

Sept. 15, 1931.

A. MITTASCH ET AL

1,823,503

MANUFACTURE OF UNSATURATED HYDROCARBONS

Filed Jan. 19, 1927

2 Sheets-Sheet 1

Fig. 1.

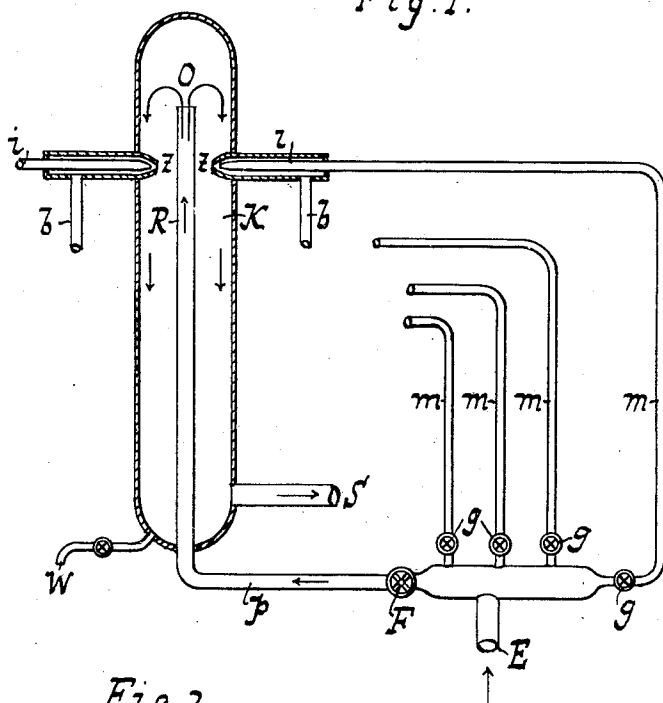
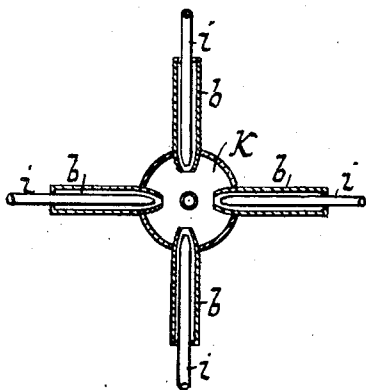


Fig. 2.



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Fig. 3.

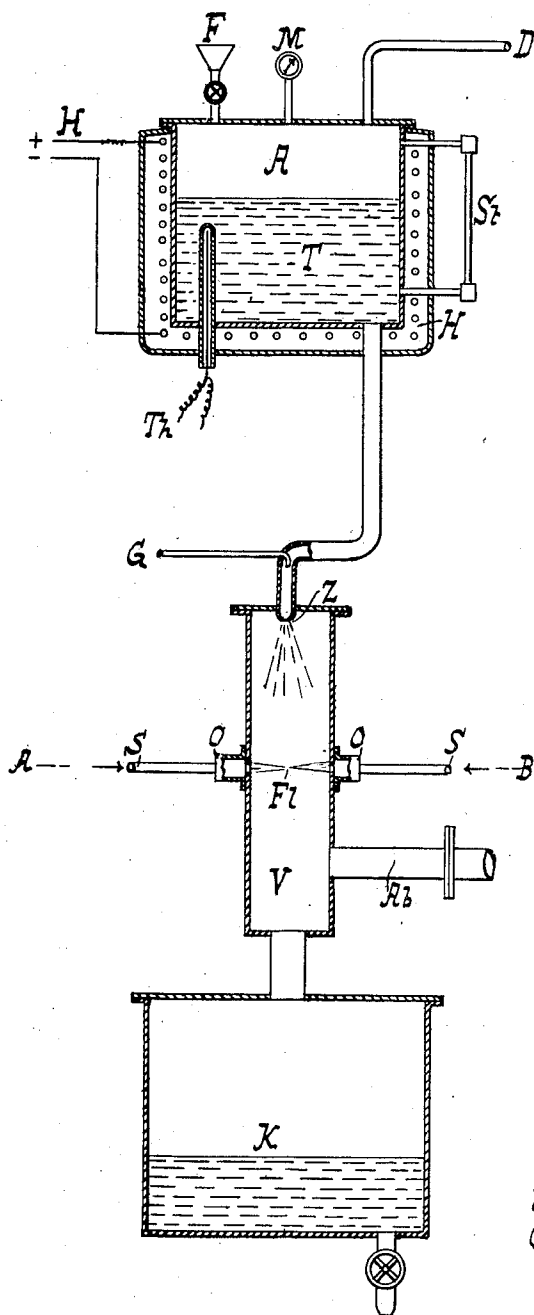
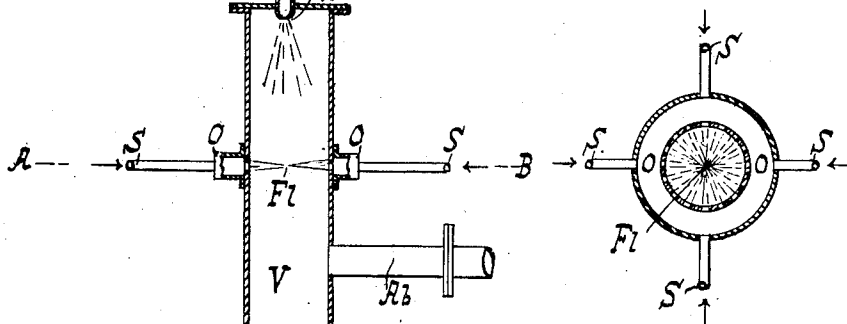


Fig. 4.



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MANUFACTURE OF UNSATURATED HYDROCARBONS

Application filed January 19, 1927, Serial No. 162,074, and in Germany January 19, 1926.

This invention relates to improvements in the manufacture of unsaturated hydrocarbons, especially acetylene, from more saturated hydrocarbons.

It is known that when saturated hydrocarbons in the form of gas or vapor, especially methane, are heated to high temperatures of more than 900° C., unsaturated hydrocarbons, especially acetylene, are formed as the result of thermochemical breaking up or decomposition. Thus by heating the said gases, for instance, in an electric arc or incandescent tube, or by incomplete combustion, more or less high yields of unsaturated hydrocarbons, especially acetylene, can be obtained.

We have now discovered that a considerably higher yield in unsaturated hydrocarbons than by the methods hitherto known can be obtained by exposing the hydrocarbons or hydrocarbon mixtures only for a short time to the action of very high temperatures. By this treatment a further conversion of the unsaturated hydrocarbons formed is prevented. As a consequence, not only is the yield in valuable unsaturated hydrocarbons much higher, when the treatment is carried out in accordance with the said principle, but serious drawbacks occurring in the usual methods are prevented to a large extent or even completely.

The said principle may be carried out in many ways.

A practicable and highly advantageous conversion of gaseous or vaporous saturated hydrocarbons into valuable unsaturated hydrocarbons especially acetylene, may be effected by passing the former alone or diluted with other gases through a flame which more or less fills a cross sectional area of a tube, such flame being, for example, arranged like a disk, which may be produced by a plurality of separate burners. The flame is generated by means of a suitable chemical reaction, preferably by the combustion of a combustible gas, gaseous mixture or vapor, with a sufficient quantity of oxygen, air or mixture of oxygen and air. Preferably care should be taken, by suitably shaping the burners, for example arranging them in the form of leads of the blowpipe type with nozzle apertures,

to restrict the extent of the flame to as narrow a zone as possible in the direction of the flow of the hydrocarbons to be converted, and to attain the highest possible flame temperature.

The flame or flames through which for example methane is to be passed, may with advantage be fed by a portion branched off from the gas to be treated together with oxygen or air. Hydrogen, coal gas and the like may also be used for this purpose. The air or the combustible gas, or both may be preheated, preferably by heat exchange with the effluent reaction gases.

In some cases it is found advisable to effect the heating of the reaction zone, not by burning the gas mixture providing the requisite temperature in a naked flame, but by the aid of substances which have a more or less catalytic influence on the combustion, effecting what is known as "surface" or "flameless" combustion. In such case, the methane or other gas is passed through the highly heated masses in any suitable manner and the combustion of the gas furnishing the requisite temperatures may be effected wholly or partially by such catalytic treatment.

Figures 1 and 2 of the accompanying drawings represent a side elevation and plan respectively of a simple apparatus suitable for carrying out the present invention, in which the auxiliary flame can be generated by burning in association with air a branched off portion of the gas, for example methane, under treatment. The whole of the methane enters at E, and is divided, by means of the regulating taps F and G into the main portion, which flows through the pipe P and R, the branched off portion passing into the pipes M and serving to feed the flames. The feeding pipes M terminate in burners I having tapered nozzles and projecting into the reaction vessel K, the said burners being surrounded by concentric nozzle pipes H through which the air or oxygen is supplied. Four of these burners are shown arranged radially in a horizontal plane. On the flames being lit by means of an ignition device (not shown in the drawings) such as the sparks from a small induction appa-

ratus, a highly heated zone Z, in the form of a disk, is produced by the blowpipe flames. The main portion of the methane flows through the pipe R, enters the end part of the vessel K at O and traverses the zone Z, thereby undergoing thermal breaking up. The hot effluent gases consisting of methane, hydrogen, carbon monoxide and acetylene preheat the fresh gas flowing through the inlet pipe R and issue from the reaction vessel at S, whereupon they are submitted to further treatment, for example to the separation or to further chemical transformation of the acetylene.

By suitably treating the gases after the reaction product has been separated therefrom, with a view to correct their composition for example by catalytically producing methane from the carbon monoxide and hydrogen contained in the gases, and introducing fresh gas in the required amount, the process hereinbefore described may also be developed into a cyclic process.

A similar method is applicable for the treatment of liquid hydrocarbons or hydrocarbon mixtures. The employment of such initial materials offers the great advantage that, under otherwise equal conditions, the yield of the desired products is considerably higher than when starting from methane. We have found that, as a rule, the yield of the desired products is considerably increased if the original hydrocarbons contain carbon chains with a plurality of carbon atoms. This is the case, for example, with mixtures of liquid hydrocarbons. The rapid heating of these substances is, however, attended with the serious drawback that, in addition to the splitting up into the desired products, there is considerable separation of carbon and consequent obstruction of the reaction chambers and piping, and this occurs whether the substances under treatment are highly superheated in the state of vapor or in form of a liquid mass.

We have found that this serious drawback can be prevented to a large extent by spraying the liquid hydrocarbons, or mixtures of such, in small drops and subjecting them in this condition of distribution, to the rapid heating to high temperatures. The thermal breaking up or decomposition of the oils or tars or the like then takes place within the individual drops, in the heated zone, without any considerable amount of carbon being deposited on the walls of the reaction chamber. The chief hydrocarbons which come under consideration for treatment in this manner are heavy oils, such as high-boiling fractions of petroleum, coal tars, low-temperature tars, brown-coal tars and the like.

It is possible, according to this invention, to raise the temperature of the heating zone, and consequently the yield of the decomposition products, to a far greater extent than

has been found practicable, in view of the drawback above referred to, in the treatment of the oils, tars, and the like in the state of vapor or in form of a liquid mass. A suitable method of carrying out the process consists in spraying the liquid hydrocarbons into a combustible gas, such as methane, ethane, hydrogen and the like and to effect the rapid heating of the finely divided drops by the combustion of a portion of the mixture under treatment with oxygen or gases rich in oxygen, the combustion being preferably so effected as to produce a disk-like flame, the temperature of which is preferably above 800° C.

An apparatus suitable for carrying out this process is shown diagrammatically in Figures 3 and 4 of the accompanying drawings.

A tank A is provided in which the oil intended for combustion is preheated, for example by an electric heating device H, the oil being forced, by means of pressure admitted by pipe D through a discharge pipe at the bottom of the said tank into a combustion chamber V. Shortly before entering the latter, the oil is mixed with a combustible gas, such as methane, hydrogen or water-gas, admitted through a supply pipe G. The mixture then passes through an atomizing nozzle Z and enters the combustion chamber V as a fine liquid mist. This chamber is provided with an annular chamber O having a ring of perforations through which oxygen or a gaseous mixture rich in oxygen, enters the combustion chamber in which it is ignited. The partial combustion of the mixture of oil and gas produces a narrow, highly heated zone of flame FZ in which the decomposition is effected, on the level of the ring perforations and at right angles to the direction of flow. After passing the reaction zone, the mixture of gas and vapor issues from the combustion chamber through a pipe Ab, any portions of particularly low volatility collecting in a second tank K provided for that purpose. The mixture then passes through a series of condensers in which the vaporous constituents are condensed, after which the acetylene is separated or subjected to further treatment, for example for the production of acetaldehyde.

By means of this, or similar arrangements, a gas containing, in addition to relatively small quantities of carbon monoxide, a relatively high percentage of hydrogen and acetylene, may be obtained from liquid hydrocarbons by treating them with such quantities of oxygen that about one molecule of oxygen will be present for every four atoms of carbon in the molecules of the said hydrocarbons. Analysis of the liquid products recovered from the reaction gases or vapors, reveals the fact that, in addition to the formation of acetylene, other products of lower

boiling point than the original material are also present, and that, consequently, a considerable cracking effect is produced by the sudden heating of the liquid mist.

Another way of carrying out our invention consists in subjecting the hydrocarbons to be treated to incomplete combustion at temperatures above 850° C. with pure oxygen, or with gas mixtures containing at least 50 per cent of oxygen. The quantity of oxygen employed must be so small that a considerable part of the methane or other hydrocarbon remains unaltered in the said combustion. According to this process, the heating of a very considerable volume of nitrogen, acting as a diluent, which always occurs in the combustion of a mixture of hydrocarbons and air in the usual manner, is completely, or to a large extent, obviated, so that the gases or vapors to be converted attain far higher temperatures and are heated within a very short time. Owing to this circumstance, the state of the thermal equilibrium is considerably modified in favor of the formation of acetylene. Moreover, in comparison with the employment of air, this process affords the additional advantage that the absence of nitrogen, or the presence of merely small amounts of that gas, completely or almost so avoids the formation of cyanogen, hydrocyanic acid and other nitrogenous compounds which otherwise may be a source of trouble.

The combustion may be carried out in various ways. For example, the flow of the combustible gas may serve to draw in certain quantities of oxygen, or gas rich in oxygen, through lateral orifices, on the principle of the Bunsen burner, the resulting gaseous mixture being then ignited. On the other hand, the oxygen, or gas rich in oxygen, may be introduced into the current of combustible gas through separate tubes, preferably with tapered nozzles, and the resulting mixture may be ignited at the point of this introduction. Again, it may be advantageous to influence the combustion, by the arrangement of refractory, ceramic porous material, in such a way that it more or less completely assumes the form of surface combustion, without the production of any soot.

The effect of the incomplete combustion may also be increased by afterwards raising the gases which have been heated in the zone of combustion, to still higher temperatures by the provision of an electric heating device or other suitable means. In this way, temperatures up to 1300° C. may be easily attained.

This process is applicable not only to gaseous or vaporous hydrocarbons, but is also specially suitable above 650° C. for treating liquid and solid hydrocarbons, such as tars, petroleum residues, bitumen and the like or substances containing the same, without these

being separately vaporized. According to this manner of working a gas rich in olefines is obtained which can be subjected to further chemical treatment in a suitable manner, for example by then passing it over contact materials such as pumice, carbonates or other salts of the alkaline earth metals, including magnesium and beryllium, phosphates, heavy metals and the like capable of causing formation of benzene. The gas rich in olefines may also be used for the production of ethylene chlorid, ethylene glycol, higher alcohols or other valuable organic products. We have further found that the yield of olefines may be increased when water, either in the liquid form or as vapor, is added as well as oxygen, this provision also reducing or entirely preventing the coking which otherwise is liable to occur in the reaction chamber. The treatment must not be too violent, for example the temperature should not be too high or the rate of flow too low, because otherwise the olefines formed undergo further conversion.

Another way of carrying out our invention in practice consists in a catalytic treatment of hydrocarbons, especially those in the gas or vapor state, with contact masses of the kind suitable for the production of aromatic hydrocarbons from aliphatic hydrocarbons by passing the aliphatic hydrocarbons, either alone or in admixture with other gases or vapors, over contact masses at elevated temperature. The said contact masses may consist for example of carbonates or other salts of the alkaline earth metals including magnesium and beryllium, either singly or mixed together or with other metallic compounds. It has also been suggested to employ for this process as contact masses the oxides or hydroxides of magnesium or beryllium, or compounds of selenium, tellurium or thallium, or active silica, or active charcoal, or mixtures of the same.

For the production of unsaturated hydrocarbons, saturated hydrocarbons, and especially methane or gas mixtures containing methane, are passed under any desired pressure over contact masses of the said kind at temperatures of from 700 to 1000° C. or higher, at a sufficiently rapid rate to preclude further condensation of the primary products, such as acetylene or ethylene, into higher-molecular hydrocarbons, especially aromatic hydrocarbons. For this purpose the heating should be effected and the gases should be removed from the hot reaction zone as rapidly as possible. Generally speaking acetylene forms the chief product at very high temperatures, and ethylene when somewhat lower temperatures are employed.

The reaction gases containing unsaturated hydrocarbons, for example, acetylene or the like may either be rapidly cooled, for the recovery of these valuable compounds, or they

may be subjected directly to further operations, especially condensation into benzol hydrocarbons, for example by passing them over suitable contact masses, in which operations their sensible heat is preferably utilized to a greater or smaller extent.

The following examples will further illustrate how the said invention may be carried into practical effect but the invention is not limited to these examples.

Example 1

Methane or natural gas is converted in a device according to the apparatus shown in Figures 1 and 2, by subjecting two-thirds of the gas, all of which is admitted at the rate of 300 litres per hour, to the heat treatment, whilst the remaining one-third is employed, in conjunction with a volume of a mixture of air and oxygen in the proportion of 2:1, sufficient for its complete combustion, to feed the heating flame. The gas mixture leaving the highly heated zone is quenched by cooling with water. It contains several units per cent of acetylene, which is separated by suitable means, or is transformed into compounds such as acetaldehyde, benzene and the like. The residual gas is either used for heating purposes, or is wholly or partially made use of again in the process itself.

Example 2

An iron apparatus, constructed in accordance with Figures 1 and 2 but provided, instead of the burners, with 32 radially disposed oxygen nozzles, is fitted internally, at the level of the said nozzles, with a horizontally arranged tungsten wire gauze, covering the whole cross section of the pipe. This gauze supports a loose layer, about 3 millimetres deep, of platinized asbestos, the catalytic action of which effects the incomplete combustion of part of the methane. By introducing about 50 cubic metres of methane and 14 cubic metres of oxygen per hour, the temperature of the narrow, circular contact zone rises to about 1100° C. The effluent gases, amounting to about 75 cubic metres per hour, contain, in addition to about 38 per cent of unaltered methane, about 23 per cent of carbon monoxide, about 34 per cent of hydrogen and about 3.5 per cent corresponding to about 2.6 cubic metres of acetylene.

Example 3

The tungsten wire gauze, supporting a layer of platinized asbestos, mentioned in Example 2, is replaced by a plate of highly porous, refractory material, for example of so-called Marquardt composition, mounted about 1 centimetre below the oxygen nozzles. The combustion, which then proceeds to some extent as surface combustion raises the temperature of the said plate to about 1050° C. The same quantity and same initial gas as in

Example 2, will furnish an effluent gas giving a yield of about 2.7 to 3 per cent of acetylene.

Example 4

Methane is passed through a quartz tube of 30 millimetres internal diameter at the rate of 264 litres per hour, and is preheated to a temperature of 900° C. on the counterflow principle, by the effluent gases of combustion. The incomplete combustion of the methane is effected in a flame zone fed by four oxygen nozzles, the flow of oxygen being at the rate of 70 litres per hour. The gases of combustion, which have a temperature exceeding 1000° C., issuing per hour consist of 189 litres of unaltered methane, 94 litres of water vapor, 42 litres of hydrogen, 47 litres of carbon monoxide and 14 litres of acetylene. The amount of soot formed is small, and, in any event, not a source of trouble. The amount of acetylene produced is thus 1 litre for every 5 litres of oxygen supplied. The acetylene thus obtained may be easily isolated in any known manner, as for example by dissolving it in acetone, or it may be directly transformed, from the gaseous mixture, into other compounds, such as acetaldehyde and acetic acid by suitable chemical treatment.

Example 5

A porcelain tube, 100 centimetres in length and 19 millimetres inside diameter, filled with coarse fragments of pumice, is heated to a temperature of 900° C. in an electric resistance furnace. The external heating is then discontinued, and 300 litres of high-grade ethane such as may be recovered from low carbonization gas by means of active charcoal or silica, is passed through the reaction tube per hour, in mixture with 104 litres of oxygen. No difficulty is experienced in maintaining the temperature of the tube at the most suitable temperature of 840° C. The resulting gas contains over 25 per cent of ethylene, which can be further treated without difficulty. The ethane may be replaced by still higher homologues of methane, or mixtures containing them, such as are easily obtainable in the form of, or producible from, distillation gases from coal or tar, or gases from the cracking process.

Example 6

An iron tube, lined with refractory material, of 6 centimetres inside diameter, is filled, in a zone 10 centimetres in length, with lumps of a porous refractory material, such as earthenware sherds. Methane is passed through the tube at the rate of 4 cubic metres per hour. Oxygen, at the rate of about 1 cubic metre per hour is introduced through a number of nozzles, in star arrangement into the zone charged with the filling material and transversely to the direction of the flow of the methane. The gas mixture being ignited, 130

a cylindrical hot zone, at a temperature of about 1000° C. results in the interior of the tube. The resulting gases contain acetylene at about the rate of 160 litres per hour, together with methane, carbon monoxide, hydrogen and water vapor. If, after leaving the zone of combustion, the gases be immediately raised to a temperature of about 1200° C. by an electric furnace arranged therefor, the yield of acetylene is increased to about 180 litres per hour.

Example 7

Brown-coal tar, preheated to about 250° C. is introduced at the rate of 240 grammes per hour, into a porcelain tube 120 centimetres long and 24 millimetres inside diameter, which may be partially filled with refractory material and is heated to a temperature of about 800° C. At the same time, oxygen is admitted into the tube at the rate of 78 litres per hour. A gas containing over 20 per cent of olefine hydrocarbons, especially ethylene, propylene and butylene, is formed, about 50 per cent of the tar being decomposed. The tarry residue may be used over again.

Example 8

Preheated brown-coal tar (viscous tar) is introduced, at the rate of about 500 grammes per hour, into the same apparatus as that described in Example 7, 105 litres of oxygen and 340 grammes of steam per hour being admitted at the same time. A gas containing over 30 per cent of olefine hydrocarbons is formed. About 50 per cent of the tar is decomposed to form gas, leaving a thin tar as residue. On passing the still hot gases over pumice, a thin oil very rich in aromatic hydrocarbons is obtained.

Example 9

The central section, 18 centimetres long, of a tube made of fused rock crystal, 70 centimetres long and of 12 millimetres inside diameter, is filled with fragments of magnesia (mean edge length, 6 millimetres). This contact is heated to a temperature of 950° C. in a small electric furnace, 15 centimetres in length. If a slow current of methane, say at a rate of flow, up to 6 litres per hour, be passed through this contact tube, about 4 per cent of the methane will be converted into acetylene, and 5 to 6 per cent into naphthalene and benzene, accompanied by the formation of carbon and hydrogen. If, on the other hand, in accordance with our invention, methane is passed rapidly over the contact say at a rate of flow exceeding 20 litres per hour, about 12 per cent of the methane will be converted into acetylene and hydrogen, and about 4 per cent decomposed into carbon and hydrogen.

What we claim is:

1. The process of producing unsaturated

hydrocarbons which comprises passing more saturated hydrocarbons in a finely divided state through a flame disk of high temperature of more than 900° C. produced by combustion.

2. The process of producing unsaturated hydrocarbons which comprises passing more saturated hydrocarbons in a gaseous state through a flame produced by the combustion of a branched off part of the gas to be treated and having a temperature of more than 900° C.

3. A process of producing acetylene which comprises passing a gas containing methane through a flame disk of high temperature of more than 900° C. produced by combustion.

4. A process of producing acetylene which comprises passing methane through a flame disk of high temperature of more than 900° C. produced by combustion of methane.

In testimony whereof we have hereunto set our hands.

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WALTER FRANKENBURGER.

GUSTAV WIETZEL.