PATENT SPECIFICATION

487,250

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797

COMPLETE SPECIFICATION

Production of Hydrocarbons

We, GEWERKSCHAFT AUGUSTE, of 11, Wilmstrasse, Oberhausen (Rheinland), Germany, a body Corporate, organised under the Laws of Germany, 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 production of hydrocarbons and more particularly to a process which renders it possible to carry out on an industrial scale reactions of a strongly endothermic character, which hitherto forbade their large-scale utilisation, between gases or between gases and liquids.

The invention is especially concerned with the production of valuable hydrocarbons from methane and the oxides of carbon.

We have found that strongly endothermic reactions can be held under control and utilised in the production of hydrocarbons by causing reactions of exothermic character, such as for instance the reaction

$$CO + 3H_2 = CH_4 + H_2O \qquad (a)$$

(which are hereinafter termed "steering reactions"), to occur simultaneously, thereby steering the algebraic sum of the free energies of the two reactions into thermodynamically favourable regions. We thus succeed in obtaining the final products of reactions, which, owing to the particular thermal conditions, i.e. owing to their highly endothermic character, could hitherto be carried out on an industrial scale, if at all, only with great difficulty.

The free energies are the measure of the course of a reaction. According to this invention their algebraic sum must not exceed the value of + 5500 gram/calories per mol. of hydrocarbon produced (calculated according to the method disclosed by Lewis and Randall, for instance in "Thermodynamics" published by McGraw & Hill, 1923). This sum may also have a negative value.

The control of the free energies achieved by this rule of working offers the great advantage of allowing the reactions to be carried out under high pressure. High pressure is a necessity because under normal pressure the methane molecule is very stable and does not readily enter into any reaction.

A sufficiently high pressure activates (polarises) the methane molecule, which then becomes a readily reactive compound. According to the law of mass action the high pressure also acts towards increasing the yield, so that we are now enabled to carry out successfully even reactions which possess a comparatively small physico-chemical constant K and accordingly also only a low negative or even a positive free energy (not exceeding 5500 g./cal.). Apart therefrom the high pressure offers the further advantage of highly accelerating the reaction.

We have found that in this manner we can produce hydrocarbons (or their polymers or isomers) which may carry side chains, from mixtures of (a) carbon monoxide, which may be wholly or partly replaced, in such mixture, by carbon dioxide, (b) hydrogen, which may be wholly or partly replaced by water and (c) methane, being enabled so to influence the reaction that either aliphatic or hydroaromatic or aromatic hydrocarbons predominate in the product of the process.

According to the present invention a process is provided of selectively producing under high pressure mixtures of hydrocarbons including those with side chains in which predominate either aliphatic or hydroaromatic or aromatic hydrocarbons which is characterised in that in an endothermic reaction (fundamental reaction), according to the equation of which the desired compounds can

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form from methane and carbon oxides, part of the methane is replaced by a mixture of hydrogen or water and carbon monoxide and/or carbon dioxide, from which mixture methane can form in accordance with the equation of an exothermic reaction (steering reaction), so that the fundamental reaction equation is changed into a reaction equation, the free energy of which, if calculated according to the method indicated by Lewis and Randall, does not exceed +5500 gram calories per mol. of the product to be produced, and which value may also be negative, the molecular quantity of methane present in the starting gas mixture being at least one fourth of the molecular quantity of carbon oxides present in the mixture.

Our invention will first be explained more in detail with reference to the synthetic production under pressure of the aliphatic compound octane. The process is here carried out in such a manner that in the fundamental reaction equation

$$17CH_4 + 7CO = 3C_8H_{18} + 7H_2O$$

which, being strongly endothermic, can be utilised as such, if at all, only with great difficulty, part of the methane is replaced, by way of the steering reaction (a), by a mixture of hydrogen and carbon monoxide in the molecular proportion of 3 H_2 to 1 CO. H_2 and CO are gradually introduced into the endothermic fundamental reaction equation until a reaction equation has been reached, the free energy of which remains below + 5500 g./cal. per mol. of octane. By introducing H_2 and CO in the molecular proportion mentioned above we thus steer the process from the thermodynamically unfavourable region into a region which under high pressure conditions is thermodynamically favourable.

If the whole of the CH_4 to be introduced in accordance with the basic reaction

$$17CH_4 + 7CO = 3C_8H_{18} + 7H_2O$$

were replaced by a mixture of 3 parts H_2 and 1 part CO, there would result the equation

$$17H_2 + 8CO = C_8H_{18} + 8H_2O$$

(end reaction equation) which at technically favourable temperatures is so strongly exothermic that it cannot be controlled. Even if this reaction were carried out under vigorous cooling, inevitable local overheating would lead to a decomposition of the hydrocarbon to be produced and to the formation of methane as an undesired by-product. The technical difficulties which prevent the sufficiently rapid removal of the large quantities of heat evolved, are felt particularly when operating under high pressure, since in this case the heat is evolved in a smaller space and leads to a more rapid and more accentuated rise of temperature. We thus avoid reactions, which, under the conditions of operation chosen, are strongly exothermic. In the production of octane for instance such reactions are preferably selected in which the free energies lie below +5500 and between +5500 and −10000 g./cal. per mol. of octane produced.

Between the fundamental reaction and the end reaction equation mentioned above a large number of different reaction equations can be formed by replacing any fraction of the quantity of methane, which is required according to the fundamental reaction equation, by the corresponding quantity of a mixture of $3H_2 + CO$. The free energies of these intermediate equations lie between the free energy of the fundamental reaction and that of the end reaction. They are determined in a well known manner, and the starting materials are brought together in those molecular proportions which correspond to an intermediate reaction, the free energy of which at the working temperature does not exceed the value of +5500 g./cal. per mol. of octane, and may thus also be negative. It is advisable to start from gas mixtures which under the pressure and at the temperature used will not evolve any heat or too large quantities of heat, for instance mixtures which correspond to the following equations:

$$11CH_4 + 13CO + 18H_2 = 3C_8H_{18} + 13H_2O \quad - - - - \quad 1$$

(−1056 g./cal. per mol. C_8H_{18} at 550° absolute)
(+5037 g./cal. per mol. C_8H_{18} at 575° absolute)

or:

$$10CH_4 + 14CO + 21H_2 = 3C_8H_{18} + 14H_2O \quad - - - - \quad 2$$

(−7573 g./cal. per mol. C_8H_{18} at 550° absolute)
(− 989 g./cal. per mol. C_8H_{18} at 575° absolute)

or:

$$9CH_4 + 15CO + 24H_2 = 3C_8H_{18} + 15H_2O \quad - \; - \; - \; - \quad 3$$

$$(-14091\ \text{g./cal. per mol. } C_8H_{18} \text{ at } 550° \text{ absolute})$$
$$(-\ 7015\ \text{g./cal. per mol. } C_8H_{18} \text{ at } 575° \text{ absolute})$$

The figures indicate the approximate values of the free energies at 550° and 575° absolute (degrees Kelvin), respectively. When working at 550° absolute it is preferred to use equation 1 or 2 and when working at 575° absolute it is preferred to use equation 2 or 3.

The synthetic production of octane according to the fundamental equation

$$17CH_4 + 7CO = 3C_8H_{18} + 7H_2O$$

can also be steered or directed with the aid of the reaction

$$2H_2O + 4CO = CH_4 + 3CO_2 \qquad (b)$$

The strongly exothermic end reaction then reads

$$9H_2O + 25CO = C_8H_{18} + 17CO_2.$$

Again the free energies of the intermediate stages are determined and a suitable stage is selected for the practical operation according to the principles developed above.

In the production of octane one may also start from the fundamental reaction equations

$$9CH_4 + 14CO = 2C_8H_{18} + 7CO_2$$
$$\text{or} \quad 25CH_4 + 7CO_2 = 4C_8H_{18} + 14H_2O$$

Besides the steering reactions (a) and (b) mentioned above we may also avail ourselves of the steering reaction

$$2H_2 + 2CO = CH_4 + CO_2 \qquad (c)$$

With all fundamental reaction equations there may further be combined the steering reaction

$$4H_2 + CO_2 = CH_4 + 2H_2O \qquad (d)$$

The above explanations have been developed with respect to octane because this compound is considered to be the most important representative of the benzine group and occupies the centre of the aliphatic series of the benzine hydrocarbons. In the practical operation of the reactions, however, no chemically pure octane will be produced, because for instance the following combinations represent the same amounts of free energy:

$$2C_8H_{18} = C_7H_{16} + C_9H_{20} = C_6H_{14} + C_{10}H_{22}.$$

Therefore these different products will be formed simultaneously.

In substantially the same manner as explained above for the production of aliphatic compounds products may also be produced which contain aromatic or hydroaromatic (alicyclic) compounds as the predominant constituents. In the production of these compounds a relatively higher percentage of carbon monoxide is used than in the production of the corresponding aliphatic compounds, since these latter are richer in hydrogen.

Strongly endothermic reactions in which either benzene or hexahydrobenzene is formed from methane and carbon oxides, may for instance be steered into regions which are thermodynamically favourable when operating under high pressure, i.e. into such regions in which the reactions, which actually proceed, possess free energies lying below +5500 g./cal.

This is again effected for instance by causing to proceed simultaneously, in the manner described above the highly exothermic reaction.

$$3H_2 + CO = CH_4 + H_2O$$

Thus the production of benzene from methane and carbon monoxide can for instance be assumed to proceed according to the following fundamental reaction equation

$$3CH_4 + 3CO = C_6H_6 + 3H_2O.$$

This reaction is very highly endothermic. Its free energy amounts for instance at 327° C. to +14.019 g./cal., so that it could be carried out on an industrial scale, if at all, only with the greatest difficulty. According to our invention we now partly replace in this fundamental reaction equation the CH_4 by H_2 and CO in the molecular proportion of 3:1, introducing into the said reaction equation that quantity of this mixture which according to equation (a) corresponds to the quantity of methane which is to be replaced in the fundamental reaction equation. We replace so much of the CH_4 by a mixture of 3 parts H_2 and 1 part CO that the free energy of the resulting reaction does not exceed, at the operating temperature +5500 g./cal. per mol. of the hydrocarbon to be produced.

The following example illustrates in a somewhat different manner how to replace the methane by hydrogen and carbon monoxide in the manner described above:

Fundamental reaction:

$$
\begin{array}{rl}
 & 3CH_4 + 3CO = C_6H_6 + 3H_2O \\
+n(& 3H_2 + CO = H_2O + CH_4) \\
\hline
\text{Sum total:} & 3nH_2 + (3-n)CH_4 + (3+n)CO = C_6H_6 + (3+n)H_2O
\end{array}
$$

Here n may possess any integral or fractional value above zero, which value however in the preceding example, corresponding to the number of CH_4-molecules in the fundamental reaction equation, cannot exceed 3. For if n becomes equal to 3, the whole of the methane is replaced and the fundamental reaction equation

$$3CH_4 + 3CO = C_6H_6 + 3H_2O$$

is changed by the addition of

$$3(3H_2 + CO = H_2O + CH_4)$$

into the end reaction

$$9H_2 + 6CO = C_6H_6 + 6H_2O.$$

By varying n any number of reaction equations may be formulated, which lie between these two equations and the free energies of which lie between the free energy of the fundamental reaction and that of the end reaction. Of these intermediate equations we select for practical use one which at the reaction temperatures chosen possesses a free energy which is thermodynamically favourable for carrying out under high pressure. In other words: by introducing the reaction equation:

$$3H_2 + CO = CH_4 + H_2O$$

(or a fraction or a multiple of the same) there result equations, with the aid of which the free energies may be varied at will within the limits determined by the free energies of the fundamental reaction equation and that of the end reaction equation.

In all these calculations one may of course also start from the exothermic end reaction. In this case the hydrogen and the carbon monoxide must be partly replaced by methane.

In a similar manner toluene may be produced as the main product, the reaction according to the equation

$$11CH_4 + 10CO = 3C_7H_8 + 10H_2O$$

being used for instance as the highly endothermic fundamental reaction. At 327° C. the free energy of this reaction amounts to +50865 g./cal., thus being, as in the preceding example, so strongly positive that the reaction is unfit for industrial use. In order to be enabled to successfully produce in spite thereof toluene from methane and carbon monoxide, this reaction is steered by means of the steering reactions mentioned above into regions, in which the free energy reaches values which, according to the principles of thermodynamics, secure a technically favourable course of the reaction under high pressure. These regions lie below +5500 g./cal. per mol. of toluene produced.

The production of other aromatic compounds can be carried through in accordance with the same principles.

If preponderantly hydro-aromatic compounds, for instance hexahydrobenzene, are to be produced, one may start from the strongly endothermic fundamental reaction equation

$$4CH_4 + 2CO = C_6H_{12} + 2H_2O.$$

This equation has a large positive free energy, for instance at 327° C. +34780 g./cal., being thus so strongly endothermic as not to be fit for practical operation. In order nevertheless to be able to produce hexahydrobenzene from methane and carbon monoxide, this fundamental reaction equation is steered, for instance by replacing part of the methane by a mixture of carbon monoxide and hydrogen in the molecular proportion of 3:1, into regions in which the free energies possess values, which render the formation of hexahydrobenzene under high pressure possible without difficulty.

The preceding fundamental reaction equation can be steered in the same manner with the aid of the other steering reactions described above.

The steering of the fundamental reactions with the aid of these steering reactions is effected in the same manner as in the preceding examples, i.e. for instance in applying the steering reaction (c) one replaces part of the methane, which occurs on the left hand side of the fundamental reaction equation (similarly as with the steering reaction (a)) by such a quantity of a mixture of hydrogen and carbon monoxide—in which mixture however hydrogen and carbon monoxide are now present in the molecular proportion of 2 : 2—that the molecular quantity of the methane forming according to the equation of the steering reaction (c) corresponds to the molecular quantity of methane to be replaced in the equation of the fundamental reaction.

In all cases the fundamental reaction equation is combined with the steering reaction equation in such proportion that there results a reaction equation, the free energy of which lies below +5500 g./cal., and the starting materials are caused to react with each other in the proportions indicated by the equation of the resulting reaction, by exposing them to suitable conditions of temperature and pressure in accordance with the principles mentioned above. Obviously by applying the above principle one is enabled to reach the region which is most favourable for the carrying out of the reactions under high pressures, in which the free energies lie below +5500 g./cal. and for instance between +5500 and −10000 g./cal.

The following fundamental reaction equations can for instance be steered by means of one of the steering reactions mentioned above in accordance with the principle underlying this invention :

$$17CH_4 + 7CO = C_8H_{18} + 7H_2O$$

$$3CH_4 + 3CO = C_6H_6 + 3H_2O$$

$$4CH_4 + 2CO = C_6H_{12} + 2H_2O$$

$$9CH_4 + 14CO = 2C_8H_{18} + 7CO_2$$

$$3CH_4 + 18CO = 2C_6H_6 + 9CO_2$$

$$3CH_4 + 6CO = C_6H_{12} + 3CO_2$$

$$25CH_4 + 7CO_2 = 4C_8H_{18} + 14H_2O$$

$$15CH_4 + 9CO_2 = 4C_6H_6 + 18H_2O$$

$$9CH_4 + 3CO_2 = 2C_6H_{12} + 6H_2O.$$

The preceding fundamental reaction equations represent primary types for the production of aliphatic, hydroaromatic and aromatic hydrocarbons, respectively. The invention is, however, not limited to these primary types. One may start in the same manner also from fundamental reaction equations according to which are formed homologues of these primary types, such as toluene, xylene, methylcyclohexane or the like, and these fundamental reaction equations may be steered with the aid of one of the steering reactions mentioned above.

In a similar manner, as explained in the preceding examples with reference to the production of hexahydrobenzene from methane and carbon monoxide, tetrahydrobenzene may for instance be produced as predominant product by choosing different molecular proportions according to the fundamental reaction equation

$$11CH_4 + 7CO = 3C_6H_{10} + 7H_2O$$

The production of other hydro-aromatic compounds can be carried out on the same principle.

From the free energies the well known equilibrium constant may be calculated, which forms a criterion for the calculation of the yield and of the pressures required.

Since the heat energy produced in the reaction can be controlled by means of a steering reaction, we are enabled to operate on a large scale under high pressure. Apart therefrom the high pressure not only serves to increase the yield in accordance with the law of mass action, but also to activate (polarise) the methane molecular. The pressure employed in the process must be high enough to cause such an activation; this is, however, attained at comparatively low pressures, if in the mixtures there are present larger quantities of CO, the molecule of which is relatively unstable, i.e. relatively readily highly polarised and operates in the polarisation of the methane by influence.

It will be useful in most cases to operate at high total pressures, for instance above 500 atmospheres and preferably above 1000 atmospheres. The working temperature may as a rule be chosen with advantage between 450° and 800° absolute (degrees Kelvin).

In the practical operation the reactions here in question can only be carried out with advantage, if the molecular quantity of CH_4 present in the starting gas mixture amounts to at least one fourth of the quantity of carbon oxides present.

The presence of CH_4 in the starting gas mixture also offers the advantage that the undesired formation of CH_4 is suppressed and prevented according to the law of mass action. The use of CH_4 instead of H_2 also leads to a diminution of the proportion of carbon oxides in the starting gas mixture and thus also to a diminution of the highly exothermic formation of H_2O. This is particularly advantageous when operating under very high pressures, at which it is difficult, in consequence of the small specific volume to carry away the excess heat with sufficient speed.

As already mentioned above, as a rule the starting materials do not react with each other according to only one reacting equation, but several reactions will always proceed simultaneously, so that a mixture of various substances is obtained. According to the quantities of CH_4, CO or CO_2 used, i.e. in accordance with the fundamental reaction equations used in practical operation aliphatic or aromatic or hydroaromatic compounds will predominate in the resultant product.

The starting materials need not be chemically pure; inert gases which will not participate in the reaction may be present in the reaction mixture. For instance natural gas or certain industrial gases containing hydrogen, carbon oxides and/or methane may be used as starting material, which may previously have been subjected to a thermal treatment or a conversion according to well known methods.

For the purpose of accelerating the reactions, particularly when operating at not too high pressures, catalysts may be used, which are produced and employed in a manner well known to a person skilled in the art. If catalysts are used having a selective efficacy, i.e. which accelerate with different effect the formation, from the same starting materials, of different compounds, the composition of the end products may be influenced according to well known principles. In such case the above explanations apply with equal force to the fundamental reaction equations, which are preferably accelerated by the respective catalyst.

In the practical operation of our invention we may for instance proceed as follows:

EXAMPLE I.

Through a contact tube filled with an iron-molybdenum-catalyst are continuously forced, after the reduction of the catalyst, 1000 cubic metres per hour of a gas mixture having the following compositon: 38% (by volume) of H_2, 31% of CO and 31% of CH_4. The pressure is maintained at 850 atmospheres above normal, the temperature at 250° C. There result 315 kgs. of hydrocarbons, consisting mainly of octane, and 195 kgs. of water per hour.

In the main the reaction

$$5H_2 + 4CO + 4CH_4 = 4H_2O + C_8H_{18}$$
(free energy: −283 g./cal.)

has occurred. The steering reaction

$$3H_2 + CO = CH_4 + H_2O$$
(free energy: −21019 g./cal.)

was used to change the strongly endothermic fundamental reaction

$$17CH_4 + 7CO = 3C_8H_{18} + 7H_2O$$
(free energy: +104,774 g./cal.)

into the reaction

$$12CH_4 + 12CO + 15H_2 = 3C_8H_{18} + 12H_2O$$
(free energy: −849 g./cal.)

which is equal to

$$4CH_4 + 4CO + 5H_2 = C_8H_{18} + 4H_2O$$

EXAMPLE 2.

1000 cubic metres of a gas mixture consisting of 33.3% (by volume) of H_2, 33.3% of CO and 33.4% of CH_4 are passed per hour through a contact tube containing reduced molybdenum-iron, the pressure being maintained at 800 atmospheres above normal, the temperature at 225 to 230° C. There are formed per hour 330 kgs. of hydrocarbons, consisting mainly of cyclohexane, and 240 kgs. of water.

Here the reaction

$$3H_2 + 3CH_4 + 3CO = 3H_2O + C_6H_{12}$$

has been carried out, the free energy of which at the working temperature amounts to +2698 g./cal. per 1 mol. C_6H_{12}. The reaction results from the fundamental reaction equation

$$4CH_4 + 2CO = 2H_2O + C_6H_{12},$$

(the free energy of which at the working temperature amounts to +25 178 g./cal.) by replacing therein exactly $1CH_4$ by $3H_2 + 1CO$ in accordance with the steering reaction

$$3H_2 + CO = CH_4 + H_2O,$$

the free energy of which at the working temperature amounts to −22 480 g./cal. per 1 mol. of CH_4.

Example 3.

Through a contact tube charged with the same catalyst as in Example 1 are continuously forced 1000 cubic metres per hour of the following gas mixture: 33.3% (by volume) of H_2, 22.2% of CH_4 and 44.5% of CO. The pressure is maintained at 890 atmospheres above normal, the temperature at 370 to 380° C. There are formed per hour 212 kgs. of aromatic hydrocarbons, consisting mainly of benzene, and about 200 kgs. of water.

Here the reaction

$$3H_2 + 2CH_4 + 4CO = C_6H_6 + 4H_2O,$$

has been carried out, which at the temperature mentioned has a free energy of +3295 g./cal. per mol. of benzene. The fundamental reaction equation used:

$$3CH_4 + 3CO = 3H_2O + C_6H_6$$

has at 370 to 380° C. the free energy +16917 g./cal. per mol. of benzene and is steered by the steering reaction (a)

$$3H_2 + CO = H_2O + CH_4$$
$$\text{(free energy: } -13622 \text{ g./cal.)}$$

into the above mentioned area which is thermodynamically favourable with a view to the conditions of operation employed.

Example 4.

Through a contact tube charged with the same catalyst as in Example 1 are forced 1000 cubic metres per hour of a gas mixture composed of 41.7% (by volume) of H_2, 16.7% of CH_4 and 41.6% of CO. The pressure is maintained at 1450 atmospheres above normal, the temperature at 370 to 380° C. There are formed per hour 273 kgs. of aromatic hydrocarbons, consisting mainly of toluene, and about 270 kgs. of water. The formation of the toluene took place according to the equation

$$5H_2 + 2CH_4 + 5CO = C_7H_8 + 5H_2O$$
$$\text{(free energy: } -2061 \text{ g./cal.)}$$

In the endothermic fundamental reaction

$$11CH_4 + 10CO = 10H_2O + 3C_7H_8$$
$$\text{(free energy: } +61927 \text{ g./cal.),}$$

steered by the steering reaction (a)

$$3H_2 + CO = CH_4 + H_2O$$
$$\text{(free energy: } -13622 \text{ g./cal.)}$$

5 mols. of CH_4 have been replaced by a mixture of $5CO. + 15H_2$, so that there results the reaction

$$15H_2 + 6CH_4 + 15CO = 15H_2O + 3C_7H_8$$
$$\text{(free energy: } -6184 \text{ g./cal.)}$$

equal to

$$5H_2 + 2CH_4 + 5CO = 5H_2O + C_7H_8$$

to which correspond the percentage of starting materials stated above.

Example 5.

Through a contact tube charged with the same catalyst as in Example 1 are forced 1000 cubic metres per hour of a gas mixture consisting of 22.2% (by volume) CH_4 and 77.8% CO. The pressure is maintained at 1300 atmospheres above normal, the temperature at 370 to 380° C. There are formed per hour 329 kgs. of hydrocarbons, mainly benzene, 76 kgs. of water and 556 kgs. of CO_2.

Here the reaction

$$2CH_4 + 7CO = C_6H_6 + H_2O + 3CO_2$$

played the main role, the free energy of which at the working temperature amounts to −6768 g./cal. per mol. of benzene produced. The fundamental reaction equation

$$3CH_4 + 3CO = C_6H_6 + 3H_2O$$
$$\text{(free energy: } +16917 \text{ g./cal.)}$$

was changed by the steering reaction (d)

$$2H_2O + 4CO = 3CO_2 + CH_4$$
$$\text{(free energy: } -23685 \text{ g./cal.)}$$

into the resulting reaction equation given above.

Example 6.

Through a contact tube charged with the same catalyst as in Example 1 were forced 1000 cubic metres per hour of a gas mixture consisting of 16.7% (by volume) of H_2, 16.7% of CH_4 and 66.6% of CO. The pressure was maintained at 1270 atmospheres above normal, the temperature at 370 to 380° C. There were formed per hour 259 kgs. of cyclic hydrocarbons, preponderantly cyclohexane, and 543 kgs. of CO_2.

Mainly the conversion

$$2H_2 + 8CO + 2CH_4 = C_6H_{12} + 4CO_2$$

took place, the free energy of which under the working conditions amounts to −1057 g./cal. The fundamental reaction

$$6CO + 3CH_4 = C_6H_{12} + 3CO_2,$$

which cannot be carried out practically under the working conditions mentioned in consequence of its having a free energy of 15919 g./cal. per mol. of cyclohexane, was steered by the steering reaction (b)

$$2H_2 + 2CO = CO_2 + CH_4$$
(free energy: −16976 g./cal.)

into the thermodynamically favourable area of the reaction actually carried out.

EXAMPLE 7.

Through a contact tube filled with a reduced vanadium iron contact are forced 1000 cubic metres per hour of a gas mixture consisting of 62% (by volume) of H_2, 23.8% of CO_2 and 14% of CH_4. The pressure is maintained at about 868 atmospheres, the temperature at about 250° C. There are formed per hour 50 kgs. of benzines, which mainly consist of octane, and 78 kgs. of water.

The formation of the benzines takes place according to the equation

$$13H_2 + 3CH_4 + 5CO_2 = C_8H_{18} + 10H_2O$$
(free energy: +1770 g./cal.)

which results, when the endothermic fundamental reaction

$$25CH_4 + 7CO_2 = 4C_8H_{18} + 14H_2O$$
(free energy: +50985 g./cal.)

is caused to proceed simultaneously with the steering reaction (d)

$$4H_2 + CO_2 = CH_4 + 2H_2O$$
(free energy: −16405 g./cal.)

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 of selectively producing under high pressure mixtures of hydrocarbons including those with side chains in which predominate either aliphatic or hydroaromatic or aromatic hydrocarbons characterised in that in an endothermic reaction (fundamental reaction), according to the equation of which the desired compounds can form from methane and carbon oxides, part of the methane is replaced by a mixture of hydrogen or water and carbon monoxide and/or carbon dioxide, from which mixture methane can form in accordance with the equation of an exothermic reaction (steering reaction), so that the fundamental reaction equation is changed into a reaction equation, the free energy of which corresponds to a value, which, if calculated according to the method indicated by Lewis and Randall, does not exceed +5500 gram. calories per mol. of the product to be produced, and which value may also be negative, the molecular quantity of methane present in the starting gas mixture being at least one fourth of the molecular quantity of carbon oxides present in the mixture.

2. A process as claimed in claim 1, in which the operation is carried out under a total pressure of at least 500 atmospheres.

3. A process as claimed in claim 1, in which the operation is carried out under a total pressure of at least 1000 atmospheres.

4. A process as claimed in any one of the preceding claims, characterised in that the operation is carried out at temperatures ranging between 450° and 800° absolute (degrees Kelvin).

Dated this 17th day of December, 1936.

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20 to 23, Holborn, London, E.C.1,
Agent for the Applicants.

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ERRATA

SPECIFICATION No. 487,250.

Page 5, line 94, *for* " molecular " *read* " molecule "
Page 7, line 49, *for* " 5CO." *read* " 5CO "
Page 7, line 54, *for* " percentage " *read* " percentages "

THE PATENT OFFICE,
September 6th, 1938.