

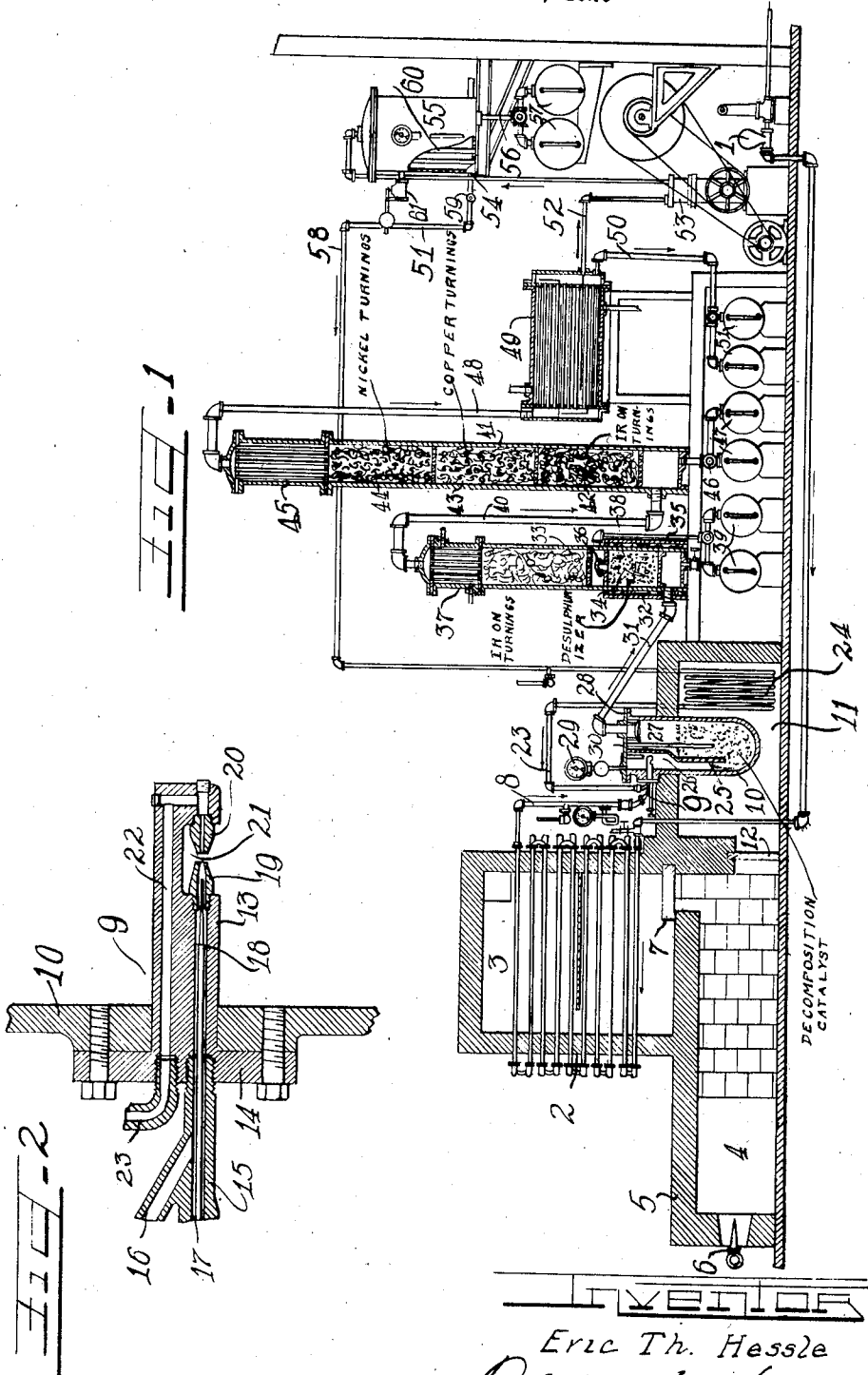
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CONTINUOUS PROCESS FOR THE REFINING OF OILS

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CONTINUOUS PROCESS FOR THE REFINING OF OILS.

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This invention relates to a continuous process for the conversion of hydrocarbon oils into other hydrocarbons of lower boiling points. More particularly it relates to a continuous catalytic process for refining oils, such as crude petroleum oils, its distillates and residues, tar oil, brown coal tar oil, shale oil and similar products.

In so far as it relates to the same subject matter, this application is a continuation in part of my application, Serial No. 678,924, filed December 6th, 1923, for "a continuous process for the refining of mineral oils", now Patent No. 1,661,826.

In the so called "cracking processes", the heavy oils are submitted to temperatures in substantial excess of their normal boiling points by maintaining the oils under relatively high pressures. The cracking of the oils is brought about solely by virtue of heat reactions.

Temperatures used in modern commercial plants are in excess of 450° C.

High temperatures mean correspondingly large fuel consumptions, the B. t. u. value of such fuel being equivalent to that of from 6 to 12 per cent of the "through put" oil.

Local overheating tends toward the oxidation of the iron of the cracking apparatus, resulting in frequent bursting of the tubes.

Considerable difficulty is experienced in cracking processes from the formation of carbon, in an amount equivalent to 5 to 15 percent of the through put oil, depending upon the character of the oil. This carbon renders the iron brittle through the formation of iron carbides. The consequent result is that the ordinary cracking process is not continuous, for the reason that the plant must be shut down to remove the adhering carbon.

In order to remove the suspended carbon in the oil, settling tanks or digesters are in general necessary.

Besides the loss due to the formation of carbon, a further loss occurs from the formation of non-condensable gases, representing from 6 to 12 percent of the through put oil, according to the nature and character of the oil.

Pressures used in modern commercial plants range from 100 to 1000 lbs. and over.

Beause of the high pressures employed both in the tubes and in the settling tanks there is an ever present danger of explosions.

Furthermore, high pressures require high

powered pumps of special design for circulating the oil through the system.

Because the desired cracking effect is not produced in a single stage of the operations, a great deal more heat must be applied in re-cracking the reflux oil than would be needed for all preheating purposes. The process therefore requires large fractionators and enormous quantities of cooling water.

In order to get away from local overheating in the tubes of the still, it has been proposed to use external or internal metal baths. Among the metals suggested for such baths are those metals or alloys having melting points below 700° C., excluding, however, metals which easily form carbides.

One of the better known so called catalytic processes employs tin, or its alloys, in reaction kettles coated on the inside with tin and provided with baffles also coated with tin. In that process the reaction chamber is either heated up to a read heat (800° C.), at which cracking would take place even without the presence of tin or its alloys, or else the process is carried out at lower temperatures employing a certain pressure and longer reaction time. In neither instance is the process, strictly speaking, a catalytic one. Even where the conversion of the oil has been carried out in the presence of tin and excess quantities of hydrogen, the process cannot be considered a truly catalytic one for the reason that tin is not a commercial hydrogenation catalyst.

My process, however, is not a cracking process in the sense in which the term is used, nor is it similar to the known so called catalytic processes. I do not maintain a super atmospheric pressure in the reaction kettle. Furthermore, the temperature of the reaction kettle is always kept below the boiling point of the oil to be treated and is, if working on heavy residue oils, not in excess of 400° C.

In my process the decomposition of the heavier hydrocarbon oils into oils of lower boiling point, or, as in the production of blaugas, into gases, is accomplished by true catalytic action of high efficiency on the oil in a fog like state. I obtain higher yields than are realized in the ordinary cracking processes or in known catalytical processes.

Where in the prior art, it has been suggested to carry out the conversion process with the oil in an atomized condition, it is evident that the conversion does not actually

take place with the oil in a liquid phase, since at the temperatures of red heat employed the oil must necessarily be vaporized.

Moreover, by "atomized" has been meant a relatively finely dispersed condition of the liquid oil effected by, (1) mechanically spraying the oil through a nozzle into a stationary body of gas, or (2) by drawing the oil into a moving stream of the gas, on the Bunsen principle, or (3) on the Koerting principle. In either case the globules of oil produced are so large and the surface of the globules so relatively small that where the process is supposedly a catalytic one, efficient catalytic action is impossible. In the second place the globules of oil by virtue of their size and density are subject to the action of gravity and tend to coalesce, especially when in contact with the catalyzer. The consequence is that an oil layer is always formed on the surface of the catalyzer, which layer distills off, leaving immediately a residue of coke.

My process contemplates not the atomization of the oil in the manner before described and with the attendant disadvantages enumerated, but rather the production of a true fog of oil. The fog which I have reference to cannot be compared with the atomized or sprayed oil of the literature, as it is entirely different in physical properties and in its behavior toward a decomposition catalyst. It is of such an extreme state of subdivision that it has all the properties of a true fog, being semi-opaque to the transmission of light, and comparatively insensible to the attraction of gravity, remaining in a floating condition for an indefinite period of time.

It is therefore a very important object of this invention to provide a fog producing device of special construction whereby the oil is discharged under a definite pressure against a counterstream of gas and thus to effect the conversion of the oil while the same is in a highly dispersed liquid phase. In this way a greater capacity of the reaction vessels is realized and a greater efficiency of catalytic action is had than when the conversion takes place in the vapor phase.

Other and further important objects of my invention will be apparent from the disclosures in the following specification and appended claims.

In carrying out my process, I employ a form of apparatus such as illustrated in the accompanying drawings in which:

Figure 1 is an elevational view of my apparatus, with parts in section.

Figure 2 is an enlarged sectional detail view of my oil fog producing device.

The oil to be converted is pumped by means of a pump 1 through a preheating coil 2, mounted in a chamber 3 above the firebox 4 of a furnace 5. Said furnace 5 may suitably be provided with a gas or oil type burner 6 adapted to be easily controlled. A damper

or gate 7 between the firebox 4 and the heating coil chamber 3 serves to regulate the temperature in said chamber. The oil in the coil 2 is preheated to a temperature of 200 to 350° C. under a pressure of 3 to 8 atmospheres, depending upon the characteristics of the oil to be treated. The oil then passes from the preheater coil 2 through an insulated pipe 8 into an oil fog producing device 9 of my special construction. Said oil fog producing device 9 extends through a side wall of a re-action kettle 10 which is supported in the brick work of the furnace 5 and is suspended, as shown, in a compartment 11 thereof. A control damper 12 is located between the fire-box 4 and the compartment 11 to enable the temperature of said compartment 11 to be easily regulated.

The oil fog producing device 9 (Figure 2) comprises a passaged body portion 13 which extends through the wall of the kettle 10 and is bolted thereto through an integral flange portion 14. A Y-fitting 15, threaded into said body portion, provides an oil passage 16, adapted to be connected to the pipe 8 and a communicating passage 17 having a needle valve 18 for controlling the flow of oil through a nozzle 19 on the inner end of said passage 17. Said nozzle 19 together with an opposing nozzle 20 are positioned in a recess 21 provided for the purpose in the lower side of said body portion 13. The nozzle 20 is connected by means of a passage 22 to a pipe 23, which serves to introduce some suitable gas or vapor into the fog producing device, as will later be explained. Said pipe 23 leads back to a preheating coil 24, positioned in the compartment 11 and serving to preheat the gas or vapor to substantially the temperature of the reaction kettle 10.

Said kettle 10 is preferably a relatively deep round bottomed kettle having a vertical partition 25 therein which extends from the top of the kettle to a point near the bottom thereof, as shown, and divides the kettle into two compartments 26 and 27 communicating with each other at the bottom of the kettle. Compartment 26, which includes the fog producing device 9 is preferably smaller than compartment 27. The top of the kettle 10 has a flanged cover 28 in which are mounted a pressure gauge 29 and a thermometer well 30. The temperature within the reaction vessel is in general maintained between 250 and 400° C., depending upon the nature of the oil which is being treated. If working on gas oil the temperature employed is usually 280 to 350° C., but if working on lower boiling hydrocarbons the temperature may be less. On the other hand, if operating on high boiling residues and asphalts the temperature rises to 400° C.

Within the kettle 10 is placed a decomposition catalyst of my invention. Tin, tin-

lead or tin-antimony alloys can be used but I prefer to use an alloy composed of tin containing less than ten percent of antimony. This alloy is not one of the common alloys of tin, nor has it to my knowledge ever been used as a catalyst. Such a catalyst gives very satisfactory results in effecting the decomposition of the hydrocarbon oils. Specifically, I have found from experiment that if only 1% of antimony is used, the highest decomposition factor is obtained. This is illustrated in the following table, which shows for different percentages of tin and antimony, the corresponding decomposition factors and the corresponding yields of gasoline. Tests were made under the same operating and temperature conditions in an experimental plant, using the same oil each time, which was a gas-spindle oil with a specific gravity of 0.88, a viscosity of 1.9 at 50° C. and a flash point of 140° C.

In these tests, the fractions having boiling points over 150° C. were first condensed in a bubble tower (fractionator) by temperature control and the resulting reflux pumped back once more through the system. The vapors leaving this bubble tower were lead into a gasoline tower where they were condensed. For the test—marked "heat-pressure test" in the following table, a pipe connection was made from the tube still direct to the first bubble tower leaving out the reaction kettle, and by regulating a needle valve on the end of this connecting line the pressure in the furnace was maintained at 75 atmospheres and a temperature of 525° C. A high powered steam pump pumped the oil to the furnace and this pump was later connected to the reflux.

The decomposition factor referred to is based upon the number of c. c. of gasoline, having an initial boiling point of 55° C. and an end boiling point of 150° C., which is obtainable from 100 c. c. of the aforesaid spindle oil. By assuming arbitrarily a unit decomposition factor for lead as a catalyst, I have been able to express a simple relation between the decomposition factors of the catalysts used.

The table is as follows:

Description of process	Decomposition factor	Yield of gasoline
Heat-pressure test.....	(525°—75 atmospheres)	Per cent
100% lead catalyst.....	1	28
100% tin catalyst.....	1.2	30
94% tin 6% antimony.....	2.1	36
99% tin 1% antimony.....	2.5	63
		75

It is thus apparent that a catalyst composed of tin containing approximately 1% of antimony possesses remarkable value in the conversion of hydrocarbon oils.

The catalyst within the kettle 10 is maintained in a molten state at the temperature

above mentioned of between 250° and 400° C. The oil arriving from the preheater 2 through the piping 8 is discharged through the valve regulated nozzle 19 against the gas issuing from the opposing nozzle 20. In first starting up my refining unit this gas may be either hydrogen, illuminating gas, water gas or some other hydrogen containing gas. Hydrogen containing gas is used in the present case for the reason that my process contemplates subsequently hydrogenating the unsaturated conversion products. However, the hydrogen plays no rôle other than as a carrier medium in the decomposition step of my process, since the catalyst there used is not a hydrogenation catalyst, and the hydrogen may therefore be subsequently introduced in the hydrogenation towers, if desired. After the unit has been operating, the fresh hydrogen supply may be partially cut off and the residue or tail gases of the process may be substituted in part. These gases would naturally contain a certain percentage of hydrogen, since only a small fraction of the hydrogen originally introduced is consumed in the hydrogenation stage. It is evident that any deficiency in the quantity of hydrogen may be made up from time to time by introducing fresh hydrogen into the system, or by constantly adding a small fraction of this gas. I do not use large excesses of hydrogen. Whatever the source of the gas, it is first preheated in the coil 24 located in the chamber 11 up to the temperature of the oil delivered from the preheating coil 2. In practice it has been found essential that the pressure of this gas should be greater by a certain proportional amount than the pressure of the oil delivered from the coil 2, this proportion depending upon the gravity and viscosity of the oil. This tends to a more balanced delivery of the oil and gas through the nozzles of the fog producer 9, and produces a real fog intermediate the opposing nozzles.

The concussion of the oil from the nozzle 19 and the gas from the nozzle 20 results in the formation of a grayish yellow fog. It is important for the formation and maintenance of this fog that the temperatures of the oil and gas be the same, and that the impact of both constituents take place in a space which shares the temperature of the reaction kettle. Accordingly, I have found that the atomization is most satisfactory if brought about within the reaction kettle itself. By utilizing hydrogen, or gases containing hydrogen, I obtain the advantage of preventing a slow poisoning of the decomposition catalyst, which advantage is sometimes especially marked when operating on heavy oils, asphalt and sulphurous oils. Any metal sulphides or oxides which might be formed are reduced immediately by the hydrogen, so that the tin and antimony re-

main in the metal state practically indefinitely.

As previously explained, the oil fog is produced in the smaller compartment 26 of the reaction vessel. The pressure of fog formed depresses the molten catalyst, which rises by a corresponding amount in the other compartment 27, until the head of molten metal substantially but not quite equals the pressure of the gas within the compartment 26. Since no pressure of gas is maintained above the metal in compartment 27, the fog and gas in compartment 26 is forced by its own pressure down through the body of metal in compartment 26 and under the lower edge of the baffle 25 and from there is forced to the surface in compartment 27 by reason of the greater density of the metal. The oil in passing through the catalyst remains in its condition as a fog, until by virtue of the decomposing action of the catalyst it is converted into hydrocarbons of such lower boiling points that, under the conditions of temperature and pressure obtaining, such oils are vaporized. It is evident, therefore, that the conversion into hydrocarbons of lower boiling point takes place strictly in the liquid phase. This is of enormous advantage since the volume of the catalyst and reaction vessel need not be nearly so great as if the decomposition occurred in gaseous state. The internal pressure of the molten metals on the globules of oil, and also the protecting action of the gas surrounding the oil particles, act to prevent in part the vaporization of the hydrocarbon conversion products while passing through the catalyst.

I have found that a fog of oil such as formed in my process will pass through the molten catalyst as stated but that oil in bulk, or in finely divided streams or in an atomized or finely dispersed condition, when forced through the same molten catalyst, will rise to the surface practically undecomposed and there undergo ordinary distillation, leaving the usual coke and carbon residues on the surface of the catalyst and plugging up the whole system in a few hours. The formation of the fog, therefore, is a most important step in my process.

The vapors of the converted hydrocarbon oils accumulating in the open space in compartment 27 are led off through a conduit 31 into the base 32 of a tower 33. The base 32 is filled with an absorbing medium 34, such as iron and manganese oxides, or any other suitable desulphurizer, for the purpose of removing any sulphurous compounds that may be present. The oxides may be removed and regenerated from time to time as required. It will be noticed that the base 32 is insulated as at 35. This is for the purpose of preventing undue cooling with consequent condensation of the vapors at this point.

The oil vapors and hydrogen containing

gases next pass through a condensate trap 36 into the main portion of the tower, which is filled with iron or steel turnings. The upper part of tower 33 is provided with a straight tube condenser 37, from which the condensates formed therein trickle down onto the trap 36. From there the condensates are discharged through a pipe 38 into rundown tanks 39. From the top of the tower 33, the vapors and gases are led through a pipe 40 into the base of a tower 41. Said tower 41 is divided into three horizontal compartments 42, 43 and 44, containing iron, copper and nickel turnings respectively. These different metal turnings all act as hydrogenation catalysts and are arranged in accordance with their respective temperature requirements for efficient catalytic action. The use of various hydrogenation catalysts is old in the art but I claim as new the arrangement of catalysts according to their most efficient reacting temperatures. For instance, iron shows greatest activity as a hydrogenation catalyst at higher temperatures than either copper or nickel, and copper at higher temperatures than nickel. They are accordingly arranged with due regard to the temperatures naturally obtained in the different compartments of the tower.

The top of tower 41 is provided with a condenser 45, which together with the rest of the tower serves as a fractional condenser to remove the greater portion of the converted oil vapors. The condensates from tower 41 run by way of a pipe 46 into run-down tanks 47. The uncondensed vapors and gases are conducted from the top of the condenser 45 by way of a pipe 48 into a final condenser 49. From said condenser 49, the condensates pass through pipe 50 into run-down tanks 51. The uncondensed gases from the final condenser 49 are conducted by a pipe 52 to a compressor 53. Said compressor 53 subjects these gases to a pressure of approximately 15 atmospheres and delivers the compressed gases through a pipe 54 into a pressure tank 55, which is cooled inside by means of straight water tubes 60. At the side of this tank is a pressure relief valve 59, which is so arranged that it blows off to maintain the gas in the return pipe 58 at a definite pressure, depending upon the oil to be treated. Another relief valve 61 is used for relieving the amount of gas not needed for recirculation to gas burners under the still. The cooling of the compressed vapors in the pressure tank results in the condensation of a portion of the gases. The condensate so formed is led through a pipe 56 into pressure run-down tanks 57. The uncondensed hydrogenous tail gases are expanded from the side of the tank 55 and led through the return piping 58 back to the preheater 24 and thence to the fog producing device 9.

I am aware that numerous changes may be

made without departing from the principles of this invention, and I therefore do not purpose limiting the patent granted hereon otherwise than necessitated by the prior art.

5 I claim as my invention:

1. A process of converting hydrocarbon oils into lower boiling products which includes the step of directing a hydrocarbon oil against a counter current stream of a gas under sufficient pressure to form a true fog of oil and then passing said fog through a molten decomposition catalyst consisting of an alloy of tin and antimony containing less than 10% antimony, whereby decomposition of the oil takes place in the liquid phase, the resulting lower boiling products being released from said catalyst in vapor form.

2. A process of converting hydrocarbon oils into lower boiling products which includes the step of directing a hydrocarbon oil against a counter current stream of a gas under sufficient pressure to form a true fog of oil and then passing said fog through a molten decomposition catalyst consisting of an alloy of tin and antimony containing less than 10% antimony, said catalyst being maintained at a temperature of between 250° and 400° C., whereby decomposition of the oil takes place in the liquid phase, the resulting lower boiling oils being released from said catalyst in vapor form.

3. A process of converting hydrocarbon oils into lower boiling oils, which includes the step of forming a true fog of oil suspended in a gas, said oil and gas having been preheated to substantially the temperature employed in the subsequent decomposition step and then passing said fog through a molten decomposition catalyst, consisting of an alloy of tin and antimony containing less than 10% antimony, said catalyst being maintained at a temperature of between 250 and 400° C., whereby decomposition of the oil takes place in the liquid phase, the resulting lower boiling oils being released from said catalyst in vapor form.

4. A process of converting hydrocarbon oils into lower boiling hydrocarbons, which includes the step of forming a true fog of oil suspended in a gaseous medium, said oil and gaseous medium having been preheated to substantially the temperature employed in

the subsequent decomposition step and then passing said fog at substantially atmospheric pressure through a molten decomposition catalyst consisting of an alloy of tin and antimony containing less than 10% antimony, said catalyst being maintained at a temperature of between 250 and 400° C., whereby decomposition of the higher boiling oil takes place in the liquid phase, the resulting lower boiling hydrocarbons being released from said catalyst in vapor form.

5. The process of refining oils, which includes subjecting the oil in the form of a true fog at a temperature above atmospheric to the action of a decomposition catalyst comprised of tin and antimony, the latter being present in an amount equal to less than 10% of the tin.

6. The process of refining oils, which includes subjecting the oil at a temperature about atmospheric while in a highly dispersed fog-like liquid phase to the action of a decomposition catalyst comprised of tin antimony alloy containing less than 10% antimony.

7. The process of refining oils, which includes subjecting the oil while in a highly dispersed fog-like liquid phase to the action of a decomposition catalyst comprised of tin antimony alloy containing less than 10% of antimony and maintained in a molten condition at a temperature of between 250 and 400° C.

8. The process of refining oils, which includes subjecting the oil while in a highly dispersed fog-like liquid phase at a temperature above atmospheric to the action of a decomposition catalyst comprised of tin antimony alloy containing less than 10% of antimony and maintained in a molten condition at a temperature below the normal boiling point of the oil.

9. The process of refining oils, which includes subjecting the oil while in the form of a true fog and at substantially atmospheric pressure to the action of a decomposition catalyst comprised of tin antimony alloy containing less than 10% of antimony and maintained in a molten condition at a temperature of between 250 and 400° C.

In testimony whereof I have hereunto subscribed my name.

ERIC TH. HESSLE, PH. D.