

Sept. 15, 1936.

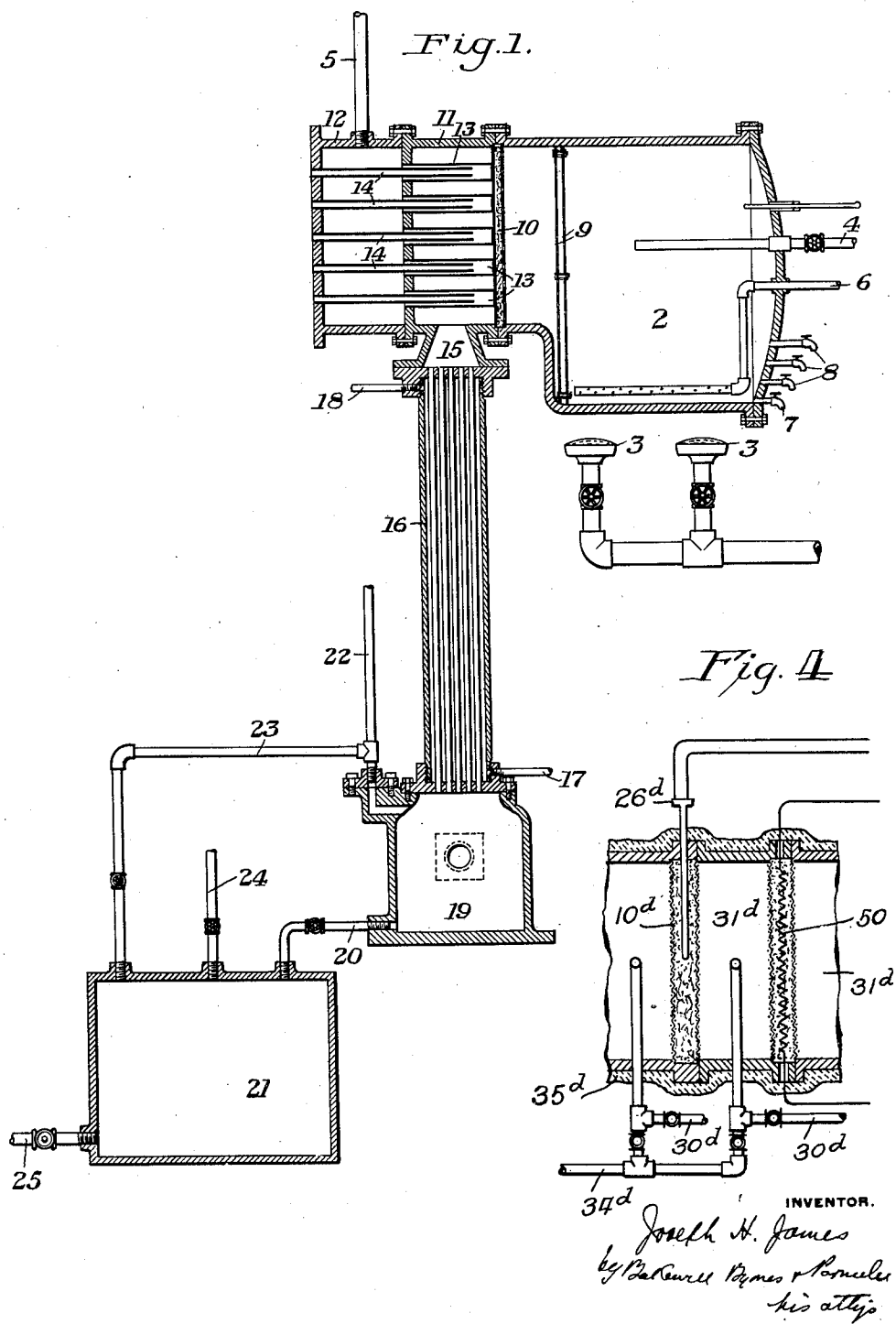
J. H. JAMES

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PARTIAL COMBUSTION METHOD FOR TREATING ALIPHATIC HYDROCARBONS

Filed Jan. 6, 1921

2 Sheets-Sheet 1



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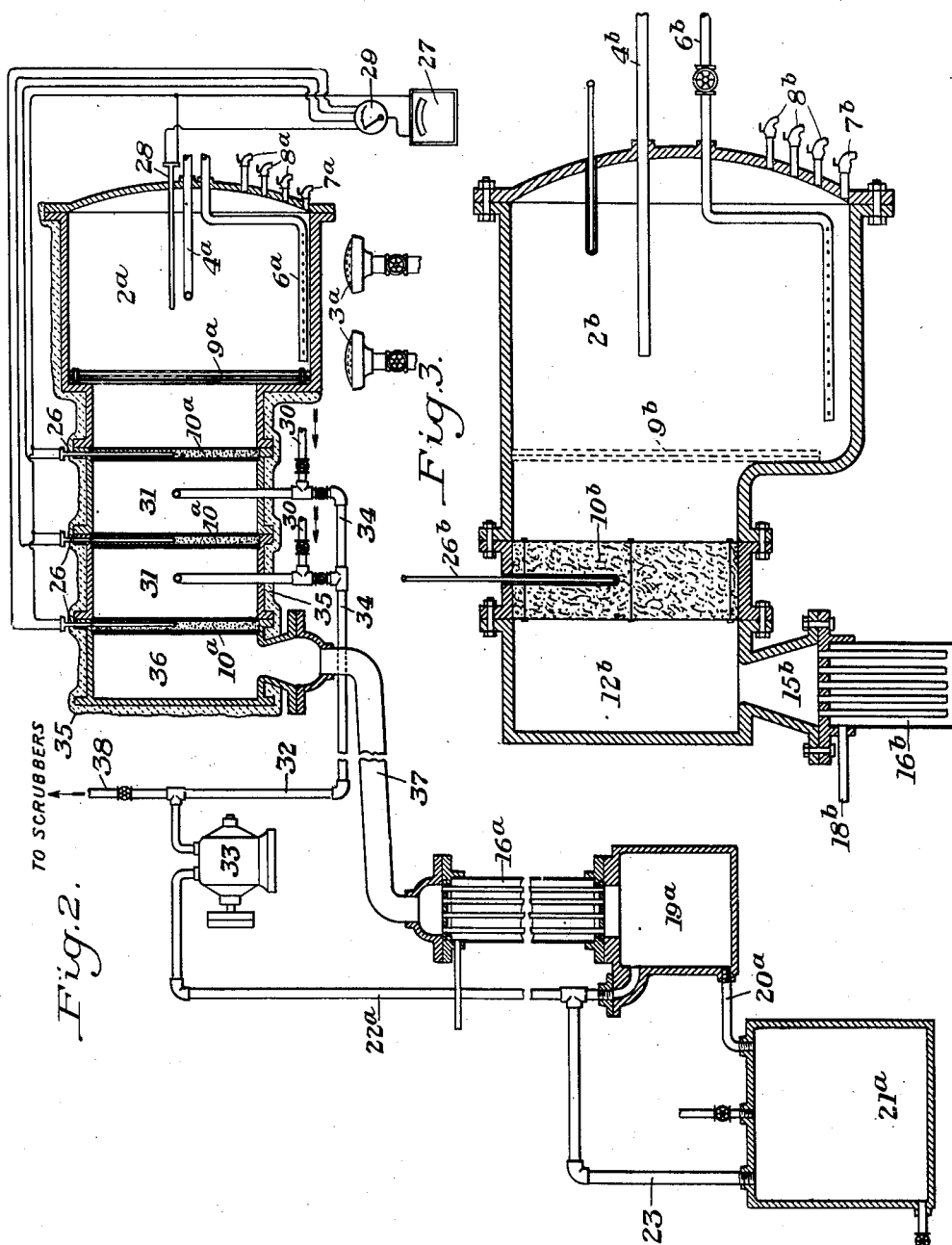
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2 Sheets-Sheet 2



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UNITED STATES PATENT OFFICE

2,054,571

PARTIAL COMBUSTION METHOD FOR
TREATING ALIPHATIC HYDROCAR-
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Application January 6, 1921, Serial No. 435,355

37 Claims. (Cl. 260—116)

The present invention relates to improvements upon the method set forth in my pending application Serial No. 272,567, filed January 22, 1919, and certain other pending applications. In a large amount of further work done on such meth-

ods, I have discovered means and methods for controlling the temperature of the reactions, and for increasing the percentages of useful products obtained and improving their quality for certain uses. I have also discovered that I can, simultaneously therewith, produce material percentages of hydrocarbon products, such as motor spirit, of less molecular weight than the hydrocarbon treated, owing to thermal decomposition. I have also found an improved way of handling hydrocarbons of high molecular weight such as are contained in large amounts in the cheaper petroleums; and which are difficult to vaporize and even when subjected to my main process give poorer products. For example, taking a heavy fraction from Mexican or California petroleum, I subject this or still heavier fractions, to the old-fashioned atmospheric pressure cracking distillation in vertical stills, as in the former process used to increase the amount of kerosene produced. By suitable regulation of the step it is possible to convert 70 to 80% of a heavy hydrocarbon fraction into a product having a specific gravity about the same as that of Pennsylvania gas oil. This contains a considerable percentage of olefin hydrocarbons, being made up partly of those already present and partly from the cracking operation. It also may contain some acetylene hydrocarbons. This distillation may be completely carried out so that all the material is cracked and distilled except a layer of cake which remains and is dug out of the still.

This operation lowers the boiling point and permits of easier handling in my main partial combustion process. If, for producing motor spirit, or special flotation oil, for example, by my process, a hydrocarbon of still lower molecular weight is desired, this "cracked" product may be subjected to vapor phase cracking, preferably at about 400° C. and in the presence of a catalyst. Such catalyst may be any of those hereinafter mentioned, and in addition finely divided metals, such as nickel. In either case the product oxidizes more easily in my process of partial combustion, and may in many cases be oxidized at a lower temperature, even as low as 170° to 180° C.

I have also discovered that, by increasing the depth or thickness of the catalytic layer in such

processes, I can improve both the quality and quantity of products obtained for certain purposes; while at the same time increasing the amount of lower boiling point hydrocarbons produced. Under this phase of the invention, I may increase the total depth or thickness of the catalytic layer either by increasing the thickness of a single layer of the material, or by using a series of separated layers, or by both. I prefer to use a succession of separated layers, and in such case I prefer to admit additional air to the hot mixed vapor material between each pair of catalytic layers; and to mix only a portion of the total amount of air required, with the vapor passing to the first layer.

I also prefer to suck the vapor-air-mixture through the apparatus by a suction or exhaust device at the outlet end, located either between the catalyst and the condenser, or beyond the condenser and between the condenser and the scrubbers, if the latter are used.

Where catalytic layers of relatively large area are employed under my method, I have found that there is difficulty in controlling the temperature in the reaction zone. The partial combustion reaction gives out heat, and with layers of large area the temperature tends to build up and to rise with considerable rapidity as the reactions proceed. With larger area layers, the heat generated will, of course, escape less easily than with those of smaller area.

I have found several ways of overcoming this trouble with relatively large area layers.

First.—I decrease the amount of air supplied for the mixture and which I would otherwise supply to considerably above that theoretically required to combine with and oxidize the vapor. I cut down this air percentage to more nearly the theoretical amount, or to such theoretical amount, or even below it, as the temperature rises above that desired, during the run.

Second.—I supply a diluent, such as steam supplied as water fed into the vaporizer in regulated amounts; or I may use fume gas fed into the mixture.

Third.—I employ several separated layers of catalytic material and supply only a portion of the total air to the mixture passing to and through each screen. This is my preferred form.

Fourth.—I may artificially cool the layer, particularly where only one layer is used; by applying cooling fluid, directly or indirectly, to the outlet side of the layer.

Any one, or several, or all of these systems of controlling the temperature may be used.

Reducing the air percentage or supplying steam or other diluent tends to retard the reactions in the reaction zone. Where the amount of air is reduced, or steam is supplied to hold down the temperature, the amount of partial combustion products will be somewhat reduced, where a single screen is used; though this system is entirely practicable without the use of special cooling devices.

By using a series of separated catalytic layers with regulated air inlets between them, I can carry out the reactions in a step-by-step manner while more effectually controlling the temperature and keeping it within the desired limits at each layer. In this system the added air supplied later will make up for the original deficit and for the dilution by nitrogen after the first reaction.

If a cooling system is used, cooling pipes with closed ends may be applied at the outlet side of the catalytic layer, the blind ends being either in contact with the layer, or embedded therein, or spaced at a slight distance therefrom. If the asbestos or other carrier coated or impregnated with the catalytic material is packed between wire mesh screens, as I prefer, the wire screen may be cut away or punctured to receive the closed ends of the pipes; or these ends may simply contact with the wire screen. By controlling the flow of cooling fluid through this cooling system, I can aid in controlling the temperature and keeping it within the desired limits. Water or air cooling may be used, and the latter, if used, may pass through the cooler by natural or forced draft. In all cases this cooling should be on the outlet side, as the hot vapor mixture must be kept in the vapor phase as it passes into and through the reaction zone. Hence strong cooling of the vapor-air mixture as it approaches the reaction zone would be objectionable.

In many cases, particularly where larger screens are used, my new discoveries will, especially for certain products, avoid the need or desirability of re-vaporizing the condensed products and again treating them in accordance with my partial combustion process; and at the same time, the total value of the products is increased, both by the production of a light hydrocarbon and by the improved quantity and quality of the partial combustion products obtained, especially where a greater total thickness of layer or layers is used.

With a succession of separated layers, the aldehyde fatty acids produced are of better quality, being more free from substances which polymerize and impart objectionable odors and colors to the products, such as soaps, made therefrom, than with a thin screen. Materials having objectionable odors may be largely deodorized by heating the product and blowing air through it for a few hours.

In the drawings,

Figure 1 is a vertical section showing one form of apparatus for carrying out my invention;

Figure 2 is a vertical section of a plural layer system;

Figure 3 is a vertical section of apparatus having a single relatively thick catalytic layer; and

Figure 4 is a broken section showing electrical heating means for the first screen where cracking or formation of unsaturated compounds is desired thereat.

Referring to the form of Figure 1, 2 represents the vaporizing and air mixing chamber, and 3, 3, suitable gas burners beneath the same.

4 represents an oil inlet pipe from which the oil may drop upon a baffle plate, if desired. 6 is the air inlet pipe. 7 is a drain cock, and 8 designates try-cocks. At the outlet end of the chamber, it is decreased in size somewhat, and in this portion are arranged two metallic screens 9, 9, consisting of thin metallic plates with perforations through them, the perforations in one plate preferably being staggered relatively to those in the next. These serve to more thoroughly mix the vapor and air, and also aid in preventing any unvaporized oil from reaching the reaction zone. 10 is a catalytic layer which may contain a thermometer or pyrometer couple for giving a preferably continuous reading of the temperature at the reaction zone.

In this form, I show means for cooling the outlet side of the screen or cooler. This means, as shown has two circular castings 11 and 12, secured to each other and to the outlet flange of the retort chamber. The casting 11 has closed end tubes 13, with their open ends secured in its rear wall, and the casting 12 has smaller open end tubes 14, with their rear ends secured in its rear wall. Water or air is circulated through this pipe system, the cooling fluid either entering the small tubes and passing back through the large tubes to a stack or outlet 5, or vice versa. The closed ends of the large tubes may contact with the outlet face of the catalytic layer or the enclosing metal screen, or may be embedded in the layer, or may be spaced a slight distance apart from the layer and screen. In all cases the intent is to abstract heat from the reaction zone to a regulable amount in order to control the temperature.

The bottom of the casting 11 is provided with an outlet channel 15, which leads to an ordinary condenser 16 having water inlet 17 and water outlet 18. The products condensing in the tubes of this condenser drop into the condenser vessel 19, from which they may be tapped out through a pipe 20 into a product receiver 21. A pipe 22 leads from the closed vessel 19 to a vacuum pump, and an equalizing vacuum pipe 23 preferably connects the two vessels 19 and 21, to provide freer discharge of the liquid product. 24 is a valved vent pipe, and 25 a valved tap for the receiver.

In the use of this apparatus, the oil entering in a regulated feed is vaporized in the chamber 2 and mixed with a regulated amount of air entering through the pipe 6. The hot hydrocarbon vapor and air mixture passes through the perforated plates 9, and thence through the catalytic layer, where the partial combustion reactions take place. On leaving the layer, the products strike the cooling system and pass down through the condenser into the collector.

Steam may also be fed in in regulated amounts to the vaporizing chamber, although this is not necessary where the cooling system is properly arranged and handled. A thin screen or a thicker screen may be used in this apparatus, depending partly upon the kind of product desired. If the heavier petroleum fractions are being used, steam will aid in vaporization and also as a temperature equalizer. It also aids in keeping the catalyst free from heavy organic materials, such as tars, which may tend to coat it and retard the passage of the mixture. In fact, although steam retards the action of the process, it is in some cases of industrial advantage, especially with a greater depth of catalyst; or with a series of catalytic layers, the continued action of which will

compensate for this retardation and complete the reactions to aldehyde fatty acids.

In carrying out these partial oxidation processes on this single screen form without lagging, the screens or catalytic layers sometimes become clogged, due to deposits which are apparently made up of carbon, tars or similar material. This difficulty, if it occurs, can be overcome by blowing out or burning up the layer. In carrying this out, I shut off the oil feed and while keeping on the burners pass heated air through the screen for a sufficient time to clean it, or use steam in the same way or both. By subjecting the screen to this action, at desired intervals, it can be kept in the desired porous and active condition. This clogging appears to be largely mechanical, and I have thus far found no chemical "sickening" action on the catalytic material, which, when properly prepared, remains active indefinitely. Another way of cleaning the layer consists in switching off the heavier oil feed and switching in a kerosene feed for a short interval of, say, one-half hour, at suitable periods, when desired. This will serve to clear the catalytic layer probably by dissolving and releasing the gummy compounds. A wire screen may be embedded in the catalyst layer and this may be connected to a source of electric current to heat the same to incandescence, when desired, in order to start combustion of the carbonaceous substances collecting in and clogging the catalytic material.

In this apparatus, the temperature of the reaction zone may be controlled by regulating the vaporizing burners, by regulating the amount of air introduced, by introducing regulated amounts of a diluent, such as steam or fume gas, and by passing cooling fluid through the cooling pipes at a regulated speed.

As illustrating the effect of a cooling system, I will describe the following example:

With a layer of catalytic material 15" in diameter and $\frac{3}{8}$ " thick and the cooling system having the closed pipe ends set against the outer screen plate which holds the catalytic material in place, an experiment was made without any water circulating through the cooling system. In this case, the temperature of the catalyst rose too rapidly for good practice, the oil being fed at 9.7 liters per hour and the air at about 7 cu. ft. per minute. This test shows that the temperature rose so rapidly that with the particular hydrocarbon air ratio used, it would soon reach a point where the reactions would pass into another and undesirable phase.

The cooling system above shown was then connected so that cold water was circulated in through the smaller pipes and back through the other pipes and the water exit. Under these conditions, another experiment was carried out. In this case, with oil fed at the rate of 9.7 liters per hour and air at the rate of 6 cu. ft. per minute, with suitable regulation of the heat under the vaporizer, the temperature was held at the desired point of about 370 to 380° C. The oil treated was Waverly gas oil with a specific gravity of .832 and the water entered at a temperature of about 10° C. and was at a temperature of 27° C., as it emerged from the condenser. The total oil fed in this case was about 37.5 liters and the product recovered amounted to 19 liters containing about 45% of aldehyde fatty acids insoluble in water. The reaction was kept under good control and a good quality of products produced.

I will now describe a multiple screen form of my apparatus, one type of which is shown in

Figure 2. In this figure, 2^a is the vaporizing and air mixing chamber, and 3^a the burners underneath the same. 4^a is the oil admission pipe; 6^a the air admission pipe; 7^a the drain cock, and 8^a try-cocks. 9^a are separated metallic screens consisting of thin metallic plates with staggered perforations, these serving to give an excellent mixture and prevent liquid spray from reaching the reaction zone. 10^a are three catalytic layers spaced apart from each other. Each catalyst layer is preferably formed of asbestos carrying the catalyzing material, and is about one-half inch thick. This material is preferably packed between metallic screens, there being about three screens on each side of the layer, the inner screen being of finer mesh than the outer ones, thus giving stiffness. Embedded in the catalyst layers are thermocouples 26, the wires of which lead to a common galvanometer 27, from which the temperatures may be read. Another thermocouple 28 is placed in the vaporizer, and a switch 29 acts to connect any of the thermocouples to the galvanometer to show the temperature at any desired point. 30 are valved supplemental air pipes, leading into chambers 31 between the three catalyst layers to supply air to the mixture emerging from the catalyst zones. That is, after the mixture with a partial amount of air admitted to it in the vaporizer has passed through the first catalytic layer, a further amount of air is mixed with it, and the new mixture is passed through the second catalytic layer. Further air may then be added to the further oxidized mixture, which is then passed through the third catalytic layer.

I also preferably add a diluent to the mixture, this diluent being either steam, or fume gas taken from the exit of the apparatus. If steam is used, I preferably add it in the vaporizing chamber by feeding measured amounts of water into the oil pipe 4^a. The steam thus added acts both as a diluent and also as an aid to vaporizing heavier distillates. In the form shown, I also employ fume gas for diluting the mixtures between the screens. Thus, the return pipe 32 leads a portion of the fume gas back from the vacuum or exhaust pump 33, through valves 34 into the valved air pipes 30. By this means, a carefully regulated measured amount of fume gas may be introduced as a diluent into the mixtures, between the catalytic layers.

I have shown the vaporizing chamber and the remainder of the apparatus thus described as lagged or covered with heat-insulating material 35, except where the burners act on the vaporizing chamber. This lagging is found to be of advantage, as I have discovered that quick cooling of the vapor mixture tends to throw down tarry deposits, etc. From the outlet chamber 36 of the apparatus, a long pipe 37 leads to the condenser 16^a, thus giving gradual cooling in passing to the condenser. From the condenser, the products drop into the vessel 19^a, from which they may be tapped out through the pipe 20^a, into the receptacle 21^a. The exhaust pump 33 has a pipe 22^a connected to the upper part of the vessel 19^a, and also the upper part of the collecting vessel 21^a, through the pipe 23^a. 38 is a valved pipe leading from the exhaust pump to the scrubbers and the atmosphere. Referring now to a run with an apparatus such as that shown in this Figure 2:—the diameter of the catalytic screens was about 15" and oil was fed at the rate of 6 liters per hour with 6/10 of a liter of water per hour. The oil used was a re-

fining waste obtained at a plant running on Pennsylvania petroleum and showing the following distillation:

5	Up to 200° C.....	None
	200 to 250° C.....	11%
	250 to 300° C.....	51%
	300 to 350° C.....	34%
	A residue above 350° C.....	4%

- 10 The specific gravity of the oil at 15.6° C. was .819. The amount of olefinic hydrocarbons as shown by the sulphuric acid test was 7.5%.

In a run of nearly four hours, the temperature in the vaporizer was maintained about 310°.

- 15 The temperature of the first layer was about 330 to 340°. The temperature of the second layer was about 365 to 380°. The temperature of the third layer was about 365 to 370°. The volume of air at room temperature and pressure passing into the vaporizer was about 2.5 to 3 cu. ft. per minute. The volume of air passing into the mixture between the first and second layers was about 1 to 1.5 cu. ft. per minute. The volume of air passing to the mixture between the second and third layers was about 1 to 1.5 cu. ft. per minute.

- 20 In the latter part of the run, fume gas was fed into the mixture passing to No. 2 layer at the rate of about 2 cu. ft. per minute, no additional fume gas being fed to the mixture passing to the third layer. A vacuum was maintained in the vaporizer equal to about 2½ to 3 inches of mercury. The oil was fed at the rate of about 100 cubic centimeters per minute. The water was fed at the rate of about 10 cubic centimeters per minute. The gas leaving the apparatus showed about the following analysis:

		Percent by volume
40	CO ₂	2.9
	O ₂	2.9
	Olefine hydrocarbons.....	2.5
	CO.....	4.8

- A total volume of 25.5 liters of oil was fed and 45 19.6 liters of oily product insoluble in water was obtained, giving a recovery of 80%. The acid and other products soluble in water are not included in this, and the latter usually amount to 7.5% by weight of the total oil fed. The oily product gave the following analysis:

	Percent
Aldehyde fatty acids.....	31
Aldehydes above 200° C.....	20
Alcohols, other products and hydrocarbons	
55 (by difference).....	49

An Engler distillation of the product gave the following:

		Percent
60	Up to 100° C.....	.5
	100° to 150° C.....	2.5
	150° to 200° C.....	11.0
	200° to 250° C.....	21.5
	250° to 300° C.....	38.5
65	300° to 340° C.....	23.0
	Above 340° C.....	3.0

- In this preferred multiple layer type, by proper regulation of the air admitted to the various chambers and of the temperature in the successive reaction zones, I am able to carry the oxidation to the point of maximum yield of aldehyde fatty acids and of low molecular weight hydrocarbons. In this system, I may employ, for the first or the first and second catalytic 75 layers, a material which gives predominant oxida-

tion to one stage, for example, the aldehyde stage. This effect is quite marked with the intermediate oxides of uranium and their compounds as a catalyst. For the remaining layers, it is desirable to use catalytic material which has the particular characteristic of carrying the oxidation to the acid stage, such as molybdenum trioxid or the intermediate oxides of molybdenum. It will be understood that I regulate the temperature in the reaction zone or at each catalytic layer according to the catalyst used and the degree of oxidation which has previously been reached before passing the succeeding layers.

In this case again, steam will aid in vaporizing heavier petroleum fractions and also in keeping the catalyst freed from deposits which would tend to coat it and retard the flow. While the steam will retard the action in one layer, this is more than compensated for by the total depth of catalyst, either in one layer or the series of layers shown.

In this case, the temperature may also be controlled within the desired limits, by regulating the amount of air fed, and if desired, by cooling, regulating the vaporizing and heating burners, etc., as well as by adding the diluent.

I may also, in this multiple screen form, vaporize the oil and pass it through the first layer (in this case preferably a relatively deep one) without adding air before contact. This will give thermal decomposition and increase the olefin content; and then by adding air between the first and second layers and beyond, if desired, in the proper amount, the partial oxidation will proceed in the succeeding layers more easily on account of the increase in unsaturated bonds in the hydrocarbon chains. Similarly, the thermal treatment with a catalytic layer may be carried out and the product condensed and then re-vaporized, air added and passed through a layer for partial oxidation.

In Figure 3, I show a simple form of apparatus with a deep catalytic layer 10^b, 2^b being the vaporizing and air-mixing chamber and 15^b the outlet to the condenser and suction device, if this is used. I have used a small apparatus of this kind with a diameter of catalytic layer of 38 centimeters and a depth of 28 centimeters. A thermometer is placed at the entrance to the catalytic layer.

With this apparatus, I employed two condensers and six scrubbers, each of the latter being filled with gas oil.

In the first run, I used gas oil having at 15° C. a specific gravity of .841. The oil feed was 100 cubic centimeters per hour, and the air rate two liters per minute. The total oil fed was 380 cubic centimeters, and the temperature of the reaction zone about 400° C.; 245 cubic centimeters of product were obtained from the condensers and absorbers.

Analysis of the product gave 17.4% of a motor spirit distilling under 200° C.; 19.7% of aldehyde fatty acids; 14% of aldehydes, and 13.3% of alcohols and unconverted hydrocarbons; these percentages being figured back on the oil fed.

In the second experiment with the same apparatus, and conditions the same, except that steam was added to the system equal to 20% of water relative to the oil fed, I obtained 11.2% of a motor spirit distillate distilling under 200° C.; 24.9% of aldehyde fatty acids; 27.1% of aldehydes and 22.1% of alcohols and hydrocarbons; these percentages being figured on the oil treated.

In a further experiment, similar to that of the first experiment, except that the temperature was reduced to 380° C., the total recovery of product increased to 86%, with a corresponding lowering in the gas loss. This shows, in accordance with many other experiments, that the reaction is so sensitive that slight changes in the factors make great changes in the proportion of the various products of yield in a given run.

In carrying out my process, it may be varied in accordance with the material treated, and the conditions in several ways. By varying the aliphatic raw material employed, I have found that in most cases and for many purposes the shorter the range of the cut or distillate, the narrower is the range of the desired products. Thus, for certain grades of products, I may employ gas oil or fuel oil distillates; distill these to obtain two fractions, and treat these fractions for certain purposes. Again, I may take "topped" California crude oil, give it one distillation and use the upper fraction for my process. Crude oils and their distillates vary in several ways some having a paraffin base and some an asphaltic base. The crude contains saturated straight chain or branched chain aliphatic hydrocarbons. It may also contain unsaturated straight chain or branched chain hydrocarbons, such as those of the olefin type and those of the acetylene type. It may also contain aromatic hydrocarbons with side chains, the latter being saturated or unsaturated, and naphthenes. My process which is a low temperature, vapor phase air oxidation, relates to attacking the chain hydrocarbons, as distinguished from the aromatic hydrocarbons of the benzene ring type, and it operates more easily on the aliphatic hydrocarbons of the unsaturated type. Because of the highly unsaturated condition of a considerable portion of the hydrocarbons of the cheaper petroleum, I find that the formation of oxidation products by my process takes place easier than with the saturated aliphatic hydrocarbons. For that reason, I prefer in some cases to prepare material for my improved process by the "cracking" distillation of crude oil from the Western States, or of Mexican crude oil, or of heavy distillates thereof; followed by applying my partial combustion process to either the entire distilled oil, or to separate fractions thereof. Olefin kerosenes and heavier fractions high in olefins can be made by cracking distillation of gas oil and other heavy fractions at atmospheric pressure. Then by submitting the same to my process, a good percentage of light oil, such as motor spirit, and at the same time a large proportion of intermediate combustion products can be obtained, such as aldehyde fatty acids, aldehydes, alcohols, waxes, etc.

For the same reasons as noted above, I can successfully treat shale oil by my process. This oil has too high a percentage of olefins to be easily worked up into ordinary petroleum products.

I may, for example, take topped California crude oil or a heavy distillate thereof, such as fuel oil, and distill it in a high vertical still. After distilling in the ordinary manner to take off the kerosene fraction, I lower the heat and slow down the distillation so that the vapor rising into the upper part of the still will fall back and be subjected to repeated thermal treatments causing cracking. This operation will convert the heavy fraction into oil lying in the heavier kerosene range and in the gas oil range. It will also produce a considerable proportion of olefins, usually from 20 to 25%. I preferably continue this slow

cracking distillation, either until nothing is left but coke, which must be dug out, or until the residue has just enough fluidity to tap out of the still. If this cracking distillation is carried on to where the residue is coked, the operation is stopped when the distilling operation shows no condensate forming from the vapors. The products then formed are merely gases. I then take this distillate which consists of heavy olefin kerosene and olefin gas oil (since olefins are present to a large extent), and subject them to the partial combustion process. The olefin end of this distillate greatly aids in producing partial combustion products, since these are more easily oxidized owing to their unsaturated nature than are the corresponding saturated hydrocarbons. The atmospheric pressure cracking still formerly used to increase the kerosene fraction may be used for this purpose.

I may distill the oil (preferably by a cracking distillation) and pass the oil vapor from the still directly into my apparatus in any desired form thereof. In this case the vapor may be passed through a preliminary heated layer where further thermal decomposition may take place, and then be mixed with air and passed on through the catalytic screen or screens and partially converted into intermediate oxidation products. Or after the thermal decomposition, the vapors may be condensed, the light oil removed, and the remainder passed through my partial combustion process.

The total depth of catalyst has an influence on the products, particularly as regards the amount of light oil produced and the percentage of the partial combustion product which will polymerize.

The particular catalyst employed is also of importance, as some catalysts are more active than others. Thus, for producing mainly alcohols and aldehydes, I preferably employ a catalyst of lower activity. For single layer work, in producing aldehyde fatty acids, I preferably employ catalytic material of greater activity.

The temperature at the reaction zone, the percentages of air supplied relative to the hydrocarbon feed, the velocity of the current of mixed vapor and air, the use of steam or other diluent, and other factors also are useful in affording elasticity to the process and varying the amount and character of the product. By such variations, I can make a larger proportion of alcohols and aldehydes, or a larger proportion of aldehyde acids; and I can vary the quality of these products and the percentages of light oil obtained.

As regards the catalyst employed, I prefer the complex oxides or compounds of metals having a varying valence. All parts of the complex may consist of oxides of the same metal or of different metals. For example, an excellent catalyst in this connection consists of the so-called "blue oxides" of molybdenum, which contain molybdenyl molybdenate (MoO_2MoO_3) and molybdenyl molybdenite, and are probably all chemical compounds of two or more oxides of molybdenum representing different states of oxidation. These complexes may be regarded as salts; that is, compounds of one or more basic with one or more acid oxides.

Other complexes of value for such catalysts are chromic chromate, $\text{Cr}_2\text{O}_3\text{CrO}_3$, tungsten tungstate, WO_2WO_3 , the manganese complexes, the vanadium complexes, etc.

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. Examples of this class are:

Uranyl uranate.....	UO_2UO_3
Cobalt molybdate.....	CeOMoO_3
Cobalt molybdate.....	CeOMoO_2
Di-uranyl vanadate.....	$(\text{UO}_2)_2\text{V}_2\text{O}_5$
etc.	

These metals whose complexes I prefer to employ as the acid part of the catalyst, since I have found them to be of high activity in this field, are the metals of high melting point electronegative low-atomic-volume metals 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, descending side of the fourth peak, and the descending side of further peaks developed since the date of this diagram. The class includes the following metals: titanium, vanadium, chromium, manganese, zirconium, niobium, molybdenum, tantalum, tungsten and uranium. The basic oxides may be the lower oxides of these metals or may be the oxides of iron, copper, nickel, lanthanum, cobalt, thorium and the eight or nine rare earth metals. In both acid or basic portions there may, of course, be two or more of these combined.

In Figure 4, I show a means consisting of embedded electric resistance 50 for heating the first screen in case it is desired at this first screen to crack the hydrocarbon or increase the unsaturated compounds in the vapor. Other parts are the same as shown in Figure 2, the letter *d* being applied to the corresponding numbers.

I may first distill the condensed product to remove the low boiling point hydrocarbons. This may be done, for example, by distilling up to about 200° C., thus obtaining motor spirit which may be used as a fuel in internal combustion engines. The percentage of this light oil may be increased by properly varying the process, particularly as regards the oil used and factors effecting thermal decomposition, such as the total depth of the catalytic layer or layers. The amount of low boiling point hydrocarbons thus distilled off will be increased by the amount of this product recovered in the scrubbers, preferably by the oil-absorption process.

In case, by suitable regulation of the temperature and the air, I shape the process so as to obtain a product relatively low in aldehyde fatty acids, free and combined, and high in alcohols and aldehydes, I then preferably treat the remainder, after distillation of the low boiling point hydrocarbons, at a boiling temperature with an alkali metal hydroxide or alkaline earth metal hydroxide, to remove the free aldehyde acids. The remainder consisting mainly of alcohols, aldehydes and waxes with any unchanged hydrocarbons, is suitable for use as a lubricant of a certain grade without further treatment. For example, this material is well adapted to the lubrication of steam engines or ordinary machinery lubrication. It may, if desired, be blended or mixed with other hydrocarbons for this purpose, or treated further.

Instead of removing the free acid after distilling off the light oil, ie alkali or lime boil may be carried to the point of decomposing the waxes present.

Again, after distilling off the light oil and saponifying the acids, I can take the non-saponifi-

able oily residue containing alcohols and aldehydes, etc., and return it to the next oxidizing apparatus for further oxidation. I have found that this second oxidation is very easily effected, giving a product high in aldehyde fatty acids and waxes. This is particularly true as regards oils containing unsaturated bodies, as California or Mexican oils, on account of the easy production of olefins.

I may also operate the partial combustion process with steam under such conditions that a relatively large percentage of alcohols will result; and then combine this product with that of a run arranged to produce a relatively large percentage of aldehyde fatty acids.

It will be evident that these acids serve nicely as the starting point for the manufacture of greases of all kinds.

If it is desired to make soaps as one of the main products, the process is conducted to obtain a high percentage of aldehyde fatty acids. The original oxidized product, after distillation to remove the light oils, is saponified by the alkali or lime treatment to convert the free and combined acids into soaps. The oily non-saponifiable residue will now contain the alcohols originally present, the alcohols liberated by the saponification, aldehydes, aldehyde alcohols and any unchanged hydrocarbons. This residue may be returned to the oxidizing apparatus for further treatment where acids or soaps are the main products desired.

These processes may be applied to the material produced either by the thin-layer catalyst or the deep-layer catalyst process, or by the multiple-screen process with successive air admission. It may also be applied to double-run or re-run material, in which the oxidizing step has been repeated.

By the words "sufficient depth" in referring to the depth of catalyst in the claims, I intend to cover not only a single catalytic layer, but the plural catalytic layer in separated sections. By the words "temperature below that of red heat" or similar words, I intend to cover a temperature below that where a distinct red heat color appears and within the range wherein oxygen is chemically tied in; and by the words "temperature below that of continuous self-sustained combustion" or similar words, I intend to cover a temperature below the ignition point for complete combustion, that is, below a point where the majority of the material is completely consumed by complete combustion to CO_2 in water and within the range wherein oxygen is chemically tied in.

I claim:

1. In the production of partial oxidation products, the steps consisting of feeding a gaseous phase mixture of hydrocarbon and a gas containing free oxygen through a hot reaction zone at a reactive temperature below that of continuous self-sustained complete combustion, then increasing the percentage of free oxygen in the exit gas, and then passing it through another hot conversion zone at a reactive temperature below that of continuous self-sustained complete combustion.

2. In the production of partial oxidation products, the steps consisting of feeding a gaseous phase mixture of hydrocarbon and a gas containing free oxygen through a hot reaction zone at a reactive temperature below that of continuous self-sustained complete combustion, then increasing the percentage of free oxygen in the exit gas and cooling the same, and then passing

it through another hot conversion zone at a reactive temperature below that of continuous self-sustained complete combustion.

3. In the production of partial oxidation products, the steps consisting in passing a mixture of hydrocarbon and a gas containing free oxygen in gaseous or vapor phase through a conversion zone at a temperature producing partial oxidation products, adding a gas containing free oxygen, and again passing the hot vapor mixture through a conversion zone at a temperature producing partial oxidation products.

4. In the production of partial oxidation products, the steps consisting in passing a mixture of hydrocarbon and a gas containing free oxygen in gaseous or vapor phase through a conversion zone at a temperature producing partial oxidation products, adding a further portion of a gas containing free oxygen, and again passing the hot mixture through a conversion zone at a temperature producing partial oxidation products, and supplying external energy to the stream to cause circulation of the mixture.

5. In the production of partial oxidation products, the process which comprises passing a mixture of hydrocarbon and a gas containing free oxygen over a hot catalyst, withdrawing the products prior to complete utilization of the oxygen in oxidizing reactions, supplying further oxygen, and then passing the mixture over another hot catalyst.

6. In the production of partial oxidation products, the steps consisting of feeding hydrocarbon in finely divided condition mixed with a gas containing free oxygen over a hot catalyst at a temperature producing partial oxidation products, adding further oxygen, passing the same over another catalyst, condensing the product, and fractioning said product.

7. In the making of partial oxidation products, the steps consisting in passing a mixture of hydrocarbon in finely divided condition and a gas containing free oxygen over a catalytic layer, and maintaining the reaction zone temperature below that of continuous self-sustained complete combustion at such a temperature as to produce material quantities of oxygen derivatives of hydrocarbons and of lighter hydrocarbons than the oil treated.

8. In the making of partial oxidation products, the steps consisting in passing a mixture of hydrocarbon in finely divided condition and a gas containing free oxygen over a catalytic layer, maintaining the reaction zone temperature below that of continuous self-sustained complete combustion at such a temperature as to produce material quantities of oxygen derivatives of hydrocarbons and of lighter hydrocarbons than the oil treated, and fractioning the product.

9. In the production of partial oxidation products, the steps consisting of increasing the unsaturated compounds in a mineral oil fraction, mixing the same in finely divided condition with a gas containing free oxygen, and passing the same through a hot conversion zone at a reactive temperature below that of continuous self-sustained complete combustion.

10. In the production of light oil, the steps consisting in passing a mixture of oil-vapor through a hot conversion zone, introducing air, and passing the mixture through another hot conversion zone at a temperature below that of continuous self-sustained complete combustion.

11. In the production of partial oxidation products, the steps consisting in passing a mixture

of oil-vapor and air through a hot conversion zone, producing alcohols and aldehydes, introducing further air, and passing the mixture through another hot conversion zone, wherein part of the alcohols and aldehydes are further oxidized and the percentage of aldehyde acids is increased.

12. In the process of making partial oxidation products, the steps consisting of passing a mixture of vaporized hydrocarbon and air over a catalytic mass at a temperature below that of continuous self-sustained complete combustion and within the partial oxidation range, supplying further air to the hot mixture and passing it over another catalytic mass.

13. In the process of making partial oxidation products, the steps consisting of passing a mixture consisting of a vaporized hydrocarbon, air and a diluent through a hot reaction zone at a temperature below that of continuous self-sustained complete combustion, supplying further air to the mixture, and passing it through another hot reaction zone at a temperature below that of continuous self-sustained combustion.

14. In the production of partial oxidation products, the steps consisting in sucking a mixture of oil-vapor and air through a reaction zone at a temperature producing partial oxidation products, supplying further air, and sucking the mixture through another conversion zone.

15. In the production of partial oxidation products, the steps consisting of passing a mixture of oil-vapor and air through a hot conversion zone, producing aldehydes, supplying further air, and then passing the hot vapor mixture through another conversion zone, and converting the aldehydes into aldehyde acids.

16. In the production of partial oxidation products, the process which comprises passing a mixture of hydrocarbon and a gas containing free oxygen in gaseous phase over a hot catalyst at such a rate of speed and at such a temperature that free oxygen is present in substantial amount in the exit gas stream, and then adding further oxygen and passing the mixture over another hot catalyst at such a speed and at such a temperature that free oxygen is present in the exit gas stream therefrom.

17. In the production of partial oxidation products, the steps consisting of sucking a mixture of hydrocarbon in finely divided condition and a gas containing free oxygen over a hot catalyst at a temperature producing partial oxidation products, then increasing the percentage of oxygen in the stream, and then passing the same over another hot catalyst at a temperature producing partial oxidation products.

18. In the production of partial oxidation products, the steps consisting of feeding hydrocarbon in finely divided condition mixed with a gas containing free oxygen over a hot catalyst, increasing the oxygen content of the stream, and then passing the stream over another hot catalyst at such a speed and at such a temperature that free oxygen is present in the exit gas therefrom.

19. In the production of partial oxidation products, the steps consisting of feeding a mixture of hydrocarbon in finely divided form mixed with a gas containing free oxygen over a hot catalyst at a temperature producing partial oxidation products, then increasing the percentage of oxygen in the exit gas and then cooling the same, and then passing it over another hot

catalyst at a temperature producing partial oxidation products.

20. In the production of partial oxidation products, the steps consisting of mixing hydrocarbon in finely divided condition with a gas containing free oxygen to an amount less than theory demands for the production of the desired derivatives, passing the mixture over a catalyst at a reactive temperature below that of continuous self-sustained complete combustion, increasing the amount of free oxygen in the exit stream and then passing the stream over another catalyst and maintaining the latter catalyst at a reactive temperature below that of continuous self-sustained complete combustion.

21. In the production of partial oxidation products, the steps consisting of mixing hydrocarbon in finely divided condition with a gas containing free oxygen to an amount less than theory demands for the production of the desired derivatives, passing the mixture over a catalyst at a reactive temperature below that of continuous self-sustained complete combustion, increasing the amount of free oxygen in the exit stream, and then passing the stream over another catalyst and maintaining the latter catalyst at a reactive temperature below that of continuous self-sustained complete combustion at such speed and at such a temperature that free oxygen is present in the exit gas therefrom.

22. In the production of partial oxidation products, the steps consisting of feeding hydrocarbon in finely divided condition mixed with a gas containing free oxygen over a hot catalyst at a reactive temperature below that of continuous self-sustained complete combustion, increasing the amount of free oxygen in the exit stream, then passing the stream over another hot catalyst and maintaining the same at a reactive temperature below that of continuous self-sustained complete combustion at such a speed and at such a temperature that free oxygen is present in the exit gas, condensing the product and fractioning said product.

23. In the making of partial oxidation products, the steps consisting in passing a mixture of oil-vapor and air through a catalytic layer, preserving the temperature below that of continuous self-sustained complete combustion, and maintaining the reaction zone temperature at such point and the air percentage at such a ratio as to produce material quantities of alcohols, aldehydes, aldehyde acids and light hydrocarbons.

24. In the making of partial oxidation products, the steps consisting in passing a mixture of oil-vapor and air through a catalytic layer, cooling the catalytic layer and preserving a reactive temperature below that of continuous self-sustained complete combustion, and maintaining the reaction zone temperature at such point and the air percentage at such a ratio as to produce material quantities of alcohols, aldehydes, aldehyde acids and light hydrocarbons.

25. In the making of partial oxidation products, the steps consisting in sucking a mixture of oil-vapor and air through a catalytic layer, preserving the temperature below that of continuous self-sustained complete combustion, and maintaining the reaction zone temperature at such point and the air percentage at such a ratio as to produce material quantities of alcohols, aldehydes, aldehyde acids and lighter hydrocarbons than the oil treated.

26. In the partial oxidation of aliphatic hydro-

carbons, the steps consisting of passing a mixture of mineral oil-vapor and air through a catalytic layer at a temperature producing partial oxidation products, slowly cooling the mixture thereafter, and then condensing the same.

27. In the production of partial oxidation products, the steps consisting of passing a hydrocarbon in vapor form over a hot catalyst, cracking the same, adding a gas-containing free oxygen to the exit stream, and passing the same over a hot catalyst at a reactive temperature below that of continuous self-sustained complete combustion.

28. In the production of partial oxidation products, the steps consisting in passing a mixture of hydrocarbons in finely divided condition and a gas containing free oxygen over a hot catalyst, maintaining the catalyst at a reactive temperature below that of continuous self-sustained complete combustion, and withdrawing the stream from the catalytic zone prior to complete utilization of the oxygen in oxidizing reactions.

29. In the making of partial oxidation products, the steps consisting in passing a mixture of hydrocarbon in finely divided condition and a gas containing free oxygen over a catalytic layer, maintaining the reaction zone temperature below that of continuous self-sustained complete combustion at such a temperature as to produce material quantities of oxygen derivatives of hydrocarbons and of lighter hydrocarbons than the oil treated, fractioning the product, and reoxidizing a resulting fraction.

30. In the making of partial oxidation products, the steps consisting of treating a mixture of finely divided hydrocarbon and a gas containing free oxygen through a hot reaction zone at a reactive temperature below that of continuous self-sustained complete combustion, then cooling the exit stream, and then passing it through another hot reaction zone at a reactive temperature below that of continuous self-sustained complete combustion.

31. In the making of partial oxidation products, the steps consisting of passing a mixture of hydrocarbon in finely divided condition with a gas containing free oxygen over a hot catalyst at a reactive temperature below that of continuous self-sustained complete combustion, condensing the product, and reoxidizing the same by applying a gas containing free oxygen thereto while in the vapor phase.

32. In the making of partial oxidation products, the steps consisting of passing a mixture of hydrocarbon in finely divided condition with a gas containing free oxygen over a hot catalyst at a reactive temperature below that of continuous self-sustained complete combustion, condensing and fractioning the product, and reoxidizing one of the fractions.

33. In the partial oxidation of hydrocarbons, the steps consisting in passing a mixture of hydrocarbon and a gas containing free oxygen through a reaction zone, cooling the reaction zone by applying another cooling fluid thereto, and maintaining the zone below the temperature of continuous self-sustained complete combustion.

34. In the partial oxidation of hydrocarbons, the steps consisting in passing a mixture of hydrocarbon and a gas containing free oxygen in vapor or gaseous phase over a catalyst at a temperature producing partial oxidation products, and applying another fluid to the catalytic zone to control the temperature thereof.

35. In the production of partial oxidation prod-

ucts, the steps consisting in passing a mixture of hydrocarbon and a gas containing free oxygen in gaseous or vapor phase through a conversion zone at a temperature producing partial oxidation products, adding a further portion of a gas containing free oxygen and a diluent, and passing the hot mixture through a hot conversion zone at a temperature producing partial oxidation products.

36. The process which comprises passing cracked oil and air over a catalyzer at such a rate of speed and at such a temperature that free

oxygen is present in substantial amount in the exit gases whereby oxygen-containing organic products are obtained.

37. The process which comprises passing cracked petroleum oil and air over a catalyzer at such a rate of speed and at such a temperature that free oxygen is present in substantial amount in the exit gases whereby oxygen-containing organic products are obtained.

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