

1,411,255.

Inventor

Oliver M. Alexander

By *A. P. M. Ely*
his Attorney

UNITED STATES PATENT OFFICE.

CLIVE M. ALEXANDER, OF PORT ARTHUR, TEXAS, ASSIGNOR TO GULF REFINING COMPANY, OF PITTSBURGH, PENNSYLVANIA, A CORPORATION OF TEXAS.

PROCESS OF MAKING LOW-BOILING HYDROCARBONS.

1,411,255.

Specification of Letters Patent.

Patented Apr. 4, 1922.

Application filed March 14, 1916. Serial No. 84,211.

To all whom it may concern:

Be it known that I, CLIVE M. ALEXANDER, a citizen of the United States, residing at Port Arthur, in the county of Jefferson and State of Texas, have invented certain new and useful Improvements in Processes of Making Low-Boiling Hydrocarbons, of which the following is a specification.

This invention relates to processes of making low boiling hydrocarbons; and it comprises a method of producing low boiling hydrocarbon oils, such as gasoline, benzol, toluol, etc., but more particularly benzol and toluol, wherein oil gas from any suitable source, oil-containing gas, such as the natural gases from which casing head gasoline, is obtained, etc., is submitted to a high heat under a comparatively high pressure; as by taking natural gas, still gases, gases made by heating oil, etc., placing the gas under a pressure of, say, 50 to 100 or more pounds and heating to a suitable temperature to produce decomposition of the gas with rearrangement thereof to form vapors of low boiling or liquefiable hydrocarbons, such temperature being advantageously between, say, 500° and 1000° C.; all as more fully hereinafter set forth and as claimed.

In view of the present active demand for low boiling hydrocarbon oils, both of the nature of gasoline and of that of benzol and toluol, for various purposes there has been an active search for new sources of these bodies. I have found that by taking the permanent gases, that is the gases which are permanent at the ordinary temperature and pressure, produced in the cracking distillation of the oil, and heating such gases under heavy pressure, I can produce therefrom by molecular rearrangement various low boiling oils useful in the arts. By heating to a comparatively low temperature, say, about 500° to 750° C. under 50 to 100 pounds pressure and then cooling, the oils produced will be largely of a petroleum character; i. e., will be gasoline, and to some extent kerosene. By using a higher temperature I can produce aromatic low boiling oils of the nature of benzol and toluol. In this latter operation a somewhat higher pressure is useful; say up to 150 or 200 pounds.

Oil gas from a variety of sources may be employed for these processes. I may make the oil gas from the cheaper forms of petroleum and petroleum products by passing the

same or the vapors thereof through a heating zone, such as a hot tube, at a temperature of 700° to 1000° C.; but preferably for the present purpose I use a temperature around 700° C. I then cool to condense and recover any low boiling products thereby formed. I then submit the residual permanent gases to heat under pressure. Or I may take the gases coming from any type of cracking operation, as in distilling oil in a cracking still with or without pressure. These gases also are best cooled, and (if necessary) compressed to remove substantially all liquefiable low boiling hydrocarbons. Or the gas may be scrubbed with a little oil for the same purpose. Or it may be both compressed and scrubbed with oil. I am not restricted in this operation to the use of oil gas coming from breaking down oil since I may also use various natural gases of the same type containing more or less liquefiable components; the type of natural gas yielding what is known as "casing head" gasoline. This type of natural gas is particularly advantageous in the present process. The dry natural gases, consisting mainly of methane, do not yield so readily to this treatment.

Any suitable apparatus may be employed in the performance of the described process. I ordinarily take the gas and free it of liquefiable hydrocarbon oils by cooling or compressing or both and thereafter deliver it under heavy pump pressure, using any suitable type of pump, to a heated zone through which it is passed under pressure. This heating zone may be a tubular retort of any desired structure of any suitable material. Iron or steel piping is perfectly suitable. Any suitable means of heating, such as flame heating, electric heating, etc., may be employed. The temperature of the heating zone should be between 500° and 1000° C.; the particular temperature employed depends upon the time of heating afforded. Catalysts may or may not be present. Their presence is often useful as lowering the necessary heat and pressure. Most of the common metals have the power of catalyzing or facilitating the operation. Copper, nickel, cobalt, iron, etc., or their oxids may be used. In order to present a larger surface for action and to distribute the heat more uniformly, the heating zone may be provided with a charge of an inert carrier

material, such as kieselguhr, pumicestone, brick fragments, etc., carrying one of the stated catalysts. An advantageous catalyst may be produced, for instance, by impregnating terra cotta fragments with a solution of nickel nitrate and heating and reducing it at a low temperature. However, as stated, catalysts are not necessary although often convenient. After passing the heated zone the effluent gases may be sent through any suitable type of condenser, being condensed therein under pressure or not as the case may be. It is advantageous to pass the gases and vapors preliminarily through an air cooled condenser of limited extent to cause a preliminary deposition of tar and then pass the gases through an ordinary water cooled condenser of any desired type. By placing a reducing valve beyond the condenser the condensation may be effected under the pressure of the system. This is useful as causing the condensate to take up some of the more volatile liquefiable products formed in the action; and is particularly useful when the process is applied to the manufacture of gasoline.

In making benzol and toluol, the condensed product may be refractionated in any suitable type of distilling apparatus.

In one specific embodiment of my invention I take the gases coming from any ordinary cracking still, compress these gases at, say, 100 pounds pressure, and cool as by water cooling, removing any liquid which may form in this cooling. The cooled gases still under pressure are then transmitted through a heated steel tube kept at a temperature between 500° and 1000° C.; the higher temperatures being better adapted to the manufacture of low boiling aromatic oils while the lower temperatures are better adapted for the manufacture of gasoline. The gases coming from the hot tube are cooled and otherwise treated as just described.

In lieu of using the described permanent gases in a modification of the present invention the more volatile normally liquid hydrocarbons, say those that are liquefiable at temperatures below 50° C. may be employed. By cooling and condensing certain types of natural gas, a mixture of very volatile low boiling hydrocarbons is obtained; many of these mixtures boiling at the heat of the air. These "wild" gasolines are not highly desirable for commercial purposes because of the difficulty in handling them; some grades indeed it is impossible to ship by rail under the ordinary legal restrictions. By passing gasolines of this type through the heated zone in the same manner as described for permanent gases more valuable liquefiable products of the nature of ordinary gasoline are obtained. These very low boiling gasolines

may be converted either into ordinary gasoline or into low boiling aromatic oils as the case may be.

In another advantageous embodiment of my invention, I take the natural gas itself ("casing head gas"), without separating condensable vapors therefrom, and submit it to heat and pressure in the described manner.

In the described operation in treating oil gas, casing head gas, etc., under heat and pressure, I find it is often advantageous to dilute the gas going into the heated zone with more or less of the gas which has already been treated and which had been freed of liquefiable constituents by cooling. This gas contains more or less hydrogen and under the familiar rule its presence tends to restrain the formation of more hydrogen; and to cause the hydrocarbon oils produced to be of less unsaturated material. The effect of this returned gas may be somewhat heightened by superheating it to a high temperature prior to the return in order to produce more free hydrogen therein.

In the accompanying drawing I have shown more or less diagrammatically, partly in elevation and partly in section, an apparatus useful in the performance of my process.

In the drawings, element 1 is the fire chamber of a still 2 heated by means of the burners 3 and 4. Exhaust gases escape at 5. Fresh oil may be supplied at 6 and any pressure may be indicated at 7. The distilled vapors pass through line 8 to preliminary air cooled condenser 9 which is provided with a back trap 10 to return heavy condensates to the still for further operation. From the air cooled condenser 9 the vapors pass through valved pipe 11 to the water cooled condenser 12. This condenser is provided with inlet 13 and outlet 14 for the water. Condensates are collected at 19. Uncondensed gases and vapors pass through valved line 15 to the compressor 16 or may if desired be passed through lines 31 and 30 to join the pipe 20 on the pressure side of the compressor. When vapors or gases from another source, as for instance casing head gasoline from a well, is to be operated upon, it is sent through pipe 18 and pipe 17 to the compressor 16. From 16 the vapors and gases which have passed the condenser 12 or the vapors and gases which have been admitted through 18 are sent by line 20 to the cracking tube 21 which is mounted in the fire chamber 22. This furnace may be heated by burners, not shown. The cracking tube is provided with pressure gage 23. The tube 21 may be provided with catalytic material 24 as described. Cracked products pass through line 25 to the air cooled condenser 26 from which heavy oils condensed may be withdrawn for use. Uncondensed

vapors and gases pass this air cooled condenser through valved line 27 to the water cooled condenser 28. The condensate from the water cooled condenser may be withdrawn at 29. The uncondensed vapors and gases may be sent back to the cracking tube 21 through line 30 on the pressure side of the compressor 16 or may be sent through line 31 to the suction side of the compressor 16. The operation is obvious from the foregoing description.

What I claim is:—

1. The process of producing low boiling oils which comprises passing permanent gases from a petroleum source through a heated zone at a temperature between 500 and 1000° C. and under heavy pressure, cooling the effluent gases and condensing liquefiable hydrocarbons formed.

2. The process of producing volatile low

boiling oils which comprises heating gaseous hydrocarbons from a petroleum source having boiling point slower than the boiling points of the oil to be produced to a temperature between 500 and 1000° C. under heavy pressure, cooling the gases and vapors resulting from such heating, and condensing the volatile low boiling liquefiable hydrocarbons produced from such low boiling hydrocarbons.

3. The process of producing volatile low boiling oils which comprises heating hydrocarbon gases under pressure in the presence of returned gases, cooling the mixture of gases and vapors formed, separating liquefiable hydrocarbons from such mixture and returning a portion of the permanent gases for admixture with fresh hydrocarbon gas.

In testimony whereof, I affix my signature.

CLIVE M. ALEXANDER.