—310° C.	7 ,, ,,	(25 per cent. olefins)
Over 310° C.	11 ,, ,,	

The pentane fraction from the gasoline had the following composition, as determoned by spectroscopic analysis:—

Pentene-1 - - -	14.0%
Pentene-2 - - -	29.5%
Isopropylethylene -	00.3%
Methylethylethylene -	22.0%
Trimethylethylene -	Trace
Isopentane - - -	17.5%
n-Pentane - - -	26.7%

This illustrates the substantial formation of branched chain hydrocarbons. The CO : H_2 ratio of the effluent gas was 1 : 0.3 40% of the input ethylene reacted to products other than ethane. In addition to the hydrocarbon products an amount of alcohols, aldehydes, esters and acids equivalent to about 5% of the hydrocarbon yield was obtained from the aqueous layer. These compounds were principally C_2 and C_3 derivatives and methyl alcohol.

On raising the temperature to 250° C. conditions otherwise being as before, the yield of products over C_3 was 153g. per standard cubic.metre, the CO : H_2 ratio of the effluent gas being 1 : 0.7.

EXAMPLE 3.

The operation was carried out in the presence of propylene under the same conditions of pressure and temperature, and with the same catalyst as in Example 2. The gas composition was (moles %):—

N_2 - - - -	11
H_2 - - - -	45
CO - - - -	22
Propylene - -	22

The yields of C_4 and higher obtained in g. per standard cubic metre were:—

C_4	35.6 (60% olefins)
Oil over C_4	158.9 Total 194.5g.

The mean gas contraction was 68% and 74% of the input CO reacted, 25% of the added propylene reacting to products other than propane, and 21% remaining unconverted. The CO : H_2 ratio of the effluent gas was 1 : 0.3.

The composition of the oil over C_4 was as follows:—

Boiling Range °C.	Weight %	% Olefins
To 35.5	8.7	61
35.5—36.6	6.3	56
36.5—65.5	7.5	55
65.5—90	14.6	57
90—128	17.4	42
128—200	26.0	34
200—232	12.6	16
Over 282	6.9	—

Dated this 12th day of June, 1946.

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Agents for the Applicants.

COMPLETE SPECIFICATION

Improvements relating to the Synthesis of Hydrocarbons and Other Compounds from Mixtures of Carbon Monoxide and Hydrogen

We, ANGLO-IRANIAN OIL COMPANY LIMITED, of Britannic House, Finsbury Circus, London, E.C.2, a British joint-stock Corporation, and STANLEY FRANCIS BIRCH and JOHN HABESHAW, both of the Research Station of Anglo-Iranian Oil Company Limited, Chertsey Road, Sunbury-on-Thames, and both of British Nationality, 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:—

The invention relates to the synthesis of hydrocarbons and other compounds from mixtures containing carbon monoxide and hydrogen and has among its objects to increase the production of olefins in the operation and to render practicable the utilisation of natural gas and petroleum fraction that are otherwise of little value.

The Fischer-Tropsch synthesis of hydrocarbons from carbon monoxide hydrogen mixtures is well known.

Fischer (Brennstoff Chem. 16, 1—11 (1935)) discloses an optimum operating temperature of 180°—200° C. for cobalt catalysts. Fischer and Pichler used temperatures with a cobalt catalyst in the range 175° C.—213° C. (Brennstoff Chem. 20, 41—48, 221—228 (1939)) in atmospheric and medium pressure synthesis. Higher temperatures have, however, been used. Tsuneoko and Murata (See Papers Inst. Phys. Chem. Res. (Tokyo) 30, 1—14 (1936)) cite about 230° C. as the optimum temperature of silicon-cobalt catalysts. With cobalt catalysts the optimum synthesis temperature from the literature thus lies in the range 170° C.—240° C. Normal synthesis temperatures, employed in the use of iron catalysts, lie in the range 200° C.—300° C. as described in the prior art, for example, Fischer in Oel und Kohle (with Brennstoff) Chem. Vol 39, Pages 517—522 (1943); Fujimura in J. Soc. Chem. Ind. Japan Vol. 34, suppl. binding Pages 136—138 (1931).

Many modifications of this synthesis to produce high yields of olefins have been proposed. These methods involve the use of gases containing a high proportion of carbon monoxide, for example, water gas having a $CO:H_2$ molar ratio of about 1:1, or in some cases of gases containing even more CO than this. The use of such gas mixtures has some disadvantages. For example, with gases of such a high carbon monoxide content the tendency to deposit carbon on the catalyst with a consequent loss of catalyst activity is much increased. Proposals have therefore been made to overcome this by dilution of the feed gas, and this is most usually done by recycling to the process relatively large amounts of exit gas, containing principally methane, nitrogen, unconverted carbon monoxide and hydrogen, but only small amounts of other compounds. Such processes to operate successfully require an initial feed gas of high CO content. The production of such gas mixtures from methane or other hydrocarbons presents difficulty.

According to another proposal, carbon monoxide and hydrogen are reacted in the presence of a hydrogenating catalyst, such as cobalt or iron, at a pressure not exceeding half an atmosphere and, if desired, in the presence of a diluent such as hydrocarbon gases or vapours. If desired, hydrocarbons produced in an earlier stage may be recycled. Hydrocarbons so recycled may contain unsaturated hydrocarbons.

According to a further proposal, carbon monoxide, hydrogen and ethylene or its homologues are reacted at high temperature and pressure in the presence of a methanol forming catalyst, the ethylene or homologues constituting 10—40% of the total volume of gas.

In refining petroleum relatively large amounts of hydrocarbons of little value are produced, for example, methane, ethane, propane and some of the residual fractions of petroleum. Also, the light gases from cracking plants contain large amounts of the lower paraffins and olefins (C_2 and C_3) which are not generally utilised. The partial combustion with oxygen of these hydrocarbons, using a deficiency of oxygen, leads to the production of carbon monoxide, hydrogen and cracked hydrocarbon mixtures of high olefin content. The $CO:H_2$ molar ratio of the gas so produced is however considerably below 1:1 and is generally close to 1:2. Thus in processing petroleum and natural gas it is easy to produce a gaseous product comprising carbon monoxide and hydrogen in the molar ratio of approximately 1:2.

The value of the hydrocarbons produced normally by Fischer-Tropsch synthesis from gas mixtures of $CO:H_2$ molar ratio of 1:2 or more is low, since the products are almost entirely straight chain and of relatively low olefin content (about 25 per cent olefins).

We have now found that the synthesis from carbon monoxide and hydrogen may be carried out in the presence of olefins with the following advantageous results:—

1. The olefine content of the oil produced is much increased.
2. The oil produced contains appreciable quantities of branch chain hydrocarbons, and is thus of greater value both for use as motor or aviation fuel and for the production of chemicals.
3. The quantity of valuable oxygen containing compounds (alcohols, aldehydes, etc.) produced is very considerable.
4. The synthesis temperature in the presence of olefins becomes much less critical than is the case without their addition, and the design of full scale convertors for the purpose is therefore simplified.

According to the present invention hydrocarbons and oxygen-containing compounds are synthesised by a process in which a feed gas containing carbon monoxide, hydrogen and one or more olefins is reacted at a pressure in the range 1—50 atmospheres in the presence of a catalyst to form hydrocarbons other than, or in addition to, methane, the catalyst used being cobalt or iron, and the reaction temperature being in the range 170° C.—250° C. in the use of cobalt as catalyst and in the range 200° C.—310° C. in the use of iron as catalyst. The iron or cobalt catalysts are used either alone or on porous supports and with or without the addition of promoters. Nickel catalysts are less suitable on account of the excessive methane production occurring with these catalysts and also because of the ready formation of nickel carbonyl under the reaction conditions.

Generally also we prefer to operate the process at temperatures a few degrees higher than those usual in hydrocarbon synthesis with a given catalyst. We have found, however, that with our method the temperature is considerably less critical than in normal Fischer Tropsch synthesis. Thus with a cobalt catalyst, a 10° C. rise in temperature had very little effect, although the effect of such a temperature rise in normal synthesis would have been appreciable.

As stated hereinbefore, normal synthesis temperatures lie in the range 170° C.—240° C. in the use of a cobalt catalyst and 200° C.—300° C. in the use of an iron catalyst.

The temperature range in the process of the present invention is accordingly 170° C.—250° C. when a cobalt catalyst is employed and 200° C.—310° C. when an iron catalyst is employed.

The optimum temperature of operation is governed by a number of factors such as $CO:H_2$ ratio of the feed gas, the proportion of added olefin, pressure, and the nature and age of the catalyst.

The synthesis is carried out at pressures of 1 to 50 atmospheres, pressures below 20 atmospheres being generally suitable, and good results being obtained even at atmospheric pressure.

The olefins added are those which are normally gaseous or boiling in the gasoline range. They may be added alone, or as is generally more convenient in practice, in admixture with inert gases or paraffin hydrocarbons with which they usually occur. Normally, the olefins will constitute not more than 30% of the combined weights of olefin, hydrogen and carbon monoxide in the feed gas.

It will be understood that olefins and other materials passed to the synthesis must be substantially free from sulphur compounds.

With gas mixtures in which the molar content of hydrogen is less than three times the molar content of carbon monoxide, the amount of hydrogen consumed relative to carbon monoxide is much increased, whereby the $CO:H_2$ molar ratio of the exit gas is much greater than that of the feed gas. Thus the process may advantageously comprise two or more synthesis stages, since the addition of olefin in the first stage produces an effluent gas having an increased $CO:H_2$ molar ratio which is therefore advantageous in the production of highly olefinic products in the later stages of the process, irrespective of whether olefin is added in the later stages.

Thus according to one mode of operation of the process of the invention, a gas mixture having a $CO:H_2$ molar ratio of about 1:1.2 to 1:2 is passed with the added olefin to the first synthesis stage. About 50% of the input CO is converted in this stage and after separation of the C_4 and higher products, the gas is passed to a second synthesis stage, together with sufficient of the initial gas mixture to make up the $CO:H_2$ molar ratio of the feed gas to 1.25:1. With such a feed gas a highly olefinic product is obtained in the second stage.

The amount of olefin employed should be such that the ethylene-propylene content of the feedstock to the synthesis stage is at least 2 moles per cent and preferably at least 5 moles per cent of the combined carbon monoxide and hydrogen in the feedstock.

We have found that a particularly suitable olefinic fraction for use in the process of the invention is the C_2—C_3 fraction obtained from a cracked petroleum product.

If desired effluent gas from the synthesis stage of a single stage process may be recycled to the synthesis stage.

Mixtures of carbon monoxide and hydrogen suitable for use in the process of the invention are conveniently made by the partial combustion of hydrocarbons using a deficiency of oxygen. Preferred hydrocarbons for this purpose are methane and natural gas although liquid hydrocarbons may be used for this purpose if desired. In this way a gas consisting mainly of carbon monoxide and hydrogen in the molar ratio of 1:1.2 to 1:2 is obtained. Any condensible material in the mixture may be removed before the mixture is passed to the synthesis stage.

If desired effluent gas from the synthesis stage, or in the case of a multi-stage process, from the final synthesis stage can be recycled to react with oxygen for the further production of carbon monoxide and hydrogen. Build-up of inert gases in the recycle gas system may be avoided by passing the necessary proportion of effluent gas to waste.

A gas recycle process using C_2 and C_3 hydrocarbons obtained from a cracked petroleum product has been found to be of particular value. Thus by recycling the effluent gas, containing ethane and propane to be converted to carbon monoxide and hydrogen, the utilisation of the fraction is substantially complete.

Our invention is illustrated but in no way limited by the following examples in which all parts given are by weight unless otherwise specified.

EXAMPLE I.

The process was carried out using a feed gas consisting of carbon monoxide, hydrogen and diisobutylene and as catalyst, a cobalt synthesis catalyst having the composition :—

Cobalt - - -	100 parts
Thoria - - -	6 parts
Magnesia - - -	12 parts
Keiselguhr - -	200 parts

The feed gas used had a $CO:H_2$ molar ratio of 1:2. Diisobutylene was added at the rate of 0.2 grams per litre of gas processed. Other conditions of the operation are as follows :—

Mean gas rate = 0.94 litres/gram cobalt/hour.
Pressure = Atmospheric.
Temperature = 190—195° C.
Gas contraction = 83 per cent.
Total running time = 270 hours.

85 per cent of the input CO reacted. The yield of all hydrocarbons was 179 grams/standard cubic metre, made up as follows :—

Methane - - -	12 per cent
$C_2 - C_4$ - - -	20 per cent
Over C_4 - - -	68 per cent

The weight of added diisobutylene being deducted from these yields. The yield of synthesised oil (C_4 and over) was 142 grams per standard cubic metre. The composition of the product over C_4, excluding unchanged diisobutylene, was as follows :—

Gasoline to 165° C. - -	55 per cent	(35 per cent olefins in fraction)
Oil 165—260° C. - -	19 per cent	(15 per cent olefins in fraction)
Oil 260—310° C. - -	13 per cent	(10 per cent olefins in fraction)
Over 310° C. - - -	13 per cent	

The olefin content of the corresponding gasoline fraction in normal Fischer Tropsch synthesis was 30 per cent.

The $CO:H_2$ molar ratio of the exit gas was 1:1. 25 per cent of the added diisobutylene reacted, an appreciable part to isobutylene.

EXAMPLE II.

The process of Example I was repeated, but with a synthesis temperature of 250° C. Under these conditions practically no condensible oil is formed in normal synthesis but a yield of synthesised oil over C_4 (excluding added diisobutylene) of 110 grams/standard cubic metre was obtained, the gasoline fraction containing 45 per cent of olefins. In addition 83 grams per cubic metre of C_2—C_4 hydrocarbons were obtained, having an olefin content of 60 per cent.

EXAMPLE III.

The process was carried out using a gas feed having the composition :—

N_2 - -	13 moles per cent
H_2 - -	44 moles per cent
CO - -	22 moles per cent
Ethylene -	21 moles per cent

The same catalyst as in Example I was used, and the process conditions were as follows :—

Synthesis temperature	193—210° C.
Pressure	Atmospheric.
Mean gas rate (total)	0.8 litres/gram cobalt/hour.
Total running time	400 hours.

51 per cent of the input CO reacted. The yields of total hydrocarbons over C_2 obtained was 185 grams per standard cubic metre of gas. The product had the following composition (weight per cent):—

C_3	14	(65 per cent propylene)
C_4	17	(65 per cent olefins)
Oil over C_4	69	

The composition of the oil over C_4 was (weight per cent):—

Up to 120° C.	51 per cent.	(55 per cent. olefins)
120—200° C.	23 per cent.	(45 per cent. olefins)
200—266° C.	8 per cent.	(30 per cent. olefins)
266—310° C.	7 per cent.	(25 per cent. olefins)
Over 310° C.	11 per cent.	

The pentane fraction from the gasoline had the following composition, as determined by spectroscopic analysis:—

Pentene-1 - -	14.0 per cent.
Pentene-2 - -	29.5 per cent.
Isopropylethylene	00.3 per cent.
Methylethylethylene	22.0 per cent.
Trimethylethylene	Trace
Isopentane - -	17.5 per cent.
n-Pentane - -	26.7 per cent.

This illustrates the substantial formation of branched chain hydrocarbons. The $CO:H_2$ molar ratio of the effluent gas was 1:0.3. 40% of the input ethylene reacted to products other than ethane. In addition to the hydrocarbon products an amount of alcohols, aldehydes, esters and acids equivalent to about 5% of the hydrocarbon yield was obtained from the aqueous layer of the synthesis product. These compounds were principally C_2 and C_3 derivatives and methyl alcohol.

On raising the temperature to 250° C. conditions otherwise being as before, the yield of products over C_3 was 153 grams per standard cubic metre, the $CO:H_2$ ratio of the effluent gas being 1:0.7.

EXAMPLE IV.

The operation was carried out in the presence of propylene under the same conditions of pressure and temperature, and with the same catalyst as in Example II. The gas composition was:—

N_2 - -	11 moles per cent.
H_2 - -	45 moles per cent.
CO - -	22 moles per cent.
Propylene -	22 moles per cent.

The yields of C_4 and higher obtained in grams per standerd cubic metre was:—

C_4	35.6 (60% olefins)
Oil over C_4	158.9

The mean gas contraction was 68% and 74% of the input CO reacted, 25% of the added propylene reacting to products other than propane, and 21% remaining unconverted. The $CO:H_2$ molar ratio of the effluent gas was 1:0.3.

The composition of the oil over C_4 was as follows:—

Boiling Range °C.	Weight %	% Olefins in fraction
To 35.5	8.7	61
35.5—36.5	6.3	56
36.5—65.5	7.5	55
65.5—90	14.6	57
90—128	17.4	42
128—200	26.0	34
200—282	12.6	16
Over 282	6.9	not estimated

EXAMPLE V.

The process was carried out using a gas feed comprising normal butenes and having the composition:—

N_2 - -	18 moles per cent.
H_2 - -	52 moles per cent.
CO - -	26 moles per cent.
CO_2 - -	1.4 moles per cent.
n-butenes -	2.6 moles per cent.

The same catalyst was used as in Example I, the process conditions being as follows:—

Synthesis temperature	190° C.
Pressure	Atmospheric.
Mean gas rate (total)	1 litre/gram cobalt/hour.
Total running time	143 hours.

84% of the input CO reacted. The yield was:—

Methane - -	27 grams per standard cubic metre of gas.
C_2—C_4 inclus. -	82 grams per standard cubic metre of gas.
Oil over C_4 - -	131 grams per standard cubic metre of gas.

The oil over C_4 contained 41 per cent of gasoline to 120° C. the olefin content being 43 per cent. Under normal Fischer Tropsch synthesis conditions, in the absence of olefin in the synthesis feed, the corresponding olefin content is 30 per cent.

The effluent gas had a $CO:H_2$ molar ratio of 1:1.1.

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 the synthesis of hydrocarbons and oxygen-containing compounds in which a feed gas containing carbon monoxide, hydrogen and one or more olefins is reacted at a pressure in the range 1—50 atmospheres in the presence of a catalyst to form hydrocarbons other than, or in addition to methane, the catalyst used being cobalt or iron, and the reaction temperature being in the range 170° C.—250° C. in the use of cobalt as catalyst and in the range 200° C.—310° C. in the use of iron as catalyst.

2. A process according to claim 1, in which the molar ratio of carbon monoxide to hydrogen in the feed to the synthesis zone lies between 1:1.2 and 1:2.

3. A process according to either claim 1 or claim 2, in which the feed gas to the synthesis zones comprises a mixture of one or more olefins with carbon monoxide and hydrogen obtained by the partial combustion of hydrocarbons using a deficiency of oxygen.

4. A process according to claim 3, in which the feed gas to the synthesis zone comprises a mixture of one or more olefins with carbon monoxide and hydrogen obtained by the partial combustion of methane or natural gas using a deficiency of oxygen.

5. A process according to any of the preceding claims, in which effluent gas from the synthesis zone is recycled to the feed to the synthesis zone.

6. A process for the synthesis of hydrocarbons and oxygen-containing compounds, in which effluent gas from an initial synthesis zone operated according to claim 1 is passed, with or without the addition of one or more olefins, to a subsequent synthesis zone operated under conditions, and in the presence of cobalt or iron as catalyst, capable of yielding hydrocarbons other than methane from carbon monoxide and hydrogen alone.

7. A process according to any of the preceding claims, in which effluent gas from a synthesis zone is caused to undergo partial combustion, using a deficiency of oxygen, for the production of a mixture of carbon monoxide and hydrogen for incorporation in the feed gas to a synthesis zone.

8. A process according to any of the preceding claims, in which the feed gas to a synthesis zone comprises carbon monoxide, hydrogen and the distillation fraction of a cracked petroleum consisting essentially of hydrocarbons containing 2—3 carbon atoms.

9. A process according to any of the preceding claims, in which the olefin content of the feed gas is at least 2 moles per cent of the total carbon monoxide and hydrogen in the feed gas.

10. A process according to claim 9, in which the olefin content of the feed gas is at least 5 moles per cent of the total carbon monoxide and hydrogen in the feed gas.

11. A process according to any of the preceding claims, in which the pressure is from 1—20 atmospheres.

12. A process according to any of the preceding claims, in which the olefin content of the feed gas is not in excess of 30 per cent of the combined weight of olefin, carbon monoxide, and hydrogen in the feed gas.

13. A process for the synthesis of hydrocarbons and oxygen-containing compounds substantially as described with reference to any of the foregoing examples.

14. Hydrocarbons whenever produced by a process as claimed in any of the claims 1—13.

Dated this 12th day of June, 1947.
EDWARD EVANS & CO.,
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