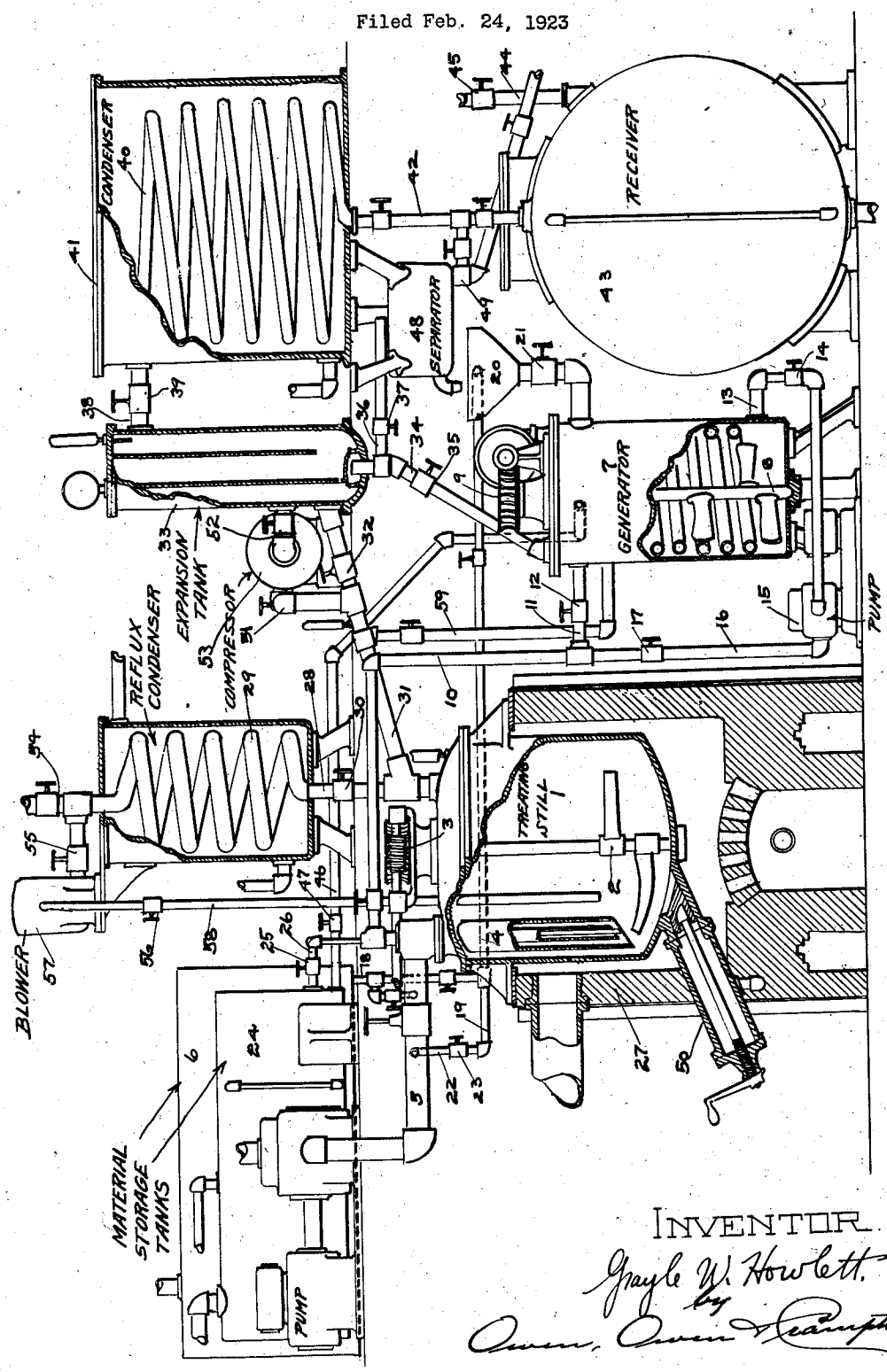
Oct. 13, 1931. G. W. HOWLETT 1,826,787

TREATMENT OF ALIPHATIC HYDROCARBONS

Filed Feb. 24, 1923



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Patented Oct. 13, 1931 1,826,787

UNITED STATES PATENT OFFICE

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TREATMENT OF ALIPHATIC HYDROCARBONS

Application filed February 24, 1923. Serial No. 620,887.

My invention relates to methods of treating aliphatic hydrocarbons and more particularly to the treatment of petroleum oils, their distillates and residues.

My invention has for its object the production of the more desirable lower boiling compounds from the less desired higher boiling petroleum hydrocarbons.

In achieving my object, I make use of my discovery that a non-metallic halogen derivative acts upon aliphatic hydrocarbons present in petroleum oils their distillates, or intermediate compounds formed therefrom, to form lower boiling compounds. Various non-metallic halogen derivatives are more or less effective in achieving my purpose, among which may be mentioned aromatic or aliphatic acid chlorides, acetyl bromide, phosgene, etc., but they are costly and not readily available, therefore, the substance which I prefer to use, because of its cheapness and availability, is an alkyl halide. The alkyl halide may be introduced into the oil as such, or reagents may be used which will produce the alkyl halide within the oil under treatment. I prefer the latter method, and the substances which I have found efficient for the purpose, and most readily available commercially, are the monohydric alcohols, sodium chloride, and sulphuric acid. The sodium chloride and sulphuric acid react to form hydrochloric acid, which, in turn, interacts with an alcohol such as methanol, to form methyl chloride.

There are many modifications of my process possible, according to the substances to be treated and the materials available for treatment, and I shall not attempt to state all of the various ways in which the process may be modified, but will indicate a few of them in connection with the following description of my preferred process.

In the preferred form of the process, I use an apparatus such as is shown in the accompanying drawing, to which reference is had in the following description of the process.

Oil to be treated is placed in a still 1, having therein agitating means 2, driven by worm gearing 3. The materials are introduced into the still through an inlet pipe 4, the higher boiling hydrocarbons being directed into the pipe 4 from the pipe 5. A tank 6 contains one of the alkyl halide forming reagents such as methanol. This material may be introduced into the still, with the heavier hydrocarbons; but I prefer to introduce it into the still with the other chemicals with which it may be mixed, in a mixer 7, provided for this purpose. The mixer 7 is equipped with agitating means 8 driven by gear train 9. The materials are passed from the mixer 7 to the inlet pipe 4 through a pipe 10, into which they may pass through a pipe 11, controlled by a valve 12 or through a pipe 13, valve 14, circulating pump 15, pipe 16 and valve 17. The methanol, if desired, may be passed from the receptacle 6 through pipes 18 and 19, to the hopper 20, and sodium chloride may be introduced into the hopper 20, and passed with the oil through the valve 21 into the mixer 7. I prefer to mix a certain quantity of the higher boiling hydrocarbons, with the salt and alcohol, and for this purpose connect pipe 5 to pipe 19 through pipe 22 and valve 23. Sulphuric acid from container 24 is passed through valve 25 and pipe 26 into the inlet pipe 4. A suitable furnace, as illustrated at 27, surrounds the still 1. The still vapors may proceed through this pipe 31, and expansion valve 32, to the chamber 33 and if desired the reflux coil 29 may be used by allowing the vapors to pass through the pipe 28, whereby the vapors may be condensed and the condensate returned to the still and any fixed gases returned to the still through pump 57 and line 58.

From the chamber 33, the compounds, which have not been changed to the desired lower boiling compounds, are passed back through the pipe 34 and valve 35, into the mixing chamber 7, from whence they may be returned to the still 1. In some cases, this product, which is condensed in chamber 33, may be collected and used without further treatment. In such cases, the valve 35 is closed and this condensed product is passed off through the pipe 36 and valve 37. If it is necessary to remove foreign matter, such as carbon, from these distillates, they are passed

through the separator 48 and directed to the hopper 20, or passed through the outlet 49 to storage. The vapors, which are not condensed in chamber 33, pass out through pipe 38 and valve 39 into the condensing coil 40 in condensing chamber 41, and pass from this chamber down through the pipe 42, into the receptacle 43. Permanent gases collecting in the receiver 43 may be released through the line 44 and valve 45, and conveyed by suitable means to a gas storage receptacle (not shown), from which receptacle the gas may be distributed for fuel purposes, if desired, or used as a component in the preparation of treating material. An outlet device 50 is provided for removal of deposits from the still, or for the removal of residual oil therefrom.

This apparatus is adapted to intermittent or continuous operation of the process. If the oil is to be treated intermittently the entire amount to be treated is charged into the still and the reagents added continuously or intermittently or both.

In treating topped Pennsylvania crude, I have found it desirable to add about 5%, by volume, of methanol and 2%, by weight, of sodium chloride to the charge of oil in the still. The charge is then brought to a refluxing temperature of about 600° F. and refluxed for one hour with the gradual addition of sulphuric acid. The total amount of sulphuric acid found advisable for such treatment is approximately 1%, by weight, of the original charge of oil, the sulphuric acid, however, being added at such a rate as to avoid the formation of an excess of hydrochloric acid. A large proportion of the charge is converted to lower boiling compounds, which are recovered by distillation. It is found that about 7% of the charge of topped oil has been changed to gasoline, with an end point of 400° F., while about 70% of the charge has been changed to kerosene distilling under 590° F. The kerosene may be treated in a similar manner, resulting in a total yield of about 65½% of the original crude, as water white gasoline, including that gasoline first removed by topping, and about 22% as kerosene, of .8 specific gravity and 590° F. end point. The residue, after such treatment, contains about 8% of the original charge in the form of oil suitable for burning purposes mixed with sodium sulphate, carbon, etc. These figures are, of course, given as merely an example of what may be accomplished in applying this process, as the time and manner of treatment, degrees of heat, pressure, etc., may be varied as desired, with different materials and in accordance with the end products desired. It should be understood that conversion takes place at many temperatures between that of the boiling point of the lowest boiling fraction, say 170° F., and that of the highest boiling fraction, about 800° F. When lower treating temperatures are employed I find a proportionately longer time and greater quantity of treating materials are required than where higher treating temperatures are used.

I prefer to conduct the method continuously wherein the materials are being constantly added to the contents of the still, as the lower boiling hydrocarbons are being distilled off. The qualities of the material which I have found advisable to employ are such, that, with a fixed distillation rate, they are continuously replenished in such manner that their quantities and proportions remain practically constant, notwithstanding the removal of materials by distillation and as residues or gas.

Essentially the same apparatus may be used for various modifications of the process. If desired, an alkyl halide may be introduced directly into the charge, instead of introducing the chemicals which will ultimately form an alkyl halide. As for example, methyl chloride may be secured from any desired source and passed into the still. The methyl chloride may be formed in any suitable generator such as the mixer 7 and passed to the still through pipes 10 and 11 and valve 12. Methyl alcohol and sodium chloride may be treated with sulphuric acid in a receptacle and the resultant methyl chloride directed into the still.

I have found that a charge of kerosene, heated to about 500° F., and refluxed for one hour, with the introduction of methyl chloride continuously to a total amount of about 1% by weight of the charge of oil used, resulted in the conversion of about 50% of the original charge of kerosene to gasoline distilling between 170° F. and 400° F.

The alkyl halide may also be produced by the interaction of gases of the methane series with a halogen. A desirable method of treatment, where such materials are readily available, is the treatment of methane with chlorine, whereby methyl chloride and hydrochloric acid are produced. I have found considerable of the alkyl halide is recovered in the tail gases and that hydrochloric is produced in the reaction.

I prefer to operate at substantially atmospheric pressures, although the process may be used with higher pressures, or pressures below atmospheric, and the treatment may take place while the materials are in the gaseous or vaporous state. As shown in the drawing, a by-pass around the valve 32, having a pump 53, is controlled by valves 51 and 52. The by-pass, and the vapor line 31, form the intake line of the compressor member 53, through which vapors from the still 1 are drawn, and directed into the compressor. The non-metallic halogen derivative, used in treating the oil vapors, is drawn from the generator 7 through the line 59 into

the vapor line 31, the valve 32 being closed. This mixture of oil and treating materials, in the vapor phase, is subjected to compression in the member 53. conversion being assisted by compression and the resulting products are expanded to any desired pressure in the expansion chamber 33. Where pressures above atmospheric are maintained on the still, the chamber 33 may act as an expansion member.

Various other modifications of the manner of using this same apparatus will readily occur; for example, where gases are given off, during the refluxing the connection of coil 29 with the atmosphere may be closed by valve 54, and valves 55 and 56 opened, and the gases returned by circulating pump 57 through pipe 58 to the still.

As will be seen from the foregoing, my invention relates broadly to the treatment of the higher boiling aliphatic hydrocarbons, with a non-metallic halogen derivative, preferably an alkyl halide such as methyl chloride. The methyl chloride, or other non-metallic haloid, may be introduced directly, as such, or formed within the body of the oil under treatment, or used in contact with the vapors of such oils, as desired; however I prefer to form the alkyl halide in the nascent state, and preferably by the reaction of a monohydric alcohol, either present, introduced or produced in the oil, with a halogen acid such as hydrochloric acid. The hydrochloric acid, likewise, may be introduced as such, or formed in any desirable manner within the oil, as by the treatment of sodium chloride with sulphuric acid, or by the action of a hydrogen containing gas such as methane, with a halogen such as chlorine, or by the action of water on an anhydrous metallic chloride, or in any other manner which will readily occur to those skilled in the art. Apparently the alkyl group disappears in the reaction, combining with the higher boiling aliphatic hydrocarbons, or intermediate compounds formed therefrom, to produce an unstable compound. Through a molecular rearrangement induced by heat lower boiling aliphatic compounds are formed. The reagents may be used somewhat more efficiently, when introduced so as to form the alkyl halide within the oil being treated.

Where gases of the methane series are present in the oil under treatment, or are formed during the process, or are available in a cheap form, it is sometimes advisable to treat these gases with a halogen, such as chlorine, to form an alkyl halide, and a halogen acid such as hydrochloric acid; the halogen acid thus formed may be employed to treat an alkyl derivative of benzene, such as xylene, or an alcohol, such as methyl alcohol, to form an alkyl halide, such as methyl chloride.

In general, it will be seen that the process can be varied by the use of different chemicals, introduced in different ways, and treated under varying degrees of pressure and heat, and which will form alkyl halide in accordance with the adaptability of the various materials and the particular purpose of the treatment and without, necessarily, the aid of metallic halogen compounds, although metallic halogens may be used in the processes involving the use of my invention without departing from the spirit thereof, the objective of the invention being to produce lower boiling hydrocarbons by the use of non-metallic halogen derivatives. I therefore do not wish to be confined to any of the processes set forth above as they have been selected and described merely as illustrations of the various processes wherein my invention is utilized.

In the appended claims I use the term "petroleum hydrocarbons" and I wish it understood that by the terms I include crude petroleum oils, their distillates, intermediate compounds and residues.

I claim:

1. The process consisting in treating heated petroleum hydrocarbons with a non-metallic halogen derivative contaning an alkyl radical and without the aid of metallic halogen derivatives and thereby producing unstable compounds and heating the mixture at a temperature suitable for conversion action of the alkyl halide to produce the lower boiling compounds.

2. The process consisting in treating heated petroleum hydrocarbons with an alkyl halide and without the aid of metallic halogen derivatives and thereby producing unstable compounds and heating the mixture at a temperature suitable for conversion acion of the alkyl halide to produce the lower boiling compounds.

3. The process consisting in treating heated petroleum hydrocarbons with a methyl halide and without the aid of metallic halogen derivatives and thereby producing unstable compounds and heating the mixture at a temperature suitable for conversion action of the halide to produce the lower boiling compounds.

4. The process consisting in treating heated petroleum hydrocarbons with methyl chloride and without the aid of metallic halogen derivatives and thereby producing unstable compounds and heating the mixture at a temperature suitable for conversion action of the chloride to produce the lower boiling compounds.

5. The process consisting in treating petroleum hydrocarbons with a non-metallic halogen derivative contaning an alkyl radical and without the aid of halogen metallic derivatives and thereby produce unstable compounds, heating the mixture at a temperature suitable for conversion action of the halide to produce the lower boiling com-

pounds, distilling off the lower boiling compounds as formed, and returning for further treatment the higher boiling of the distillates while the mixture is subjected to a conversion temperature.

6. The process consisting in treating petroleum hydrocarbons with an alkyl halide and without the aid of metallic halogen derivatives and thereby producing unstable compounds, heating the mixture at a temperature suitable for conversion action of the alkyl halide to produce the lower boiling compounds, distilling off the lower boiling compounds as formed, and returning for further treatment the higher boiling of the distillates while the mixture is subjected to a conversion temperature.

7. The process consisting in treating petroleum hydrocarbons with methyl chloride and without the aid of metallic halogen derivatives and thereby producing unstable compounds, heating the mixture at a temperature suitable for conversion action of the chloride to produce the lower boiling compounds, distilling off the lower boiling compounds as formed, and returning for further treatment the higher boiling of the distillates while the mixture is subjected to a conversion temperature.

8. The process consisting in treating petroleum hydrocarbons with an alkyl halide and without the aid of metallic halogen derivatives applying heat and thereby producing unstable compounds, heating the mixture at a temperature suitable for conversion action of the alkyl halide to produce the lower boiling compounds, adding materials to the hydrocarbons under treatment to maintain a substantially constant proportion and at a conversion temperature.

9. The process consising in treating petroleum hydrocarbons with an alkyl halide and without the aid of metallic halogen derivatives applying heat and thereby producing unstable compounds, heating the mixture at a temperature suitable for conversion action of the alkyl halide to produce the lower boiling compounds, adding to the petroleum hydrocarbons under treatment to take the place of the compounds removed, and maintaining the distillation at such a rate that the amount of materials entering the treatment is approximately equal to the amount removed and at a conversion temperature.

10. The process of converting higher boiling petroleum oils into lower boiling oils which comprises maintaining a boiling body of the said higher boiling oils in the presence of a non-metallic halogen derivative containing an alkyl radical and without the aid of metallic halogen derivatives and at a temperature suitable for conversion action of the halogen to produce the lower boiling compounds.

11. The process consisting in treating petroleum hydrocarbons with an alkyl halide and without the aid of metallic halogen derivatives, applying heat at a temperature suitable for conversion action of the alkyl halide to produce the lower boiling compounds.

In testimony whereof I have hereunto signed my name to this specification.

GRAYLE W. HOWLETT.