METHOD OF PRODUCING GAS

Filed Nov. 16, 1933

Fig. 2.

HOT LEAN GAS

COOL CARBURETTED GAS

CHILLED CARBURETTED GAS

Fig. 1.

COOL CARBURETTED GAS

VAPOR FLASHED OIL AND HOT LEAN GAS MIXTURE

HOT OIL UNDER PRESSURE

HOT LEAN GAS

OIL-CONE WELL CLEAN-OUT

INVENTOR

Theodore Nagel

BY

Kiddie, Ruckel & Montgomery

ATTORNEYS
My invention relates to a process for making hydrocarbon fixed gases from oil or hydrocarbon vapors and provides a method for obtaining the maximum yield of non-condensable hydrocarbons or fixed gases with a minimum yield of condensate. A return of 20% to 30% condensate is considered good practice with present commercial methods for converting oil hydrocarbons into fixed gases, whereas my invention provides a method wherein the condensate yield is reduced to not substantially more than 10% by weight of the hydrocarbons charged.

It is well recognized that the time required for heating a unit weight of matter varies inversely as its volume, i.e. directly as its density. An exceedingly longer time, therefore, is required for heating a given quantity of liquid oil than is required for heating the equivalent weight of hydrocarbon gases, because the volume of the gas is exceedingly greater than the volume of the equivalent weight of liquid hydrocarbons.

By heat intensity oil can be converted from a liquid to vapor and finally to gas. When subjected to a pressure around 200 pounds per square inch or higher pressures, oil can be heated to within a temperature range of approximately 700° F. to approximately 900° F. while maintaining the oil as a liquid. On release of the pressure, by injecting the hot oil into a heat insulated chamber, for example, the liquid flashes almost instantly into vapor and gas with a temperature drop in the order of 50° F. This is an endothermic action. On cooling, the major portion of the mixture will condense, only a minor portion remaining as hydrocarbon permanent or fixed gases.

If, on the other hand, instead of merely injecting the hot oil into a heat insulated chamber, the heated oil under pressure be released into a hot zone in which the temperature of the vapor gas mixture is raised to within a temperature range of approximately 1200° F. to approx. 1500° F., for example, I find that while on cooling the proportion of condensate to hydrocarbon fixed gases produced has been greatly decreased, nevertheless the condensable gases will still amount to from 20% to 30% by weight of the original charge. This is far in excess of the results obtained by my processes.

I have found by extensive research into the pyrolysis of hydrocarbons, i.e., dissociation and reactions of the hydrocarbons produced by the application of heat, within the temperature range of 1200° F. to 1600° F., that the complex hydrocarbon gases are almost instantly broken down into the simpler aliphatic lower molecular weight gaseous hydrocarbons (an endothermic action), and that this primary endothermic dissociation is followed by secondary reactions, exothermic in character. During the exothermic secondary reactions olefinic portions of the primary decomposition products recombine to form higher molecular weight condensable complex hydrocarbons. In the pyrolysis of hydrocarbons these reactions are known as polymerizing. In other words, there is a uniting of lower molecular weight reagents to form complex hydrocarbons of higher molecular weights—polymerization products that are condensable.

I propose, therefore, by the method of my invention to control the primary dissociations and secondary reactions above referred to by controlling the heating and cooling so that overlapping of the periods for primary and secondary reactions is reduced to a minimum, thereby converting substantially all the oil to substantially all non-condensable hydrocarbon gases, with the yield of condensate reduced to around 10% or less by weight of the original hydrocarbons charged as compared with from two to three times this quantity of condensate yield from commercial operating practices prior to my invention.

In other words, the present invention provides for regulating the yield of hydrocarbon fixed gases from oil or from hydrocarbon vapors by control of the heating and cooling so that the maximum yield of hydrocarbon fixed gases is attained with minimum yield of condensate as compared with the 20% to 30% condensate yield of prior methods.

Figs. 1 and 2 of the accompanying drawings illustrate diagrammatically embodiments of my invention.

As a practical example of my improved method, the following procedure may be followed:

Oil subjected to superatmospheric pressure of not less than 150 pounds pressure to the square inch is heated in any suitable fashion to a vaporizing temperature ranging approximately from 700° F. to 900° F. under conditions to maintain the oil as a liquid. If the pressure on this heated oil is released by injecting the oil into a heat insulated chamber it will instantly flash into a vapor gas mixture with a temperature drop of 50° to 80° F. I propose, however, to release the pressure on the hot oil by injecting the oil as shown at 1 in Fig. 1 into a hot zone such as chamber 2 which, by supplying hot lean gas thereto as shown at 3, is at such a temperature that the vapor gas...
mixture will instantly flash into gas and immediately attain a temperature ranging from 1200°F to 1600°F. Under these conditions, as above explained, the complex hydrocarbon gases almost instantly decompose into the more simple aliphatic lower molecular weight gaseous hydrocarbons—an endothermal action. Before the secondary reactions, above referred to as exothermic in the presence of oxygen, can take place to a substantial amount, I cool the gas formed on the heating cycle to below 1000°F, by adding cool carbon retted gas thereto as indicated at 4 with the result that not more than 10% of the original amount of hydrocarbons charged reverts to a condensate, associated with the relatively high yield of 20% to 30% condensate obtained in the practice of prior methods.

It will be appreciated, therefore, that as far as described, my improved method provides for producing hydrocarbon fixed gases from oil by heating the oil under controlled temperature and pressure conditions whereby the oil will be maintained a liquid, the pressure on the heated oil being released by injecting the oil into a hot zone to be converted almost instantly into gas and the complex hydrocarbons decomposed into the more simple aliphatic lower molecular weight gaseous hydrocarbons, cooling being thereafter immediately effected before a substantial portion of the olefins of the primary decomposition products recombine, thereby providing a method involving controlled heating and cooling for obtaining the maximum yield of hydrocarbon fixed gases and the minimum yield of condensate by avoiding a substantial amount of polymerization.

I have found, however, that even more desirable results may be obtained by varying somewhat the procedure described above.

I have found that the principal polymerizing reagents entering into the secondary reactions, which I avoid as far as practicable by rapid heating and cooling, are mostly the highly unsaturated hydrocarbons of the primary dissociation products, which as I have already mentioned come under the classification of the olefine portions of the primary decomposition products. I may take advantage of this condition, therefore, by effecting primary dissociation in a hot zone passions of reaction to effect partial saturation of the highly unsaturated hydrocarbons, thereby reducing the polymerizing reagents and to the extent further decreasing the yield of condensate.

It will be appreciated of course that the hydrocarbon may be supplied from any suitable source. For example, from carbon monoxide hydrogen gas in connection with the making of a carburetted carbon monoxide hydrogen gas mixture.

In the making of such gas mixture the leaner gas, i.e., the uncarburetted carbon monoxide hydrogen gas mixture can be produced by any desired process, such as the continuous flow process of my copending application Serial No. 653,619, filed January 26, 1933. Oil heated under pressure as above described is then injected into this leaner gas as indicated at 8 in Fig. 2 the leaner gas being at sufficiently high temperature to provide the sensible and latent heat requirements for instantly decomposing the hydrocarbons of the oil into the primary dissociation products above referred to. The enriched or carburetted carbon monoxide hydrogen gas mixture thus produced is immediately thereafter rapidly cooled to the temperature range where polymerization cannot take place, thereby retarding and avoiding to a substantial amount the secondary reactions throughout the heating and cooling.

Rapid cooling may be effected in any practicable manner as for hydrocarbon from the hot carburetted gas in countercurrent flow through the heater for the oil, for heat recuperation, to supply the heat deficiency of the lean gas; or gas cooling may be effected by passing the hot carburetted gas through a waste heat boiler; or water spray may be employed. I prefer, however, to inject cooled carbon monoxide hydrogen gas or cooled carburetted carbon monoxide hydrogen gas into the hot hydrocarbon fixed gases as shown at 6 in Fig. 2 in sufficient volume to instantly cool the hot gas by contact to below 1000°F, cooling to room temperature being effected thereafter by any suitable means.

The time consumed in heating and cooling after flashing the hot liquid oil into a vapor gas mixture may be varied but should not exceed six seconds. When the higher temperatures are employed the time may not exceed one second or even less.

This variation in time will be appreciated when it is understood that dissociation and polymerizing reactions take place with increasing rapidity with increase in temperature. Consequently the higher the temperature employed within specified limits, the shorter will be the period for heating and cooling in order to prevent the slower polymerizing reactions occurring to a substantial amount before substantial completion of the more rapid primary dissociation on heating and to retard or avoid polymerizing reactions during cooling, so that little or substantially no polymerization occurs during the period of heating and cooling, namely, before the gas has been cooled to a temperature where polymerizing reactions do not occur.

From all the foregoing, therefore, it will be appreciated that I have provided a process for generating hydrocarbon fixed gases in which a vapor gas mixture is heated almost instantly to a temperature at which practically all the more complex hydrocarbons are converted into primary dissociation products; the gas mixture immediately after attaining the desired high temperature being rapidly cooled to retard or avoid a substantial amount of secondary or polymerizing reaction which through this controlled heating and cooling the yield of hydrocarbon fixed gases is regulated enabling the maximum yield of hydrocarbon fixed gases to be obtained with a minimum yield of condensate.

In addition to the advantages accruing to my invention by reason of the fact that I can regulate the yield of hydrocarbon fixed gases from oil by control of the heating and cooling so as to obtain the maximum yield of hydrocarbon fixed gases and the minimum yield of condensate as distinguished from the 20% to 30% condensate hereofore considered good practice, my invention possesses another and very material advantage.

It is well known that unrefined or straight run heavy oils, for example A.P.I. 16° to 30° Bé, oils free of moisture and refinery residues, have higher heating values, namely, higher B. t. u. value of the hydrocarbon gas mixture than gas oils, such for example as A.P.I. 30° to 40° Bé, oils currently used for gas carburetion. These heavier oils contain heavier hydrocarbons, boiling at higher temperatures than the hydrocarbons of gas oils. By employing the heavier oils in the practice of my invention in place of gas oils and controlling the heating and cooling as above set out, it will
be appreciated that more desirable gaseous carburants can be generated from these heavier oils than from the gas oils because the heavier oils yield larger quantities of olefins, which are desirable carburants for gas enrichment than gaseous paraffins.

Under present methods of carburetting no control is maintained to prevent polymerization of the olefins, with the result that the heavier oils yield more drip oil and tar condensate than the gas oils.

With my invention, however, the yield of condensate from the heavier oils may be kept to as low as 10%, thereby enabling the lower cost heavier oils to be used for carburetting with the advantage of yielding a more desirable gaseous carburant.

Throughout the foregoing and in the appended claims the expression “hydrocarbon non-condensible, permanent or fixed gases” is to be interpreted to mean the hydrocarbons that remain as gases under the usual temperatures and pressures encountered in public utility gas distribution.

What I claim is:

1. The process of generating hydrocarbon fixed gases from oil, which process comprises supplying substantially maximum heat to the oil while maintaining substantially all of the oil as a liquid by preheating the oil to within a temperature range of approximately 700° F. to 900° F. while the oil is subjected to a pressure of at least 150 pounds per square inch, injecting the preheated oil into a hot gaseous medium, the volume and temperature of which are such that the hydrocarbons are approximately instantly heated to a temperature within a temperature range of 1200° F. to 1600° F. substantially instantly to decompose the hydrocarbons to gaseous hydrocarbons the unsaturated hydrocarbons of which are composed of olefins, and before polymerization in excess of 10% takes place contacting the hot gases in direct heat exchange relation with a relatively cool fluid to cool the gaseous hydrocarbons below 1000° F. and excluding polymerization during cooling, thereby to retain the maximum heating value of the gaseous hydrocarbons.

2. The process of generating hydrocarbon fixed gases from oil, which process comprises supplying substantially maximum heat to the oil while maintaining substantially all of the oil as a liquid by preheating the oil to within a temperature range of approximately 700° F. to 900° F. while subjected to a pressure not less than 150 pounds per square inch, injecting the preheated oil into a hot gaseous medium, the volume and temperature of which are such that the hydrocarbons are approximately instantly heated to a temperature within a temperature range of 1200° F. to 1600° F. substantially instantly to decompose the hydrocarbons to gaseous hydrocarbons the unsaturated hydrocarbons of which are composed of olefins, and before polymerization in excess of 10% takes place contacting the hot gases in direct heat exchange relation with a relatively cool fluid to cool the gaseous hydrocarbons below 1000° F. and excluding polymerization during cooling, thereby to retain the maximum heating value of the gaseous hydrocarbons.

THEODORE NAGEL.