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COMPLETE SPECIFICATION

Process for the Separation of Hydrocarbons from Oxygenated Derivatives

We, NAAMLOOZE VENNOOTSCHAP DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ, of 30, Carel van Bylandtlaan, The Hague, The Netherlands, a Company organised under the laws of The Netherlands, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the separation of mixtures of organic compounds containing hydrocarbons and derived substantially water-insoluble oxygenated compounds and to the compounds so obtained and is particularly but not exclusively applicable to the separation of substantially water-insoluble oxygenated compounds from the reaction products obtained from the synthetic manufacture of hydrocarbons from carbon monoxide and hydrogen (e.g. from the Fischer Tropsch process).

Some of the oxygenated compounds in such reaction products are water-soluble and their separation with aqueous solvents is accordingly a simple operation and will precede the separation of the substantially water-insoluble compounds to which the present invention relates. It will thus be appreciated that the process of the present invention is not applied to the crude mixture of reaction products from the synthetic manufacture of hydrocarbons from carbon monoxide and hydrogen but to the substantially water-insoluble portion of this mixture.

The substantially water-insoluble oxygenated compounds to which the present invention refers include alcohols, aldehydes, ketones and carboxylic acids.

The separation of these mixtures by extraction with a single solvent, such as liquid sulphur dioxide or aqueous methanol, possessing selective solvent action for the substantially water-insoluble oxygenated compounds has proved difficult and uneconomic in practice because of the large quantities of solvent required to give a substantially pure extract with the result that the extraction of the substantially water-insoluble oxygenated compounds is not generally carried out; they are left as impurities and thus lost, although, once separated, they are valuable compounds. For example, the Fischer Tropsch process normally produces a product containing about 2 per cent of substantially water-insoluble oxygenated compounds which are not recovered. However, by modifying the catalyst, this quantity could be raised to 10 per cent or more and the processes would therefore provide a valuable source of oxygenated compounds if an economic process for the extraction of the substantially water-insoluble oxygenated products could be evolved.

The desired economic separation is achieved according to the present invention by subjecting a mixture of organic compounds containing hydrocarbons and substantially water-insoluble oxygenated compounds derived from hydrocarbons to extraction with two solvents flowing in countercurrent to each other, one solvent consisting substantially of liquid sulphur dioxide and the other solvent consisting substantially of paraffinic hydrocarbons boiling outside the boiling range of said mixture.

Paraffinic hydrocarbons suitable for use in the process of the invention are pure hydrocarbons, for example normal heptane or mixtures of paraffinic hydrocarbons such as occur in mineral oil fractions, for example gasoline, substantially free from aromatic hydrocarbons. A substantially aromatic-free mineral oil fraction of boiling range sufficiently above the boiling range of the initial mixture to permit subsequent ready

[*Price* 2/-]

separation of solvent and extracted material is preferred, for example, medicinal paraffin oils. Paraffinic solvents having a boiling range above that of the initial mixture are also preferred for the reason that they are less miscible with sulphur dioxide than paraffinic solvents having a boiling range below that of the initial mixture.

The extraction process is preferably carried out at temperatures below –10° C., because at these temperatures the vapour pressure of the liquid sulphur-dioxide is so low as to make it possible to operate at atmospheric pressure; the working-temperature is preferably about –25° C. It is also possible to operate at higher temperatures, for example 20° C., but the extraction then has to be effected at higher pressures with less favourable results.

The principal advantage of using sulphur dioxide and a paraffinic hydrocarbon in a double solvent extraction according to the present invention lies in the high partition coefficients of the oxygenated components with respect to these two solvents. Thus the partition coefficients of various oxygenated compounds with respect to equal volumes of sulphur dioxide and medicinal paraffin oil were determined at –25° C. The concentration of oxygenated compounds in the mixture of oxygenated compounds, liquid sulphur dioxide and medicinal paraffin oil was 17% by volume or less.

The following partition coefficients were found :—

	Parts by vol. present in SO_2 layer	*Parts by vol. present in hydrocarbon layer*
diethyl ketone ..	15	1
methyl isobutyl ketone	12	1
di-isobutyl ketone	5.5	1
n.butanol-1 ..	18	1
hexanol	4.5	1

It has previously been stated that mixtures of hydrocarbons, especially of the heavy type such as lubricating oils, may be fully fractionated by counter-current extraction with the aid of benzine and liquid sulphur dioxide.

The present invention is further illustrated with reference to the following examples.

EXAMPLE 1

A feed mixture consisting of :—

1 part by volume of methyl isobutyl ketone,
1 part by volume of n.butanol and
8 parts by volume of a paraffinic hydrocarbon fraction with 8–10 C-atoms per molecule

(boiling range 115–167° C.) was extracted at –25° C. in a four stage extraction system through which liquid sulphur dioxide and medicinal paraffin oil flowed in countercurrent to each other. Eight parts by volume of medicinal paraffin oil were introduced into the first stage of this system and ten parts by volume of liquid sulphur dioxide were introduced into the fourth stage of this system. Ten parts by volume of the feed mixture were introduced into the third stage of this system.

The liquid sulphur dioxide phase was removed from the first stage and after the removal of the sulphur dioxide, yielded an extract consisting of methyl isobutyl ketone and butanol, contaminated with less than 0.5% by volume of hydrocarbons. The paraffin oil phase, which was withdrawn from the extraction system at the fourth stage, contained the hydrocarbons present in the feed mixture contaminated with about 0.5% by volume of oxygen compounds.

EXAMPLE 2

An extraction of the same feed material as that described in Example 1 was carried out with liquid sulphur dioxide and n-heptane flowing in countercurrent to each other. It was found that, in order to obtain the same degree of separation as in Example 1, a seven-stage extraction system was necessary; eight parts by volume of n-heptane were introduced into the first stage of this system and ten parts by volume of liquid sulphur dioxide were introduced into the seventh stage of this system. Ten parts by volume of the feed mixture were introduced into the fifth stage of the system. The liquid sulphur dioxide phase was withdrawn from the first stage and the n-heptane phase was withdrawn from the seventh stage of the system.

On comparing Examples 1 and 2, it appears that the use as paraffinic solvent of a hydrocarbon fraction with a higher boiling point than the mixture to be separated is preferable to the use of a paraffinic hydrocarbon with a boiling range lower than that of the initial mixture.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is :—

1. A process for separating a mixture of hydrocarbons and substantially water-insoluble oxygenated compounds derived from hydrocarbons, in which the mixture is subjected to extraction with two solvents flowing in countercurrent to each other, one solvent consisting substantially of liquid sulphur dioxide and the other solvent consisting substantially of one or more paraffinic hydrocarbons, the boiling range of which is outside the boiling range of the initial mixture.

2. A process according to claim 1, wherein the paraffinic solvent is a mineral oil fraction substantially free from aromatics, the boiling

range of which exceeds that of the mixture to be separated.

3. A process according to claim 2 in which the paraffinic solvent is medicinal paraffin oil.

4. A process for separating a mixture of hydrocarbons and substantially water-insoluble oxygenated compounds substantially as hereinbefore described.

5. Alcohols, aldehydes, ketones or carboxylic acids whenever separated from hydrocarbons by the process claimed in any one of the preceding claims.

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