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PROCESS AND APPARATUS FOR CRACKING HYDROCARBON OILS OR THEIR DISTILLATES BY DISTILLATION UNDER PRESSURE

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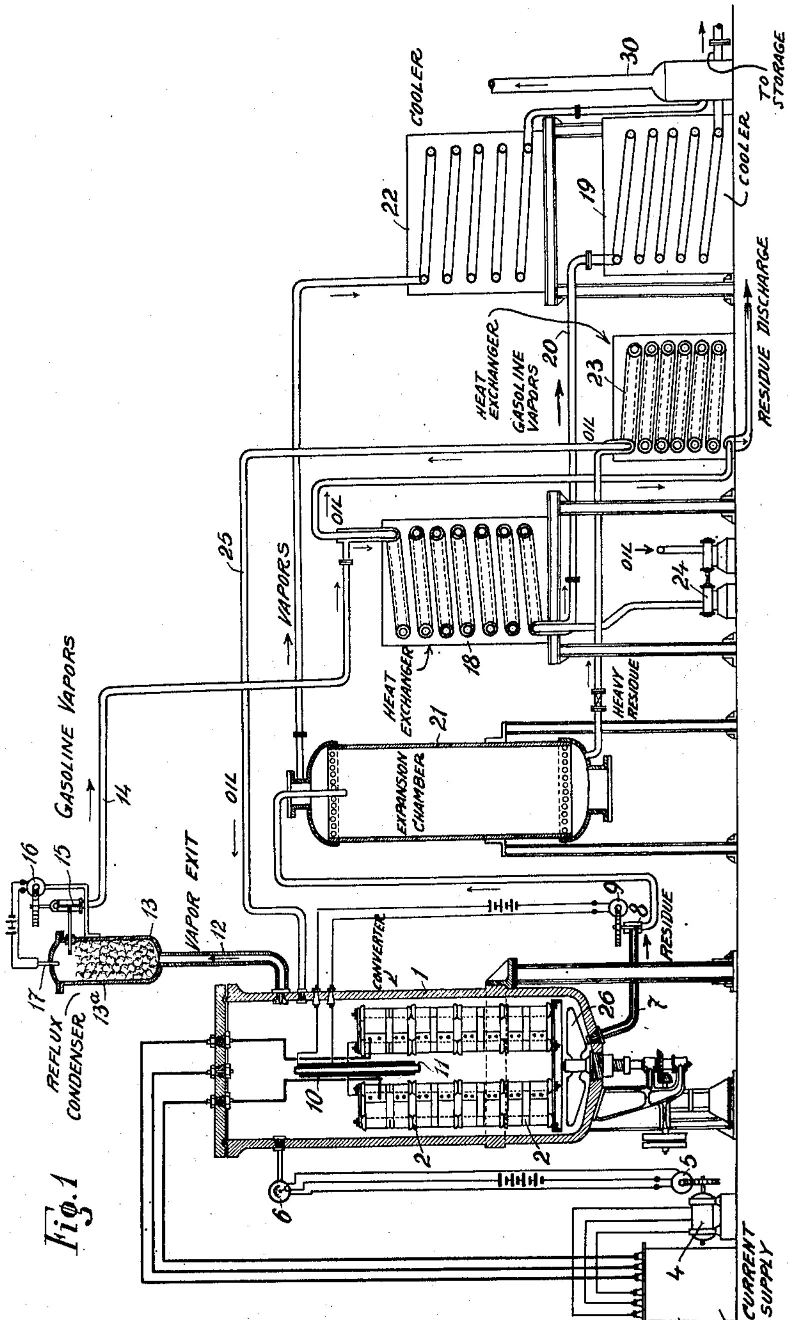

Fig. 1

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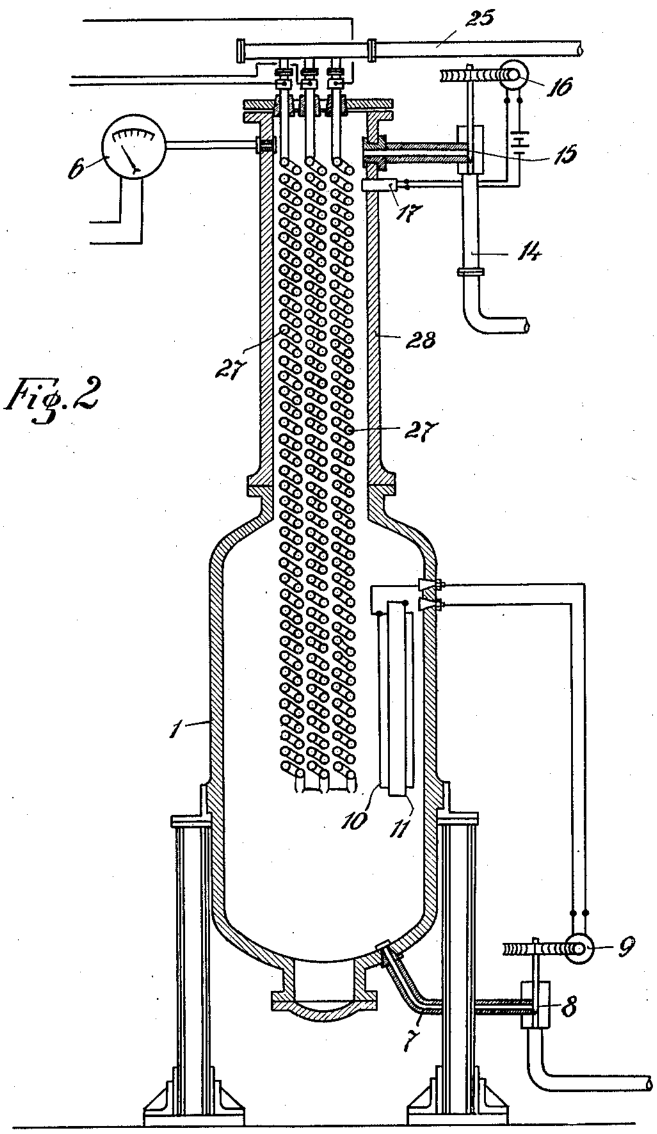

Fig. 2

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UNITED STATES PATENT OFFICE

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PROCESS AND APPARATUS FOR CRACKING HYDROCARBON OILS OR THEIR DISTILLATES BY DISTILLATION UNDER PRESSURE

Application filed March 1, 1927, Serial No. 171,859, and in Austria March 18, 1926.

This invention relates to the cracking of hydrocarbon oils or of distillation products by distillation under pressure.

There are numerous processes known for cracking high boiling oils by distillation under pressure, in which processes very high pressures, up to 100 atmospheres and even more are necessary. Moreover these cracking processes take place at rather high temperatures and consequently the apparatus usually employed for such distillation under pressure are subjected to very high stresses. As very large quantities of heat are to be transferred to the material to be distilled in order to attain said pressures and temperatures, the walls of the still must therefore be of considerable thickness.

Several ways have been tried for avoiding the drawbacks connected with externally heating such thick walled stills in the usual manner. For instance the material to be cracked is heated in tubes instead of in a still for the purpose of providing the required surface for the transfer of heat. According to another method molten metal, for example molten lead is injected in the liquid state into the reaction chamber, or else the material to be distilled is caused to rise within molten metal. In all these cases great difficulties result from the deposit of coke on the heating surfaces, because in the course of the reaction a considerable amount of gaseous cracking products are generated corresponding to a high waste in coke, so that the yield of low boiling-point liquid cracking products is diminished. This is for the reason, that the cracking of higher boiling hydrocarbons into low boiling ones under pressure by the usual methods involves a hydrogen migration, the low boiling products being enriched in hydrogen and the residue becoming poorer. The extreme limiting case would be attained, if free hydrogen and gases with a high hydrogen contents (methane) would be generated on the one hand and petroleum coke as residue on the other. But if it were possible to succeed in effecting the cracking in such manner, that e. g. from the saturated hydrocarbons of the type C_nH_{2n+2} fragments of the type C_nH_{2n} (olefines) would be formed, or from naphthenes of higher molecular weight olefines of lower molecular weight, there could take place, theoretically speaking, altogether no formation of free carbon and of free hydrogen.

The present invention starts with the assumption that the above indicated limiting case, that is, the forma ion of free hydrogen and of gases with a high hydrogen content on the one hand and of petroleum coke on the other, will take place at higher temperatures, as is now somewhat analogously known in the manufacture of oil gases. The deposit of coke sets in to a particularly great extent on the heating surfaces, as there the surplus of temperature causing the formation of coke is present. By the coke deposit on the heating surface the transfer of heat from the external heating means to the contents of the still is lessened, while on the other hand, by this latter fact, the overheating is increased and consequently the deposit of coke is also increased.

Now we have found that in realizing the cracking of high boiling hydrocarbons into low boiling ones of the gasolene type under pressure the maintenance of particularly high temperatures is not nearly of such essential importance as hitherto had mostly been believed. On the contrary, by most carefully performed and exhaustive experiments it has been shown that the cracking sets in at relatively low temperatures, when the pressure has attained a certain value. But these reactions in question are reversible, so that a chemical equilibrium will be established; that is to say a state, in which the products of the reaction and the unchanged reactants are present in a certain amount and these amounts will be constant so long as the conditions are not altered. This equilibrium has hitherto been disturbed by increasing the temperature and thereby the progress of the cracking has been forced, but at the same time the formation of gaseous products and of coke has been favored.

According to the present invention, after attaining the temperature sufficient for initiating a cracking of the material under treatment, a self-imposed pressure corresponding to this temperature being generated thereby, this temperature is maintained constant and the said equilibrium is disturbed by removing the formed low boiling hydrocarbons very quickly from the reaction mixture by presenting to the liquid a large amount of heating surfaces the temperature of which not considerably exceeds that of the liquid undergoing cracking, and provoking an immediate fractional distillation of the lower boiling-point hydrocarbons at the instant of their formation by allowing a permanent free escape of the evolved vapors of desired volatility into a condensing system being under a lower pressure than that maintained in the heated system, while the heavier constituents of the evolved vapors are by reflux condensation returned to the converter under the self-imposed pressure existing therein. While in the usual methods of cracking the fire tubes at the end of the operation are heated up to dark red, which state corresponds to a temperature of 500 to 600° C., in the present method the temperature is not raised substantially above 400° C. and in the case of readily crackable oils may even be considerably lower.

Moreover, we have found, that another factor influences the result of the destructive distillation, if not in a decisive manner, but all the same to a very substantial extent, namely the mutual relation of the volumes of the liquid phase and that of the gaseous one, that is to say of the retort space for liquids and for gases. For provoking and maintaining the reaction pressure a certain percentage of the liquid has to be vaporized. If the gas space is too large, a correspondingly large part of the uncracked high boiling hydrocarbons has to be vaporized until the required pressure will be attained, so that consequently the mixture of vapors contains a smaller percentage of low boiling parts. On the other hand, if the gas space is too small, the vapors of the low boiling parts will, owing to the violent boiling of the liquid, be charged with clouds and little drops of the high boiling parts still unconverted. Consequently in rapidly effecting the cracking it is necessary that the gas chamber be not so greatly enlarged above the size required for preventing the mechanical entrainment of liquid that undecomposed high boiling parts of the material to be treated will have to be vaporized uselessly, except only for the one purpose of obtaining the necessary reaction pressure. The most favorable relation between the volume of the liquid and the gas volume has to be found out empirically at the beginning of the operation for each different kind of raw material and this relation has then to be maintained constant through the entire operation.

The process derived from these new discoveries cannot be carried out by the plants used heretofore, as the heating surfaces of the latter are not sufficient for introducing into the material to be distilled those amounts of heat which are indispensable for disturbing, without surplus temperatures, the equilibrium only by rapidly distilling off of the formed light volatile hydrocarbons, that is to say at the moment of their generation. In carrying out the distillation by employing the usual means the acceleration of the distillation process is limited by the fact that the entire mass of the material to be distilled must lose too much heat owing to the large heat of vaporization. For this reason the formation of low boiling parts would be considerably reduced. The new method, however, can be realized in a very advantageous and simple manner by electrically heating the material to be distilled by means of resistances placed inside the still. A device of this kind consists of resistances of very large total heating surface disposed and distributed throughout the entire space of the still to be occupied by the liquid and thus adapted for transferring great quantities of heat from these resistances to the liquid in such manner that the difference between the temperature of the resistances and that of the material to be distilled is a very small one.

For obtaining the optimum result it is preferable to combine a device for internal heating of this kind with means for provoking an agitation of the liquid to be treated. By heating the material to be distilled by means of resistances having large heating surfaces distributed throughout the entire space to be occupied by the liquid it is possible to reduce the separation of carbon and the formation of gases to a minimum. If in addition the liquid is kept in rapid motion during the cracking reaction so that no part of the still can be overheated and that the heat given off by the resistances is as rapidly as possibly conveyed all over the space, the advantages of the internal heating will turn out all the more markedly and the result will be a most considerable increase of the final yield of liquid hydrocarbons of the gasolene type.

By employing the electric means for internal heating there exists also the possibility of carrying out the reaction in a normal vessel or still of cylindrical form, which in constructive respect is the most advantageous one, as this form, while requiring the least material, offers the relatively greatest strength. The reaction vessel can be entirely covered on its exterior surface with some heat insulating layer, whereby a considerable amount of heat is saved.

Thus by the use of electric internal heating in a still provided with means for agitating the material to be distilled the latter can be worked up to a residue amounting to about 10% of the initial materials or even less, the extremely small amount of coke generated during the process being contained therein in a finely divided state as powder. The residue can be removed from the reaction vessel without interrupting operations. The formation of gas is also reduced to a minimum and seldom surpasses 8% of the weight of the starting material.

The process has been developed in such way that all the necessary operations owing to the most exact regulation of the heat supply by the electrical means take place so to say automatically. By pyrometers automatically varying resistances or operating switches or the like, and by devices regulating the pressure, the temperature and the pressure are kept constant within the desired limits, whereby great safety as to reliable working and a perfect uniformity of the reaction product is assured. The method permits of continuous operation even when using a single distillation apparatus. For large plants two or more distillation apparatus may be mounted in series in such manner, that the liquid to be distilled flows through them one after the other.

By means of the described method it is possible to effect the cracking of high boiling hydrocarbons into low boiling ones of the gasolene type in an automatically working compendious plant, whereby for instance from Galician gas oil outputs of 60% with boiling points within the limits of 35° to 170° C. have been obtained. Owing to the prevention of any surplus of temperature during the entire time of heating, the reaction temperature most favorable for the respective material to be cracked can easily be maintained constant, and it is for this reason, that a great output with a constant composition of the reaction product is obtained.

In the drawings two apparatus adapted for carrying the invention into practice are illustrated by way of example by diagrammatical sectional views.

In Fig. 1 the cylindrical still is designated by the numeral 1 and 2 represents the electric resistances of large surface placed therein. The latter are fed by a transformer 3 receiving the current over a potential adjusting device 4. 5 is the motor of the latter, the working of which is automatically adjusted in connection with the vapor pressure in the vessel 1. For this purpose a pressure gauge 6 is provided, which is subjected to the pressure of the vessel and adapted for influencing the current driving the motor, but not influencing it at a certain determined pressure. For this purpose a regulating contact of known type with a series of contact blocks is combined with the moving member of the gauge, the strength and direction of the current being thus altered in the known way. When the pressure is rising or sinking, the motor is influenced in such manner, that the supply of electrical energy is diminished or increased. This arrangement controlled in response to the vapor pressure within the vessel may be substituted by one controlled in response to the temperature existing in the vessel. The control system based on variations in the pressure, however is to be preferred, since for the alterations of state under consideration in the present case relatively great variations of pressure correspond to relatively small variations of the temperature.

If the bottom of the vessel 1 an outlet for drawing off the residue is provided and a conduit 7 connected thereto with a reduction valve 8 inserted therein, which valve is controlled by a motor 9 which in turn is controlled by the level of the liquid in the vessel. According to the illustrated example a condenser is inserted into the circuit of the motor, which condenser consists of two concentrically arranged tubes 10 and 11 immerging into the liquid. The dielectric constant of the condenser changes according to the rise or lowering of the liquid level, as the values of the constants are different for liquid oil and for a gasified one. Consequently by variations of the level the capacity is altered and thereby also the alternating current for the motor 9 passing through the condenser.

The vapors generated in the vessel pass through a pipe 12 into the reflux condenser 13 filled with Raschig-rings 13*a* and from there through a conduit 14, the reduction valve 15 of which is controlled in response to the temperature existing at the top of the reflux condenser. For this purpose a pyrometer 17 is inserted into the circuit of the motor 16 controlling the reduction valve 15, which pyrometer is exposed to the temperature existing at the top of the column 13 and influences in known manner the current so as to alter either its strength or its direction. If this temperature rises above a determined limit, the throttling effect of the valve will be increased, in the other case diminished. Thus the result is obtained that only cracked products of the desired volatility will permanently escape.

The conduit 14 is connected to a counter current apparatus 18, the exterior tubes of which are passed by the vapors coming from the condenser 13. The condensation of the vapors takes place in the cooler 19 connected to the counter current apparatus by the duct

20. To the throttling valve 8 of the pipe 7 serving for the removal of the residue a pressureless expansion chamber 21 is connected, within which the residue is allowed to expand for the purpose of obtaining the low boiling parts thereof, which then escape at the top of this receptacle and are condensed in the cooler 22 connected to a stack 30. The heavy residue is drawn off at the bottom of the receptacle 21 and led to a counter current apparatus 23.

For operating this plant the pressure gauge 6 is adjusted for the desired pressure, the pyrometer 17 for the desired temperature and the condenser 10, 11 to the level found empirically to be the most favorable. The hydrocarbons to be distilled are first of all driven by the pump 24 at a uniform rate of flow into the counter current apparatus 18, pass from there into the counter current apparatus 23 and then through the conduit 25 into the vessel 1, where they are heated by the electric resistances. An agitator 26 driven by a motor keeps the liquid in permanent motion for the purpose of preventing the formation of coke. The temperature and the pressure of the vapors are kept permanently constant at a determined point, as the pressure gauge 6 adjusts the supply of electric energy to the resistances. Also the relation of vapor space to the volume of liquid remains constant, the throttling valve 8 being controlled by the condenser 10, 11, the dielectric constant of which is depending upon the level of the liquid. For adjusting this level any other automatically working known means may be utilized, for instance the so called "Arca" level regulator. Finally the vapors escaping from the reflux condenser 13 will always have the same temperature, because its condensing action is adjusted in dependence from the temperature by the position of the throttle valve 15.

In the apparatus as shown by Fig. 2 the utilization of the electric heat energy is improved by a special form and arrangement of the resistances, owing to which the agitator can also be dispensed with. In said Figure, 1 is a retort surmounted by a cylindrical crown or dome 28, freely communicating with the retort space for vapors. The electric heating means are composed of hollow tortuous heating elements 27, partly located in the dome 28 and partly in the vessel 1 itself so, that the coils lead into the retort space for liquid. These hollow tortuous electric heating elements are made of metal or of a suitable alloy, for instance of an alloy composed of chromium, iron and nickel. The lower part of the retort is provided with auxiliary heating means (not shown in the drawings). This converter is destinated to be substituted for the vessel 1 of the plant according to Fig. 1, all the other parts of this plant and the controlling and actuating devices are the same as described in connection with Fig. 1. The means for discharging vapors controllable in response to the volatility of the evolved vapors are in this case mounted directly on the top of said dome 28.

The hydrocarbons to be cracked are passed through the coils 27 to be heated and are discharged into the retort space for liquid after having been brought to the temperature required for cracking. The exterior surfaces of the spiral heating coils 27 act simultaneously as a condenser on the vapors rising from the vessel, the heavy parts of which vapors will be condensed and will give off their condensation heat to the liquid flowing within the coils, while the light parts will escape without being condensed at the top of the dome 28 through the reduction valve 15, which is controlled in response to the temperature existing at the top of the dome by controlling means as described in connection with Fig. 1.

By this construction of the converter the utilization of the heat is considerably improved, as the condensation heat of the condensing heavier vapors is utilized for heating up the liquid under treatment. Moreover the use of the coils offers the advantage that the liquid is during the heating kept in strong motion, so that no special device for agitating is required.

What we claim is:

1. In combination, a converter for heating liquid hydrocarbons held under a self-imposed super-atmospheric vapor pressure having a space for the liquid and a vapor-space, electrical heating means located in said converter in intimate contact with the liquid under treatment and adapted to cause spread of heat through the body of the liquid material, a reflux condenser being in free communication with the vapor-space of the said converter, controllable means for discharging vapors from said condenser and means for automatically controlling the said vapor discharging means in response to the volatility of the evolved vapors independently from the pressure within the communicating converter-condenser system, and means for condensing the evolved vapors of desired volatility and collecting the distillation products.

2. In combination, a converter for heating liquid hydrocarbons held under a self-imposed super-atmospheric vapor pressure having a space for the liquid and a vapor-space, electric heating means located in said converter in intimate contact with the liquid under treatment, a reflux condenser being in free communication with the vapor-space of the said converter, controllable means for discharging vapors from said condenser, and means for automatically controlling the said vapor discharging means in response to the variations of temperature in the upper part of the condenser, and means for condensing

the evolved vapors and collecting the distillates.

3. In combination, a converter for heating liquid hydrocarbons held under a self-imposed super-atmospheric vapor pressure having a space for the liquid and a vapor-space, electric heating means located in said converter intimate contact with the liquid under treatment, controllable means for passing electric heating currents through the heaters and means for automatically controlling the electrical heating current supply in response to the variations of pressure within the converter, a reflux condenser being in free communication with the vapor-space of the said converter, controllable means for discharging vapors from said condenser and means for automatically controlling the vapor discharging means in response to the volatility of the evolved vapors independently from the pressure within the communicating converter-condenser system, and means for condensing the evolved vapors of desired volatility and collecting the distillates.

4. In combination, a converter for heating liquid hydrocarbons held under a self-imposed super-atmospheric vapor pressure having a space for the liquid and a vapor-space, electric heating means located in said converter in intimate contact with the liquid under treatment, controllable means for passing electric heating currents through the heaters and means for automatically controlling the current supply in response to the variations of pressure within the converter, controllable means for drawing off the residue from the converter and independent means for automatically regulating the quantity of residuum drawn off by these means in response to variations in the level of the liquid in the converter, a reflux condenser being in free communication with the vapor-space of the said converter, controllable means for discharging vapors from said condenser and independent means for automatically controlling the said vapor discharging means in response to the volatility of the evolved vapors, and means for condensing the evolved vapors of desired volatility and collecting the distillates.

5. In combination, a retort for distilling liquid hydrocarbons held under a self-imposed super-atmospheric pressure having a space for the liquid and a vapor-space, tubular coil electric heating elements located in said vapor-space through which heating elements the liquid charging materials to be cracked are passing to be discharged into the retort space for fluids, a reflux condenser being in free communication with the vapor space of the retort, controllable means for discharging vapors from said condenser, means for automatically controlling the said vapor discharging means in response to the volatility of the evolved vapors, and means for condensing the said vapors.

6. In combination, a retort for distilling liquid hydrocarbons held under a self-imposed super-atmospheric pressure having a space for the liquid and vapor-space, a tubular coil electric heating element located in the upper part of said retort through which heating element the liquid charging materials to be cracked flow downward to be discharged into the retort space for the liquid, a reflux condenser being in free communication with the vapor space of the retort, controllable means for discharging vapors from said condenser, means for automatically controlling the said vapor discharging means in response to the volatility of the evolved vapors, and means for condensing the said vapors and collecting the distillates.

7. In combination, a retort for distilling liquid hydrocarbons held under a self-imposed super-atmospheric pressure having a space for the liquid and a vapor-space, a tubular coil electric heating element located in the upper part of said retort through which heating element the liquid charging materials to be cracked flow downward to be discharged into the retort space for the liquid, a reflux condenser being in free communication with the vapor space of the retort, controllable means for discharging vapors from said condenser, means for automatically controlling the said vapor discharging means in response to the volatility of the evolved vapors independently from the pressure in the communicating converter-condenser system and means for condensing the said vapors and collecting the distillates.

8. In combination, a retort for distilling liquid hydrocarbons held under a self-imposed super-atmospheric pressure having a space for the liquid and a vapor-space and being surmounted by a dome freely communicating with the retort space for vapors, a tubular coil electric heating element located in said dome through which the liquid charging materials are passed into the retort space for liquid, and the exterior surface of which acts simultaneously as a condenser, controllable means for discharging vapors from the overlying dome, means for automatically controlling the said vapor discharging means in response to the volatility of the evolved vapors, and means for condensing the said vapors and collecting the distillates.

9. In combination, a retort for distilling liquid hydrocarbons held under a self-imposed super-atmospheric pressure having a space for the liquid and a vapor-space, and being surmounted by a dome freely communicating with the retort space for vapors, a tubular coil electric heating element located in said dome through which the liquid charging materials are passed into the retort space

for liquid and the exterior surfaces of which act simultaneously as a condenser, controllable means for discharging vapors from the overlying dome, means for automatically controlling the said vapor discharging means in response to the variations of temperature in the upper part of the said dome, and means for condensing the said vapors and collecting the distillates.

10. In combination, a retort for distilling liquid hydrocarbons held under a self-imposed super-atmospheric pressure having a space for the liquid and a vapor-space and being surmounted by a dome freely communicating with the retort space for vapors, a tubular coil electric heating element located in said dome through which the liquid charging materials are passed into the retort space for liquid and the exterior surfaces of which act simultaneously as a condenser controllable means for passing electric heating currents through said heating element and means for automatically controlling the current supply in response to the variation of pressure within the retort, controllable means for discharging vapors from the overlying dome and means for automatically controlling the said vapor discharging means in response to the variations of temperature in the upper part of said dome, and means for condensing the said vapors and collecting the distillates.

11. In combination, a retort for distilling liquid hydrocarbons held under a self-imposed super-atmospheric pressure having a space for the liquid and a vapor-space and being surmounted by a dome freely communicating with the retort space for vapors, a tubular coil electric heating element located in said dome through which the liquid charging materials are passed into the retort space for liquid and the exterior surfaces of which act simultaneously as a condenser, controllable means for passing electric heating currents through said heating element and means for automatically controlling the current supply in response to the variations of pressure within the retort, controllable means for drawing off the residue from the retort space for liquid and means for automatically regulating the quantity of residuum drawn off by these means in response to variations in the level of liquid in the retort, controllable means for discharging vapors from the overlying dome and means for automatically controlling the said vapor discharging means in response to the variations of temperature in the upper part of the said dome, independently from the pressure maintained upon the liquid hydrocarbons within the retort, and means for condensing the said vapors and collecting the distillates.

12. A process in the art of distilling liquid hydrocarbons under superatmospheric pressure for the purpose of obtaining therefrom products having lower boiling points which consists in continuously charging the hydrocarbons to a converter, heating the liquid hydrocarbons up to a temperature just sufficient to initiate a cracking of the material under treatment in the converter without the aid of hydrogenizing agents or catalysts, by electrical heating means having a large amount of metallic heating surfaces and automatically controlled in response to the pressure in the converter to a temperature not considerably surmounting that of the liquid undergoing cracking, a self-imposed pressure corresponding to the temperature just sufficient for initiating cracking being generated thereby in the converter, maintaining the volume ratio of liquid to vapor constant in said converter by continuously drawing off residuum through discharge means automatically controlled in response to the liquid level therein and starting an immediate spontaneous distillation of the formed lower boiling point hydrocarbons by permitting vapors of predetermined volatility to permanently escape through vapor discharging means automatically controlled in response to the volatility of the evolved vapors but independently from the pressure existing within the converter into a condensing system being under a lower pressure than that existing in the heated system, and while returning the heavier constituents of the evolved vapors by reflux condensation directly to the bulk of the liquid under treatment.

13. A process in the art of distilling liquid hydrocarbons under superatmospheric pressure for the purpose of obtaining therefrom products having lower boiling points which consists in preheating the charging stock by heat exchange with residuum and vapors withdrawn from the process and then further heating said stock to a temperature just sufficient to initiate a cracking of the material under treatment in a converter without the aid of hydrogenizing agents or catalysts, by internal electrical heating means having a large amount of metallic heating surfaces and automatically controlled in response to the pressure in the converter to a temperature not considerably surmounting that of the liquid undergoing cracking, a self-imposed pressure corresponding to the temperature just sufficient for initiating cracking being generated thereby in the converter, maintaining the volume ratio of liquid to vapor constant in said converter by continuously drawing off residuum through discharge means automatically controlled in response to the liquid level therein, and starting an immediate spontaneous distillation of the formed lower boiling point hydrocarbons by permitting vapors of predetermined volatility to permanently escape through vapor discharging means automatically controlled in response to the volatility of the evolved vapor but in-

dependently from the pressure existing within the converter into a condensing system being under a lower pressure than that existing in the heated system, and while returning the heavier constituents of the evolved vapors by reflux condensation directly to the bulk of the liquid under treatment.

In testimony whereof we have affixed our signatures.

SIEGMUND STRANSKY.
FRITZ HANSGIRG.