

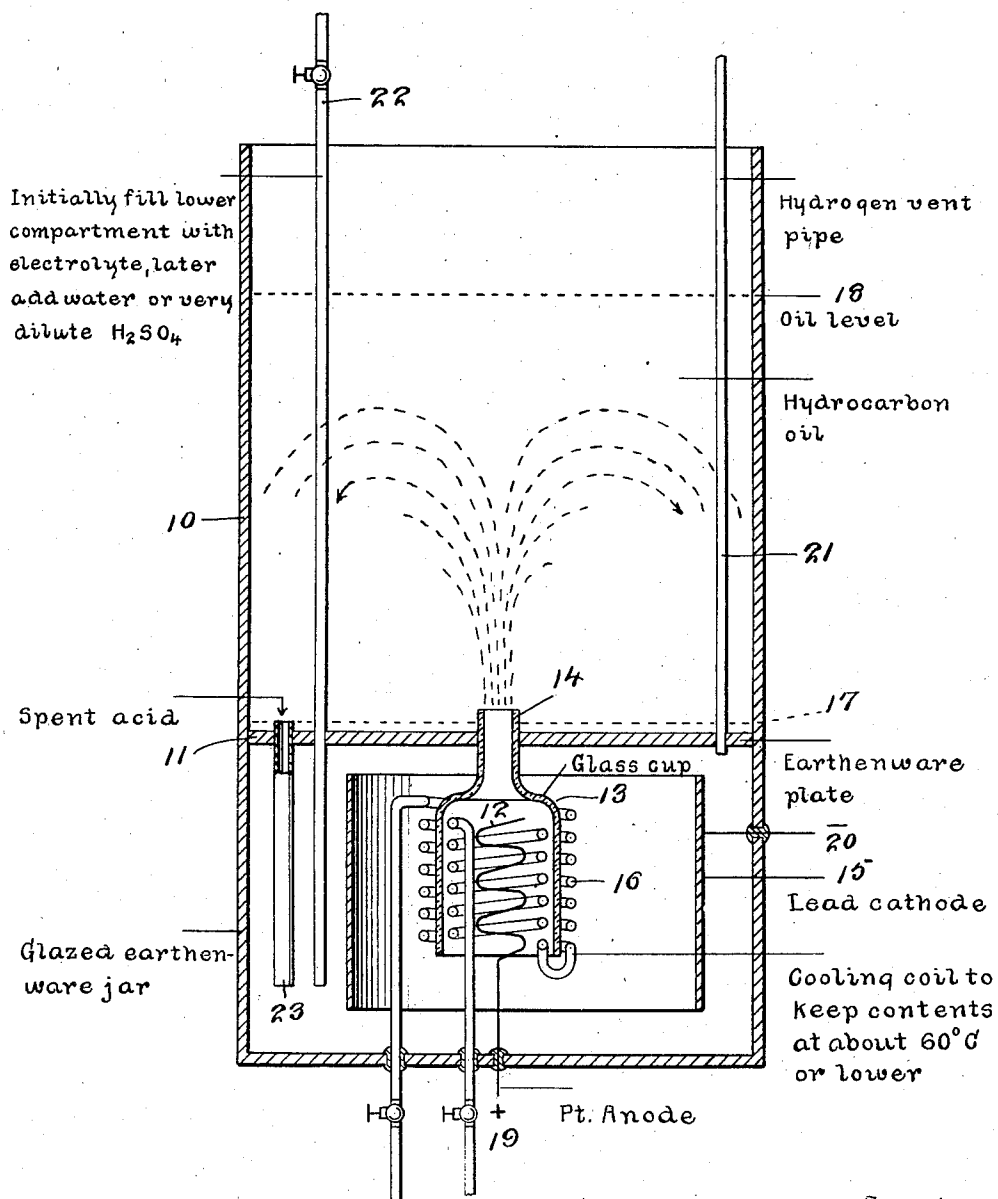
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OXIDATION OF HYDROCARBONS

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OXIDATION OF HYDROCARBONS

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The present invention relates to the production of oxidation products of hydrocarbons, such as alcohols, aldehydes and fatty acids, and the applications is based upon electrolytic oxidation of an electrolyte, which is then brought, while in an oxidized condition, and preferably very soon after the electrolysis, into contact with a hydrocarbon in a liquid state, for the production of oxidation compounds. The oxidation compounds of the hydrocarbons are generally soluble, to a considerable extent at least, in the electrolyte and can be separated therefrom by a suitable method, for example fractional distillation, after which the electrolyte, after suitable dilution if desired, can again be oxidized in the electrolytic cell.

In a copending application 390,657 filed September 5, 1929, I have described a process of refining petroleum products including gasoline and various others, by treating with an electrolytically oxidized refining agent consisting for example of dilute sulphuric acid of 35 to 80 per cent, and preferably around 50 per cent strength. In the present process I also use such an electrolyte which is oxidized electrolytically, and contacted with the liquid oil or petroleum distillate, the contacting preferably being effected very shortly after the formation of the oxidized sulphuric acid.

The oxidation of the sulphuric acid may be performed by passing a direct current of electricity through sulphuric acid of say 50 per cent, although the strength may vary between about 30 per cent and about 80 per cent, the object of the electrolysis being to form considerable quantities of oxidation products of sulphuric acid, such as persulphuric acid, Caro's acid, and hydrogen peroxide. Ozone or oxygen may also be produced to a considerable extent.

The oxidation of the electrolyte may conveniently be performed in a cell having a platinum anode, and a lead cathode, separated by a suitable ceramic diaphragm, the latter may be in the shape of an inverted bowl, and the platinum anode may be water-cooled, for example it may consist of a coil of platinum tubing through which cooling water is caused to flow. The cathode may be a strip of lead or a lead cup, in the outer compartment of the cell surrounding the bowl above referred to.

From the anode compartment, which thus may consist of the inverted bowl a small open tube leads upwardly into a superposed receptacle containing the hydrocarbon liquid to be treated.

The oxidized electrolyte from the anode compartment of the electrolytic cell passes up through this tube bubbling into the hydrocarbon, and at once reacts vigorously therewith giving the hydrocarbon the appearance of boiling, and bubbles of gas being formed and escaping from the said oil. The alcohol produced in the oil by such oxidation, as well as the aldehydes and fatty acids mostly dissolve in the acid electrolyte and the exhausted electrolyte carrying the organic oxidation products in solution, settles to the bottom of the oil receptacle, being drawn off again into the outer compartment of the electrolytic cell. This operation is continued until it is found that a desired amount of oxidation has been performed, when the electrolyte may contain say 5 to 10% of dissolved oxidation products of the oil, and the electrolyte can then be passed to a still and the alcohol, aldehyde and fatty acids distilled off, during which operation of course a good deal of the water content of the electrolyte would also distill off, and the sulphuric acid can then be diluted to about 50 per cent and cooled and again introduced into the electrolytic cell. If desired a portion of the electrolyte can be continuously drawn off, distilled to recover the oxidation products of the hydrocarbon, diluted, cooled and again continuously reintroduced into the electrolytic cell. This mode of separation is given by way of example, and any suitable mode of separation can be employed.

The process can be continued until as much as half of the body of hydrocarbon has been converted into oxidation products.

The temperature of the liquid in the electrolytic cell is preferably kept down, for example by the cooling water in the tubular anode or in any other suitable manner, preferably to as low as 60° F., or lower. The lower the temperature of the electrolyte the more stable is the persulphuric acid and other oxidation products of the electrolyte.

The hydrocarbon liquid in the treating receptacle should be kept cool enough to prevent excessive amounts of vaporization of the same, this material may be at about ordinary room temperature.

The hydrocarbon liquid may be sulphur-free or not, and it may contain substantial amounts of unsaturated hydrocarbons or not, as desired. When the said material contains considerable amounts of olefines or other unsaturated hydrocarbons of the open chain type, the product of the process may consist largely of alcohols of the ethylene series (dihydric alcohols) it is also

possible to produce alcohols containing more than two OH groups.

Without restricting the invention to details, it is stated that the voltage may be at about 7 to 17, at 5 to 15 amperes. In a particular case 18 volts at 10 amperes gave very satisfactory results.

This corresponded to about 50 amperes per square decimeter of anode area, and the ratio of cathode surface to anode surface was about 15:1.

Without restricting the invention to details, the following examples of the process are given.

Example 1

A straight run (uncracked) petroleum ether boiling between 40° and 70° C. constituted the starting material. This consisted largely of pentane, hexane and heptane, and was substantially free from unsaturated hydrocarbons and was also substantially free from sulphur. The liquid was put into the flask above described, which was positioned over the electrolytic cell with two glass tubes passing through the bottom of the flask forming the two passageways above referred to. The current was passed between the electrodes, in this case a current from a 10 volt line, at about 8 amperes was employed. The acid from the anodic compartment passed up through the vertical tube into contact with the petroleum ether, and the bubbles and flow produced gave the latter the appearance of boiling. The dilute acid separated out from the hydrocarbon in the bottom of the flask, and was allowed to run back into the outer compartment (cathode compartment) of the electrolytic cell, adjustment being had by a suitable valve in the said outlet tube. The temperature in the electrolytic cell was maintained between 55 and 62° F., and the temperature of the petroleum ether was about 70 to 72° F. After being allowed to run for 3 to 5 minutes the electrolyte was found to contain a considerable amount of alcohols, including butyl, amyl, hexyl and heptyl. After running for 10 to 15 minutes, the corresponding aldehydes were found to be present in the electrolyte to a considerable extent, and after running for half an hour it was found that the corresponding fatty acids were present in the electrolyte, the concentration of the same being about 5%.

The solution of the electrolyte was run through a still, and the organic compounds above referred to were separated from the same by distillation. The residual acid was then diluted to 50% and cooled and brought back into the electrolytic cell, for regeneration of the oxidizing agent.

Example 2

A cracked petroleum ether, that is to say a petroleum ether or liquid having a boiling point range of from about 40 to about 70° C., made by cracking a heavier petroleum product, was used as the starting material. The procedure was carried on as in the above example, and it was found that a large percentage of dihydric alcohol was produced, and that continued oxidation gave aldehydes and acids of smaller number of carbon atoms than the alcohols referred to, a portion of the same being in the hydrocarbon oil, but most of the oxidation products going into solution in the electrolyte. The oxidation products were separated from the acid by the method above referred to, and the final quantities of oxidation products were recovered from the petroleum ether at the end of the operation.

The oxidation product in this case was largely glycols and oxidation products of the same.

Example 3

Gasoline was first treated in accordance with the example of the prior application 390,657 above referred to, for the removal of sulphur. The sulphur was largely removed from the gasoline during the first four minutes of treatment. The treatment was then continued giving results similar to the above, but higher alcohols being largely produced. In some cases considerable amounts of butyric acid, together with some of the higher acids were also produced.

In some cases cracked gasoline high in olefines and other unsaturated compounds are found to give considerable amounts of higher glycols.

It will be understood that the process can be accelerated to some extent by the use of suitable catalytic agents, thus for example cerium sulphate can be used as a constituent of the electrolyte, along with the sulphuric acid as above described.

My tests have indicated that up to 40 or 50%, more or less, of the petroleum ether can be converted into the oxidized bodies, by continuing the running.

While I have referred particularly to low boiling oils, such as petroleum ether and gasoline, I call attention to the fact that the invention embraces the treatment of oils of any degree of volatility or boiling point range, such as kerosenes, motor oils, and heavier oils, and is not restricted to the lighter distillates. The invention is equally applicable whether or not the oils contain sulphur compounds or other impurities.

A highly important feature of the present invention resides in bringing the oxidized electrolyte very promptly after its formation into contact with the oil. An electrolyte which has been allowed to stand, even for a few minutes is not nearly as effective. A mixture containing sulphuric acid and persulphuric acid, made for example by adding potassium persulphate to a large excess of 50% sulphuric acid is not very effective (if useful at all) for producing the results of the present process.

The process can be carried out in apparatus such as is illustrated diagrammatically in the annexed drawing, forming a part of this application.

A receptacle 10, which may be in the form of a large earthenware jar is provided, and this contains a plate 11 which also can be made of earthenware, thereby forming an upper and a lower compartment. The lower compartment can be filled with sulphuric acid of the concentration referred to above. The anode may be a platinum wire or platinum foil indicated at 12, this being positioned within a glass bowl or cup 13, which has a spout projecting upwardly through a hole in the central part of the plate 11, as indicated at 14. The cathode may be a cylindrical lead cup, open at the top and bottom, as indicated at 15. Within the lower compartment, and preferably located in and around the anode cup 13 is a refrigerating coil 16, for maintaining the liquid in and near the cathode compartment at a low temperature, for example at 60° C. or lower.

The receptacle 10 is first filled with electrolyte up to about the level 17, after which the apparatus is filled with the hydrocarbon oil to be treated, say up to the level 18. A direct current is then passed in from the lead 19 to the anode 12, the cathode 15 being connected to the lead 20. When the current of electricity is passed, hydro-

gen is given off at the cathode, which finds its exit through the pipe 21, and can be suitably utilized. Water or very dilute sulphuric acid is added from time to time, through the pipe 22, for maintaining the acid level at 17, and a portion of the electrolyte, will flow upwardly through the passage 14, and will cause considerable stirring in the oil, oxidizing the oil as indicated above, the spent sulphuric acid flowing back through the pipe 23, for reuse in the process.

I have shown the electrical connections and the pipe to the refrigerating coil, as passing through suitable holes in the earthenware tank, but it will be understood that these can be introduced through the open upper end of the said tank or jar, if desired.

I call attention to the fact that gases liberated at the anode will immediately pass upwardly, and will thereby assist the flow of the electrolyte from the compartment 13 into the oil, whereby the said electrolyte is brought into contact with the oil very soon after formation of the electrolyte, and without allowing such decomposition of the electrolyte as would take place on standing for a protracted period.

I claim:—

1. A process of producing oxidation products from hydrocarbons which comprises oxidizing sulphuric acid by electrolytic oxidation to form a product containing oxidation products of sulphuric acid, and promptly bringing such oxidized material into contact with the said hydrocarbon, whereby the latter is in part oxidized, and separating the oxidation product of the hydrocarbon from said electrolyte.

2. A process of oxidizing hydrocarbons by bringing oxidation products of sulphuric acid, containing persulphuric acid, Caro's acid and hydrogen peroxide and containing at least about 20% of water, which oxidation products are unstable and would substantially change with loss of activity, if they were allowed to stand for any substantial period, into contact with said hydrocarbons, such bringing together of said materials being effected promptly after the production of said oxidation products, and continuing the treatment until the aqueous acid liquid contains the desired products of oxidation of said hydrocarbons, in a substantial amount.

3. A process which comprises circulating a dilute sulphuric acid electrolyte containing about 30 to 80% of H_2SO_4 , through an electrolytic cell and bringing the anodic oxidation product at once into contact with a petroleum hydrocarbon, and continuing such treatment until said electrolyte has accumulated a substantial amount of oxidation products of said hydrocarbon, separating the oxidation products of the hydrocarbon from the sulphuric acid and reintroducing the latter, as dilute acid, into said cycle.

4. A process which comprises circulating a dilute sulphuric acid electrolyte through an electrolytic cell and bringing the anodic oxidation products at once into contact with a petroleum hydrocarbon not substantially more volatile than gasoline, and continuing such treatment until said electrolyte has accumulated a substantial amount of oxidation products of said hydrocarbon, separating the oxidation products of the hydrocarbon from the sulphuric acid and reintroducing the latter, as dilute acid into said cycle.

5. A process which comprises circulating a dilute sulphuric acid electrolyte through an electrolytic cell and then at once into contact with a hydrocarbon consisting largely of petroleum

ether, and continuing such treatment until said electrolyte has accumulated a substantial amount of oxidation products of said hydrocarbon, separating the oxidation products of the hydrocarbon from the sulphuric acid and reintroducing the latter, as dilute acid into said cycle.

6. A process which comprises circulating a dilute sulphuric acid of about 30 to 80% strength, preferably around 50% strength through an electrolytic cell and bringing the anodic oxidation products at once into contact with an open chain hydrocarbon, and continuing such treatment until said electrolyte has accumulated a substantial amount of oxidation products of said hydrocarbon, separating the oxidation products of the hydrocarbon from the sulphuric acid and reintroducing the latter, as dilute acid into the said cycle.

7. A process of electrolytically oxidizing an electrolyte containing dilute sulphuric acid in an electrolytic cell, surmounted by a treating receptacle at only a short distance therefrom, passing the oxidation product of such electrolysis upward directly into said treating receptacle into contact with a low-boiling petroleum fraction, whereby the latter becomes oxidized and taken up to some extent at least by the acid, and thereafter removing the oxidation products of the petroleum fraction from the residual acid, whereby the latter is again suitable for use as electrolyte.

8. A process which comprises circulating a dilute sulphuric acid electrolyte through an electrolytic cell under conditions capable of oxidizing the same and into contact with kerosene, and continuing such treatment until said electrolyte has accumulated a substantial amount of oxidation products of said hydrocarbon, separating the oxidation products of the hydrocarbon from the sulphuric acid and reintroducing the latter, as dilute acid into said cycle.

9. A process which comprises circulating a dilute sulphuric acid electrolyte through an electrolytic cell under conditions capable of oxidizing the same and into contact with a petroleum fraction less volatile than kerosene, and continuing such treatment until said electrolyte has accumulated a substantial amount of oxidation products of said hydrocarbon, separating the oxidation products of the hydrocarbon from the sulphuric acid and reintroducing the latter, as dilute acid into said cycle.

10. A process which comprises circulating a dilute sulphuric acid electrolyte through an electrolytic cell capable of oxidizing such acid and then in contact with a hydrocarbon consisting largely of petroleum ether, and continuing such treatment until said electrolyte has accumulated a substantial amount of oxidation products of said hydrocarbon, separating the oxidation products of the hydrocarbon from the sulphuric acid by distillation and reintroducing the latter, as dilute acid into said cycle.

11. A process which comprises circulating a dilute sulphuric acid of about 30 to 80% strength, preferably around 50% strength through an electrolytic cell to oxidize the same and into contact with a petroleum oil hydrocarbon containing impurities, and continuing such treatment until said electrolyte has accumulated a substantial amount of oxidation products of said hydrocarbon, separating the oxidation products of the hydrocarbon from the sulphuric acid by distillation and reintroducing the latter, as dilute acid into said cycle.

12. A process which comprises circulating a di-

lute sulphuric acid electrolyte containing about 30 to 80% of H_2SO_4 , through an electrolytic cell and bringing the anodic oxidation product at once into contact with a petroleum hydrocarbon, and
5 continuing such treatment until said electrolyte has accumulated a substantial amount of oxidation products of said hydrocarbon containing at least one of the herein described group consisting of alcohol, aldehyde and fatty acid, separating such oxidation products of hydrocarbon from the sulphuric acid and reintroducing the latter, as dilute acid, into said cycle. 5

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