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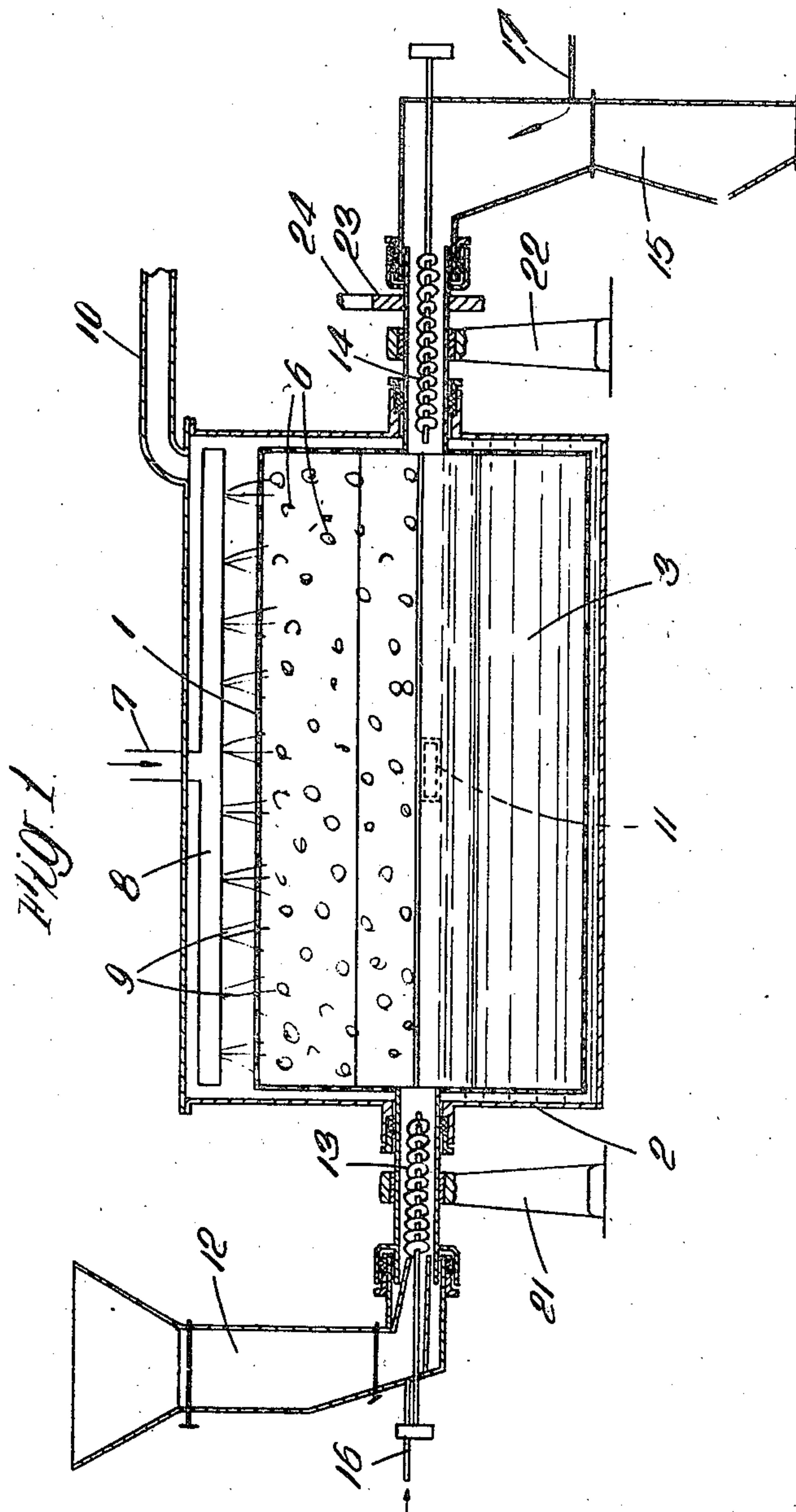
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TREATMENT OF PETROLEUM CRACKING RESIDUES

Filed Aug. 17, 1945

2 Sheets-Sheet 1



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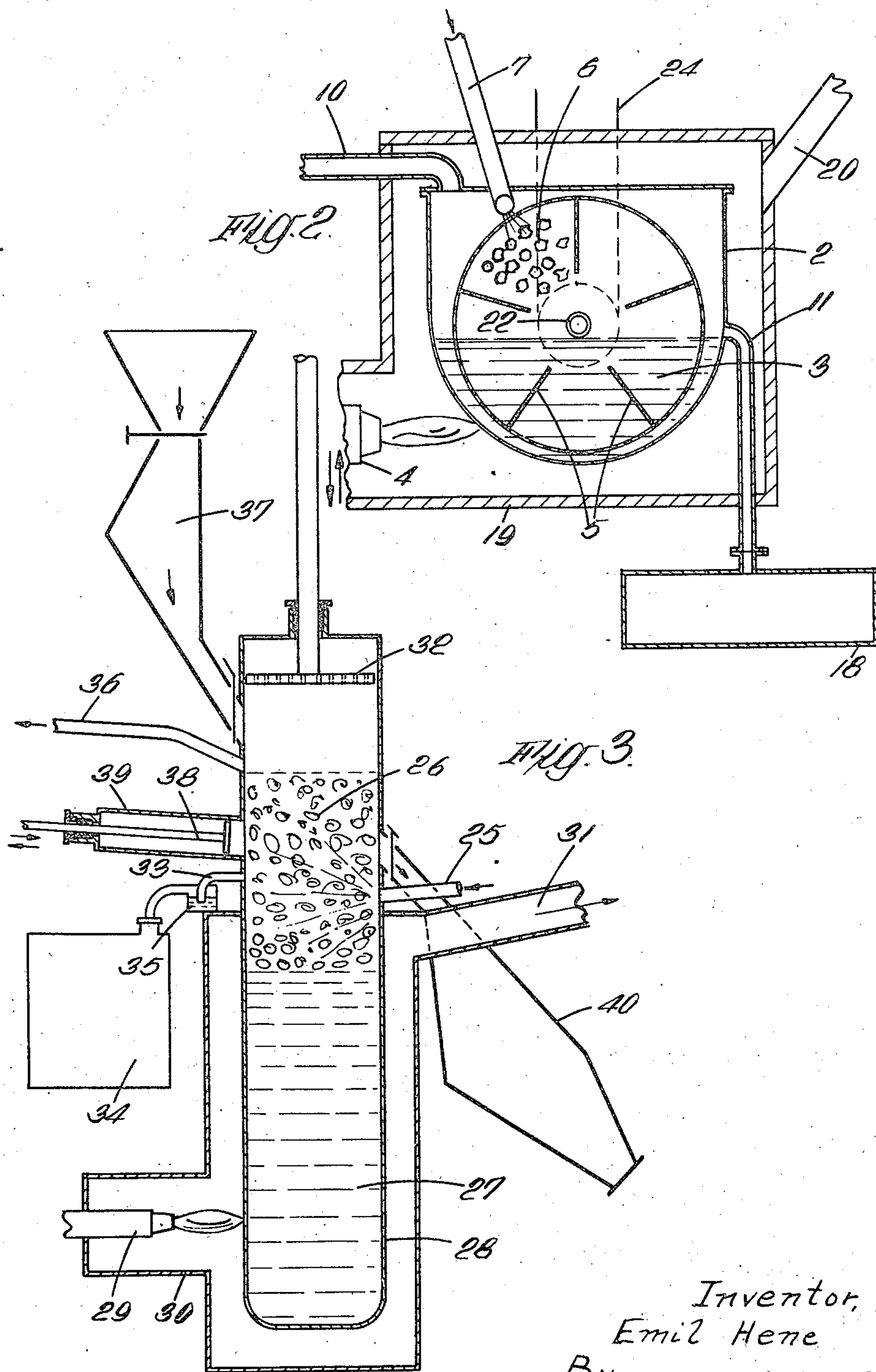
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UNITED STATES PATENT OFFICE

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TREATMENT OF PETROLEUM CRACKING
RESIDUES

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5 Claims. (Cl. 196—79)

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This invention relates to the treatment of petroleum cracking residues.

A number of processes are known to produce distillates and coke from petroleum cracking residues (hereinafter referred to as "residues") by heating such residues on coke lumps.

A close examination of the behaviour of such residues showed that during such heat treatment a variety of heavy asphalt-like hydrocarbons either present in the original residue or formed during the heat treatment coat the coke lumps for a considerable time in the liquid phase before final coking can be achieved. During this period no fresh charge of residue can be admitted as otherwise a pitchy mass would result making any mechanical or continuous operation impossible. The decomposition of these hydrocarbons was, therefore, considered necessary and it has been effected either by raising the temperature or by allowing sufficient time for the decomposition to take place.

A number of experiments has shown that such decomposition of these hydrocarbons occurs only very gradually by releasing volatile hydrocarbons and leaving hydrocarbons with a lower ratio of hydrogen to carbon, their colour becoming gradually darker, their softening points higher while at the same time their resistance to decomposition increases constantly during their approach to coke. Therefore, if only coke and distillates are to be produced, the throughput is to a great degree dependent on the time required for the coking of these refractory hydrocarbons.

Even when these hydrocarbons represent only 10% of the weight of the charge, the time necessary for their decomposition will be several times greater than that necessary to reach that point.

It has now been found according to this invention to be possible to remove these hydrocarbons without their destruction and to recover them as such so that not only a very considerably increased throughput but also, as the examination of these hydrocarbons showed, a convenient recovery of very useful hydrocarbons can be achieved.

Accordingly, the present invention provides a process for the manufacture of hydrocarbon distillates, coke and asphaltic material from residues obtained in the cracking of petroleum which comprises soaking lumps of coke or like porous carrier with the residue, heating the same in a gaseous or vaporous atmosphere so as to evaporate the more volatile hydrocarbons and leave a coating of the less volatile hydrocarbons and of

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coke, and submerging the thus coated lumps in a molten metal or salt at a temperature above the softening point of the hydrocarbons forming the coating so as to cause liquid products to rise to the surface of the molten material.

Instead of coke I may use a like forming carrier, for example wood charcoal.

Preferably both steps are carried out within the temperature range of 400° C. to 550° C. Preferably a molten lead bath is used and the action of the molten metal or salt seems to be to squeeze out the liquid hydrocarbons which collect on the top thereof from whence the liquid hydrocarbons can easily be removed and recovered as such, while the solid hydrocarbons stick to the surface of the lumps which after a short period of heating are ready to receive a fresh charge of residue.

It will thus be seen that the process of the present invention enables distillates, asphalt-like fractions and coke to be obtained from cracking residues in one operation with high throughput and heat efficiency.

Cracking residues useful for the process of the invention may be obtained by cracking hydrocarbons as they occur in natural or synthetic petroleum, in asphalts, bituminous or waxy deposits and removing the lighter fractions. They may be blended with hydrocarbons from cracked or uncracked stocks.

Two embodiments of the invention will now be described in greater detail by way of example with reference to the accompanying drawings in which:

Fig. 1 is a front sectional view of one embodiment of this apparatus with furnace removed.

Fig. 2 is an end sectional view corresponding to Fig. 1 but including the furnaces, and

Fig. 3 is a front sectional view of a second embodiment.

Referring to Figs. 1 and 2 of the drawings a perforated cylindrical iron drum 1 is rotatably mounted in a bath 2 containing molten lead 3 heated by heating means 4 disposed in furnace 19 provided with flue 20, the axis of the drum being horizontally disposed. The level of the lead is below the axis of the drum and the drum is divided into sections by means of radially disposed perforated plates 5, and about two-thirds of the space within the drum is filled with lumps of coke 6. The pre-heated charge is introduced into the drum 1 through a pipe 7 at the top of the bath, the pipe leading to a horizontal manifold 8 with a plurality of openings 9. The vapours evolved escape through a pipe 10 at the top of the bath and are condensed, and the liq-

liquid hydrocarbons displaced by the metal bath escape through an overflow pipe 11 at the side of the bath slightly above the level of the molten metal. Fresh coke can be charged from a hopper 12 by means of an axially disposed screw conveyor 13, while coke which has sufficiently increased in weight is removed by means of a further axially disposed screw conveyor 14 at the other end of the drum to a hopper 15. Tubes 16 and 17 may be provided through which gas under pressure can be introduced into the conveyor housing, to prevent vapours entering the conveyors. A lead trap 18 may be connected with the overflow for the liquid products. The drum 1 is supported in bearings 21 and 22 and is driven through pulley 23 and belt 24.

Referring to Fig. 3 of the drawings the pre-heated charge of residue is fed through a pipe 25 on to hot coke lumps 26 floating on a bath of molten lead 27 contained in a cylindrical vessel 28 having a vertical axis. The lead is heated by heating means 29 disposed in furnace 30 having a flue 31. After the coke has soaked sufficiently in the residue, a short time is allowed for evaporation of volatile constituents. Then a perforated disc 32 fitting inside the cylinder is pushed down until all the coke is submerged in the molten lead, the lead content of the cylinder being such that the lead rises up to an overflow pipe 33 so that the liquid hydrocarbons formed run into a container 34 connected to the pipe. A lead trap 35 is provided in the pipe and retains any molten lead that might have been carried over. Vapours produced are removed through a pipe 36 near the top of the cylinder and condensed.

The coke is charged from a hopper 37 above the aforesaid vapour pipe and the excess after treatment is removed by the aid of a plunger 38 disposed in a sleeve 39 fitted at the side of the cylinder.

The coke removed is received in a hopper 40.

When the coke has been submerged for a sufficient time, the disc 32 is moved up and a fresh charge of residue applied to the rising coke.

In both embodiments the area above the lead bath is well lagged or provided with additional heating means.

The composition and proportion of the various fractions obtainable from a given charge can be varied.

(a) By varying the temperature of the lead bath; if the temperature is increased the proportion of distillates increases as well as that of the coke, but they may become darker if the pressure is not also increased. The proportion of asphalt-like hydrocarbons decreases.

(b) By the application of increased or reduced pressure; an increase of pressure will lead to an increase of the asphalt-like hydrocarbons and of coke, the latter especially when the temperature is increased at the same time.

A similar effect to that obtained by the use of reduced pressure can be obtained by the use of carrier gas or vapours or the addition of lower boiling fractions to the charge.

(c) By varying the period during which the coke lumps are inside or outside the lead bath; an increase of the period during which the coke lumps are outside the bath will lead to a reduction of the proportion of the asphalt-like hydrocarbons while the other two fractions increase; at the same time the softening point of the asphalt-like hydrocarbons will rise and their

composition change, as can easily be ascertained by solvent extraction.

The longer the period of submersion of the coke in the lead bath the lower becomes its volatility; a similar result is obtained by using higher temperatures.

It may be remarked that the composition of the residue is of great importance and the properties of the fractions can be modified very considerably by varying the original cracking conditions or by blending.

The following are the general properties of the three fractions obtained, in addition to which a small proportion of gas ($\frac{1}{2}$ –3%) is also obtained;

1. *Distillates*.—They range from hydrocarbons boiling at ordinary temperatures to resinous hydrocarbons, the proportions depending on the nature of the residue and the conditions of the treatment. They may be recovered by fractional condensation, the heavier fractions being stocks for lubricating oils and drying oils. A large variety of useful products can be obtained from them with the aid of solvents.

The hydrocarbons in the gas oil range may be used as a fuel or for blending; thus a large proportion of residue can be converted into a useful fuel by treating a proportion according to the process and blending the suitable distillates with untreated residue.

2. *Asphalt-like hydrocarbons*.—They have the appearance of asphalt and may be used for purposes for which asphalt is used, either as such or after blending with suitable material. They can be obtained with a high softening point, making transport and storage easy. By solvent treatment useful hydrocarbons of resinous nature can be extracted.

A proportion can, for example, be extracted with petroleum ether. These hydrocarbons are resins of low softening point. They can be further separated by treatment with furfural into various types, the part in the lower layer generally having drying properties or being lubricating stock; but in some cases these products were found in the top layer and the lower layer contained resins of somewhat higher softening points. A variation of the proportions of furfural and the temperature of its application will enable a variety of products to be produced and the desired method of treatment to be found. However, other solvents may be employed to obtain a different variety of products.

Generally, these hydrocarbons are easily emulsifiable and compatible with nitrocellulose and, therefore, very useful for painting and coating when used as such or in mixtures with other products. Drying oils obtained by the process are miscible with linseed oil in all proportions without reducing the drying property of the mixture.

The same observations were made regarding the heavier fractions of the distillate.

The residue from the petroleum ether extraction contains a proportion of hydrocarbons soluble in benzole and a larger one soluble in solvent naphtha. These hydrocarbons are very often black, shiny, very resistant to acids, and they dry from their solution with a hard, glossy, black film. They are useful for incorporation in paints and lacquers. The softening point of the dry resin is often about 70 to 90° C.

The residue from this extraction consists of hydrocarbons which are an intermediate stage in the production of coke, while those having proceeded further were removed as solids by

absorption by the coke lumps. They are solid at ordinary temperatures, but very soft and, for example, very useful as pigments as they are almost free from coke.

3. *Coke*.—The coke can be recovered as loose lumps which makes continuous and automatic operation very easy and increases its value for many purposes.

It can be used as a fuel or for chemical reactions. If it is intended for use for making carbon disulphide, where normal coke (for example gas coke) is unsatisfactory, the original coke lumps may be wood charcoal or crushed lumps from previous operations. If it is desired to obtain coke with some inorganic matter fairly homogeneously distributed, such matter may be mixed with the charge in powdered form. Organic matter (for example sawdust) may be used in the same way to increase porosity.

It may be remarked that the process of the invention can easily be controlled by the softening point of the asphalt-like hydrocarbons or the proportions of the various distillates during fractional condensation.

The term "gaseous" as used in the appended claims includes "vaporous."

I claim:

1. A process for the manufacture of hydrocarbon distillates, coke and asphaltic material from residues obtained in the cracking of petroleum which comprises soaking lumps of porous carrier material with a residue obtained in the cracking of petroleum, heating the soaked lumps in a gaseous atmosphere so as to evaporate the more volatile hydrocarbons and leave a coating of the less volatile hydrocarbons and of coke on the lumps of porous carrier, and submerging the thus coated lumps in a molten material selected from the group consisting of molten metals and molten salts, at a temperature above the softening point of the hydrocarbons forming the coating so as to cause liquid products to rise to the surface of the molten material.

2. A process for the manufacture of hydrocarbon distillate coke and asphaltic material from residues obtained in the cracking of petroleum which comprises soaking lumps of coke with a residue obtained in the cracking of petroleum, heating the soaked lumps in a gaseous atmosphere so as to evaporate the more volatile hydrocarbons and leave a coating of the less volatile hydrocarbons and of coke on the lumps of porous carrier, and submerging the thus coated lumps in a molten material selected from the group consisting of molten metals and molten salts, at a temperature above the softening point of the hydrocarbons forming the coating so as to cause liquid products to rise to the surface of the molten material.

3. A process for the manufacture of hydrocarbon distillates, coke and asphaltic material from residues obtained in the cracking of petroleum which comprises soaking lumps of coke with a residue obtained in the cracking of petroleum, heating the soaked lumps in a gaseous atmosphere at a temperature of between 400 and 550° C. so as to evaporate the more volatile hydrocarbons and leave a coating of the less volatile hydrocarbons and of coke on the lumps of porous carrier, and submerging the thus coated lumps at a temperature of between 400 and 550° C. in a molten material selected from the group consisting of molten metals and molten salts so as to cause liquid products to rise to the surface of the molten material.

4. A process for the manufacture of hydrocarbon distillates, coke and asphaltic material from residues obtained in the cracking of petroleum which comprises soaking lumps of porous carrier material with a residue obtained in the cracking of petroleum, heating the soaked lumps in a gaseous atmosphere so as to evaporate the more volatile hydrocarbons and leave a coating of the less volatile hydrocarbons and of coke on the lumps of porous carrier, and submerging the thus coated lumps in molten lead at a temperature above the softening point of the hydrocarbons forming the coating so as to cause liquid products to rise to the surface of the molten lead.

5. A process for the manufacture of hydrocarbon distillates, coke and asphaltic material from residues obtained in the cracking of petroleum which comprises soaking lumps of coke with a residue obtained in the cracking of petroleum, heating the soaked lumps in a gaseous atmosphere at a temperature of between 400 and 550° C. so as to evaporate the more volatile hydrocarbons and leave a coating of the less volatile hydrocarbons and of coke on the lumps of porous carrier, and submerging the thus coated lumps at a temperature of between 400 and 550° C. in molten lead so as to cause liquid products to rise to the surface of the molten lead.

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