April 26, 1938. P. C. KEITH, JR 2,115,144

METHOD FOR CRACKING OILS IN VAPOR PHASE

Original Filed Dec. 1, 1928 3 Sheets-Sheet 1

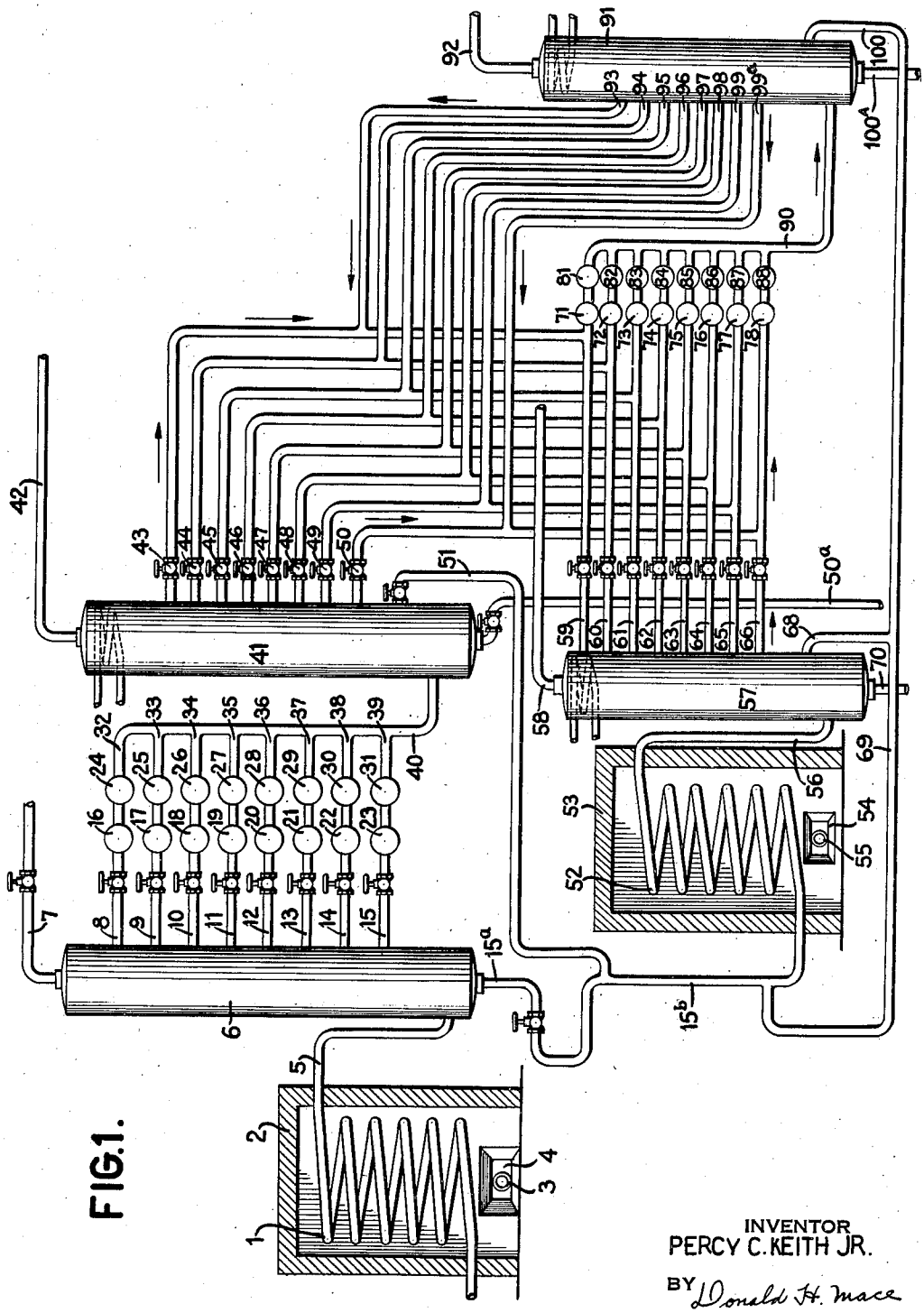


FIG.1.

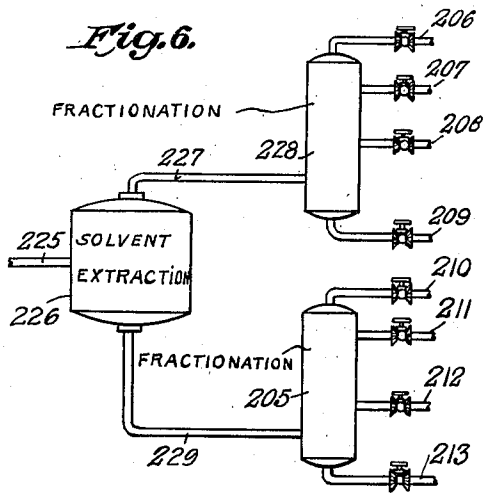
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Fig. 6.



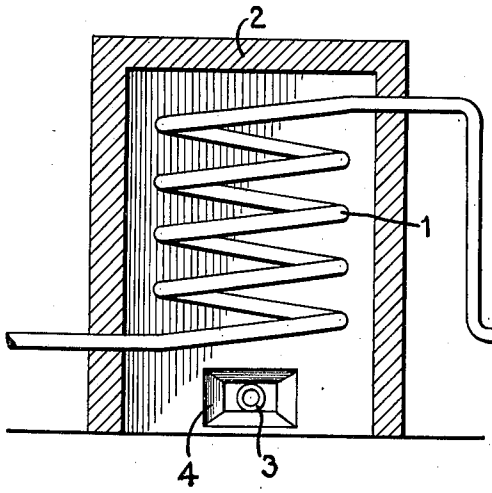
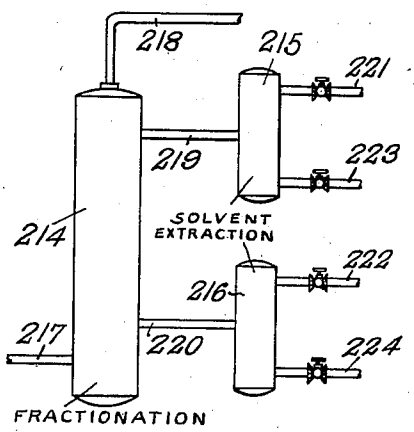


Fig. 7.



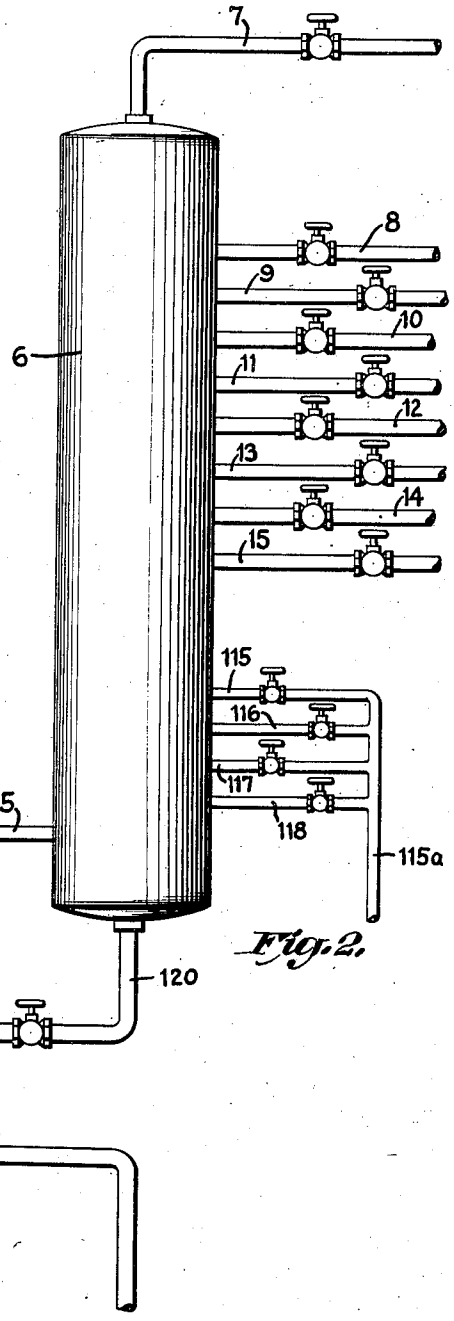


Fig. 2.

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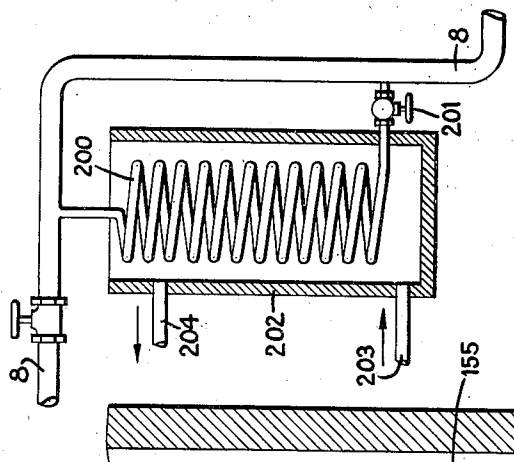


FIG. 5.

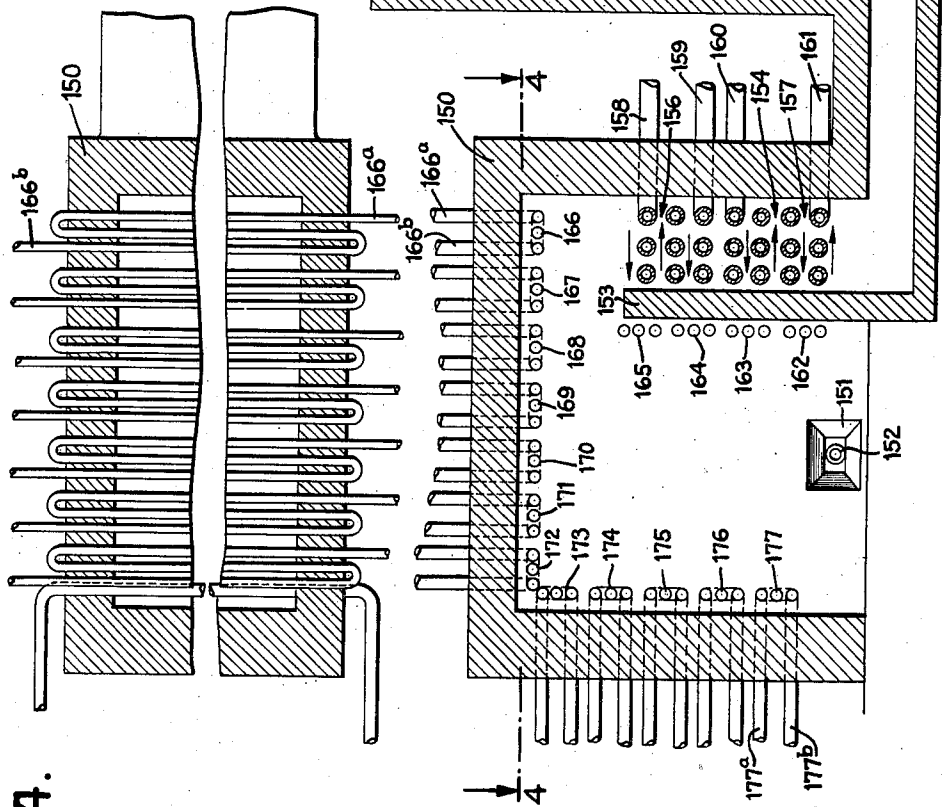


FIG. 4.

FIG. 3.

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UNITED STATES PATENT OFFICE

2,115,144

METHOD FOR CRACKING OILS IN VAPOR PHASE

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Original application December 1, 1928, Serial No. 323,005. Divided and this application November 9, 1933, Serial No. 697,282

6 Claims. (Cl. 196—50)

This invention relates to the pyrogenesis of petroleum oils and is a division of application Serial No. 323,005 filed December 1, 1928. The invention will be fully explained in the following description and accompanying drawings, in which:

Fig. 1 is a diagrammatic representation of a preferred embodiment of apparatus in which my process may be carried out;

Fig. 2 is a diagrammatic representation of an alternative form;

Fig. 3 is a vertical section through a form of apparatus which may be employed in conjunction with my process;

Fig. 4 is a cross section taken on the line 4—4 of Fig. 3;

Fig. 5 is a side elevation with parts in section of a form of apparatus employed in conjunction with my process and with the apparatus shown in Figs. 3 and 4;

Fig. 6 is a diagrammatic representation of apparatus for applying a selective solvent treatment to my process; and

Fig. 7 is a diagrammatic representation of an alternative arrangement of apparatus for applying the solvent treatment.

The pyrogenesis of petroleum oils for production of oils of lower boiling point is carried out by heating crude petroleum, or such of its distillates as may economically be utilized in this manner, to cracking temperatures with or without pressure. The fraction intermediate between kerosene and lubricating oils known as gas oil is frequently utilized for this purpose because of its lesser market value, although kerosene, lubricating oil fractions and fuel oils are also employed at times. The fractions so employed are composed of an extended range of compounds as indicated by the range of molecular weights and boiling points. The conglomerate of compounds is subjected to cracking conditions until a certain quantity of material falling within a desired boiling range is produced. Simultaneously with the formation of this product, or products, materials are produced which do not fall within the desired range, for example, when cracking to produce a substantial proportion of gasoline which is a product composed of a large variety of different hydrocarbon compounds, there is simultaneously produced a quantity of tarry and coky materials. Some elements of a conglomerate stock, for reasons which will be given more fully later, require cracking to a degree less than others, and because of the fact that the stock as a whole is subjected to the same conditions the cracking reaction will be carried too far in the case of some of the constituents of the stock in order to secure the desired quantity of material of a predetermined boiling point range and with the resultant formation of compounds which do not fall within the said range or which are deleterious to the operation, for reasons which will be more fully pointed out. The different cracking rates of some of the constituents of the stock tend to accentuate the condition referred to above. I have discovered that a fundamental increase in the efficiency of the cracking process may be obtained by separating the cracking stock into a number of distinct fractions of different boiling point ranges and thereafter cracking the individual fractions so generated. I prefer to obtain as nearly as possible, having regard to the conditions imposed by practice, a number of charging stocks all the constituents of each of which will respond in the same degree to the conditions to which each of the stocks is subjected. I preferably apply to each such fraction the degree of time, temperature, and/or pressure necessary to its optimum conversion into desired products. These conditions may in any case be determined by preliminary tests. Thus, when conditions have been established by such tests as to yield the same quantity of desired end products from a series of segregated fractions as is obtainable from cracking conglomerate stock the concomitant loss in gas and/or tarry or coky materials is diminished, or for an equivalent loss the yield of the desired end products is relatively increased.

My process is applicable generally in the pyrogenesis of petroleum oils to produce lower boiling point oils, as, for example, cracking to produce either gas, gasoline, kerosene, gas oil or lubricating oil from stocks of respectively higher boiling point.

In the ideal embodiment of my process the stock is segregated into a plurality of charging stocks of such character that under the conditions of heat, time, and pressure imposed cracking of the various individual compounds composing the fraction will take place at substantially the same rate. However, the limitations imposed by practice require segregation into a smaller number of stocks than in the ideal method and I therefore segregate into an appropriate number of charging stocks and subject each of such stocks to optimum conditions for the particular segregate.

I have discovered that in high molecular weight hydrocarbons of straight chain structure the ini-

tial scission on cracking frequently occurs adjacent the center of the molecular chain. In one application in my process I aim to obtain by cracking the products of first scission of the molecule, and I therefore prepare charging stocks which upon their initial scission yield products which fall within the range of physical characteristics of the material desired to be obtained. Thus in the case of gasoline I may proceed by dividing my charging stock into a number of fractions each of which has a molecular weight substantially twice that of a constituent of gasoline, then by cracking the stocks to the extent of one scission I obtain a number of products whose molecular weights fall within the range of molecular weights of the constituents of gasoline. In cases in which the original charging stock contains constituents so heavy that the products of their initial scission will not fall within the range of physical characteristics of the desired products, these constituents may be separated from the remainder of the original charging stock, as by distillation, and treated in one of two ways; i. e. (1) by segregating them from one another as by distillation into individual fractions and then subjecting each segregated fraction to such conditions as will produce from each segregated fraction a product which will yield, upon refractionation, products which may be decomposed as above into gasoline constituents. This procedure enables me to separate unsaturated constituents to a degree and to then subject such fractions to appropriate treatment. (2) In view of the limitations of practice I may subject the entire heavier conglomerate cut to cracking conditions best suited to obtain the maximum yield of products which can be segregated into charging stocks of the nature described and cracked in the manner above set forth so as to yield gasoline constituents.

Alternatively, I may prepare a number of fractions of charging stock, including some which cannot be converted by a single scission adjacent the center of the molecule into products falling within the desired range, and subject each such fraction to the degree of time, temperature and pressure necessary to its conversion into products of the desired boiling point range. I may, however, in such cases crack each such fraction to yield a cracked material having a position with respect to the average molecular weight of the series of cracked materials obtained which corresponds to the position held by the parent fraction with respect to the other members of the parent series.

In addition to the foregoing I may make a further separation based on chemical characteristics. Thus, I may separate the original cracking stock into two fractions, one containing a preponderance of saturates and the other containing a preponderance of aromatics and unsaturates, as, for example, by the application of selective treatment with liquid sulphur dioxide. These individual products may thereafter be separated each into products of different boiling point ranges to be separately cracked as hereinabove described. Alternatively, the fractions of separate boiling point ranges may be first prepared and each thereafter separated into fractions of different chemical characteristics, as, for example, by treatment with liquid sulphur dioxide.

In any event, where several fractions of the original charging stock are prepared, as by distillation, the decomposition products from the several fractions will preferably have average molecular weights whose ratio to each other is approximately the same as the ratio of molecular weights of the parent fractions. For example, in cracking gas oil to produce gasoline the gas oil may be segregated by fractionation into a series of several cuts, each of which has 90% of constituents boiling within a different 50° F. range. The average molecular weights of these fractions are in some ratio to their boiling points, the fraction of relatively high boiling point having the highest molecular weight. In cracking these individual fractions conditions are adjusted to produce a series of cracked products having the same general relationship. Thus, the fractions of lower average molecular weight will have been cracked to produce a cracked material of lower average molecular weight than will have been produced from the parent fractions of relatively higher molecular weight. In this way the lighter constituents of the end product gasoline will have been predominantly produced from those fractions of the cracking stock of lower molecular weight, whereas those fractions of the gasoline of relatively higher molecular weight will have been predominantly produced from the fractions of cracking stock of relatively higher molecular weight.

I achieve a number of distinct advantages by this process, for example, the cracking is carried out on each of the individual cuts under conditions which may be predetermined in view of the rate of dissociation of the particular stock to produce the optimum conversion, while the total number of dissociations or the degree of pyrogenesis to produce any given yield of end product is relatively less than would be necessary with the indiscriminate cracking of a conglomerate stock, and thus the concomitant losses in gas and/or tar or coke are greatly diminished. A further distinct advantage is that polymerization to form products of a greater molecular weight than the parent stock does not occur to the same degree as when cracking a conglomerate stock. It is unnecessary to carry the cracking reaction on some of the constituents of the original stock to the point of forming polymers of a character deleterious to the operation of the process. Thus, in operating upon a conglomerate stock in the manner used at the present time it may be unavoidable to carry the cracking reaction to the point of third, fourth, fifth or higher scission in the case of some of the constituents of the initial charge and to the scission of polymerized products formed therefrom in order to obtain the desired yield of the end product, whereas in my process I prefer to confine the reaction to the formation of the products of scission of a lower order. The scissions of higher order result in an increase in the products of decomposition, or polymerization, which contributes to the formation of the products known as tar and coke.

One of the preferred methods of operating my process is to crack each individual cut of the cracking stock to produce a cracked material having an average molecular weight substantially half of that of the parent cut, for example, ranging from 75 to 25% of the average molecular weight of the parent cut. In this way, to an extent at least, with a single decomposition of the various molecules composing the gas oil fraction, I am enabled to convert them into fractions of the gasoline series, and by working upon a series of individual fractions I am enabled to produce an entire series of products boiling within the

gasoline range with a minimum of individual molecular dissociations, or polymerization. The conditions outlined may, of course, be varied in view of the particular stock or in view of the particular characteristics of the product desired, as, for example, to produce a gasoline having a certain definite proportion of material boiling within a certain predetermined range.

The particular method of cracking the individual stocks may be any one of the methods at present employed or hereafter developed. I may, for example, crack these individual cuts in either liquid or vapor phase or in a combination of the two and under any degree of pressure. In a preferred embodiment of my invention, however, I subject the individual cuts to a vapor phase cracking of relatively short duration ranging, for example, from the order of one second up to times of the order of five minutes, at temperatures which may range between 750° and 1500° F. and at pressures which may range from a few atmospheres to partial vacuum. In this way I am enabled to effect a carefully controlled dissociation of the individual stocks and accurately control the amount of dissociation applied to each of these stocks so that a large proportion of the individual cuts is subjected to a single dissociation, thereby automatically throwing it into the boiling point range of the desired end product with a minimum production of undesired products. A further advantage of this procedure that I have discovered is that owing to the relatively short times involved, the temperature range in which cracking is effected and the low specific volume of the gases in the cracking zone, the tendency to polymerization, or reformation of heavier products, is inhibited, the efficiency of the operation is increased and I am enabled to diminish the formation of tar and/or coke.

In determining the conditions under which individual cuts of the initial conglomerate charging stock are to be cracked consideration must be given to the formation of fixed gas. I believe that the theory at present held that fixed gas produced by a cracking operation is substantially produced by the cracking of tar to coke is mistaken and that in fact such fixed gas is substantially produced by the cracking of constituents falling within the gasoline range. I therefore so select the conditions of operation in the preferred form of my process as to prevent the cracking of such gasoline constituents, as, for example, by removing them from the zone of reaction as quickly as possible. In this respect my process is radically different from those at present practiced in which the products falling within the gasoline range, or some of them, are held in the zone of reaction for considerable periods of time. In the processes in use at the present time these products which are extant in the zone of reaction are either retained there by reason of the nature of the apparatus which does not permit of their evacuation immediately upon formation, or are retained there by reason of their solution in liquid since they are in contact with large bodies of heavier liquid content in the system. This effect is considerably aggravated in many processes by the use of pressure. It will be noted that in my improved process because of the nature of the apparatus and the charging stock used there is substantially no liquid present in the system at any time and the apparatus is such that products falling within the gasoline range are removed substantially as quickly as formed.

The selection of the temperature bears a definite relation to the time element involved in the operation of the apparatus, the more rapid the evacuation of the products from the zone of reaction the higher the temperature which may be used, sufficient time being provided to permit the reaction to take place. The effect of removing the products from the zone of reaction is to arrest the reaction, and it may be desirable to cool immediately the products removed to prevent further reaction by reason of the contained heat.

My process will now be described with specific reference to the apparatus diagrammatically indicated in the drawings. Referring specifically to Fig. 1 a cracking stock such as gas oil is passed through the tubular heater 1, surrounded by the refractory setting 2, and heated by means of a burner such as 3 communicating with the setting through the port 4. Any alternative means of heating this stock to a temperature of complete or partial vaporization may be employed, such as a heat exchanger or a still. The partly vaporized cracking stock is delivered through the pipe 5 into the fractionating column 6. This column may be suitably insulated and provided with a number of rectifying devices such as the customary transverse partitions carrying down flow pipes and vapor contacting devices, not shown. The design of this column is not a feature of the invention and any column or corresponding device which is appropriately designed to separate petroleum oil into a number of fractions by rectification may be alternatively employed. Provision is made for taking off an overhead cut in vapor phase from the column by means of the vapor outlet 7 and a number of side cuts (ordinarily in liquid phase, but which may be in the vapor phase) from the side outlets 8, 9, 10, 11, 12, 13, 14 and 15. The side cuts may be rectified or stripped in a secondary rectifying column, if desired, to eliminate light ends, or, alternatively, any other means for obtaining an enhanced degree of separation may be employed. Any bottoms or heavy ends formed in the column will be removed, preferably in a continuous fashion, by means of the bottom draw-off 15A. The column may be supplied with cooling coil adjacent to the top or intermediate points and with a heating coil adjacent to the bottom or with reboiler sections at intermediate points. All such modifications will be incorporated to the degree necessary to obtain the desired separation of the individual fractions. The cuts taken off through outlets 7 to 15, inclusive, are, in view of the necessities of practice, relatively close cut fractions having, for example, 90% of constituents boiling within a 50° F. range, and while these ranges to some extent overlap, the cuts represent a complete series of charging stocks, each of which approaches, within the limits of commercial practicability, an ideal charging stock as above defined. This series of cuts has a range of boiling points and corresponding molecular weights which increases throughout the series. These various cuts are passed to individual crackers through control apparatuses 16 to 23 inclusive which will be hereinafter more fully described, and from the control apparatuses the cuts pass respectively to the individual cracking apparatuses which have been diagrammatically indicated by the numerals 24 to 31, inclusive. I may employ any form of cracking apparatus, such as stills which may be adapted to operate under pressure or tubular crackers with or without reaction chambers or tubular stills operated in the vapor phase. In

any event, the cracking is carried out under conditions which may be ascertained in advance by tests to be suited to the individual cut. Preferably, when operating to make gasoline the individual cuts are cracked to such an extent that the average molecular weight of the cracked material produced from an individual cut ranges from 25 to 75% of that of the parent fraction. I obtain in this way a series of cracked products with serially larger molecular weights corresponding in order to the molecular weights of the original fractions of cracking stock. The desired end product is therefore obtained by the selective cracking of preferred stocks and with less actual molecular disruptions and recombinations than would be incidental to handling a cracking stock as a conglomerate. For convenience all of the cracked materials discharged from the crackers **24** to **31**, inclusive, through outlets **32** to **39**, inclusive, may be conducted by means of the manifold **40** into the rectifying column **41** which is of suitable construction to permit the separation thereof into the desired end product, as, for example, gasoline which may be taken off in vapor phase, if desired, through the outlet **42**, and a number of side cuts taken off through the side outlets **43** to **50**, inclusive. These side cuts taken off through the outlets **43** to **50**, inclusive, are preferably fractionated so that 90% of the constituents of each cut boil within a range of 50° F. and will be hereinafter more fully considered. The column **6** may be operated under any pressure at which appropriate fractionation may be secured, and for purposes of heat economy, is preferably operated under a pressure in excess of atmospheric, say, for example, a pressure not exceeding 100 pounds per square inch. I achieve in this way the additional advantage that the cuts taken off from the outlets **8** to **15**, inclusive, may, in this manner, be supplied by virtue of their initial pressure to the respective cracking apparatuses **24** to **31**, inclusive. The column **41** may be operated under pressure preferably less than that obtaining in column **6** so that the progress of material through the entire system is effected by virtue of the initial pressure obtaining in column **6**. The side cuts from column **6** fall within the gas oil range and are such as may, to a large extent, be converted into constituents boiling within the gasoline range, particularly where the cracking is so controlled as to produce molecular disruptions occurring at or near the mid-point of the molecule.

The plant illustrated is only an approach to the ideal and some polymerization may occur to products whose molecular weight is higher than those taken off through the side outlets **8** to **15**, inclusive, of column **6**. Such polymerized products are preferably separately processed as outlined in the preferred manner of processing the cut withdrawn through **15***a*, but for commercial reasons may be removed from column **41** through the side outlets **51** and diverted through pipe **15***a* to pipe **15***b* to be combined with and processed with the products withdrawn from column **6** through outlet **15***a*.

The materials delivered through the pipe **15***b* represent materials which cannot be converted into constituents of the gasoline series by a single disruption adjacent the center of the molecule and, while I may segregate these bottoms by fractionation in the manner described and thereafter crack selectively the individual components and then refractionate and then recrack the individual components falling within the gas oil range to gasoline range, I find it sufficient to subject these components to a mild cracking by forcing the same through the tubular heater **52** surrounded, for example, by the refractory setting **53** heated through the port **54** by means of the burner **55**. The cracking effected in the heater **52** is not intended to convert the stock treated therein predominately to gasoline, but rather to convert a substantial proportion of the stock into stocks having molecular weights approximating those removed from column **6** through the side outlets **8** to **15**, inclusive. There is of course, the incidental production of a small quantity of gasoline where the operation is not accurately controlled. The stock cracked in this manner is delivered through the outlet **56** into the rectifying column **57**, which may be of any suitable construction, in which it is fractionated to form an overhead distillate, for example, taken off through the outlet **58** which may consist of gasoline and a series of intermediate cuts taken off through the side outlets **59** to **66**, inclusive, which are preferably cut to have 90% constituents boiling within a range of 50° F. These constituents boiling within the kerosene and gas oil ranges are such as may to a large extent be converted into constituents of gasoline by a single disruption occurring at or adjacent the mid-point of the individual molecule. Any heavy ends may be taken off through the side outlet **68**, and, while they are preferably handled by separation and cracking of the individual segregates, as above outlined, I find it sufficient in commercial practice to carry these compounds by means of the pipe **69** back into the inlet side of the tubular heater **50** for a second cracking operation. Any tarry products collecting in the base of the towers **41**, **57** and **91** are withdrawn by means of bottom outlets **50***a*, **70** and **100***a*, and diverted from the system. The products obtained from the side outlets **59** and **66** inclusive, represent products which have been cracked and separated into products having a molecular weight approximating those removed from the side outlets on column six. As segregates they are passed through the control apparatuses diagrammatically indicated by the numerals **71** to **78**, inclusive, discharging into cracking apparatuses **81** to **88**, inclusive, which may be of any suitable construction, although they are preferably of the type hereinafter described. The cuts obtained from tower **41** from the side outlets **43** to **50**, inclusive, are cuts which have been subjected to cracking and subsequent fractionation. These preferably will be cracked in the same manner as cuts **8** to **15**, inclusive, derived from tower **6**, but for commercial reasons they may be blended with cuts **59** to **66**, inclusive, and passed through the crackers **81** to **88**, inclusive. In the ideal embodiment of my process all polymerized cuts, even of the same molecular weight as the cuts **8** to **15**, inclusive, will be treated separately. This is desirable for two reasons, the first being that the dissociation speed of these polymers may be different than those of **8** to **15**, inclusive, and further, because I have discovered that the presence of polymerized cuts in contact with undecomposed cuts will enhance the formation of tar.

The cracking accomplished in these cracking apparatuses is conducted under conditions ascertained by test or experience to be best for the particular cuts and may be so adjusted as to produce cracked material having an average molecular weight ranging from 25 to 75% of the average molecular weight of the cut from which the

cracked material is derived. In this way a series of cracked materials of serially larger average molecular weight is produced which have been cracked under conditions conducive to the maximum efficiency, under conditions so controlled that the lighter parts of the end product, for example, gasoline, are predominately derived from the lighter cuts of cracked stock, whereas the heavier portions of the end product are predominately derived from the heavier portions of the cracked stock, and under conditions producing the minimum of fixed gas and polymerized material. The cuts which have been cracked through apparatuses 81 to 88, inclusive, may be diverted through the common flow line 90 into the rectifying column 91 which may be of any suitable design. From this rectifying column gasoline may be removed through outlet 92. From the side of column 91 a series of cuts, shown as 93 to 99*a*, inclusive, may be withdrawn and because of their small quantity may be diverted through crackers 81 to 88, inclusive. It will be understood that if the pressure in, or the location of, the tower 91 is not such as to cause liquid to flow through the lines 93 to 99*a*, inclusive, into the lines leading to the crackers 81 to 88, inclusive, suitable pumps and check valves or other well-known apparatus may be employed for effecting this purpose.

The cut 100 may be diverted back to the tubular heater as in the case of cut 51 as is the case likewise with cut 68 from column 57. The cut 68 differs from cuts 100 and 51 in that it represents to a large extent products which have not been converted into those of the desired molecular weight, whereas cuts 51 and 100 are substantially products which have been formed by polymerization since the plant shown is only an approach to the ideal. For the same reason as before outlined, tarry matter may be removed through line 100*a*.

Referring specifically to Fig. 2 which is the diagrammatic elevation of apparatus adapted to processing crude oil or other petroleum oils containing constituents of higher boiling point than gasoline. The charging stock is passed through the tubular heater 1 surrounded by the suitable refractory setting 2, heated by means of the burner diagrammatically indicated at 3, communicating with the setting through the port 4. The crude oil may be heated in heater 1 to a temperature of substantially complete or partial vaporization and is thereafter discharged through pipe 5 into the rectifying column 6. In the event that it is desired to produce a quantity of gas oil or cracking material in addition to that normally occurring from the crude, conditions in the tubular heater 1 may be adjusted to produce a cracking effect, preferably of a moderate character, to convert heavier materials to a considerable extent into products such as kerosene and gas oil, which products are in turn susceptible to being converted into gasoline by a minimum number of molecular disruptions. This operation is not, of course, conducted under the ideal cracking conditions which I have hereinabove described, but is utilized only as a matter of expediency. The rectifying column 6 may be of any suitable type. Provision may, for example, be made to take an overhead cut of gasoline by means of the vapor outlet 7 and a series of side cuts from the outlets 8 to 15, inclusive, and 115 to 118, inclusive. It will, of course, be understood that any alternative number of side cuts may be employed, the design in any case being determined by the character of the stock to be treated and the number of side cuts which it is desired to make. Assuming that cuts such as kerosene and gas oil are taken off from the side outlets 8 to 15, inclusive, these are preferably fairly closely fractionated so that 90% of the total constituents of each cut will boil within a range of say 50° F. Products evolved from the tower 6 which are heavier than gas oil, or so heavy that they cannot be converted into gasoline to a large extent by a single disruption adjacent the midportion of the molecule, may be taken off from the column 6 by means of the side outlets 115 to 118, inclusive, combined in the manifold 115*a* and thereafter treated in the same manner as the products obtained from the outlet 15*a* of Fig. 1. Any heavy residue resulting during the operation may be diverted from the system by means of the outlet 120.

The several side cuts taken from column 6 through the side outlets 8 to 15, inclusive, may be handled in the identical manner as the side cuts taken from column 6 of Fig. 1 through the side outlets 8 to 15, inclusive, and inasmuch as the product taken from column 6 through the side outlets 115 to 118, inclusive, is handled in the identical manner as the products taken from the column 6 in Fig. 1 through the pipe 15*a*, the subsequent progress of these materials may be ascertained by reference to the previous description relating to Fig. 1 and need not be more fully illustrated or described.

Referring specifically to Figs. 3 and 4, the form of cracking apparatus which I prefer to employ for cracking the individual closely fractionated cuts which have been described from time to time is detailed, which apparatus has been designated for example by numerals 24 to 31, inclusive, and 81 to 88, inclusive. This apparatus consists of a refractory setting 150 and may be heated through the port 151 by means of the burner diagrammatically indicated as 152. A baffle wall such as 153 may be provided and a down draft section 154 communicating with a stack 155. The tubular heaters 156 and 157 in the down draft section may comprise a number of tubes through which oil may circulate by means of inlets and outlets 158, 159, 160, 161, respectively, and sections of this character may be utilized for heating or cracking the cuts of relatively wide boiling point corresponding to the operations which have been previously described as conducted in tubular heaters 1, 52. The walls of the setting 150 are preferably lined with a number of relatively short tubular heaters 162 to 177, inclusive, each of which is adapted to the circulation of hydrocarbon materials by means of inlets and outlets such as 166*a* and 166*b*, etc. These sections are relatively short being composed of only a few lengths of tubing adapted to be heated to a large extent by the radiant products of combustion evolved. In operation I prefer to maintain these heaters 162 to 177, inclusive, at temperatures intermediate between 750° and 1500° F. and to conduct cracking operations therein at relatively low pressures ranging from a few atmospheres to subatmospheric. The total time of heating of the hydrocarbon gases at these temperatures is preferably limited to a period ranging from one second up to the order of five minutes, which conditions I find to favor a symmetrical dissociation which is amenable to control with a simultaneous formation of a relatively small quantity of the products of re-association or polymerization. In vapor phase cracking apparatus, such as that

shown, I may admix with the petroleum oil undergoing cracking in the vapor phase a material to limit the formation of polymers. I have discovered the formation of polymers is influenced, among other things, by the concentration of the unsaturates produced by decomposition per unit of space and that this concentration and consequent polymerization may be inhibited or limited by admixing with the petroleum oil a substance which does not deleteriously affect the cracking reaction. In vapor phase reactions I prefer to use a material which is gaseous at the temperature of operation, such as a fixed gas, steam, carbon dioxide, hydrogen, etc. All such substances which are not petroleum oils undergoing cracking and which do not deleteriously affect the cracking reaction, will be hereinafter referred to as diluent gases. The cracked and heated hydrocarbons delivered through the respective outlets of coils 162 to 177, inclusive, are preferably quenched by cooling them immediately either by contact with a liquid or a vapor at temperature below cracking, for example, by contact with steam or by conducting them against relatively cool metal surfaces, for example, through a relatively cool large exchanger. I am thus enabled to control the extent to which the reaction is permitted to proceed and thus determine the constitution of the product. The combination, rectification and subsequent disposition of these products has been hereinabove described.

Referring specifically to Fig. 5, this is a diagrammatic representation of control apparatus which has been indicated by the numerals 16 to 23, inclusive, 71 to 78, inclusive. This apparatus comprises the side outlet, such as 8, carrying a fraction from any one of the rectifying columns hereinabove described, discharging into cracking apparatus such as diagrammatically indicated by the numeral 24. A cooling coil such as 200 is connected into the outlet 8, preferably adjacent the under side thereof. This coil, controlled by the valve 201, discharges into the pipe 8 at a point below its origin. The coil 200 may be surrounded by a receptacle, such as 202, through which a cooling fluid is circulated by means of inlets and outlets, such as 203 and 204, respectively, so that any petroleum oil, either in liquid or vapor form, passing through the coil 200 is automatically cooled and discharged in cooled condition back into pipe 8. By manipulation of the valve 201 the amount of cooled material which is reintroduced into the pipe 8 may be carefully controlled, and in this way the temperature of the products passing into the cracking apparatus 24 may be controlled, and hence the temperature of the products discharged from the cracking apparatus 24 may be correspondingly controlled. The form of apparatus which I have just described is particularly adapted to the close control of vapor phase cracking, which I prefer to conduct in apparatus such as 24 and to which I prefer to subject the various fractions into which I separate my original cracking stock.

Figures 6 and 7 show apparatus for the solvent treating of oil in accordance with my invention. In Fig. 6 the oil to be treated enters through pipe 225 and is subjected to solvent extraction at 226, the constituents comprising a preponderance of saturates being removed through pipe 227 for fractionation in tower 228, while the constituents comprising a preponderance of aromatics and unsaturates are removed through pipe 229 for fractionation in tower 205. From tower 228 the fractionated vapors are removed through 206 and a plurality of reflux condensate fractions of different boiling point ranges are withdrawn through pipes 207, 208 and 209 for further cracking similarly, for example, to the fractions removed as side streams from fractionator 6 in Fig. 1. Reference numeral 210 indicates a pipe through which vapors are withdrawn from fractionator 205, while 211, 212 and 213 indicate conduits for the withdrawal of reflux condensates of different boiling point ranges for further cracking, for example in a manner similar to those withdrawn from fractionator 6 shown in Fig. 1. In Fig. 7 the reverse operation is shown, the fractionation taking place in tower 214 and the solvent extraction in 215 and 216. The oil to be treated is introduced through pipe 217 and fractionated in 214, from which light vapors are removed through 218 and a plurality of side streams of reflux condensate through 219 and 220, these being subjected to solvent extraction in 215 and 216 to form fractions 221 and 222 which include preponderantly saturates and fractions 223 and 224 comprising mainly aromatics and unsaturates.

I claim:

1. The process of treating hydrocarbon oil which comprises separating said oil, by treatment with sulphur dioxide, into two fractions, one containing a preponderance of saturates and the other containing a preponderance of aromatics and unsaturates, dividing each of said fractions into smaller fractions the greater part of the constituents of each which boil within a range of 50° F., independently cracking said smaller fractions and forming a desired blended gasoline distillate from the resulting cracked products.

2. A process in accordance with claim 1 wherein said smaller fractions are cracked in the vapor phase for a short period of time under a pressure ranging between a partial vacuum and a few atmospheres.

3. The process of treating hydrocarbon oil which comprises separating said oil, by treatment with a selective solvent, into two fractions, one containing a preponderance of saturates, and the other containing a preponderance of aromatics and unsaturates, dividing each of said fractions into smaller fractions of different boiling point ranges, independently cracking the said smaller fractions under optimum conditions for the formation of the gasoline distillates and blending gasoline obtained from the resulting cracked products to form the final desired product.

4. The process of treating hydrocarbon oil which comprises separating fresh relatively heavy charging stock into a plurality of components by selective solvent action, one of said components containing a preponderance of saturates and the other containing a preponderance of aromatics and unsaturates, fractionating said components in separate fractionating zones to form a plurality of fractions of different molecular weights, separately cracking resulting fractions under such conditions that the fractions of lower molecular weight form mainly the lower molecular weight fractions of gasoline and the fractions of higher molecular weight form mainly the higher molecular weight fractions of gasoline, separating the resulting cracked products into vapors and liquid residue and forming a desired gasoline distillate from vapors so obtained.

5. The process of treating hydrocarbon oil

which comprises separating said oil, by treatment with sulfur dioxide, in two components, one containing a preponderance of saturates and the other containing a preponderance of aromatics and unsaturates, dividing each of said components into smaller fractions of relatively narrow boiling point ranges, independently cracking said smaller fractions and forming a desired blended gasoline distillate from the resulting cracked products.

6. The process of treating hydrocarbon oil which comprises heating gas oil to a distilling temperature to cause vaporization, fractionally condensing resulting vapors to separate a plurality of fractional condensates of different boiling point ranges, each of said fractional condensates having the greater part of the constituents thereof boiling within a 50° F. range, separating the fractional condensates into a plurality of components, by selective solvent action, in separate zones, one of said components containing a preponderance of saturates and the other containing a preponderance of aromatics and unsaturates, independently cracking said components and forming a final desired blended gasoline distillate from the resulting cracked products.

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