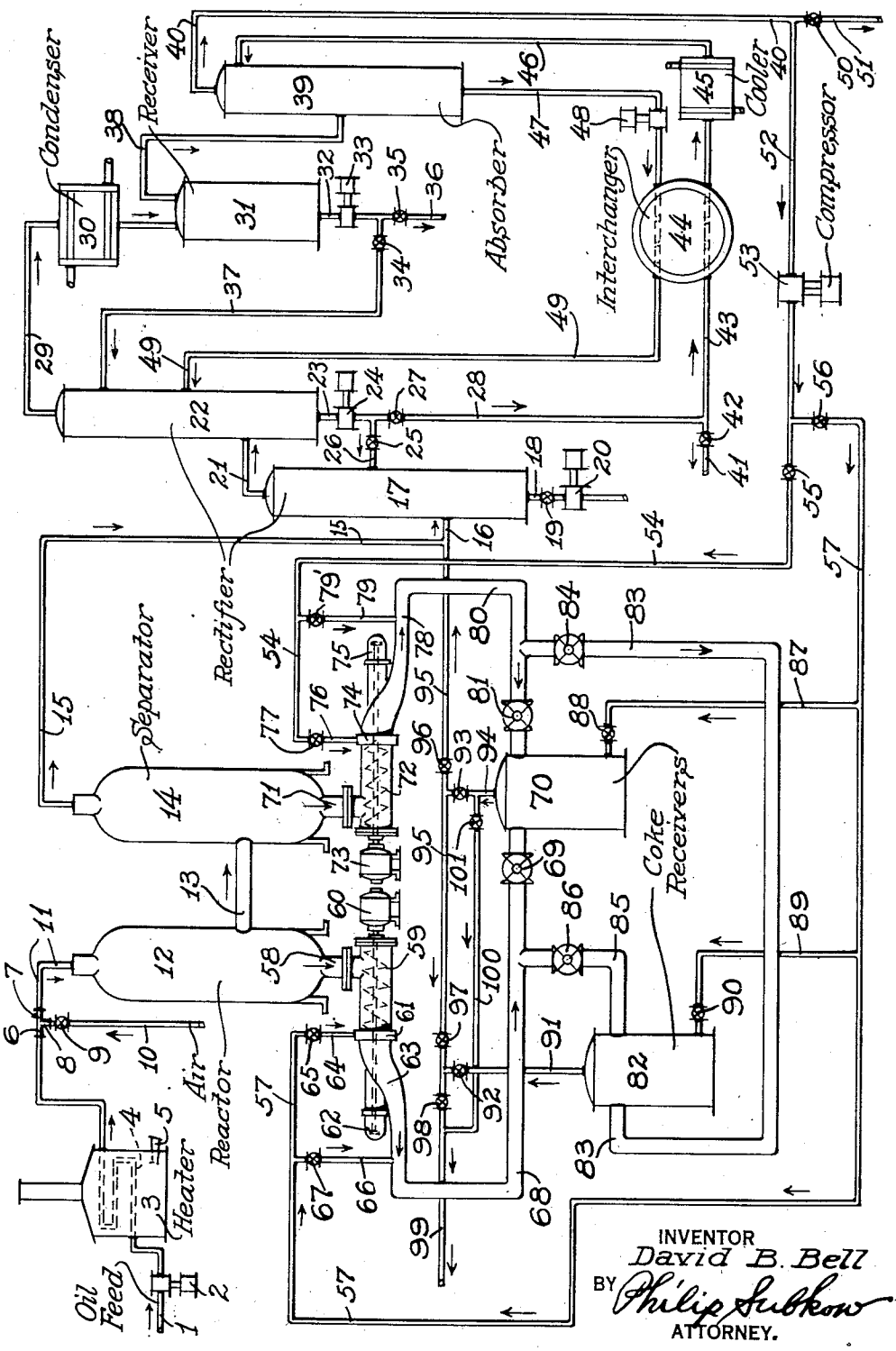
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METHOD OF CONVERTING OIL

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METHOD OF CONVERTING OIL

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This invention relates to a method for conversion of hydrocarbon oils, particularly petroleum residual oils and lighter oils. This application is a continuation in part of application Serial No. 310,908, filed December 26, 1939.

The invention of this application is directed to a process of conversion of petroleum oils, of high molecular weight, as for instance, the conversion of crude oils and residual oils into gas oil and gasoline, and the conversion of gas oil and kerosenes into gasoline and fractions lighter and heavier than gasoline.

Petroleum oils and particularly heavy oils such as residual fuel oils, crude oils, heavy gas oils and heavy oils produced by cracking may be converted by the process of this invention into lighter bodies with high yields of gasoline, light gas oils by reaction of the oil with air or other oxygen-containing gas.

In the process of my invention air has two functions. When employing heavy oils at a temperature insufficient to completely vaporize the oils, the air has the property of disintegrating the oil entering the reaction into small particles, and it has the property of dehydrogenating the oil, whether liquid or vapor, and in so doing apparently is accompanied by cission, cyclization and aromatization.

The air and oil must be mixed in a mixing device to permit the disintegration of the unvaporized oil into very fine particles if it is liquid, or to cause an intimate commingling of the oil if a vaporized feed is employed. This mixture is usefully carried out at a relatively low temperature to inhibit reaction in the mixer, and its flow controlled to the proper degree, as hereinafter explained. Preferably the mixing temperature should be below the thermal cracking temperature of the oil. It preferably should be at a temperature at which the reaction rate between the oil and air is low so that substantially no reaction occurs in the mixing zone. If a relatively high temperature is attained in the mixing zone the reaction proceeds rapidly in the zone with the formation of coke, excessive gas and excessive combustion. The control of temperature in the mixer may be accomplished by limiting the temperature of the oil entering the mixer, also by employing air at a relatively low tempertaure and also by employing a mixer which is cooled, as for instance, by exposure to the air, where any temperature rise is minimized by loss in radiation and convection.

The mixture, after it is formed in the mixing tube, is expanded into an enlarged reactor-expander where there is a material drop in pressure. The nature and the effects of the expansion is controlled by the pressure drop occurring on expansion and by the rate of flow of the feed hydrocarbons. By such proper control a proper disintegration of the oil and a proper mixture is made in the reactor expander to obtain the results of my process.

I have found, as a result of extensive experimentation, that the reaction between oil and oxygen-containing gas such as air, may be controlled to produce high yields of high knock rating gasoline from heavier oils, with low losses to gas and coke and with substantially no formation of products of combustion such as carbon monoxide and carbon dioxide. Fuel oils, gas oil and kerosenes, may be converted to gasoline hydrocarbons, and gasoline hydrocarbons of low knock rating, such as paraffinic and naphthenic gasolines, into high knock rating gasoline fractions which contain high contents of aromatic hydrocarbons boiling in the gasoline range, by employing air to dehydrogenate and convert the oil without burning any substantial amounts of the feed hydrocarbons, as is evidenced in the process of this invention, by the formation of gases substantially free of carbon monoxide and carbon dioxide.

The reaction between air and oil at high temperatures occurs in a series of steps, involving the formation of alcohol, and as further oxygen reaction occurs, aldehydes are formed. The aldehydes may break down to carbon monoxide and hydrogen, or the aldehydes may be burned completely to carbon dioxide and water. If sufficient oxygen is available for combustion, carbon monoxide is converted to carbon dioxide. Part of the aldehydes may be oxidized to acids. These acids are unstable at high temperature and break down to carbon dioxide without reaction with oxygen. This chain process of combustion is well known in the art of combustion and has been given the name of "hydroxylation process of combustion." While I do not wish to be limited by this theory of chemical combustion, I believe that it may be accepted as a valid explanation of the process of combustion. Whatever theory of combustion is used, it is well known and I have been able to establish this fact in my own experience, that if oxygen and air are mixed under conditions to permit the establishment of the combustion process, that is, of this chain of combustion reactions, the gases contain large quantities of carbon monoxide. A large proportion of the oxygen used appears as carbon monoxide in the gases and a substantial proportion of the feed hydrocarbons are converted to carbon monoxide. If an amount of air is used insufficient to completely convert the feed hydrocarbons into carbon dioxide and carbon monoxide, the process of combustion raises the temperature of the hydrocarbons to thermal cracking temperature, under which conditions the oil is cracked into lighter hydrocarbons under a condition of imperfect combustion, with the generation of large amounts

of coke and lamp black and a high conversion of the hydrocarbons to gas. These processes are characterized by the presence of relatively large amounts of carbon monoxide in the gases, tell tale of imperfect combustion. The generation of large amounts of coke and large conversion of the feed to gas, the presence of large percentages of carbon monoxide, are among some of the characteristic features of imperfect combustion cracking processes.

I have found that by the proper control of the reaction I am able to direct the reaction between the oil and air into an entirely different channel or course of reaction. Apparently the reaction proceeds primarily as a cission dehydrogenation proces. In this process a major proportion of the oxygen is used to abstract hydrogen from the molecule to form water. This is accompanied by a cission reaction in which hydrocarbons of lower molecular weight are formed. The gases are substantially free of carbon monoxide and in my process I have been able to conduct the reaction so that no or only a trace of carbon monoxide appears in the gases. There is no free oxygen present and the gas formation and the amount of coke generated when operating on heavy oils is far less and of a different order of magnitude than that present in imperfect combustion cracking reactions. The process of dehydrogenation and cission is accompanied or followed by processes of cyclization and aromatization, since I produce gasoline fractions of high aromatic content from hydrocarbons of naphthenic and paraffinic nature. The process of conversion is accompanied by the formation of only small amounts of carbon dioxide. This I believe is a result of the conversion of the oxygenated bodies which form as a result of secondary reaction in this process. These oxygenated bodies are in the inevitable consequence of the presence of the reaction between oxygen and oil. The amount of carbon dioxide and the percent of oxygen which goes to carbon dioxide is therefore an index of the oxygenation process which goes on and I have found that by the proper control of the air while maintaining efficient conditions of mixing and expanding, I can keep this oxygenation process at a minimum, as evidenced by the very limited conversion of the oxygen and the feed to carbon dioxide.

I have observed, however, that under conditions of my operation in which the control is such as to inhibit the formation of carbon monoxide, a dehydrogenation and cyclization process occurs in which the oxygen acts to extract hydrogen from the molecule to form aromatic type gasolines.

While I do not wish to be limited to any particular theory of the physical and chemical processes which occur and wish to embrace within the limits of my invention the full scope thereof within the claims forming a part hereof, I believe that the reactions described below explains the results of and the process occurring in my invention. This dehydrogenation reaction in my process apparently occurs preferentially to an extent sufficient to inhibit or prevent the combustion reaction. The hydroxylation process of combustion requires a relatively long series of steps before the combustion chain is completed. If the oxygen is robbed from this process by another mechanism, as for instance, by the dehydrogenation reaction of my process, then the chance for the completion of the chain of combustion will be materially reduced and the formation of carbon monoxide will be inhibited or prevented.

I have found that one of the important considerations in attaining my results is the control of the mixing process and the control of the expansion process in the reaction.

I have found that in a maldistributed condition of oil and gas in the reactor, at the temperature occurring in this process, there will be a region in which the ignition and combustion takes place. By forming the mixture in a uniform condition and by maintaining the composition of the mixture, that is, the ratio of air to oil, and its pressure sufficiently low, I am able to control the reaction in the reaction zone so that ignition and combustion do not occur and the reaction proceeds in the non-combustion reaction region rather than in the combustion region or partial combustion region.

The pressure in the mixer is always higher than in the reactor. The partial pressure of the oxygen is high both because the pressure is high and the condition at the initial stages of the mixing contains the oil in a maldistributed condition. There are regions in the mixer where there are high air/oil ratios.

The condition of ignition and combustion in the mixer is accelerated by increasing temperatures in the mixer. At any given pressure in the mixer, and at any given ratio of oil to air, and for a given velocity of flow, there is a maximum temperature above which ignition and combustion starts. I prefer to maintain the temperature in the mixer below this temperature and to permit sufficient time in the mixing tube to form an intimate mixture. The mixture is discharged from the mixing tube before any substantial reactions between the oil and air occurs, as is hereinafter explained. When the reaction proceeds in the reactor it is accompanied by a decreasing concentration of oxygen which is being consumed in the reaction to form water and some oxygenated bodies. There is also a rise in temperature. While this rise in temperature at the given pressure may tend to move the reaction in the direction of the ignition and combustion range, this movement would be countered by the diminution in the oxygen partial pressure. A diminishing partial pressure takes a higher temperature to move the air-oil mixture to the ignition range. The reaction occurring in my process is self-limiting, that is, has an automatic break. As will be observed from the data herewith reported, the temperatures reached are far below those which are attained in combustion processes, and the conversion of air and oil to carbon monoxide and carbon dioxide are inhibited. Notwithstanding that the temperature of the reactions are increased the reaction is still maintained below the region of ignition with no formation of carbon monoxide.

But whatever theory is adopted to explain the results of my process, I find that by a proper control of the process I am able to cause a high conversion of oil to high knock rating hydrocarbons with a low loss as gas and coke and substantially no loss of feed or formation of carbon monoxide by imperfect combustion of the feed hydrocarbons.

This is attained in my process by forming the mixture at relatively low temperatures in a mixer, causing the mixture to expand into a lower pressure zone before the reaction between the air and the oil has obtained either a combustion reaction or a substantial conversion reaction. It is preferable to discharge the air-oil mixture out of the mixing tube before the reaction proceeds

very far, in other words, before the combustion chain is established. If this mixture is permitted to remain in the mixing tube too long the reaction between the air and oil in the maldistributed condition occurs in the mixing tube with relatively high pressure air, or if a high mixing temperature is permitted to exist in the mixing tube, the combustion chain would be established and a coking of the tube result.

The mixture when properly made is then expanded into the lower pressure chamber. Upon expansion the disintegration previously discussed occurs. The expansion, in addition to causing the disruption and disintegration of the oil, also reduces the partial pressure of the oxygen. This partial pressure is further diminished by the presence of the hydrocarbon gases resulting from the reaction and consumption of the oxygen in the formation of water.

By imparting to the stream a sufficient energy of flow the expansion of the oil and air into a lower pressure expander disrupts the oil into a fine fog of minute droplets of oil, uniformly dispersed in the atmosphere of air at a lower pressure. In other words before the combustion chain has reached the stage where the oxygen is reacting to form oxygenated bodies sufficient to cause the formation of carbon monoxide and coke, i. e. before imperfect combustion is obtained, or before a temperature is attained to cause any material gasoline formation, the expansion of the oil into a low pressure zone causes a diminution in the concentration of the oxygen. The presence of an excess amount of hydrocarbons far in excess of the amount of any alcohols and aldehydes which may possibly be formed by the initial oxygenation in the reactor apparently robs the oxygen from the hydroxylation-combustion reaction and the process proceeds mainly as a dehydrogenation reaction. More than 50% of the air and ranging up to 100% of the air goes to this dehydrogenation reaction.

Air and oil is thus mixed to form a uniform mixture in which the oil, if it is liquid feed such as a residual oil, is mixed with air at a temperature below its incipent vaporation point, i. e. up to 5 to 10% of the oil vaporized, in order to prevent surges of vapor and liquid in the mixture. If material partial vaporization of a liquid feed is caused in the mixer there will be sudden surges in the mixer causing improper mixtures of air and oil. This may result in momentary periods of high air/oil ratios of such magnitude as to cause the establishment of imperfect combustion in the mixer with accompanying coking up of the mixer. The mixture occurs preferably at a relatively low temperature below that which would give sufficient time in the mixing tube to cause the combustion chain to be established. The temperature will be sufficiently low to prevent any substantial conversion of the oil to gasoline in the mixing tube. Preferentially this mixing tube is a line mixer. The mixture is discharged into the expansion vessel of vastly increased diameter before the reaction has progressed far enough to attain an active reaction temperature.

The reaction of oxygen with oil proceeds through an induction period. As air is mixed with oil at sufficiently high temperature there is a period of time during which very little reaction occurs between the oxygen and the oil and then the reaction begins to accelerate, rising rapidly with a resulting increase in temperature. The higher the mixing temperature the shorter this induction period. The mixture in the mixing tube, if maintained in the mixing tube for a sufficient length of time, will, at the high pressures and temperature in the mixing tube, complete the combustion chain and combustion will occur. The inhibition of reaction in the mixing tube can be accomplished by controlling the conditions of temperature of mixing and the length of time the mixture is in the mixing tube.

The mixture is expanded into an enlarged chamber in which a substantial pressure drop occurs. The reduced partial pressure of oxygen will, as previously explained, further inhibit the generation of the completion of the combustion chain. The reduction in pressure on the air and the increase in temperature causes a tremendous expansion of the gas and a very large reduction in the oxygen concentration. The large quantity of oil both in liquid and vapor form, as compared to the relatively small quantity of oxygenated bodies, would create a condition wherein the dehydrogenation reaction would be preferred to the completion of the combustion chain. The reaction therefore proceeds in the direction of dehydrogenation. If a condition is established in which the stratification of the oxygen occurs, so that there are local high ratios of oxygen to oil, there will be available sufficient oxygen for the completion of the combustion chain. Apparently also this would result in local high temperatures, notwithstanding that the average over-all temperature would be low. At high temperature the combusion chain accelerates and may accelerate to a higher degree than the dehydrogenation stage. The results would be imperfect combustion.

In the operation of my process, sufficient energy is imparted to the stream in the mixer and sufficiently high velocities are imparted so that upon the expansion of the air-oil stream in the expander the drop in pressure across the orifice and expansion and enlargement in volume thus obtained causes an extensive disruption and disintegration of the oil stream into minute fog-like droplets of oil uniformly distributed in the atmosphere of air. In such a condition with proper control of temperatures and air rates, the oil and air undergoes a dehydrogenation reaction without formation of carbon monoxide. If, however, this disruptive energy is not available by reason of the fact that the air pressure or the oil rates are diminished, so that the pressure drop and velocity of flow across the orifice formed by the juncture of the mixing tube and the expander does not give the desired expansion and therefore does not have the disruptive energy available, no proper disintegration of the oil occurs, no proper mixture is formed. A phenomenon of stratification of oil and air occurs, permitting oil to react with air under various conditions, some of which may be such as to permit combustion and the generation of excessive and local temperatures resulting in excessive loss by degradation to gas, carbon monoxide and carbon.

The velocities of flow of air or oil through the mixer may be too great, or the mixing tube too short, so as not to give sufficient time in the mixer for an intimate commingling of the air and oil, and on discharge a stratified condition will result. It is desirable to provide sufficient mixing time in the mixer so that in cooperation with the energies of flow available the proper type of disintegration and distribution is obtained in the reactor-expander.

Additionally the rate of feed of the oil may be

reduced to so low a figure that for the particular design of mixer, even though desirable air-oil rates are employed to give the reactions when mixing conditions are properly established, the rate will be insufficient to give the desired mixing and expansion. It will be found that within the limits herein described, and taking due observance of the nature of the products produced, as herein described, a proper design of mixer and proper control can be attained.

For each mixer design there is a velocity or pressure drop, which if reached or exceeded will give the necessary disruption and mixing. This would vary with various mixer designs and a test which may be employed is the amount of carbon monoxide that is present in the gases. It will be found that if this desirable mixing and expansion is attained, the carbon monoxide content of the gases will be substantially nil. If, however, this is not attained, then the carbon monoxide content of the gases will be high.

The mixture travels from the point of mixing through a short length of tubing of restricted cross-sectional area at high velocity and high turbulence and at relatively high pressure, to cause intimate commingling of the air. The stream is discharged into a reactor of greatly enlarged cross-sectional area through which reactor it passes in commingled state without separation of components until it is discharged at a remote end of the reactor. The temperature rises upon expansion into the top of the reactor. The temperature at the top of the reactor is however below the maximum temperature obtained in the reactor. I prefer to maintain the temperature in the mixing tube to below about 750° F. so that I ensure substantially no reaction in the mixing tube. The reaction takes place substantially entirely in the reactor. This ensures that the reaction will not occur in the mixing tube where coke, if it accumulates, will cause the process to be shut down.

The mixture enters the reaction vessel at a temperature near to or below the threshold re- the reactor varied from 250° F. to 730° F. The action temperature of 700–750° F. In the examples given below the temperature at the top of the reactor varied from 250° F. to 730° F. The mixture of air and oil travels through the reaction vessel in commingled state without separation of the oil and gas in a thoroughly distributed and uniform mixture. The reaction proceeds in the passage of the stream through the reactor, with rise in temperature until the maximum temperature is attained and a substantially complete utilization of the oxygen of the air occurs.

I maintain the mixture in the reactor sufficiently long to permit the attainment of maximum temperature and preferably long enough to ensure the substantially complete consumption of the oxygen of the air by the reaction.

I have found in the apparatus and process exemplified herein that if the mixing temperature measured at the point where the mixing temperature is measured as described herein, attains 650° F. or higher, using air pressures at the inlet of the mixer of 95 lbs. or higher, coking proceeds inside the mixing tube and the process is rapidly shut down. While this temperature may vary with different sizes of mixing tubes and pressures employed, and with stocks processed, it will be found that as the temperature proceeds above this point, and up to about 700–750° F., the tendency to coke in the tube increases, and I prefer, as will be herein described, to control the mixing temperature below about 750° F., and preferably not above around 650° F. to 750° F., the lower temperature being preferred.

The maximum temperature rise obtained in the reactor-expander depends upon the air/oil ratio employed. The more air employed per barrel of feed, the higher will be the rise in temperature from the mixing temperature to the maximum reaction temperature attained in the expander. I have found that there is a maximum air ratio which may be profitably employed to obtain this necessary temperature rise and desired dehydrogenation reaction. The rate of conversion of the oil, that is, the percent of the oil which may be converted into gasoline, gas oil, and other bodies under proper conditions of reaction as herein described, to produce the dehydrogenation without any material formation of carbon monoxide, is a function of the temperature attained in the reactor. The higher the temperature the greater the yield of gasoline and other light products. I have found that I can, by the proper control of reaction, obtain relatively high conversion temperatures without causing any combustion of the oil, or any material conversion of the oxygen to carbon monoxide.

The nature of the process is also further brought out by the character of the products produced. The process may be operated to convert heavier fractions such as crude oil, fuel oil, gas oil, kerosene, into gasoline and gas oil fractions and in some cases into residuum and in others into coke. The gasolines and light gas oils are of high aromatic content, as evidenced by the boiling points, gravities and viscosities. The gasolines are of high octane rate, ranging from 75 to as high as 88 octane and higher. It has been found that unlike other conversion processes, such as catalytic and thermal conversion processes, the products of the reaction such as the residuum and gas oils formed may be recycled into the process and upon reaction give yields of products similar to that of virgin unreacted feeds. So also may cracked products, such and gas oil and residuums produced by thermal or catalytic processes, be processed by my process.

In operating the process to produce coke, I have found that unlike the coke formed in thermal cracking processes, which is massive coke and must be cut out or bored out of the reaction vessels, the coke formed is in discrete particles like grains of sand apparently formed by the coking of small droplets of oil.

I have found that in operating with sufficient air rate to supply the necessary air for the dehydrogenation reaction, there is an initial temperature, hereinafter referred to as "threshold temperature" which must be attained by the reaction between the oil and the air in order to obtain substantial conversion of the oil. This "threshold temperature" will change with various stocks which may be treated but it will be found that with each stock there will be such a temperature below which no substantial conversion of the oil occurs. As this temperature increases it will be found that the yields increase. In operating with a 17° A. P. I. gravity Los Angeles Basin fuel oil or with other types of crude or residuums or as produced in this process or by thermal cracking, it has been found that this temperature lies in the range of about 725° to about 750° F. Oil and air commingled at a tem-

perature of above about 200° to 300° F. or higher, will attain this threshold temperature under proper conditions of operation not by the combustion of the oil, but primarily by the dehydrogenation reaction. It has also been found that to obtain substantial conversion of the oil, it is desirable to employ air rates in excess of about 900 to 1000 cubic feet of air per barrel of oil. In this specification, wherever volumes of air or gas are given, it is to be understood that the volume is measured at 60° F. and 14.7 pounds absolute pressure. Wherever liquid volumes are given it is understood they are measured at 60° F. This ratio will vary with the stock charged, but it will be found that for heavy oils such as the Los Angeles Basin mixed base fuel oils, or other residuum oils as described above, this threshold value of the air rate is desirable to obtain a substantial conversion of the oil. The temperature rise which occurs as a result of the reaction of the oil increases as the air rate is increased.

As the maximum temperature attained in the reactor, which temperature hereafter will be termed the "maximum reactor temperature" rises, the yield of 400° end point gasoline rises. However there is also a rise in the amount of the charge which is converted into fixed gases lighter than gasoline and when operating on a fuel oil charge an increase in the total losses, i. e. gas, coke and other losses. There will be an economic limit as to the temperature which is to be employed and I have found that for economic operations the temperature limits may be taken approximately from 800° to 1100° F.

I prefer to cause the temperature rise from about 700° to 750° F. to the maximum reactor temperature, i. e. to 800° to 1100° F. to occur in the reaction vessel during the travel of the mixed oil and air therethrough. The chamber is designed to give sufficient time to permit of this reaction between the air and oil while traveling through the chamber.

With these criteria in mind it will be found that the useful range of temperature and air rates may be taken as about 200° F. to 700° F. in the mixer, 800° F. to 1100° F. as the maximum reactor temperature and from about 900 to 4000 cubic feet per barrel of oil as the air rates to be employed. It will be found that by properly choosing the temperatures and air rates in the ranges and by properly controlling the air rate, high yields of gasoline of high octane and low loss of feed to coke and gas may be obtained with but a minimum utilization of air and a consequent minimum amount of combustion of the feed and a minimum formation of oxidized products.

This process will be better understood by reference to the accompanying drawing which shows a schematic illustration of one application of my process.

Oil from a source of supply is fed through line 1 under pressure by a pump 2 to the coils 4 positioned in furnace 3 which furnace is heated by burners 5. The preheated oil enters the run 6 of the T mixer 7. Into the branch 8 of the T mixer 7 air is introduced under pressure through line 10 controlled by valve 9. The oil and air mixes in the mixer 7 and in line 11 and is expanded into an enlarged combined reaction, coking and separating vessel 12. The oil and air passes in commingled state without separation of component parts through 12 until it gets to the outlet line 13. At this point there is a separation of components.

The coke particles, as will be later explained, continue downwardly and deposit in the lower part of the reactor 12 to be discharged continuously through the outlet 58. The vapors and any unseparated coke particles exit through line 13 into the separator 14. In the separator the vapors continue upwardly while the coke drops out and down into the lower part of the separator 14, to be withdrawn through line 71 as explained later. The vapors exit through line 15 and enter through line 16 into the rectifier 17. In this rectifier the vapors are separated into a heavy gas oil fraction which forms a bottoms and into lighter fractions. The heavy gas oil is withdrawn through line 18 by control of valve 19 and pump 20. This gas oil may be recirculated to be mixed with the feed for reprocessing. The lighter fractions exit as vapors through line 21 into the rectifier 22. In this rectifier the vapors are separated into gasoline and lighter components and an intermediate or light gas oil fraction. This light gas oil fraction is withdrawn through line 23 by pump 24 and by the proper control of the valves 25 and 27 part of the withdrawn gas oil fraction is introduced as a reflux medium through line 26 into the rectifier 17 and the other part is passed through line 28 as will be furthed described. The gasoline and lighter fractions are withdrawn through line 29 as vapors, condensed in condenser 30 and collected in receiver 31. The crude gasoline condensate is withdrawn through line 32 by pump 33 and by the proper control of the valves 34 and 35 part is returned through line 37 to act as a reflux medium in rectifier 32 and the other part is withdrawn through line 36. The uncondensed fractions consisting of the fixed gas and the uncondensed gasoline fractions, is withdrawn through line 38 and introduced into the absorber 39 wherein it is washed with a menstruum which is introduced through line 46 as will be later described. In this absorber the gasoline fractions are removed and the fixed gases, substantially freed of gasoline fractions, are withdrawn through line 40. Part of the stripped dry gases are discharged under control of valve 50 through the line 51. Another part is passed through line 52 and recompressed by compressor 53 and introduced into headers 57 and 54 to be used in the process by proper control of valves 55 and 56. A portion of the light gas oil passing through line 28 is discharged through line 41 controlled by valve 42 to a convenient receiver. Another portion passes through line 43 into the heat exchanger 44 and through cooler 45 to be introduced through line 46 into absorber 39 from which absorber the fat oil passes through line 47 from 48 and interchanger 44 and through line 49 to the rectifier 22 in which it is stripped of its gasoline fractions.

Referring now to the handling of the coke, the coke which, as will be later described, is granular in the form of discrete particles, discharges through the discharge throat 58 of reactor 12 or discharge throat 71 of separator 14. The coke removing means is shown schematically at 59 and 72. This is one of the many methods by which such granular solid material may be moved and it is not intended as a limitation upon such method of movement but merely an illustration of one convenient method which I prefer. This pump is a combination of a screw and a pneumatic conveyer. The solids passed by the screws 59 and 72 rotated respectively by motors 60 and 73, and is fed through an air chamber where it is

met by numerous jets of gas introduced through the gas rings 61 and 74 from headers 57 and 54 respectively via lines 64 and 76 under the control of valves 65 and 77. This gas "aerates" the material and expands and causes it to "flow." There is provided "dust seals" 62 and 75. The material flows through line 63 and 73 respectively, in which lines it meets additional gas introduced through line 66 controlled by valve 67 and line 79 controlled by valve 79'. The form of pump here illustrated is a well known type of pump for solid particles, and no novelty is claimed for this particular pump construction for moving the solids, except when used in the combinations and subcombinations shown in this application.

The mixture of vapors and solids and gases traveling through lines 63 and 73 may be introduced into one of a number of receivers which are manifolded so that they can be used independently of each other. Two receivers 82 and 70 are shown in the drawing to illustrate the process. One is filled while the other is being cooled and discharged. Thus, for illustration, assume 70 is cooling and discharging, while 82 is receiving. The material in line 63 passes through line 68, and through line 85, valve 86 being opened, and valve 69 being closed. The material from line 73 passes to line 80 into line 83, valve 84 being opened and valve 81 being closed. The material discharges through these lines into the separator 82. Valve 90 being closed, valve 92 being opened, the vapors and gases separate from the coke which is deposited in the receiver 82 to accumulate therein. With valve 98 closed and valve 97 and valve 96 opened, valve 93 being closed, the mixed vapor and gases enter through line 95 into the rectifier 17. Receiver 70 now having cooled as explained herein, it is opened through a man hole provided therein, and not shown, and the coke discharged in any convenient manner to the atmosphere. The receiver is then closed. It is deaerated by opening valve 88, gas passing through the receiver, line 94, valve 101 being opened, valve 93 closed, the gas discharged through line 100 and line 99. Thus, gas will displace the air. When the receiver has been deaerated it is now ready to receive the discharge from the separators and reactors. Receiver 82 now being full, the valves 86 and 84 are closed and valves 69 and 81 are opened, valve 101 closed, valves 93 and 96 opened, 88 closed, valve 97 closed, valve 98 opened and valve 92 opened. The coke is allowed to cool in the receiver 82, gas venting through valve 98 and line 99. Cooling may be accelerated by passing a coolant through the mass as for instance by passing gases through line 89, valve 99 being opened, valve 92 being opened, valve 98 being opened, valve 97 remaining closed, valve 101 remaining closed. When the coke has cooled down sufficiently, valve 90 being closed, valve 92 being closed, the separator 82 is opened and the coke discharged, and the cycle is then repeated for these carbon receivers as is explained.

In carrying out the process of this invention and this apparatus, the control is directed to the formation of coke and vaporous fractions and not to the formation of a liquid residue. The purpose of the process is to form a solid dry coke which is in such discrete particles of such relatively small size that it may be discharged continuously from the reactors and separated. There is thus produced a continuous coking process. The oil is preheated in heater 3. It is desirable to preheat the oil to a temperature not higher than the incipient vaporization temperature, that is, to vaporize not much more than 5–10% of the feed stock. A partially vaporized stock or a stock heated to high temperature will be materially vaporized on mixing with air and surges will occur in the mixer. Such surges cause uneven mixing, maldistributed oil and air mixture, excessive local air/oil ratios, carbonization and excessive gasification. This may result in a clogged mixer due to accumulation of coke.

The preheated oil is commingled with air under conditions of control previously recited, such as to cause a conversion of the oil directly into coke and vapors without any substantial formation of liquid residue or of carbon monoxide, that is, without any substantial combustion of the oil. The oil is preheated to such a temperature that at the air rates and temperatures of air employed, the temperature of the mixture of oil and air shall be not over about 650° to 750° F., preferably not over about 650° F. The rates of flow of the products are correlated to the size of the reactor and to the size of the mixer, to obtain the control whereby substantially no formation of carbon monoxide is formed as is explained above. Thus the air and the oil may be introduced into the mixer at a pressure of about 120 to 140 pounds and the pressure in the reactor is maintained at about 35 pounds. As an example of a useful ratio of the diameter of the mixer nozzle to the diameter of the reactor, wherein the results of this process are obtained at the ratio of about 160 to 1, as given as an illustration. While one line mixer 7 is shown, it is understood of course that a plurality of such mixers may be employed in parallel, all discharging into the reactor 12. By the proper regulation of the feed rates of oil and the feed rate of air correlated to the mixer and reactor design and the pressures employed, the reaction may be controlled so as to produce a temperature at the top of the reactor of about 700° F. upward. The temperature rises as the mixture passes through the reactor until part way down it reaches a temperature of about 900° to 950° F. It has been found that if the maximum temperature attained is controlled to be in excess of about 900° F. and preferably above 925° F., under the conditions here described, the oil is completely converted to coke and to vaporous products, no liquid residue being formed.

In operating my process I commingle the oil and air at the chosen temperature and rates as expanded herein. The mixture is commingled under sufficiently high pressure and flow rates to pass the products at high velocity through the mixing tube. The time permitted in the mixing is preferably insufficient to raise the temperature to or materially above the "threshold reaction temperature" as hereinafter explained, with sufficient time in the mixer to cause proper mixing, but preferably a sufficiently small period of time in the mixing nozzle to prevent material reaction, as explained above. Observance of the principles described herein will permit a proper design of the mixer and expander combinations and a proper choice of operating conditions.

The mixture is discharged preferably substantially unreacted as above described, from the mixing tube into the reaction vessel, which is many times greater in volume and diameter than the mixing tube. There is a consequent large drop in pressure. This drop in pressure and expansion ensures a disintegration of the oil into minute droplets finely dispersed through the

gaseous atmosphere. There is therefore a uniform distribution of oil in the air. Reaction occurs and temperature rises rapidly from the threshold temperature which occurs near the top of the reactor to the maximum reaction temperature attained in travel through the reactor. The oil is converted while in a disintegrated condition in the form of fine droplets. The mixture travels through the reactor and is discharged at the bottom, the oxygen in the air being completely consumed.

If the temperature attained is about 890–950° F. or higher the fuel oil feed is completely converted into vaporous products and coke. The coke is granular in nature due to the coking of the fine droplets of oil. It is collected in the bottom of the separator and reactor and is removed as described.

As an example for carrying out the process, a feed composed of Los Angeles Basin residuum having a gravity of 17° A. P. I., flash of 230°, viscosity of 103 seconds Saybolt Universal at 122° F., and having an initial of about 470° F. and 5% distilling off at 570° F., is preheated to a temperature of about 540° F. and mixed with air charged at about 80° F. at the rate of about 2350 cubic feet per barrel of oil, the temperature attained in the mixer was about 300° F., the temperature attained at the top of the reactor is 700° F. and the maximum temperature attained in the reactor **12** is 928° F., and the temperature at the point of discharge from the reactor **13** is about 820° F. The size of the mixer **7** in this example was ⅛'' internal diameter and the internal diameter of the reactor was 20 inches. The air and oil pressure was about 130 pounds gauge at the mixer and the pressure in the reactor was 35 pounds gauge. There was produced 28.5% of gasoline as later described, 18.5% of a light gas oil, 15.5% of a heavy gas oil and no residuum. The coke deposited was of a granular nature having the appearance of sand. The coke was light and not massive. The gasoline was of the following nature:

A. P. I. gravity	degrees	49.3
A. S. T. M.–C. F. R. knock rating		75.8
Reid vapor pressure	pounds	10.2
Engler distillation:		
Initial	degrees F.	98
10%	do	132
50%	do	238
90%	do	356
End point	do	397

The heavy gas oil such as is removable through line **18** had the following characteristics:

A. P. I. gravity	degrees	5.7
Viscosity, S. F. at 122° F.	seconds	1235

The material such as will be removed through line **23** is a light gas oil having the following characteristics:

A. P. I. gravity	degrees	23
Viscosity, S. U. at 100° F.	seconds	38
Distillation:		
Initial	degrees F.	403
End point	do	653

In this process the oil is heated in furnace **3** to various temperatures at or below the incipient vaporization temperature of the oil. It is desired that no substantial vaporization of the oil occurs in order to insure proper mixing conditions. The mixer temperature, as described above, should be below the threshold reaction temperature, which for the oils of the nature illustrated in the example, run from 700–750° F. It has been found, however, that it is desirable to maintain the temperature below 650° F., since if the mixer temperature is allowed to rise to 650° F. or higher excessive coking occurs and the mixer tends to stop up when employing a feed as illustrated above. By carrying the temperature in the range of 900° F. and higher and preferably above 925° F. to 950° F., the oil, if it is of the residual nature such as described above, is converted directly to coke.

The temperature rise which occurs between the mixer temperature and the maximum reactor temperature, as illustrated above, is a function of the air/oil ratio, and the same reactor temperatures are attained by increasing the temperature of the feed and decreasing the ratio of air to oil. Thus, instead of using 2350 cubic feet per barrel of oil and a mixer temperature of 300° F., the same reactor temperature could be obtained by controlling the temperature of preheat and air/oil ratio to give a mixer temperature of 550° F. and an air/oil ratio of about 1750 cubic feet per barrel of oil. Or, the air/oil ratio may be increased to 3000 cubic feet per barrel and the mixer temperature reduced to about 228° F. by dropping the temperature of preheat and the above reactor temperature obtained. It has been found, however, that it is not desirable to raise the mixer temperature to above about 650° F. nor to drop the air/oil ratio below about 900–1000 cubic feet per barrel of oil. For practical purposes it will be found that in the range of a mixer temperature below about 600° F. and an air/oil ratio above about 1350 cubic feet per barrel of oil to a mixer temperature of about 200° F. and an air/oil ratio of about 3000–3500 cubic feet per barrel illustrates useful ranges of reactor temperatures and air/oil ratios whereby temperatures of around 900° F. to 950° F. may be attained in this process to cause the conversion of residual fractions directly to coke and gas oil and gasoline.

When controlled as herein described, it will be found that the process proceeds with substantially no combustion of the oil. The fixed gases will contain substantially no carbon monoxide and these may be as low as from 0 to .05% and will contain carbon dioxide from 0 to 2.5%, percentages being volume percent of the wet gases issuing from receiver **31**. Less than .1% to not much more than .6% of the feed will be converted into carbon dioxide, and from less than 5% to not much more than 12–15% of the air will be converted into carbon dioxide. From 70–90% of the oxygen appears as water in the process, depending on the air/oil ratios used. The lower the air/oil ratios used the smaller the amount of oxygen which will be converted to carbon dioxide and which will be used in converting the fuel to carbon dioxide and the higher the percentage of the oxygen which will appear as water.

The foregoing description of the process of the invention and the experimental data are not to be construed as limiting my invention, as they have been given for illustrative purposes only and changes and modifications may be made therein within the scope of the appended claims.

I claim:

1. A continuous process for converting residual oil into gasoline and gas oil fractions and into coke which comprises preheating oil to not more than the incipient vaporization temperature of said residual oil while still substantially in the

liquid state, commingling said oil with air in a tube of restricted cross sectional area at a temperature below about 650–750° F., discharging said commingled air and oil from said tube before said temperature reaches above about 750–800° F., while still in a liquid state commingled with the air introduced into said mixing tube and before a gasoline or carbon monoxide forming reaction occurs, into and through an enlarged space, at a materially reduced pressure, in commingled form without any substantial separation of liquid oil from said air, for a time to permit the temperature to rise to active conversion temperature of at least about 900–950° F. without combustion of said oil, substantially completely converting said liquid oil into finely divided particles of coke and into vaporous and gaseous fractions lighter than said oil charged to the process, said lighter fraction comprising gasoline, hydrocarbon fractions lighter than gasoline and gaseous fractions substantially free of carbon monoxide or carbon dioxide, said conversion and said temperature rise occurring solely by reaction between the air introduced into the said mixing zone and under a diminishing partial pressure of oxygen in said expansion zone, separating gasoline and coke from said products of reaction.

2. A continuous process for converting residual oil into gasoline and gas oil fractions and into coke which comprises preheating oil to not more than the incipient vaporization temperature of said residual oil while still substantially in the liquid state, commingling said oil with air in an unheated tube of restricted cross sectional area at a temperature below about 650–750° F., discharging said commingled air and oil from said tube before said temperature reaches above about 750–800° F., while still in a liquid state commingled with the air introduced into said mixing tube and before a gasoline or carbon monoxide forming reaction occurs, into and through an enlarged space, at a materially reduced pressure, in commingled form without any substantial separation of liquid oil from said air, for a time to permit the temperature to rise to active conversion temperature of at least about 900–950° F. without combustion of said oil, substantially completely converting said liquid oil into finely divided particles of coke and into vaporous and gaseous fractions lighter than said oil charged to the process, said lighter fraction comprising gasoline, hydrocarbon fractions lighter than gasoline and gaseous fractions substantially free of carbon monoxide or carbon dioxide, said conversion and said temperature rise occurring solely by reaction between the air introduced into the said mixing zone and under a diminishing partial pressure of oxygen in said expansion zone, and separating gasoline and coke from said products of reaction.

3. A continuous process of converting residual oil into gasoline and into gas oil fractions and into coke, which comprises preheating oil to the incipient vaporization temperature of said residual oil while still substantially in the liquid state, commingling said oil with air in a tube of restricted cross sectional area at a rate in excess of 1000 cubic feet per barrel of oil, controlling this ratio of air to oil and the temperature of preheat of said oil and said mixing to obtain a temperature of the mixture not above about 650° F. and adjusting said air and oil flow and said temperatures to discharge said air and oil from said mixing tube in substantially unvaporized form and before a gasoline or carbon monoxide forming reaction between said liquid oil and air occurs in said mixing tube, expanding said mixture of oil and air from said tube into a chamber of much greater cross sectional area maintained at a pressure materially lower than the pressure in said tube, wherein said oil is disrupted into fine particles of oil, controlling said rate of flow in said tube by controlling the rate of feed of said oil and said air to discharge said mixture into said enlarged reaction space where the temperature of the oil reaches an active conversion temperatue solely by reaction of the oil and air introduced into said mixing tube, passing said stream of air and oil particles in said reaction space in a commingled state without separation of the parts of said stream until said stream has reached a temperature in excess of around 900° F. to 950° F. under continuously diminishing partial pressure of oxygen without combustion of said oil to carbon monoxide, continuing said passage until said particles of oil have been completely converted into granular particles of coke and vaporous products, then separating the vapors from said coke, and separating a high knock rating aromatic gasoline from said vapors and separating a fixed gas from said gasoline substantially free of carbon monoxide and oxygen.

4. A process of converting residual oil into gasoline and into gas oil fractions and into coke, which comprises preheating oil to the incipient vaporization temperature of said residual oil, commingling said oil with air in a tube of restricted cross sectional area at a rate of 1000 to 4000 cubic feet per barrel of oil, controlling this ratio of air to oil and the temperature of preheat of said oil and said mixing to obtain a temperature of the mixture not above about 200° F. to 700° F. and adjusting said air and oil flow and said temperatures to discharge said air and oil from said mixing tube in substantially unvaporized form and before a gasoline or carbon monoxide forming reaction between said liquid oil and air occurs in said mixing tube, expanding said mixture of oil and air from said tube into a chamber of much greater cross-sectional area maintained at a pressure materially lower than the pressure in said tube, passing said stream of air and oil in said reaction space in a commingled state without separation of the parts of said stream until said stream has reached a temperature upward of about 900° F. to 950° F. without material conversion of said air to carbon monoxide under continuously diminishing partial pressure of oxygen without combustion of said oil, continuing said passage until said oil has been completely converted into granular coke and vaporous products, then separating the vapors from said granular coke and separating gasoline from said vapors and separating a fixed gas from said gasoline substantially free of carbon monoxide.

5. A process of converting residual oil into gasoline and into gas oil fractions and into coke, which comprises preheating oil to the incipient vaporization temperature of said residual oil, commingling said oil with air in a tube of restricted cross sectional area at a rate in excess of 1000 cubic feet per barrel of oil, controlling this ratio of air to oil and the temperature of preheat of said oil and said mixing to obtain a temperature of the mixture not above about 650° F. and adjusting said air and oil flow and said temperatures to discharge said air and oil from said mixing tube in substantially unvaporized form and before a gasoline or carbon monoxide form-

ing reaction between said liquid oil and air occurs in said mixing tube, expanding said mixture of oil and air from said tube into a chamber of much greater cross-sectional area maintained at a pressure materially lower than the pressure in said tube, passing said stream of air and oil in said reaction space in a commingled state without separation of the parts of said stream under continuously diminishing partial pressure of oxygen without combustion of said oil until said stream has reached a temperature in excess of around 900° F. without material conversion of said air to carbon monoxide, continuing said passage until said oil has been completely converted into coke and vaporous products, then separating the vapors from said coke and separating gasoline from said vapors and separating a fixed gas from said gasoline substantially free of carbon monoxide.

6. A process of converting residual oil into gasoline and into gas oil fractions and into coke, which comprises preheating oil to the incipient vaporization temperature of said residual oil, commingling said oil with air in a tube of restricted cross sectional area at a rate in excess of 1350 to 3500 cubic feet per barrel of oil, controlling this ratio of air to oil and the temperature of preheat of said oil and said mixing to obtain a temperature of the mixture of about 200° F. to 600° F., expanding said mixture of oil and air from said tube into a chamber of much greater cross-sectional area maintained at a pressure materially lower than the pressure in said tube, controlling said rate of flow in said tube by controlling the rate of feed of said oil and said air to discharge said mixture into said enlarged reaction space before said temperature has reached an active conversion temperature of upward of 750° F., passing said stream of air and oil in said reaction space in a commingled state without separation of the parts of said stream under continuously diminishing partial pressure of oxygen without combustion of said oil until said stream has reached a temperature in excess of around 900° F. to 950° F. without any substantial conversion of said oil and air to carbon monoxide, continuing said passage until said oil has been completely converted into granular coke and vaporous products, then separating the vapors from said granular coke and separating gasoline from said vapors and separating a fixed gas from said gasoline substantially free of carbon monoxide.

DAVID B. BELL.

CERTIFICATE OF CORRECTION.

Patent No. 2,336,057. December 7, 1943.

DAVID B. BELL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 4, first column, line 45, strike out the words "the reactor varied from 250° F. to 730° F. The"; and second column, line 48, for "and gas" read --as gas--; page 6, second column, line 54, for "expanded" read --explained--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 15th day of February, A. D. 1944.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.

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