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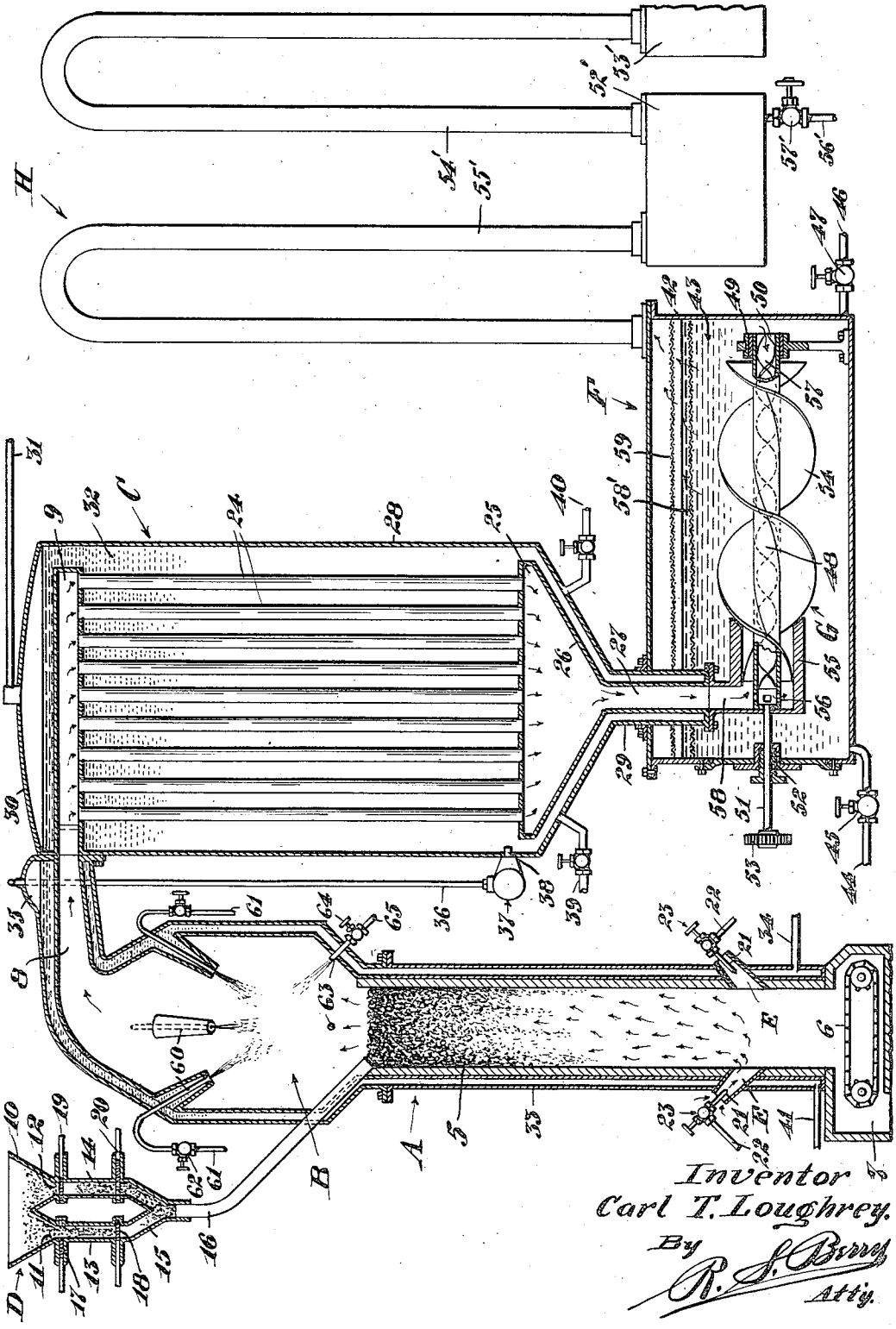

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## METHOD FOR TREATING OILS

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This invention relates to the art of refining and fractionating oils and more particularly pertains to the production of synthetic oils.

The primary object of the invention is to provide a method whereby petroleum and other hydrocarbons may be treated to effect refining and fractionation thereof and to produce synthetic hydrocarbons, and which method is applicable for use in hydrogenating, refining and fractionating oils of various characteristics, such as sweet oil, sour or sulphur containing oils, and fatty oils, with or without water content.

The invention contemplates the provision of a method whereby the oil under treatment will be subjected coincidently to the action of nascent hydrogen and hot fixed gases in such manner that the nascent hydrogen will effect hydrogenation of the oil and simultaneous desulphurization thereof if sulphur be present, and the hot fixed gases together with the nascent hydrogen effect fractionation of the oil; and also whereby the oil may at the same time be dehydrated if it has a water content.

Another object is to provide a method of the above character in which the nascent hydrogen and the fixed gases will be generated as used, with or without a dehydrating action, and in which such gas generation and the treatment of the oil will be accomplished interiorly of the one apparatus and in the one operation.

Another object is to provide a means whereby nascent hydrogen and fixed gases can be generated and impacted collectively under velocities and at predetermined temperatures into a body of oil in such manner as to effect hydrogenation and fractionation of the oil and also effect desulphurization of the oil if it have a sulphur content.

A feature of the invention resides in the provision of a method whereby the gases will be caused to impact on the oil under high velocity, and synthesis of the unsaturated constituents of the oil effected without developing a high pressure.

Another object is to provide a method whereby volatilized metallic sodium can be associated with the fixed gases and directed therewith into a water containing oil under treatment to produce nascent hydrogen directly within the oil body and thereby increase hydrogenization of the oil.

Another object is to provide an apparatus whereby gases may be generated and directed under velocity and at a predetermined temperature into a body of liquid in such manner as to impact on the liquid and in such manner as to obviate back pressure or rebound, thereby insuring against reversal of chemical action.

With the foregoing objects in view together with such other objects and advantages as may subsequently appear, the invention resides in the steps and features, hereinafter more fully described and illustrated by way of example in the accompanying drawing, in which:

The figure is a diagrammatic view in vertical section with parts in elevation illustrating an apparatus for carrying the method into effect.

The apparatus, as illustrated in the drawing, embodies a gas producer A, including a shaft 5 arranged so that sufficiently heavy materials delivered to the upper portion thereof may gravitate therethrough, and for which purpose is preferably disposed vertically. The lower end of the shaft is fitted with a grate 6 here shown as of the travelling type adapted to effect the discharge of residuum material from the lower end of the shaft through a discharge opening 7.

The upper end of the shaft 5 is in open communication with an expansion chamber B from the upper end portion of which leads a horizontally extending gas discharge pipe 8 communicating with a manifold 9 of a boiler C constituting a combined heat exchanger and steam generator.

A fuel charging device D is provided for delivering carbonaceous fuel to the upper end of the shaft 5 which is here shown as embodying a hopper 10 having twin outlets 11 and 12 connecting with a pair of parallel vertical conduits 13 and 14 terminating at their lower ends in the branches of a Y-connection 15, the stem portion of which connects with the upper end of a feed pipe 16 leading downwardly and extending through the walls of the expansion chamber B and having its lower end opening to the upper end of the shaft 5. A pair of dampers 17 and 18 are provided in the conduit 13 adjacent to the ends thereof and a corresponding pair of dampers 19 and 20 are provided in the conduit 14 adjacent its ends, which dampers are designed to be operated to effect a continuous feed of granular solid fuel materials from the charging device to the feed pipe and to the upper end of the shaft, as will be later described.

The shaft 5 is fitted at its lower end portion with a series of tuyères E, which open downwardly at an angle to the vertical center of the shaft and are open at their outer ends to form a means of air intake to the shaft. Projecting into the tuyères E are nozzles 21 connecting with feed pipes 22 through regulating and cut-off valves 23 and through which nozzles suitable fluids, gaseous

or liquid or both, are directed as desired into the charge at the lower portion of the shaft.

The boiler C is here shown as comprising a series of downwardly extending tubes 24 connecting at their upper ends to the manifold 9 and connecting at their lower ends to a manifold 25 having an inclined bottom wall 26 leading to a discharge throat 27; the boiler also including a shell 28 which encompasses the tubes 24 and manifolds 9 and 25 and has a downward extension 29 encircling the throat 27 and is formed at its upper end with a dome 30 extending above the manifold 9 with which is connected a steam take-off pipe 31. The boiler shell 28 is designed to contain a body 32 of water which surrounds the manifolds 9 and 25 and the tubes 24 and serves as a cooling medium to effect the reduction of temperature of hot gases delivered through the tube 24 and the manifolds, as will be later described.

The shaft 5, expansion chamber B, and gas discharge pipe 8 are enclosed by a water jacket 33 to which water is supplied from any suitable source through an intake pipe 34, and the upper portion of the water jacket adjacent the connection of the pipe 8 with the manifold 9 is formed with a dome 35 from which leads a conduit 36 connecting with the intake side of an injector 37, the outlet side of which opens to the interior of the boiler shell 28 through a nozzle 38 whereby steam or hot liquids generated in the water jacket 33 by heat radiated from the shaft 5 and expansion chamber B will be delivered to the boiler C.

As a further means for delivering water to the boiler C, the shell thereof is equipped with a water intake pipe 39 connecting with any suitable source of water supply. The lower portion of the boiler shell 28 is provided with a draw-off pipe 40 through which water may be drained from the boiler as occasion may require. In like manner, the water jacket 33 is equipped with a draw-off pipe 41 through which water may be drained from the water jacket as desired.

Located beneath the heat exchanger or boiler C, is a combined hydrogenator and fractionator F which embodies an enclosed still 42 adapted to contain a body 43 of oil to be treated and to which still the oil is supplied as needed through a feed pipe 44 equipped with a feed valve 45. Residuum is discharged from the still continuously or from time to time as through a pipe 46 fitted with a valve 47.

Arranged within the still 42 is a combined induction, displacement, the mixing device G which embodies a horizontally extending revoluble tubular shaft 48, the outer end of which is supported in a bearing 49 and opens at 50 to the interior of the still and the inner end of which is affixed to a shaft 51 projecting through a packing gland 52 in an end wall of the still and which shaft 51 is adapted to be driven from any suitable source of power as through a gear 53 carried thereon. The shaft may be and is preferably driven by an engine, not shown, operated by steam generated in the boiler C.

Mounted on the shaft 48 exteriorly thereof is a spiral blade 54, and encircling the inner end portion of said blade is a cylinder 55, the inner periphery of which slidably contacts the outer margin of the encompassed portion of the spiral blade.

The inner end portion of the shaft 48 is formed with openings 56 forming a communication between the interior of the shaft and the cylinder 55, and mounted interiorly of the shaft 48 is a spiral blade 57 adapted to impel a stream of liquid through the shaft 48 from the still 42 into the cylinder 55 through the openings 56. The external blade 54 is arranged with the pitch thereof extending opposite that of the internal blade 57 and operates on the rotation of the shaft 48 to effect discharge of liquid from the cylinder 55 through the outer end of the latter into the still 42, and also serves to form a void in the body of liquid 43 and to effect rotation of the liquid around the margin of the void. The cylinder 55 is formed at its inner end with an intake 58 to which the discharge throat 27 is connected whereby on rotation of the blade 54 to displace liquid in the still gases will be caused to flow under their own velocities through the throat 27 and intake 58 and be impinged onto the body of liquid 43 and caused to act thereon as will be later described.

The upper portion of the still 42 connects with a condenser H which may be of any suitable character, being here shown as including a series of condensing chambers 52' and 53' connecting with each other and with the still 42 through conduits 54' and 55; the condensing chambers being fitted with draw-off pipes 56' equipped with valves 57' as is common in condensing apparatus.

The still 42 is provided with screens 58' and 59, which extend horizontally across the still in the path of gases rising therein, the screen 58' being submerged in the body of liquid 43 for the purpose of breaking up and reducing globules rising in the liquid body and the screen 59 being spaced above the surface of the liquid and being of fine mesh to effect breaking up of bubble or foam and also to separate the gases into fine streams and thereby bring the metal of the screen into intimate contact with the gases. The screens 58' and 59 are formed of a metal which will serve as a catalyzer.

Means are provided for introducing gases and liquids into the expansion chamber B which is here shown as comprising a series of downwardly projecting nozzles 60, leading through the walls of the expansion chamber at the upper portion thereof, each of which nozzles connects with a feed pipe 61 fitted with a valve 62, and through which nozzles any desired fluids may be directed into the expansion chamber as occasion may require. Leading upwardly through the bottom portion of the expansion chamber, is a second series of nozzles 63, each of which connects through a valve 64 with a feed pipe 65, and through which nozzles a fluid, such as water or steam, may be directed into the expansion chamber.

It will now be seen that the apparatus embodies in its ensemble, a retort including the shaft 5 and the expansion chamber B, constituting a combined gas and vapor producer, to which various solids, fluids, and gases may be fed as occasion may require; the charging device D enabling the continuous feed of a granular solid carbonaceous fuel material, such as charcoal, coke, lignites, bitumen, shale, etc., together with alkali or other solids where desired, to form a stack of such materials of predetermined level in the shaft 5; the tuyères and their associated nozzles 21 serving to admit air, combustible gases, water, etc., to the lower portion of the stack to afford the maintenance of a combustion zone in the lower portion of the stack and effect the production of gases therein, and the nozzles 60 and 63 leading to the expansion chamber B enabling the introduction of gases, fluids or semi-fluids into the generated gases delivered to the expan-

sion chamber from the shaft to produce gases and vapors of desired characteristics and volume in said chamber; the substances fed to the expansion chamber including water, hydrocarbon and sodium containing material. The various materials fed to the gas producer are delivered thereto as needed and in various combinations as occasion may require.

In the operation of the invention the shaft **50** is revolved to effect rotation of the helical blade **54** within the liquid body **43** which rotation of the blade **54** will act to displace the liquid in which it is submerged in such manner as to create a large void in the body of the liquid, and at the same time impart a rotary or swirling movement to the liquid thereby creating a vortex therein beneath the surface thereof; the portion of the blade **54** surrounded by the cylinder **55** acting primarily to displace the liquid in the cylinder and to force it with a positive action through the outer open end of the cylinder where the enlarged portion of the blade **54** will act to direct such displaced liquid outwardly into the main body of the liquid in the still. The void thus created is displaced in part during continued rotation of the shaft **50** and blade **54** by liquid which will flow into the cylinder **55** through the shaft **50** under the action of the spiral blade **57** within the latter, the blade **57** forcing such liquid through the openings **56** into the cylinder **55**. This liquid flowing into the cylinder **55** serves to afford a seal between the inner periphery of the cylinder **55** and the encompassed portion of the blade **54** so as to augment the action of the blade **54** in creating a void within the cylinder **55**. On the void being created within the cylinder **55** and within the body of liquid **43** gases will be permitted to flow under their own volition into such void through the throat **27** together with such vapors as may be generated in the gas and vapor producer A and expansion chamber B.

A constant and positive displacement will thus be effected throughout the communication leading from the tuyères E, through the charge in shaft **5**, expansion chamber B, passage **8**, manifold **9**, tubes **24**, manifold **25**, and through the throat **27** to the interior of the cylinder **55**; air flowing through the tuyères E into the fuel charge to support combustion in the latter on ignition thereof whereby an incandescent zone of carbon will be formed in the lower portion of the fuel charge. Carbon dioxide will be initially produced by the combustion of the fuel, which carbon dioxide will later be reduced to carbon monoxide within the fuel charge, thus resulting in a hot fixed gas which will flow under its own volition into the expansion chamber B. In practice the volume of air drawn into the charge, and the height and width of the fuel column are so proportioned that the incandescent zone will be formed in the column spaced from the upper end of the latter, thus providing a mass of fuel above the combustion zone to afford a seal between said zone and the expansion chamber. A fluid fuel which may consist of either a hydrocarbon or combustible gas, may be introduced into the fuel charge through the tuyères E, which fluid fuel is employed in conjunction with the fuel charge in the stack **5** and water vapors, such as steam, are directed into the fuel charge through the tuyères. The water vapors will be disassociated in the carbon incandescent zone, resulting in the formation of nascent hydrogen, which with the fixed gases will flow through the interstices of the charge under its own velocity into the expansion chamber.

An important feature of the invention resides in thus causing the gases generated in the fuel charge to flow under their own velocities as such obviates any possibility of channeling of the fuel charge and consequent flow of free oxygen into the expansion chamber and whereby the combination of oxygen with the carbon is insured. This feature is further advantageous in that it obviates the generation of the gases under pressure.

In some instances the hot gases thus generated may be of such character and volume as to effect the desired action on the liquid under treatment, but in some cases it may be desirable to generate gases of a volume in excess of the capacity of the gas producer A, in which event fluids, such as hydrocarbon, steam, or water vapors, and sodium containing substances are directed into the hot gases within the expansion chamber B through the nozzles **60** and **63** according to whatever result is desired. The present invention however contemplates the delivery of metallic sodium vapors into the oil under treatment and accordingly it is essential in carrying the invention into effect that no water vapors or steam be delivered to the expansion chamber at the time of forming metallic sodium vapors therein, or at least in insufficient quantity to form an excess of sodium compounds or materially interfere with the formation of metallic sodium vapors in such volume as is required to effect hydrogenation of the oil under treatment.

The gases flowing from the expansion chamber B and passing downwardly through the tubes **24** will be reduced in temperature by the conduction of heat therefrom through the walls of the tubes **24** and their communicating manifolds into the body of water surrounding same; the heat thus exchanged being utilized to generate steam which is taken off through pipe **31** thus affording a supply of steam which may be employed as occasion may require. The temperature of the gases may be regulated as by controlling the flow of water through the heat exchanger. However, the temperature of the gases is maintained sufficiently high to effect the desired chemical action in the still **42**.

The capacity of the boiler tubes **24** is such as to permit considerable expansion of the gases; the tubes having collectively a cross sectional area greater than the area of the expansion chamber B, which increased area causes more frequent impact of the generated gases and thereby augmenting lateral radiation of heat and rapidly effecting the reduction of temperature of the gases.

It is manifest that in order to effect the delivery of metallic sodium vapors to the oil in the still F, the temperatures of the gases and vapors discharged from the boiler C through the throat **27** and into the void formed in the oil body by the rotating helical blade **54** must be in excess of the boiling point of sodium, which temperature is also such as to effect cracking of oil under treatment.

The boiler C acts as a means for controlling the temperatures of the gases and vapors delivered from the chamber B and serves to prevent the delivery of gases of too high temperature to the oil under treatment. Without the provision of some means of control of the temperatures of the gases as delivered from the

chamber B the apparatus would be liable to run wild and gases of undesirably extreme high temperatures might be delivered to the still.

The gases flowing into the void formed in the body of the liquid under treatment will be impinged upon the rotating liquid and will be occluded therein and will pass upward through the liquid thus being prevented from rebounding into the void. Thus no back pressure will be formed, and by reason of the action of the blade being continuous no pulsations will occur in the apparatus.

The gases thus directed into the body of liquid will be of such temperatures as to effect fractionation of the oil and also to cause the metallic sodium vapors to coact with water in the oil in the still and thereby form nascent hydrogen to effect combination with the unsaturates of the oil and to combine with such sulphur as may be present in the oil.

The body of liquid contained in the still comprises that which is to be treated and may consist of any liquid or mixture of liquids subject to being acted on by hot gases and vapors in the manner herein set forth, such for example as hydrocarbon or oil with or without a sulphur content and with or without a water content. However in most instances where a hydrocarbon is treated it will carry some water naturally, and also it may be desirable to add water to an oil to be treated thereby forming an emulsion.

As a means for increasing the nascent hydrogen content of the gases in the expansion chamber and for producing nascent hydrogen in the body of oil under treatment where water is present, sodium in the form of an oxide, hydroxide or carbonate, is introduced into the gas generator either at the tuyère zone, or through the fuel feed or into the expansion chamber, where it reacts with carbon and is thereby reduced to volatilized metallic sodium which mingles with the gases in the expansion chamber. A portion of the metallic sodium will react with carbon monoxide in the expansion chamber, but another portion thereof will remain in vaporous form and will pass off with fixed gases to the still.

Where it is desired to generate nascent hydrogen in the body of oil under treatment, which can be readily effected where there is water present in the oil, the metallic sodium vapors are introduced with the hot gases from the expansion chamber free of $H_2O$ into the liquid in the still where the sodium disassociates the $H_2O$ present in the oil thus liberating nascent hydrogen and producing sodium oxide or sodium hydroxide or sodium carbonate; the sodium being co-mingled with sludge or residue formed in the still, and the nascent hydrogen combining with the unsaturated carbon in the oil. The sludge or residue will then contain sodium in the form of an oxide, hydroxide or carbonate, together with carbon and affords a material which on being introduced into the gas generator will supply additional carbon for fuel and will serve as a supply of the sodium. In this manner the sodium may be used repeatedly it being alternately converted into metallic sodium and sodium oxide or sodium hydroxide or sodium carbonate. The hot gases together with the metallic sodium vapors flowing through the throat **27** into the cylinder **55** act on a portion of the liquid directed into the cylinder through the shaft **48** to convert the oil and water content of such portion into vapors and at the same time create nascent hydrogen at this point by the action of a portion of the sodium vapors on the water vapors.

Where it is desired to increase the hydrogen content of the gases in the expansion chamber, mixed hydrocarbon and $H_2O$ is sprayed into the latter, which $H_2O$ is disassociated by the metallic sodium, resulting in liberation of nascent hydrogen in the presence of the hydrocarbon and the formation of sodium oxide or other sodium compounds; the latter gravitating onto the fuel charge and the nascent hydrogen combining with the hydrocarbon and effecting saturation thereof which latter is carried over with the gasses previously generated.

A sludge or residue formed in the still **42** by the action of the hot gases and vapors of the liquid body **43** may be drawn off continuously or from time to time as may be expedient and is preferably directed into the expansion chamber B through the nozzles **60** in the form of a spray where it will be acted on by the high temperatures of the gases entering the expansion chamber from the gas producer to effect cracking thereof.

The fixed gases together with such gases as may be formed by the reaction of the nascent hydrogen on the unsaturates of the oil under treatment will flow under their own volition upwardly through the body of liquid **43** and the bubbles thereof on impacting on the screen **58'** will be broken up or reduced and the liberated gases together with such vapors as may be generated in the liquid body by the action of the heated gases thereon to pass through the screen **59** through the condensers H where the desired recoveries are made in the usual manner.

A catalytic action may be effected to facilitate the combination of the nascent hydrogen with the unsaturates of the oil under treatment as by forming the screens **58'** and **59** of a catalyzing material or by incorporating a catalyzing substance in the body of liquid under treatment.

By means of the apparatus herein set forth a continuous operation may be effected as the fuel and substances for generation of the gases and vapors may be fed continuously or as needed to effect continuous formation of the gases, while continued flow of the generated gases through the body of the liquid under treatment will occur during continuous rotation of the blade **54**, and the oil or liquid to be treated may be fed continuously or substantially so through the resorvoir **42**.

I claim:

1. The process of treating oils which consists in generating hot fixed gases by a combustion of carbonaceous fuel, impacting said hot fixed gases together with metallic sodium vapors into a body of oil containing water wherein the force of impact of the gases and vapors is that of their own velocities stimulated by heat, and maintaining the oil in a state of agitation around the zone of impact of the gases and vapors.

2. The process of treating oils which consists in generating hot gases and vapors by combustion of carbonaceous fuel thereby forming a zone of incandescent carbon and introducing a reducible sodium compound into said zone to form metallic sodium vapors consisting of fixed gases and metallic sodium vapors, creating a void within a body of liquid containing oil and water and permitting the hot gases to flow under their own velocities directly into the void.

3. The method of treating oils which consists in effecting a positive displacement within a body

of liquid containing oil and water, generating hot gases and vapors comprising fixed gases and metallic sodium vapors under the action of such displacement by combustion of carbonaceous fuel thereby forming a zone of incandescent carbon and introducing a reducible sodium compound into said zone to form metallic sodium vapors, effecting impact of such gases on the liquid under their own velocities directly at the point of displacement of the liquid and occluding the gases within the body of liquid.

4. The method of treating oils consisting in generating a mixture of hot fixed gases and metallic sodium vapors by combustion of carbonaceous fuel thereby forming a zone of incandescent carbon and introducing a reducible sodium compound into said zone to form metallic sodium vapors, and impacting and occluding said hot fixed gases and vapors as generated within a body of liquid containing oil and water.

5. The method of treating hydrocarbons to produce fractionates and synthetic products consisting in generating hot gases including fixed gases and metallic sodium vapors but free of oxygen by combustion of carbonaceous fuel thereby forming a zone of incandescent carbon and introducing a reducible sodium compound into said zone to form metallic sodium vapors, effecting positive displacement in a body of liquid including the hydrocarbon together with water and permitting the gases and vapors to flow as generated into the void formed by displacement of the liquid and to impact on the liquid under their own volition and at such temperature as to effect hydrogenation and fractionation of the hydrocarbon.

6. The method of treating hydrocarbons consisting in generating fixed gases, sodium vapors and sodium vapors by combustion of carbonaceous fuel thereby forming a zone of incandescent carbon and introducing a reducible sodium compound into said zone to form metallic sodium vapors and causing said gases and vapors to flow under the volition of the gases and at predetermined temperatures into a body of liquid including the hydrocarbon together with water by effecting positive displacement of the liquid.

7. The method of treating hydrocarbons consisting in creating a vortex beneath the surface of a body of liquid containing the hydrocarbon and water under barometric pressure, forming a zone of incandescent carbon by combustion of carbonaceous fuel and introducing a reducible sodium compound into said zone to form metallic sodium vapors and directing the resultant gases and vapors directly into the vortex.

8. The method of treating sulphur containing oils to effect fractionation and desulphurization thereof and also produce synthetic products which consists in forming a zone of incandescent carbon by combustion of carbonaceous fuel and introducing a reducible sodium compound into said zone to form metallic sodium vapors and directing the resultant gases and vapors into a liquid containing water together with the oil to be treated.

9. The method consisting in generating metallic sodium vapors by introducing a reducible sodium compound into a zone of incandescent carbon and causing said vapors to enter a body of liquid under treatment containing water.

10. The method consisting in generating metallic sodium vapors from sodium compounds by the reducing action of carbon, and causing the resultant vapors to enter a body of water containing liquid under barometric pressure.

11. The process consisting in generating metallic sodium vapors from sodium compounds by the reducing action of carbon, and directing such vapors and associated fixed hot gases through a body of liquid containing hydrocarbon and water under barometric pressure and at a predetermined reduced temperature.

12. The herein described method of treating hydrocarbon comprising generating hot fixed gases by combustion of carbonaceous material thereby forming a zone of incandescent carbon, introducing a reducible sodium compound into said zone of incandescent carbon to form metallic sodium vapors, performing the foregoing steps under barometric pressure, imparting a gyratory motion to the liquid beneath the surface of a body of liquid containing a hydrocarbon and water thereby forming a void in said body and directing the fixed gases together with the sodium vapors directly into the void.

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