Jan. 23, 1934. J. D. ZIELEY 1,944,483

METHOD OF TREATING HYDROCARBONS

Filed July 7, 1931 3 Sheets-Sheet 1

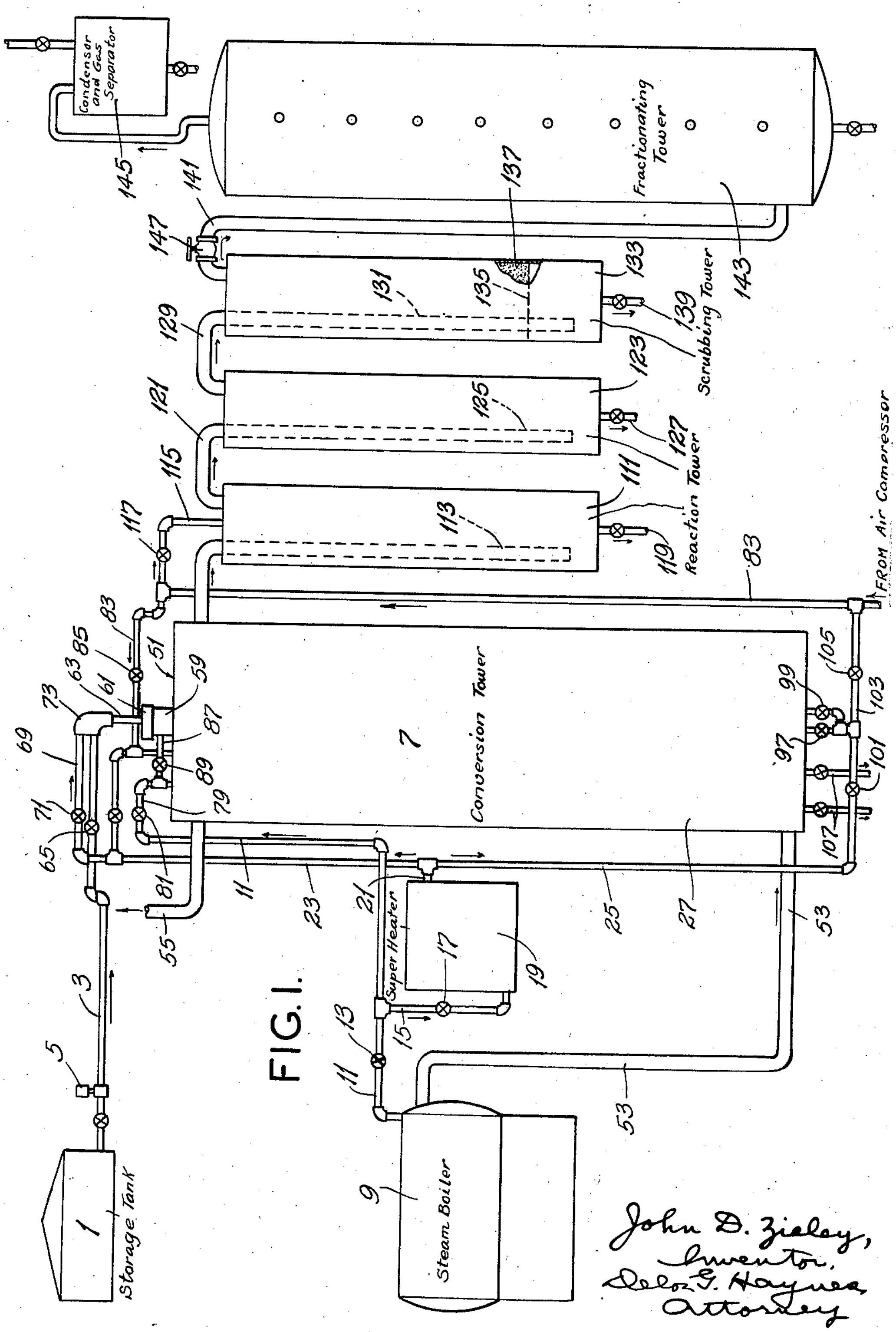

FIG. I.

John D. Zieley,
Inventor.
Deloz G. Haynes
Attorney

Jan. 23, 1934.

J. D. ZIELEY

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FIG. 2.

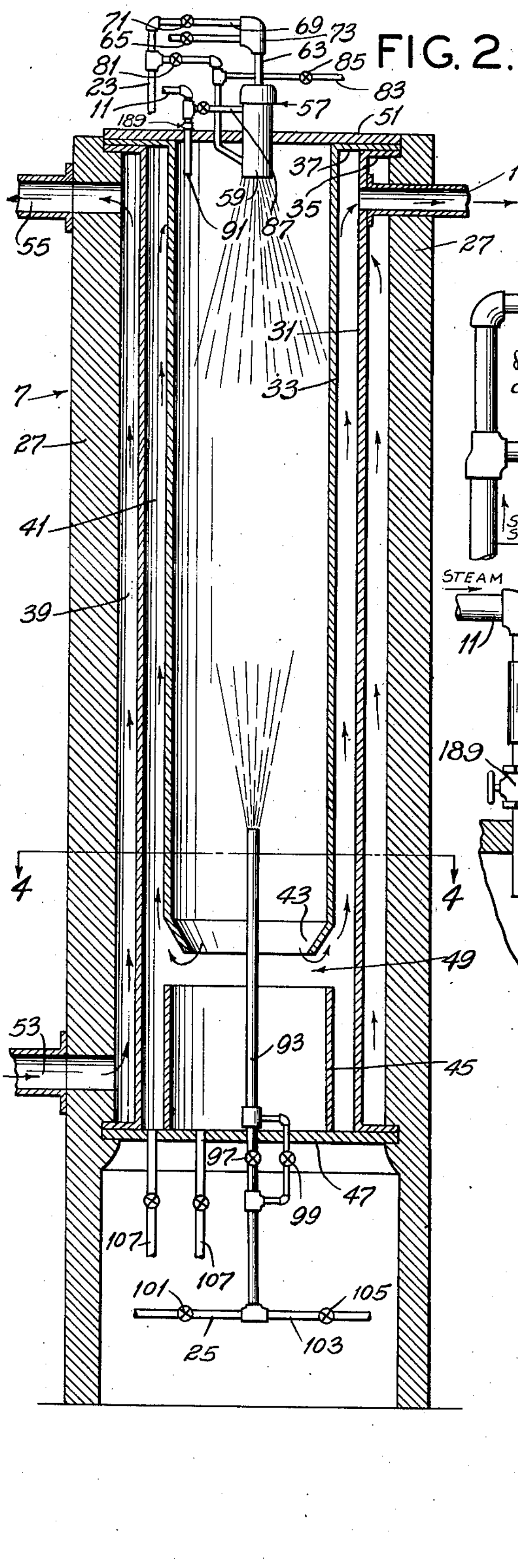
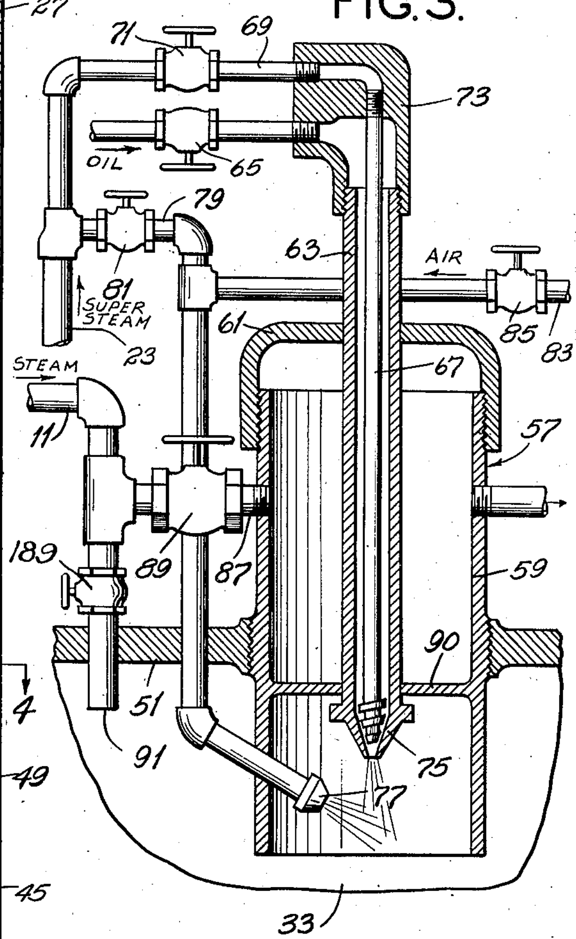


FIG. 3.



John D. Zieley,
Inventor.
Delos V. Haynes,
Attorney

FIG. 4.

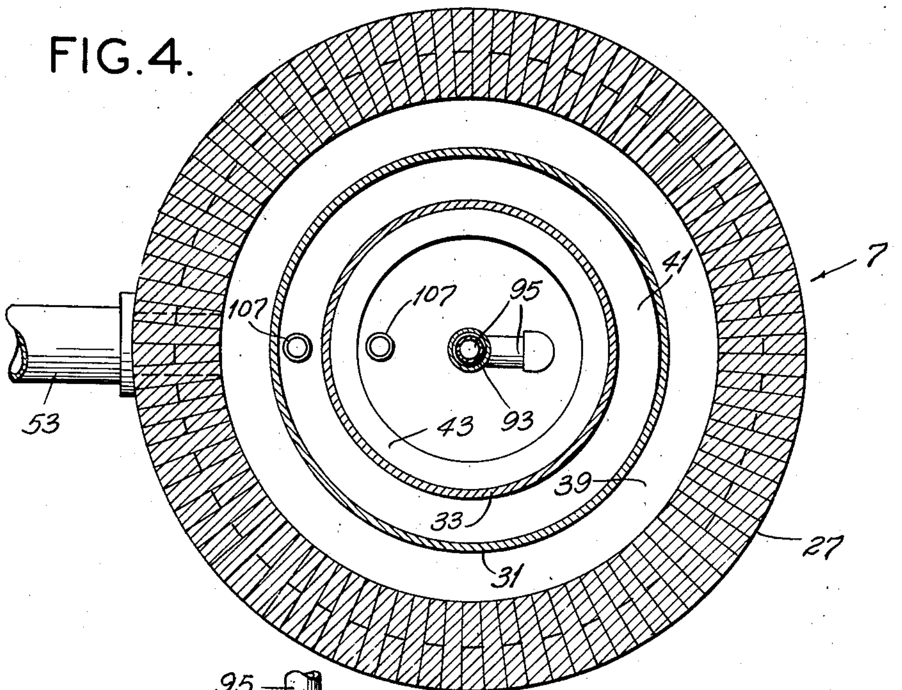
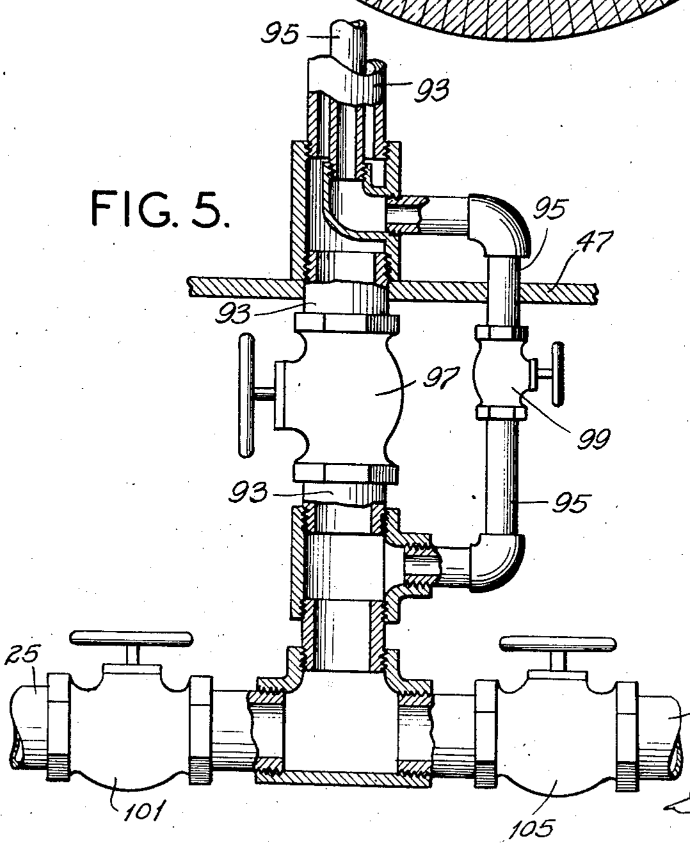


FIG. 5.



John D. Zieley
Inventor

Delos G. Haynes
Attorney

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UNITED STATES PATENT OFFICE

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METHOD OF TREATING HYDROCARBONS

John D. Zieley, Belmar, N. J., assignor to Amarel Corporation, Wilmington, Del., a corporation of Delaware

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2 Claims. (Cl. 196—65)

This invention relates to the treatment of hydrocarbons and like substances, usually of a heavy nature, for the recovery therefrom of products of a wide range of utility. With regard to certain more specific features, the invention relates to treatment of the materials described with heat under optimum conditions and at optimum speeds.

Among the several objects of the invention may be noted the provision of a method for the treatment described in which heat is applied substantially instantaneously to the raw material in its liquid, albeit atomized, phase, achieving complete treatment thereby without overheating of any portion or portions of such raw material, and in which the heat transferring medium is fluid and may thus be conducted to the point of application with maximum facility; a method which includes optionally a procedure for controllably oxidizing the raw material at the time of treatment; a method wherein deleterious cracking is inhibited, but wherein maximum yields of lighter materials are received from the raw material; a method wherein the raw material is subjected to distillation, decomposition and oxidation contemporaneously and substantially instantaneously; and a method of the class described which is economical in its use of heat and treating mediums and the like, and which involves a minimum of complicated procedures. Other objects will be in part obvious and in part pointed out hereinafter.

The invention accordingly comprises the steps and sequence of steps, composition and synthesis, which will be exemplified in the processes hereinafter described, and the scope of the application of which will be indicated in the following claims.

In the accompanying drawings, in which is illustrated one of various possible embodiments of the invention,

Fig. 1 is a diagrammatic showing of the various elements of the invention, arranged in proper sequence;

Fig. 2 is a diagrammatic vertical section of a conversion tower shown in Fig. 1;

Fig. 3 is a more detailed view illustrating a spray head associated with the tower of Fig. 2;

Fig. 4 is a horizontal section taken substantially on line 4—4 of Fig. 2; and,

Fig. 5 is a more detailed view illustrating an injecting tube associated with the tower of Fig. 2.

Similar reference characters indicate corresponding parts throughout the several views of the drawings.

Most existing processes for the heat-treatment of hydrocarbons and the like achieve such heat-treatment by indirectly contacting a heating medium (such as hot products of combustion) with the hydrocarbon, with a heat-conducting body (such as a metal pipe) interposed therebetween. Hydrocarbons, whether in the liquid or the vaporous phases, are poor conductors of heat; accordingly, in order to heat sufficiently the core or inner portion of the hydrocarbon, it is necessary that the shell, or outer portion, be overheated. In the case that heavy hydrocarbons, such as all types of crudes, including paraffine, asphaltic, or semi-asphaltic base crudes, and residues such as residuums and petrolatums and paraffins, and greases, natural asphalts, and the like, are being treated, such oveheating occassions the more or less complete decomposition of the hydrocarbon and the deposition of solid carbon, thereby clogging pipes and stills and the like and in many instances completely preventing the recovery of any valuable constituents from these raw materials.

The present invention overcomes the difficulties of overheating above set forth by treating the raw material including all such as above mentioned, directly by a heat-conducting medium, in a state of subdivision such that each particle is as thoroughly and intimately heated directly by the heat-medium as its neighbor. Broadly described, the present invention provides for such direct, thorough, uniform heating by atomizing the raw material under sufficient pressure to form a spray thereof, and impinging against said spray a continuous flow of superheated fluid such as steam.

The superheated steam utilized herein is at a temperature of the order of 1000° F. to 1400° F., and is thus above the range of temperatures ordinarily used with steam. I have discovered that such superheated steam is an efficient conductor or heat-transmitting fluid, and that with proper pipe insulation, it may be made to heat the incoming raw material with economy and efficiency.

As an important feature of the present invention, it is to be noted that the retort or confining walls are heated to no appreciably higher temperaturer than the temperature of the material under treatment, and thus the tendency to form coke by "baking out" or cracking on the walls is minimized or entirely eliminated.

Depending somewhat upon the character of the raw material being treated, I have found that the heat-treatment above described achieves not only a simple distillation of the raw material, but also a change in chemical constitution thereof such that the products are quite different than the raw material. Cracking, as the term is ordinarily defined, does not take place to a sufficient degree to account for the entire change of composition noted: this is proved by the fact that all cracking operations must produce either solid carbon, or residual fluids high in carbon and low in hydrogen, or fixed gases of a low hydrogen content in order that hydrogen may be supplied for the increased-hydrogen-content lighter hydro carbons produced by the cracking, and, treating in the manner of the present invention, neither is a large amount of solid carbon nor a large volume of low-hydrogen-content fixed gas produced. In fact, under some operating conditions, the fixed gases resulting from treatment according to the present invention contain a substantial percentage of free hydrogen gas. In addition, the fixed gases frequently contain appreciable quantities of carbon monoxide and/or carbon dioxide. The liquid products frequently exhibit aromatic characteristics associated with oxygenated hydrocarbons, such as terpenes, aldehydes, alcohols, ketones, and the like.

I explain this result in the following manner: Steam at temperatures of the order herein mentioned is considerably more dissociated into hydrogen and oxygen, its components, than it is at ordinary temperatures. Further, in the presence of hydrocarbons, this dissociation is even more pronounced. Thus, at the temperatures herein considerd, it is likely that the steam exists not as molecular H_2O, but as separate molecular or atomic H_2 and O. The affinity of carbon for oxygen is great; carbon monoxide, for example, is practically stable and undissociated at temperatures considerably higher than those herein employed. Apparently, then, instead of the carbon atom freeing itself of all hydrogen atoms, as it does in ordinary cracking procedures, in the present invention the carbon atoms combine with oxygen atoms forming oxides of carbon.

I have found further that the speed of the reaction is increased and the yield of oxygenated compounds is bettered if free oxygen, such as air, is admitted with the superheated steam. The details of this procedure will appear more fully hereinafter.

The less stable or heavier hydrocarbon fractions included in the complex initial, charging-stock hydrocarbons, tend to decompose more readily than the lighter, more stable fractions under the temperature and other conditions here provided. As a result, these heavier fractions are first to drop out carbon, probably in atomic form. The atomic carbon thus formed is immediately brought into contact with the superimposed atmosphere including oxygen from the air and the steam. Both the carbon and oxygen are in a highly reactive form and exhibit considerable affinity for each other. Thus they combine to form oxides of carbon with great rapidity. Some of the oxides of carbon thus formed are quite stable, and in subsequent cooling the oxygen remains bound to the carbon, while other carbon atoms left unstable by the heat reactions in cooling attach some of the free hydrogen molecules from the water, or elsewhere, whereby they become more saturated. Further reactions, as between a carbon atom partially saturated with oxygen and a carbon atom partially saturated with hydrogen, may also occur in the cooling, and thus form the oxygenated hydrocarbons mentioned hereinbefore. These oxygenated hydrocarbons are relatively unstable as compared with the other hydrocarbons, and as evidenced by their tendencies to decompose at lower temperatures.

A specific embodiment of the invention is illustrated in the accompanying drawings. For purposes of description the process will be carried through considering petrolatum as the raw material, although it is of course to be understood that other raw materials can be similarly treated.

Petrolatum is the heavy, viscous residue obtained in refineries when a centrifuging process is utilized to separate out waxes and greases and the like. It contains a high percentage of wax (paraffine base), considerable quantities of grease, and oil. Heretofore it has been considered impossible to recover any substantial amounts of utilizable substances from petrolatum, on account of the difficulty of separating these three constituents, all of which have substantially the same boiling range. Petrolatum is thus considered to be worthless, and the losses sustained thereby, especially in the case of high wax-content petroleums (such as Pennsylvania crude oil) have been large.

Referring now more particularly to Fig. 1, numeral 1 indicates a storage tank for the raw petrolatum. A pipe 3 leads from the tank 1, and a pump 5 is used to force the relatively viscous material to a conversion tower 7. It is desirable, to facilitate flow, that the petrolatum in tank 1 be preheated by customary means (utilizing, preferably, waste heat from some source in the process).

A conventional boiler 9 is provided to generate steam. A steam line 11 leads from the boiler 9. A valve 13 in line 11 controls the amount of steam delivered to the process per se. Branching from the line 11 is a steam line 15, controlled by a valve 17, and leading to a steam superheater 19. The superheater 19 may be of any suitable form: a twenty-pass tube still, fired by a steam-oil burner, has proved to be quite successful. A line 21 leads the superheated steam from the superheater 19. Line 21 branches, one portion 23 going to the top of the conversion tower 7 and the other portion 25 going to the bottom of said conversion tower 7. It is desirable that all of the steam lines be heat-insulated as, for example, with asbestos covering.

The conversion tower 7 is illustrated in more detail in Fig. 2, wherein numeral 27 indicates a brick or like stack, supported on suitable steel or like standards. Held within the stack 27 are a pair of concentric cylinders 31 and 33, having flanged ends 35 and 37 respectively. The diameter of the cylinders is such that cylinder 31 is spaced from the stack 27, leaving an annular jacket 39, while the cylinder 33 is spaced from cylinder 31 leaving an annular jacket 41. The inner cylinder 33 terminates at its lower end in a sort of inwardly tapered portion 43. A short cylinder 45, of substantially the same diameter as cylinder 33, rests on the bottom 47 of the tower, leaving a space 49 between itself and the tapered portion 43. Except as hereinafter provided, the several cylinders, bottom 47, and top 51 are welded or otherwise sealed together to provide an air-tight container.

The outer annular jacket 39 is used as a heat-insulating jacket, and for this purpose is provided with an inlet 53 and outlet 55. The spent products of combustion from the steam boiler 9, or from the superheater 19 (see Fig. 1) are advantageously introduced at inlet 53 and discharged into a suitable stack from outlet 55. Thus it is seen that the interior of the tower 7 is heat-insulated both by the brick wall 27 and the jacket of hot gases 39. Accordingly there is substantially no heat dissipation by radiation or conduction from the reaction zone, or central portion of tower 7.

In the top 51 of tower 7 is sealed an atomizer 57. The atomizer 57 and the connections thereto are illustrated in more detail in Fig. 3. A threaded pipe 59, to which a cap 61 is screwed, is welded or otherwise sealed to the top 51 of tower 7. Welded in the cap 61 is a tube 63, carrying the petrolatum supply from line 3, as controlled by a valve 65. Concentrically supported in the tube 63 is a small tube 67, supplied with superheated steam from line 23 by way of a bypass line 69 and valve 71. A special type of fitting 73 permits connections to tubes 63 and 67. Terminating the tubes 63 and 67 is an atomizing nozzle 75, of conventional design, adapted under pressure of superheated steam in tube 67 to atomize the petrolatum flowing in tube 63.

For imparting an initial heat to the atomized petrolatum, a nozzle 77 is provided to direct a mixed stream of superheated steam (via line 79 and valve 81 from line 23) and compressed air, if desired, from a line 83 controlled by a valve 85, against the atomized petrolatum. The heat thus imparted is sufficient to maintain the petrolatum in an atomized condition until it is further heat-treated, as provided hereinafter.

Under some conditions, the character of the petrolatum or other raw material is such that were the superheated steam to be brought in contact therewith, in the atomizer, coking might ensue, and the apparatus become clogged. For such contingencies, a cooling system is provided around the atomizer system. For example, relatively cool boiler steam from line 11 is admitted to the pipe 59 by way of a by-pass line 87, controlled by a valve 89. The pipe 59 is provided with a partition 90, preventing the cool steam from entering the tower 7. It is thus seen that a relatively cool jacket of steam is provided around the atomizer 57, and clogging due to coking is prevented. A control valve 189 is positioned in the boiler steam line 11, beyond the by-pass line 87, in order that the supply of wet steam to the atomizer cooler may be used without the necessity of also discharging wet steam into the reaction chamber by way of outlet 91.

Line 11, carrying boiler steam, continues and enters tower 7 directly through its top 51, and terminates as at 91 within said tower. Line 11 serves for initially warming the tower, and for a fire protecting means, as will appear more fully hereinafter.

The assembly at the bottom of tower 7 is illustrated in Fig. 5. Numeral 93 indicates a tube or pipe projecting well into the center portion of tower 7. Within the pipe 93 is a coaxial, but relatively smaller pipe 95 (see Figs. 4 and 5). The connections are illustrated in Fig. 5. Flow in pipe 93 is controlled independently of flow in pipe 95 by means of a valve 97. Similarly, flow in pipe 95 is individually controlled by a valve 99.

Feeding the pipes 93 and 95 is accomplished through superheated steam line 25, by way of valve 101, while air is fed from a pipe 103 branching from line 83, controlled by valve 105. Thus air and/or steam may flow in either or both of the tubes 93, 95.

Drain pipes 107 lead from the jacket 41 and central portion of tower 7, whatever sumps, or residuums, are not vaporized. Such are usually not utilized, but with the recycling thereof, additional products may be obtained.

Returning to Figs. 1 and 2, numeral 109 indicates a vapor discharge line leading from the top of inner jacket 41. The line 109 passes to a first reboiling or reaction tower 111, and terminates in a pipe 113 leading nearly to the bottom of said tower 111. A branch air line 115, controlled by a valve 117, leads from main air line 83 to the top of tower 111. The tower 111 is normally empty. A drain 119 is provided for withdrawing knock-back liquid fractions (obtained only in small volumes). A discharge line 121 leads from first reaction tower 111 to a second reaction tower 123, having a pipe 125 similar to pipe 113, a drain 127 similar to drain 119, and a discharge line 129 similar to line 121. The tower 123 is likewise empty.

The discharge line 129 leads to a pipe 131 extending nearly to the bottom of a scrubbing tower 133, having a perforated plate 135 near the bottom thereof supporting crushed porous brick and the like 137. A drain 139 is provided for the scrubber 133, although no substantial condensation takes place therein. A discharge line 141 leads from the top of scrubber 133 to a fractionating tower 143 and condenser and gas separator (all conventional) indicated at numeral 145. A pressure relief valve 147 is provided in line 141.

It is to be understood that the entire system subsequent to the tower 7 is shown by way of example only, and that any suitable condensing and fractionating system may well be employed.

The operation from a process standpoint, is as follows:

The petrolatum, desirably preheated as hereinbefore indicated, is forced by pump 5 through line 3 to the atomizer 57. Here it meets superheated steam, and is sprayed from nozzle 75 as a mist of fine droplets, its phase, nevertheless, remaining liquid. By the time the petrolatum reaches nozzle 75 it is quite thoroughly liquefied, by being indirectly heated by steam in the pipes and jackets of the atomizer.

The downwardly-directed spray of petrolatum, in the central portion of tower 7, almost immediately meets the upwardly-directed spray of superheated steam from pipe 93 (or 95). The heating effect is substantially instantaneous. However, the force of the upwardly-directed blast of superheated steam prevents the now vaporized petrolatum from falling to the bottom of tower 7 too fast to avoid heat treatment, and also prevents any substantial mechanical carrying-over of droplets and the like.

Finally, after a sufficient time in direct contact with the superheated steam, the vaporized petrolatum, together with the somewhat cooled steam, passes downwardly and out into the inner annular jacket 41. Any liquid fractions not vaporized fall to the bottom of tower 7 and may be withdrawn by draw-offs 107. However, very little if any of the petrolatum will be found not vaporized after the steam treatment.

Oxygen, or air, is desirably admitted with the steam into tower 7 from above and below, in order to secure the advantageous reactions hereinbefore mentioned.

The mixed steam and petrolatum vapors rise relatively slowly in the inner annular jacket 41, and the chemical reactions therebetween commence. When the mixed vapors reach the top of tower 7 they are drawn off through line 109 to reaction tower 111, where the reaction continues with substantially no condensation. Additional air may be admitted to tower 111 through line 115 if it is desired further to oxidize the products.

From the first reaction tower 111 the vapors pass to the second reaction tower 123, where the chemical reaction is substantially completed. Subsequent passage through the scrubber 133 removes objectionable foam and the like which might be present. The vapors pass from the scrubber 133 to fractionators and condensers and gas separators, where they are condensed and separated into various fractions.

A back pressure, say of the order of 60–70 pounds, may be maintained on the system by means of relief valve 147. This relatively slight back pressure, I have determined, inhibits cracking to an optimum extent and also increases the speed of chemical reaction.

The products obtained from the treatment of petrolatum as described are (1) a greatly increased amount of wax, or paraffine, quite desirably free of grease or oil, (2) a series of relatively low boiling oils, of oxygenated character, the complete composition of which is not yet fully determined, and (3) a combustible fixed gas. Thus the original grease and oil in the petrolatum appear to have been completely converted into new oxygenated oils and partially oxidized paraffine. The paraffine is valuable commercially in the manufacture of fatty acids for soap making.

The temperatures and pressures achieved during treatment of petrolatum as described are as follows:

The boiler steam passes to the superheater at a temperature of the order of 275° to 300° F., the pressure being seventy to eighty pounds. In the superheater, the steam is heated to the order of 1000° to 1400° F., but the increased pressure is compensated for, at least in part, by increased velocity.

The petrolatum entering the atomizer is preheated to the order of 400° to 450° F. Its pressure is somewhat lower than that of the superheated steam, to secure proper atomization. The spray issuing from the atomizer is at a temperature of the order of 400° to 500° F.

The primary, central, contacting zone of the tower 7 is at the order of 1000° F. If no air is being admitted, the pressure is of the order of forty pounds; but with air admission, valve 147 is preferably regulated to secure a pressure of the order of seventy pounds. The vapors issue from tower 7 at a temperature only slightly below the primary, central zone temperature.

It is to be understood that these values are by way of example only, and that varying raw materials naturally require change thereof for optimum results.

To start operations in the cold tower 7, steam is preferably admitted to warm said tower to operating temperature through lines 91 and 93. Under running conditions, the small line 95 carries the steam for the heating purpose in sufficient volume, and at a desirably greater velocity, than the pipe 93. The pipe 91, carrying relatively cool boiler steam, is not ordinarily open during normal running conditions, but it may be used at any time for putting out possible fires and the like.

It is thus seen that from a comparatively valueless raw material, petrolatum, a series of valuable, saleable products are obtained.

Attention is directed to the flexibility of the invention as hereinbefore described. Temperatures, pressures, and even reaction constituents may readily be varied. Without the admission of air, oxidation is relatively slight, and the process is comparable to a simple distillation. When air is admitted, or under conditions of great decomposition of the steam, complete structural, chemical rearrangement of the raw material may be secured.

This flexibility of control may be advantageously utilized in treating various raw materials. Several examples, in addition to the case of petrolatum described hereinbefore, will suffice to show the wide range of applicability of the invention:

(1) Crudes or topped crudes are desirably preheated to a temperature just below their decomposition point and then atomized into the superheated steam jet, at the proper temperature and flow velocity. Temperatures are controlled so that the highly viscous base (asphalt or paraffine or both) is dropped out as a residue, and the lighter fractions are carried overhead to be fractionated and condensed. Oxidation may be added with the admission, with the superheated steam, of air. With paraffine base crudes, the entire charge may optionally be taken overhead.

(2) Residuums, tars, and asphalts are similarly treated, the temperatures being such as to drop out insoluble matter. In this case, oxidation is desirably utilized to enhance the lightness of the product distillates.

(3) Vegetable oils, fats, fatty acids, and the like are desirably liquefied by preheating and then treated as above. Oxidation causes the production of an entirely new range of products.

In view of the above, it will be seen that the several objects of the invention are achieved and other advantageous results attained.

As many changes could be made in carrying out the above constructions, compositions and processes without departing from the scope of the invention, it is intended that all matter contained in the above description or shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

I claim:

1. The process of treating petrolatum which comprises atomizing said petrolatum with steam, spraying superheated steam at a temperature of the order of 1200° Fahrenheit, together with oxygen, directly into said atomized petrolatum, allowing the hot mixture of steam, oxygen, and petrolatum vapors to remain in contact sufficiently long for reactions to take place therebetween, and then fractionating and condensing the resulting vapors, the said reactions being effective to yield an increased amount of wax or paraffine desirably free of grease or oil and a series of relatively low boiling oils of oxygenated character.

2. The process of separating paraffine from grease and oil in petrolatum, which comprises atomizing said petrolatum, and contacting superheated steam and air with the atomized petrolatum in a reaction zone maintained at a temperature of the order of 1000° F., the time of reaction being such as to avoid deleterious cracking.

JOHN D. ZIELEY.