Conversion of Gas Oils by Oxidation

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Vapor phase oxidation may be used to convert both light and heavy gas oils to olefins and/or oxygenated compounds in a reaction vessel utilizing circulating solids to remove the exothermic heat of reaction. Such a process is of potential use in producing alpha olefins as well as fuels. At high temperatures the products consist largely of olefins rich in alpha olefins while at low temperatures oxygenated compounds rich in ketones and other oxygenated compounds predominate. In most cases the product distribution differs from that obtained either by catalytic or thermal cracking; such comparisons are made. Product analyses through the twelve-carbon-atom range are given.

THE UTILITY of noncatalytic vapor phase oxidation of hydrocarbons in a raining-solids-type reactor (*5–7*) has been extended to heavier compounds, namely gas oils, for the production of olefins, oxygenated compounds, and fuels. This article reports the results obtained from the vapor phase oxidation of selected gas oil feedstocks and compares the results with data from the thermal and catalytic cracking of similar feedstocks (*4*).

EXPERIMENTAL

Apparatus. The basic apparatus has been described (*6*). The solids used in the present work were zircon silica (The Carborundum Co.) of 35 to 40 mesh size. Oxygen (99.9%) was used as an oxidant and was distributed equally through four inlets. The contact time between hydrocarbon and oxygen was from 5 to 10 seconds. Steam was used as a solids lift in all experiments and was also injected into the hydrocarbon feed to vaporize high boiling compounds for the case of the heavy gas oil.

Procedures. The experiments were exploratory in nature to determine the type products formed under different temperatures and different oxygen to hydrocarbon "mole ratios" for two gas oils. The "mole ratio" of hydrocarbon to oxygen fed was based on the average molecular weight of the gas oil. The effect of temperature was noted.

Quantities of hydrocarbon from 1200 to 3100 grams were subjected to oxidation. Material balances showed 95 to 99% recovery of hydrocarbon and oxygen. All results were corrected for losses and are expressed on the basis of the feed charged and the feed reacted for the case of the light gas oil, and on the basis of the feed charged and the product boiling below the feed for the case of the heavy gas oil. The hydrocarbon conversion is defined as the percentage of the feed converted to products other than the feed, these products being lighter or heavier than the feed.

Source of Materials. The gas oils used as feed stocks are characterized in Table I.

Product Analyses. The products of the oxidation consisted of noncondensable gas, a liquid organic layer rich in hydrocarbons and oxygenated compounds, and an aqueous layer consisting mainly of water from the steam used for the solids lift and to vaporize the feed, but also containing water soluble oxygenated compounds. The

Table I. Analysis of Gas Oil Feed Stocks

Feed stock	Heavy gas oil	Light gas oil
Specific gravity, 60° F. (15.5° C.)	0.900	0.841
Refractive index [° F. (° C.)]	1.479[152.6(67)]	1.4689[68(20)]
Pour pt., ° F. (° C.)	100(38)	. . .
Bromine No.	3.2	2.5
Sulfur, Wt. %	0.26	0.11
Av. mol. wt.	385	261
ASTM distillation (atm., % off)		
5 ° F. (° C.)	662(350)	520(271)
10	691(366)	545(285)
30	750(399)	586(308)
50	824(440)	606(319)
70	901(483)	622(328)
90	1022(550)	642(339)
Final b.p.	1099(593)	662(350)
Refractive index-density-mol. wt. analysis (wt. % of total carbon)		
Aromatic	27.5	10.5
Naphthenic	40.8	25.2
Paraffinic	31.7	64.3

products of oxidation were analyzed as outlined below. Gas liquid and gas solid chromatographic techniques were employed extensively using Models 154C and 154D Perkin-Elmer vapor fractometers.

Noncondensable Gas. A column packed with Molecular Sieves (5A) was used at 212° F. (100° C.), as well as a helium flow rate of 44 cc./min. for determining hydrogen, oxygen, nitrogen, methane, and carbon monoxide. Carbon dioxide and all hydrocarbons (C_2–C_5) were determined using a column packed with hexamethylphosphoramide supported on an inert carrier and operated at 86° F.(30° C.), with a helium flow rate of 50 cc./min. Ethane and ethylene appeared as a single peak on this column and were resolved on a column packed with Molecular Sieves (13X) operated at 212° F. (100° C.) with a helium flow rate of 130 cc./min. Oxygenated compounds other than the carbon oxides were assumed to be negligible in the gaseous products.

Organic Products Condensed in a Dry Ice–Acetone Trap. Two separate gas liquid chromatographic columns were employed. Hydrocarbons (C_2–C_6) were separated using the hexamethylphosphoramide substrate described previously while oxygenated compounds were separated on a similar type column employing β,β'-oxydipropionitrile as the substrate operated at 212° F. (100° C.) and a helium flow rate of 64 cc./min.

Aqueous Layer Products. The organic material boiling below 212° F. (100° C.) was separated from the water by distillation through a 20-plate column packed with glass helices. The organic material was analyzed with the β,β'-oxydipropionitrile chromatographic column described previously. The water was stripped from the residue by simple vacuum distillation. The small amount of polymeric material collected did not warrant any further analysis. Formaldehyde determinations were made directly on the aqueous layers by the method of Bricker and Johnson (*2*).

Major Organic Layer. A sample of the organic layer was fractionated under vacuum through a spinning band distillation column (Nester and Faust) having approximately 20 theoretical plates. The fractions obtained were analyzed in the following manner.

Low Boiling Ends [Initial Boiling Point, –212° F. (100° C.)]. Gas liquid chromatographic techniques were employed using substrates of hexamethylphosphoramide for C_4 through C_6 hydrocarbons and β,β'-oxydipropionitrile for oxygenated compounds operated as previously described. A squalane substrate operated 122° F. (50° C.) and a helium flow rate of 70 cc./mm. was used for determination of C_6 and C_7 hydrocarbons.

Upper Naphtha Range [212–430° F. (100-221° C.)]. Fluorescent indicator adsorption methods as described by Criddle and Le Tourneau (*3*), were used to estimate the percentages of unsaturates, saturates, and aromatics plus oxygenated compounds in the products boiling in this range. Hydrogen flame ionization gas liquid chromatography using a 150-foot capillary column impregnated with squalane and operated at 212° F. (100° C.), and a nitrogen flow rate of 0.3 cc./min. was used to determine the *n*-paraffin and α-olefin content of certain fractions and to estimate the complexity of the mixture. Infrared absorption spectra were used to determine the characteristic functional groups present in representative fractions. Bromine numbers determined by a modified ASTM method (*1*) were used to establish the olefin content of representative fractions.

Heating Oil Range [429.8–649.4° F. (221–343° C.)]. Fluorescent indicator adsorption methods as described by Knight and Groennings (*8*) for heavier oils were used as previously described along with infrared absorption spectra.

Heavy Gas Oil Range [649.4+° F. (343+° C.)]. The distillation residues comprised the major portion of this cut. Carbon and hydrogen microanalyses were used to determine the apparent average molecular weight and possible average structure.

Silica gel adsorption methods were utilized in several experiments to separate hydrocarbons from oxygenated compounds after which the aforementioned procedures were used in ascertaining the composition of the products.

RESULTS

Oxidation of a Heavy Gas Oil. The product distribution resulting from the atmospheric pressure, single-pass, vapor phase oxidation of a heavy gas oil (characterized in Table I) at 932° F. (500° C.) and oxygen to hydrocarbon mole ratios of 1.0 and 1.7 is summarized in Table II.

The addition of only 2.5% of the amount of oxygen needed for the complete combustion of the gas oil was sufficient to convert at least 43% of the feed, while the addition of 4% of the amount of oxygen needed for complete combustion converted more that 54% of the feed. Only small amounts of tar were produced in the two experiments. An experiment carried out at the same conditions, but in the absence of any oxygen was essentially a blank run and only 13% of the feed was converted to products boiling below the feed.

The boiling point range of the gas oil feed and of the products of the oxidation experiments is shown in Figure 1. These curves show that as the oxygen to hydrocarbon mole ratio is raised, the hydrocarbon conversion is increased.

Approximate pour point data taken on selected fractions indicate that oxidation raised the pour point of any particular fraction, although the pour point of the total product was necessarily lowered by oxidation.

The product distribution for the liquid hydrocarbon layer for each experiment indicates the presence of a large concentration of olefins together with carbonyls and alcohols.

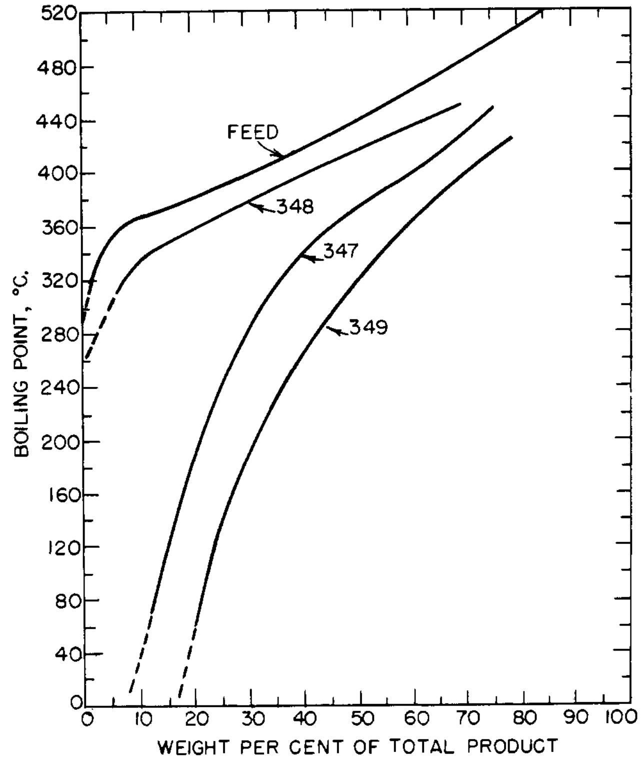

Figure 1. Heavy gas oil oxidations product distribution by boiling point

[Reaction Temperature, 932° F. (500° C.)]

Experiment	O_2/Feed, "Mole Ratio"
348	0
347	1.0
349	1.7

Table II. Summary of Products Isolated from Oxidation of Heavy Gas Oil

Oxygen/feed, "mole ratio"	1.0		1.7	
Av. reaction temp., ° F. (° C.)	941(505)		932(500)	
Oxygen conversion, %	97		97	
Hydrocarbon conversion, %	>43		>54	
Contact time, sec.	9.7		8.4	
	Production, Pounds per 100 Lb.			
	Feed	Product boiling below feed	Feed	Product boiling below feed
C_4^-	6.3	14.7	9.6	17.9
Olefins, totals[a]	5.1	11.9	7.5	14.0
Ethylene	1.8	4.2	2.9	5.4
Propylene	1.9	4.4	2.8	5.2
1-Butene + isobutylene	1.2	2.8	1.5	2.8
2-Butenes	0.2	0.5	0.3	0.6
Paraffins, totals	1.2	2.8	2.1	3.9
Methane	0.5	1.2	0.9	1.7
C_2—C_4	0.7	1.6	1.2	2.2
C_5—430° F. (221° C.) fraction[b] totals	13.9	32.3	17.2	32.0
Saturates	1.1	2.6	0.0	1.5
Unsaturates	11.4	26.5	12.1	22.5
1-Pentene	0.7	1.6	0.0	1.3
2-Pentenes	0.1	0.2	0.2	0.4
Isopentenes	0.5	1.2	0.5	0.9
1-Hexene	0.9	2.1	1.4	2.6
Other hexenes	0.1	0.2	0.4	0.7
1-Heptene	0.6	1.4	0.8	1.5
Other heptenes	0.1	0.2	0.2	0.4
1-Octene	0.4	0.9	0.1	0.2
1-Nonene	0.5	1.2	0.9	1.7
1-Decene	0.5	1.2	0.1	0.2
1-Undecene	0.2	0.5	0.2	0.4
Other olefins	6.8	15.8	6.5	12.0
Aromatics + oxygenated compounds	1.4	3.3	4.3	8.0
430-650° F. (221-343° C.) fraction, totals	15.6	36.3	20.4	37.9
Saturates	1.1	2.6	1.0	1.9
Unsaturates	5.6	13.0	5.5	10.2
Aromatics + oxygenated compounds	8.9	20.7	13.9	25.8
650+° F. (343+° C.) fraction, totals	57.0[c]	...	46.2[c]	...
Miscellaneous, totals	7.3	17.0	12.3	22.9
CO	2.7	6.3	4.3	8.0
CO_2	0.8	1.9	1.9	3.5
Hydrogen	<0.1	<0.1	<0.1	<0.1
Acetaldehyde	0.6	1.4	0.9	1.7
C_3 + C_4 aldehydes	0.2	0.5	0.3	0.6
Methanol	0.5	1.2	0.8	1.5
Ethanol + acetone	0.6	1.4	1.0	1.9
Other low boiling oxygenated compounds	0.7	1.6	1.2	2.2
Organic material b.p. > 100° C. from aqueous layer	1.1	2.6	1.9	3.5
Grand totals	100.1	100.3	105.7	110.7

[a] Alpha olefins may be present in larger quantities than indicated. The total olefin content, however, includes these amounts.

[b] Compositions estimated from FIA and gas chromatographic analysis.

[c] Largely unreacted feed. Some oxygenated compounds present.

The approximate olefin content was initially determined from the bromine numbers of selected fractions of distillate from the organic layer distillations. These data indicate that the lower boiling products contain a large proportion of oxygenated compounds—the olefin content reaching a peak in the 16 carbon atom range. The olefin content drops off sharply after this point, the major portion of the remaining product being unreacted feed. In both experiments about 25 lb. of olefins were formed per 100 lb. of feed with about half of the olefins produced falling in the five-to-twelve carbon atom range. Types I (alpha), II (beta), and III olefins were present in the oxidation products, Type I predominating in most cases and reaching as high as 50% of the total olefin content. The experiment using no oxygen yielded only about 4 lb. of olefins per 100 lb. of feed.

To predict the utility of oxidation as a conversion process, the results of these experiments were compared with present-day catalytic cracking data. In general, oxidation at 932° F. (500° C.) converted less of the feed to products boiling below the feed than did catalytic cracking of the same gas oil at 932° F. (500° C.). Table III shows the difference in product distribution between the two processes. Noteworthy, however, are the higher production of olefins

Table III. Comparison of Oxidation and Cracking

(Heavy gas oil)

Production (Wt. % of Feed)	Oxidation at 932° F. (500° C.)	Catalytic Cracking at 932° F. (500° C.)
C_4^-	6–10%	13–20%
Olefin/paraffin ratio	3.6–4.3	4.5–7.7
C_5—430° F. (221° C.)	14–17%	32–39%
Unsaturates	70–82%	43%[a]
Saturates	5–8%	35%[a]
Oxygenated compounds	10–25%	0
Aromatics		22%[a]
430–650° F. (221–343° C.)	16–20%	16–25%
650+° F. (343+° C.)	46–57%	17–27%
Coke + carbon	0	2–7%

[a] Volume per cent of a typical experiment.

and the production of little tar and no coke by oxidation.

Oxidation of a Light Gas Oil. The product distribution from similar oxidations of a light gas oil (characterized in Table I) at temperatures of 734° to 1022° F. (390° to 550° C.) and at oxygen-to-hydrocarbon mole rations of 1.1 to 1.9 are summarized in Table IV.

The addition of 4 to 7% of the amount of oxygen necessary for the complete combustion of the gas oil converted from 79 to 85% of the feed. An experiment carried out in the absence of oxygen showed a conversion of only 28% of the feed, the majority of the products consisting of polymerization and condensation products boiling above the feed.

The boiling range of the oxidation products for each experiment is given in Figure 2. This analysis includes gaseous products, products recovered from the aqueous layer, and all organic layer products. The degree of oxidation can be seen to increase with the temperature of the oxidation. The oxygen-to-hydrocarbon mole ratio also produces a change in the boiling range of the products for oxidation at any given temperature, the olefin content also increasing with the severity of reaction-olefins predominating for oxidation at 1013° F. (545° C.); oxygenated compounds predominating at 734° F. (390° C.).

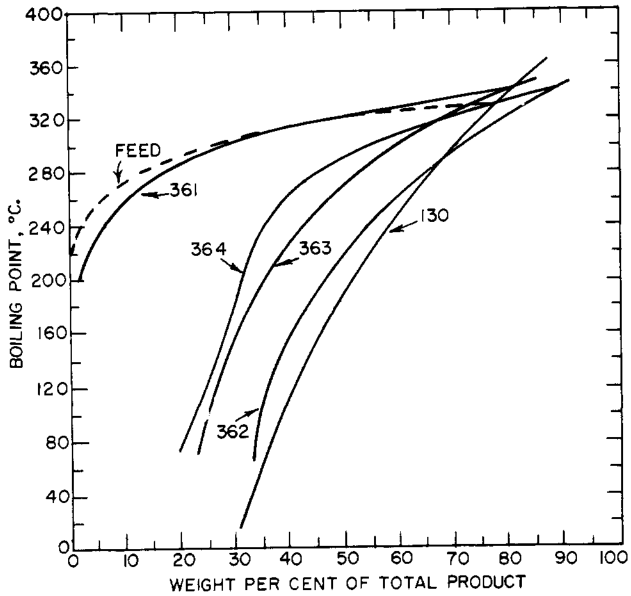

Figure 2. Light gas oil oxidations product distribution by boiling point

Experiment	Reaction Temp.,	O_2/Feed, "Mole Ratio"
130	1013(545)	1.9
361	914(490)	0
362	932(500)	1.7
363	932(500)	1.1
364	734(390)	1.8

Infrared analysis indicated that Types I (alpha), II (beta), and III olefins were present in the products of oxidation. At 734° F. (390° C.), only 21 lb. of olefins was formed per 100 lb. of feed while about 40 lb. was formed at 932° F. (500° C.) and 52 lb. at 1013° F. (545° C.).

The oxygen distribution to the various products formed during the oxidations based on the amount of oxygen reacting per pass is reported in Table V. The water of reaction from the various experiments accounted for 50 to 70% of the oxygen consumed, the water of reaction being indicative of the amount of dehydrogenation (olefin formation) occurring.

Comparisons of the data obtained from oxidation with those from thermal (steam) and catalytic cracking are shown in Table VI.

DISCUSSION

The vapor phase oxidation of gas oils at temperatures of 932° to 1022° F. (500° to 550° C.) is a potentially important method for producing products that in some cases are similar to and in others different from those presently made by means of catalytic and thermal cracking processes depending on the reaction temperature and oxygen to hydrocarbon feed mole ratio.

At present the commercial demand for olefinic hydrocarbons is met by means of endothermic cracking reactions using either thermal or catalytic processes. These processes are useful in forming low molecular weight olefins while higher molecular weight olefins are made by polymerization of the lower olefins. The present methods of producing gasolines are adequate. However, with the rising consumption of jet and diesel fuels, a method of conversion to these products is necessary. Oxidation may prove to be useful for such an application.

The oxidation technique is especially advantageous since the reaction is exothermic and no heat need be supplied to the reactor—in fact heat needs to be removed and can be used as a source of energy elsewhere in any commercial operation. Oxidation also is favorable since neither coke nor carbon is produced in the reaction. On the other hand, in the case of catalytic or thermal cracking processes as much as 2 to 7 wt. % of the feedstock may be converted to these undesirable by-products.

By using only 2.5 to 7% of the theoretical amount of oxygen necessary to burn the gas oil feeds completely to carbon dioxide and water, substantial conversion of the gas oils to useful products was accomplished. High reaction temperatures 932° to 1013° F. (500° to 545° C.) favored the production of olefins while low reaction temperature 734° F. (390° C.) favored the production of oxygenated compounds. The degree of reaction was found to vary with the severity of oxygen attack as well as that of the temperature range. In general, as the conditions became more and more severe the olefin content increased. Further, the yield of low molecular weight olefins also increased with the severity of oxidation. The oxygenated compounds appeared to consist largely of ketones having the same carbon skeleton as that of the feed. Such products could readily be converted to alcohols which in turn could be dehydrated to give additional olefins. It is also possible that on catalytic treatment the ketones could also be changed to olefins. Thus, the presence of oxygenated compounds (which are not encountered in thermal or catalytic cracking reactions) need not be considered detrimental. They may be valuable fuel components as such.

Table IV. Summary of Products Isolated from Oxidation of a Light Gas Oil

Experiment No.	362[a]	363[a]	364[a]	130[b]
Oxygen/feed, "mole ratio"	1.7	1.1	1.8	1.9
Av. reaction temp.,	932(500)	932(500)	734(390)	1013(545)
Oxygen conversion, %	99	99	97	97
Hydrocarbon conversion, %	81.5	79.0	79.7	84.6
Contact time, sec.	6	6	6	9

	Production; Pounds per 100 Lb.							
	Feed	Reacted	Feed	Reacted	Feed	Reacted	Feed	Reacted
C_4^-, totals	12.4	15.2	8.8	11.1	3.4	4.3	26.4	31.0
Olefins, totals	9.6	11.8	6.5	8.2	2.8	3.5	20.8	24.4
Ethylene	4.0	4.9	2.3	2.9	0.9	1.1	6.4	7.5
Propylene	3.0	3.7	1.9	2.4	0.9	1.1	16.9	14.4
1-Butene + isobutylene	2.2	2.7	2.0	2.5	0.9	1.1		
2-Butenes + butadiene	0.4	0.5	0.3	0.4	0.1	0.2		
Paraffins, totals	2.8	3.4	2.3	2.9	0.6	0.8	5.6	6.6
Methane	1.5	1.8	1.3	1.6	0.3	0.4	4.9	5.8
C_2–C_4	1.3	1.6	1.0	1.3	0.3	0.4	0.7	0.8
C_5—430° F. (221° C.) fraction, totals	23.5	28.8	20.5	25.9	18.0	22.6	20.9	24.4
Saturates	1.6	1.9	1.7	2.1	2.1	2.6	0	0
Unsaturates	16.6	20.4	14.9	18.9	9.9	12.5	16.1	18.8
1-Pentene	1.2	1.5	1.2	1.5	0.5	0.6	7.1	8.3
2-Pentenes	0.2	0.3	0.3	0.4	0.1	0.1		
Isopentenes	0.7	0.9	0.6	0.8	0.3	0.4		
1-Hexene	1.5	1.8	1.3	1.6	0.7	0.9		
Other hexenes	0.1	0.1	0.5	0.6	0.3	0.4		
1-Heptene	1.0	1.2	0.7	0.9	0.3	0.4		
Other heptenes	0.1	0.1	0.1	0.1	0.1	0.1		
1-Octene	0.6	0.7	0.5	0.6	0.3	0.4	2.0	2.3
1-Nonene	0.9	1.1	0.5	0.6	0.4	0.5		
1-Decene	1.0	1.2	0.7	0.9	0.2	0.3	6.4	7.5
1-Undecene	9.3	11.5	0.8	1.0	6.7	8.4		
Other olefins			7.7	9.9			0.6	0.7
Aromatics + oxygenaged compounds	5.3	6.5	3.9	4.9	6.0	7.5	4.8	5.6
430–650° F. fraction, totals	39.8	26.2	40.6	24.8	47.4	34.0	29.1	17.3
Saturates	10.3	...	15.0	...	15.8	...	12.9	...
Unsaturates	6.0[c]	7.4	11.4	14.4	4.0	5.0	7.9	9.9
Aromatics	8.2[c]	...	6.0	...	4.5[c]	...	1.5	...
Oxygenated compounds	15.3[c]	18.8	8.2[d]	10.4	23.1[c]	29.0	6.8	8.0
650° F. + fraction, totals	9.6	11.8	20.7	26.2	21.1	26.5	10.3	12.0
Miscellaneous, totals	16.7	20.5	9.1	11.5	13.2	16.6	16.9	19.6
CO	5.8	7.1	3.6	4.6	3.9	4.9	2.5	2.9
CO_2	1.2	1.5	0.7	0.9	0.5	0.6	9.5	1.1
Hydrogen	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	0.1
Acetaldehyde	1.0	1.2	0.7	0.9	1.0	1.3	1.2	1.4
C_3 + C_4 aldehydes	0.5	0.6	0.3	0.4	0.4	0.5	...	...
Methanol	0.8	1.0	0.5	0.6	1.2	1.5	...	...
Ethanol + acetone	0.8	1.0	0.5	0.6	0.9	1.1	...	...
Other low boiling oxygenated compounds	4.0	4.9	1.8	2.3	2.7	3.4	2.8	3.2
Material b.p. > 100° C. from aqueous layer	2.6	3.2	1.0	1.2	2.6	3.3	0.8	0.9
Water of reaction	11.0	13.5	10.0	12.7	16.8	21.1	13.4	15.6
Grand totals	113.0	116.0	109.7	112.2	119.9	125.1	117.0	119.9

[a] Analysis based on FIA and gas chromatographic methods. [b] Analysis based on silica gel and distillation procedures. The composite olefin yields include branched olefins as well as alpha olefins which were not determined quantitatively. [c] Estimated from silica gel adsorption analysis. [d] Estimated to be approximately 20% oxygenated.

Table V. Oxygen Distribution

(Light gas oil oxidations)

Experiment No.	362	363	364	130
Av. reaction temp., ° F. (° C.)	932(500)	932(500)	734(390)	1013(545)
Oxygen/feed mole ratio	1.7	1.1	1.8	1.9
Oxygen consumed, grams per 100 grams of feed	20.4	13.2	21.8	23.8
Constituent		Oxygen, Wt. %		
Water[a]	48.0	67.3	68.3	50.0
Carbon monoxide	16.2	15.9	10.0	5.9
Carbon dioxide	4.4	3.8	1.8	29.0
Oxygenated compounds boiling below 212° F. (100° C.)	9.8	8.5	8.8	4.4
High boiling residue from aqueous layer	2.5	1.5	2.4	0.6
Oxygenated compounds[b] boiling above 212° F. (100° C.)	19.1	3.0	8.7	10.1
Total	100.0	100.0	100.0	100.0

[a] Based on the actual water of reaction as calculated by material balance. [b] By difference.

Table VI. Comparison of Oxidation and Cracking

(Light gas oil)

	Oxidation		Catalytic Cracking,	
Production (% of Feed)	950° F. (500° C.)	1013° F. (545° C.)	932° F. (500° C.)	1022° F. (550° C.)
C_4^-	9–12%	26%	15–21%	24%
Olefin/paraffin ratio ·	2.8–3.4	3.7	4.5–7.7	1.7
C_5—430° F. (221° C.)	21–24%	21%	29%	27%
430+° F. (221+° C.)	49–61%	40%	44–53%	45%
Coke + carbon	0	0	4%	> 2%
	Oxidation, 932–1013° F.		Steam Cracking, 1274–1508° F.	
Production (% of Feed)	(500–545° C.)		(690–820° C.)	
C_4^-	9–26%		47–58%	
Olefin/paraffin ratio	2.8–3.7		2.1–3.4	
C_5—430° F. (221° C.)	21–24%		21–27%	
430+° F. (221+° C.)	40–61%		1–15%	
Tar	[a]		10–19%	

[a] Small amount.

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