Dec. 15, 1931. J. H. JAMES 1,836,325

MANUFACTURE OF INTERMEDIATE OXIDATION PRODUCTS

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Fig. 2.

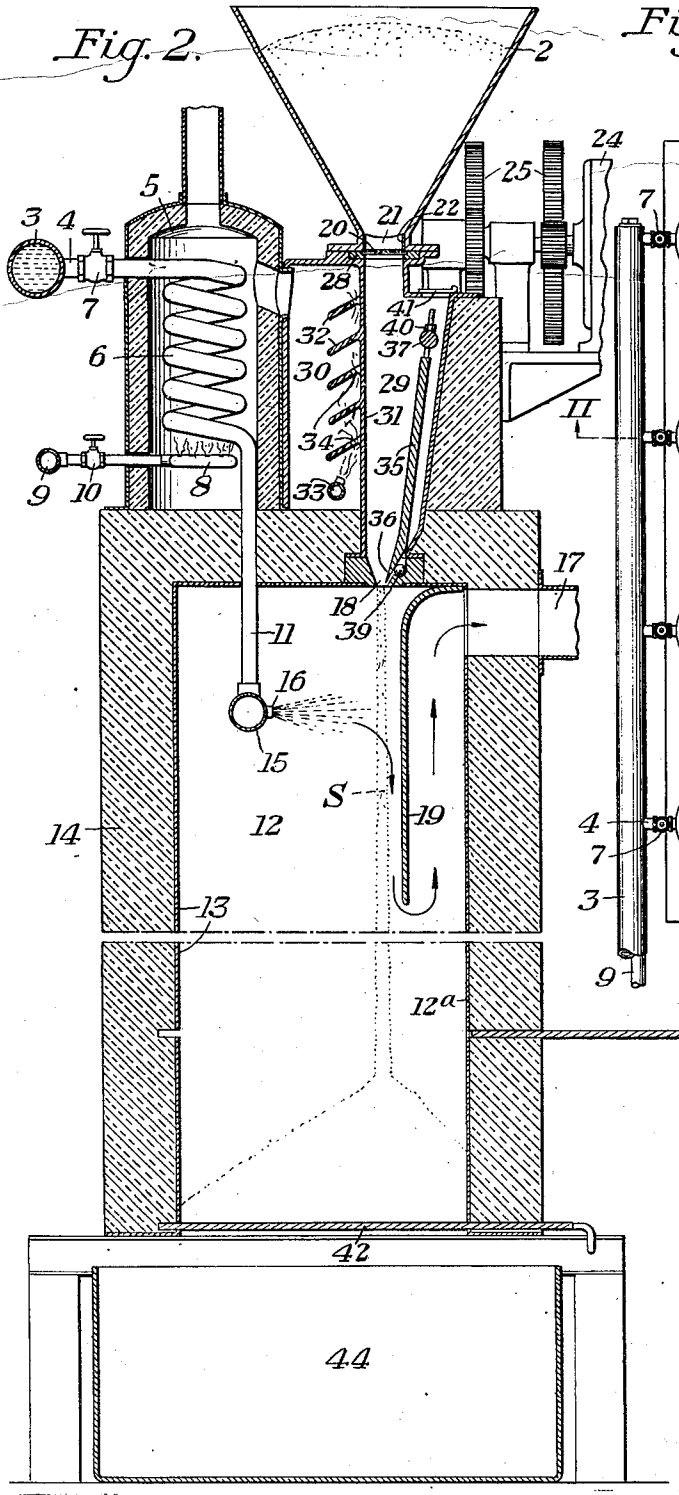
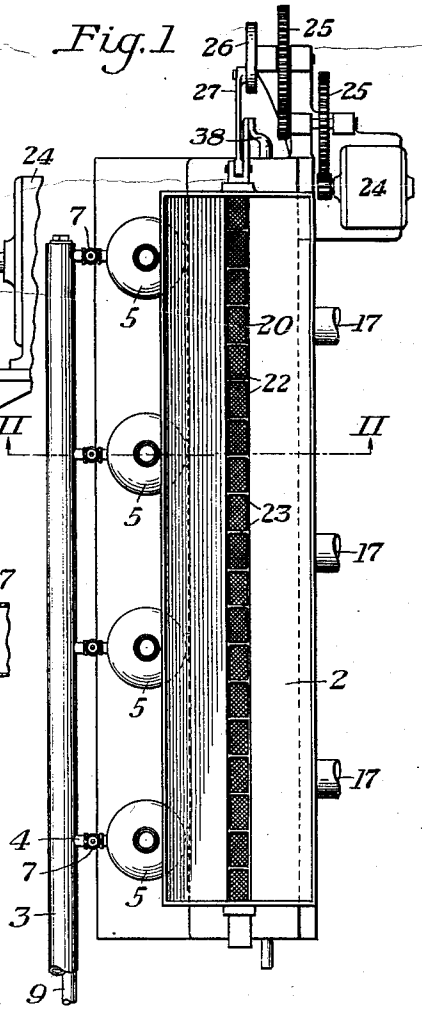


Fig. 1



INVENTOR

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by Hyman Steblin & Rumelle

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MANUFACTURE OF INTERMEDIATE OXIDATION PRODUCTS

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Fig. 4.

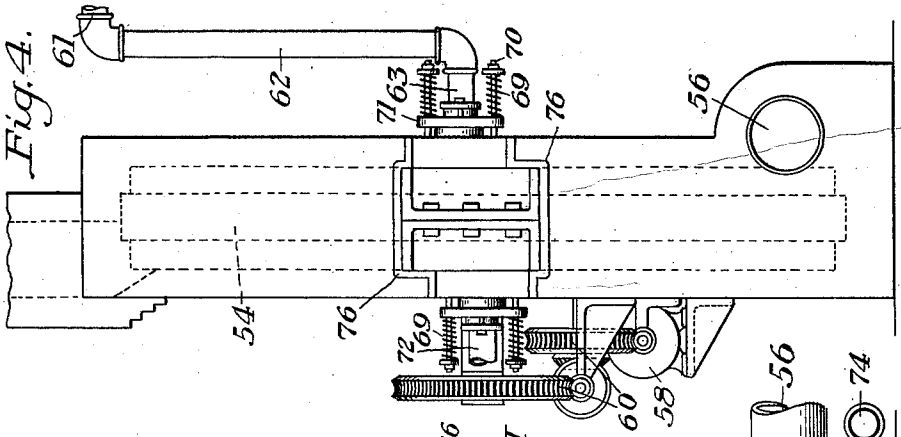
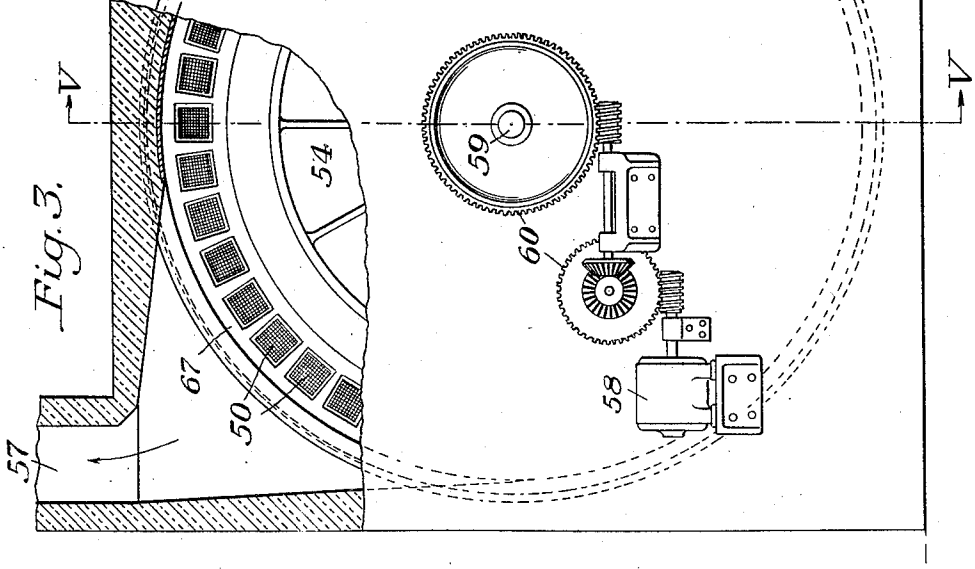


Fig. 3.



INVENTOR

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MANUFACTURE OF INTERMEDIATE OXIDATION PRODUCTS

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Fig. 5.

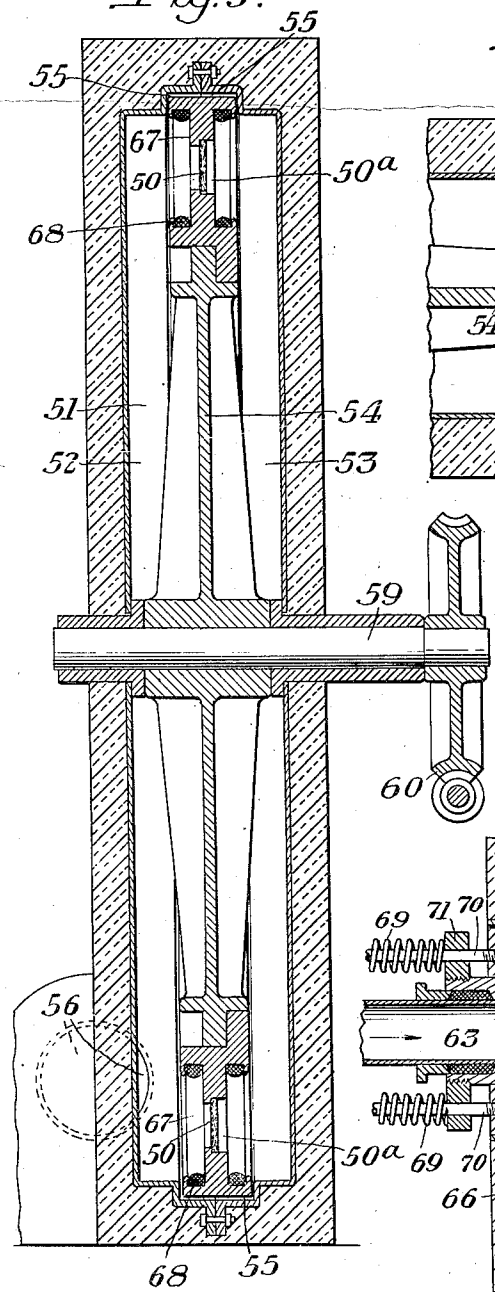


Fig. 6.

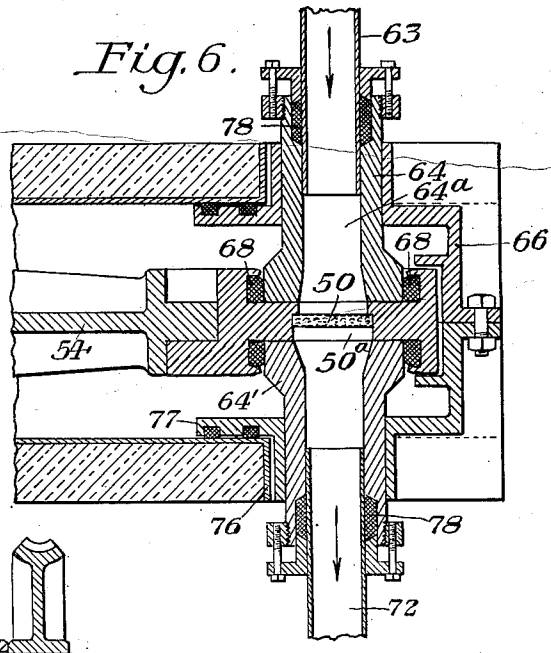
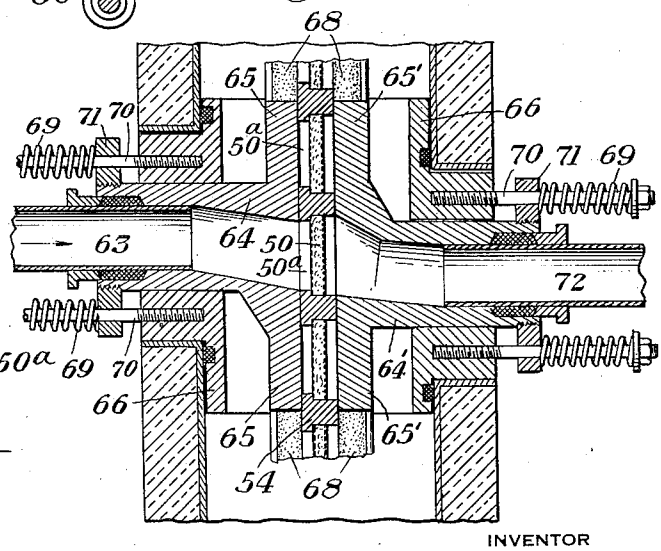


Fig. 7.



INVENTOR

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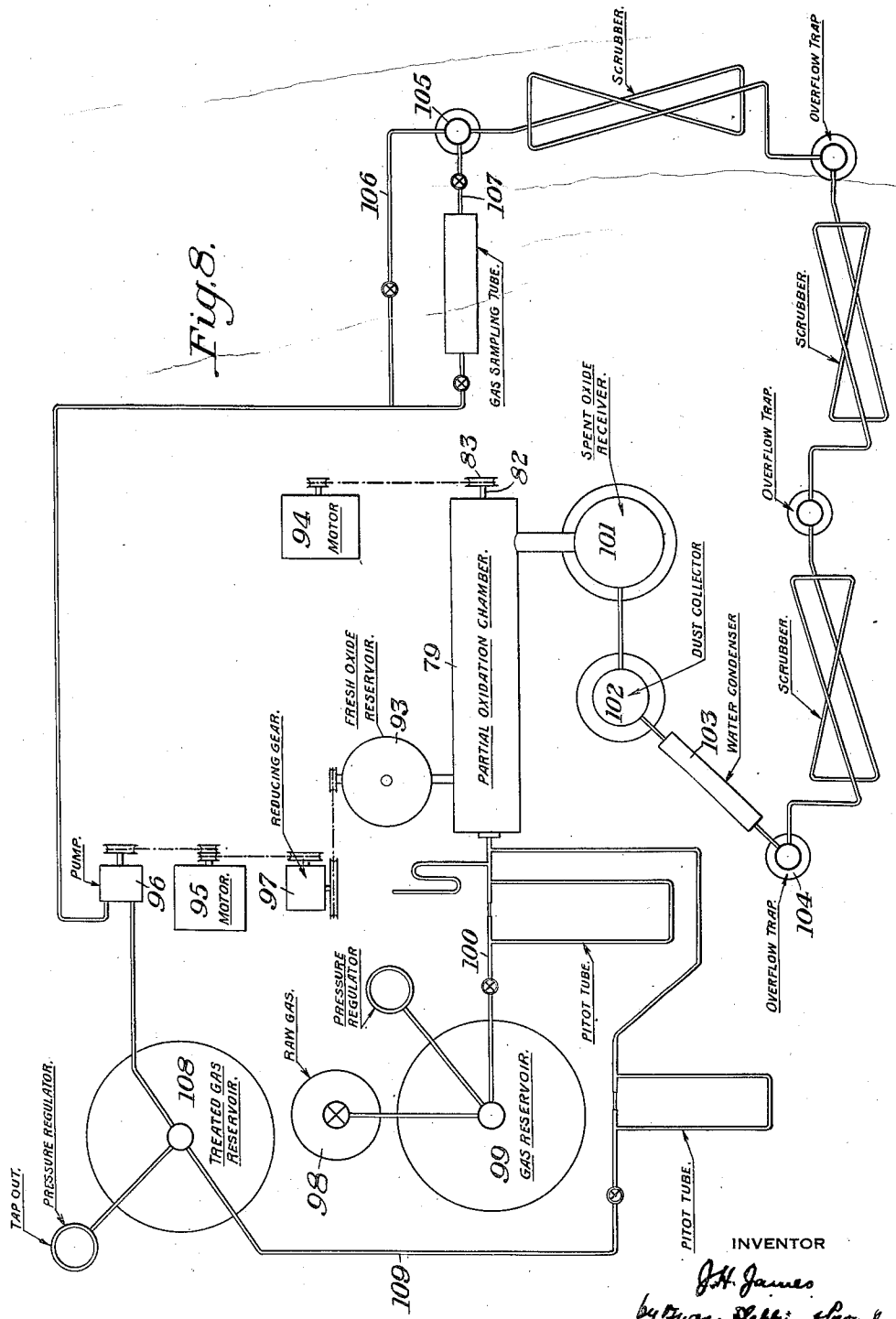
his attys.

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MANUFACTURE OF INTERMEDIATE OXIDATION PRODUCTS

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Fig. 8.



INVENTOR

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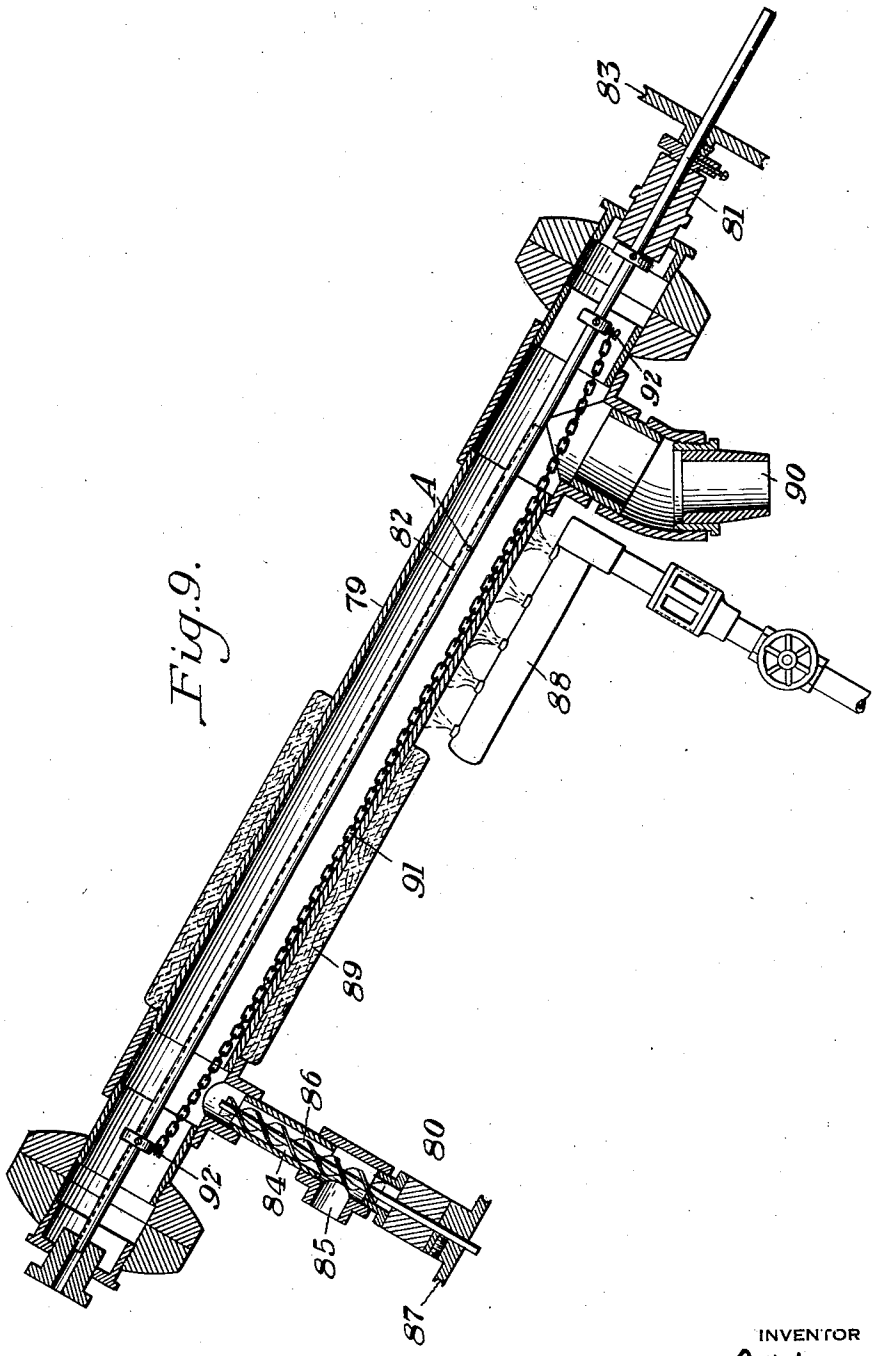
his attys

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MANUFACTURE OF INTERMEDIATE OXIDATION PRODUCTS

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Fig. 9.



INVENTOR

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Patented Dec. 15, 1931

1,836,325

UNITED STATES PATENT OFFICE

JOSEPH H. JAMES, OF PITTSBURGH, PENNSYLVANIA, ASSIGNOR TO CLARENCE P. BYRNES, TRUSTEE, OF SEWICKLEY, PENNSYLVANIA

MANUFACTURE OF INTERMEDIATE OXIDATION PRODUCTS

Application filed January 18, 1926, Serial No. 81,963. Renewed June 27, 1927.

In the drawings:

Figure 1 is a top plan view of a treating apparatus embodying the invention;

Figure 2 is a vertical section on the line II—II of Figure 1;

Figure 3 is a side elevation, partly broken away, of another apparatus embodying the invention;

Figure 4 is an end elevation of the apparatus shown in Figure 3;

Figure 5 is a vertical section on the line V—V of Figure 3;

Figure 6 is a horizontal section on the line VI—VI of Figure 3;

Figure 7 is a vertical section on the line VII—VII of Figure 3;

Figure 8 is a diagrammatic plan view showing another system for carrying out my invention; and

Figure 9 is a side elevation, partly broken away, on a larger scale, showing the reaction chamber and connections of the system of Figure 8.

My invention relates to the manufacture of intermediate oxidation products from organic bodies such for example as hydrocarbons or hydrocarbons derivatives. It is especially advantageous in producing intermediate oxidation products from hydrocarbons or hydrocarbon derivatives of the lower molecular weights such as those which are gaseous at normal temperatures and pressures, or those hydrocarbon liquids which are more volatile.

In a number of copending applications, for example, Serial No. 272,567, filed January 22, 1919, Serial No. 281,124, filed March 7, 1919, Serial No. 335,939, filed November 5, 1919, Serial No. 435,355, filed January 6, 1921, and Serial No. 520,283, filed December 6, 1921; I have disclosed processes for making intermediate oxidation products from mineral hydrocarbons such as petroleum or fractions thereof, the products from the low temperature distillation of coals, and from shale oil, whether or not said products have been "cracked" prior to oxidation. In said processes the hydrocarbon, in vapor or gaseous phase, was mixed with oxygen or an oxygen containing gas such as air, and the mixture passed through a reaction zone at a temperature between 160° C. and 500° C. with or without a catalyst. The condensed products of such processes were in the range from aliphatic alcohols to aldehyde fatty acids including aldehydes, aldehyde alcohols, esters, ketones, etc.

Such processes, while generally applicable, are specially desirable for liquid hydrocarbons having a boiling range from that of kerosene on through the mineral oil fractions of heavier molecular weights; but for fractions lighter than the lower kerosene limit, including gaseous hydrocarbons, the diluting effect of the nitrogen of the air makes it difficult to procure and recover the products. Furthermore, in the lighter hydrocarbons below the kerosene range, the explosive range of such hydrocarbons when mixed with air becomes wider, thus increasing the hazard of working with the more volatile or gaseous hydrocarbons.

The present invention is designed to overcome or reduce these difficulties, and the main novel feature thereof lies in partially oxidizing organic bodies such as hydrocarbons or hydrocarbon derivatives while in finely divided condition, such for example, as vapor or gaseous phase, by means of oxygen derived from a material containing chemically-combined oxygen; instead of using a gaseous stream containing free oxygen, as for example, by mixing the finely divided hydrocarbon with air. The operation is preferably carried out in an atmosphere free or substantially free of air or free oxygen and at a reactive temperature which will cause oxygen to pass from the oxygen-containing material into the hydrocarbon or hydrocarbon derivative. The material which is thus partially or wholly deoxidized is withdrawn from the reaction zone and preferably regenerated by reoxidizing it and then re-used in the process. The oxidant material containing the chemically-combined oxygen may be supplied to the reaction zone and removed therefrom either continuously or intermittently, and is preferably in finely divided form. It may thus be supplied in the form of a continuously or intermittently flowing stream or shower of

finely divided solid material which may be collected and trapped out; or it may be supplied either continuously or intermittently by means of a moving carrier such as a disk provided with an oxidant screen or screens which may be rotated or moved either continuously or intermittently, and through a portion of which the hydrocarbon stream is passed at a temperature within the reaction range. In either case, the material which has been deoxidized either partially or wholly within the reaction zone, is preferably reoxidized, as for example, by subjecting it at a proper temperature to the action of air and may then be re-used in the process.

When the powdered or finely divided oxidant material is used in shower form, it may be trapped out and reoxidized and again fed through the reaction zone; and in the case of the moving oxidant screen the portions other than the portions through which the finely divided hydrocarbon is passing may be subjected to heated air or kept heated in the presence of air to cause the reoxidation before such portions again pass within the reaction zone.

In the preferred form, the operation is cyclic. In one passage of the finely divided hydrocarbon through the oxidant, only a portion of the hydrocarbon will be partly oxidized. The vapor stream will then pass through a condensation scrubbing and washing system to extract the partial oxidation products. The remainder of the exit stream will then again pass through a reaction zone and the oxidizing operation be repeated, using either the same apparatus or another apparatus of similar type. Fresh hydrocarbon is preferably supplied to the exit stream after extraction of the intermediate oxidation products and I usually prefer to also tap out a portion of the remaining gaseous stream and supply fresh hydrocarbon sufficient to replace both the tapped out portion and the recovered portion which has been converted into intermediate oxidation products; before repeating the oxidation process either in the same or a similar apparatus.

The material which I preferably employ as the oxidant preferably consists of metallic oxides and I have discovered that for this purpose the class of metallic oxides which I have disclosed as catalysts in the pending applications above referred to gives the best results. Such oxides are those of the high melting-point, electronegative, low-atomic-volume metals, particularly those having an atomic weight above 40. These metals appear on the Lothar-Meyer diagram of the periodic series beginning on the descending side of the third peak and extending on the descending side of the fourth peak and the descending side of further peaks later developed. This class includes the following metals: titanium, vanadium, chromium, manganese, zirconium, niobium, molybdenum, tantalum, tungsten and uranium. An excellent oxidant for my present purposes consists of the tri-oxide of molybdenum. I prefer to employ the complex oxides of metals having a varying valence. The parts of the complex may consist of oxides of the same metal or of different metals. Such complexes may be regarded as salts, that is, compounds of one or more basic acid oxides. The basic and acid parts of these complexes may be formed from oxides of different metals, in which case each metal or group of metals used should possess varying valence. The basic oxides may be the lower oxides of the metals in the class named or may be the oxides of iron, copper, nickel, lanthanum, cobalt, thorium or eight or nine rare earth metals. In both acid or basic portions there may, of course, be two or more of these combined. I may use chromic-chromate, tungsten-tungstate, etc., for example.

It will be noted that in my new method the hydrocarbon or hydrocarbon derivative is in finely divided form, preferably in the vapor or gaseous phase, while the oxygen derived from a material containing chemically-combined oxygen and preferably in solid finely divided condition. The temperature will vary according to the hydrocarbon or hydrocarbon mixture being treated. Under the conditions named, the hydrocarbon can be partially oxidized to form intermediate products, such as alcohols, aldehydes and acids. During the process, if a solid oxide is employed, the oxide will pass to a lower state of oxidation or to the metal itself.

In the preferred form, the operation is carried out in such a way and the factors, such as rate of gas or vapor flow and feed of oxide, are so controlled that only a part of the total hydrocarbon present is converted during one passage. In such case, the residual hydrocarbon, together with any carbon dioxide present, is preferably returned to the system after adding fresh hydrocarbon to replace that converted and taken up in the absorption system, as well as that which is tapped out if this tapping out is used. The tapping out of a portion of the exit gas beyond the absorbing system is specially desirable in the partial oxidation of hydrocarbons which are gaseous at ordinary temperatures and pressures.

In order to carry out this process, it is necessary to bring fresh oxygen-containing material in contact with the stream of gas or vapor of the organic body being treated. In this process, the hydrocarbon must be in finely divided form, preferably either in the form of a gas or vapor, and hence, if normally a liquid or solid, it should be vaporized, the vapors or gases being brought in contact with the oxidant at a reactive temperature which varies according to the hydrocarbon or hydrocarbon mixture being treated. For example, in the

case of gases from cracking stills containing olefin contents, the temperature may be relatively low (170° and upwards) on account of the unsaturated compounds present. In the case of natural gas, for example, the temperature should be much higher and nearer to but preferably below 600° C.

Throughout the specification and claims, where I use the word "hydrocarbon," I intend to include hydrocarbon derivatives of different kinds.

Where tri-oxide of molybdenum is employed as an oxidant, I have found that this material becomes sticky or gummy as it changes from the higher oxide to one of the lower oxides while the reaction is taking place. In my early experiments, I employed furnaces of the rotating kiln type which are fitted with scrapers acting on the oxide as it traveled through the reaction zone. In this operation trouble was experienced due to the sticking and gumming of the oxide and in the several types of apparatus herein shown, means are provided for overcoming this difficulty.

Referring to the embodiment of the invention illustrated in Figures 1 and 2, 2 is a hopper or bin containing the powdered oxidant and 3 a supply pipe for the fluid hydrocarbon or other organic compound to be treated. Branch pipes 4 lead from the pipe 3 to stoves 5, each containing a heating coil 6 for vaporizing the material to be oxidized. A valve 7 is provided for regulating the flow of hydrocarbon to each stove. Suitable heaters 8 are provided in each stove, these being shown as gas heaters supplied from a gas line 9 and regulated by valves 10.

Each heating coil 6 has a downwardly extending leg 11 terminating inside a common treating chamber 12. This chamber is made of a substantially gas-tight metal casing 13 provided with suitable insulation 14 to conserve the heat.

The legs 11 terminate in a horizontal header 15 provided with nozzles 16 by which the vaporized or gaseous hydrocarbon from the heater 6 is jetted across the treating chamber 12. Outlets 17 are provided on the side of the treating chamber 12 opposite the nozzles 16, and a slot 18 for supplying powdered oxidant from the hopper 2 extends along the top of the treating chamber. Suction means (not shown) are preferably provided for causing the vapors leaving the nozzles 16 to travel across the chamber and find on outlet through the openings 17, and in their travel the vapors encounter the screen S of powdered oxidant issuing from the slot 18. A baffle 19 is provided so that the path of the vapors leaving the nozzle is substantially as indicated by the arrows. The baffle is preferably used to reduce the carrying out of spent oxidant with the gas stream. The solid oxidant tends to drop out of the stream as it turns upwardly. The baffle may also be varied in length to vary the time of contact of the gas and the oxidant in accordance with the materials used, etc.

The powdered oxidant should be heated before it enters the chamber and the quantity supplied should also be carefully regulated. I provide means between the hopper 2 and the slot 18 for attaining both these objects.

The hopper is provided at its bottom with a screen 20 over which there lies a slide 21. This slide consists of side members 22 and cross members 23 and the entire slide is adapted for reciprocation at any desired speed. The reciprocating means is shown in the drawings as consisting of a variable speed motor 24, suitable gearing 25, and a crank disk 26 connected to the slide by a connecting rod 27. By varying the speed of the motor 24 the slide 21 can be reciprocated at any desired rate and the flow of powdered material thus controlled. The screen 20 is preferably carried in a withdrawable slide member 28 for easy replacement.

The material passing through the screen 20 falls through a chamber 29 in which it is raised to the desired temperature. The chamber lies adjacent a heating chamber 30 and the metal division wall 31 is provided with baffles 32 extending into the heating chamber. A burner 33 is placed under the lowest of these baffles and the hot gases from the burner pass upwardly through staggered openings 34 in the baffles. This arrangement maintains the wall 31 at a high temperature and insures proper heating of the oxidant. The other wall may be heat insulated as shown or may be heated in the same way. The chamber 29 terminates in the slot 18 and it will be seen from Figure 2 that a clear path is provided from the hopper into the treating chamber 12. This is desirable as the material used tends to become sticky at higher temperatures and care must be used to prevent it from collecting or building up at any point.

To prevent the material from clogging the slot 18 I provide in the chamber 29 a reciprocating plate 35 having a portion 36 extending adjacent or into the slot 18. The plate 35 is mounted on a rod 37 which extends outside the heating chamber 29 and is provided with an extension 38 connecting the rod to the slide 21. Antifriction bearing balls 39 are provided adjacent the portion 36 so that the entire plate may reciprocate freely. This arrangement effectually prevents clogging of the slot 18. Adjusting nuts 40 are provided so that the plate 35 may be raised or lowered as desired. It is therefore effective not only for keeping the slot 18 free of obstruction but also acts as a regulator for the width of the slot whereby a supplemental adjustment of the amount of material may be effected. The adjusting nuts 40 are reached through

opening in the chamber 29, these openings being provided with covers 41.

The spent oxidant falls to the bottom of the treating chamber 12 where it collects in a pile on a slide 42. At desired intervals the material is withdrawn from the chamber by pushing a slide 43 inwardly so as to seal off the lower portion of the chamber and then withdrawing the slide 42 so that the material thereon falls into a box 44, after which it may be suitably treated and then returned to the hopper 2. The slide 43 substantially prevents the ingress of air to the treating chamber 12 and permits continuous operation of the apparatus without its being affected by outside conditions. The powdered material collects on the slide 43 while the material therebelow is being dumped and the side wall 12^a of the chamber 12 in each case acts as a stripping means for breaking the material loose from the slides 42 or 43 in case it should tend to adhere.

Referring now to the embodiment of the invention illustrated in Figures 3 to 7, the oxidant instead of being used in powdered form is carried by previous screens 50. In a complete cycle of the process the hot hydrocarbon vapors or gases are passed through one of these pads and are thus oxidized, after which the pad is again supplied with oxygen, preferably by subjecting it to heated air. In order to carry out these steps I provide a heating chamber 51 divided into two compartments 52 and 53 by a wheel 54 provided with a series of openings 50^a in which the screens 50 are secured. The periphery of the wheel fits into a recess 55 which acts as a seal so that substantially the only comunication between the portions 52 and 53 of the chamber is through the screens 50. Hot air is supplied to the chamber 52 through a conduit 56 at one side and below and this air passes through the screens 50 and finds an outlet through a stack 57 at the other side of the top. The hot air reoxidizes the oxidant screens for the next treatment of the hydrocarbon vapor, gas or other organic compound being treated.

The oxidation of the hydrocarbons is carried out at a treating station indicated generally by the reference character T and the screens are successively carried through this station by rotating the wheel 54. In Figure 3 there is shown a motor 58 connected to the shaft 59 of the wheel through suitable gearing 60 for causing rotation of the wheel at any desired speed.

The heated vapor is supplied from a conduit 61 having a downwardly extending portion 62 and a horizontal portion 63 extending into the treating station. The construction is shown in detail in Figures 6 and 7. The conduit 63 terminates in a contact member 64 which terminates in a cheek plate 65 and is slidably mounted in the frame 66.

The cheek plate 65 fits into an annular recess 67 in the wheel 51 and it will be noted from Figures 5 and 6 that the openings 50^a in which the pads 50 are fitted terminate in the recess. The contact member 64 is provided with an opening 64^a adapted to register with one of the openings 50^a, while the cheek plates 65 extend vertically so as to cover the adjacent openings 50^a and thus prevent any leakage of hydrocarbon vapors from the conduit 63 into the chamber 52 proper. The annulus 67 is provided with packings 68 extending entirely around the wheel, which serve to materially reduce leakage. Leakage is further prevented by the provision of springs 69 carried by studs 70, mounted in the frame 66 and bearing against a collar 71 secured to the contact member 64. By this arrangement the contact member is continually urged against the wheel and a relatively tight sliding joint is secured.

The contact member 64 is duplicated on the other side of the wheel, this being indicated in Figures 6 and 7 at 64′. The contact member 64′ is provided with a cheek plate 65′ which is coextensive with the cheek plate 65, as best shown in Figure 7.

In operation the vapors to be treated enter through the pipe 63, pass through one of the screens 50 and leave the treating station through a conduit 72. The conduit 72 leads into a downwardly extending conduit 73 connected to an outlet 74 through a swivel joint 75.

It will be noted that the arrangement of inlet and outlet conduits is such that there is a general downflow of the vapors at all times, so that no condensed hydrocarbons can collect anywhere in the apparatus. As shown in Figure 7 the openings through the contact members 64 and 64′ are so arranged that condensed vapors cannot collect therein.

The frame 66 is slidably mounted in a guide 76 built into the furnace wall to permit movement of such frame toward or away from the center of the furnace with expansion or contraction of the wheel. In apparatus of this character the variation in wheel diameter will be a material amount and the arrangement shown prevents jamming of the apparatus. The frame 66 is provided with interior flanges 77 which are packed to prevent leakage. With the movement of the frame 66 inwardly or outwardly, it is of course necessary to move the conduits 63 and 72 correspondingly and the swivel joint 75, together with a similar swivel joint (not shown) on the conduit 61, make this movement possible. Packings 78 are provided on the contact members 64 and 64′ for the conduits 63 and 72 so that expansion longitudinally of these conduits may be provided for while maintaining a tight joint and at the same time permit the slight rotation of the conduits which will be occasioned on a movement of the frame 66.

The wheel illustrated in Figures 3 to 7 has been shown as continuously rotated, but it will be understood that a Geneva movement or similar apparatus for providing an intermitten motion on the wheel may be provided if desired. As shown in Figure 7, the screens 50 are separated from one another only a relatively short distance and when so arranged the continuous rotation is advantageous.

The treating chamber is maintained at suitable temperature by the hot air entering through the opening 56 and the treating station T is so located with respect to the openings 56 and 57 that it will be suitably heated without any undue pressure differential, which would tend to cause leakage, existing at that point. The wheel proper may be made of any suitable material such as cast iron, but it is desirable to make the rim of a close-grained metal which will take a high polish and will not be subject to warping, such as nichrone, invar, or Monel metal. The contact members 64 and 64′ should be made of material which is not subject to warping and preferably has a low coefficient of expansion and contraction. This species of Figures 3 to 7 is not specifically claimed herein, although it is covered and included within the broader method and apparatus claims. It is covered in a divisional application, Serial No. 212,103 filed August 10, 1927.

Referring to Figures 8 and 9, I show in these figures a system and apparatus which I have employed in the carrying out of the process. In Figure 9, 79 represents a stationary tubular casing mounted in an inclined position and carried on upper and lower supports 80 and 81. Through the center of this tubular casing extends a rotary tube 82, rotated by pulley 83 and to the upper end of which the stream of vapor or gas is supplied. The oxidant enters the worm feed chamber 84 through channel 85, the worm 86 driven by pulley 87 carrying the material up into the upper portion of the tubular casing. External heat is applied to the lower portion of the tubular casing, as for example, by a burner conventionally shown at 88, to bring the reactive elements to the reactive range. The upper part of the stationary tubular casing is preferably provided with a surrounding jacket of non-conducting material 89. This heat is applied to the descending granular oxidant which, in turn, heats the gas or vapor stream passing down through the inner rotating tube. The heated stream of vapor or gas preferably emerges from the inner tube at about the point marked A and contacts with the heated stream or shower of the oxidant, both passing out through the connection 90 into a closed trap or reservoir. A chain 91 is shown as connected to pins 92, at the upper and lower portions of the inner tube within the tubular casing and the inner rotation of the inner tube. This chain has a hammering and scraping effect giving a more uniform flow of the oxide down through the casing, and particularly through the reaction zone, stirring it up and causing it to feed out in spite of its stickiness.

The receptacle into which the vapor and oxide material are fed is kept sufficiently heated to allow the products of oxidation to remain in vapor condition until they are carried on into the absorbing system, preferably comprising condensers and scrubbers.

In the preferred form, the general arrangement is shown in the diagram of Figure 8, wherein a cycling system is disclosed which will be understood generally from the names applied to the various parts. The partial oxidation chamber 79 proper is shown in Figure 8 in the center of the diagram, the oxidant material being fed in through channel 85 from the reservoir 93 for fresh or revivified oxidant material. 94 is the motor arranged to drive the pulley 83 fixed to the rotary tube 82 and 95 is another motor arranged to drive the circulating pump 96 and also through the reducing gear 97, the oxidant feed from the fresh oxide reservoir. 98 indicates a supply of raw gas feeding to the gas reservoir 99 from which the gas is led through valve pipe 100 to the gas tube 82 of the partial oxidation chamber. 101 is the spent oxide receiver and 102 is a dust collecting chamber. Both the spent oxide receiver and the dust collector are heated so that the products of partial oxidation can be carried over into the recovery system. These products pass from the dust collector 102 through water condenser 103 to overflow trap 104 and thence through scrubbers and overflow traps as shown. The residual gas stream passes from the last scrubber to the receiver 105 and thence through pipe 106 having bypass 107 with the gas sampling tube and back to the pump 96. From the pump 96 it passes to the treated gas reservoir 108, this having a pressure regulator and a tap out as shown, and from this treated gas reservoir it passes through tube 109 back to the inlet to the partial oxidation chamber where it meets the fresh stream coming from the raw gas reservoir 99.

In carrying out my process with the above described apparatus, the temperatures were recorded by a thermocouple placed either at the center of the outlet from the stationary casing or on the outer wall of said outlet. The readings from the outer wall were about 100° C. higher than those from the thermocouple when placed at the center of the outlet passage.

Inasmuch as natural gas requires a higher reaction temperature than heavier gases, I experimented with hydrocarbon gases heavier

than methane. For example, the so-called "liquid gas" made from casing head gas by removal of the gasoline therein. This was supplied in liquid form and consisted of ethane about 20%, propane about 60% and butane about 20%. In the first run with this material, the rate of gas flow was $\frac{1}{10}$ liter per minute (without cycling) and the feed of molybdenum tri-oxide was approximately 4.3 grams per minute. The temperature at the spent oxide exit was 400° C. The length of the run was 2½ hours. A sample of the gas collected at about the middle of the run when conditions were substantially normal showed the following by volume:

	Per cent
Carbon dioxide (CO_2)	None
Oxygen (O_2)	1.7
Unsaturated hydrocarbons of the C_nH_{2n} series	.7
Carbon monoxide	None

The products caught in the water scrubbers on one passage were:

	Per cent
Aldehyde (calculated as propionic) based on weight of gas fed	.096
Acid (calculated as propionic) based on weight of gas calculated as propane	.42

This run showed that a higher temperature was needed, so the next run was as follows:
Rate of gas flow—$\frac{1}{10}$ liter per minute (without cycling)
Rate of oxide (MoO_3) feed—5.65 grams per minute
Temperature—400° C.
Length of run—two hours
The gas analysis with percentages by volume gave:

	Per cent
Carbon dioxide (CO_2)	2.4
Oxygen (O_2)	.2
Unsaturated hydrocarbons of the C_nH_{2n} series	1.3
Carbon monoxide	None

The products gave aldehyde (calculated as propionic) .77% based on the weight of gas treated; acid (calculated as propionic) .93% based on the weight of gas treated calculated as propane.

In the next experiment, a still higher temperature was employed as follows:
Rate of gas flow—$\frac{1}{10}$ liter per minute (without cycling)
Rate of oxide feed—approximately 6 grams per minute
Temperature—520° C. at the center of the outlet
Length of run—45 minutes
The gas analysis showed:

	Per cent
Carbon dioxide	5.8
Oxygen	1.3
Unsaturated hydrocarbons	2.9
Carbon monoxide	None

The products showed:

	Per cent
Aldehyde (calculated as propionic)	1.77
Acid (calculated as propionic)	2.55

These examples were based on the weight of the gas treated (calculated as propane).

In this run, the acid and aldehyde products represent 47.3% of the gas actually attacked, the remainder of the hydrocarbon appearing unchanged in the exit gas.

In the fourth run, the conditions were as follows:
Rate of gas flow—$\frac{1}{10}$ liter per minute (without cycling)
Rate of oxide feed (MoO_3)—4.5 grams per minute
Temperature taken on the outside of the exit tube—430° C. (estimated as 530° C. on the inside)
Length of run—1 hour, 40 minutes.
The gas analysis showed:

	Per cent
Carbon dioxide	13.0
Oxygen	None
Unsaturated hydrocarbons	2.8
Carbon monoxide	None

The products from the absorbing system showed:

	Per cent
Aldehyde (calculated as propionic)	3.95
Acid (calculated as propionic)	4.07

These are based on the weight of gas calculated as propane.

Since the remainder of the exit gas is unchanged hydrocarbon, calculating the above acids and aldehydes as a percentage of the gas actually attacked, the results showed that approximately 53% of the gas so attacked passed into acid and aldehyde in the proportion above given.

Run 5

Rate of gas flow—$\frac{1}{10}$ liter per minute (without cycling)
Rate of oxide feed—4.2 grams per minute
Temperature—measured on the outside of the exit tube—500° C., giving an estimated temperature of 600° C. at the inside of the exit.

The gas analysis was:

	Per cent
Carbon dioxide	30.6
Oxygen	.6
Unsaturated hydrocarbons	4.2
Carbon monoxide	None

The products showed:

	Per cent
Aldehyde (calculated as propionic)	4.8
Acid (calculated as propionic)	5.1

These are based on the weight of gas calculated as propane. This percentage of product is 41.5% of the hydrocarbon actually attacked, the remainder being unchanged in the exit gas.

The aldehyde and acid in the above tests were calculated to the propane derivatives, since the gas treated was 60% propane at the beginning and as the liquid evaporated, this would give a gas largely propane at about the middle of the tank contents. The evidence also shows that the acid was largely propionic.

In the above experiments, the gas was not cycled. From the calculations where the acid and aldehyde are based on the hydrocarbon actually attacked, it will be seen that the products represent from 40% to 50% of the hydrocarbon actually attacked. Hence, the unchanged hydrocarbon should be converted by resubjecting it to the process either in the same or successive apparatus. It will further be noted that the carbon dioxide in the exit gas will (by the mass action effect) serve to reduce and retard the formation of more carbon dioxide on the second and further passages. Hence, by cycling the gas, the yields will amount to at least 50% of the total hydrocarbon treated.

In carrying out the "cycling" operation, I may employ the apparatus of Figure 8, in which case the gas is supplied to the inner rotary tube of the oxidation chamber while at the same time fresh oxide is fed around the tube into the upper end of said chamber. After its descent through this stationary tube the oxidant becomes heated and thereby heats the gas in the tube. The gas then issues from the tube toward its lower portion and meeting the oxidant withdraws oxygen therefrom. The gas mixture and the spent oxidant then pass out into the spent oxide receiver 101, thence through the dust collector, water condenser, scrubbing system, etc., back to the circulating pump which feeds the residual gas stream into the treated gas reservoir where a portion may be tapped out as above described if desired. From the treated gas reservoir the gas is then passed through suitable controls back to the entrance to the partial oxidation chamber where it is mixed with the fresh gas coming from the raw gas reservoir.

I have also found that the sticking or gumming of the molybdenum oxide in the reactive zone may be reduced or partly obviated by adding finely divided inert material to the powdered oxidant. Thus, I may employ with the oxidant an equal volume of uniformly graded fine silica sand with advantage. In this case, the passage through the apparatus was more easily accomplished.

It will be noted that in all cases, the hydrocarbon in vapor or gaseous phase or other finely divided condition is brought in contact with an oxidant under a temperature such as to give a reaction, causing oxygen to leave the oxidant and become chemically tied into the hydrocarbon. The temperature will vary from a relatively low temperature where the vapor or gas stream contains a large amount of unsaturated compounds, such as cracking still gases, to a relatively high temperature around 500° to 600° or 700° C. in the case of methane or fixed gases requiring higher temperatures for the reaction.

I prefer to employ a short time of sojourn or contact between the vapors or gaseous stream and the oxidant to carry the exit gases away from the reactive zone as rapidly as possible to avoid secondary reactions, particularly where the lighter hydrocarbons are being treated.

I do not intend to confine my process to saturated aliphatic hydrocarbons. The method may be used for the production of valuable products from unsaturated hydrocarbons of the aliphatic series, as well as from naphthenic, terpenic and aromatic hydrocarbons. Thus, the process is readily adapted to the production of benzaldehyde and benzoic acid from toluene, as well as to the production of phthalic anhydride from naphthalene and to the production of maleic acid from benzene. It may also be applied to the treatment of alcohols to form aldehydes and acids, such for example, as ethyl alcohol or other derivatives as the raw material treated, or to mixtures of hydrocarbons and hydrocarbon derivatives.

I consider myself the first to partially oxidize hydrocarbons in the vapor or gaseous phase by means of oxygen derived from a material in which the oxygen is chemically combined and is transferred from the oxidant to the hydrocarbon or hydrocarbon derivative in the reaction zone. While the class of oxidants I have disclosed is preferable, other oxidants may be employed.

In carrying out my process I may employ either sub-atmospheric pressure or superatmospheric pressure within the partial oxidation chamber. In the form where the rotary carriage having catalytic screens is employed in the vapor feed pipe and the outlet pipe may be moved in a circular path instead of moving the screens. In other words the movement may be relative.

The advantages of my invention are especially important in connection with lighter hydrocarbons, although the process may be employed on heavier hydrocarbons.

By the term "solid oxidant material" in my claims, I intend to cover any solid material which, under the general conditions recited herein, will yield oxygen to the organic material and become chemically tied thereinto, and which oxidant material if reused in the process, must be renewed or revivified by adding oxygen thereto, this being preferably at a point removed from the reaction zone and at a higher temperature than normally exists in the reaction zone, such temperature being obtained by the addition of heat.

I do not claim herein the metallurgical method of reducing metallic oxides to metals

herein disclosed, as that invention is covered in the claims of my copending divisional application Ser. No. 550,147, filed July 11, 1931.

I claim:

1. In the method of partially oxidizing organic bodies, the steps consisting of feeding in finely divided condition an organic body containing hydrogen and carbon as its major constituents in a substantially non-oxidizing atmosphere into contact with solid oxidant material at a reactive temperature, said oxidant material being capable of yielding oxygen to the organic body, thereby causing oxygen to pass from the oxidant material into the organic body, and withdrawing the oxidant material from the reaction zone and reoxidizing it.

2. In the method of partially oxidizing organic bodies, the steps consisting of feeding in finely divided condition an organic body containing hydrogen and carbon as its major constituents in a substantially non-oxidizing atmosphere into contact with solid oxidant material at a reactive temperature, said oxidant material being capable of yielding oxygen to the organic body, thereby causing oxygen to pass from the oxidant material into the organic body, and withdrawing the oxidant material from the reaction zone during a reaction period.

3. In the method of partially oxidizing organic bodies, the steps consisting of feeding in finely divided condition an organic body containing hydrogen and carbon as its major constituents in a substantially non-oxidizing atmosphere into contact with solid oxidant material at a reactive temperature, said oxidant material being capable of yielding oxygen to the organic body, thereby causing oxygen to pass from the oxidant material into the organic body, and withdrawing the oxidant material from the reaction zone during a reaction period and reoxidizing it.

4. In the method of partially oxidizing organic bodies, the steps consisting of feeding in finely divided condition an organic body containing hydrogen and carbon as its major constituents in a substantially non-oxidizing atmosphere into contact with solid oxidant material at a reactive temperature, said oxidant material being capable of yielding oxygen to the organic body, thereby causing oxygen to pass from the oxidant material into the organic body, and withdrawing the oxidant material from the reaction zone and reoxidizing it and reusing it in such process.

5. In the method of partially oxidizing organic bodies, the steps consisting of feeding in finely divided condition an organic body containing hydrogen and carbon as its major constituents in a substantially non-oxidizing atmosphere into contact with solid oxidant material at a reactive temperature, said oxidant material being capable of yielding oxygen to the organic body, thereby causing oxygen to pass from the oxidant material into the organic body, and withdrawing the oxidant material from the reaction zone and reoxidizing it.

6. In the method of partially oxidizing organic bodies, the steps consisting of passing through a hot reaction zone having a substantially non-oxidizing atmosphere, solid oxidant material which will yield oxygen to an organic body, passing an organic body containing carbon and hydrogen as the major constituents in finely divided condition through said reaction zone in contact with the oxidant material at a reactive temperature, thereby causing oxygen to pass from the material into the organic body, and withdrawing the oxidant material.

7. In the method of partially oxidizing organic bodies, the steps consisting of passing through a hot reaction zone having a substantially non-oxidizing atmosphere, solid oxidant material which will yield oxygen to an organic body, passing an organic body containing carbon and hydrogen as the major constituents in finely divided condition through said reaction zone in contact with the oxidant material at a reactive temperature, thereby causing oxygen to pass from the material into the organic body, and withdrawing the oxidant material and reoxidizing it.

8. In the method of partially oxidizing organic bodies, the steps consisting of passing through a hot reaction zone having a substantially non-oxidizing atmosphere, solid oxidant material which will yield oxygen to an organic body, passing an organic body containing carbon and hydrogen as the major constituents in finely divided condition through said reaction zone in contact with the oxidant material at a reactive temperature, thereby causing oxygen to pass from the material into the organic body, and withdrawing the oxidant material during a reactive period.

9. In the method of partially oxidizing organic bodies, the steps consisting of passing through a hot reaction zone having a substantially non-oxidizing atmosphere, solid oxidant material which will yield oxygen to an organic body, passing an organic body containing carbon and hydrogen as the major constituents in finely divided condition through said reaction zone in contact with the oxidant material at a reactive temperature, thereby causing oxygen to pass from the material into the organic body, and withdrawing the oxidant material and reoxidizing it and reusing it in such process.

10. In the method of partially oxidizing organic bodies, the steps consisting of passing through a hot reaction zone having a substantially non-oxidizing atmosphere a relatively thin layer of solid oxidant material which will yield oxygen to an organic body,

passing an organic body containing carbon and hydrogen as the major constituents in finely divided condition through said reaction zone in contact with the oxidant material at a reactive temperature, thereby causing oxygen to pass from the material into the organic body, and withdrawing the oxidant material.

11. In the method of partially oxidizing organic bodies, the steps consisting of passing through a hot reaction zone having a substantially non-oxidizing atmosphere, solid oxidant material which will yield oxygen to an organic body, passing an organic body containing carbon and hydrogen as the major constituents in finely divided condition through said reaction zone in contact with the oxidant material at a reactive temperature, thereby causing oxygen to pass from the material into the organic body, and trapping out the oxidant material.

12. In the method of partially oxidizing organic bodies, the steps consisting of passing through a hot reaction zone having a substantially non-oxidizing atmosphere finely divided solid oxidant material which will yield oxygen to an organic body, passing an organic body containing carbon and hydrogen as the major constituents in finely divided condition through said reaction zone in contact with the oxidant material at a reactive temperature, thereby causing oxygen to pass from the material into the organic body, and withdrawing the oxidant material.

13. In the method of partially oxidizing organic bodies, the steps consisting of passing an organic body containing carbon and hydrogen as the major constituents while in finely divided condition in contact with solid oxidant material which will yield oxygen to the organic body and will reoxidize on exposure to oxygen, in a substantially non-oxidizing atmosphere at a reactive temperature, thereby causing oxygen to pass from the oxidant material into the organic body, and cycling at least a part of the exit stream through such a reaction zone.

14. In the method of partially oxidizing organic bodies, the steps consisting of passing an organic body containing carbon and hydrogen as the major constituents while in finely divided condition in contact with solid oxidant material which will yield oxygen to the organic body and will reoxidize on exposure to oxygen, in a substantially non-oxidizing atmosphere at a reactive temperature, thereby causing oxygen to pass from the oxidant material into the organic body, and cycling at least a part of the exit stream including carbon dioxide.

15. In the method of partially oxidizing organic bodies, the steps consisting of passing an organic body containing carbon and hydrogen as the major constituents while in finely divided condition in contact with solid oxidant material which will yield oxygen to the organic body and will reoxidize on exposure to oxygen, in a substantially non-oxidizing atmosphere at a reactive temperature, thereby causing oxygen to pass from the oxidant material into the organic body, removing products from the exit stream and cycling some of said stream.

16. In the method of partially oxidizing organic bodies, the steps consisting of passing an organic body containing carbon and hydrogen as the major constituents while in finely divided condition in contact with solid oxidant material which will yield oxygen to the organic body and will reoxidize on exposure to oxygen, in a substantially non-oxidizing atmosphere at a reactive temperature, thereby causing oxygen to pass from the oxidant material into the organic body, removing products from the exit stream, adding an organic body of the same type and again passing the mixture through a reactive zone.

17. In the method of making organic compounds, the steps consisting of feeding a stream of an organic compound of the hydrocarbon type through an enclosed reactive zone, bringing it into contact in said zone with successive portions of a solid chemical compound, chemically tying an element of the solid chemical compound into said organic compound, and withdrawing and recovering products from the stream.

18. In the method of making organic compounds, the steps consisting of feeding a stream of an organic compound of the hydrocarbon type through an enclosed reactive zone, bringing it into contact in said zone with successive portions of a solid chemical compound at a temperature below red heat, chemically tying a normally gaseous element of the solid chemical compound into said organic compound, and withdrawing and recovering products from the stream.

19. In the method of making organic compounds, the steps consisting of feeding a stream of an organic compound through an enclosed reactive zone, passing all parts of said stream through and in intimate contact in said zone with successive portions of a solid chemical compound, chemically tying a normally gaseous element of the solid chemical compound into said organic compound, and withdrawing and recovering products from the stream.

20. In the method of making organic compounds, the steps consisting of feeding a stream of an organic compound of the hydrocarbon type through an enclosed reactive zone, bringing it into contact in said zone with successive portions of a solid chemical compound at a temperature below a temperature of continuous self-sustained combustion, chemically tying a normally gaseous element of the solid chemical compound into said or-

ganic compound, and withdrawing and recovering products from the stream.

21. In the method of partially oxidizing organic bodies, the steps consisting of feeding a gaseous-phase stream of a compound containing hydrogen and carbon through a hot reaction zone having a sufficient supply of a non-gaseous chemical compound containing chemically combined oxygen and having the property of releasing the combined oxygen under the conditions in the hot reaction zone to supply oxygen to combine with a material proportion of the hydrogen-carbon compound, maintaining in said zone reactive conditions which cause oxygen to be withdrawn from its compound and combine with the hydrogen-carbon compound to form the major portion of hydrogen-carbon-oxygen compounds produced therein, and causing relative movement between the compounds to bring the gaseous-phase stream in contact with further non-gaseous oxygen-containing compounds.

22. In the method of partially oxidizing organic bodies, the steps consisting of feeding a gaseous-phase stream of a compound containing hydrogen and carbon through a hot reaction zone having a sufficient supply of a non-gaseous chemical compound containing chemically combined oxygen and having the property of releasing the combined oxygen under the conditions in the hot reaction zone to supply oxygen to combine with a material proportion of the hydrogen-carbon compound, maintaining in said zone reactive conditions which cause oxygen to be withdrawn from its compound and combine with the hydrogen-carbon compound to form the major portion of the hydrogen-carbon-oxygen compounds produced therein, causing relative movement between the compounds to bring the gaseous-phase stream in contact with further non-gaseous oxygen-containing compounds, and regenerating the non-gaseous oxygen-containing material by chemically combining oxygen therewith.

23. In the method of partially oxidizing organic bodies, the steps consisting of feeding a gaseous-phase stream of a compound containing hydrogen and carbon through a hot reaction zone having a sufficient supply of a non-gaseous chemical compound containing chemically combined oxygen and having the property of releasing the combined oxygen under the conditions in the hot reaction zone to supply oxygen to combine with a material proportion of the hydrogen-carbon compound, maintaining in said zone reactive conditions which cause oxygen to be withdrawn from its compound and combine with the hydrogen-carbon compound to form the major portion of hydrogen-carbon-oxygen compounds produced therein, causing relative movement between the compounds to bring the gaseous-phase stream in contact with further non-gaseous oxygen-containing compounds, and supplying heat and oxygen to the non-gaseous oxygen-containing material exteriorly of the reaction zone to regenerate it.

24. In the method of partially oxidizing organic bodies, the steps consisting of feeding a gaseous-phase stream of a compound containing hydrogen and carbon through a hot reaction zone having a sufficient supply of a non-gaseous chemical compound containing chemically combined oxygen and having the property of releasing the combined oxygen under the conditions in the hot reaction zone to supply oxygen to combine with a material proportion of the hydrogen-carbon compound, maintaining in said zone reactive conditions which cause oxygen to be withdrawn from its compound and combine with the hydrogen-carbon compound to form the major portion of hydrogen-carbon-oxygen compounds produced therein, and supplying fresh oxygen-containing material to the reaction zone and removing spent material therefrom.

25. In the method of partially oxidizing organic bodies, the steps consisting of feeding in a finely divided stream a compound containing hydrogen and carbon, said stream being substantially free from free oxygen, through a hot reaction zone having a sufficient supply of a chemical compound containing oxygen and having the property of releasing the oxygen under the conditions in the hot reaction zone to supply oxygen to combine with a material proportion of the hydrogen-carbon compound, maintaining in said zone reactive conditions which cause oxygen to be withdrawn from its compound and combine with the hydrogen-carbon compound to form the major portion of hydrogen-carbon-oxygen compounds produced therein, and causing relative movement between the compounds to bring the gaseous-phase stream in contact with further oxygen-containing compounds.

26. In the method of partially oxidizing organic bodies, the steps consisting of feeding in a finely divided stream a compound containing hydrogen and carbon, said stream being substantially free from free oxygen, through a hot reaction zone having a sufficient supply of a chemical compound containing oxygen and having the property of releasing the oxygen under the conditions in the hot reaction zone to supply oxygen to combine with a material proportion of the hydrogen-carbon compound, maintaining in said zone reactive conditions which cause oxygen to be withdrawn from its compound and combine with the hydrogen-carbon compound to form the major portion of hydrogen-carbon-oxygen compounds produced therein, causing relative movement between the compounds to bring the gaseous-phase

stream in contact with further non-gaseous oxygen-containing compounds, and regenerating the non-gaseous oxygen-containing material by chemically combining oxygen therewith.

27. In the method of partially oxidizing organic bodies, the steps consisting of feeding in a finely divided stream a compound containing hydrogen and carbon, said stream being substantially free from free oxygen, through a hot reaction zone having a sufficient supply of a chemical compound containing oxygen and having the property of releasing the oxygen under the conditions in the hot reaction zone to supply oxygen to combine with a material proportion of the hydrogen-carbon compound, maintaining in said zone reactive conditions which cause oxygen to be withdrawn from its compound and combine with the hydrogen-carbon compound to form the major portion of hydrogen-carbon-oxygen compounds produced therein, and supplying fresh oxygen-containing material to the reaction zone and removing spent material therefrom.

In testimony whereof I have hereunto set my hand.

JOSEPH H. JAMES.