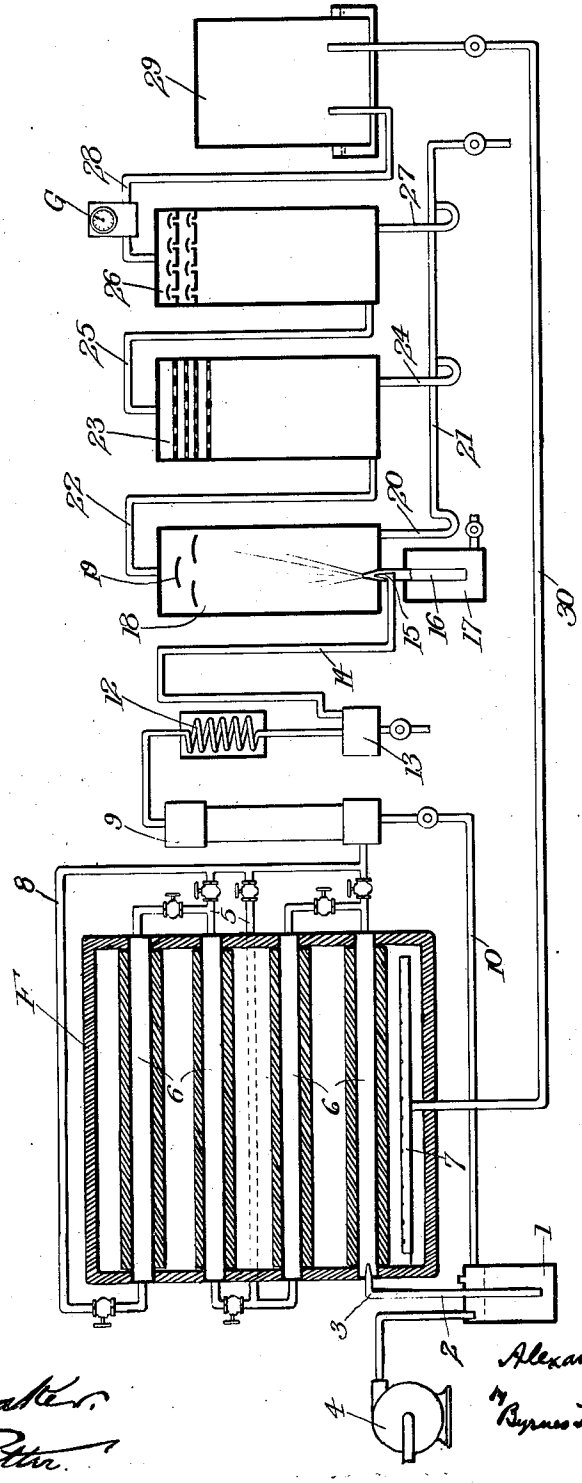
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PROCESS OF TRANSFORMING MINERAL OILS.

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Witnesses

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PROCESS OF TRANSFORMING MINERAL OILS.

1,224,787. Specification of Letters Patent. Patented May 1, 1917.

Application filed April 27, 1916. Serial No. 94,068.

To all whom it may concern:

Be it known that I, ALEXANDER S. RAMAGE, a subject of the King of Great Britain, residing at Detroit, in the county of Wayne and State of Michigan, have invented certain new and useful Improvements in Processes of Transforming Mineral Oils, of which the following is a specification.

My invention is a process whereby hydrocarbons are transformed, by restricted oxidation effected through the agency of a suitable reducible metallic oxid, into other hydrocarbons containing proportionately less hydrogen, water being produced in the reaction. According to my invention I am enabled to transform paraffin hydrocarbons into olefins, as for example pentane into amylene, etc.; or into terpenes such as pinene and limonene; or into aromatic hydrocarbons of the benzol type. Presumably the formation of olefins, terpenes and aromatic hydrocarbons represents the successive stages in the restricted oxidation of a paraffin, so that each of these groups may conveniently be regarded as derived from the preceding group richer in hydrogen, by removal of a portion only of this hydrogen. On this assumption some of the reactions involved might be thus expressed, using generalized formulæ:—

(1) Conversion of a paraffin into an olefin

$$C_nH_{2n+2}+O=C_nH_{2n}+H_2O$$

(2) Conversion of an olefin into a terpene

$$C_nH_{2n}+O_2=C_nH_{2n-4}+2H_2O$$

(3) Conversion of a terpene into an aromatic hydrocarbon

$$C_nH_{2n-4}+O=C_nH_{2n-6}+H_2O$$

It will be understood however that the production of an aromatic hydrocarbon, for example, may with equal propriety be regarded as taking place directly by the restricted oxidation of a paraffin or an olefin, the intermediate reaction stages, if such there be, being disregarded; thus—

(4) Conversion of a paraffin into an aromatic body

$$C_nH_{2n+2}+4O=C_nH_{2n-6}+4H_2O \text{ or}$$

(5) Conversion of an olefin into an aromatic body

$$C_nH_{2n}+3O=C_nH_{2n-6}+3H_2O.$$

Similarly an equation may be written to represent the direct transformation of a paraffin into a terpene—

(6) $C_nH_{2n+2}+3O=C_nH_{2n-4}+3H_2O.$

In the practice of my process, at least when carried out under conditions substantially as specified below, there is reason to believe that the reaction does in fact occur in successive stages, inasmuch as I usually find among the reaction products representatives of most or all of the above-mentioned groups (olefins, terpenes and aromatic bodies).

It will be observed that there occurs in each case an oxidation of a portion only of the hydrogen component of the hydrocarbon, whereby a hydrocarbon of any given series (paraffin, olefin or terpene) is transformed or converted into a hydrocarbon or hydrocarbons of a series relatively poorer in hydrogen. Another product of this restricted oxidation is in each case water, and the amount of water produced, relative to the amount of hydrocarbon treated, is an accurate index of the extent to which the oxidation has progressed. Therefore by collecting the water of oxidation and determining its quantity I am enabled definitely to control the reaction.

I accomplish the results above set forth by subjecting a hydrocarbon, or usually a mixture of hydrocarbons, to restricted oxidation by a reducible metallic oxid, under conditions of temperature and time which are carefully regulated according to the oxid used, the character of the hydrocarbon to be transformed, and the nature of the products desired. In the preferred embodiment of my invention, the hydrocarbon, in a state of vapor, is caused to pass over or through a bed of reducible oxid contained in a tube, retort or other chamber which may be heated by a burner or by means of an electric resistance coil. The temperature within the tube is maintained, by suitable regulating devices, at a point which is sufficient for the reduction of the oxid in question: and the time and temperature are regulated with reference to the yield of water in order to produce the particular hydrocarbon or hydrocarbon mixture desired.

As reducible oxids suitable for my purposes, I may mention the oxids of copper, nickel, cobalt and iron, the last mentioned being preferred. Copper oxid is reduced at a relatively low temperature (250°–300°

C.) and the reaction is extremely rapid and not readily controlled.

Using ferric oxid (Fe_2O_3) a temperature range of 580°–750° C. is suitable. Within these limits, provided a sufficient excess of iron oxid be present, no appreciable separation of carbon has been observed. At higher temperatures, or if the reduction of the oxid is carried too far, cracking sets in and the reduced metal contains carbon.

Ferric oxid employed as above undergoes successive reduction to Fe_3O_4, FeO and metal. For the best operating conditions it is preferred to arrest the treatment when the charge in the tube or retort has been largely reduced to ferrous oxid FeO, containing usually some iron. The reduced charge may be regenerated by blasting it with steam while maintaining a temperature of approximately 750° C., without removing it from the tubes. In the course of this regeneration hydrogen is produced, which may be collected and utilized for hydrogenation, or for other purposes. In case hydrogen is not desired the regeneration may be accomplished by means of air or a mixture of air and steam.

Between the approximate temperature limits above mentioned (580°–750° C.) I effect a careful adjustment between the temperature of the oxid and the boiling-point of the hydrocarbon to be transformed. Thus for a hydrocarbon fraction boiling between 150° and 200° C., the lower temperature ranges, say 580° to 625° C., are used; whereas for a fraction boiling between 250 and 300° C., the higher temperature ranges, say between 700° and 750° C., are used; the intermediate fractions requiring intermediate temperatures for the best results. In practice the boiling-point of the material under treatment is observed and the temperature of the oxid regulated accordingly: For example, when treating an oil fraction of which the boiling-point rises progressively, the temperature of the oxid is progressively and correspondingly increased.

It will be apparent from the foregoing that the precise working conditions of the process may vary within somewhat wide limits, according to the character of the hydrocarbon to be transformed, the nature of the product or products desired, and the specific reducible oxid used. I will therefore describe my invention by reference to one specific illustrative example thereof, it being understood that the invention is not limited to the manipulative features detailed in this example.

Example: The material treated was a complex hydrocarbon mixture consisting largely of olefins and containing constituents boiling all the way from 150° to 300° C. The reaction vessel consisted of a malleable iron tube three feet six inches long by four inches in diameter, electrically heated by nichrome wire set in alundum cement, a rheostat being provided for accurate control of the temperature. The tube was filled with a pure iron oxid of paint grade, prepared from copperas, the tube being nearly filled with the unground material, in lump and powder form. The temperature was measured by means of a thermocouple on the outside of the tube which had previously been calibrated with a thermocouple in the center of the oxid, so that the temperatures mentioned are internal.

The oil was vaporized, and the vapors carried through the tube and discharged into a condensing system. At the beginning of the operation the temperature reading was 580° C., for a boiling-point of the hydrocarbon introduced of 150° C., and this temperature was gradually increased in proportion to the rising boiling-point of the hydrocarbon to an ultimate temperature of 750° C. The pressure within the system was sufficient only to maintain the regulated flow of the vapor therethrough. The condensate amounted to upward of ninety per cent. of the oil treated. Of the recovered product forty-seven per cent. boiled under 180° C. The remaining high-boiling material was refluxed to be again subjected to oxidation.

The material boiling under 180° C. was fractionated, yielding a series of fractions as follows:—

Up to 40° C.,	about 7%,	largely amylene.
40 " 75° C.,	" 8%,	" hexylene.
75 " 95° C.,	20–25%,	containing about 70% of benzol, the balance olefins.
95 " 120° C.,	15–20%,	containing nearly 75% toluol, the balance olefins.
120 " 130° C.,	3%,	containing some octylene.
130 " 150° C.,	10–15%,	containing xylenes, olefins and some pinene.
150 " 180° C.,	25–30%,	of which approximately 18% was limonene, the balance largely olefins and aromatic hydrocarbons.

Practically no paraffins were discoverable in the reaction products, which are therefore very readily purified in order to recover their values. For the purpose for example of recovering benzol and toluol, it is merely necessary to remove the olefins by the usual treatment with sulfuric acid leaving the aromatic compounds in excellent condition for rectification.

A suitable apparatus for carrying out the process is diagrammatically shown in the accompanying drawing, and comprises a tank 1 for containing the starting material from which it is delivered by pipe 2 to a nozzle 3, by pressure upon the liquid in the tank 1 supplied by a suitable air-compressor 4. The hydrocarbon is thus injected into a series of connected tubes 6 containing the reducible oxid, these tubes being mounted in a suitable furnace F and heated in the arrangement shown by a burner 7. From the tubes 6, a pipe 8 leads to a reflux condenser 9, maintained at a suitable tempera-

ture. From this condenser the residual high-boiling-point material returns through pipe 10 to tank 1, for re-treatment.

The uncondensed vapors and gases pass to a second condenser 12, kept at a lower temperature, the condensate being collected in tank 13. The residual gases are then subjected to a scrubbing operation, passing through pipe 14 to the nozzle of an injector 15, supplied with wash-oil (which may be some heavier paraffin oil or kerosene, boiling-point 180°–200° C.), through the pipe 16 from the tank 17. This wash oil is sprayed into a chamber 18, provided with baffles 19, the separated liquid passing through trapped pipe 20 to the collecting main 21. The vapors and gases pass from chamber 18 through pipe 22 to a tower 23, provided with a series of perforated plates, the separated liquid passing through pipe 24 to the main 21. The gases from tower 23 pass through pipe 25 to a "bell" tower 26, from which the separated liquids pass through pipe 27 to main 21. The gases, principally hydrogen, pass through pipe 28, provided with a suitable gas meter G, to a gas-holder 29, from which they may be carried to the burner 7 through the pipe 30. The wash oils and condensates recovered from main 21 may be re-used, preferably after fractioning off the light products, and are returned to tank 17.

The references in certain claims to the introduction of the hydrocarbon "in a state of vapor substantially unmixed with reactive oxygen" is intended to indicate that the hydrocarbon vapors entering the retorts are substantially undiluted by air, steam or oxygen in any other reactive form, whereby the oxidizing effect to which the vapors are subjected is essentially or substantially that of the reducible metallic oxid.

I claim:—

1. The process of transforming hydrocarbons into other hydrocarbons relatively poorer in hydrogen, which consists in bringing the hydrocarbon to be transformed, in a state of vapor substantially unmixed with reactive oxygen, into contact with a reducible metal oxid, and so regulating the temperature of said oxid and the time of contact of the vapor therewith as to oxidize a part only of the hydrogen component of the hydrocarbon, producing thereby as reaction products hydrocarbons relatively poorer in hydrogen, and steam.

2. The process of transforming hydrocarbons into other hydrocarbons relatively poorer in hydrogen, which consists in bringing the hydrocarbon to be transformed, in a state of vapor substantially unmixed with reactive oxygen, into contact with iron oxid at a temperature of 580°–750° C., and so regulating the time of contact between the vapor and the oxid as to oxidize a portion only of the hydrogen component of the hydrocarbon, producing thereby as reaction products hydrocarbons relatively poorer in hydrogen, and steam.

3. The process of transforming paraffins and olefins into terpenes and aromatic hydrocarbons, which consists in subjecting said paraffins and olefins, in a state of vapor substantially unmixed with reactive oxygen, to restricted oxidation by means of a reducible metal oxid maintained at a suitable temperature, producing thereby as reaction products hydrocarbons relatively poorer in hydrogen, and steam.

4. The process of transforming paraffins and olefins into terpenes and aromatic hydrocarbons, which consists in subjecting said paraffins and olefins, in a state of vapor substantially unmixed with reactive oxygen, to restricted oxidation by means of iron oxid maintained at a temperature of 580°–750° C., producing thereby as reaction products hydrocarbons relatively poorer in hydrogen, and steam.

5. The process of subjecting mixtures of hydrocarbons of differing boiling-point to restricted oxidation, which consists in progressively vaporizing said mixtures, conducting the vapors into contact with a reducible metal oxid, at a temperature above the reduction point of said oxid, and progressively raising the temperature of the oxid in correspondence with the rising boiling-point of the hydrocarbon.

6. The process of subjecting mixtures of hydrocarbons of differing boiling-point to restricted oxidation, which consists in progressively vaporizing said mixtures, conducting the vapors into contact with ferric oxid at a temperature above the reduction point thereof, and progressively raising the temperature of the oxid in correspondence with the rising boiling-point of the hydrocarbons.

7. The process of transforming hydrocarbons into other hydrocarbons relatively poorer in hydrogen, which consists in bringing the hydrocarbon to be transformed, in a state of vapor substantially unmixed with reactive oxygen, into contact with a reducible metal oxid, and so regulating the temperature of said oxid and the time of contact of the vapor therewith as to oxidize a part only of the hydrogen component of the hydrocarbon, and to effect incomplete reduction of the oxid, producing thereby as reaction products hydrocarbons relatively poorer in hydrogen, and steam, while avoiding material separation of carbon.

8. The process of transforming hydrocarbons into other hydrocarbons relatively poorer in hydrogen, which consists in bringing the hydrocarbon to be transformed, in a state of vapor substantially unmixed with reactive oxygen, into contact with iron oxid

at a temperature of 580°–750° C., and so regulating the time of contact between the vapor and the oxid as to oxidize a part only of the hydrogen component of the hydrocarbon, and to effect incomplete reduction of the oxid, producing thereby as reaction products hydrocarbons relatively poorer in hydrogen, and steam, while avoiding material separation of carbon.

9. The process of transforming paraffins and olefins into terpenes and aromatic hydrocarbons, which consists in subjecting said paraffins and olefins, in a state of vapor substantially unmixed with reactive oxygen, to restricted oxidation by means of a reducible metal oxid maintained at a suitable temperature, producing thereby as reaction products hydrocarbons relatively poorer in hydrogen, and steam, while providing such excess of the reducible oxid as to avoid material separation of carbon.

10. The process of transforming paraffins and olefins into terpenes and aromatic hydrocarbons, which consists in subjecting said paraffins and olefins, in a state of vapor substantially unmixed with reactive oxygen, to restricted oxidation by means of iron oxid maintained at a temperature of 580–750° C. producing thereby as reaction products hydrocarbons relatively poorer in hydrogen, and steam, while providing such excess of the reducible oxid as to avoid material separation of carbon.

11. The process of subjecting mixtures of hydrocarbons of differing boiling-point to restricted oxidation, which consists in progressively vaporizing said mixtures, conducting the vapors into contact with a reducible metal oxid, at a temperature above the reduction point of said oxid, and progressively raising the temperature of the oxid in correspondence with the rising boiling-point of the hydrocarbon, while maintaining throughout the operation a sufficient excess of oxid to avoid material separation of carbon.

12. The process of subjecting mixtures of hydrocarbons of differing boiling-point to restricted oxidation, which consists in progressively vaporizing said mixtures, conducting the vapors into contact with ferric oxid at a temperature above the reduction point thereof, and progressively raising the temperature of the oxid in correspondence with the rising boiling-point of the hydrocarbons, while maintaining throughout the operation a sufficient excess of oxid to avoid material separation of carbon.

In testimony whereof I affix my signature in presence of two witnesses.

ALEXANDER S. RAMAGE.

Witnesses:
CHARLES FENER,
FLORENCE JACOBI.