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DESULPHURIZATION AND OXIDATION OF HYDROCARBONS

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The present invention relates to the desulphurization and oxidation of hydrocarbons.

We have found that for the production of organic products containing oxygen, such as alcohols, aldehydes, non-aromatic carbonic acids, by incomplete oxidation of crude materials which are solid or liquid at ordinary temperature and which consist of or contain substantial amounts of hydrocarbons, which hereinafter are referred to as "crude coherent hydrocarbon materials", it is advantageous to subject these materials to a preliminary desulphurization.

This desulphurization may be effected by any known method, for example by subjecting the said crude solid or liquid hydrocarbons to a suitable treatment with fuming sulphuric acid or liquid sulphur dioxide. By the said methods of desulphurization the unsaturated hydrocarbons are partly or wholly removed from the treated materials but can often be recovered from the purifying agents employed, such as sulphuric acid, only with difficulty.

We have further found that it is particularly advantageous for the subsequent incomplete oxidation of the hydrocarbons employed, in particular those consisting mainly of or containing paraffin waxes, to purify the impure materials to be incompletely oxidized only to such an extent that the sulphur compounds only are wholly or partially removed and that the main portion of unsaturated hydrocarbons contained in the said materials is not separated therefrom. These unsaturated hydrocarbons remain in the bulk of the treated materials either unconverted or they are converted into saturated compounds by hydrogenation. The purification may be effected by the usual desulphurizing agents, the reaction conditions, such as temperature, concentration and the like, being so selected that a removal of the unsaturated hydrocarbons is avoided as far as possible. It is particularly advantageous to effect the purification by hydrogenation at temperatures ranging from 150° to 450° C., preferably from 200° to 350° C. and under a pressure ranging from 5 to 200 atmospheres. The sulphur thereby escapes in the form of hydrogen sulphide. In this hydrogenation the unsaturated hydrocarbons contained in the initial materials may be partly or wholly converted into saturated hydrocarbons, if the conditions as regards temperature and pressure are chosen sufficiently strong. The special temperature and pressure to be employed depend on the kind of the initial material to be treated and on the catalyst employed. In any case the conditions for obtaining the desired degree of purification and saturation may be readily ascertained.

As catalysts coming into question for the said purifying hydrogenation treatment may be mentioned molybdenum, cobalt, molybdenum sulphide, cobalt sulphide, if desired deposited on carbon, or compounds, in particular oxides, of the alkaline earth metals or earth metals, or oxides of the metals of groups 4 to 7 of the periodic system, if desired, activated with sulphides. As the initial materials according to the present invention, aliphatic or naphthene-like solid or liquid hydrocarbons from any source and mixtures of the same, as for example the middle oils from petroleum, mineral or brown coal tars or low temperature carbonization tars, and also the hydrocarbons obtained from hydrogenation products of coals, petroleum residues and the like may be employed.

If in the purifying hydrogenating treatment it is not desired to saturate the unsaturated hydrocarbons or to saturate them only partially, milder conditions as regards temperature and pressure are to be employed. For this purpose temperatures as low as 200° C. are often sufficient.

The subsequent incomplete oxidation of the purified materials is then effected with gases containing or supplying oxygen at elevated temperatures. It is carried out in the liquid phase. Temperatures ranging from about 100° to 200° C. are usually employed; as oxidizing agents may be mentioned oxygen, air and nitrogen oxides; compounds of manganese, barium or mercury, such as the salts thereof with stearic acid or cinnamic acid are suitable as catalysts.

As is well known in the art for example from Journal of the Chemical Society 121 (1922) page 496, Berichte der Deutschen Chemischen Gesellschaft vol. 53 (1920), pages 66, 922 and 1569 and Mitteilungen des Deutschen Forschungsinstitutes für Textilstoffe 1918, page 108, in the liquid-phase oxidation of paraffin no substantial cracking of the hydrocarbons occurs if the oxidation be carried out below 200° C., and especially when carried only to such an extent that unattacked

hydrocarbon material remains. When obtained under the said conditions, the oxygenated products of the liquid-phase oxidation will contain about the same number of carbon atoms as the initial materials, of which paraffin is known to contain hydrocarbons containing from about 12 to 36 carbon atoms, mainly from about 12 to about 24 carbon atoms (compare for example Berichte der Deutschen Chemischen Gesellschaft, vol. 40 (1907), page 4779). In accordance with the said statements water-insoluble fatty acids containing from 10 to about 35 carbon atoms, mainly from 11 to 24 carbon atoms, have been identified in the liquid-phase oxidation products from paraffin (according to the aforesaid citations, Chemiker Zeitung 49 (1920), page 311, and Zeitschrift für angewandte Chemie 1918, page 69). Similarly, alcohols in the said oxidation products contain from about 10 to 25 carbon atoms (see Journal of the Chemical Society 1926, page 2377), lauryl, myristyl, palmityl and stearyl or octodecyl alcohols together with alcohols containing 22, 24 and 25 carbon atoms having been found besides the corresponding myristic, palmitic, isopalmitic, stearic and arachic acids, the alcohols having from about 12 to about 20 carbon atoms constituting generally the predominant portion of the whole mixture of alcohols.

Since no substantial cracking of the hydrocarbons occurs in the said oxidation and the resulting products contain about the same number of carbon atoms as the initial materials the said oxidation is hereinafter referred to as a non-destructive one.

The advantage of working according to the present invention consists in the fact that the unsaturated hydrocarbons are present during the subsequent oxidation so that increased yields of valuable oxidation products are obtained.

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

Example 1

American gas oil containing 0.6 per cent of sulphur is treated with hydrogen at 350° C. under a pressure of about 150 atmospheres in the presence of a catalyst consisting of a mixture of nickel sulphide and molybdenum sulphide precipitated on carbon. The oil purified in this manner only contains 0.01 per cent of sulphur. It is then blown with air for 5 hours at 150° C. in the presence of manganese stearate. The yield of carboxylic acids amounts to about 60 per cent. The remainder consists of about 25 per cent of neutral oxygen-containing compounds such as high molecular alcohols and ketones and of about 15 per cent of unchanged initial material.

Example 2

An oil fraction which is obtained by cracking distillation of a brown coal low temperature carbonization tar and which boils between 130° and 310° C. under a pressure of 6 millimeters mercury gauge, is passed, while maintaining a partial pressure of hydrogen of 200 atmospheres and a temperature of 360° C., over a catalyst consisting of a mixture of zinc oxide, magnesium oxide and molybdenum oxide deposited on carbon. The hydrogenated product is practically odorless and has a slightly yellow coloration. Further properties of this product are given in the following table in which it is compared with the initial material:

	Iodine number	Content of sulphur in percent	Content of paraffins in percent
Hydrogenated product	2.6	0.02	38
Initial material	46	0.8	37

Products of similar properties are obtained, if instead of the aforesaid catalyst insensitive to sulphur, oxides or sulphides of the elements of groups 3, 4 and 6 of the periodic system, if desired together with zinc oxide and/or magnesium oxide, may be employed for the desulphurization and hydrogenation. Similarly the temperature and the pressure may be varied within wide ranges. The temperature may be selected between 300° and 450° C. The pressure should preferably be higher than 25 atmospheres.

The hydrogenation product, in which 1 per cent of the manganese salt of naphthenic acid is dissolved, is then treated for five hours and at 160° C. with air blown therethrough with a velocity of flow of 0.7 cubic meter per hour per each kilogram of said hydrogenation product. The product thus obtained contains 30 per cent of acids which are separated therefrom. The remainder may be again subjected to a hydrogenating treatment, if desired together with fresh initial material, and then to oxidation.

Example 3

A paraffin distillate derived from a Pennsylvanian crude oil is passed, while maintaining a partial pressure of hydrogen of 200 atmospheres and a temperature of 370° C., over a catalyst consisting of a mixture of zinc oxide, magnesium oxide and molybdenum oxide. The hydrogenation product obtained is colorless and odorless and differs from the initial material as shown in the following table:

	Iodine number	Content of sulphur in percent	Content of paraffin in percent
Hydrogenated product	2.0	0.019	25
Initial material	17.2	0.8	26

The said hydrogenation product, in which 1 per cent of the manganese salt of naphthenic acid is dissolved, is then treated for 4½ hours and at 160° C. with air blown therethrough with a velocity of flow of 1000 liters per hour per each kilogram of hydrogenation product. The resulting product contains 38 per cent of acids which are separated therefrom. The remainder may be again subjected to hydrogenation, if desired together with fresh initial material, and then to incomplete non-destructive oxidation.

What we claim is:—

1. In the production of organic products containing oxygen from aliphatic hydrocarbon oils containing unsaturated compounds, the steps which comprise desulphurizing the said materials while precluding the removal of said unsaturated compounds and then subjecting the desulphurized materials to incomplete non-destructive oxidation in the liquid phase.

2. In the production of organic products containing oxygen from aliphatic hydrocarbon oils containing unsaturated compounds, the steps which comprise desulphurizing the said materials by hydrogenation at temperatures between

150 and 200° C. and under a pressure of from 5–200 atmospheres, and subjecting the desulphurized materials to incomplete non-destructive oxidation in the liquid phase.

3. In the production of organic products containing oxygen from a crude coherent hydrocarbon material containing unsaturated compounds, the steps which comprise desulphurizing the said material while precluding the removal of said unsaturated compounds and then subjecting the desulphurized material to incomplete non-destructive oxidation in the liquid phase.

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