

UNITED STATES PATENT OFFICE

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PRODUCTION OF ALCOHOLS

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The present invention relates to the production of alcohols.

It is already known that the oxidation of hydrocarbons may be carried out for example by treating the initial materials in the liquid phase with air or other gaseous oxidizing agents in the presence of alkali or solutions of alkali. In this manner the oxidation proceeds with the information of acids and at least some portion of the acids is obtained in the form of their salts.

We have now found that alcohols are mainly obtained in the oxidation of difficultly volatile, i. e. from liquid to solid, hydrocarbons having a boiling point of above 180° C. by adding at least 2 per cent by weight, calculated with reference to the initial materials, of non-gaseous i. e. from liquid to solid acids having a dissociation constant between 10⁻⁴ and 10⁻¹³, to the hydrocarbons to be oxidized with the aid of oxygen, air or other gaseous oxidizing agents containing free oxygen such as mixtures of oxygen with carbon dioxide or nitrogen or air diluted by inert gases such as carbon dioxide, nitrogen and the like. As suitable acids according to the definition given above may be mentioned in particular organic acids of low molecular weight, as for example formic acid, acetic acid, propionic acid, maleic acid, benzoic acid and the like. Weak inorganic acids such as boric acid or its anhydride, antimony pentoxide, stannic acid and the like may also be employed. Since water is immediately formed in the oxidation, the anhydrides of the aforesaid acids may be employed, which are immediately converted into the acids and are therefore considered as equivalents to the acids and comprised within the term acids. These additions which apparently interrupt and prevent the oxidation from proceeding beyond the alcohol stage of oxidation and render the products more uniform, are employed in large amounts, at least 2 per cent calculated with reference to the hydrocarbons to be oxidized, and the addition may be effected in any suitable manner, the best results being generally obtained with quantities of from 5 to 10 per cent, the yields being gradually decreased with higher quantities of acid. For example the current of gas to be oxidized may be laden with the vapours of the acids and the like before its entry into the oxidizing chamber, or the acids and the like may be added all at once or in consecutive fractions to the hydrocarbons to be oxidized. The duration and reaction temperature of the process depend on the initial materials but in most cases blowing with the gaseous oxidizing agent for from 2 to 3 hours at tempera-

tures between about 100° and 200° C. is sufficient. The operation is stopped as soon as a sample shows a saponification value of 70, the reaction being not allowed to proceed further since otherwise a too far reaching oxidation and destruction would occur. The recovery of the acids, which are partly contained in the vapour phase in the gases leaving the reaction vessel, may be carried out in any suitable manner, as for example by boiling up under a reflux condenser together with water or by washing out and the like.

Aliphatic hydrocarbons, as for example petroleum fractions such as middle oils, paraffins, ceresine and the like or naphthene hydrocarbons, such as are contained in certain paraffin oil, gas oil and the like or synthetic hydrocarbons, as for example hydrocarbons obtained by the hydrogenation of tars and the like are especially suitable as initial materials for the process according to the present invention. The oxidation of the initial materials may be carried out at atmospheric or higher pressures, such as up to 100 atmospheres if liquid initial materials are employed, whereas pressures up to 50 atmospheres are usually sufficient on working with solid initial materials. The reaction is preferably accelerated, in the manner already known, by the presence of catalysts such as naphthenates or resinsates, whereby, in combination with the said additions of acids and the like, the formation of alcohols is still further promoted.

The reaction products, which besides unattacked initial material and acid constituents mainly consist of free alcohols and esters thereof, are separated in the manner already known as for example by extraction with organic solvents, as for example ethyl alcohol, or crystallization, after removal of the acid constituents. The alcohols thus obtained are liquid or solid according to the nature of the initial materials employed.

The following examples will further illustrate the nature of this invention, but the invention is not restricted to these examples. The parts are by weight.

Example 1

Hard paraffin wax is fused and heated to 160° C. and for each kilogram of the wax 1 cubic metre of air, which has been laden with 22 grams of acetic acid by passing it at 18° C. through a vessel filled with concentrated acetic acid, is blown per hour through the heated wax. After 3 hours a pale coloured oxidation product is obtained containing 40 per cent by weight cal-

culated with reference to the initial material of alcohols.

Example 2

Hard paraffin wax is fused and heated to 175° C. and for each kilogram of the wax 50 grams of boric anhydride are added and 1 cubic metre of air, which has been laden with 16 grams of acetic acid by passing it at 15° C. through a vessel filled with concentrated acetic acid, is blown per hour through the heated wax. After 3 hours a pale coloured oxidation product is obtained containing 44 per cent by weight calculated with reference to the initial material of alcohols.

Example 3

A fraction of Pennsylvania crude mineral oil boiling between 180° and 350° C. is mixed with 1 per cent of its weight of manganese naphthenate and air is blown through at 160° C. at the rate of 1 cubic metre per hour and per kilogram of the oil, the air having been laden with 37 grams of acetic acid per each cubic metre before its introduction into the reaction vessel by passing it at 20° C. through a vessel filled with concentrated acetic acid. After 3 hours an oxidation product is obtained which contains 35 per cent calculated with reference to the initial material of alcohols. When working without acetic acid about 1/3 of the said yield of alcohols is obtained.

Example 4

800 parts of molten hard paraffin wax are incorporated with 16 parts of benzoic anhydride and the whole is blown with air at 160° C. at a velocity of 1 cubic metre of air per hour and per each kilogram of the wax. In the course of two hours further 10 parts of benzoic anhydride are added and blowing is stopped after two and a half hours. The yield of reaction product is 106 per cent by weight of the initial material. After separating off unsaponifiable material (esters, lactones and free acids) 75 per cent of the whole oxidation product of neutral products is obtained, which possess a hydroxyl value of 84.3.

Example 5

1000 parts of American hard paraffin wax are incorporated with 50 parts of antimony pentoxide and then blown with air at 180° C. at a velocity of 1 cubic metre per hour and per each kilogram of the wax. After 3 hours blowing, an oxidation product is obtained in a yield of 105 per cent of the initial material. After separating off unsaponifiable material (esters, lactones and free acids) about 70 per cent of the whole oxidation product of a neutral product is obtained which possesses a hydroxyl value of 80.5.

Example 6

100 parts of a fraction of crude Pennsylvania mineral oil boiling between 180° and 350° C. are blown with air at 160° C. at a velocity of 1 cubic metre per hour and per 1 kilogram of the oil after the addition of 1 part of manganese naphthenate. Before entering the oxidation vessel the current of air passes a vessel filled with concentrated acetic acid the temperature of which

is kept at 20° C. so that each cubic metre of air contains 37 grams of acetic acid. After 3 hours blowing, an oxidation product is obtained which contains about 35 parts of alcohols.

What we claim is:—

1. In the liquid phase oxidation of difficultly volatile non-aromatic hydrocarbons boiling above 180° C. with gaseous oxidizing agents while heating at atmospheric pressure, the step which comprises carrying out the oxidation from the start in the presence of an added organic acid having a dissociation constant between 10^{-4} and 10^{-13} , the quantity of the organic acid added during the whole reaction being at least 2 per cent by weight of the initial hydrocarbons and the reaction being stopped at least as soon as the saponification value of the reaction product is 70.

2. In the liquid phase oxidation of difficultly volatile non-aromatic hydrocarbons boiling above 180° C. with gaseous oxidizing agents while heating to a temperature between about 100° and 200° C. at atmospheric pressure, the step which comprises carrying out the oxidation from the start in the presence of an added organic acid having a dissociation constant between 10^{-4} and 10^{-13} , the quantity of the organic acid added during the whole reaction being about from 2 to 10 per cent by weight of the initial hydrocarbons and the reaction being stopped at least as soon as the saponification value of the reaction product is 70.

3. In the liquid phase oxidation of difficultly volatile non-aromatic hydrocarbons boiling above 180° C. with air while heating to a temperature between 100 and 200° C. at atmospheric pressure, the step which comprises carrying out the oxidation from the start in the presence of an added organic acid having a dissociation constant between 10^{-4} and 10^{-13} , the quantity of the organic acid added during the whole reaction being from 5 to 10 per cent by weight of the initial hydrocarbons and the reaction being stopped at least as soon as the saponification value of the reaction product is 70.

4. In the liquid phase oxidation of a paraffin boiling above 180° C. with air while heating to a temperature between 100° and 200° C. at atmospheric pressure, the step which comprises carrying out the oxidation from the start in the presence of an added organic acid having a dissociation constant between 10^{-4} and 10^{-13} , the quantity of the organic acid added during the whole reaction being from 5 to 10 per cent by weight of the initial paraffin and the reaction being stopped at least as soon as the saponification value of the reaction product is 70.

5. In the liquid phase oxidation of a liquid paraffin boiling above 180° C. with air while heating to a temperature between 100° and 200° C. at atmospheric pressure, the step which comprises carrying out the oxidation from the start in the presence of added acetic acid, the quantity of acid added during the whole reaction being from 5 to 10 per cent by weight of the initial paraffin and the reaction being stopped at least as soon as the saponification value of the reaction product is 70.

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