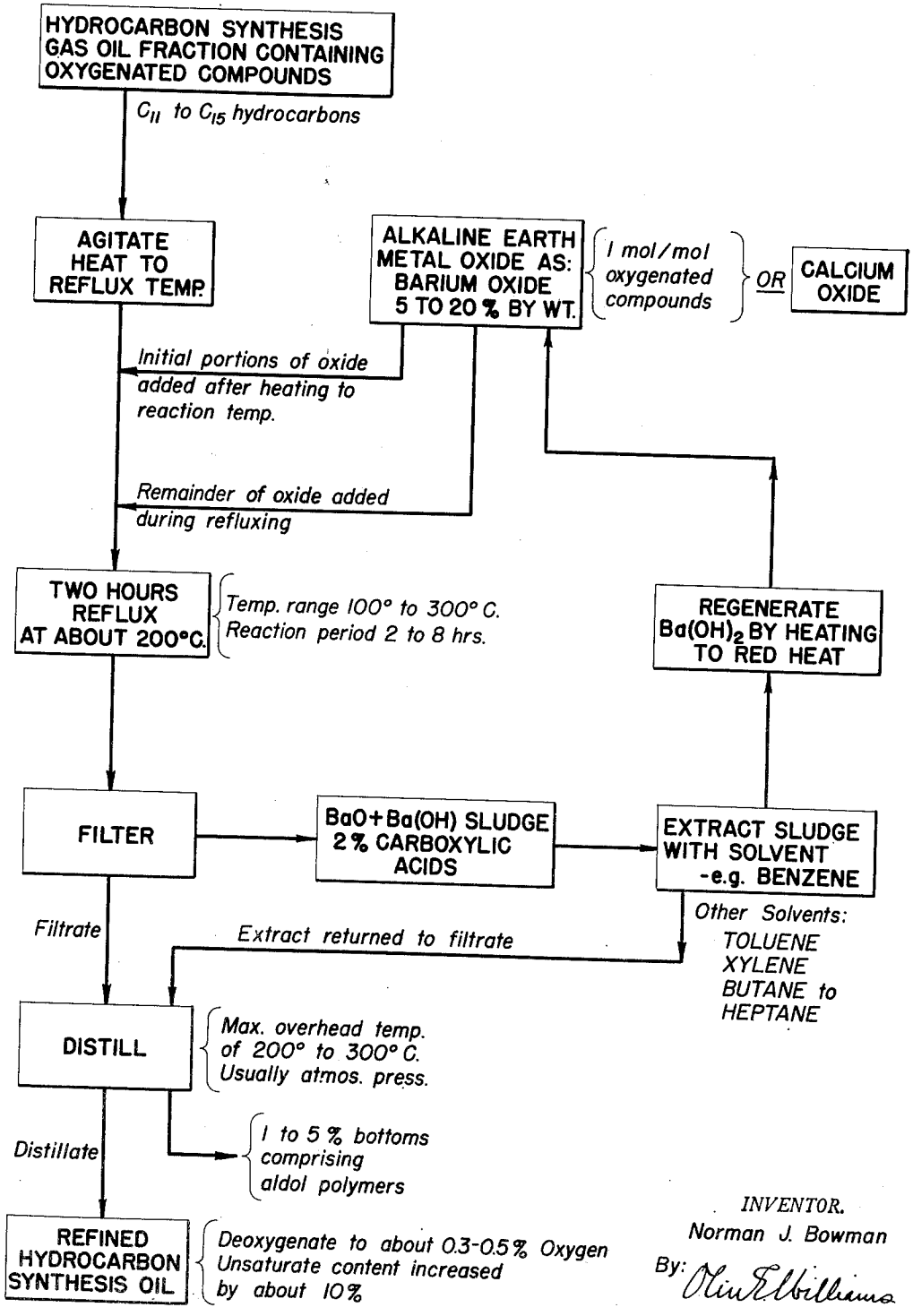
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REMOVAL OF OXYGENATED ORGANIC COMPOUNDS FROM HYDROCARBON MIXTURES THEREOF

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REMOVAL OF OXYGENATED ORGANIC COMPOUNDS FROM HYDROCARBON MIXTURES THEREOF

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This invention relates to the refining of hydrocarbon oils by the removal of oxygenated compounds from such oils. The invention relates more particularly to the deoxygenation of hydrocarbon mixtures containing oxygenated compounds such as the gas oil obtained from hydrocarbon synthesis.

The products of various oil-preparing or treating processes, for example the controlled oxidation of hydrocarbons or the synthesis of liquid hydrocarbons from carbon monoxide and hydrogen, are known to contain various oxygenated compounds including alcohols, acids, ketones, esters, and aldehydes. The presence of these compounds is sometimes undesirable; they tend to interfere with useful reactions of the olefins contained in the oils and deleteriously affect the stability of the oil. It is desirable in other cases to remove oxygenated compounds in order to refine the product for use as gasoline.

As the oxygenated compounds often boil in the range of their associated hydrocarbons, it is difficult or infeasible to remove them by distillation. On the other hand, the oxygenated compounds of high molecular weight are not soluble in water and, therefore, cannot be removed by aqueous extraction.

An object of the present invention is the removal of oxygenated compounds from hydrocarbon mixtures containing the same, thereby refining the aforesaid hydrocarbons. It is another object of the invention to provide an economical process for the removal of oxygenated compounds from the said hydrocarbon mixtures by means of easily regenerated reagents. It is a further object of the invention to convert the oxygenated compounds of the said hydrocarbon mixture to hydrocarbons, particularly olefinic hydrocarbons, so that an increased yield of useful hydrocarbons can thereby be economically obtained. Yet another object of the invention is the provision of a process for increasing the olefinic content of hydrocarbon mixtures so as to enhance their value for certain chemical applications. Other objects and advantages of the invention will be apparent in the specification and claims hereinafter made.

Briefly stated, the process of this invention comprehends heating a hydrocarbon mixture containing oxygenated compounds at temperatures between 100° and 300° C. in the presence of an alkaline earth metal oxide wherein the term "alkaline earth metal" is interpreted strictly to include only the left hand members of Group II of the Periodic Table, or more specifically, calcium, strontium, and barium; refluxing the mixture for a period of from 2 to 8 hours; and thereafter filtering alkaline earth compound from the mixture, and preferably distilling the filtrate and separating therefrom a minor portion of polymerized heavy material. The alkaline earth metal oxide can be present in substantially pure form or can be present in a mixture of anhydrous materials; for example, as the mixture of calcium oxide and magnesia obtained by calcining certain dolomitic limestones. The alkaline earth metal oxide can be added to the hydrocarbon oil before heating or the oil can be heated to desired temperature and the oxide reagent can then be added or it can be added at any intermediate period during heating. To be effective, alkaline earth oxide must be substantially anhydrous. The hydrocarbon oil mixture must be stirred or otherwise agitated during heating to prevent local overheating and consequent polymerization.

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It appears that several reactions occur involving the oxygenated compounds during the aforesaid treatment. An analysis of the product indicates a dehydration of alcohols to olefins, a saponification of the esters with dehydration of the produced alcohols, a condensation and dehydration of aldehydes and ketones (in which case it appears that some of the aldols or other condensation products subsequently are decomposed), and possibly, to a very minor extent, a dehydrogenation of alcohols to acids. The above treatment provides a refined hydrocarbon product from which about 90 per cent of the oxygenated product compounds are removed or converted and in which the olefinic content is increased as much as 10 per cent. Approximately 2 per cent by weight of the original charge has been recovered as carboxylic acids by acid treatment of the alkaline earth oxide.

The accompanying drawing that is employed solely to illustrate the present process is a schematic diagram constituting a flow sheet of a preferred embodiment of the present invention.

In the embodiment of the invention that is illustrated by the drawing, a hydrocarbon-synthesis gas-oil fraction having predominantly C_{11} to C_{15} hydrocarbons is treated for removal of oxygenated compounds. The said gas oil usually contains from about 15 to 30% by weight of the oxygenated compounds. These compounds are primarily alcohols, acids, and aldehydes and include also ketones and esters. The hydrocarbon synthesis oil fraction is usually alkali washed for removal of particularly the

lighter carboxylic acids before treatment as hereinafter described. The oil is stirred and heated to a desired reflux temperature which can be between 100° and 300° C., and preferably between 150° and 250° C., depending upon the character of the gas oil fraction. After the oil has been heated, one portion of an alkaline earth metal oxide, such as, for example, barium oxide, is added to the agitated and heated oil. After this addition of alkaline earth metal oxide is made, has become dispersed through agitation of the oil, and an excess heat of solution has been dissipated, a second portion of oxide can be added if a more complete deoxygenation is desired. A total amount of oxide corresponding to 5 to 30 per cent by weight of the oil is added to the heated oil. Preferably, substantially one mol of alkaline earth metal oxide is added per mol of oxygenated compounds, because the said oxides act primarily as reagents to remove hydrogen and hydroxyl radicals from the oxygenated compounds and react therewith to form alkaline earth metal hydroxide. After the total amount of oxide has been added, the oil should be refluxed for at least about two hours, although substantial reduction in concentration of oxygenated compounds can be accomplished in shorter periods. The total reaction period, including heating the oil to reaction temperature, is from about 2 to 8 hours.

The above treatment will effect primarily a dehydration of the alcohols in the oil and also a polymerization of aldehydes and ketones and a saponification of the esters present therein. The said saponification is accompanied by formation of the alkaline earth metal salt of the carboxylic acid and a subsequent dehydration of the alcohol that is liberated by the said esterification. The resultant reaction mixture will be cooled or permitted to cool and the supernatant oil will be decanted from a so-formed alkaline-earth metal oxide and hydroxide sludge, or the two phases can be separated by a filtering or centrifuging step. The alkaline earth metal sludge will contain alkaline earth metal carboxylates of an amount depending on whether the gas oil fraction was acid washed before the described dehydration step and upon the residual amount of acids and esters present in the washed oil. The sludge is washed with a solvent to remove oils that are occluded therewith. Solvents which can be used are benzene, toluene, xylene, or polynuclear aromatic hydrocarbons. The alkane hydrocarbon solvent, for example butane, pentane, hexane, or heptane, and their isomers, are also well adapted to this extraction. Other hydrocarbon solvents can be used if they boil at sufficiently low temperature that their removal from extracted material can be effected without a close fractionation.

The treated deoxygenated gas oil to which the dissolved sludge extract is added is distilled at temperatures between about 200° and 300° C. and usually at atmospheric pressure to separate the said oil from polymers such as the aldols formed during the treating step. The distillation can be performed continuously or intermittently and in case of the former, the employed hydrocarbon solvent, for example benzene, is fractionated overhead from the charge. Ordinarily, however, a simple batch distillation can be performed wherein the hydrocarbon solvent is first flashed off the oil and then the oil is distilled from the polymers constituting the bottoms product. The bottoms comprising aldol polymers constitutes from about 1 to 5 per cent of the volume of the filtrate.

The deoxygenated product is reduced by the above described treatment to an oxygen concentration of about 0.3 to 0.5 per cent by weight. This oxygen concentration represents about 5 per cent by weight of oxygenated compounds and represents, therefore, a reduction in oxygenated compounds of 75 to 90 per cent. The refined hydrocarbon synthesis gas oil so-produced exhibits an increased content of unsaturated hydrocarbons of about 10 per cent. The increase in unsaturated products is apparently greater than can be accounted for by a dehydration of the alcohol content of the original gas oil; some of the increased olefin must result from either a saponification of the esters present and a dehydration of the resulting alcohol or from a dehydration of other more complex oxygenated compounds.

It is further observed that no cracking whatsoever is effected by the above described treatment. The dehydration of oxygenated compounds and the retention of the olefins in the gas oil will, however, lower somewhat the overall boiling range of the hydrocarbon mixture because the resultant olefins will boil in a range lower than the oxygenated compounds from which they were derived.

The following specific examples illustrate the present invention when employing either barium or calcium oxide as the deoxygenating reagent and particularly illustrate the effect of various reaction variables.

Example 1

One hundred parts of a hydrocarbon synthesis light gas oil having a boiling range of 160° to 280° C. and an average carbon number of about 13 (containing predominantly C_{12} to C_{15} hydrocarbons) was alkali washed. The alkali washed oil contains 2.7 per cent by weight of oxygen which corresponds to about 28 per cent of oxygenated compounds. The gas oil was heated in a vessel having a stirrer to provide adequate agitation. The oil was heated to about 150° C. To the heated oil about eight parts by weight of powdered barium oxide were added with continuous stirring and the temperature was increased to 200° C. where it was maintained. The oil was refluxed in the presence of the so-called barium oxide for one hour and then an additional eight parts by weight of barium oxide were added and the agitation was continued for an additional three hours. The treated oil was cooled and subsequently decanted from solid residue. The residue was extracted with 88 parts by weight of benzene. The benzene extract and the decanted treated oil were distilled at atmospheric pressure to a maximum overhead temperature of 260° C. About 5 per cent by volume of distillation bottoms were retained in the vessel and comprised predominantly aldehyde polymers. Approximately 90 per cent of the original washed oil was recovered as treated oil. The resultant oxygen content was .65 per cent by weight of product representing a removal of 78 per cent of the contained oxygenated compounds. The efficiency of the reagent was measured by the result of multiplying the yield times the per cent removal of oxygen compounds divided by theoretical yield, which was in this instance .93.

Example 2

In three other examples the same light gas oil was treated under substantially entirely the

same conditions as were employed in Example 1; that is, with 10 per cent BaO and for an overall period of four hours with the exception that temperature of reaction was varied. In these runs the oil was treated at temperatures of 175°, 150°, and 100° C. The removal at 100° C. was 61 per cent of the oxygenated compounds; at 150° C., 67 per cent; and at 175° C., 70 per cent, with an efficiency in the latter instance of .84.

Example 3

A series of tests were made in which the same oil was treated at 200° C. and in exactly the same manner as is described in Example 1, except that in this instance the amount of added barium oxide was varied to see what influence such changes would have. As before noted, when a total weight of 10 per cent barium oxide was added to the gas oil, a removal of 78 per cent of the oxygenated compounds was obtained. When this deoxygenated oil was treated with an additional 10 per cent by weight of barium oxide, a cumulative removal of 82 per cent of the oxygenated compounds was accomplished.

In another instance where the light gas oil was treated with 10 per cent by weight of barium oxide at 200° C. for a period of four hours, 73 per cent of the oxygenated compounds was removed. In a second treatment of this deoxygenated oil an added 5 per cent by weight of barium oxide effected a cumulative removal of 84 per cent by weight of the oxygenated compounds.

In another instance, operated also at 200° C., 85 per cent of the oxygenated compounds was removed by a second treatment constituting the addition of 5 per cent by weight of additional barium oxide. When this treated oil was again heated and refluxed in the presence of another 5 per cent by weight of barium oxide, no substantial decrease of oxygenated compounds was observed.

It appears, therefore, that 20 per cent of alkaline earth metal oxide reagent is substantially the maximum amount necessary for efficient removal of oxygenated compounds from hydrocarbon synthesis gas oil or the like containing in the order of 25 to 30 per cent oxygen compounds. It is observed that 5 per cent appears to be too low an amount of alkaline earth metal oxide when the oil to be treated contains as high a concentration of oxygenated compounds as did the oil used in the present example. A ratio of one mol of alkaline earth metal oxide per mol of oxygenated compound in the oil to be treated has been found to be most generally suitable. If some of the aldehydes polymerize rather than reacting with the alkaline earth metal oxide, this is off-set by the saponification of contained esters and the formation thereby of an alcohol which is dehydrated by the alkaline earth metal oxide and an acid which reacts therewith. Therefore, the above ratio of one mol per mol of oxygenated compounds is the preferable weight for thorough treatment. It is to be noted, however, that much lower percentages, for example 5 per cent, reduces the oxygen content more than half and will in many instances be a sufficiently effective treatment.

Example 4

The influence of the time factor was investigated in runs which were otherwise conducted precisely in the manner described in Example 1. When 10 per cent by weight of barium oxide was added and the gas oil was refluxed at 200° C.

for only one hour, 71 per cent of the oxygenated compounds were removed. A check run on this provided a removal of 67 per cent by weight. Runs conducted with alkaline earth metal oxides for periods as long as four hours, as above indicated, provided removals of about 80 per cent of the oxygenated compounds. No appreciable improvement was obtained by extending the period of treatment to as much as eight hours. Four hours operating, therefore, is preferred and apparently optimum, and any extension beyond a few hours would not be economically warranted. On the other hand, shorter treatments remove as much as 70 per cent of the oxygenated compounds and in many circumstances this short reaction period may prove adequate.

Example 5

Several runs were made employing anhydrous calcium oxide as the reagent. Ten per cent by weight of calcium oxide was added to portions of the same light gas oil used in Example 1. The gas oil was treated by the conditions of operation used in Example 1. The calcium oxide was refluxed with a gas oil in one run at a temperature of 150° C.; another, 175° C.; and another, 200° C. The effect of the increased temperature is most noteworthy in this case employing calcium oxide; the percentage of oxygen removal at the various temperatures was 43 per cent at 150° C.; 67 per cent at 175° C.; and 73 per cent at 200° C.

It is preferable, therefore, when employing calcium oxide to use a minimum temperature of 200° C.

Example 6

A series of the runs was made using the process of invention as defined in Example 1 in which the deoxygenating treatment was carried out using 10 per cent by weight of calcium oxide at 200° C. and for periods of 1, 2, and 4 hours. Treatment for one hour effected a 50 per cent oxygen removal; two hours, 67 per cent; and 4 hours, 73 per cent.

Example 7

A further series of runs was made in which a gas oil was treated with 10 per cent by weight of calcium oxide for four hours at 200° C. by the method described in Example 1 and was distilled from any aldol polymers present. The deoxygenated gas oil was treated with an additional 5 per cent by weight of calcium oxide. A cumulative removal of oxygenated compounds of 83 per cent was obtained. Again, the treated oil from the above second treatment was treated for a third time with an additional 5 per cent by weight of calcium oxide, the total amount of reagent being 20 per cent by weight. An oxygen removal of 85 per cent was obtained. Further runs of similar type emphasized the fact that treatment with substantially more than 10 per cent by weight of alkaline earth metal oxide and the extra time involved is rarely warranted because of the only slight increase in refining of the light gas oil.

A study of the data obtained in the above experiments revealed the fact that not only are olefins formed from the alcohol present in light gas oil, but in order to account for the total volume of olefins present in the product, it is apparent also that other oxygenated compounds have been dehydrated to form olefins. For example, esters present may have become saponified and olefins may have been formed from the resultant alcohols.

A selection between calcium and barium oxide must be made according to prevalent conditions as they are substantially equivalent in reaction. However, calcium oxide appears to be less efficient except at the higher temperatures. This may be off-set by price or ease of regeneration. The oxides are regenerated by well-known calcining operations.

The observed increase in olefinic compounds in the gas oil (which can be as high as 10 to 20 per cent) is surprising insofar as it has been generally believed that an alkaline earth metal oxide will not dehydrate higher than C_5 alcohols without encountering excessive resinification. Very slight resinification occurs in the present instance and must be entirely due to aldehydes because a greater yield of olefins was obtained in the above specific examples than can be accounted for by alcohol content alone.

The product can be simultaneously or subsequently hydrogenated by conventional catalytic methods so that the ultimate product will be a mixture of saturated aliphatic hydrocarbons. Hydrogenation of the product is a particularly useful step in the manufacture of a fuel oil.

In accordance with the foregoing description, I claim as my invention:

1. A process of refining a hydrocarbon oil containing oxygenated compounds comprising heating the hydrocarbon oil in liquid phase to a temperature between 100° and 300° C., adding thereto from 5 to 20 per cent, by weight of the contained oxygenated compounds, of an anhydrous oxide of an alkaline earth metal selected from the group consisting of calcium, strontium and barium, maintaining the oil in contact with the said oxide at the said temperature for a sufficient time to convert oxygenated compounds to hydrocarbons and alkaline earth metal oxide to a hydroxide sludge and separating so-refined deoxygenated hydrocarbon oil from the said sludge.

2. A process of refining a hydrocarbon oil containing oxygenated compounds comprising heating the hydrocarbon oil in liquid phase to a temperature between 150° and 250° C., adding thereto substantially one mol of anhydrous oxide of an alkaline earth metal selected from the group consisting of calcium, strontium and barium per mol of said oxygenated compounds and maintaining the oil in contact with the said oxide at the said temperature for a period of from 2 to 8 hours, whereby oxygenated compounds are converted to hydrocarbons and alkaline earth metal oxide to a hydroxide sludge, separating so-refined deoxygenated oil from the sludge and regenerating alkaline earth metal oxide by heating the sludge to at least red heat.

3. A process of refining a hydrocarbon oil containing oxygenated compounds comprising heating the hydrocarbon oil in liquid phase to a temperature between 150° and 250° C., adding thereto substantially one mol of anhydrous oxide of an alkaline earth metal selected from the group consisting of calcium, strontium and barium per mol of contained oxygenated compounds, refluxing the oil and admixed oxide for a period of from 2 to 8 hours to convert oxygenated compounds to hydrocarbons whereupon the alkaline earth metal oxide is converted to a hydroxide sludge containing occluded oil, separating refined deoxygenated oil from oil bearing sludge, washing occluded oil from the sludge with a hydrocarbon solvent, adding the extracted oil to the said deoxygenated oil, distilling the oil admixture to separate therefrom a bottoms fraction containing oxygenated compounds polymerized by the said treatment, and regenerating alkaline earth metal oxide by heating the sludge to at least red heat.

4. The process of claim 3 in which the alkaline earth metal oxide is calcium oxide.

5. The process of claim 3 in which the alkaline earth metal oxide is barium oxide.

6. The process of claim 3 in which the selected reflux temperature is substantially 200° C. and the period of refluxing is about four hours.

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