

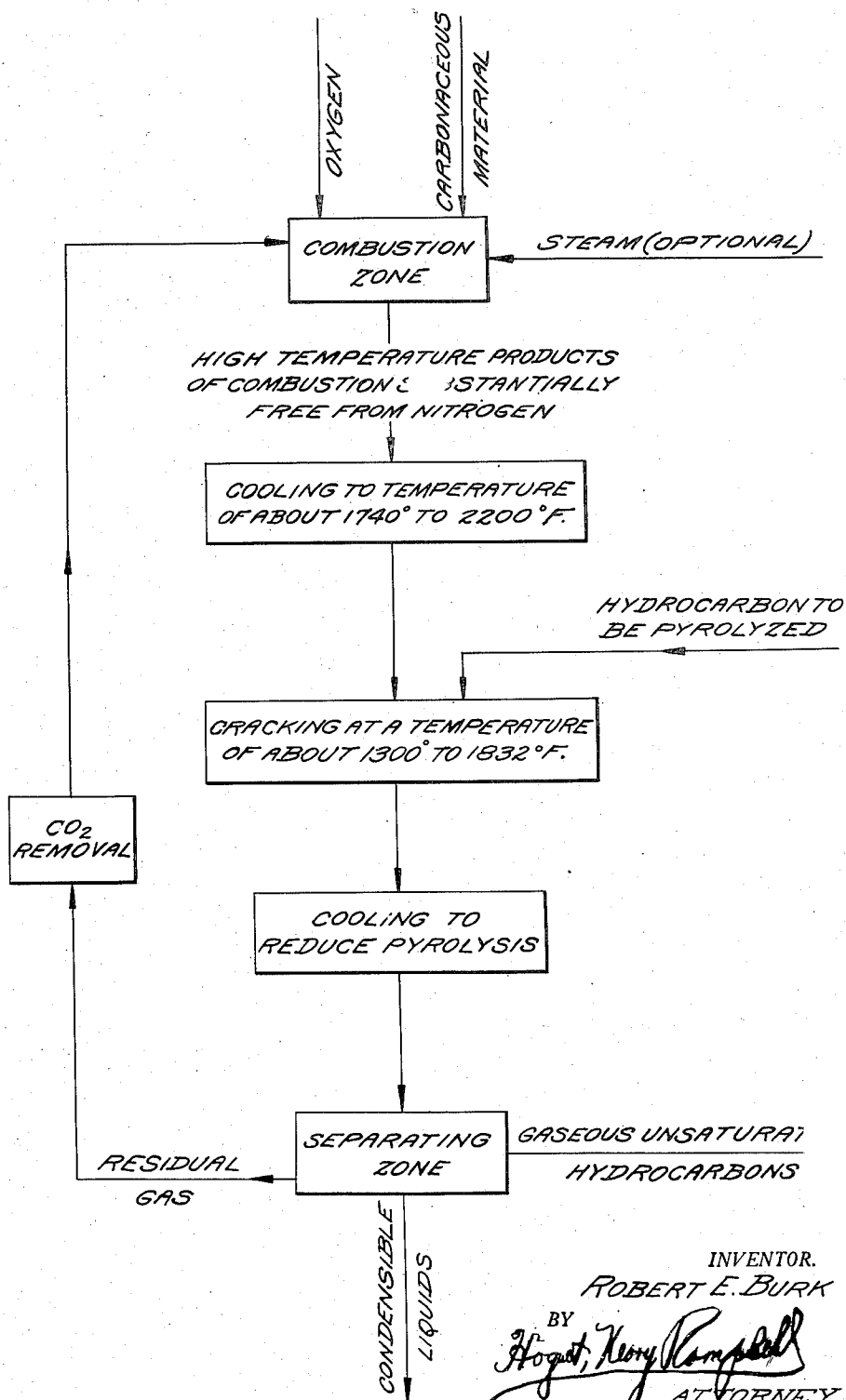
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PREPARATION OF UNSATURATED ALIPHATIC GASEOUS HYDROCARBONS, ETC

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PREPARATION OF UNSATURATED ALIPHATIC GASEOUS HYDROCARBONS, ETC.

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While ethylene and the like is obtainable by heating oil vapors under various conditions, including simple tube heating and heating with super-heated steam, the efficiency, particularly the heat efficiency has been poor. The rate of heat transfer from a hot surface is low, and the rate of heat transfer from super-heated steam is also low. A procedure therefore characterized by feasibility and heat economy making possible a controlled output is of fundamental importance and highly desirable.

To the accomplishment of the foregoing and related ends, the invention, then, comprises the features hereinafter fully described, and particularly pointed out in the claims, the following description setting forth in detail certain illustrative embodiments of the invention, these being indicative however, of but a few of the various ways in which the principle of the invention may be employed.

The accompanying drawing is a diagrammatic flow sheet of my process with self-explanatory legends identifying the various steps.

In accordance with my invention unsaturated aliphatic gaseous hydrocarbons are produced by pyrolyzing oil vapors, effecting heat transfer by direct inter-mixture of highly heated gases, and the reaction mass is then abruptly shock-cooled. When burning carbonaceous material such as gas, oil, coal, coke, etc. in a closed chamber with approximately the theoretical amount of air for combustion, a resultant gas substantially free from oxygen is obtained, and at a temperature range of 3500–4000° F. The oxygen is consumed out of the air and the resultant gas is particularly nitrogen with a minor per cent of combustion gas, as carbon dioxide. In such procedure however, there is a loss in about 15 per cent methane which is formed when the hot gas is subsequently contacted with hydrocarbon vapors to be pyrolyzed, as such methane being mixed with and diluted by the large amount of nitrogen cannot be recovered. In accordance with the present invention such loss is obviated, and an improved control on the production of the hot gas and the operation of such heat transfer medium is made possible with particularly high efficiency. I prepare the hot gas by burning the carbonaceous material above noted, without substantially introducing nitrogen into the products of combustion. Oxygen is supplied to the combustion zone or burners in controlled amount to consume the carbonaceous material, and where the temperature of the hot products of such combustion is too high for the character of unsaturated aliphatics to be pro-

duced by its heating action upon hydrocarbon vapors, I reduce the temperature thereof to a range of 1740–2200° F., and then pyrolyze the hydrocarbon or oil vapors. This reduction of temperature may be accomplished best by injecting or spraying a suitable amount of hydrocarbon which is cracked in reducing the excess high temperature and with the formation of condensible products. The gaseous mass now at the desired temperature range receives an admixture of oil vapors to be pyrolyzed for the production of ethylene and the like, and the feed of the oil vapors is controlled such that the pyrolysis thereof goes on at a temperature of 1300–1832° F. Preferably the oil is vaporized before its admixture, although in some cases the hot gas may be employed to atomize and vaporize the oil. The oil employed is desirably a petroleum distillate, kerosene or other distillate heavier than gasoline. The contact time between the oil vapor and the hot pyrolyzing gas depends somewhat upon the apparatus and its efficiency for mixing, but involves a reaction time of the order of 0.005 to 0.5 second. In some cases a catalyst may be present to advantage, such as oxides of metals of groups VI, also oxides of groups II, III and IV of the periodic system. As the desired reaction is rapid, extension into decomposition is now avoided by abruptly shock-cooling the reaction mass. In a continuous type of operation with the mixture forwarded through a pyrolyzing zone and then to a cooling zone, such shock-cooling may be effected desirably by injecting residual petroleum, or crackable petroleum as for example gas oil. By injecting the residual petroleum such as a topped crude into the products for shock-cooling, a distillate oil for charging stock for the process is obtained and yields also motor fuel, or by injecting gas oil a yield of motor fuel and the like is obtained. Of course, the shock-cooling may be effected by other means, wasting the heat, but the efficiency is correspondingly lowered.

With operation thus, particularly high yields of ethylene may be obtained. Small amounts of propylene and less butylene also occur.

In a preferred form of operation, I burn the carbonaceous material, such as gas, oil, coal, coke, etc. in a closed combustion zone, supplying to the burner oxygen for controlled combustion providing combustion products of intermediate temperature range, and then admix hydrocarbon vapors to be pyrolyzed, such as of kerosene or gas oil. The hot products are then quickly cooled down to at least below the range of further decomposition, by controlled injection of hydrocarbons such

as topped crude or gas oil, the feed being limited to avoid excessive cooling, and then the ethylene and other olefines are removed, such as by direct polymerization, by fractionation, by solvent extraction, or by selective adsorption such as charcoal, or by selective reaction such as with sulphuric acid, and the gaseous residue is passed into contact with a catalyst eliminating carbon dioxide carried in the products by hydrogenation with the contained hydrogen, thereby forming methane and carbon monoxide if nickel is used as a catalyst, or forming some liquid hydrocarbons if other catalysts are used, such as metals or partially reduced oxides of group VIII of the periodic system, especially iron and cobalt, which may be promoted with oxides of chromium, zinc, beryllium, etc., the temperature in this catalytic zone being around 200° C., and pressure about atmospheric. It is advisable to remove sulphur from the gas before passing over the catalyst. The products then being passed through a condensing zone condense out the normally liquid constituents. The residual gas, thus after the removal of the olefines, diolefines, and acetylene if desired, and being now also free from objectional carbon dioxide, is recycled to the combustion zone or burner where it goes into admixture with the feed of oxygen-rich gas for combustion.

In the combustion zone, according as the feed of oxygen is proportioned and the temperature is controlled, merely the hot combustion products for pyrolyzing the hydrocarbon vapors in the next stage may be produced, or desirably by suitable control of the oxygen and a surplus feed of the combustion material, for example oil, not only is there provided a desired supply of hot combustion gas (substantially free from nitrogen) for the next or cracking stage, but some yield of olefines and other unsaturates may be obtained in this stage, augmenting the yield which follows in the next or pyrolyzing stage proper.

In some cases, a small controlled feed of steam may be introduced in the combustion zone.

In applying oxygen for the production of the hot gases, it now becomes possible furthermore, to operate the combustion zone at a particularly high temperature range if desired, and acetylene and diolefines may be thereby emphasized in production, in that particularly high temperatures of pyrolysis are thus available, and the acetylene can be segregated from the end products, as by absorption in a selective solvent, such as acetone, etc., and the diolefines and ethylene and other olefines may be segregated in succession. Where proceeding by such particularly high temperature operation, it is also desirable to raise the overall efficiency by removing carbon dioxide from the residual gas and re-cycling the final residual gas to the combustion zone or burner, the carbon dioxide being removed by hydrogenating with the hydrogen present, by passing through the catalytic zone as already described to form methane and carbon monoxide or some normally liquid hydrocarbon, depending upon the catalyst used.

In some cases, in the procedure involving removal of carbon dioxide for re-cycling to the combustion zone, other means of removing the carbon dioxide may be availed of if desired, such as extracting the carbon dioxide or scrubbing with caustic alkali solution, etc.

This application is a continuation, in part and as to common subject matter, of my application Ser. No. 60,887, filed Jan. 25, 1936.

Other modes of applying the principle of the

invention may be employed, change being made as regards the details described, provided the features stated in any of the following claims, or the equivalent of such, be employed.

I therefore particularly point out and distinctly claim as my invention:

1. In a process of making unsaturated aliphatic gaseous hydrocarbons pyrolytically, burning carbonaceous material with substantially pure nitrogen-free oxygen to produce products of combustion at a high temperature, cooling the same to a temperature of about 1740 to 2200° F., admixing an amount of a hydrocarbon with said cooled products of combustion to pyrolyze the hydrocarbon and form unsaturated aliphatic hydrocarbons at a temperature of about 1300 to 1832° F., quickly cooling the products, separating resultant condensible hydrocarbons, separating unsaturated aliphatic gaseous hydrocarbons, removing carbon dioxide from the residual gas, and returning the nitrogen-free residual gas including methane that is formed in said previous steps to be burned with more carbonaceous material in said first mentioned step.

2. In a process of making unsaturated aliphatic gaseous hydrocarbons pyrolytically, burning carbonaceous material with substantially pure nitrogen-free oxygen to yield products of combustion at a temperature above 3500° F., admixing hydrocarbon oil with the hot products of combustion to lower the temperature to about 1740 to 2200° F., admixing hydrocarbon vapors with the resultant mixture at said lower temperature to pyrolyze the vapors and form unsaturated aliphatic hydrocarbons at a temperature of about 1300 to 1832° F., adding liquid hydrocarbons to shock cool the products and crack said hydrocarbons, eliminating condensible hydrocarbons from the products, eliminating gaseous unsaturated aliphatics therefrom, passing the residual methane-containing gas over a catalyst to remove carbon dioxide at an elevated temperature, and returning the nitrogen-free residual gas including methane that is formed in said previous steps to be burned with more carbonaceous material in said first mentioned step.

3. In a process of making unsaturated aliphatic gaseous hydrocarbons pyrolytically, burning carbonaceous material with substantially pure nitrogen-free oxygen, admixing a hydrocarbon to cool the hot products of combustion to a temperature of 1740-2200° F., then admixing hydrocarbon vapors therewith at said cooled temperature to pyrolyze the same and form unsaturated aliphatic hydrocarbons, quickly cooling the products, separating unsaturated aliphatic gaseous hydrocarbons from the products and separating condensible hydrocarbons to leave a residual nitrogen-free gas including methane that is formed in said previous steps which may be burned in said first mentioned step.

4. In a process of making unsaturated aliphatic gaseous hydrocarbons pyrolytically, burning carbonaceous material with substantially pure nitrogen-free oxygen, cooling the hot products of combustion to a temperature lower than the combustion temperature by injecting petroleum therewith, admixing hydrocarbons of more than two carbon atoms therewith to pyrolyze the same at a temperature of about 1300-1832° F., and form unsaturated aliphatic hydrocarbons, segregating condensible hydrocarbons, and segregating ethylene to leave a residual nitrogen-free gas including methane that is formed in said

previous steps which may be burned in said first mentioned step.

5. In a process of making unsaturated aliphatic gaseous hydrocarbons pyrolytically, burning carbonaceous material with substantially pure nitrogen-free oxygen, admixing hydrocarbons with the hot products of combustion to cool the products to a temperature of not over 2200° F., admixing hydrocarbons with the cooled products of combustion to pyrolyze the same and form unsaturated aliphatic hydrocarbons at a temperature within the range of 1300 to 1832° F., admixing further hydrocarbons with such products in turn to cool the same and reduce pyrolysis, and segregating unsaturated aliphatic gaseous hydrocarbons from the product and burning the residual nitrogen-free gas including methane that is formed in said previous steps.

6. In a process of making unsaturated aliphatic gaseous hydrocarbons pyrolytically, burning carbonaceous material with substantially pure nitrogen-free oxygen, admixing hydrocarbons to cool the products of combustion to a temperature less than the combustion temperature, admixing hydrocarbons of more than two

carbon atoms with the hot products at said temperature less than the combination temperature to pyrolyze the same and form unsaturated aliphatic hydrocarbons, segregating the unsaturates, and recycling nitrogen-free gaseous fuel products formed in the process to be burned as at least a part of the carbonaceous material in the first step.

7. In a process of making unsaturated aliphatic gaseous hydrocarbons pyrolytically, burning carbonaceous material with substantially pure nitrogen-free oxygen to produce products of combustion at a high temperature, cooling the same to a temperature of about 1740 to 2200° F., admixing an amount of a hydrocarbon with said cooled products of combustion to pyrolyze the hydrocarbon and form unsaturated aliphatic hydrocarbons at a temperature of about 1300 to 1832° F., quickly cooling the products, and segregating unsaturated aliphatic gaseous hydrocarbons from the products and burning the residual nitrogen-free gas including methane that is formed in said previous steps.

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