Dec. 24, 1946. E. HENE 2,412,983

PROCESS FOR THE CONVERSION OF HEAVY HYDROCARBON LIQUID

Filed June 17, 1943 2 Sheets-Sheet 1

FIG. 1.

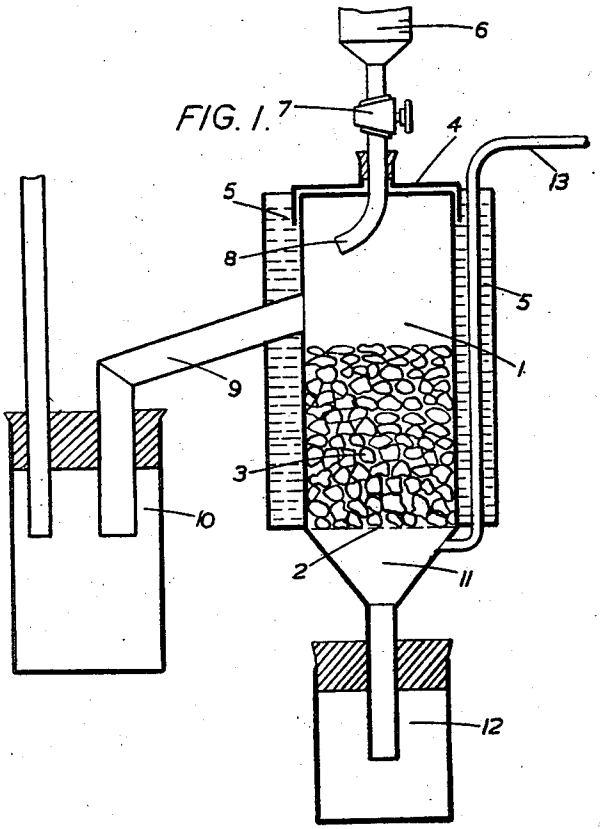


FIG. 2.

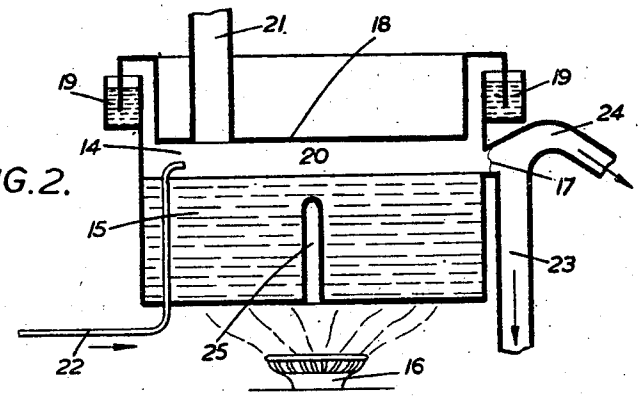
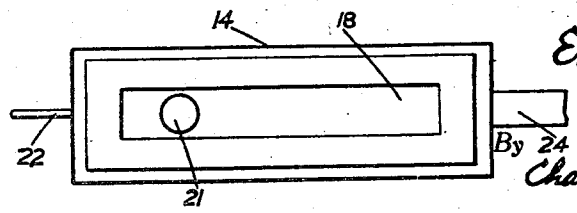


FIG. 3.



Emil Hene
Inventor

By Charles M. Thom
Attorney

Dec. 24, 1946. E. HENE 2,412,983

PROCESS FOR THE CONVERSION OF HEAVY HYDROCARBON LIQUID

Filed June 17, 1943 2 Sheets-Sheet 2

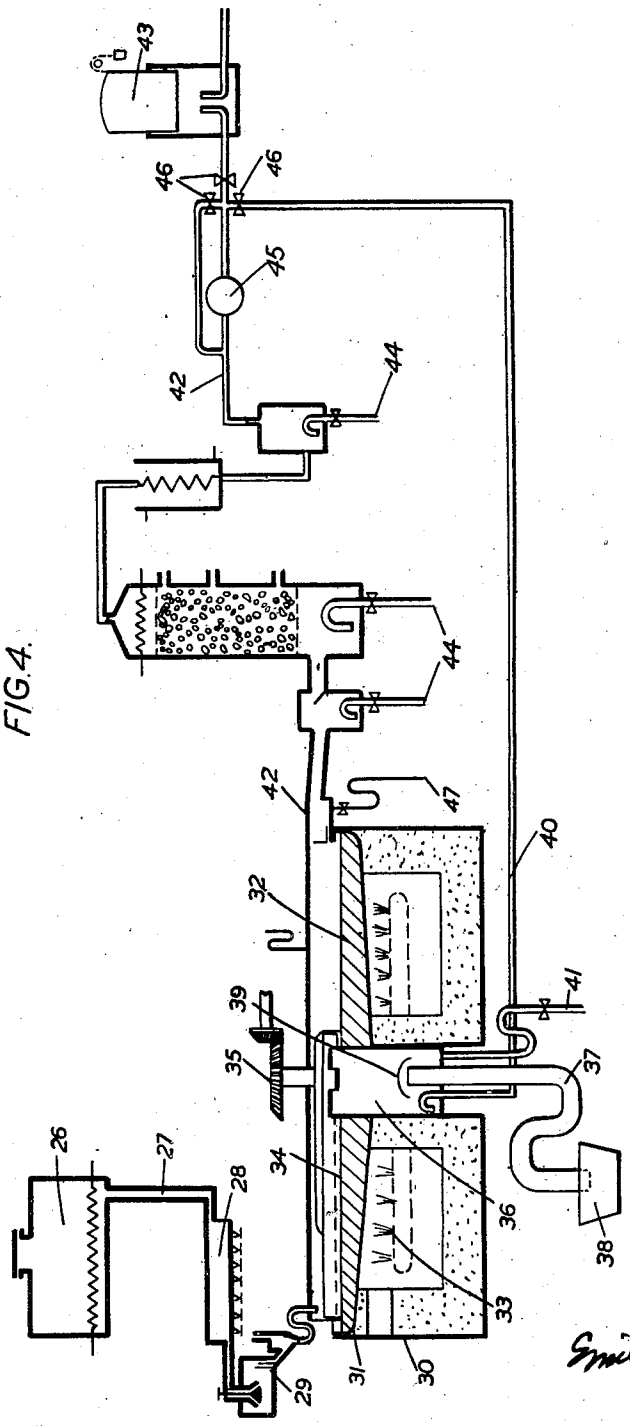


FIG. 4.

Emile Hene
Inventor

By Charles M. Thomas
Attorney

Patented Dec. 24, 1946 2,412,983

UNITED STATES PATENT OFFICE

2,412,983

PROCESS FOR THE CONVERSION OF HEAVY HYDROCARBON LIQUID

Emil Hene, London, England

Application June 17, 1943, Serial No. 491,190
In Great Britain April 14, 1942

1 Claim. (Cl. 196—70)

1

This invention is concerned with improvements in or relating to the heat treatment of petroleum and like hydrocarbon products and/or hydrocarbon products obtained from the liquefaction or heat treatment of coal and the like and to the production therefrom of other products.

In my application Serial No. 347,146, filed July 24, 1940, I have described a process for the treatment of heavy residua and distillates so as to obtain from them hydrocarbon products boiling mainly in the gas oil range with a minimum production of gasoline, gas and coke, wherein the oil is very rapidly heated by being sprayed or dripped on to the surface of a body composed of porous lumps, such as coke, heated to a temperature of from 400°–600° C., the rate of feed and distribution of the oil and the size of the lumps being such that only a thin film of oil is formed on any lump at any instant of time, the vapours formed being rapidly withdrawn. In that process the hydrocarbons are recovered as vapours, most of which are condensed into liquid oils, and no liquid residuum remains.

In a later application Serial No. 481,923, filed April 5, 1943, I have shown that under certain conditions the effect of heat on petroleum products or alternatively the speed of the reaction or the response of the charging stock to the treatment can be greatly increased by the addition of a small quantity of one or more catalysts or accelerators belonging to the fifth periodic group of elements. For example, as described in said application 481,923, I may use as the catalyst some of the catalyst-containing distillate obtained from a previous run with the same catalyst or catalysts. The use of these substances enables the throughput to be increased, and also increases the paraffinicity of the hydrocarbons produced, whilst tending to decrease the formation of gas.

Continuing my investigations on processes of the kinds described in the said prior applications, I found and described in my British specification No. 31/42 and in my corresponding United States application Serial No. 487,323, filed May 17, 1943, that by selecting charging stocks in which paraffinic bodies did not predominate such for example as cracked residua, and by operating the process at a temperature of from 400°–460° C. which constitutes the lower portion of the range covered in my application Serial No. 347,146 it is possible to modify the nature of the resulting product and to produce in the main not ordinary gas oils, but oils of lubricating properties together with some jellies and resinous products.

2

As a result of further investigations relating to the processes described in my said earlier applications, it has now been found that the reaction passes through one or more intermediate stages, there being a tendency for some of the hydrocarbons to increase in saturation, probably owing to a re-arrangement of large molecules or by reaction of molecules with one another or by a variety of changes which are often accompanied by the formation of small quantities of products of a lower boiling range. It has further been found that when the charging stock consists, wholly or partly of heavy residua, either cracked or uncracked, the first or one of the first of these intermediate stages results in the formation of products which cannot be distilled without decomposition under the conditions of the reaction, and which thus decompose with the formation, in the main, of hydrocarbons, gas and coke, unless they are rapidly removed in the liquid phase from the sphere of the reaction.

It has been found that these products comprise very valuable hydrocarbons such as resinous products, lubricating oils including drying oils, jellies and the like and the present invention is concerned inter alia with the production and separation of such products, which, we have found, can be effected by carefully controlling the reaction and either stopping it at a desired intermediate stage or removing the said products from its sphere.

The most suitable temperature range for bringing about the surface reaction is comparatively low, lying between 430° and 485° C., in the case of petroleum products and although we do not desire to be limited by any theoretical explanations it may be said that it appears probable that under the conditions of the process an actual conversion of products takes place, whereby substances which are still of high molecular weight and of increased saturation are produced by inter-reaction of components of the hydrocarbon mixture partly at the expense of the more asphaltic material, the hydrogen to carbon ratio of which is more and more reduced until it becomes immiscible with the remainder of the material and settles together with a part of the substances produced on the surface where, being undistillable under the existing conditions, it is converted into coke. If, however, the coking of this material is prevented by its removal from the reaction surface in liquid phase it will be found to contain various valuable products of the initial stages of the convertive reaction.

Accordingly the invention consists inter alia

in a process for the treatment of heavy petroleum residua and the like in which the material is so sprayed, dripped or otherwise applied to a heated surface under such conditions of temperature that each particle of the liquid is rapidly raised to the temperature at which, in addition to some vapours, liquid and non-distillable conversion products are formed on the surface, said vapours and said liquid conversion products being as far as possible rapidly removed, in the vapour and liquid phases respectively from the reaction sphere before any substantial decomposition of said liquid conversion products takes place.

For the purpose of controlling the progress of the reaction, it is usually desirable to collect any distillate and the liquid conversion products in separate receivers, but these will not in general enable a complete separation to be effected, and the contents of each receiver are liable to contain varying quantities of the material which should have been collected in the other. In such cases and to facilitate a satisfactory separation and working-up of the products, the contents of the two receivers may be mixed and subjected to any suitable separation treatment. Details of a preferred method of separation are given in the examples.

Alternatively, a direct separation, which will in most cases be preferable, can generally be carried out in a suitable large scale plant, such for example as that illustrated in Figure 4. Where such a method is adopted, the liquid phase product will generally contain little, if any, light oil, so that it will not usually be necessary to remove such oil by distillation, thus avoiding heating it to a high temperature, which might have undesired effects.

The process can be carried out either with or without the aid of catalysts or accelerators as described in the stated prior applications, and besides collecting the valuable products referred to, any distillate from the surface reaction can of course be separately condensed and collected whilst any gas and/or coke which may be formed can likewise be collected and used.

In the case of petroleum products the temperature will generally lie between 430° and 485° C. whilst in the case of gas tars, pitches and the like it may in some cases be desirable to use temperatures of over 500° C. (see Example 9).

The necessary control of the reaction and removal from its sphere of the converted liquid phase can be effected in various ways.

Thus, if for any given plant and charging stock the temperature remains constant, the rate of throughput will control the contact time and the rate of removal of the liquid phase from the hot surface, which liquid can be collected as such, whilst distillate vapours can be separately collected. An inert or carrier gas may be used to remove or to assist in the removal of the liquid from the reaction sphere. Moreover, the heat capacity of the plant and the rate of heat application can be selected to assist in bringing about the necessary conditions.

The products obtained according to the invention may contain hydrocarbons of more paraffinic character which in the higher boiling range (above 400° C.), are often of the character of a petroleum jelly. These can be separated by solvents of the furfural type. Such a separation might in many cases be desirable, as resins containing a considerable proportion of such products require a much longer time for drying especially without drying agents. But such more paraffinic hydrocarbons are generally more volatile than the resins, and it is therefore possible, by efficient separation of the vapour phase and liquid phase products, to obtain a liquid phase product, which by simple treatment with a solvent e. g. solvent naphtha, results in producing a solution of resins which can be used without further treatment.

The liquid phase product may also be used as such for coating, etc.

As a rule, the vapour phase products contain lighter resins, and thus a further variation in the number of resins of different properties can be obtained.

If desired some oil might be left with the resins thus reducing their softening points but such products will still give a hard film, as these oils have drying properties.

The process may be carried out in any convenient apparatus or plant which provides a suitable contact or conversion surface, adapted to be maintained at the desired and properly controlled temperature with means for feeding the charge in the desired small portions, rapidly removing the liquid conversion products and collecting any distillate.

The optimum rate of feed for a given surface depends on the character of the charge and on the extent to which it is desired to carry the conversion and therefore the optimum conditions can readily be determined in any particular case by measuring the ratio of distillate to liquid undistilled conversion products and by ascertaining the extent to which the distillate contains hydrocarbons of a lower boiling range than would be produced by a straight distillation of the charge.

If the contact surface consists of lumps of suitable material, as for example coke, I have found it to be desirable gently and regularly to disturb the surface, so as to prevent agglomeration. The lumps may if desired be removed either continuously or discontinuously from the reaction vessel, broken down to the desired size and recharged on to the top of the layer, if necessary after heating to a higher temperature than that of the reaction, so as if necessary to accelerate the complete coking of any deposit.

We have found that in many cases a liquid contact or conversion surface, as for example a surface of molten lead, can with advantage be used, suitable means being of course provided for removing and collecting the liquid conversion products. The use of such a surface has the advantages of combining increased rate of heat transmission and consequent increased throughput with ease of control of contact time and temperature.

A tendency exists to form a layer of coke which would interfere with heat transmission. It may therefore be advisable to remove it continuously or discontinuously.

A solid heated metal surface can also be used, but owing to the tendency to coke formation, the heat conductivity will gradually decrease unless the coke is regularly removed from the surface.

The following examples of results obtained according to our improved process are given by way of illustrations only, and to facilitate a better understanding of the invention.

Examples

Apparatus.—The various experiments details of which are given below were all carried out in one or other of two forms of apparatus illustrated

in Figures 1–3 of the accompanying drawings in which:

Figure 1 is a sectional elevation of an experimental apparatus using a bed of coke as contact surface,

Figure 2 is a sectional elevation of a different apparatus in which the contact surface consists of molten metal, and

Figure 3 is a plan of the apparatus illustrated in Figure 2.

Figure 4 is a diagrammatic and partly sectional representation of one form of plant suitable for continuous operation of the process on a large scale.

Referring to Figure 1, the experimental reaction vessel 1 was of circular cross-section, the diameter being 3" and the height 6". The vessel 1, which was constructed of iron, was fitted with a perforated plate 2 on which was arranged a bed of lumps of coke 3 of approximately ⅓" in average diameter, and with a rotatable lid 4, the downturned flange of which dipped into a bath of molten lead 5, which surrounded the vessel 1, and which was heated by a laterally disposed burner not shown. A funnel 6 for feeding the charge was centrally disposed in the lid 4, and was provided with a cock 7, the delivery end 8 being bent so that by rotation of the lid the charge could be spread over the periphery of the coke bed, although the delivery end 8 was so arranged as to avoid any of the charging stock being delivered closer than about ⅓" to the inner wall of the vessel. The vapourous distillate from the reaction vessel was allowed to pass through the laterally disposed pipe 9 and was condensed and collected in the vessel 10, whilst liquid reaction products were removed through the conical end 11 and collected in the vessel 12. A pipe 13 was provided for admitting a suitable carrier gas below the plate 2, for the purpose of accelerating the withdrawal of the vapourous distillate.

In the apparatus illustrated in Figures 2 and 3 the reaction vessel 14, which was of rectangular shape, contained a quantity of lead 15 maintained in a molten state by means of a burner 16, the amount of lead being such that in the molten state its upper surface was flush with or very slightly lower than the lower part of a discharge outlet 17 arranged at one end of the vessel. The cover or lid 18 was arranged to provide a liquid seal, as at 19 and a shallow space 20 adjustable as to its depths, above the surface of the molten lead. A feed pipe 21 was disposed near the end remote from the outlet 17 and a carrier gas pipe 22 enabled a stream of non-oxidising gas to be discharged just above the level of the molten lead so as to facilitate rapid removal of all products of the reaction. The outlet 17 discharged into a two-way pipe, one limb of which 23 was downwardly directed for the passage of liquid products, whilst the other limb 24, was upwardly directed and adapted for the passage of vapourous distillate to a receiver not shown. A pocket 25 for housing a pyrometer was arranged in the vessel 14.

The vessel illustrated in Figures 2 and 3 enabled a higher reaction temperature to be employed than with the apparatus according to Figure 1, as by lowering the lid or cover 18 the velocity of the vapours could be increased, thus reducing the risk of decomposition of the liquid conversion products or of cracking the vapours.

In a plant constructed according to Figure 4 the charging stock flows from a charge tank 26 fitted with a heating coil through the pipe 27, gas fired preheater 28, feed control and vapour trap assembly indicated generally at 29 to the converter 30. The converter is preferably of circular shape and comprises a shallow and preferably dished or slightly conical metal bath 31 filled with lead 32 which is kept molten by means of a gas-fired furnace 33. A rotary scraper 34, for scraping the surface of the lead bath is provided and is driven through the gears 35. A centrally disposed cylindrical chamber 36, closed at its lower end and having one or more parts or openings at or near its upper end serves as an overflow weir for the rapid and continuous removal of liquid conversion products which collect in the lower end of the said chamber, through which projects an outlet pipe 37 for discharging the said products into a mould or other receiver 38. A spreader or shield 39 is so disposed over the open end of the pipe 37 as to leave a clearance space for the passage of the liquid. A gas return pipe 40, described below is adapted to blow returned vapours through the liquid collected in the bottom of the chamber so as to liberate any entrained vapours. A spilled lead drawoff pipe 41 is preferably provided. The vapours are discharged through the pipe 42 and pass through any desired series of dephlegmators and condensers to a gasometer 43 where they are stored for use as fuel or for any other desired purpose. A series of draw-off pipes 44 is provided at convenient points of the dephlegmating and condensing part of the plant, for the purpose of removing any heavy distillate which may have collected. At a convenient point of the system near the gasometer, we provide an exhauster 45 for drawing the vapours through the plant, and forcing them into the gasometer. The gas return pipe 40, which is branched off the pipe 42, on suitable operation of the cocks or other controlling devices indicated at 46, enables a controlled proportion of the gases and/or vapours to be returned and blown through the liquid conversion products collected in the lower end of the chamber 36.

Valve-controlled drain pipe 47 is provided for the drainage from pipe 42 of any liquid which may have been entrained in and then deposited from the vapors and gases passing through pipe 42.

Examination of products.—The examination of the products obtained in all the undermentioned experiments was carried out as follows:

The distillate and the liquid conversion product (hereinafter referred to as "L. C. P.") from the experiment were mixed and treated with petroleum ether (B. P. 100/120° C.) by mixing them thoroughly at about 60/80° C. and then allowing them to cool. On standing the mixture separated into two layers: (*a*) a portion insoluble in petroleum ether, which was a resin which solidified from the molten stage into a hard shiny black product with a softening point of about 60°–80° C. This resin, which in the examples given below, is referred to as extract 1, was found to be soluble in benzole. The solution, on application to a smooth surface and on being allowed to evaporate, yielded an excellent hard shiny brown film which dried very quickly. In its original form the resin sometimes contained matter of a more or less coke-like nature, which can be separated by filtering the benzole solution. It depends on the conditions of the test whether such carbonaceous matter can be filtered off easily and immediately or only after some additional treatment such as standing for some hours. The insoluble matter

dried to a "coke-like residuum" and this term is used in the examples.

(*b*) *Portion soluble in petroleum ether.*—The petroleum ether was evaporated and the residue extracted with furfural and the two fractions thus obtained treated separately. Two separate resins were obtained, one from the bottom layer (extract 2) and one from the top layer (extract 3). The various oils referred to as having been obtained in the following examples were all obtained by distillation of one or other or the two fractions resulting from the furfural extraction of the soluble portion (*b*).

It will of course be obvious that other solvents and/or working conditions than those described could if desired be used for examining and working up the conversion products.

Moreover the properties of the extracts vary according to the conditions of the operation, that is, according to the state of transition which the products are allowed to attain. Thus, resinous extracts having softening points which differ from those mentioned in the examples, may be obtained by varying the charging stock or the treatment, whilst still further variations may be effected by using different solvents and/or conditions of separation.

Extract 1.—This can be obtained as a very hard, highly glossy resin generally melting between 60 and 80° C. and solidifying without any immiscible matter. A film from benzole solution is transparent, hard and shiny, drying within a few minutes (Example 8). The extract will sometimes be found to contain coke-like matter which can be separated either by filtering the benzole solution or by separating and removing the upper layer in the molten stage. The resin will still be hard, less shiny and somewhat more brittle but the film formed from benzole solution will still be hard and shiny.

Extract 2.—The resin can be obtained as a hard transparent shiny brown product which is not brittle. The film from benzole or petrol ether solution is hard, shiny and of a brown to yellow colour. If the reaction has not reached the proper stage, the resin is brittle and becomes so again if the reaction is carried too far, in which case its proportion is reduced, mainly in favour of lubricating oil.

Extract 3.—This extract always contains a hard and somewhat ductile resin, representing probably a more saturated part of extracts 1 and 2. A film of this resin from benzole solution is less hard and has less grip on the surface than that of extracts 1 and 2 and the resin resembles an extract 1 produced from a straight-run residuum.

While the process is not confined to petroleum hydrocarbons, the following examples were mainly carried out with a residuum from liquid phase cracking, as this product is readily available and represents at present a product of very small value. One example is given for a straight-run product to indicate the influence of the charging stock on the reaction and another one in which a proportion of pitch tar distillate is added as representing aromatic compounds.

It seems that hydrocarbons boiling above 300° C. but below the asphaltic matter contribute considerably to the formation of resins or other products of large molecular size. The examples given show the influence of the catalyst. The catalyst used was in all cases in the form of a distillate obtained from a treatment of the metal and residuum as described in application Serial No. 481,923.

As already stated, other solvents may be used either instead of or in addition to those already mentioned, for the purpose of effecting extraction or separation, whereby the variety of resinous products obtainable may be increased; thus, for example, butyl acetate might be used to separate a lighter resin from extract 1.

Example 1.—The apparatus shown in Figure 1 was used and the charge, pre-heated to about 100° C., was dripped on to the coke while the funnel was slowly turned in order to allow the coke lumps to become almost free from the previous charge before a fresh charge could reach them. The charging stock used was straight-run residuum from Venezuelan crude, topped to 360° C., with a specific gravity of 0.98 at 60° F. The temperature in the lead bath was 450° C. The rate of feed was 2 gms. per minute. 100 ccs. of CO_2 per minute were used as carrier gas. The yield of distillate and L. C. P. was 80%, coke 16%, gas and loss 4%. The catalyst was arsenic, one part per 500,000 parts of charge.

Analysis of L. C. P. and distillate

	Per cent by weight of the charge
Extract 1 (black film from benzole solution not very hard)	10
Extract 2 (hard, transparent)	5
Extract 3 (9% representing petroleum jelly)	12
Lubricating oil	33
Gas oil (Diesel Index 58)	12
Oil boiling below 230° C	5
Coke-like residuum, obtained from insoluble portion (*a*) by benzole extraction	3

Example 2.—The conditions of the experiment were exactly the same as in Example 1, but the charge was a residuum from liquid phase cracking, topped to 340° C. and had a specific gravity of 1.1. The yield of distillate and L. C. P. was 86%, coke 11%, gas and loss 3%.

Analysis of L. C. P. and distillate

	Per cent by weight of the charge
Extract 1 (black, hard, film hard, very adherent)	14
Extract 2 (hard, transparent)	39
Extract 3 (2% representing petroleum jelly)	3
Lubricating oil	20
Oil boiling below 300° C	1
Coke-like residuum	9

Example 3.—The apparatus shown in Figures 2 and 3 was used and the charge and catalyst were the same as in Example 2. The charge was pre-heated to 225° C., the rate of feed was 10 gms. per minute. The temperature of the lead bath was 440/445° C. No carrier gas was used. The yield of distillate and L. C. P. was 99%, gas and loss 1%.

Analysis of distillate and L. C. P.

	Per cent by weight of the charge
Extract 1 (as from Example 2)	33
Extract 2 (as from Example 2)	38
Extract 3 (Black, fairly hard film)	6
Lubricating oil	12
Oil boiling below 330° C	4
Coke-like residuum	6

Examples 4 and 4a.—The charge consisted of 95% of topped cracked residuum and 5% topped straight-run residuum. The conditions employed were the same as in Example 3, except that the

rate of feed was reduced to 2.5 gms. per minute while Example 4 was carried out with arsenic as catalyst, no catalyst was employed with Example 4*a* and in both cases 100 ccs. of CO_2 per minute were used as carrier gas. The yield of distillates and residuum was in both cases 97% and gas and loss 3%.

Analysis of distillate and L. C. P. (all percentages are by weight of the original charge)

	4	4*a*
	Per cent	*Per cent*
Extract 1	29	24.5
Extract 2	32	35
Extract 3	4.5	14
Lubricating oil	11	5
Oil boiling below 340° C	15	7
Coke-like residuum	5.5	11.5

The extract 1 of Example 4 gave a harder shinier film from benzole solution than extract 1 from 4*a*. Extract 2 from 4 was hard and shiny, while that from 4*a* was soft and sticky. Extract 3 from 4 contained 3.5% of a good petroleum jelly, while that from 4*a* was a soft and sticky mass. The oil boiling below 340° C. from 4 had an aniline point of 153° F. and a specific gravity of 0.879 at 60° F., while that from 4*a* had an aniline point of 147° F. and a specific gravity of 0.889 at 60° F. The addition of saturated products to a cracked product often has the effect of producing extracts of lighter colour.

Examples 5 and 5a.—The charge was a mixture of 95% topped cracked residuum and 5% topped straight-run residuum (Cumarabo) the catalyst consisting of one part per 200,000 parts of the charge of a mixture of phosphorus, bismuth and vanadium of equal proportions and prepared in the form of a distillate as described in application Serial No. 481,923. The apparatus shown in Figures 2 and 3 was used. The rate of feed was 10 gms. per minute, the temperature in the lead bath being 455/460° C. for Example 5 and 480/485° C. for Example 5*a*. No carrier gas was employed. The yield of distillate and L. C. P. was 99% for Example 5 and 98% for Example 5*a*.

Analysis of distillate and L. C. P.

Per cent by weight of charge	5	5*a*
Extract 1	26	19
Extract 2	27	24
Extract 3	15	6
Lubricating oil	11	13
Other oils	16	21
Coke-like matter	4	15

All the products in the desired range showed better qualities from Example 5 than from 5*a*.

Extract 1.—The extract from Example 5, when directly melted, was a very hard and shiny resin with almost no top layer of carbonaceous matter. The film from benzole solution was very hard, smooth, shiny and transparent and stuck firmly to the surface. Similar tests on the product from 5*a* showed a very brittle resin with a considerable top layer of carbonaceous matter, while the film from benzole solution could comparatively easily be removed from the surface.

Extract 2.—The extract from Example 5 was much less brittle than that from 5*a*.

Extract 3.—The extract from Example 5 was a mixture of a hard and somewhat ductile resin 8% and an excellent petroleum jelly 7%, which were separated as described. No jelly was obtained from 5*a*.

The lubricating oil from 5 was superior to that from 5*a*. The paraffinic oil boiling from 360/385° C. contained almost no wax from Example 5, while it was very waxy from Example 5*a*.

Example 6.—A Gulf Venezuela crude was treated with furfural and the paraffinic layer topped to 375° C. The residuum was an asphalt, soft at ordinary temperature. It was treated in the apparatus shown in Figures 2 and 3 (*a*) as such (*b*) mixed with 40% of its weight of extract 1 derived from Example 5. (*c*) mixed with 40% of its weight of extract 2 derived from Example 5.

Catalyst: Mixture of P, As, Bi, V in equal parts—1 part in 200,000 parts of the charge.
Rate of feed—3 ccs. per minute.
No carrier gas was used.
Temperature in lead bath 440–445° C.

Yield of L. C. P. and distillate

	(*a*) 99%	(*b*) 99%	(*c*) 99%
Extract 1		16	15
Extract 2	33	16	11
Extract 3	1	7	5
Gas oil	35	44	47
Coke-like residuum	30	16	21

REMARKS.—In the case of (*a*) a separation of the residuum from the petrol ether extraction was not satisfactorily possible and the product dried as such, when it resembled the coke-like residuum from the previous test. Its proportion is, therefore, given in that column.

The extracts 1 and 2 from tests (*b*) and (*c*) were very good representatives of those types, while extract 3 from (*b*) was a petroleum jelly and from (*c*) a hard and shiny resin.

Example 7.—The apparatus of Figures 2 and 3 was used and the charging stock was a mixture containing 35% of extract 2 in experiment (*a*) and 35% of extract 1 in experiment (*b*) and 65% of a distillate obtained from the cracked residuum used in previous experiments; the distillate had a specific gravity 1.022 (60° F.) and 91% boiled from 320–400° C. (50% at 360° C.)

Temperature 465° C.
Catalyst: P, As, V in equal parts—1 part taken together in 200,000 parts of the charge.
Rate of feed 3 ccs. per minute.
No carrier gas was used.

	(*a*)	(*b*)
Yield of liquid phase products and distillate.	99%	99%
I. B. P.	290° C.	305° C.
By weight of charge of extract 1	9%	7%
By weight of charge of extract 2	30%	22%
By weight of charge of extract 3	2%	3.5%
Oil boiling below 350° C	10%	25%
Lubricating oil above 350° C	48%	29.5%
Coke-like residuum.		12%

Extract 1 (*a*) could be molten without separating carbonaceous matter and was a hard shiny black resin. Extract 1 (*b*) could not be treated in the same way but the carbonaceous matter had to be separated. Extracts 2 were in both cases of almost the same appearance, medium hard, ductile, brown and transparent. Extracts 3 contained petroleum jellies in both cases (1.5% and 3% respectively).

Example 8.—The charge was a mixture of two parts of a topped cracked residuum as used in the previous examples, with one part of distillate of the same stock, with a boiling range as

referred to in Example 7. The catalyst consisted of one part in 500,000 parts of the charge of a mixture of phosphorus, bismuth and vanadium in equal proportions and prepared in the form of a distillate as described in application Serial No. 481,923. The apparatus shown in Figures 2 and 3 was used. The rate of feed was 5 gms. per minute, the temperature in the lead bath was 455/460° F. No carrier gas was employed. The yield of distillate and L. C. P. was 99%.

Analysis of distillate and L. C. P.

	Per cent by weight of the charge
Extract 1	33
Extract 2	24
Extract 3	7
Lubricating oil	15
Oil boiling below 350° C.	20

Extract 1 was very hard, exceptionally glossy and not brittle, melting without forming a top layer of coke-like matter.

Extract 2 was hard and transparent, not brittle.

Extract 3 was a mixture of a hard ductile resin and petroleum jelly (5%).

Oil boiling below 350° C. contained 0.7% below 200° C. and 2.5% below 300° C. Initial boiling point 108° C.

Example 8a.—The cracked distillate as treated in Example 8 was treated without any admixture of asphaltic matter under exactly the same conditions as in Example 8. Practically no gas was produced and yields of 2% of extract 1, 9% of extract 2 were obtained, while the boiling range for recovered products was only slightly changed. The non-paraffinic part of the oil boiling above 350° C. (40% by weight of the charge) was an excellent lubricating oil. About 20% of paraffinic oil boiling from 302/400° C. was obtained.

Example 9.—The charge was a mixture of 75% of a cracked paraffinic crude, sp. gr. 0.934 at 60° F. of which 43% boiled above 350° C., and of 25% of a coal tar pitch distillate sp. gr. 1.215 at 60° F.

The catalyst was vanadium (1 part per million) used as described in previous examples.

The temperature was 495–505° C., charge preheated to 180° C.

The lead bath was 15 in. wide and 12 in. long.

Rate of feed: 4 gallons/hour.

Yield: 97%.

Approx. 87% was recovered in liquid phase, and 10% as a distillate.

In this case both fractions were collected and analysed separately.

Liquid phase products

	Per cent
Petroleum jelly	4
Non-paraffinic oil above 350° C.	10
Paraffinic oil above 350° C.	15
Resin type 2 (hard, excellent film)	13
Resin type 1 (ductile, film very glossy)	11
Final residuum	4
Oil boiling below 350° C.	Remainder

Vapour phase products

	Per cent
Petroleum jelly	8
Non-paraffinic oil above 350° C.	9
Paraffinic oil above 350° C.	18
Resin type 2 (soft, film light in colour)	11
Oil boiling below 350° C.	Remainder

Extracts 1, 2 and 3.—The method described for the separation of the material referred to as "extract 1" is similar to a method already known for the separation of asphaltenes from asphalt, but although the presence of asphaltenes in the charging stock may to some extent contribute to the formation of extract 1, it is clear from experiment 7*a* that their presence is not essential for such formation.

If the proportion of asphaltic matter in the charge is too great, some part would remain unconverted, and would be obtained with extract 1, in which case the molten product would not be homogeneous. When such a product is allowed to cool, two layers are clearly visible, the top layer having a very brittle and almost coke-like appearance, whilst the lower layer clearly appears to have been molten.

To avoid the presence of unconverted asphaltenes the charge may if necessary be blended with a proportion of a charge containing less asphaltic matter (Example 8) or some paraffines may be added, or the conditions of the reaction may be made more severe, e. g. by increasing the temperature and/or contact time or a combination of these methods may be applied.

Extract 2 is in some ways similar to a resin which is known to occur in asphaltic products and which can be obtained from it by the same process of extraction as described in this application for extract 2.

Although it may be that a part of extract 2 is derived from such a resin it is not necessarily so for all of it as shown in Example 7*b*.

While the original resin in the asphaltic matter was very brittle even when oil was only removed to a maximum boiling temperature of about 345° C. the extracts 2 showed a different behaviour and could be obtained as a ductile, clear, transparent and shiny resin even when oil was taken off to 375° C. and higher. Such oils are lubricating or drying oils.

Extracts 3 show the greatest variation. It may be that they are formed, at any rate to some extent, by further conversion of extracts 1 and 2, so that extracts 3 obtained by the method as described herein, and which are not jellies, but resins, might be the more paraffinic parts of extracts 1 and 2 which have become immiscible with furfural.

Some of these products occur with the jelly and can be separated by topping the paraffinic layer from furfural treatment to about 370°–400° C. dissolving the residuum in petrol ether and filtering off the insoluble resin. The filtrate is treated with acid and the clear filtrate freed from the ether, when the jelly remains.

It should be noted that in every case the substances produced according to the invention are different from those which would be produced by an ordinary distillation. The reaction which occurs according to the invention appears to consist in part of a distillation and in part of a conversion which takes place in liquid phase, and the process may therefore be described as one of "convertive distillation," which term could also appropriately be used to describe the reactions which form the subjects of my said earlier applications. Inasmuch as the reaction produces a minimum amount of gas and low boiling hydrocarbons, the bulk of the products obtained being more saturated than the charging stock, the process can in no sense be regarded as a "cracking" process, or as one of destructive distillation in which large proportions of coke, gas and low-boiling hydrocarbons are formed.

The invention is not limited to use with residua,

but heavy distillates will be found to undergo a similar conversion, with formation of products different from those contained in the charge, whilst a considerable part of the products recoverable will be found to have good lubricating properties or to be useful as drying oils.

The reaction can be carried out under reduced, normal or increased pressure and it should be noted that the relation between the volume of the distillate and converted products, as well as their properties can be widely varied by suitably varying one or more of the reaction conditions such as the catalyst, the rate of feed, temperature, and nature and heat capacity of the contact surface according to the charging stock to be used.

Moreover it may be found that some mixtures of hydrocarbons, after treatment will contain resinous products which are softer or harder than indicated in the examples, and even the order of softening points may be different: e. g. an extract 2 might be harder than an extract 1.

I claim:

A process for the conversion of heavy hydrocarbon liquid having a boiling point of at least

350° C. and containing a substantial proportion of unsaturated compounds into valuable hydrocarbons of high molecular weight and mainly of a more saturated nature than said heavy hydrocarbon liquid, said process comprising maintaining in a reaction zone for said heavy hydrocarbon liquid a molten surface at a temperature of from about 430° C. to about 500° C., distributing said heavy hydrocarbon liquid over the molten surface at a controlled rate of feed such that each particle of the liquid is rapidly raised to a temperature at which it is partially vaporized and the unvaporized portion thereof remains in liquid condition, immediately removing the resultant vaporous and liquid conversion products from the zone of reaction before any substantial coking of the liquid occurs, said process being further characterized in that the said heavy hydrocarbon liquid is one yielding a resinous material in the liquid conversion products, and said liquid conversion products are subjected to a solvent extraction to separate said resinous material therefrom.

EMIL HENE.