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E. T. HESSLE

PROCESS FOR REFINING OIL

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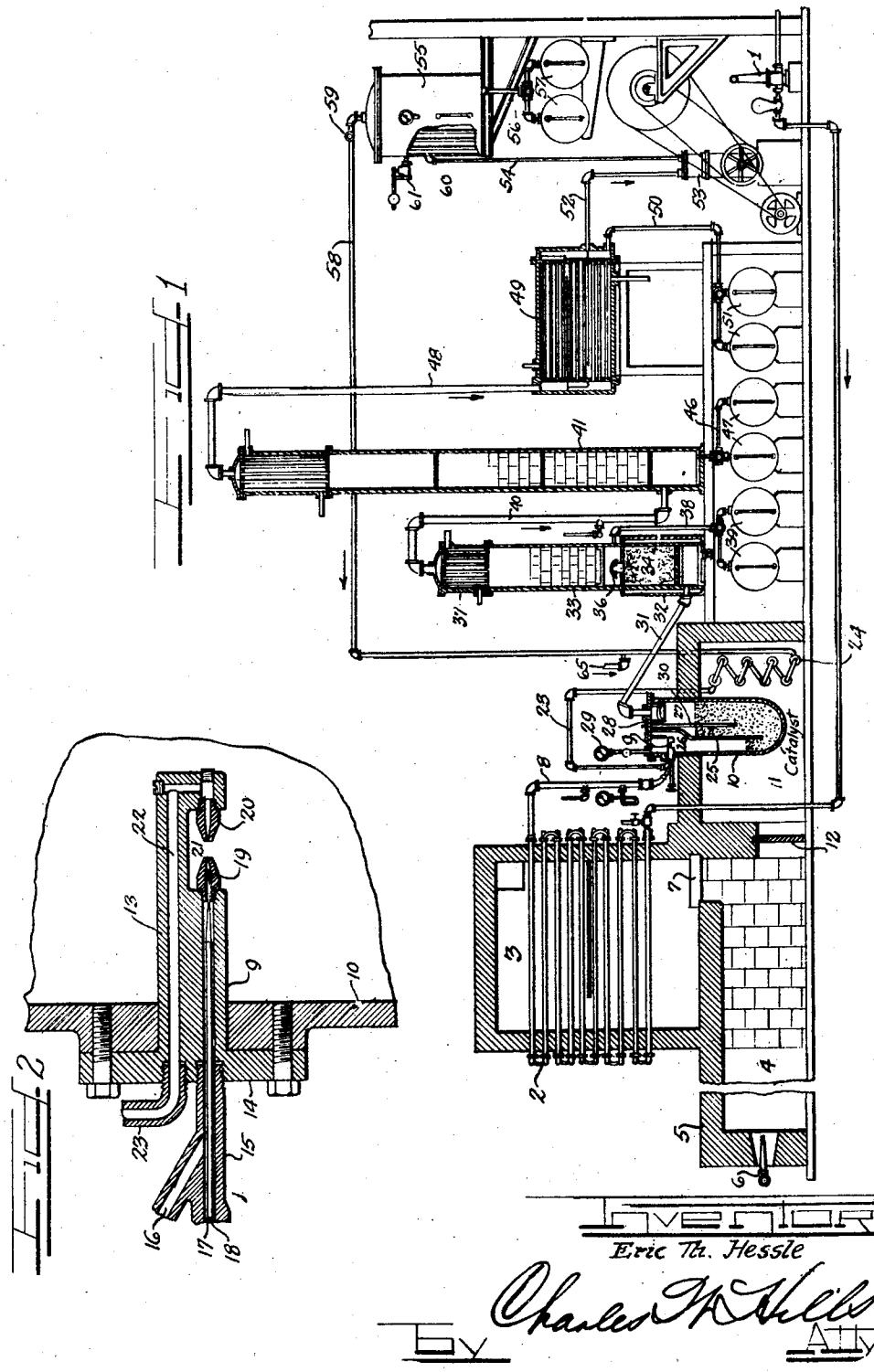


FIG. 1

FIG. 2

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PROCESS FOR REFINING OIL.

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

In my copending application for a "continuous process for the refining of oil", Serial No. 678,924, filed Dec. 6, 1923, I have described a catalytic process for the conversion of hydrocarbon oils into products having lower boiling points. In that process I bring the oil into a suitable state for being acted upon most efficiently by the catalyst by producing a fog of oil and hydrogen or a gas containing hydrogen. I now propose to use in place of the hydrogen containing gas, the vapors of oils or distillates having lower boiling points than the oil to be treated, such as paraffin oil, light lubricating oil, gas oil, kerosene, gasoline, and the like, and thereby to produce lower boiling conversion products of unsaturated character.

It is generally conceded at the present time, that for motor fuel, gasolines containing unsaturated hydrocarbons possess desirable advantages over saturated hydrocarbons belonging to the C_nH_{2n+2} series. Among these advantages is the anti-knock property, which is characteristic of unsaturated gasolines and benzenes. Therefore, the addition of hydrogen during the conversion of the higher boiling hydrocarbon oils is no longer a desirable step.

Furthermore, it is unnecessary to add hydrogen for the reason that in the ordinary processes the tail gases usually contain approximately 6% to 10% of hydrogen. Much more than 6 to 10% of hydrogen is present in statu nascendi during the cracking reaction, and this hydrogen takes care of a certain amount of hydrogenation. If fuel or gas oil is to be cracked enough hydrogen is present naturally during the cracking process to take care of a certain amount of hydrogenation. About one-quarter of the cracked gasolines are olefines, but an even larger percentage would be desirable in view of their anti-knock properties.

For cracking very heavy hydrocarbons, or heavy, or half solid, residues and asphalts, which do not contain enough hydrogen in the molecules to form lighter hydrocarbons, it would ordinarily be advisable to add hydrogen in order to prevent carbon deposits, but by using the vapors of lighter distillates as a medium for the production of a fog, as in my present process, some hydrogen is formed by the breaking down of these vapors. This hydrogen, which is in statu nascendi and therefore more active, is sufficient, although present in only limited quantities, to serve the same purpose as larger quantities of added hydrogen.

It is therefore an object of this invention to provide a process for the conversion of hydrocarbons into products of lower boiling point in which kerosene or other light distillate vapors are employed to assist in the process.

It is a further object of this invention to employ an oil fog producing device using the vapors of lighter distillates as the carrier-medium for the fog.

It is a further object of this invention to provide a process for converting hydrocarbon oils into unsaturated compounds, of the olefine, naphthene and aromatic series.

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 fire-box 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 reaction 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, first, to vaporize the oils or distillates having lower boiling points than the hydrocarbons to be treated, and secondly, to preheat these vapors as well as the tail gases.

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 vary. On the other hand if operating on high boiling residues and asphalts the temperature rises to between 350 and 400° C.

Within the kettle 10 is placed a decomposition catalyst of my invention, composed of tin containing a small percentage of antimony. 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.

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 running from the preheater 2 through the pipe 8 is discharged through the valve regulated nozzle 19 against the vapor issuing from the opposing nozzle 20. This vapor may be any vaporized lighter distillate than the oil to be treated. This vapor used is first preheated in the coil 24, having radiant disks for the better distribution of the applied heat and located in the chamber 11, up to the temperature of the oil delivered from the preheating coil 2. The lighter oil or distillate vapor is introduced in the heating coil 24 through an intake pipe 65, under a pressure greater than the pressure of the oil delivered from the preheater 2. This tends toward a more balanced delivery of the gas in the fog producer 9, and produces a real fog intermediate the opposing nozzles.

The concussion of the oil from the nozzle 19 and of the vapor 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 vapor be the same and that the fog be produced at the temperature of the reaction kettle. Accordingly I have found that the production of the fog is most satisfactory if brought about within the reaction kettle itself.

The pressure of the fog formed in the smaller compartment 26 of the reaction kettle depresses the molten catalyst, which rise by a corresponding amount in the other compartment 27. Since no pressure of gas is maintained above the molten metal in compartment 27, the fog in compartment 26 is forced by its own pressure down through the body of the metal in compartment 26 and up into compartment 27. The oil in passing through the catalyst remains in its condition as a fog until by virture of the decomposing action of the catalyst it is converted into oils of such lower boiling points that under the conditions and pressures obtaining said oils are vaporized. It is evident, therefore, that the conversion into hydrocarbon oils of lower boiling point take place strictly in a liquid phase. This is an enormous advantage since the volume of catayist and reaction vessel need not be nearly so great as if the decomposition occurred in a gaseous state.

The vapor used as a carrier medium for the fog will also be subject to the decomposition action of the molten catalyst, this vapor being largely broken down into lower boiling products. A certain amount of hydrogen may be formed from the decomposition of these, but not in sufficient quantity to hydrogenate to any substantial degree the conversion products of the oil. These conversion products will therefore contain a considerable quantity of unsaturated hydrocarbons, which are now deemed desirable in the motor fuels. Furthermore the small amount of hydrogen formed is sufficient to prevent the molten catalyst from being poisoned.

The vapors of the converted hydrocarbon oils accumulating above the molten metal in

compartment 27 are led off through a conduit 31 into the base 32 of a fractionating column 33. The base 32 is filled with an absorbing medium 34, such as iron and manganese oxides, or other suitable desulphurizer, for the purpose of removing any sulphurous compounds that may be present. The fractionating column 33 may be provided with a condensate trap 36, above which the tower 33 may be filled with suitable packing rings, or it may be arranged in any of well known manner for effecting fractionation of the oil vapors. At the top of the tower 33 is provided 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 run-down tanks 39. From the top of the tower 33, the vapors and gases are led through a pipe 40 into the base of a second fractionating column 41 which may be similar in its design to the fractionator 33. From the column 41 the condensates pass by way of pipes 46 into run-down tanks 47. The vapors and gases from said fractionator 41 pass out at the top of the column through a pipe 48 into a final condenser 49. From said condenser 49 the condensates pass through a pipe 50 into run-down tanks 51. The uncondensed gases from the final condenser 49 are conducted by the pipe 52 to the compressor 53 which delivers said gases at the pressure of approximately 15 atmospheres through the pipe 54 into a pressure tank 55, cooled within by means of straight water tubes 60. On the top of this tank there is a pressure relief valve 59, which is so regulated that it blows off to maintain the gas in the return pipe 58 at a certain pressure depending upon the gravity and viscosity of the oil. Another relief valve 61 is provided 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 55 results in the condensation of a portion of the gas. The condensates so formed are led through the pipe 56 into pressure run-down tanks 57 and the uncondensed tail gases are led off, as explained, at a certain pressure from the tank 55, through the return pipe 58 back to the preheater 24 and thence to the fog producing device 9. In this way the tail gases supplement the lighter oils or distillates introduced into the system under pressure through the pipe 65.

When treating heavy hydrocarbons, asphalts and the like, a lower boiling oil may be mixed with these heavy hydrocarbons to make them more fluid and this mixture then passed through the fog producing device and there formed into a fog with the vapor of some lighter oil, preferably paraffine oil.

The advantage of employing lighter oils or distillate vapors in my process is (1) that the lighter oils or distillates are easily obtainable at the oil refinery plant, (2) that they are much cheaper than hydrogen or hydrogen containing gases, (3) that their conversion products form a valuable part of the final product obtained, (4) that certain parts of tail gases are converted into valuable hydrocarbons having motor fuel value, and, (5) that olefines and aromatic compounds are formed that have desirable anti-knock properties.

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 otherwise than necessitated by the prior art.

I claim as my invention:

1. A process of converting hydrocarbon oils into lower boiling products, which includes directing the oil against a counter current stream of a hydrocarbon vapor under sufficient pressure to form a true fog of highly dispersed liquid oil suspended in said vapor, and passing said fog through a decomposition catalyst whereby decomposition of the oil and vapor take place to form lower boiling products.

2. A process of converting hydrocarbon oils into lower boiling products, which includes directing the oil against a counter current stream of a hydrocarbon vapor under sufficient pressure to form a true fog of highly dispersed liquid oil suspended in said vapor, and passing said fog through a molten decomposition catalyst, said catalyst being maintained at a temperature of between 250 and 400° C; whereby decomposition of the oil and vapor take place to form lower boiling products.

3. A process of converting hydrocarbon oils into lower boiling products, which comprises directing the oil against a countercurrent stream containing a hydrocarbon vapor under sufficient pressure to form a true fog of highly dispersed liquid oil suspended in said vapor, and bringing said fog into contact with a decomposition catalyst comprising a mixture of tin containing a small quantity of antimony to effect decomposition of the oil and vapor into lower boiling products.

In testimony whereof I have hereunto subscribed my name.

ERIC TH. HESSLE, PH. D.