

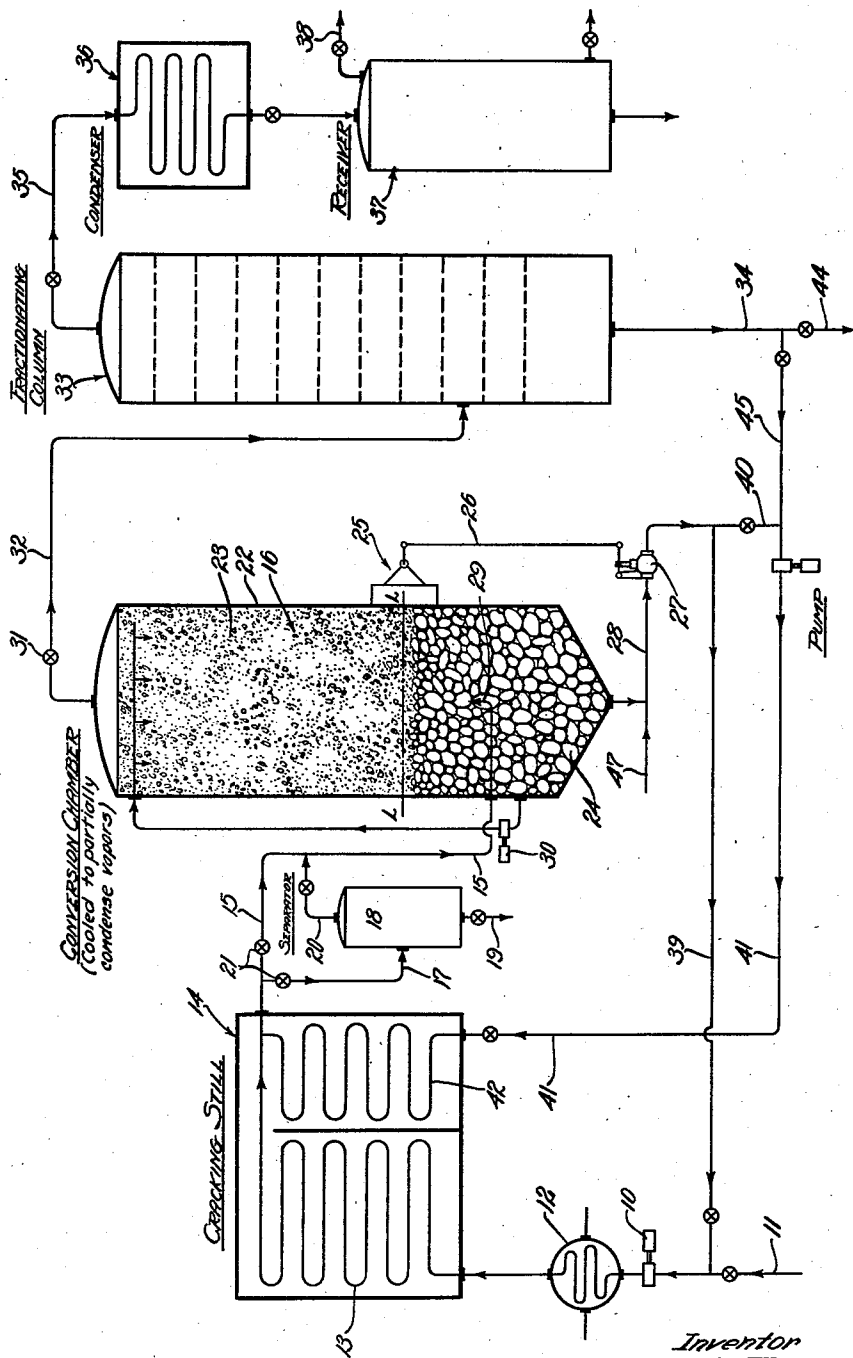
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W. T. HANCOCK

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METHOD OF REFINING HYDROCARBONS BY CRACKING AND CATALYSIS

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Inventor
WILLIAM T. HANCOCK

Alfred White
Attorney

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METHOD OF REFINING HYDROCARBONS BY
CRACKING AND CATALYSIS

William T. Hancock, Long Beach, Calif.

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11 Claims. (Cl. 196—52)

This invention has to do with the refining of petroleum hydrocarbons, and relates particularly to an improved method whereby the hydrocarbons may be subjected to conversion in the presence of catalytic material, under conditions conducive to maximum effectiveness of the catalyst and most extensive conversion of the hydrocarbons.

The present method may be characterized as one whereby the hydrocarbons first are heated to a temperature at which the desired conversion will take place in the presence of a particular catalyst or combination of catalysts, and vaporized hydrocarbons then delivered to a conversion zone wherein mixed liquid and vapor fractions of the hydrocarbons are maintained in intimate contact within a body of material containing the catalyst. The temperature to which the hydrocarbons are heated for treatment in the conversion zone will depend upon, and become subject to variation in accordance with, the particular catalyst used and the nature of the conversion to be accomplished. Similarly, the pressures to be employed may vary for this same reason. I have found this method particularly effective for the conversion of the charging stock to high percentage yields of high-octane motor fuels, by subjecting the charging stock to an abnormally high degree of dissociation or cracking to produce a high potential yield of compounds capable of conversion to condensable fractions, and polymerizing such compounds to produce motor fuel characterized by its high octane values and low sulphur and gum content. According to this method, therefore, the charging stock may first be heated to cracking temperature before introducing the vapors to the conversion zone, or to a temperature at which cracking will occur in the conversion zone in the presence of the catalyst.

The invention is concerned primarily with an improved method for maintaining mixed liquid and vapor fractions of the hydrocarbons in contact with the catalytic material, independently of the nature or composition of the catalyst, excepting however that the class of catalysts contemplated and claimed herein are those that may be termed a non-adsorptive type, or combination of non-adsorptive and adsorptive catalysts, since similar processes directed to the use of adsorptive materials are claimed in my copending application Serial Number 306,345, filed November 27, 1939, on Cracking of light petroleum stocks, and another application Serial Number 306,346 filed November 27, 1939, on System for

cracking and polymerizing hydrocarbons. Accordingly, it will be understood that the invention broadly contemplates the use of any suitable catalyst of the type claimed, since the conditions under which the hydrocarbons undergoing conversion are maintained in contact therewith, increase and maintain the efficiency of all such catalysts as well as provide a most favorable relationship between them and the mixed phase hydrocarbons affected thereby. Certain catalysts, or combinations of catalysts, may however be regarded as preferred.

As illustrative, the catalyst employed may be selected to accomplish any or a combination of the following types of reactions or effects, all of which are included under the general term "conversion"; dehydrogenation, dissociation or cracking, isomerization, cyclization, alkylation and polymerization. To accomplish dehydrogenation, catalysts such as chromic oxide, nickel mixed with alumina (Al_2O_3), alumina alone, chromic oxide-phosphoric acid mixture, or phosphoric acid on a carrier, may be employed as the catalyst. The principal cracking catalyst is aluminum chloride, although some value is found in certain metals such as aluminum, magnesium, nickel, cobalt, copper and iron, and the metal oxides. Reactions of isomerization may be catalyzed by chromic acid, aluminum, boron phosphate, and nickel mixed with alumina. Catalysts for cyclization to change chain hydrocarbons into ring hydrocarbons, include chromic oxide, alumina at high temperatures, and metals such as tin and lead. At present, the principal alkylation catalysts appear to be sulphuric acid, aluminum chloride and phosphoric acid.

For purposes of distinction and general designation, the particular catalysts mentioned above may be termed non-adsorptive catalysts to distinguish them from the usual adsorptive materials such as fuller's earth, bauxite, Death Valley and Muroc clays, hydrated aluminum silicate, and activated clays in general. Such adsorptive materials are known and employed generally as polymerization catalysts (although other known polymerizing catalysts such as the metal chlorides, and oxides of chromium, molybdenum, vanadium and titanium, may be used). Since the invention contemplates the use of a combination of catalysts to obtain a single catalytic effect, or combination of catalytic effects, as for example to induce both cracking and polymerization in the same conversion zone, I may employ any suitable combination of non-adsorptive and adsorptive catalysts, as designated above.

Frequently, adsorptive clays are used as a base or carrier for other catalysts. For example, adsorbents of the fuller's earth type may be impregnated with other catalysts such as phosphoric or sulphuric acids, active salts such as aluminum chloride, ferric chloride and zinc chloride, oxides of chromium, nickel and cobalt, and metals including chromium, iron, nickel, copper and aluminum.

Among the various possible combinations of catalysts that may be employed, the invention contemplates particularly the use of a suitable catalyst to promote cracking within the conversion zone to produce a high yield of low molecular weight compounds reformable into the final product, together with a polymerizing catalyst adapted to convert such lower molecular weight products of dissociation, into higher boiling hydrocarbons within the motor fuel range. For this purpose, the catalytic material may comprise the combination of a cracking catalyst such as aluminum chloride, and an adsorptive clay, the aluminum chloride acting to promote dissociation, and the clay to polymerize the products of dissociation to recoverable gasoline fractions. The use of aluminum chloride as the cracking catalyst may also serve to considerably reduce the conversion zone temperature required for cracking.

The physical steps of the process involve first heating a suitable charging stock to cracking temperature, or to a temperature sufficiently high that the desired conversion will take place in the presence of the catalyst. After passage through the heating zone, wherein the charging stock may be heated to the required initial temperature either in liquid or vapor phase, the hydrocarbons may be discharged directly into the conversion zone, or first through a separating chamber for the removal of any unvaporized residue. Preferably, the conversion zone comprises a vertically extending chamber containing a stationary foraminant body of the catalytic material, into which the vapors are introduced so as to flow upwardly within and in intimate contact with the material. The vapors in the conversion zone are subjected to partial condensation which, within the broad contemplation of the invention, may be accomplished by any suitable method, and mixed liquid and vapor fractions of the hydrocarbons are maintained in a state of continuous admixture and washing agitation within the body of catalytic material.

The principal advantages of the present method result from the conditions under which the mixed hydrocarbon phases are maintained within the conversion zone. By virtue of their intimate contact and constant washing agitation within the catalytic material, the liquid and vapor hydrocarbons approach an equilibrium state favoring the conversion reactions and at the same time insuring thorough and intimate contact with the catalyst. Simultaneously, the catalyst is conditioned for maximum and continued high effectiveness by reason of the fact that residual reaction products, such as high boiling polymers and other bodies of a contaminating character, are constantly being washed out of the clay and removed from the conversion zone with the condensate. So effective are these conditions that it is found possible to obtain abnormally high yields of recoverable gasoline distillate, and at the same time maintain the catalytic material in an efficient state over long periods of time.

The invention will be understood more fully

and to better advantage from the following detailed description of a typical refining system in which hydrocarbons are subjected to heating and conversion in accordance with the general method outlined above. Reference is made to the accompanying drawing illustrating the system diagrammatically and in flow sheet form.

The charging stock to be subjected to heating and conversion may be of any suitable type, although I prefer generally to employ stocks within the Kerosene distillate-gas oil range. The charging stock may be discharged by pump 10 from line 11 through a suitable preheater 12 to coil 13 in a cracking still 14, wherein the hydrocarbons are heated to a suitable conversion temperature ranging generally between 800 to 1100° F., under suitable pressure, for example 150 to 400 pounds per sq. in. Lower temperatures may be employed where a particular cracking catalyst in the conversion chamber is capable of effecting the desired degree of cracking at relatively low temperatures. Where the charging stock consists of lower boiling hydrocarbons, as for example within the kerosene distillate range, the heated hydrocarbons may be discharged from the cracking still directly through line 15 to the conversion chamber 16. Ordinarily, however, I prefer to remove all unvaporized residue before passage of the hydrocarbons into the conversion chamber, as by first passing the heated or cracked hydrocarbons through line 17 to a separator 18, from which the unvaporized residue is withdrawn through line 19 and the separated vapors discharged through line 20 to the conversion chamber. If desired, the pressure on the heated hydrocarbons may be reduced in advance of the conversion chamber by regulation of valves 21.

The conversion chamber 16 comprises a vertically extending shell 22 containing a foraminant body 23 of the previously described catalytic material which may be placed above a bed of relatively coarse stone 24 within the bottom portion of the chamber. Suitable provision may be made for maintaining a predetermined minimum level L—L' of condensate within the conversion chamber, as by the conventionally illustrated float control 25 connected by linkage 26 with a valve 27 in the condensate outlet line 28 leading from the bottom of the conversion chamber. The vapors are discharged through line 15 into the conversion chamber preferably at a location 29 below what would be the static level L—L' of condensate within the chamber. Consequently, the vapor stream rising within the conversion chamber constantly displaces the condensate upwardly from the accumulated body within the lower portion of the chamber, with the result that mixed liquid and vapor hydrocarbon fractions are maintained in a state of washing agitation within a large portion of the body of catalyst. Simultaneously, the hydrocarbons are undergoing conversion, i. e. both dissociation and polymerization, with resultant formation of heavy residual bodies. These bodies however are constantly being washed out of the catalytic material by the agitated condensate, and are removed from the conversion zone through the condensate outlet line 28.

The conversion chamber 16 may be maintained at a temperature at which the vapors will undergo partial condensation within the catalytic material, and particularly is this desirable where partial condensation may not result from other conditions, such as delivery of the vapors directly into a body of condensate within the lower portion of the chamber. Adequate cooling of cham-

ber 16 to partially condense the vapors may result from normal heat losses to the atmosphere. If desired, the vapors may be subjected to reflux condensation, as by a stream of oil circulated by a pump 30 from the bottom to the upper interior of the chamber. As previously stated, the temperatures maintained in the conversion chamber ordinarily will be sufficiently high to cause a considerable degree of cracking to occur in the presence of the catalyst, and in general this temperature may range from around 800 to 1100° F., although it is preferred to maintain the vapor outlet temperature not substantially above 900° F., in order to avoid excessive fixed gas losses. It is found that within the temperature range indicated, it is possible to effect simultaneously both substantial cracking and association or polymerization of the cracked products i. e., to produce by the effect of the cracking catalyst, further or more complete dissociation of the vapors heated to cracking temperature in the cracking still, and to polymerize the resulting reformable hydrocarbons by the effect of the polymerizing catalysts. Valve 31 in the vapor outlet line 32 may be set to maintain any desired pressure on the hydrocarbons within the conversion chamber.

The vapors leaving the conversion chamber through line 32 may be fractionated or subjected to further treatment by any suitable method. As illustrative, the vapors are shown to be delivered to fractionating column 33 for removal of higher boiling fractions above the gasoline range, which are condensed and withdrawn through line 34. The vapors then are taken through line 35 for final condensation in condenser 36 and the product gasoline is collected in receiver 37. Fixed gases and uncondensed vapors are discharged through the valved line 38. Where the hydrocarbons have been subjected to polymerization within the conversion chamber by intimate contact with adsorptive clays of the character described, the product gasoline is found to be relatively low in sulphur and possessed of water white color stability by reason of the effective removal of polymers and gum forming bodies.

Preferably the condensate stream and its contained polymers removed from the conversion chamber through line 28, are recirculated for further cracking. The condensate may be returned through line 39 and combined with the charging stock in line 11 for cracking in coil 13, or the condensate may be recirculated through lines 40 and 41 to an independent heating or cracking coil 42 connecting at its outlet with line 15. Instead of introducing the charging stock initially through line 11, it may be fed to the system through line 47 and combined with the recirculated condensate. By thus recirculating the condensate for further cracking, impurities such as sulphur containing compounds and polymers removed from the conversion chamber, are re-cracked, thus permitting recovery in the system of desirable condensable constituents of the impurities and providing for elimination of sulphur compounds either as residue from the separator 18, or in the form of fixed gases through the final outlet gas line 38. As illustrated, condensate withdrawn from the fractionating column through line 34 may be taken to storage through line 44, or recirculated through lines 45 and 41 to the cracking still.

I claim:

1. The method of refining petroleum hydrocarbons that includes, passing a stream of the

hydrocarbons through a cracking zone wherein the hydrocarbons are heated to cracking temperature, passing vapors from said zone into a conversion zone containing a foraminant body of material comprising a non-adsorptive catalyst, and thereby subjecting the hydrocarbons to conversion within said material, introducing the vapors into a body of condensate maintained within the lower interior of said conversion zone and thereby subjecting mixed liquid and vapor fractions of the hydrocarbons to intimate contact within said material by upward displacement of the condensate therein, so that the liquid fractions constantly wash the material in the presence of hydrocarbons undergoing conversion and constantly remove residual bodies resulting from the conversion, removing the vapors from said conversion zone, and separately removing the condensate and its contained residual bodies.

2. The method of refining petroleum hydrocarbons that includes, passing a stream of the hydrocarbons through a cracking zone wherein the hydrocarbons are heated to cracking temperature, passing vapors from said zone into a conversion zone containing a foraminant body of material comprising a non-adsorptive catalyst, and thereby subjecting the hydrocarbons to conversion within said material, introducing the vapors into a body of condensate maintained within the lower interior of said conversion zone and thereby subjecting mixed liquid and vapor fractions of the hydrocarbons to intimate contact within said material by upward displacement of the condensate therein, so that the liquid fractions constantly wash the material in the presence of hydrocarbons undergoing conversion and constantly remove residual bodies resulting from the conversion, maintaining the hydrocarbons in said conversion zone at a temperature at which cracking occurs in the presence of said catalyst, removing the vapors from said conversion zone, and separately removing the condensate and its contained residual bodies.

3. The method of refining petroleum hydrocarbons that includes, passing a stream of the hydrocarbons through a cracking zone wherein the hydrocarbons are heated to cracking temperature, passing vapors from said zone into a conversion zone containing a foraminant body of material comprising a combination of different catalysts one adapted to induce cracking and the other polymerization of the hydrocarbons, and thereby subjecting the hydrocarbons to cracking and polymerization within said material, introducing the vapors into a body of condensate maintained within the lower interior of said conversion zone and thereby subjecting mixed liquid and vapor fractions of the hydrocarbons to intimate contact within said material by upward displacement of the condensate therein, so that the liquid fractions constantly wash the material in the presence of hydrocarbons undergoing cracking and polymerization and constantly remove polymers being formed, removing the vapors from said conversion zone, and separately removing the condensate and its contained polymers.

4. The method of refining petroleum hydrocarbons that includes, passing a stream of the hydrocarbons through a cracking zone wherein the hydrocarbons are heated to cracking temperature, passing vapors from said zone into a conversion zone containing a foraminant body of material comprising a combination of a metallic cracking catalyst and an absorptive polymer-

izing catalyst together adapted to induce both cracking and polymerization of the hydrocarbons, and thereby subjecting the hydrocarbons to cracking and polymerization within said material, introducing the vapors into a body of condensate maintained within the lower interior of said conversion zone and thereby subjecting mixed liquid and vapor fractions of the hydrocarbons to intimate contact within said material by upward displacement of the condensate therein, so that the liquid fractions constantly wash the material in the presence of hydrocarbons undergoing cracking and polymerization and constantly remove polymers being formed, removing the vapors from said conversion zone, and separately removing the condensate and its contained polymers.

5. The method of refining petroleum hydrocarbons that includes, passing a stream of the hydrocarbons through a cracking zone wherein the hydrocarbons are heated to cracking temperature, passing vapors from said zone into a conversion zone containing a foraminant body of material comprising a combination of aluminum chloride and adsorptive clay catalysts together adapted to induce both cracking and polymerization within said material, introducing the vapors into a body of condensate maintained within the lower interior of said conversion zone and thereby subjecting mixed liquid and vapor fractions of the hydrocarbons to intimate contact within said material by upward displacement of the condensate therein, so that the liquid fractions constantly wash the material in the presence of hydrocarbons undergoing cracking and polymerization and constantly remove polymers being formed, removing the vapors from said conversion zone, and separately removing the condensate and its contained polymers.

6. The method of refining petroleum hydrocarbons that includes, passing a stream of the hydrocarbons through a cracking zone wherein the hydrocarbons are heated to cracking temperature, then removing unvaporized residuum from the hydrocarbons and passing the vapors into a conversion zone containing a foraminant body of material comprising a non-adsorptive catalyst, and thereby subjecting the hydrocarbons to conversion within said material, introducing the vapors into a body of condensate maintained within the lower interior of said conversion zone and thereby subjecting mixed liquid and vapor fractions of the hydrocarbons to intimate contact within said material by upward displacement of the condensate therein, so that the liquid fractions constantly wash the material in the presence of hydrocarbons undergoing conversion and constantly remove residual bodies resulting from the conversion, removing the vapors from said conversion zone, and separately removing the condensate and its contained residual bodies.

7. The method of refining petroleum hydrocarbons that includes, passing a stream of the hydrocarbons through a cracking zone wherein the hydrocarbons are heated to cracking temperature, then removing unvaporized residuum from the hydrocarbons and passing the vapors into a conversion zone containing a foraminant body of material comprising a combination of different catalysts one adapted to induce cracking and the other polymerization of the hydrocarbons, and thereby subjecting the hydrocarbons to cracking and polymerization within said material, introducing the vapors into a body of condensate

maintained within the lower interior of said conversion zone and thereby subjecting mixed liquid and vapor fractions of the hydrocarbons to intimate contact within said material by upward displacement of the condensate therein, so that the liquid fractions constantly wash the material in the presence of hydrocarbons undergoing cracking and polymerization and constantly remove polymers being formed, removing the vapors from said conversion zone, and separately removing the condensate and its contained polymers.

8. The method of refining petroleum hydrocarbons that includes, passing a stream of the hydrocarbons through a heating zone wherein the hydrocarbons are heated to a temperature suitable for catalytic cracking and polymerization of the hydrocarbons, passing vapors from said zone upwardly within a conversion zone containing a foraminant stationary body of material comprising a non-adsorptive cracking catalyst and an adsorptive polymerizing catalyst, and thereby subjecting the hydrocarbons to both cracking and polymerization within said material, partially condensing the vapors and subjecting a considerably large quantity of the condensate to intimate contact with vapor fractions within said material so that the condensate is upwardly displaced therein by the vapors and is thereby caused to repeatedly contact and be acted upon by said material, said condensate also serving to constantly wash and remove from the material residual bodies resulting from the cracking and polymerization, withdrawing the vapors from said conversion zone, and separately removing the condensate and its contained residual bodies.

9. The method of refining petroleum hydrocarbons that includes, passing a stream of the hydrocarbons through a heating zone wherein the hydrocarbons are heated to a temperature suitable for catalytic cracking and polymerization of the hydrocarbons, passing vapors from said zone into a conversion zone containing a foraminant stationary body of material comprising a combination of different catalysts, one adapted to induce cracking and the other polymerization of the hydrocarbons, and thereby subjecting the hydrocarbons to both cracking and polymerization within said material, partially condensing the vapors and subjecting a considerably large quantity of the condensate to intimate contact with vapor fractions within said material so that the condensate is upwardly displaced therein by the vapors and is thereby caused to repeatedly contact and be acted upon by said material, said condensate also serving to constantly wash and remove from the material residual bodies resulting from the cracking and polymerization, withdrawing the vapors from said conversion zone, and separately removing the condensate and its contained polymers.

10. The method of refining petroleum hydrocarbons that includes, passing a stream of the hydrocarbons through a heating zone wherein the hydrocarbons are heated to a temperature suitable for subsequent catalytic cracking and polymerization, removing unvaporized residuum from the hydrocarbons, passing the vapors into a conversion zone containing a foraminant stationary body of material comprising a combination of different catalysts, one adapted to induce cracking and the other polymerization of the hydrocarbons, and thereby subjecting the hydrocarbons to cracking and polymerization within said material, partially condensing the vapors and subjecting a considerably large quantity of the

condensate to intimate contact with vapor fractions within said material so that the condensate is upwardly displaced therein by the vapors and is thereby caused to repeatedly contact and be acted upon by said material, said condensate also serving to constantly wash and remove from the material residual bodies resulting from the cracking and polymerization, withdrawing the vapors from said conversion zone, and separately removing the condensate and its contained polymers. 10

11. The method of refining petroleum hydrocarbons that includes, passing a stream of the hydrocarbons through a heating zone wherein the hydrocarbons are heated to a temperature suitable for catalytic cracking and polymerization of the hydrocarbons, passing vapors from said zone upwardly within a conversion zone containing a foraminated stationary body of material 15

comprising aluminum chloride supported on a solid adsorptive carrier, and thereby subjecting the hydrocarbons to both cracking and polymerization within said material, partially condensing the vapors and subjecting a considerably large quantity of the condensate to intimate contact with vapor fractions within said material so that the condensate is upwardly displaced therein by the vapors and is thereby caused to repeatedly contact and be acted upon by said material, said condensate also serving to constantly wash and remove from the material residual bodies resulting from the cracking and polymerization, withdrawing the vapors from said conversion zone, and separately removing the condensate and its contained residual bodies.

WILLIAM T. HANCOCK.