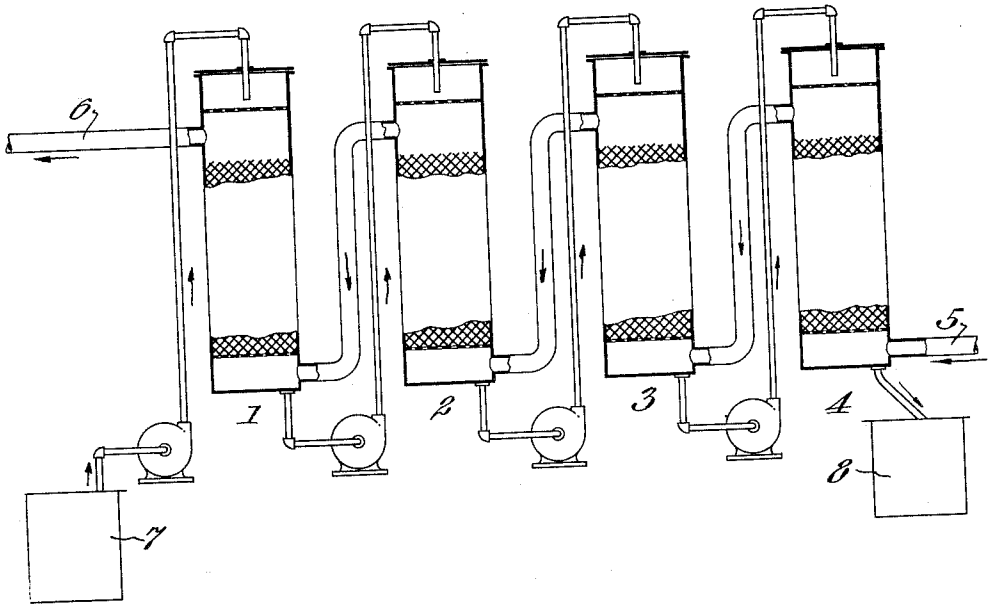
July 24, 1928.

1,678,078

A. S. RAMAGE

PROCESS OF TRANSFORMING LIGHT PARAFFIN HYDROCARBONS INTO OTHER PRODUCTS

Filed June 19, 1925



Inventor:
Alexander S. Ramage
Byrnes Townsend & Brickenstein
his Attorneys.

Patented July 24, 1928.

1,678,078

UNITED STATES PATENT OFFICE.

ALEXANDER S. RAMAGE, OF DETROIT, MICHIGAN, ASSIGNOR TO BOSTAPH ENGINEERING CO., OF DETROIT, MICHIGAN, A CORPORATION OF NEW YORK.

PROCESS OF TRANSFORMING LIGHT PARAFFIN HYDROCARBONS INTO OTHER PRODUCTS.

Application filed June 19, 1925. Serial No. 38,302.

The present invention relates to the transformation of mixtures of light paraffin hydrocarbons such as those found in natural gas and those produced by weathering casing head gasolene, for instance, ethane, propane, butane and pentane, into other useful products. In United States Patent No. 1,224,787 I have described a process for the conversion of paraffin hydrocarbons into other hydrocarbons containing proportionately less hydrogen, such as olefines, terpenes and aromatic hydrocarbons, by subjecting the paraffin hydrocarbons to restricted oxidation or dehydrogenation by contacting them with a reducible metallic oxid, such as ferric oxid, at a temperature of say 580 to 750° C. I have now found that the dehydrogenation of light paraffin hydrocarbons may be so regulated that the dehydrogenation does not go materially beyond the olefine stage, by limiting the temperature of the oxidizing or dehydrogenation reaction to about, but not materially above, 550° C. The first step in the process of my present invention therefore consists in passing a mixture of light paraffin hydrocarbons or a gas containing the same, such as natural gas or the wild gas from weathered casing head gasolene, over and in contact with a reducible metallic oxid such as ferric oxid at a temperature not materially above 550° C. This step may be carried out precisely as is described in the Patent No. 1,224,787 above referred to, excepting with respect to the temperature employed which is regulated so that the temperature of the gases leaving the apparatus does not materially rise above 550° C. The product of this operation is a gaseous mixture containing olefines such as ethylene, propylene, butylene and amylene, together with fixed gases. An average composition is about 25% of ethylene, 25 to 35% of higher olefines and 40% of other gaseous products which so far as the present invention is concerned may be regarded as impurities. This gaseous mixture, even when passed through a condenser and cooled with an ice and salt mixture, does not give any appreciable quantity of condensate; but as I have found by cooling the gas mixture and then contacting it with a body of a solvent oil such as a hydrocarbon oil of the type known as wash oil, the olefinic hydrocarbons are absorbed and polymerized. This may be regarded as a continuation of my earlier invention, as disclosed in United States Patent No. 1,527,079, of a process for the polymerization of ethylene by absorbing it in a solvent hydrocarbon oil. This operation of absorbing the olefines from the gaseous mixture produced by the dehydrogenating operation frees the olefines from fixed gases which are not absorbed in the wash oil.

The next step in my process is the recovery of the olefines which may be accomplished by distillation of the wash oil mixture. In the distilling operation the polymerized olefines contained in the wash oil mixture are depolymerized or split up (this depolymerization occurs at about 120° F), giving a gaseous product consisting essentially of olefines and having an average composition corresponding to the formula C_4H_8. This gas has a calorific value of from 3000–3500 B. t. u. per cubic foot.

In accordance with my invention this gaseous mixture of olefines may be treated in two ways: (*a*) to produce a liquid consisting essentially of polymerized olefines admirably suited, due to its ability of withstanding high compression, for use as fuel in aeroplane and other high-compression internal combustion engines, or (*b*) to produce a mixture of alcohols suitable for use for solvent purposes.

The production of a mixture of the polymerized olefines is accomplished by cooling the gas mixture distilled from the wash oil mixture and contacting it as by bubbling it into a body of the liquefied product thereof. By so doing the olefines contained in the gas are absorbed and polymerized to liquid products. This process of course requires as a starting material a quantity of the polymerized and liquefied olefines. Such a body of liquid may be provided in starting the process, for instance, by bubbling the olefinic gases into an absorbent oil such as wash oil and continuing the operation until the proportion of wash oil in the resulting liquid is negligible. Once the process has been started, the absorbing liquid may be supplied from a previous operation. The liquefied product obtained as described above, which is practically a pure mixture of the polymerized olefines is, as stated, admirably suited for use as motor fuel.

For the production of a mixture of al-

cohols suitable for use as a solvent the procedure is analogous to that employed for the production of ethyl alcohol from ethylene.

In the following description of an illustrative procedure reference is made to the accompanying drawings in which one form of apparatus suitable for the carrying out of the procedure is diagrammatically illustrated.

Referring to the drawings, 1, 2, 3 and 4 are towers of conventional design which may be, for instance, about 30 feet in height and 4 feet in diameter and filled with a suitable acid-proof filling material such as fire-clay rings or balls. 5 is an inlet for the olefinic gases and 6 is an outlet for unabsorbed gases; 7 is a supply of fuming sulfuric acid and 8 is a receiver for the liquid or solution produced by the absorption. The towers are provided with pumps and conduits, as are usual for conveying the gases from the top of the last tower of the series numbered 4 into the bottom of tower 3 and from the top of tower 3 into the bottom of tower 2 and so on as indicated, and for conveying the acid to the distributor at the top of tower 1 and from the bottom of tower 1 to the top of tower 2 and so on as indicated.

In the tower 4 the gases first come into contact with acid which has in the previous towers absorbed a quantity of the olefines and therefore is partially exhausted with respect to its absorbing capacity. In this tower the higher and more easily absorbed olefines are absorbed. As the gases approach the tower 1 the more readily absorbed olefines are removed until in the tower 1 the most difficultly absorbed olefine, ethylene, comes in contact with fresh fuming sulfuric acid and is absorbed thereby and the unabsorbed gases are discharged. As stated, fuming sulfuric acid is used for the absorption. I am aware that I might use instead of fuming sulfuric acid hot sulfuric acid of 1.84 gravity, but I prefer to use fuming acid and to operate at normal temperatures.

The liquid product delivered from the tower 4 into the receiver 8 is diluted or mixed with an equal volume of water and the mixture heated in a lead-lined tank, whereupon it separates into an upper layer of a tar-like material and a lower layer of diluted sulfuric acid. The sulfuric acid may be disposed of in any suitable way, for instance it may be concentrated and re-used in the absorbing operation. The tar-like mass is then treated with an aqueous solution of caustic soda in quantity sufficient to produce a practically neutral reaction mixture. This operation gives a thick, brown, oily liquid which is then distilled in the usual way, preferably to a coke residue. The distillate is a light yellow, pleasant-smelling oil consisting essentially of a mixture of alcohols and having excellent solvent properties, being for instance a good solvent for gun-cotton. If desired, it may of course be fractionally distilled to separate the various alcohols.

It is of course understood that my invention is not limited to the specific procedures and apparatus described in the foregoing specification, as it is evident that other procedures and other apparatus may be employed. The principal points of my invention are the dehydrogenation of light paraffin hydrocarbons under controlled conditions to produce a mixture of olefines, the recovery of the olefines by absorbing them in a solvent liquid, the production of a liquid product by condensing the olefines in a liquid product thereof and the conversion of the mixture of olefines into a mixture of alcohols. With the foregoing disclosure as a guide, various methods of accomplishing these main points of my invention will be apparent to one skilled in this art.

It is possible, and may under certain circumstances be desirable, to eliminate the step of absorbing the olefines from the gas mixture produced by the limited dehydrogenation in wash oil and to pass the gases directly from the dehydrogenating operation to the operations for the production of a liquid product suitable for use as motor fuel or for the production of alcohols. That is, the gases may be cooled and absorbed directly in their own condensate or the gases may be passed directly after cooling to the sulfuric acid absorption.

I claim:—

1. Process which comprises contacting a mixture of light paraffin hydrocarbons substantially unmixed with reactive oxygen with a reducible metal oxid at a reacting temperature not substantially in excess of 550° C.

2. Process which comprises contacting a mixture of hydrocarbons similar in hydrocarbon content to natural gas substantially unmixed with reactive oxygen with ferric oxid at a reacting temperature up to but not exceeding 550° C.

3. Process for the conversion of light paraffin hydrocarbons not heavier than pentane into the corresponding olefines without further substantial dehydrogenation which comprises contacting said paraffin hydrocarbons substantially unmixed with reactive oxygen with ferric oxid at a temperature of about 550° C.

In testimony whereof, I affix my signature.

ALEXANDER S. RAMAGE.