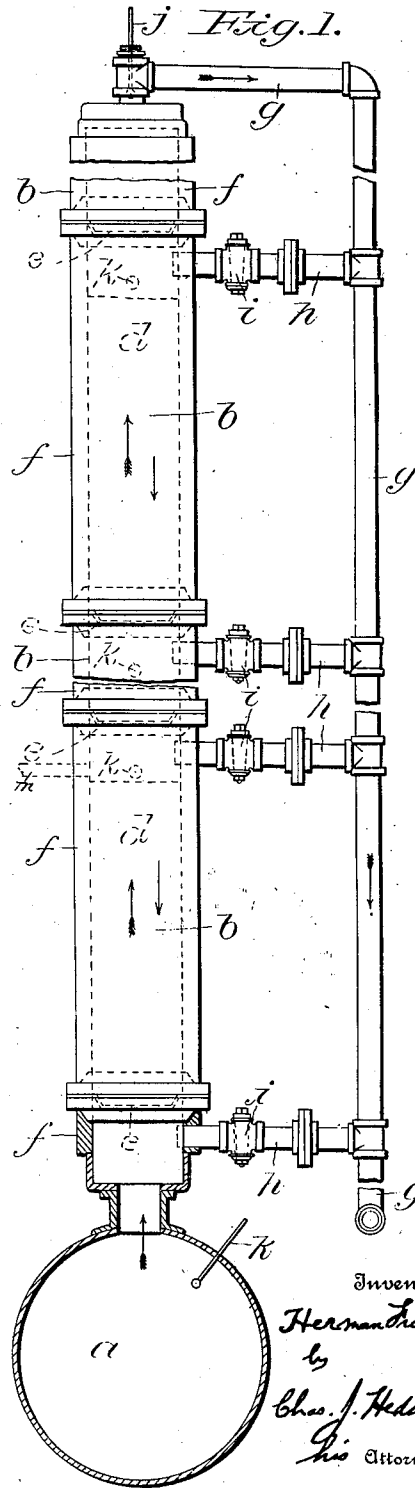
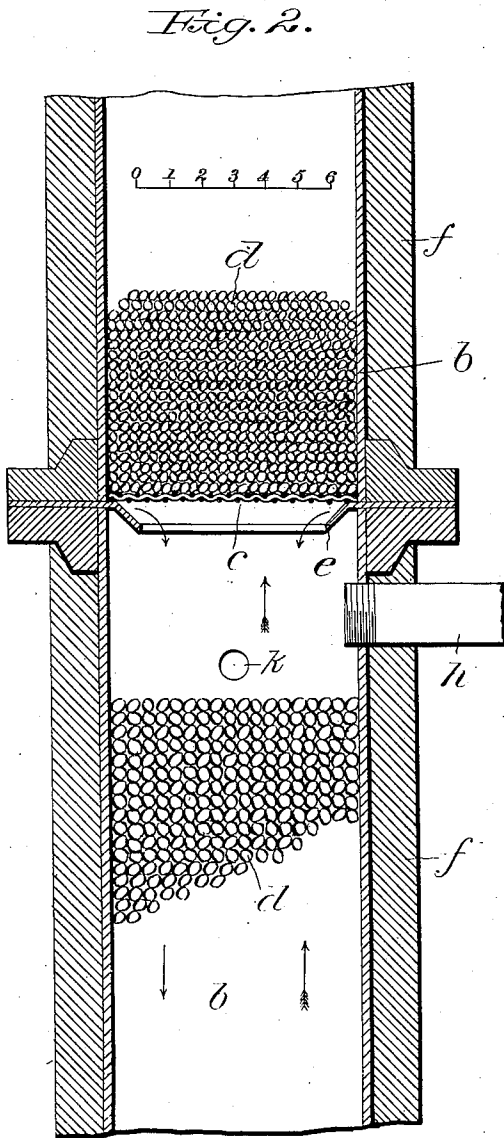


H. FRASCH.
OBTAINING PETROLEUM PRODUCTS.
APPLICATION FILED JUNE 30, 1902.

968,760.

Patented Aug. 30, 1910.



Witnesses

E. H. Walker
M. C. Masie

Inventor
Herman Frasch
by
Chas. J. Hedrick
his Attorney

UNITED STATES PATENT OFFICE.

HERMAN FRASCH, OF NEW YORK, N. Y., ASSIGNOR TO STANDARD OIL COMPANY, OF BAYONNE, NEW JERSEY, A CORPORATION OF NEW JERSEY.

OBTAINING PETROLEUM PRODUCTS.

968,760.

Specification of Letters Patent. Patented Aug. 30, 1910.

Application filed June 30, 1902. Serial No. 113,768.

To all whom it may concern:

Be it known that I, HERMAN FRASCH, a citizen of the United States, residing at New York, Manhattan borough, in the county of New York and State of New York, have
5 invented certain new and useful Improvements in Obtaining Petroleum Products; and I do hereby declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled
10 in the art to which it appertains to make and use the same.

This invention relates more particularly to the obtainment of useful products from a certain kind of petroleum which is characterized as hereinafter set forth and is herein
15 termed Coalinga oil or Coalinga petroleum for convenience of reference. It is found in the neighborhood of the town of Coalinga, in the county of Fresno and State of California; but the expression is intended to include
20 crude petroleum of the same or substantially similar character wherever found and also distillates of like character derived from such crude oil. Ordinarily on distilling petroleum and testing the gravity of successive
25 samples of the distillate as it runs from the tail pipe of the condenser, it will be found that the distillate becomes gradually denser (heavier in gravity) and less volatile (of higher average boiling point) as the
30 temperature in the still rises. In other words, the boiling points and densities of the hydrocarbons of petroleum usually increase together; and the greater the density of a
35 hydrocarbon from a given crude petroleum, the higher boiling point may it ordinarily be expected to have. I have discovered, to wit, in the said Coalinga petroleum an extraordinary exception to this general rule;
40 that is to say, I have discovered in Coalinga petroleum an oil which on distillation may at intervals exhibit retrogressions of density in the distillate, while the volatility of the
45 latter continues to decrease. Coalinga oil, therefore, contains hydrocarbons which are specifically heavier than others of higher boiling point in admixture therewith. Further, petroleum ordinarily consists, as is
50 known, of hydrocarbons of the paraffin series (C_nH_{2n+2}) with usually more or less olefines (C_nH_{2n}). This is the case with crude oil from the Pennsylvania and Lima (Ohio) fields, as well as from those of Ontario,
55 Canada. Russian oil consists mainly, as is

known, of isomers of the olefines (C_nH_{2n}). Traces of aromatic hydrocarbons of the benzene (C_nH_{2n-6}) and naphthalene (C_nH_{2n-12}) series are said to have been found in petroleum; but, so far as I am
60 aware, they have never (prior to the present invention) been known to occur naturally in petroleum from any field in sufficient proportion to be utilized industrially. I have discovered that the apparent retrogression in density of the distillate of Coalinga oil (such retrogression consisting in
65 the fact that the distillate becomes lighter instead of heavier with increase in its average boiling point) is due to the presence in such distillate in a notable and industrially utilizable proportion of hydrocarbons of the benzene and naphthalene series. On the coming over of such hydrocarbons in sufficient proportion in the distillate the density
70 of the latter increases so much more than would have been the case but for their presence that as they disappear or diminish in amount the density of the distillate diminishes, notwithstanding its continued rise in
75 boiling point. After a time when the amount coming over has diminished sufficiently, the distillate again increases in density as well as in average boiling point, and so continues until another retrogression of density occurs.
80

My present invention, which comprises new products as well as new processes, is based in part at least on these discoveries. It must not be understood, however, that the
85 nature, or even the exceptional behavior, of Coalinga petroleum necessarily exhibits itself in any and every form of distillation. On the contrary, with the ordinary petroleum distillation, in which a charge of oil is
90 evaporated in a box-like chamber and the vapors pass to a water cooled condenser immediately on their exit from said chamber, the retrogressions of density of distillate are inconsiderable and by no means such (if noticeable at all) as to indicate either the substantial amount or the special nature of the
95 hydrocarbons therein which are denser than those of higher boiling point. I have, moreover, encountered practically the same lack of substantial retrogressions of density of distillate after subjecting the vapors on their way to a condenser to such a rectification as will be obtained by their passage through
100 the rectifying columns ordinarily used for

alcohol distillation. Of these the stills of Coffey and Derosne are representative. Nor am I aware that prior to my present invention any industrial rectifying process had been devised which (if applied to Coalinga petroleum) would effect a satisfactory (if industrially useful) separation of the benzene and naphthalene hydrocarbons from those of other series in the Coalinga oil.

10 In accordance with the present invention, Coalinga petroleum, also petroleum in general which is analogous to Coalinga oil in containing sufficient hydrocarbons of the benzene and naphthalene series to exhibit a
15 retrogression of density with contemporaneous diminution of volatility of the distillate received in distilling said petroleum as herein set forth, is subjected to distillation, with such rectification of the vapors as to result at
20 intervals in retrogressions in the density of distillate, while the volatility of said distillate continues to diminish; those portions of the distillate which come over near the beginnings of the respective retrogressions are
25 collected apart from those less dense and less volatile portions which come over near the respective endings thereof; and said denser portions are utilized, in whole or in part, after the manner of hydrocarbons of the benzene and naphthalene series. For example, they are utilized (with or without further purification) for the obtainment
30 therefrom of substitution products of the benzene series by treatment with concentrated sulfuric acid, fuming sulfuric acid, sulfuric anhydrid, nitric acid, or other known or suitable reagents and of naphthalene by appropriate cooling to solidify the naphthalene, followed by separation of the
40 solidified naphthalene from the liquid hydrocarbons; or they are utilized directly for those purposes for which hydrocarbons of the benzene and naphthalene series are applied (as the mesitylene product for solvent
45 naphtha for one instance).

Those portions of the distillate which come over near the endings of said retrogressions are utilized, in whole or in part, as burning oil (kerosene). Portions unsuited
50 for any other purpose may be utilized, for example, for fuel or for the manufacture of illuminating gas.

The aforesaid rectification and collection of products can be applied in the further
55 distillation of distillate as well as in the original distillation of crude oil; and distillate to be thus further distilled can be obtained from crude oil by distillation in the ordinary way, if preferred. There may be
60 two or more successive distillations with the aforesaid rectification and collection of products in each.

It is, in fact, considered an advantage and special improvement once, or oftener, to distil again (with the aforesaid rectification

and collection of products) parallel products collected apart in a number of former distillations of crude oil or of distillate and mixed together in order to constitute the stocks for such further distillation.

70 It is also considered an advantage and special improvement, in one or more distillations with the aforesaid rectification and collection of products, to collect by themselves intermediate portions of the distillate, as
75 well as those denser and less dense, and to distil again such intermediates with the aforesaid rectification and collection of products, intermediates being again separated or not, as preferred. Intermediates separated
80 in the final (or in any prior) distillation can be returned for further distillation, say with other intermediates or with the crude oil.

Further, it is considered an advantage and special improvement to employ for the aforesaid rectification a new rectifying process
85 which will now be described and which forms part of the invention for application to petroleum and other liquids in general to which it may be applicable, as well as to Coalinga
90 or analogous petroleum in particular. This new process of rectification involves the passage of the mixed vapors given off from the body of oil in distillation upward through a tall column (say, about five feet, more or
95 less, as a minimum, or, more advantageously, about eight feet or upward) of finely divided solid material (such as gravel whereof the individual stones have diameters of between a half inch and a quarter inch, both inclusive) under subjection to such cooling influences as will allow a gradual fall of temperature to occur in the column and will
100 further, with or without the aid of a more energetic condensation at about or above the top of said column, keep the pieces of solid material effectively covered with coherent coatings of the downflowing liquid of condensation. I have discovered that if
105 the pieces of solid material are too large, it is impossible to effect a satisfactory separation; and I have further discovered that, with pieces of the dimensions given above, a satisfactory result is dependent upon a proper
110 adjustment of the cooling influences; for if the cooling is too feeble the hydrocarbons are not separated as desired, which result I attribute, in the light of my investigations, to the fact that the downflowing liquid of condensation is too meagre fully to cover
115 the solid matter; and so also, on the other hand, if the cooling should be too energetic, the hydrocarbons are not separated as desired. In this latter case I find that the cohesion of the descending liquid of condensation is so overcome by the rising vapors that said liquid is carried about by said vapors; and it is to this disturbance of the descending liquid, or perhaps the reciprocal disturbance of the rising vapors, or both, to which
120 125 130

(in the light of my investigations) I attribute the unsatisfactory result in the case of too energetic cooling.

With respect to the tallness of the column, several feet seem to be essential for industrial working; for, although a good separation can be effected in the laboratory with a column as short as eight inches (in a glass tube), a column of two feet (eight inches in diameter) scarcely brought about any retrogression of the density of the distillate in distilling crude Coalinga petroleum in a fifty-gallon still and collecting the distillate in two per cent cuts; whereas, with an eight-foot column, the density of distillate under the same conditions has diminished with the progress of the distillation by amounts equivalent to more than five degrees of Baumé's hydrometer. To give a precise illustration (of course, merely by way of example) in one run the thermometer at the top of the eight-foot column rose from 223° F. to 229° F., while a gallon of the distillate was running from the tail pipe of the condenser; and this gallon of distillate had a density of 41 2/10 degrees Baumé (specific gravity .818); whereas, the two per cent. cut (one gallon) collected while the same thermometer was rising from 241° F. to 261° F. had a density of only 50 9/10° B. (specific gravity .774). In the same run the two per cent. cut collected between the thermometer readings 282° F.-287° F. had a density of 36 8/10° B. (specific gravity .839); while that collected between 310° F. and 316° F. had a density of only 42 1/10° B. (specific gravity .813).

In rectification by a column containing finely divided solid matter, I have discovered it to be advantageous for the down-flowing liquid of condensation to be directed horizontally between overlying and underlying portions of said matter from points of lower to points of higher temperature (that is, for example, from the walls to the axis of the column); and the improvement in such rectification based upon such discovery is included in the invention, as well with a column and solid material in loose lumps or pieces of any dimensions and any cooling, as with the column and such solid material of the dimensions and cooling of the character above stated. By such horizontal direction of condensate, the volume of the latter at said points of higher temperature in each underlying portion is larger and the solid matter in such portion is consequently more uniformly covered with condensate than would be the case without such deflection of the condensate.

The distillation may be carried on intermittently; that is to say, by filling the still, and then distilling off the vapors through the rectifying column; but the invention is not restricted to an intermittent mode of

working. If a stream of the liquid to be distilled should be introduced at an intermediate part of the column during the run, so that there would be a continuous distillation, the process would likewise be within the invention, provided the conditions herein specified (or, rather, those of any one or more of my hereinafter written claims) should be fulfilled. In such continuous distillation part of the necessary rectification may occur in the distillatory portion of the column (that is, in the portion of the column below the inlet of the liquid to be distilled).

The new products of the present invention are as follows: First. Benzene-containing petroleum distillate, evaporating over 50 per cent. below 190° F. and having a density greater than 56° B. (specific gravity .753). Second. Toluene-containing petroleum distillate, evaporating over 50 per cent. between 200° F. and 245° F. and having a density greater than 45° B. specific gravity .800). Third. Xylene-containing petroleum distillate, evaporating over 50 per cent. between 250° F. and 320° F. and having a density greater than 40° B. (specific gravity .824). Fourth. Mesitylene-containing petroleum distillate, evaporating over 50 per cent. between 300° F. and 350° F. and having a density below 40° B. (specific gravity .824). Fifth. Naphthalene-containing petroleum distillate, evaporating over 50 per cent. between 400° F. and 435° F. and having a density below 35° B. (specific gravity .848). Sixth. Petroleum distillate containing hydrocarbons of the benzene series, evaporating over 50 per cent. within that temperature interval of 50° F. which extends from 25° F. below to 25° F. above the boiling point of the contained hydrocarbon of the benzene series and having a density greater than hydrocarbon of similar boiling point of the paraffin series by more than 20° B. All of these products are distinguished from products most nearly resembling the same, obtained from coal tar, by having the characteristics of petroleum rather than of coal tar. For example, in the products from coal tar the bodies which are present in greater or less proportions with the hydrocarbons of the benzene and naphthalene series are unlike those associated with the hydrocarbons of those series in my said new products. The differences not only constitute marks of identification for my said products, but are of importance in the utilization of the products, in that the presence of the associated petroleum hydrocarbons do not interfere to the like extent (if at all) in the utilization of my new products as the associated coal tar bodies would be liable to do. Thus, for example, to prepare substitution products of hydrocarbons of the benzene and naphthalene series, from coal tar products, these

must be much freer from associated bodies than my new petroleum products.

The following is a description of what is considered the best mode of carrying the invention into effect so as to obtain the products above named, it being understood that modifications can be made and parts omitted, so long as the substance of any one or more of my hereinafter written claims is retained.

10 In carrying out the invention, any appropriate apparatus can be used, one form being shown by way of example in the accompanying drawings which form part of this specification, and in which:

15 Figure 1 is an elevation, partly in section, of a still with rectifying column, and Fig. 2, a section, on a larger scale, of a portion of said column.

The still *a* is to be supported and heated 20 in any known or suitable way. The column *b* is shown as made in sections, and has a perforated or reticulated floor plate *c* at the bottom of each section, which floor plate supports the finely divided solid material *d*, say, two feet of gravel for each section. The 25 gravel in the two lower sections may be such as to pass through a sieve of two meshes to a linear inch and to be arrested by one of three meshes to the linear inch; that in the 30 upper sections may be a little smaller, say, gravel which will pass through the last mentioned sieve and be arrested by one of four meshes to the linear inch. Either size of gravel could be used in all the sections, but 35 it is considered better to have the gravel of the lower sections a little larger on account of the larger volume of liquid of condensation therein.

Below each floor plate *c* is a collar *e* for 40 directing the downflowing liquid of condensation from the walls of the column toward the axis thereof.

The column *b* is covered with a coating *f* of an inch and a half of asbestos cement.

45 The vapor pipe *g* leads from the top of the column *b* to the condenser, of known or suitable construction (not shown). Branch pipes *h* with valves *i* therein are shown connecting with the space below each column 50 section, for enabling the vapors to pass to the condenser direct from the still *a* or after passing through any one or more of the column sections as may be desired.

A thermometer *j* is placed in the top of 55 the column *b* to indicate the temperature of the vapors entering the vapor pipe *g*; and there may be thermometers at the points *k*.

This or other appropriate distilling and 60 rectifying apparatus being at hand, the still is supplied with the crude Coalinga petroleum; and the temperature of the still and contents is raised to the distilling point. After a time the vapors pass over by the 65 pipe *g* to the condenser (not shown), where they are condensed to a liquid (the petro-

leum distillate) which runs out of the tail pipe into the customary box, which is so arranged that the flow can be observed and samples taken for testing, as customary. As the mixed vapors rise through the tall 70 (eight-foot) column of finely divided solid material, they become partially condensed to a liquid, which immediately commences to descend toward the still *a*, covering the 75 pieces *d* of solid material in its passage. The cooling by the air, modified by the asbestos jacket *f*, gives a gradual fall of temperature in the column from the bottom upward, and keeps the solid pieces effectively covered 80 with coherent coatings of the downflowing liquid, the supply of which is being constantly renewed by condensation at points above.

Since the cooling takes place at the outside of the column, the temperature at outside 85 points is naturally lower than it is at interior points at the same level; and the tendency, therefore, is for the flow of condensate to be greater at the outside than in interior parts of the column. The collars *e* 90 between overlying and underlying portions (sections) of the column counteract this tendency (at least in part) by deflecting the current of condensate from the outside of each overlying portion horizontally toward 95 the interior parts of each underlying portion. A more uniform distribution of condensate over the solid matter of the underlying portion (or section) of the column is thus effected. 100

At any given point in the column the rising vapors, which consist of a mixture of hydrocarbons of different boiling points, are meeting and coming into intimate contact 105 with the descending liquid, which consists likewise of a mixture of hydrocarbons of different boiling points. Of these liquid hydrocarbons, some are of lower and some of higher boiling points than a part at least of the vaporized hydrocarbons, which meet 110 them in any particular point. There are consequently repeated fractional condensations from the vapors, and fractional re-evaporations from the liquid of condensation, until the well rectified vapors escape by 115 the vapor pipe *g*.

The fire under the still *a* may be so regulated as to distil off about two per cent. per hour of the charge placed in the still *a* at the beginning of the run. As distillation 120 proceeds, the temperature in the still *a* and column *b* rises; the density of the distillate at the tail pipe of the condenser for the most part increases; and the volatility of said distillate steadily diminishes; but at certain periods said density gradually diminishes; 125 while said volatility continues to decrease. Such a retrogression in density of distillate takes place before the thermometer *j* reaches 260° F.; and when this temperature is 130

reached, the distillate receiver may be changed, so that distillate next collects in the new receptacle.

- The distillation being continued, the density of distillate gradually increases with the rise of the distilling temperature until another retrogression of such density takes place; which occurs before the temperature at the top of the column *b* reaches 320° F.
- When this temperature is attained, the distillate receiver may be again changed. The distillation may then be continued until the temperature at the top of the column reaches 400° F., when the top section may be cut out by opening the valve *i* in topmost branch pipe *h*, so that the vapors pass through it to the vapor pipe *g*. The distillation may then be continued until the temperature at the top of the third section reaches 485° F.
- It could be continued longer; or stopped earlier. The residuum is then discharged from the still *a* and column *b*, in preparation for another run.

- By the distillation described, three fractions of Coalinga petroleum will have been obtained, namely: (1) the fraction collected before 260° F. is reached, (2) the fraction collected between 260° F. and 320° F., and (3) the fraction collected between 320° F. and, say, 485° F., more or less. The first contains the benzene and toluene of the crude oil, the second the xylene and some of the mesitylene, and the third the rest of the mesitylene and the naphthalene. This separation is not expected to be perfect, however. In making it as described, the hydrocarbons which come over near the beginnings of the respective retrogressions would not be collected apart from those which come over near the endings thereof.

- Each of the so obtained fractions is distilled by itself with rectification in the column *b*, or with other rectification able to effect the aforesaid retrogressions of density of distillate contemporaneously with continued decrease of volatility; and the hydrocarbons which come over near the beginnings of the respective retrogressions are collected apart from those which come over near the endings thereof. There would best be a collection separately of intermediate portions also. The following tables indicate the different portions which would best be collected apart and the temperatures at top of column *b* during their collection.

Table I—Redistillation of Benzene-Toluene Fraction.

	Below 165° F., burning oil portion.
60	Between 165° F. and 184° F., benzene portion.
	" 184° F. " 215° F., burning oil portion.
	" 215° F. " 227° F., intermediate portion.
	" 227° F. " 232° F., toluene portion.
	" 232° F. " 246° F., intermediate portion.
	" 246° F. " 252° F., burning oil portion.
	" 252° F. " 279° F., intermediate portion.
65	Above 308° F., mesitylene portion.

Table II—Redistillation of Xylene Fraction.

Below 308° F., as in Table I.
Between 308° F. and 352° F., mesitylene portion.
Above 352° F., intermediate portion.

Table III—Redistillation of Mesitylene-Naphthalene Fraction.

Below 352° F., as in Tables I and II.
Between 352° F. and 408° F., intermediate portion.
" 408° F. and 420° F., naphthalene portion.
Above 420° F., intermediate portion.

The parallel portions from the several redistillations can be united and distilled again with collection of the different portions as before; and this union can be repeated as often as may be desired. As the denser products become purer, the limits between which they are collected can be made closer to the boiling points of the corresponding benzene hydrocarbons. In the case of intermediates below mesitylene, the parallel portions (that is, the portions coming over between the same limits of temperature) from all the distillations can be united and redistilled; or they can be added to the crude oil.

In collecting the mesitylene portion in the first and other redistillations, whatever portions are not too smoky for burning oil (kerosene) can be cut out. The proper cuts can be determined by burning samples of the distillate in an ordinary flat flame lamp and seeing if they smoke. The test may be made with the wick down so that the top of the flame appears between an eighth and a quarter of an inch above the cone of the lamp burner. Let a porcelain dish be supported by a wire tripod on top of the lamp chimney over its mouth at such distance therefrom, say, between a half inch and an inch, as not to interfere with the draft. If no deposit of soot (or substantially none) is found on the dish after the lamp has burned in this way for half an hour, the test shows satisfactorily that a non-smoking oil has been under investigation.

In collecting the intermediate portion between mesitylene and naphthalene, whatever portions are not too smoky or otherwise unsuited to burning oil (kerosene) can be cut out. The portions of the intermediates above mesitylene, not applicable to burning oil, are disposed of as may be thought most profitable at the time. It is always open to use them as fuel.

The burning oil portions are mixed together and refined by the usual sulfuric acid treatment, the subjection of the oil to the sulfuric acid being followed by washing with water and alkaline solution as sufficiently understood by those skilled in refining petroleum.

To utilize the portions containing the hydrocarbons of the benzene and naphthalene series after the manner of hydrocarbons of these series requires no additional directions

here. The foregoing description, in connection with the knowledge and skill of those accustomed to work with such hydrocarbons will suffice. The new products containing hydrocarbons of the benzene series can by rectification, as described, be so far freed from other matters as to be in condition for treatment with known or suitable reagents for converting said hydrocarbons into their sulfo, nitro and other substitution products. Additional purification or admixture with products from other sources can be resorted to, if thought necessary or expedient.

The mesitylene-containing portion can be so far freed from other matters by rectification as to be applicable to the uses of solvent naphtha with or without admixture with solvent naphtha from other sources.

The naphthalene is readily separated from the naphthalene-containing portion, by cooling the latter with ice and salt, and draining off the liquid hydrocarbons from the crystallized naphthalene. The extracted oil can be used as fuel; or otherwise, as may be found profitable.

Where the denser products of the fraction coming over between 320° F. and 485° F. (mesitylene-naphthalene fraction) are not desired for utilization after the manner of benzene and naphthalene hydrocarbons, a useful procedure is to continue the distillation of the crude oil, after the benzene-toluene and xylene fractions have been obtained, with or without passage of the subsequently given off vapors through all or part of the rectifying column, so long as the distillate does not become too smoky for use as burning oil, the distillation of the crude oil being then arrested, and the still *a* and column *b* being emptied preparatory to receiving oil for another run.

A pipe *m* is shown in dotted lines in Fig. 1 at an intermediate part of the column to indicate that through such a pipe liquid to be distilled continuously could be introduced in a stream into the column; if it should be preferred to employ continuous distillation. Intermittent distillation is considered more advantageous and has, therefore, been particularly described.

I claim as my invention or discovery:

1. The process of obtaining petroleum products, by distilling Coalinga or analogous petroleum with such rectification of the vapors thereof as to result in substantial retrogressions of density of distillate while the volatility of said distillate continues to diminish, collecting apart the portions which come over near the beginnings of such retrogressions, and utilizing the said portions after the manner of hydrocarbons of the benzene and naphthalene series, substantially as described.

2. The process of obtaining petroleum products, by distilling Coalinga or analogous

petroleum with such rectification of the vapors thereof as to result in substantial retrogressions of density of distillate while the volatility of said distillate continues to diminish, collecting the portions which come over near the beginnings of such retrogressions apart from those received near the endings thereof, and utilizing the latter portions for burning oil and the first mentioned portions after the manner of hydrocarbons of the benzene and naphthalene series, substantially as described.

3. The process of obtaining petroleum products, by distilling Coalinga or analogous petroleum with such rectification of the vapors thereof as to result in substantial retrogressions of density of distillate while the volatility of said distillate continues to diminish, collecting apart the portions received near the endings of such retrogressions, and utilizing said portions for burning oil, substantially as described.

4. The process of obtaining petroleum products, by distilling Coalinga or analogous petroleum with such rectification of the vapors thereof as to result in substantial retrogressions of density of distillate while the volatility of said distillate continues to diminish, collecting apart the portions which come over near the beginnings of such retrogressions at temperatures below 320° F., and subjecting said portions to reagents for obtaining substitution products of benzene hydrocarbons, substantially as described.

5. The process of obtaining petroleum products, by distilling Coalinga or analogous petroleum with such rectification of the vapors thereof as to result in substantial retrogressions of density of distillate while the volatility of said distillate continues to diminish, collecting apart the portions which come over at temperatures between 300° F. and 350° F., and utilizing said portions as solvent naphtha, substantially as described.

6. The process of obtaining petroleum products, by distilling Coalinga or analogous petroleum with such rectification of the vapors thereof as to result in substantial retrogressions of density of distillate while the volatility of said distillate continues to diminish, collecting apart the portions which come over between 400° F. and 435° F., cooling said portions to solidify the naphthalene therein, and separating the so solidified naphthalene from the liquid hydrocarbons, substantially as described.

7. The process of obtaining petroleum products, by distilling Coalinga or analogous petroleum with such rectification of the vapors thereof as to result in substantial retrogressions of density of distillate while the volatility of said distillate continues to diminish, and collecting the portions which come over near the beginnings of such retrogressions apart from those received near

the endings thereof, substantially as described.

8. In the process of obtaining petroleum products, by distilling Coalinga or analogous petroleum, the improvement consisting in preliminarily fractionating the crude oil, then redistilling the so-obtained fractions with such rectification of the vapors thereof as to result in substantial retrogressions of density of distillate while the volatility of said distillate continues to diminish, and in the redistillation collecting the portions which come over near the beginnings of such retrogressions apart from those received near the endings thereof, substantially as described.

9. In the process of obtaining petroleum products, by distilling Coalinga or analogous petroleum with such rectification of the vapors thereof as to result in substantial retrogressions of density of distillate while the volatility of said distillate continues to diminish, the improvement consisting in collecting the portions which come over near the beginnings of such retrogressions apart from those received near the endings thereof in such manner as to leave intermediate portions, and redistilling the said intermediate portions with such rectification of the vapors thereof as to result in substantial retrogressions of density of distillate while the volatility of said distillate continues to diminish, and collecting the portions which come over near the beginnings of such retrogressions apart from those received near the endings thereof, substantially as described.

10. The process of obtaining petroleum products, consisting in distilling Coalinga or analogous petroleum with rectification of the vapors thereof by passage of the same through a five to eight-foot or taller column of solid material in pieces between a half and a quarter inch in diameter under subjection to such cooling influences as will allow a gradual fall of temperature to occur in the column and will keep the pieces of solid material effectively covered with coherent coatings of the downflowing liquid of condensation and so will result in substantial retrogressions of density of distillate while the volatility of said distillate continues to diminish, collecting apart the portions which come over near the beginnings of such retrogressions, and utilizing said portions after the manner of hydrocarbons of the benzene and naphthalene series, substantially as described.

11. The process of obtaining petroleum products, consisting in distilling Coalinga or analogous petroleum with rectification of the vapors thereof by passage of the same through a five to eight-foot or taller column of solid material in pieces between a half and a quarter inch in diameter under sub-

jection to such cooling influences as will allow a gradual fall of temperature to occur in the column and will keep the pieces of solid material effectively covered with coherent coatings of the downflowing liquid of condensation and so will result in substantial retrogressions of density of distillate while the volatility of said distillate continues to diminish, collecting the portions which come over near the beginnings of such retrogressions apart from those received near the endings thereof, and utilizing the latter portions for burning oil and the first mentioned portions after the manner of hydrocarbons of the benzene and naphthalene series, substantially as described.

12. The process of obtaining petroleum products, consisting in distilling Coalinga or analogous petroleum with rectification of the vapors thereof by passage of the same through a five to eight-foot or taller column of solid material in pieces between a half and a quarter inch in diameter under subjection to such cooling influences as will allow a gradual fall of temperature to occur in the column and will keep the pieces of solid material effectively covered with coherent coatings of the downflowing liquid of condensation and so will result in substantial retrogressions of density of distillate while the volatility of said distillate continues to diminish, collecting apart the portions received near the endings of such retrogressions, and utilizing said portions for burning oil, substantially as described.

13. The process of obtaining petroleum products, consisting in distilling Coalinga or analogous petroleum with rectification of the vapors thereof by passage of the same through a five to eight-foot or taller column of solid material in pieces between a half and a quarter inch in diameter under subjection to such cooling influences as will allow a gradual fall of temperature to occur in the column and will keep the pieces of solid material effectively covered with coherent coatings of the downflowing liquid of condensation and so will result in substantial retrogressions of density of distillate while the volatility of said distillate continues to diminish, collecting the portions which come over near the beginnings of such retrogressions apart from those received near the endings thereof, substantially as described.

14. The process of obtaining petroleum products, consisting in distilling petroleum with rectification of the vapors thereof by passage of the same through a five to eight-foot or taller column of solid material in pieces between a half and a quarter inch in diameter under subjection to such cooling influences as will allow a gradual fall of temperature to occur in the column and will keep the pieces of solid material covered

with coatings of the downflowing liquid of condensation of such limited thickness that said coatings are coherent and so enabled to resist the tendency of the rising vapors to carry about the liquid composing said coatings, substantially as described.

15. The rectifying process which is characterized by the passage of the mixed vapors from the liquid under distillation through a five to eight-foot or taller column of solid material in pieces between a half and a quarter inch in diameter under subjection to such cooling influences as will allow a gradual fall of temperature to occur in the column and will keep the pieces of solid material covered with coatings of the downflowing liquid of condensation of such limited thickness that said coatings are coherent and so enabled to resist the tendency of the rising vapors to carry about the liquid composing said coatings, substantially as described.

16. The process of obtaining petroleum products, consisting in distilling Coalinga or analogous petroleum with rectification of the vapors thereof by passage of the same through a five to eight-foot or taller column of solid material in pieces between a half and a quarter inch in diameter under subjection to such cooling influences as will allow a gradual fall of temperature to occur in the column and will keep the pieces of solid material effectively covered with coherent coatings of the downflowing liquid of condensation and so will result in substantial retrogressions of density of distillate while the volatility of said distillate continues to diminish, directing said liquid at intervals intermediate the top and the bottom of the column horizontally from points of lower to points of higher temperature, and collecting the portions which come over near the beginnings of such retrogressions apart from those received near the endings thereof, substantially as described.

17. The rectifying process which is characterized by the passage of the mixed vapors from the liquid under distillation through a five to eight-foot or taller column of solid material in pieces between a half and a quarter inch in diameter under subjection to such cooling influences as will allow a gradual fall of temperature to occur in the column and will keep the pieces of solid material covered with coatings of the downflowing liquid of condensation of such limited thickness that said coatings are coherent and so enabled to resist the tendency of the rising vapors to carry about the liquid composing said coatings, and directing said liquid at intervals intermediate the top and bottom of the column horizontally from points of lower to points of higher temperature, substantially as described.

18. The rectifying process, which consists in passing the vapors to be rectified through

a column of finely divided solid material, subjecting them therein to cooling influences sufficient to effect a partial condensation, allowing the resulting condensate to flow downward over said material, and directing such downflowing liquid intermediate an overlying and an underlying portion of said material horizontally from points of lower to points of higher temperature, so as thereby to distribute said liquid more uniformly over the solid material in said underlying portion, substantially as described.

19. Benzene-containing petroleum distillate, evaporating over 50 per cent. below 190° F. and having a density greater than 56° B. and the characteristics of a petroleum as opposed to a coal tar product, substantially as described.

20. Toluene-containing petroleum distillate, evaporating over 50 per cent. between 200° and 245° F. and having a density greater than 45° B. and the characteristics of a petroleum as opposed to a coal tar product, substantially as described.

21. Xylene-containing petroleum distillate, evaporating over 50 per cent. between 250° F. and 320° F. and having a density greater than 40° B. and the characteristics of a petroleum as opposed to a coal tar product, substantially as described.

22. Mesitylene-containing petroleum distillate, evaporating over 50 per cent. between 300° F. and 350° F. and having a density greater than 40° B. and the characteristics of a petroleum as opposed to a coal tar product, substantially as described.

23. Naphthalene-containing petroleum distillate, evaporating over 50 per cent. between 400° F. and 435° F. and having a density greater than 35° B. and the characteristics of a petroleum as opposed to a coal tar product, substantially as described.

24. Petroleum distillate containing hydrocarbon of the benzene series, evaporating over 50 per cent. within that temperature interval of 50° F. which extends from 25° F. below to 25° F. above the boiling point of the contained hydrocarbon of the benzene series and having a density greater than hydrocarbon of similar boiling point of the paraffin series by more than 20° B. and also having the characteristics of a petroleum as opposed to a coal tar product, substantially as described.

25. The process of obtaining petroleum products, by subjecting Coalinga or analogous petroleum to a distillation and rectification in which the distilling temperature rises to above 400° F. and in the progress of which the distillate, decreasing in volatility, exhibits at certain periods an increasing and at others a substantially retrograding density, collecting each by itself the following portions, namely: a benzene-containing distillate between about 165° F. and about

184° F., more or less, a burning oil portion
between about 184° F. and about 215° F.,
more or less, a toluene-containing portion
between about 227° F. and about 232° F.,
5 more or less, a burning oil portion between
about 246° F. and about 252° F., more or
less, a xylene-containing portion between
about 279° F. and about 308° F., more or
less, a mesitylene-containing portion between
10 about 308° F. and about 352° F., more or

less, and a naphthalene-containing portion
between about 408° F. and about 420° F.,
more or less, and mixing said burning oil
portions, substantially as described.

In testimony whereof I affix my signature, 15
in presence of two witnesses.

HERMAN FRASCH.

Witnesses:

F. W. LOTHMAN,

J. C. UPDE GROVE.