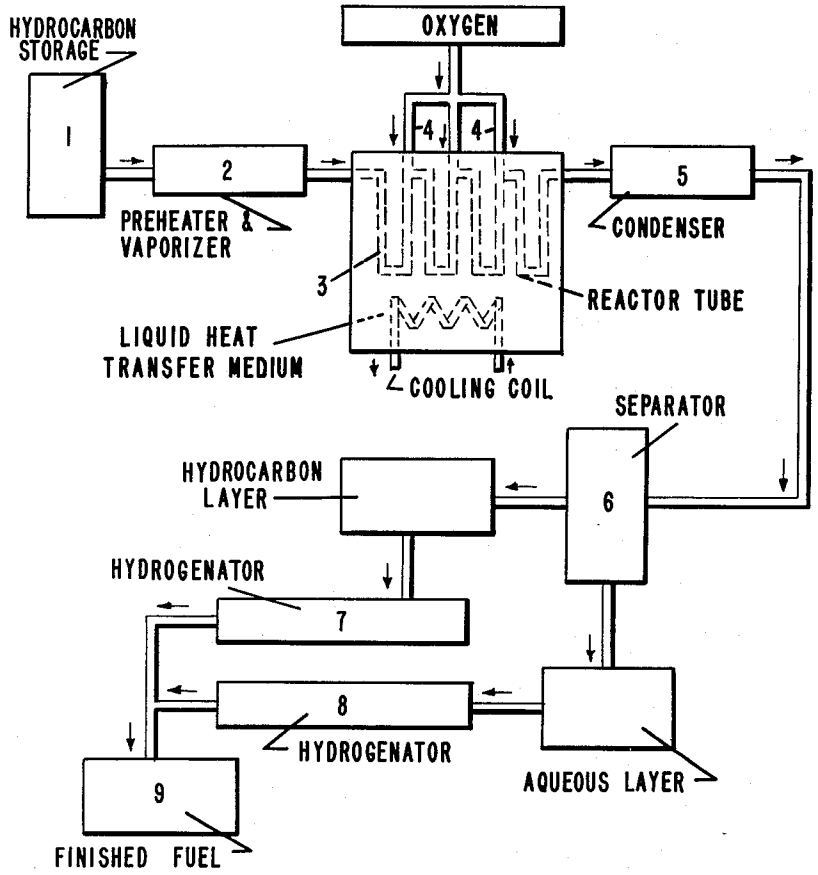
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UPGRADING OF NAPHTHAS

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UPGRADING OF NAPHTHAS

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This invention relates to upgrading of hydrocarbons such as naphthas, to produce oxygenated and olefinic compounds which improve the fuel quality of the hydrocarbons and also represent a valuable source of chemicals. In particular this invention relates to selective vapor phase non-catalytic oxidation of hydrocarbons, or naphthas, or hydrocarbon mixtures, followed by selective hydrogenation or dehydration. The invention is particularly applicable to virgin naphthas, but can be similarly used on other light normally liquid hydrocarbon feeds obtained from a variety of sources such as thermally cracked naphthas, catalytic cracked naphthas, or hydroformed naphthas.

It has been proposed in Patent No. 1,808,168 and elsewhere to dehydrogenate hydrocarbons by reacting them in vapor phase with oxygen at relatively low temperature. It has thus been possible, for instance, to obtain olefins on a small scale by treating a virgin gasoline fraction with air at temperatures of about 265° C., the air being added in amounts equivalent to not more than about 1.5 atoms of oxygen per hydrocarbon molecule. This reaction has been known to be poisoned by solid packing or by liquid reflux within the reactor, and also by active reactor surfaces. At best, this process was characterized by relatively low yields of olefins, without any substantial formation of liquid oxygenated compounds. On the other hand, when the reactor temperature was raised appreciably above the aforementioned value, and especially when high ratios of oxygen to hydrocarbon were used, all except the very light hydrocarbons were extensively degraded into carbon dioxide and water. Moreover, such liquid fuel product as was obtained, was of relatively low quality because of its gum-forming tendencies.

It is the object of the present invention to increase the oxidative conversion of hydrocarbons and particularly of naphthas so that low octane hydrocarbons are preferentially converted into olefins and other products having superior anti-knock characteristics. A further object is the conversion of hydrocarbons into oxy- compounds which either are suitable gasoline constituents or can be converted into such by selective hydrogenation, which yields alcohols, or by dehydration, which yields unsaturated hydrocarbons such as olefins. These and other objects as well as the nature of the invention will become apparent from the following description.

In the present invention naphtha is dehydrogenated and oxidized by reaction with about 0.3 to 1.2 or 1.5 moles of oxygen per mole of hydrocarbon, depending on the reaction conditions, the nature of the feed, and the degree of oxidation desired. Although it is greatly preferred to use substantially pure oxygen, air or any inert gas such as steam containing oxygen may be used. Use of oxygen in a purity of at least 90 mole per cent of a condensable gas rich in oxygen simplifies the recovery of the volatile products, for such products are then associated with fewer gaseous diluents. Also diluents may adversely affect the reaction.

Where extensive conversion is desired it is important that the oxidation be carried out in several successive steps. This can be done either by introducing the oxygen at several successive points, or by removing the oxidation product after one contact with oxygen, and preferably after separation of the resulting water layer and non-condensable gas recycling the oxidation product to the reaction zone for more contacts with oxygen. The reaction is carried out at temperatures of about 275° C. to 480° C., and at relatively low pressures of about 0 to 100 p. s. i. g., preferably at about 350° to 400° C. and a pressure of about 0 to 5 p. s. i. g. Pressure tends to increase the yield of gas at the expense of useful products. Nevertheless, this may at times be desirable since the resulting oxidized hydrocarbon layer then also contains a substantially increased proportion of valuable olefins. The best pressure to use depends on the temperature of reaction, the inherent oxidation rate of the hydrocarbon, and the completeness of the recovery of the volatile products that is desired. The more reactive the hydrocarbon, the lower the pressure. Contact times in the range of about 1 to 5 seconds, and preferably not more than 3 seconds, may be employed. No catalyst is used and, as far as known, the reaction is a homogeneous one in the gas phase. The resulting products are a non-condensable gas, a hydrocarbon layer, and a water layer.

Heat transfer is an essential part of the present invention, for the reaction is highly exothermic. It is necessary to remove this heat from the reaction zone, to keep the reaction temperatures from rising to such high levels that many of the valuable reaction products would be lost by pyrolysis. To remove the reaction heat, the contents of the reaction zone must be in good heat transfer relationship with another medium which is capable of absorbing this heat without jeopardizing the reactants or acting as an anti-catalyst for the reaction. In the present instance the reaction may be conveniently carried out in empty tubes immersed in a thermostatic bath using liquid terphenyl as the heat absorbing medium. However, other well-known stable media which are fluid and have an appreciable heat capacity in the proper temperature range such as mercury or molten salts such as mixtures of nitrates of sodium and potassium may be used similarly.

It is important that the materials constituting the reaction zone or surfaces present therein do not attain excessive temperatures. Otherwise, they tend to catalyze the formation of carbon dioxide and water and other undesirable products. For this reason it is essential that the surfaces in contact with the reactants, but not necessarily the reactants themselves, have a heat transfer coefficient, in relation to the medium picking up the reaction heat, of at least 100 B. t. u. per hour per square foot of surface per degree Fahrenheit difference in temperature between these surfaces and the heat absorbing medium. Only in this way can the reaction temperatures be maintained within the desired range and the surfaces in contact with the reactants always kept low enough in temperature to avoid undesirable catalytic effects.

Since surface has an adverse effect on the homogeneous reaction which is the basis of this invention, another important feature is to have the reaction zone contained by smooth walls or surfaces essentially free of reducible oxides, that is, surfaces which are not altered readily either by an oxidizing or reducing environment, such as exists when oxygen and hydrocarbon interact. When the surfaces are metallic, they should be selected from those metals that do not oxidize readily. When the surfaces contain oxides, the oxides should be selected from those that are not readily reduced, or prone to exert undesirable catalytic effects. Examples of metallic surfaces are stainless steel, silver, and alloys of chromium or nickel.

Examples of suitable heat resistant oxide surfaces are silica, alumina, and chromia.

In operating with multiple points of oxygen injection, the reaction temperature should be brought down to the 300 to 480° C. range before the next injection of oxygen takes place. This is accomplished by providing ample heat transfer surface, of the quality and character described, between the points of oxygen injection.

Essentially all the oxygen is used up in one pass through the reactor. The distribution of this oxygen to the various products is important for it shows what reactions are taking place. For an East Texas light virgin naphtha boiling between 158 and 216° F., the following typical oxygen distribution was obtained.

TABLE I

	Total Wt. Percent	Liquid Fuel
Oxygen Distribution:		
To Non-Condensable Gaseous Products—		
Carbon Dioxide	9	----------
Carbon Monoxide	17	----------
	26	
To Water Layer Products—		
Water	49	----------
Formaldehyde	5	5
Other Carbonyls	3	3
Other Oxygenated Material	1	1
	58	9
To Hydrocarbon Layer Products—		
Carbonyls	7	7
Epoxides	9	9
	16	16
Total	100	25

In general, about 25 to 70 weight percent of the naphtha feed may be actually converted. As a result, about 75 to 95 percent by weight of the naphtha feed appears, in partially converted form, in the hydrocarbon layer, some 5 to 12% is converted to non-condensable gas; and about 3 to 8 percent is converted to give the water layer. Typical average compositions are shown in Table II.

TABLE II

Product distribution

Gas (O_2-free and N_2-free basis):	Vol. percent
CO	About 40–60
CO_2	About 10–25
C_2H_4	About 5–10
C_3H_6	About 8–15
Saturated hydrocarbons (C_3 average)	About 5–10

Hydrocarbon layer:	Wt. percent
Olefins (C_4 to C_8)	12 to 16
Carbonyl compounds [1]	5 to 9
Epoxides [2]	13 to 20
Unconverted feed hydrocarbons	60 to 65

[1] Acetaldehyde, propionaldehyde, acetone, C_5 to C_8 ketones, etc.
[2] 2,5-dimethyl tetrahydrofuran, etc.

Water layer:	Approx. wt. percent
Formaldeyhde	10 to 15
Acetaldehyde	3
C_3 carbonyl compounds	5
Glycols, etc., B. P. 60 to 85° C.	7
Water	70 to 75

It is apparent that if the reaction were entirely one of dehydrogenation, all of the oxygen should appear as water. Actually, however, only about 40 to 55% of the original oxygen ends up as water, some 25 to 30% ends up as

oxides of carbon, and the other 20 to 30% as useful liquid oxygenated compounds. The formation of oxides of carbon represents unwanted side reactions which are wasteful of both hydrocarbon feed and oxygen. On the other hand, oxygen fixed in the hydrocarbon structure in the form of oxy compounds such as aldehydes, ketones, alcohols, and bridge-oxygen compounds or epoxides actually is desirable. Many of the formed oxygen compounds have characteristics which make them valuable fuel components, or their oxygen can be converted to water via dehydration, thereby adding to the selectivity to water and increasing the yield of desirable olefins or diolefins. Or such oxygen compounds can be converted to alcohols by selective hydrogenation as hereafter described.

While only about 25% of the reacted oxygen goes to useful oxygenated compounds, the actual production of these compounds is high because of their relatively large molecular weight. For instance, it can be seen from Table III below that the actual weight of the oxygenated compounds was 122.4 pounds/100 pounds of reacted oxygen.

TABLE III

Production of liquid oxygenated compounds

[Basis: 100 lbs. O_2 reacting; 386 lbs. naphtha charged (178 lbs. naphtha reacting.)]

Constituent	Lbs./100 Lbs. O_2	O_2 Distribution, Wt. Percent
Formaldehyde	10.0	5.3
Other Aldehydes in Water Layer	13.1	2.9
Other Oxy-Compounds in Water Layer	5.6	1.1
Carbonyls in HC Layer (assuming C_5	36.2	7.0
Epoxides in HC Layer (assuming $C_{8.5}$)	57.5	8.6
	122.4	24.9

In addition to the above products, about 40 pounds of valuable olefins are formed per 100 pounds of oxygen reacting.

Although the data presented above were obtained for a light East Texas virgin naphtha, similar results are obtained from heavy virgin naphtha (200 to 430° F. boiling) range, Bradford Pennsylvania virgin naphtha (140 to 259° F. boiling range) and also from pure hydrocarbons such as n-pentane, n-hexane, n-heptane, n-nonane, n-decane, n-hexadecane, cyclohexane, methylcyclohexane, methylcyclopentane, 1-octene, 2-octene, etc. Thus, the invention is particularly applicable to virgin naphtha hydrocarbons boiling in the range of about 158° to 430° F. (70° to 220° C.). In general, pure aromatic hydrocarbons such as benzene and toluene, and highly branched paraffin hydrocarbons such as 2,3-dimethylbutane and "isooctane," do not undergo appreciable reaction under the conditions outlined above.

In general, the liquid products resulting from the hydrocarbon oxidation consist of low molecular aldehydes (mainly formaldehyde, acetaldehyde, propionaldehyde, and some acrolein), ketones (acetone and ketones having the same carbon content as the hydrocarbon oxidized), alcohols (methanol, ethanol, and higher alcohols having the same carbon content as the hydrocarbon oxidized), epoxides (such as tetrahydrofurans, trimethylene oxide derivatives, and ethylene oxide derivatives having the same carbon content as the hydrocarbon oxidized), olefins (a mixture of olefins of the same carbon content as that of the hydrocarbon feed and lower molecular weight alpha olefins), and unreacted hydrocarbon.

The low molecular weight aldehydes, ketones, and alcohols tend to be concentrated in the water layer whereas the epoxides and higher ketones and alcohols

are concentrated in the hydrocarbon layer in admixture with the olefins and unreacted hydrocarbon or naphtha portion.

The character of the epoxides produced depends on the molecular weight and the type of hydrocarbon oxidized. Thus, for example, n-hexane yields an epoxide portion containing chiefly 2,5-dimethyltetrahydrofuran, 2-ethyltetrahydrofuran, 2,4-epoxyhexane, and 2,3-epoxyhexane. Similarly, pure n-heptane yields an epoxide mixture containing chiefly 2-methyl-5-ethyl tetrahydrofuran, 2-propyltetrahydrofuran, 2,4-epoxyheptane, and 3,4-epoxyheptane. The higher hydrocarbons such as n-nonane, n-decane, n-hexadecane, etc. also yield an epoxide portion containing similar products. On the other hand, naphthene hydrocarbons yield an epoxide portion containing mainly epoxynaphthenes. Thus, for example, cyclohexane yields 1,2-epoxycyclohexane and 1,4-epoxycyclhohexane while methylcyclohexane yields a complex mixture of epoxymethylcyclohexanes.

The various epoxides are useful as solvents and also as chemical intermediates in that they may be converted to diolefins, alcohols, glycols, ketones, phenols, polymers, chlorohydrins, esters, etc.

The olefins present in the liquid products consist, in general, of a mixture of olefins of the same carbon content as the hydrocarbon feed and lower molecular weight alpha olefins. Thus, for example, n-decane on oxidation yields a mixture of decenes, 1-hexene, 1-heptene, and 1-octene. Similarly, n-heptane yields heptenes, 1-butene, 1-pentene, and 1-hexene. Cyclohexane yields mainly cyclohexene together with some lower molecular weight alpha olefins. Thus, the described process is also suitable for the production of alpha olefins of lower molecular weight than the hydrocarbon feed. The yield of olefins resulting from the process is relatively low if low oxidation temperatures are used.

For the case of a naphtha feed the unreacted hydrocarbon portion of the liquid product resulting from the oxidation reaction consists essentially of the higher-octane number components of the naphtha, the poorer octane hydrocarbons having been selectively oxidized. This fact is illustrated by the following data obtained for a paraffinic type of virgin naphtha boiling between about 70° and 110° C. and containing a mixture of normal and monomethyl substituted paraffins.

Research Octane No. of feed	38.9
Research Octane No. of unoxidized hydrocarbon portion of the liquid product obtained by sulfuric acid extraction to remove oxygenated and olefinic materials (about 37 percent of the naphtha underwent oxidation)	53.3

To illustrate further the selective nature of the oxidation reaction, it has been found that the comparative ease of oxidizing various pure hydrocarbons under the conditions described herein decreases in the following order:

1. n-Hexadecane	8. Isopentane
2. n-Decane	9. 1-pentene
3. n-Heptane	10. 2-pentene
4. 2-methylpentane	11. Trimethylethylene
5. Methylcyclopentane	12. Benzene
6. Cyclohexane	13. Toluene
7. Methylcyclohexane	14. Isooctane

The three last-named hydrocarbons are essentially nonreactive.

From a fuel standpoint the finishing of the liquid products obtained in the selective oxidation is important in determining the yield of liquid fuel and its anti-knock quality. The volatility of the liquid product is usually not much greater than that of the feed for there is not much hydrocarbon cracking during the oxidation as carried out under this invention. Such cracking as does take place results mostly in saturated and unsaturated gaseous hydrocarbons containing, on the average, between 2 and 3 carbon atoms per molecule.

The liquid hydrocarbon and water layers obtained in the oxidation can be lightly hydrofined to convert the aldehydes and a portion of the ketones to alcohols, but without affecting epoxides or olefins. The alcohols and any ketones or epoxides, etc. can then be distilled from the water layer and combined with the oxidized hydrocarbon layer. The resulting fuel mixture, still having a boiling range closely similar to that of the naphtha charged, may have the following typical composition (by volume); 9% alcohols and ketones, 14% olefins, 17% epoxides and 60% hydrocarbons. The research octane number of the resulting mixture may be about 80 to 85 without the addition of tetraethyl lead (clear). The yield of fuel including the oxidized hydrocarbon layer and the hydrogenated material from the water layer may amount to about 80 to 90% by weight of the original naphtha.

Similar results are obtained for other feeds such as narrow-boiling hydrocarbon fractions or pure hydrocarbons. For example, n-hexane when oxidized to the extent of about 72 percent gives a 72 percent by weight yield of a liquid having the following composition (after a light hydrofining treatment).

	Liquid product wt. per cent
Hexenes	4
Oxygenated compounds from hydrocarbon layer (largely epoxides)	32
Oxygenated compounds from water layer (about 70% C_1 and C_2 alcohols, remainder epoxides)	26
n-Hexane, unreacted	38
	100

The octane number (Research, clear) of the above liquid product was found to be 76.5. The research octane number of n-hexane is 24.8. This further illustrates the usefulness of this process in upgrading hydrocarbons to make them more suitable as fuels for spark ignition engines.

The oxidized hydrocarbon layer may be selectively hydrogenated to convert undesirable carbonyl compounds into alcohols. This selective hydrogenation may be carried out either simultaneously with the aforementioned hydrogenation of the water layer, or preferably the two layers may be hydrogenated separately as described later.

In the alternative, the oxidized hydrocarbons including alcohols and epoxides can be dehydrated to olefins or diolefins by passage over synthetic or natural alumina in the form of clay or bauxite, for instance, at atmospheric pressure and 350 to 450° C.

The following specific runs will serve to illustrate the operation and advantages of the invention more clearly, though it will be understood that the scope of the invention is not limited thereto.

For carrying out the oxidation a tubular reactor has been used. This consisted essentially of twelve 0.5-inch and six 0.75-inch diameter stainless steel tubes, any number of which could be connected in series in a serpentine path and immersed in an agitated bath of molten m-terphenyl which was used as a heat transfer fluid. Each of the tubes was about 20 inches long. Variable lengths of reactor tubing were used in different runs in order to provide different reaction times as desired. Side lines of stainless steel tubing were tapped into the tubular reactor at the U-bends connecting the several tubes so as to allow addition of oxygen at numerous points in the reaction zone. The reactor was fitted with thermocouples which extended through a packing nut in each arm of the serpentine tubing.

Data of typical runs are summarized in Table IV below.

TABLE IV

Oxidation of hydrocarbons

Hydrocarbon Feed	East Texas Light Virgin Naphtha (C_6–200° F.)[A]				East Texas Heavy Virgin Naphtha[A] (200–430° F.)		N-Hexane	
Run No.	73	85	94	78	88	89	104	104/5
Feed Conversion, Percent	46	46	58	55	42	52	48	72
Total O_2/HC Feed Ratio (in moles)	0.64	0.78	1.07	0.99	0.81	1.08	0.75	1.49
Maximum O_2/HC Feed Ratio (in moles)	0.31	0.26	0.27	0.50	0.27	0.27	0.19	0.19
Percent of Theor. O_2 for Complete Combustion	6.4	7.8	10.7	9.9	5.9	7.8	7.8	15.7
O_2 Reacting, Percent	99	94.5	100	96	98.5	99.4	99.9	100
No. Points of O_2 Injection	3	3	4	2	3	4	4	8
HC Feed Rate, Lbs./Hr.	5.83	2.09	-------	2.07	-------	-------	-------	-------
Temperature of Bath, ° C.	359	362	360	362	360	360	361	361
Temperature of Reaction, Max. ° C.	450	400	400	490	420	415	456	456
Total Contact Time, Secs.	2	3	4	2.5	3	5	4.8	9.5
HC Layer/Water Layer, Wt. Ratio	4.2	3.9	2.6	3.1	6.5	4.6	1.14	3.04
C,H,O Product Distribution, Wt. Percent on Total C,H,O Charged:								
HC Layer	65	67	-------	58	-------	-------	-------	-------
Water Layer	16	17	-------	19	-------	-------	-------	-------
Non-Condensable Gas	13	14	-------	19.5	-------	-------	-------	-------
Analysis of HC Layer:								
Acids, gm. O_2/100 gm. HC Layer	0.14	0.16	0.31	0.19	0.27	0.37	0.11	0.28
Carbonyls, gm. O_2/100 gm. HC Layer	2.0	2.3	3.0	2.3	3.3	4.3	2.14	3.66
Bromine No., gm. Br_2/100 gm. HC Layer	31.7	31.7	36.3	36.3	29.3	30.8	21.0	27.7
Acid Solubility:								
Vol. Percent Sol. 95% H_2SO_4	33	36	44	42	46	54	29	43.5
Vol. Percent Sol. 90% H_3PO_4	22	24.5	34	26	25	30	26	38
Density @ 60° F.	0.743	0.746	0.756	0.754	0.807	0.818	0.701	0.731
Analysis of Water Layer:								
Acids, gm. O_2/100 gm. W. L.	1.1	1.7	1.2	1.1	1.2	1.3	1.01	-------
Carbonyls, gm. O_2/100 gm. W. L.	11.6	10.7	10.0	9.9	10.7	10.0	13.8	13.6
CH_2O, Wt. Percent	-------	12.1	11.7	-------	12.2	11.8	24.0	-------
Analysis of Non-Cond. Gas, Wt. Percent:								
CO	48.3	47.1	51.8	41.3	49.3	52.2	42.5	47.8
CO_2	14.7	13.3	18.2	20.8	13.7	15.2	10.5	11.8
Unsaturates (C_2 and C_3)	20.0	17.1	17.2	18.9	19.0	18.5	25.4	22.5
Saturates (C_2 and C_3)	6.7	6.0	5.7	6.3	6.3	6.2	8.5	7.5
CO/CO_2 Ratio	3.3	3.5	2.9	2.0	3.3	3.4	4.1	4.1
Yield, Wt. percent on HC Feed:								
HC Layer[B]	81.5	84.6	76.2	78.7	94.0	90.4	78.2	54.5
Oxygen Material from Water Layer[B]	5.1	5.8	7.1	6.7	2.9	4.6	8.5	17.3
Total Organic Liquid	86.6	90.4	83.3	85.4	96.9	95.0	86.7	71.8
C+H in Non-Cond. Gas	-------	9.3	15.6	-------	4.9	9.5	13.9	26.6
Octane No., Research, Clear:								
Combined Product[C]	-------	[C] 83.1	84.5	-------	[C] 71.5	[C] 79.5	-------	-------
Original Feed	-------	64.4	64.4	-------	43.0	43.0	-------	-------

[A] Properties of Feed	Light Naphtha	Heavy Naphtha
Acid Solubility:		
Vol. Percent Sol. 95% H_2SO_4	4.0	11.0
Vol. Percent Sol. 90% H_3PO_4	0	1.0
Density at 60° F.	0.709	0.765
Octane No., Res., Clear	64.4	43.0

[B] After light hydrogenation.
[C] Hydrofined HC layer plus organic material recovered from water layer after hydrogenation.

The data representing the percentage of naphtha undergoing oxidation was based on the solubility of the hydrocarbon layer products in 95% sulfuric acid (the acid insoluble portion was assumed to represent the proportion of unreacted naphtha present, after correction for the small soluble portion of the original naphtha). Solubility of the product in phosphoric acid has been used as a measure of the proportion of oxygenated material present in the hydrocarbon layer.

The percentage of oxygen reacting was found by making an oxygen balance based on the amount of oxygen appearing in the non-condensable gaseous products and the volume of gas produced. 98% oxygen was used.

Contact times were calculated from known flow rates and known reactor volume, assuming that no reaction occurred. Since the formation of water and gaseous products leads to shorter reaction times, the calculated values represent maximum, rather than exact actual contact times. Where multiple injections of oxygen were used, the tabulated contact times represent the sum of several calculations.

The temperatures are those of the bath and of the maximum temperature found in the reaction zone.

In several early runs in which the oxygen was preheated to about 300° F. before entering the reactor, excessive temperatures as high as about 1000° C. were observed near the entrance point where the oxygen first contacted the hydrocarbon. These excessive temperatures could be minimized by diluting the hydrocarbon with steam, but even this proved unnecessary by omitting preheating of the oxygen and introducing the latter into the reactor without preheating, i. e., at temperatures below about 50° C.

In order to initiate the vapor phase oxidation of the naphtha a minimum bath temperature of about 325 to 330° C. is required. However, bath temperatures of about 360° C. are preferred since the reaction develops at an earlier point in the reactor and the maximum temperature peak is lower. Once the oxidation reaction begins, a high temperature develops and is maintained substantially constant and at about the same point in the reactor, depending on the conditions being employed.

The maximum proportion of oxygen that may be injected into or be present in the reactor at any one point while oxidizing hydrocarbons such as light virgin naphtha is about 40 moles of O_2 per 100 moles of naphtha. At a contact time of about 3 seconds this oxygen ratio produces a maximum reaction temperature of 450° to 470° C. Still further increases in local oxygen/naphtha ratio to about 0.45 or 0.5 are less desirable, as this has tended

to produce excessive temperatures of 500 to 600° C. and made temperature control quite difficult. In the present equipment under the conditions described oxygen/naphtha molal ratios of about 0.3 to 0.4 are preferred, in order to avoid reaction temperatures of 450° C. or higher which tend to produce tar-like material at the expense of useful product. Above 500° C. even some carbon is produced and this still further decreases the yield of desired products. Of course, a total oxygen ratio greatly in excess of the foregoing limits can be tolerated, provided that the oxygen is injected into the reactor in successive portions without exceeding the stated limits at any one point. Thus, while oxygen is preferably added in a total amount of about 0.3 to 1 mole per mole of hydrocarbon feed, as much as about 1.5 moles of oxygen per mole of feed is useful as indicated above in Table IV, run No. 104/5.

In general, the regions of maximum temperature may range from 1 inch to 12 inches in length or more. When the hot point is very high in temperature, it tends to be short in length, and when the temperature is more moderate, the maximum temperature zone tends to be more extensive, the latter type of temperature distribution being preferable.

Use of diluents such as steam or nitrogen in general has been found undesirable with naphtha-type feeds since it delays the start of the oxidation reaction and actually increases the tendency to form localized hot spots in the reaction zone. However, for the case of certain highly reactive feeds the use of an inert diluent may be desirable.

Multiple oxygen injection, on the other hand, tends to minimize hot points and is also desirable in that it produces a greater yield of oxidized products as indicated by comparing runs 78, 85 and 94.

From the data of Table IV it may be noted that, depending on reaction conditions, about 5 to 20 percent of the hydrocarbon feed is converted to gas. The high ratio of C_2 and C_3 olefins to saturated hydrocarbons (about 3:1) in the gas, as well as the high percentage of carbon monoxide are worthy of note.

The water layer oxidation products contain relatively large proportions of low molecular weight oxygenated compounds, mainly as C_1 to C_3 aldehydes, and some alcohols, ketones, and epoxides. If the water layer is subjected to distillation, the majority of the oxygenated compounds, with the exception of formaldehyde and some polymers formed during distillation, may be recovered as distillate. On the other hand, if the water layer is first hydrogenated to convert the aldehydes to the corresponding alcohols, the formaldehyde may be recovered as methyl alcohol. Since formaldehyde may represent about 40 percent of the entire oxygenated organic material present in the water layer, its recovery by conversion to methyl alcohol contributes materially to the yield of useful liquid products. Thus, in run 85 the water layer upon hydrogenation and distillation yielded 27 weight percent of recoverable organic material, or about 6 pounds per 100 pounds of naphtha charged, not counting an additional 6% of the water layer which consisted of a high-boiling water soluble product.

Hydrogenation of water layer

The water layer products are hydrogenated at low temperature, i. e. predominantly below about 60° C. in order to avoid condensation reactions and the formation of high boiling, water soluble products. Temperatures above about 60° C. are undesirable at the start, since they tend to cause polymerization of formaldehyde. However, in the latter stages of the hydrogenation it may be advantageous to raise the temperature, e. g. to 80–100° C., so as to facilitate complete hydrogenation of acetaldehyde. Raney nickel is a particularly useful catalyst for this hydrogenation, though other highly active hydrogenation catalysts such as platinum or palladium may be used similarly. On the other hand, nickel supported on kieselguhr or other less active catalysts are not so desirable, since they require relatively high hydrogenation temperatures, e. g., 140° C. But at such high temperatures the formation of undesirable high boiling residue due to polymerization is much higher than at low temperature, and even then the conversion of formaldehyde does not readily go to completion.

In typical runs of this invention the water layer was hydrogenated in a shaking autoclave at about 1000 p. s. i. g. The temperature was maintained at about 50 to 60° C. for the first two to three hours, whereupon it was raised to about 90° C. for another two hours or so. Raney nickel was used as catalyst in an amount equal to 10 weight percent on feed. The catalyst was prepared as described by Adkins et al., J. A. C. S., 70, 695 (1948) "W–7" catalyst.

The hydrogenation results are summarized in subsequent Table V.

A comparison of runs 84–A and 84–B shows the advantage of Raney nickel catalyst over nickel on kieselguhr when hydrogenating a water layer of the type produced in the present invention. Specifically it is noted that Raney nickel yields more than twice the amount of valuable products such as alcohols, whereas at the temperatures required with nickel on kieselguhr the yield of alcohols is low and a substantial proportion of the organic material is turned into an undesirable high boiling residue.

A comparison of runs 85—A and 85—B shows the advantage of finishing the hydrogenation at a higher temperature, which completely eliminates any acetaldehyde from the product while increasing the useful distillate yield.

TABLE V

Hydrogenation of water layer

Run No	84–A	84–B	85–A	85–B
Analytical Data on Water Layer:				
Formaldehyde, Wt. Percent	12.1	12.1	12.1	12.1.
Carbonyl Number (Gm. O_2/100 Gm.)	9.9	9.9	10.7	10.7.
Carbonyl Number Due to HCHO	6.5	6.5	6.5	6.5.
C_3 Aldehydes and Ketones, Wt. Percent	12.3	12.3	15.2	15.2.
Hydrogenation Conditions:				
Catalyst	Ni on Kieselguhr.	Raney Ni.	Raney Ni.	Raney Ni.
Catalyst Used, Wt. Percent	10	10	10	10.
Time and Temperature	6 Hrs. at 140° C.	6 Hrs. at 50° C.	5 Hrs. at 55° C.	{3 Hrs. 55°. 2 Hrs. 85°.
Composition of Water Layer (By Distillation) Wet Basis:				
Formaldehyde, Wt. Percent	None	None	None	None
Acetaldehyde, Wt. Percent	None	None	0.8	None
Methyl Alcohol, Wt. Percent	4.6	12.8	12.6	12.1
Mtrl. B. P. 65–80° C.[1] Wt. Percent	6.7	10.2	10.0	11.3
Mtrl. B. P. 80–95° C.[2] Wt. Percent	4.0	13.5	3.0	16.1
Total Distillate	15.3	36.5	26.4	39.5
High Boiling Residue, Wt. Percent	>15	<6.5	<4	<4

[1] Contains some ethyl alcohol and isopropyl alcohol.
[2] Contains some low molecular weight epoxides.

The high boiling, water soluble, condensation products which were isolated from the hydrogenation water layer by distilling off all the low boiling organic material and water were apparently composed mainly of alcoholic products. The residue typically had a boiling range approximately as follows:

10 to 15 wt. percent_____ 50 to 92° C./12 mm. Hg.
25 to 40 wt. percent_____ 92 to 107° C./12 mm. Hg.
25 to 30 wt. percent_____ 107 to 131° C./12 mm. Hg.
25 to 30 wt. percent_____ Above 131° C./12 mm. Hg.

The approximate composition of the organic material recovered by distillation from the water layer after hydrogenation over Raney nickel catalyst was as follows:

	Boiling Range, ° C.	Amount, Wt. Percent of Water Layer
Methyl Alcohol	60–65	12
Ethyl Alcohol+Other Materials	65–80	7
Alcohols+Epoxides	80–95	8
		27
Water		73

Hydrogenation of hydrocarbon layer

The presence of low molecular weight aldehydes in the oxidized hydrocarbon products is generally undesirable because of their irritating odor and, especially where the product is to be used as a motor fuel, because of their tendency to form gummy condensation products. Accordingly, it is desirable to convert the aldehyes to the corresponding alcohols so as to eliminate the formation of condensation products, and also to further increase the octane number of the product. However, conventional hydrogenation of the oxygenated hydrocarbon product, while eliminating the undesirable aldehydes, has also tended to saturate the valuable olefins, thereby detracting from the anti-knock characteristics of the final product.

According to the present invention it has been found that copper chromite catalyst can be used under proper conditions to bring about a selective hydrogenation of the undesirable aldehydes and ketones, without saturating the desired olefins admixed with the aldehydes in the oxidation product. The desired selective hydrogenation over the copper chromite catalyst is carried out at temperatures of about 100 to 160° C. and pressures of about 500 to 1500 p. s. i. g., preferably at about 140° C. and at pressures of the order of about 1000 p. s. i. g. Selective hydrogenation is obtained by interrupting the reaction after the desired proportion of hydrogen has been absorbed, i. e. until the carbonyl number of the product has been reduced to a value less than 1.0. A suitable barium-promoted copper chromite catalyst is available from the Harshaw Chemical Co. (Code 469,931).

The advantages of the novel hydrogenation with the aid of copper chromite, as compared with the more conventional hydrogenation using nickel on kieselguhr is illustrated in Table VI below. This table contains data obtained on the hydrocarbon layer of oxidation 85, showing properties before and after hydrogenation. In each hydrogenation run about 10 wt. percent of catalyst (based on feed) was used and the hydrogenation was carried out over a period of 3 to 4 hours at 1000 p. s. i. g.

TABLE VI

Hydrogenation of hydrocarbon layer

Catalyst	Copper Chromite at 140° C.		Nickel on Kieselguhr at 60° C.	
Properties of Liquid	Before	After	Before	After
Solubility in—				
95% H_2SO_4	36	35.5	36	29
90% H_3PO_4	25	25	25	22
Bromine No.	29.6	27.9	29.6	10
Carbonyl No.	2.2	0.74	2.2	0.76

It is apparent that hydrogenation in the presence of copper chromite effectively reduces the aldehyde content, as shown by the decrease in carbonyl number, without materially affecting the olefin content as indicated by the substantially unchanged sulfuric acid solubility and bromine number. In contrast, the nickel catalyst, while effective in reducing the aldehyde content, also brings about a major decrease in bromine number as well as in acid solubility, thus indicating that olefins have been undesirably reduced. This saturation of olefins becomes even more complete at higher temperatures. The boiling range of the hydrogenated product was in each instance similar to that of the starting oxygenated material. The approximate composition of the oxidized hydrocarbon layer from run 85, before and after selective hydrogenation with the aid of copper chromite is shown in Table VII.

TABLE VII

Composition before and after hydrogenation

	Before Hydrogenation, Wt. Percent	After Hydrogenation, Wt. Percent
Carbonyls:		
C_2	8	0
C_3		0
C_4 and Higher		3
Alcohols, C_2 and Higher	0	5
Olefins:		
10% C_4 and C_5	12	12
90% C_6 and C_7		
Epoxides	16.5	16.5
Unoxidized Naphtha	63.5	63.5
	100.0	100.0

The maximum yield of useful liquid products is obtained by combining the selectively hydrogenated hydrocarbon layer product and the hydrogenated material recovered from the water layer product. In a typical run the combined product may be composed of about 5 to 10 weight percent of organic material recovered from the water layer while the other 90 to 95 weight percent represent the hydrogenated hydrocarbon layer. The boiling range of the combined product is similar to the hydrocarbon layer product alone, but somewhat richer in light ends than the original naphtha. The approximate composition of the combined hydrogenated product from run 85 was:

	Wt. percent
Methanol	3
Ethanol, isopropanol+other oxy-compounds from water layer	3.4
Higher alchols from HC layer	4.4
Carbonyls (C_4+above) from HC layer	2.8
Olefins	11.0
Epoxides	15.4
Unconverted naphtha	60.0
	100.0

The clear research octane number of the above product was 83.1, as compared with 64.4 for the naphtha charging stock. The yield of the combined product was 90.4 weight percent, or 85.5 volume percent.

It is readily apparent that the above product is a potential source of valuable chemicals which may, if desired, be separated from the hydrocarbon portion of the mixture in one of the following manners: (1) by separation on silica gel which adsorbs the oxygenated compounds in preference to the hydrocarbons, (2) by extraction with a polar solvent such as hot water, a glycol, a glycol-water mixture, ammonia, etc. to separate the oxygenated materials, (3) by first converting the trimethylene oxide derivatives and ethylene oxide derivatives to glycols by means of dilute acid and then extracting the oxygenated compounds by means of a polar solvent, (4) for the case of certain pure or narrow-boiling hydrocarbon feeds, distillation may be used to separate the various oxygenated compounds, for the latter mostly boil below and above the boiling point of the hydrocarbon being oxidized.

Dehydration of hydrocarbon layer oxidation product

Instead of selectively hydrogenating the oxidation product as described, the undesirable aldehydes may be removed therefrom even more readily by relatively simple dehydration over alumina or active clays at temperatures of about 350 to 450° C. and low pressures. A good improvement in product quality and useful yield is obtained, but the product contains substantially more unsaturates and less alcohols and epoxides than in the hydrogenation treatment.

Specifically, a portion of the hydrocarbon layer oxidation product from run 85 was passed over commercial alumina catalyst (Harshaw Chemical Co.) at a temperature of about 400° C. and a contact time of about 40 to 60 seconds at atmospheric pressure. As a result, the epoxides present in the oxidation product gave principally conjugated and non-conjugated diolefins, with small amounts of olefin. The aldehydes also gave principally olefins and diolefins. The following yields of products were obtained:

	Wt. percent
Dehydrated HC product	91.4
Water	4.6
Weight increase of catalyst	2.5
C, H, O in gas	1.5
	100.0

Approx. gas composition (dry):	Vol. percent
CO and CO_2	40
H_2	10
C_1–C_3 paraffins	25
C_2–C_3 olefins	25
	100

The following properties of the liquid hydrocarbon product before and after dehydration were determined:

	Before	After
Bromine No.	31.7	53.
Carbonyl No.	2.28	Negligible.

The above shows that simple dehydration effectively removes the undesired carbonyl compounds and materially increases the unsaturation of the product. The approximate original composition of the hydrocarbon layer oxidation product, as well as its composition after dehydration and after selective hydrogenation are compared in Table VIII.

TABLE VIII

Product composition

	Original Oxidation Product, Wt. Percent	After Hydrogenation, Wt. Percent	After Dehydration, Wt. Percent
Carbonyls	8	3	2
Alcohols	0	5	0
Olefins	12	12	18
Diolefins	0	0	10
Epoxides	16.5	16.5	2
Unoxidized Naphtha	63.5	63.5	68
	100	100	100

It will be observed that dehydration, as compared with selective hydrogenation, produces a greatly increased yield of unsaturates, a very substantial yield of diolefins, and only a very small yield of oxygenated compounds.

When the above-described dehydrated product (10 pounds) was combined with a proportionate amount (0.75 pound) of organic material recovered from the hydrogenated water layer described earlier herein, the resulting yield of useful liquid products amounted to about 83 weight percent (81 volume percent), based on the naphtha charged. This compares with a combined yield of about 90 weight percent (85 volume percent) in the case where the hydrocarbon layer was selectively hydrogenated. The clear research octane number of the combined dehydrated product was about 81–82, as compared with 64.4 for the naphtha charged, and 83.1 for the comparable combined product resulting from the selective hydrogenation.

In the attached drawing a simplified flow diagram illustrates the combined steps of operation. The hydrocarbon feed from storage vessel **1** passes through vaporizer **2**, then through reactor tube **3** with admixed oxygen from inlets **4**. The oxidation vapor products are condensed in **5**. The condensate separates into a hydrocarbon layer and an aqueous layer in separator **6**. The hydrocarbon layer may be subjected to hydrogenation or dehydration in unit **7**. The aqueous layer may be subjected to hydrogenation in unit **8**. The combined organic products from units **7** and **8** may be used to obtain a finished fuel **9**.

From the standpoint of octane improvement in a naphtha, the over-all effect of the selective oxidation is one of dehydrogenation. The hydrogen is removed either directly as water, or the original molecule is changed into such a form that it can give water upon dehydration, e. g., by catalytic treatment with dehydrating agents, such as alumina. For example, it has been shown herein that about half of the oxygen charged goes to water. And when the "potential" water is actually removed from the various oxy-compounds by dehydration, then the over-all oxygen selectivity to water (and hence its selectivity in eliminating hydrogen from the feed) is around 70%. In other words, it is apparent that only about 25 to 30% of the oxygen is used up to make oxides of carbon, which are not usable in a liquid fuel. But if the carbon monoxide is considered useful, as in OXO synthesis, then carbon dioxide represents the only waste of oxygen and thus an oxygen efficiency of about 90% can be obtained. Also, it is understood, of course, that elimination of all oxygen from the oxy-compounds formed in the oxidation step is not essential to the main purpose hereof. On the contrary, with the exception of aldehydes, the oxy-compounds generally aid in making naphthas more suitable as a fuel for internal combustion engines in terms of cleanliness, volatility and anti-knock quality. Also the freezing point is reduced, which may be of particular benefit in jet fuels. The remarkable upgrading in anti-knock quality obtainable by means of the present invention is due principally to the selective oxidation of the poor quality components of the feed such as n-hexane (octane no. 24.8) to epoxides such as 2,5-dimethyl tetrahydrofuran (octane no. 92.2) and to the presence in the final product of olefins

and alcohols such as methanol which have a good blending anti-knock value.

Having given a general description of the invention as well as specific illustrations of various phases thereof, these are not to be considered as limitations thereof. On the contrary, variations and modifications not expressly described herein may be made by persons skilled in the art without departing from the present invention, the scope and spirit of which is particularly pointed out in the appended claims.

We claim:

1. A process for upgrading a naphtha hydrocarbon feed containing normally liquid hydrocarbons of the class consisting of normal paraffins and cycloparaffins to form olefins and epoxides of the same number of carbon atoms as the feed hydrocarbon as principal conversion products thereof by non-catalytic oxidation, which comprises passing a stream of the hydrocarbon feed in vapor phase through a conversion zone maintained at a pressure between 0 and 100 p. s. i. g. and a reaction temperature between 275° C. and 480° C., injecting oxygen gas into the stream of hydrocarbon vapor in the conversion zone to form a mixture having a molal oxygen to hydrocarbon ratio at any point not above 0.5, the total amount of oxygen so admixed and reacted with said hydrocarbon feed being between about 0.3 and 1.5 moles of oxygen per mole of hydrocarbon, maintaining the hydrocarbon in contact with the admixed oxygen for a calculated total reaction period of about 1 to 5 seconds until about 25 to 70 weight percent of the hydrocarbon feed is converted, cooling the conversion zone at a sufficiently high rate of heat transfer to maintain the reaction temperature within the stated range, condensing the vapor products leaving the conversion zone, and separating the resulting liquid condensate into an aqueous phase and an organic phase product comprising principally unconverted hydrocarbon feed containing dissolved therein olefins and epoxides of the same number of carbon atoms as the feed hydrocarbon.

2. A process for upgrading a naphtha hydrocarbon feed boiling in the range of about 70° to 220° C. and containing normally liquid hydrocarbons of the class consisting of normal paraffins and cycloparaffins, which comprises passing a stream of the hydrocarbon feed in vapor phase once through a conversion zone at a pressure between about 0 and 5 p. s. i. g. and a reaction temperature between about 350° and a maximum of about 480° C., injecting oxygen gas of at least 90% purity at a temperature not above 50° C. into the stream of hydrocarbon vapor feed at a plurality of successive spaced points in amounts adapted to give at said injection points a mixture having a local molal oxygen to hydrocarbon ratio not in excess of 0.4 and to give a total amount of about 0.3 to 1.0 mole of oxygen per mole of hydrocarbon feed, maintaining the hydrocarbon in contact with the admixed oxygen for a calculated reaction period of about 1 to 3 seconds, cooling the conversion zone at a sufficiently high rate of heat transfer to keep the reaction temperature from exceeding the stated maximum, condensing the conversion zone effluent, and separating the resulting condensate into an aqueous phase and a hydrocarbon-rich organic product having a research octane number of at least 80 and comprising principally unconverted hydrocarbon feed containing dissolved therein olefins and epoxides of the same carbon content as the original hydrocarbon feed.

3. A process according to claim 2 wherein the separated organic product is contacted with hydrogen under pressure at a temperature of about 100° to 160° C. in the presence of a copper chromite catalyst until the aldehyde content of the product is selectively reduced to a carbonyl value less than 1.

4. A process for upgrading a light naphtha hydrocarbon feed containing normally liquid hydrocarbons of the class consisting of normal paraffins and cycloparaffins to form olefins and epoxides as principal conversion products thereof by non-catalytic vapor-phase oxidation, which comprises passing a stream of the hydrocarbon feed in vapor phase once through a conversion zone at a pressure between 0 and 100 p. s. i. g. and a reaction temperature between 275° and 480° C., injecting oxygen into the stream of hydrocarbon vapor feed passed through the reaction zone to form a mixture having a molal oxygen to hydrocarbon ratio at any point not above 0.5, restricting the total amount of oxygen admixed and reacted with said hydrocarbon feed to about 0.3 to 1.2 moles of oxygen per mole of hydrocarbon, maintaining the hydrocarbon in contact with the admixed oxygen for a reaction period of about 1 to 5 seconds while cooling the reaction zone at a sufficiently high rate of heat transfer to maintain the reaction temperatures therein, condensing the resulting vapor products that leave the reaction zone to obtain liquid hydrocarbon-rich and water phases and separating the hydrocarbon-rich phase characterized by a solution of principally olefins and epoxides with a minor amount of carbonyl compounds in a portion of the feed hydrocarbon left unoxidized in one passage through the conversion zone.

5. The process according to claim 4, wherein portions of the total oxygen reacted are injected at a plurality of successive spaced points into the hydrocarbon vapor stream as it passed once through the conversion zone in an amount adapted to keep the oxygen-naphtha molal ratio from exceeding 0.4 at any point and to keep the maximum reaction temperature from exceeding 450° C.

6. The process according to claim 4 wherein a normal paraffin is converted more selectively to an olefin and epoxide of the same number of carbon atoms per molecule and a branched paraffin in the feed remains substantially less reacted.

7. The process according to claim 4 wherein the hydrocarbon vapor feed is a light virgin naphtha fraction boiling between about 70° to 110° C. containing normal and monomethyl substituted paraffins.

8. The process according to claim 4, wherein the hydrocarbon-rich liquid phase separated from the water phase is chemically treated to lower its carbonyl content.

9. The process according to claim 4, wherein the separated hydrocarbon-rich phase is chemically treated by selective catalytic hydrogenation of aldehydes therein.

10. The process according to claim 4, wherein the separated hydrocarbon-rich phase is chemically treated by catalytic dehydration to lower its carbonyl content.

11. The process according to claim 4, wherein the aldehydes in the separated water phase are hydrogenated, and organic material containing the hydrogenated aldehydes from the water phase is blended with organic compounds from the hydrocarbon-rich phase.

References Cited in the file of this patent

UNITED STATES PATENTS

1,517,968	Ellis	Dec. 2, 1924
1,735,486	Young	Nov. 12, 1929
1,976,696	Ellis	Oct. 9, 1934
1,995,324	Penniman	Mar. 26, 1935
2,079,607	Ellis	May 11, 1937
2,132,968	Penniman	Oct. 11, 1938
2,321,311	Mottlau	June 8, 1943
2,369,710	Bludworth	Feb. 20, 1945
2,580,528	Dice et al.	Jan. 1, 1952
2,689,253	Robertson et al.	Sept. 14, 1954