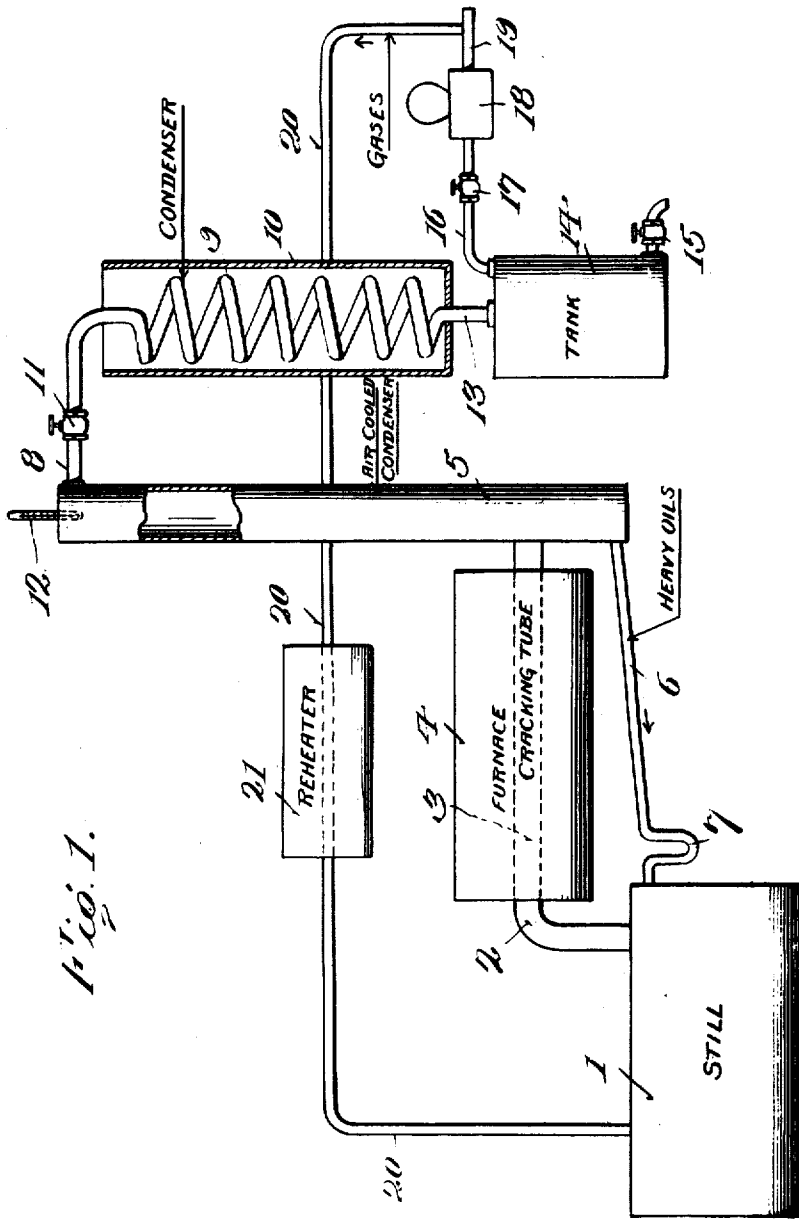


1,404,725.

Patented Jan. 31, 1922.
 2 SHEETS—SHEET 1.



Witness

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 PROCESS OF MAKING LOW BOILING HYDROCARBONS.
 APPLICATION FILED MAR. 8, 1916.

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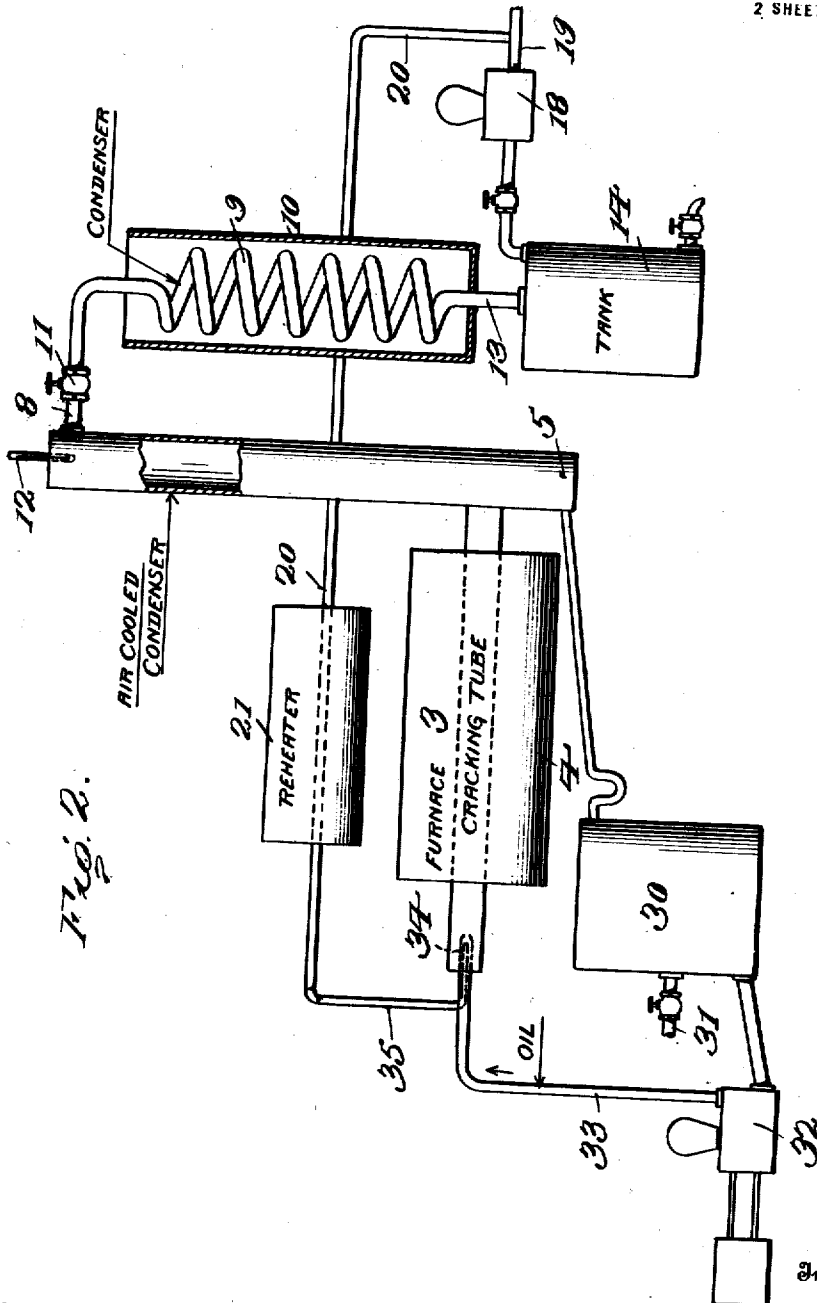


Fig. 2.

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UNITED STATES PATENT OFFICE.

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PROCESS OF MAKING LOW-BOILING HYDROCARBONS.

1,404,725.

Specification of Letters Patent.

Patented Jan. 31, 1922.

Application filed March 8, 1916. Serial No. 82,897.

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 converting petroleum hydrocarbons, and particularly the high boiling hydrocarbons contained in gas oil, fuel oil, crude petroleum, etc., into low boiling hydrocarbons, whether aliphatic, or aromatic or cyclic, such as gasoline, benzol, toluol, etc., wherein such petroleum hydrocarbons are passed through a highly heated zone maintained at a suitable cracking temperature of 500° C. or more in the presence of an atmosphere of gases produced in a like cracking operation and returned to said cracking zone together with the incoming petroleum hydrocarbon or hydrocarbons or vapors thereof, the effluent gases and vapors from said zone being fractionally condensed in order to recover high boiling hydrocarbons, which high boiling hydrocarbons are returned to the cracking zone with a mixture of fresh oil; all as more fully hereinafter set forth and as claimed.

The low boiling aromatic hydrocarbons, benzol, toluol and the xylols, are extensively used as solvents and as raw materials for explosives, for making dye stuffs, etc.; but the supply in this country is not as great as the demand. Ordinarily, they are recovered from coke oven gases. Many attempts have been made to convert the hydrocarbons of petroleum, which in large part belong to entirely different series of hydrocarbons, into these aromatic hydrocarbons; but the operation has ordinarily not been productive. It is an object of the present invention to provide a method of converting petroleum hydrocarbons into aromatic hydrocarbons giving a good yield of the latter products.

On exposure of the petroleum hydrocarbons to a high heat they break down into bodies of simpler molecular structure; the high boiling oils giving low boiling oils, gas, etc. The particular product yielded de-

pends upon the temperature and many other conditions; but in a general way it may be said that ordinarily temperatures around 450° C. give larger yields of low boiling oils and less yields of gas while temperatures above 500° C. give larger yields of gas. In the case of paraffin or saturated hydrocarbons, the liquid product formed consists of a mixture of both saturated and unsaturated hydrocarbons in variable proportions. With petroleum oils containing the polymethylene hydrocarbons the action is more obscure and is not well understood. Pressure favors the production of liquefiable or oily hydrocarbons as against the production of permanent gases while reduced pressure has the reverse effect. High boiling oils can be cracked down to give low boiling liquefiable oily products. Under some conditions, these low boiling oils are, like the original petroleum oils, of aliphatic or olefinic nature, while under other conditions they are of aromatic or cyclic nature, that is, are benzol, toluol, etc. In cracking operations aromatic compounds are supposed, ordinarily, to be formed mainly where very high temperatures are employed, with or without pressure. Their formation is favored by pressure.

I have found, however, that I can produce good yields of low boiling aromatic hydrocarbons by conducting cracking under certain particular conditions. One of these conditions is a return of the gases formed in the operation to and through the cracking zone together with the oil to be cracked or its vapors. This operation can be conducted with production of good yields without pressure. By varying the conditions somewhat, equally good results may be obtained in the production of low boiling oils of the petroleum type, that is, gasoline, naphtha, etc.

In many cases, it is an advantageous expedient to supply oil or its vapors to the cracking zone at a relatively rapid rate—a rate so rapid that a substantial proportion of oil boiling as high as the original oil can be condensed beyond the cracking zone. Such condensed high boiling oil as is here recovered may of course be returned to the cracking zone.

I find that the result of the operation depends materially upon the proportion of the gases returned to the cracking zone. If the amount of gas present in the cracking zone be relatively great as compared with the amount of oil vapors undergoing treatment and the temperature be relatively high, say around 1300° F. or 700° C. (which is an ordinary gas making temperature), the product coming from the cracking zone is rich in aromatic compounds, especially benzol and toluol. The greater the amount of gas the less is the concentration of oil vapors in the total gas-vapor mass and the greater is the tendency to form aromatics. If on the other hand, the proportion of gas so returned is less and the temperature is lower, say around 1000° F. or 540° C., then the product is more in the nature of low boiling petroleum oils (gasoline), and is less rich in the aromatic bodies. The oil or its vapors may be supplied to the cracking zone in any of a number of different ways. For example, the oil may be sprayed or misted into the cracking zone under pump pressure and flow through the cracking zone together with gas supplied in any convenient manner. Or a stream of gas under heavy pressure may be used as injecting means for misting or spraying the oil into the cracking zone. It is however better to have the oil enter under its own pressure since this makes control of the operation more feasible. Instead of introducing the oil directly into the cracking zone, its vapors may be so introduced, the cracking apparatus being directly connected with the vapor outlet of an oil still in any suitable manner.

The cracking apparatus may be of any type adapted for heating the oil vapors and gas in transit. It is conveniently tubular in structure. It may be heated in any suitable manner, as by fire heat, electric heat, etc.

Advantageously, I submit the mixture of gas and vapors going past the cracking zone to a regulated cooling such as will serve to condense unchanged high boiling hydrocarbons together with such new high boiling hydrocarbons as may be formed in the action while allowing the low boiling hydrocarbons (for instance, such as benzol and toluol or gasoline) to go beyond for subsequent condensation. This is convenient as it saves one distillation. The high boiling hydrocarbons so condensed may be directly returned to the cracking zone or to the still furnishing the vapors to the cracking apparatus. The mixture of vapors of low boiling hydrocarbons and permanent gases may now be further cooled to condense the former. It is advantageous to use rather low temperatures in this condensation. In condensation, and particularly where gasoline, is to be made, it is often advantageous

to chill artificially, since this causes the condensing oils to take up a substantial proportion of the vapors of the very low boiling hydrocarbons which might otherwise escape condensation. Or the uncondensed material passing the condenser may be compressed or scrubbed with oil, or both, to recover these liquefiable vapors. The gases passing beyond the condenser for low boiling material may be sent back (or any suitable fraction thereof may be so sent) to the cracking zone by means of any suitable pumping means. In making gasoline, it is advantageous to have the gas so returned freed of these liquefiable vapors by compression or scrubbing.

In the accompanying illustration I have shown, more or less diagrammatically, certain organizations of apparatus elements useful in the performance of the described process. In the showing,

Fig. 1 is an elevation, certain parts being in vertical section, of one type of apparatus, using a vapor feed to the cracking zone, and

Fig. 2 is a similar view of another form of apparatus wherein oil is supplied directly to the cracking zone without a preliminary vaporization.

In the showing of Fig. 1 element 1 indicates diagrammatically any suitable type of still for the production of oil vapors. Heating means and the like are omitted for the sake of clarity of presentation. Vapors leave this still through vapor conduit 2 continued as cracking tube 3 within heating chamber 4. From the cracking apparatus the vapors pass into a condensing apparatus which may be, as shown, a simple air cooled vertical tower 5. At its base it is provided with a discharge conduit 6 for condensed heavy oils, which may as shown, lead through trapped extension 7 back into the still. Uncondensed vapors from the tower leave through conduit 8 continued as condenser 9 in cooling tank 10. Adjustable valve 11 may be used to regulate the pressure through the distilling and cracking system. Thermometer or pyrometer 12 may be used to indicate the temperatures in the partial condensation column. Passing beyond this condenser, the condensable vapors of gasoline or of light oils containing benzol and toluol (as the case may be) pass through conduit 13 into tank 14 where the condensed light oils separate from the gas, being afterwards withdrawn through suitable valved outlet 15. Uncondensed gases leave this tank through outlet conduit 16, which may be valved at 17 in case it is desired to have high pressure in the system and to have this pressure to extend through the condenser. Passing beyond this valve, the gases are taken by pump 18 and delivered into conduit 19 under any suitable

pressure. It is better to leave both 11 and 17 open and use normal pressure. By this conduit they may be led to any suitable place of use. Branching from this conduit is conduit 20 returning to the still and having for its function sending through the still, cracking apparatus, and condensers, an adjusted flow of the exit gases. As shown, this gas at one point passes through a re-heater 21, by which its temperature may be raised to any point desired. This reheating of the gas has several functions. For one thing, it may be used to supply the gas to the cracking zone hot and prevent any local chilling at the point of entrance. Or by carrying the reheating temperature considerably higher than the temperature prevailing in the cracking zone, the gas may be more or less broken down with production of free hydrogen, as will be hereinafter pointed out.

As stated, I find that the results of the operation vary materially with the amount of this gas which is so returned to the cracking zone to meet the vapors of oils produced in the still 1.

In Fig. 2, the apparatus is substantially the same save that the separate still is dispensed with. The cracking zone, condensers, etc., are the same and have received the same reference numerals. In this modification, oil is sprayed directly into the cracking zone. As shown, the condensed high boiling oils coming from the tower-like preliminary condenser are delivered to a storage tank 30. Fresh oil may be added to this storage tank through pipe 31. Pump 32 and its connections are adapted to take oil from the storage tank and deliver it through 33 to any suitable type of spraying or misting nozzle 34. Pipe 35 serves to admit as much gas with the oil as may be desired.

In a typical embodiment of the present invention making benzol and toluol and using the apparatus of Fig. 1, I produce a moderately rapid distillation of oil in still 1. This oil may be gas oil or solar oil, fuel oil, residuum, crude oil, or any other high boiling petroleum oil or product. A 30° Bé. gas oil gives good results. The vapors from the still are passed through cracking tube 3 at a moderate rate. The pressure used may be the ordinary pressure incident to the structure of the still and accessory parts. Gas is returned to the still, and thence, together with the vapors, to the cracking zone in a proportion by volume greater than that of the oil vapors. The cracking zone may be kept at about 700° C. or 1292° F. The speed of gas circulation through conduit 20 should be at such a rate as to supply 1 cubic foot per minute for every gallon of oil distilled into or supplied to the cracking zone per hour. Under these conditions the low boiling oil condensate ob-

tained in 14 will generally upon redistillation begin to boil at about 150° F. and will completely distil below 450° F.; about three-fourths of it passing below 350° F. It may be redistilled to yield fractions rich in benzol and toluol. These fractions will usually contain more or less unsaturated hydrocarbons which can be removed with some sulfuric acid. The purified product may be nitrated, etc.

In using the apparatus of Fig. 2, the operation is exactly the same, save that oil is supplied through 33 in lieu of vapors. This oil is generally in part oil which has once been through the cracking zone and in part fresh oil. The ratio will of course depend upon the particular operation.

The temperature range which I find best adapted for making aromatic compounds is from 1200° F. to 1500° F. The greater the proportion of recirculated gas to that of oil vapors up to a certain maximum ratio through the system, the better the yield of benzol and toluol. Rapid passage of oil through the cracking zone so as to obtain a high percentage of recondensed high boiling hydrocarbons is also of advantage.

High yields of gasoline may be obtained in a similar manner by using a less proportion of recirculated gas to that of oil vapors and a lower temperature in the cracking zone. Using a temperature of about 550° C. or 1022° F. in the cracking zone, a low boiling condensate may be obtained, which upon redistillation begins to boil at about 120° F. and is substantially completely volatile below 350° F.

In making gasoline it is advantageous to have the returned gas freed so far as may be of liquefiable hydrocarbons and the rate of gas return is less than that best adapted for making aromatic compounds. Generally, I use one-third to one-half as much returned gas as in making the aromatic compounds.

The volume of gas returned is considerably more than the volume of the oil vapors; that is, the cracking zone always contains a greater volume of returned gases than of oil vapors.

In making gasoline, under the present invention, the return of the exit gases, which always carry more or less hydrogen, serves to heighten materially the yield of saturated hydrocarbons; whether this be by restraint of the production of more hydrogen or by the direct addition of the hydrogen so returned to the unsaturated bodies produced. By the use of the gas reheating device 21, the percentage of hydrogen in the gas so returned may be materially increased with a concomitant improvement in the quality of gasoline obtained.

It is to be noted that in this process the advantages hitherto obtained by the use of

high pressure in cracking processes are obtained without the use of pressure, or so much pressure, through the agency of recirculated gases and rapid passage of vapors through the cracking zone.

I find that in practical work the temperature of the oil vapors in the cracking zone should not be below 500° C and 450° C. may be said to be a minimum.

In a typical embodiment of the present invention making low boiling aromatics (benzol and toluol) petroleum vapors were passed through a heated tubular retort of six inches diameter and eight feet in length maintained at a temperature around 700° C. The rate of feed of vapors corresponded to 8 gallons of oil per hour. The condensate averaged about 25 per cent of aromatic bodies. The gas was recirculated at the rate of about 5 cubic feet per minute. By distillation of the oil condensed, (which contains unchanged original oil) a yield of about 7 per cent of benzol and 4 per cent of toluol (on the amount of oil used) was obtained.

In making gasoline with the same apparatus, with a temperature around 550° C. with 10 gallons of oil fed per hour and one cubic foot per minute of gas recirculated, the yield of gasoline will be about 70 to 75 per cent (on the original oil).

Instead of using the hydrocarbon gases formed in the cracking operation itself, other hydrocarbon gases, such as oil gas, the various natural gases, etc., may be used. But the gases formed in the operation itself and consisting of a mixture of gaseous hydrocarbons with more or less free hydrogen, I believe to be best adapted for the present purposes; and it is of course the most convenient gas to use. I therefore regard it as most advantageous to use the gaseous hydrocarbons from the operation itself; the gas being used with or without reheating as the case may be.

In another application Serial No. 204,635, filed Nov. 30, 1917, I have described and claimed broadly the cracking of oils in the vapor stage by means of heat so applied that some but not all of the vapors is cracked, a substantial proportion of oil like the original oil being recovered by condensing the vapors beyond the cracking zone. In the present invention I utilize this principle in

connection with the return of gases produced in the cracking operation.

What I claim is:—

1. The process of converting high boiling hydrocarbons into low boiling hydrocarbons, which comprises passing vapors of such high boiling hydrocarbons through a heated zone of 500° C. or more together with a portion of reheated and broken down returned hydrocarbon gases.

2. The process of converting high boiling petroleum hydrocarbons into low boiling aromatic hydrocarbons, which comprises passing the vapors of high boiling petroleum hydrocarbons through a heated zone maintained at a temperature of 500° C. or more together with a copious flow of gases coming from such heated zone and returned thereto after escape therefrom and after heating sufficiently to produce breaking down to a substantial extent.

3. The process of converting high boiling oils into low boiling oils which comprises transmitting the vapors of such high boiling oils through a heated cracking zone at a temperature of 500° C. or more together with a greater volume of returned gases, such returned gases coming from such operation.

4. The operation of converting high boiling petroleum hydrocarbons into low boiling aromatic hydrocarbons which comprises transmitting a mixture of the vapors of such high boiling hydrocarbons together with a larger amount of returned gases through a cracking zone at a temperature of 700° C. or more, the returned gases being gases originating in such cracking zone.

5. The process of converting high boiling petroleum hydrocarbons into low boiling aromatic hydrocarbons, which comprises passing the vapors of high boiling petroleum hydrocarbons through a heated zone maintained at a temperature of 500° C. or more together with a copious flow of gases coming from such heated zone and returned thereto after escape therefrom, such gases being reheated prior to reintroduction to the cracking zone and being greater in volume than the oil vapors mixed therewith.

In testimony whereof, I affix my signature.

CLIVE M. ALEXANDER.