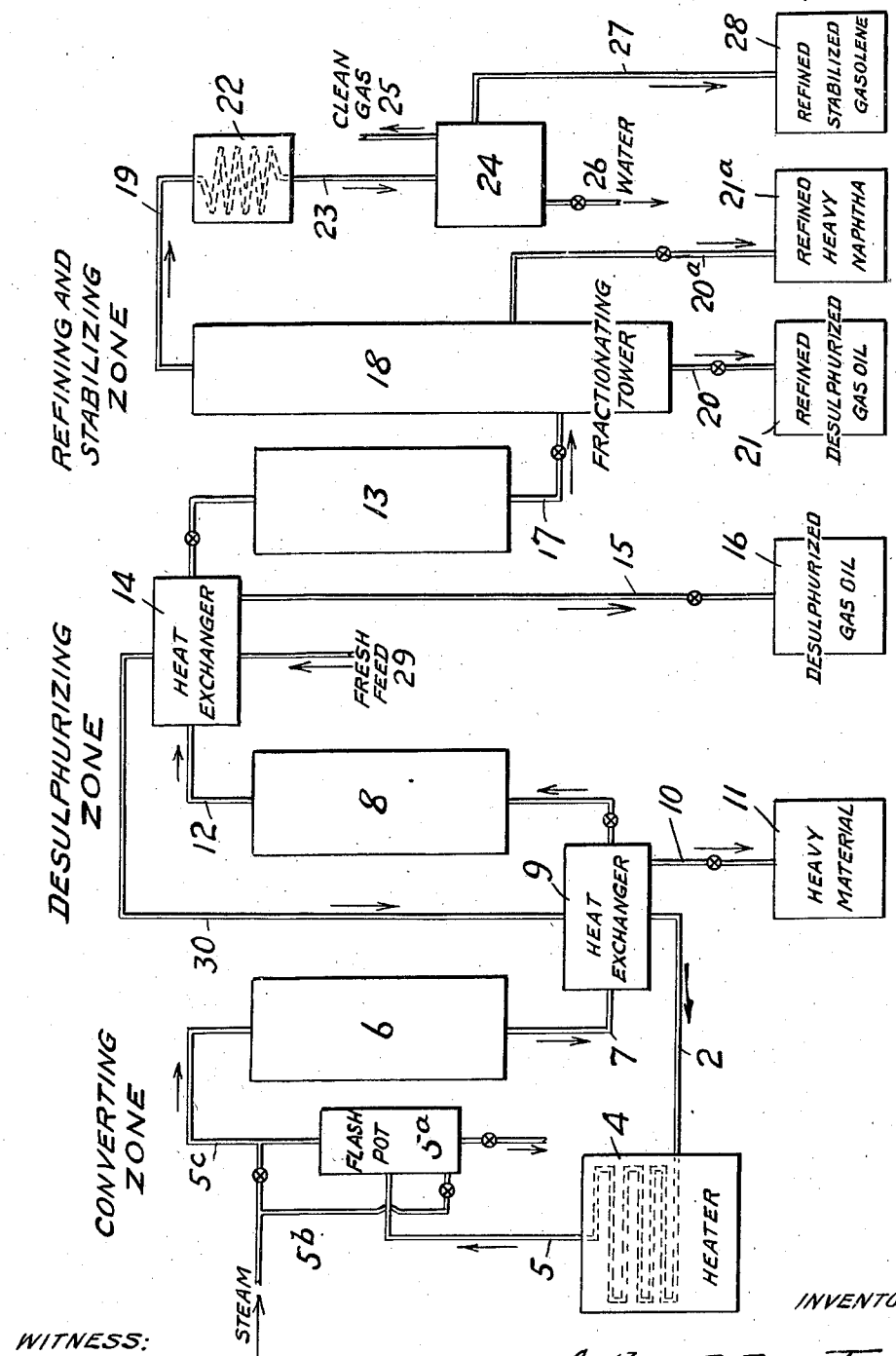
June 21, 1938. A. E. PEW, JR 2,121,046

CONVERSION AND TREATMENT OF MINERAL OILS

Filed Dec. 16, 1935



WITNESS:

Robt R. Mitchell

INVENTOR

Arthur E. Pew, Jr.

BY

Ira L. Nickerson

ATTORNEY.

Patented June 21, 1938 2,121,046

UNITED STATES PATENT OFFICE

2,121,046

CONVERSION AND TREATMENT OF MINERAL OILS

Arthur E. Pew, Jr., Bryn Mawr, Pa., assignor, by mesne assignments, to Houdry Process Corporation, Wilmington, Del., a corporation of Delaware

Application December 16, 1935, Serial No. 54,641

2 Claims. (Cl. 196—52)

This invention relates to processes for the conversion, transformation, modification, refining or other treatment of hydrocarbons including mineral oils from any source and their distillates and residues. More particularly it relates to a once-through operation involving a series of transforming or treating steps. In certain aspects, it may be considered as embodying improvements upon or further developments of the invention set forth in the copending application of Eugene J. Houdry, Serial No. 512,466, filed January 30, 1931, renewed on October 18, 1934 and refiled as Serial No. 71,341 on March 27, 1936.

One object of the invention is to produce finished products substantially without heat input into the charge after the heating of the same for the first step. Another object is to effect a progressive reduction in the temperature of the stream from step to step. Another object is to drop out of the stream at least the heaviest components at the times of reduction of temperature. Another object is to subject all of the desirable products to desulphurization and the lighter ones to refining as well. Other objects will be apparent from the detailed description which follows.

Instead of subjecting the hydrocarbon stream after the conversion or transforming step to fractionation so that the subsequent desulphurizing and refining steps are applied only to the light overhead material (as contemplated in certain forms of the invention disclosed in the aforesaid copending application), the present invention involves progressive or step-by-step reductions in the temperature of the stream so that the heat input into the charge for the first step carries through the subsequent steps. By preference, the temperature reductions are sufficient to condense the heavier components of the stream and these are withdrawn before the stream goes on into the next treating zone. Hence there is a partial cooling of the stream and removal of condensate before one, and preferably before both the desulphurizing step and the refining step but, in each instance, the remainder of the stream is left at a proper temperature for the next treating step.

In order to illustrate the invention, a preferred application or embodiment is diagrammatically indicated by the flow chart which forms the only figure on the accompanying drawing.

As indicated, a charging material, such as heavy hydrocarbons, derived from petroleum or from the destructive distillation of bitumens, or from a conversion of such materials in the gas oil boiling range or higher, is sent, preferably in preheated condition, by line 2, into a suitable heater such as a pipe still 4. The charge, then heated to conversion temperature, is sent by line 5 into a flash pot 5a for the removal of unvaporized tarry or asphaltic material and then mixed or not with extraneous gaseous material such as steam admitted within or after the flash pot from branched line 5b and passes through line 5c into a reaction vessel 6, which may be merely a soaking drum or may be a catalytic converter. The charge is here at least partly converted or transformed into light hydrocarbons, the reaction taking place within the range of 760° to 1100° F., or higher. If the reaction is promoted by a suitable catalytic mass, a good reaction range is 760° to 900° F. If the reaction is entirely thermal in character, the temperature range may be from 800° to 1100° F., or higher. The stream of transformed material passes from vessel 6 to a purifying or desulphurizing vessel 8 by a connecting line 7, and, intermediate these two reaction zones, there is a zone of temperature reduction or a condensing zone in which the stream is reduced in temperature by passing through any suitable heat exchange equipment, indicated at 9, the drop in temperature being preferably sufficient to condense out at least the heaviest components of the stream, which are withdrawn by line 10 to a suitable storage tank 11. The remainder or vapor phase portion of the stream passes at reaction temperature into vessel 8, where it is subjected to a desulphurizing or other purifying operation in contact with a desulphurizing contact material in the temperature range of 600° to 775° F. The purified material passes from vessel 8 by line 12, which connects with a refining vessel 13, the stream of purified material, however, being reduced in temperature by its passage through suitable heat exchange equipment indicated at 14, the drop in temperature of the stream being sufficient to condense out at least the then heavier or higher boiling material components of the stream which are withdrawn as desulphurized or purified oil, e. g. a gas oil by line 15 for storage in tank 16. The remainder or vapor phase portion of the stream enters vessel 13 at reaction temperature, where it is subjected to a refining and chemical stabilizing and polymerizing reaction, preferably in the presence of solid adsorptive contact material, the reaction being effected in the range of 430° to 620° F. The stream of refined material issuing from reaction chamber 13 passes, by line 17, into a fractionat-

ing tower 18, wherein end point gasoline vapors, fixed gas, and extraneous gaseous material may be taken overhead by line 19, while the heavier or higher boiling hydrocarbons, e. g. gas oil are condensed and withdrawn from the bottom of the tower by line 20 for storage in tank 21. Lighter condensed hydrocarbons may be withdrawn from the tower in a side stream by line 20a for storage in tank 21a. The overhead stream in line 19 is sent through a condenser 22 and thence, by line 23, through a separator 24, from which clean gas may be withdrawn through an upper outlet 25, water by a lower outlet 26, and refined and stabilized end point gasoline by an intermediate outlet line 27 leading to storage tank 28. The operation of tower 18 may be regulated in a conventional manner by recirculating therein condensed gasoline from separator 24 or tank 28 through suitable connections (not shown).

It is to be understood that the present invention contemplates the multistage treating operation on the charging stock substantially without heat input other than that furnished by heater or still 4. The temperature of the continuous stream of material undergoing treatment, after leaving the first or converting zone, is reduced, and the composition of the stream is modified before each of the subsequent treating steps. Removal of heat from the stream may be effected by any suitable means and by any known or desired type and arrangement of equipment. The heat thus removed may be utilized to preheat the charge, and this is indicated in the accompanying flow chart, wherein the fresh feed is shown as passing by line 29 through heat exchange means 14, thence by line 30 through heat exchange means 9, and thence into line 2 leading to still 4.

While the conversion or transformation effected in the first zone may be either thermal or catalytic, it is, by preference, catalytic, as indicated also in the aforesaid Houdry application. In fact, it is preferred, but not essential, that a contact treatment take place in each of reaction chambers 6, 8, and 13. The catalytic or contact masses may be composed of any material capable of effecting the desired reactions within the specified temperature ranges. The masses, however, are preferably in the form of lumps, fragments or molded pieces, so as to be capable of regeneration in situ. Two or more reaction chambers are intended to be utilized in each zone, in order that the process may operate continuously with the converters in each zone alternately on stream and in regeneration. Any metals or metallic compounds having the desired selective or adsorptive activity may be used for the various masses, and, if desired, these metals or metallic compounds may be incorporated, in finely divided form, into or upon porous carriers which are themselves either catalytically active or inert. Suitable carriers include those formed of china clay, pumice, fuller's earth, diatomaceous earth, and like clayey materials. A desirable carrier of this general type is disclosed in U. S. Patent No. 1,818,403, issued to A. Joseph on August 11, 1931. An inert or relatively inert carrier is preferably used in vessel 8 for the desulphurizing or purifying reaction, the bodies of porous earthenware or other support containing or carrying upon and within the same some metal or metallic compound having an affinity for mineral or other combined sulphur, such as nickel, cobalt, or copper. One method of impregnation is by soaking the support in the nitrate or other salt of the metal, and then converting the nitrate or other salt to an oxide, as by heating. For the catalytic masses in vessels 6 and 13, active or activated clayey materials, with or without the addition of other adsorptive materials such as metals or metallic compounds, may be utilized. Such active basic material may comprise natural or artificial blends of silica and alumina produced in various ways, one way being by suitable acid or other chemical treatment of naturally occurring clays or blends of clays. The contact mass for the first or conversion zone may comprise molded pieces of activated hydrosilicate of alumina of suitably controlled silica to alumina ratio. The contact mass for the last or refining and stabilizing zone may comprise the same or similar material with 10% or less of nickel, copper or cobalt in metallic or oxide form. Catalysts of this general type are disclosed in the copending application of E. J. Houdry, Serial No. 600,581, filed March 23, 1932 which issued on May 4, 1937 as Patent No. 2,078,945.

The operating conditions will be selected to suit the charging material and the type of conversion desired in the first zone. For a straight-through catalytic or contact operation in all zones, with a charging material comprising a deep gas oil cut with a portion of the bottoms from crude oil, a good operation consists in heating the charge in still 4 to 830° F. or slightly thereabove, conducting the catalytic transforming operation in converter 6 at 825° to 850° F., and reducing the temperature of the stream in heat exchange equipment 9 to remove a certain amount of the heavier material, so that the stream enters the desulphurizing zone in the range of 650° to 700° F., with the contact operation taking place at about 675° F. The stream issuing from the desulphurizing zone is reduced in heat exchanger 14 to about 450° to 500° F., and the refining and chemical stabilizing and polymerizing operation is conducted in converter 13 in the range of 430° to 500° F., or at about 475° F. It is to be understood, however, that the temperatures may be adjusted within the specified ranges as desired or required to suit the charging material or the particular finished products to be produced, and that the process may be operated at subatmospheric, atmospheric, or superatmospheric pressure. By operating under pressure, removal of condensate at heat exchangers 9 and 14 is facilitated.

Because of the wide variance in the composition of different hydrocarbon feed stocks, definite feed rates cannot be given. However, where a contact material or catalyst is used in each of vessels 6, 8 and 13, in general the rates of feed on the conversion catalyst in vessel 6 may vary, for example, from 10 to 30 liters of charge per hour per 20 liters of catalyst (i. e. 10/20 to 30/20). Much higher rates can normally be used in the refining catalyst in vessel 13, as, for example, 20/20 to 200/20 and as high or still higher rates may often be employed in the desulphurizing contact mass. An illustrative operation for gasoline production involves a rate of 16/20 in the conversion chamber 6, 100/20 in the desulphurizing chamber 8, and 60/20 in the refining chamber 13.

From the above, it is apparent that the present invention involves an operation in which material to be transformed is sent in a continuous stream through a series of reaction zones, with the removal of heat and/or a portion of the stream after each zone, the material being removed because it is already a finished product or because it is undesirable to subject it to treatment

in the succeeding zones. Thus, for example, in the operation set forth specifically in the second preceding paragraph, the material drawn off into storage tank 11 will be very heavy hydrocarbons not transformed in the preceding cracking or converting stage and which are suitable for recharge in a subsequent run, the material withdrawn into tank 16 will be purified or desulphurized oil in the gas oil boiling range suitable for use as finished product as Diesel oil or domestic fuel oil, the materials taken out of fractionating tower 18 will also be finished products comprising a still more completely refined oil in the gas oil range in tank 21 and refined kerosene and heavy naphthas in tank 21*a*, and, as final products after condensation from separator 24, there are obtained refined and stabilized end point gasoline and highly purified clean hydrocarbon gases.

I claim as my invention:

1. In the production of refined lower boiling hydrocarbons including those within the light motor fuel or gasoline boiling range in a continuous straight-through operation from a composite hydrocarbon charge boiling to substantial extent above the gasoline boiling range, the steps of process which comprise heating and passing the hydrocarbon charge through a confined conversion zone containing an adsorptive catalytic material maintained at a temperature substantially within the range of 760° to 900° F., continuously removing fluid products from said conversion zone and passing them through a condensing zone, continuously separating to substantial extent higher boiling components which condense therein at temperatures above approximately 650° F. from the remaining fluid products of conversion, passing said remaining fluid products in the absence of said higher boiling components separated therefrom through a confined desulphurizing zone containing a metalliferous contact material capable of reacting with sulphurous components of the said vaporous products by undergoing chemical change to a sulphurous form, said contact material being maintained at a temperature within the range of 600° to 775° F., continuously withdrawing fluid products from said desulphurizing zone and passing them through a condensing zone, separating to a substantial extent liquid components which condense in the zone last-mentioned at temperatures above approximately 450° F. From the remaining lower boiling components of the fluid products from the desulphurizing zone, passing said lower boiling vaporous components in the absence of said liquid components through a confined chemical stabilizing and refining zone containing an adsorptive catalytic material comprising essentially an active silicious material having incorporated therewith a relatively small proportion of a metalliferous material capable of reacting with inorganic sulphur in the vapors to form a sulphur compound of the metal, the last-mentioned catalytic material being maintained at a temperature substantially within the range of 430° to 620° F., withdrawing fluid products from said refining zone, and fractionating the last-mentioned products to separate a light motor fuel fraction of high quality from remaining hydrocarbons.

2. In the production of refined lower boiling hydrocarbons including those within the light motor fuel or gasoline boiling range in a continuous straight-through operation from a composite hydrocarbon charge boiling to substantial extent above the gasoline boiling range, the steps of process which comprise heating and passing the hydrocarbon charge through a confined conversion zone under conditions so as to effect a cracking or production of lower boiling hydrocarbons from the higher boiling hydrocarbons, said conversion zone being maintained within the temperature range of 760° to 1100° F., continuously removing fluid products from said conversion zone and passing them through a condensing zone, continuously separating at least a substantial proportion of the higher boiling components thereof which condense therein at temperatures above those of the order of 650° to 700° F. from the remaining vaporous products of conversion, passing said remaining vaporous products in the absence of said higher boiling components separated therefrom through a confined desulphurizing zone containing a metalliferous contact material capable of reacting with sulphurous components of the said vaporous products by undergoing chemical change to a sulphurous form, said contact material being maintained at a temperature approximately within the range of 600° to 775° F., continuously withdrawing fluid products from said desulphurizing zone and passing them through a condensing zone, separating to a substantial extent liquid components which condense in the zone last-mentioned at temperatures above those of the order of 450° to 500° F. from the remaining lower boiling components of the fluid products from the desulphurizing zone, passing said lower boiling vaporous components in the substantial absence of said liquid components through a confined chemical stabilizing and refining zone containing an adsorptive catalytic material comprising essentially an active blend of silica and alumina, the last-mentioned catalytic material being maintained at a temperature substantially within the range of 430° to 620° F., withdrawing fluid products from said refining zone, and fractionating the last-mentioned products to separate a gasoline fraction of high quality from remaining hydrocarbons.

ARTHUR E. PEW, JR.