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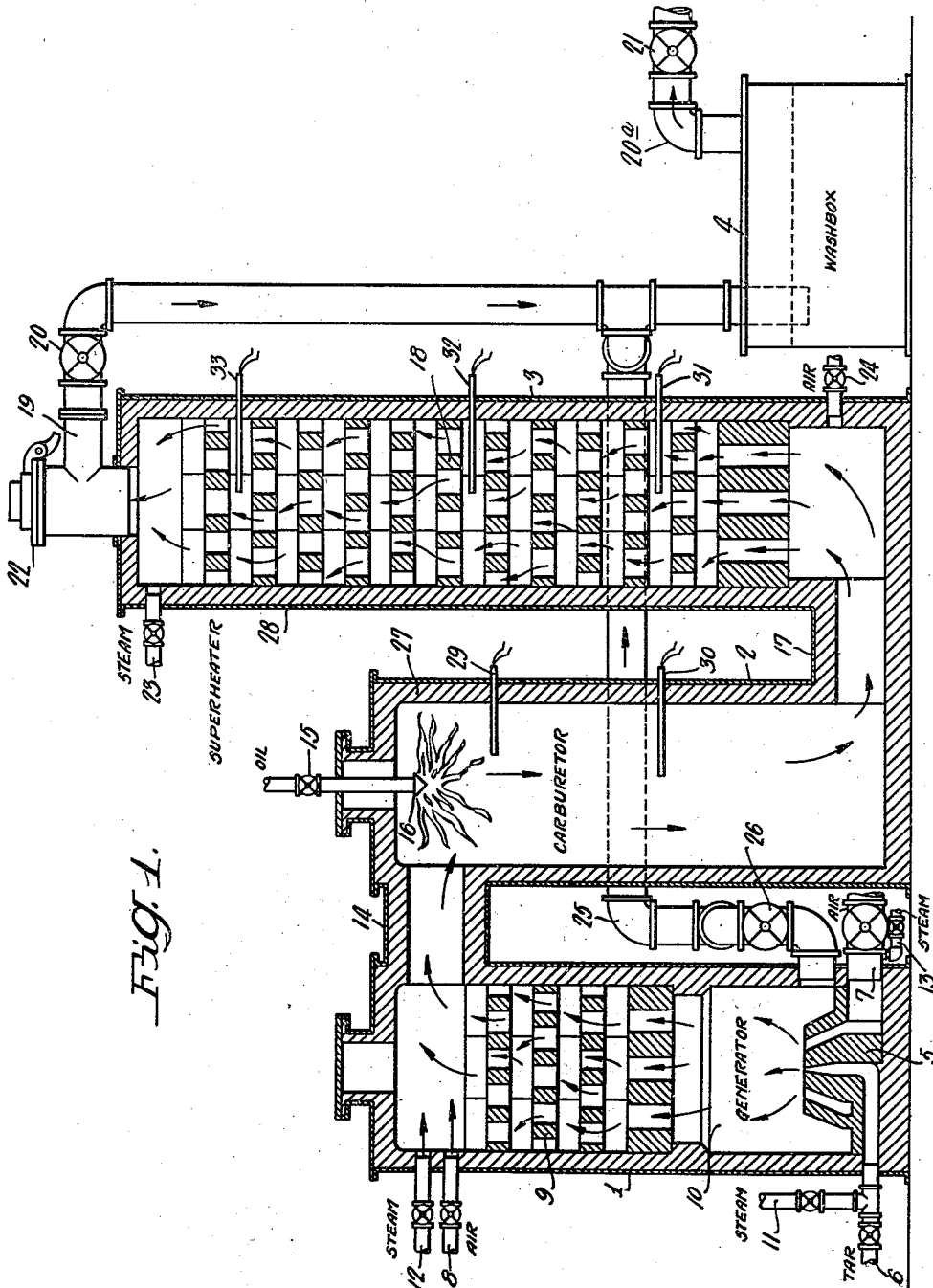
N. K. CHANEY ET AL

2,383,772

PRODUCTION OF VALUABLE HYDROCARBONS

Filed Dec. 28, 1940

3 Sheets-Sheet 1



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3 Sheets-Sheet 2

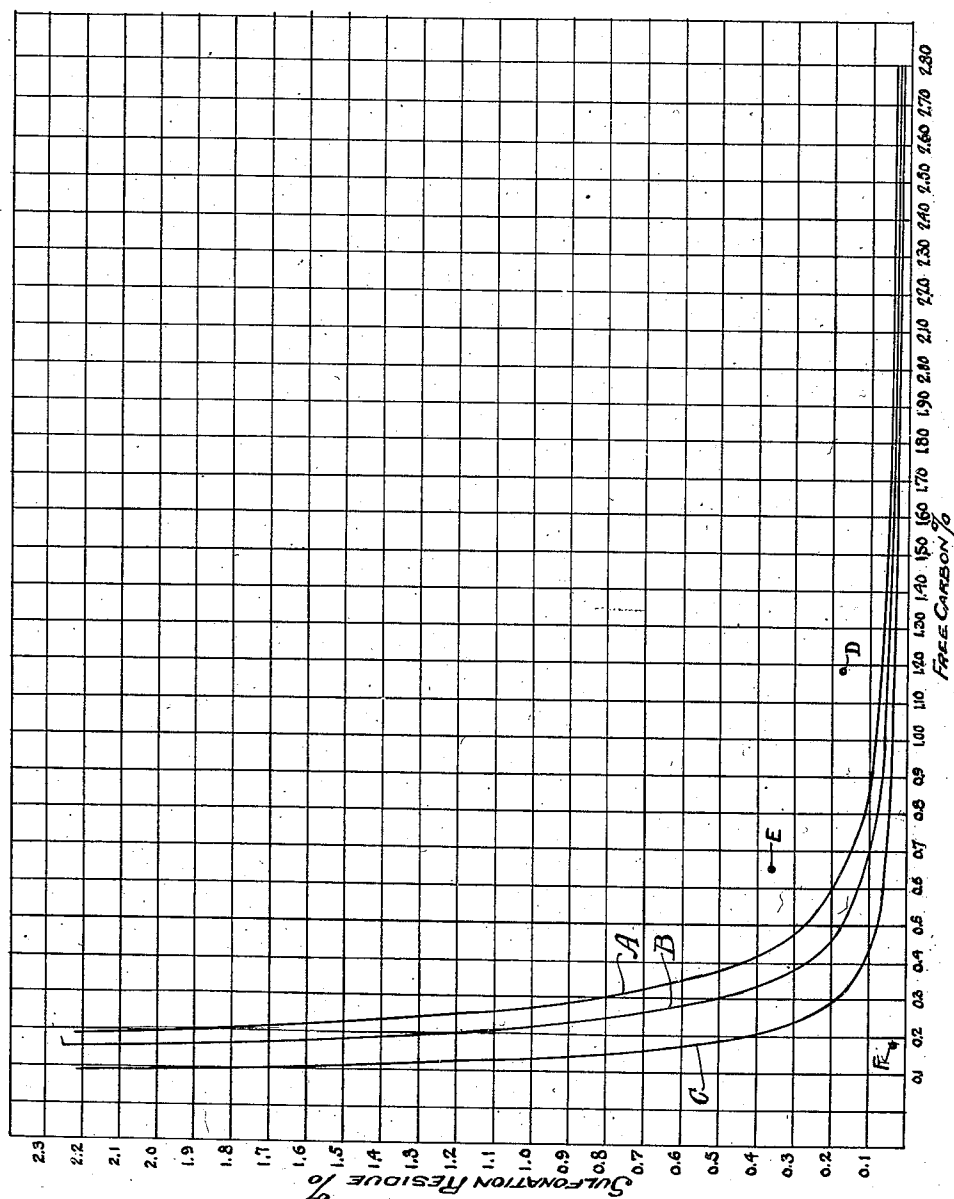


Fig. 2.

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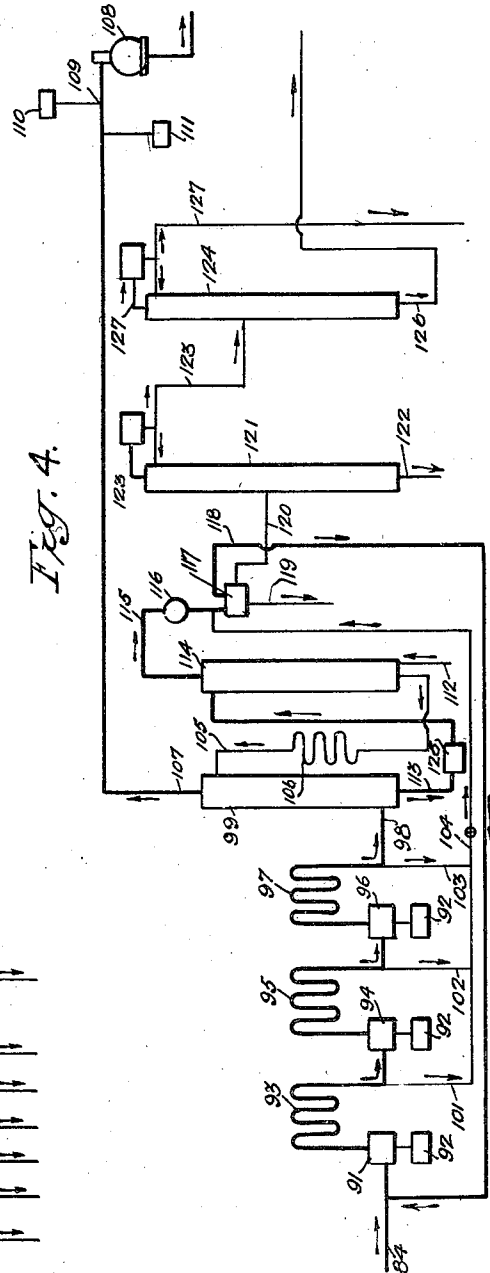
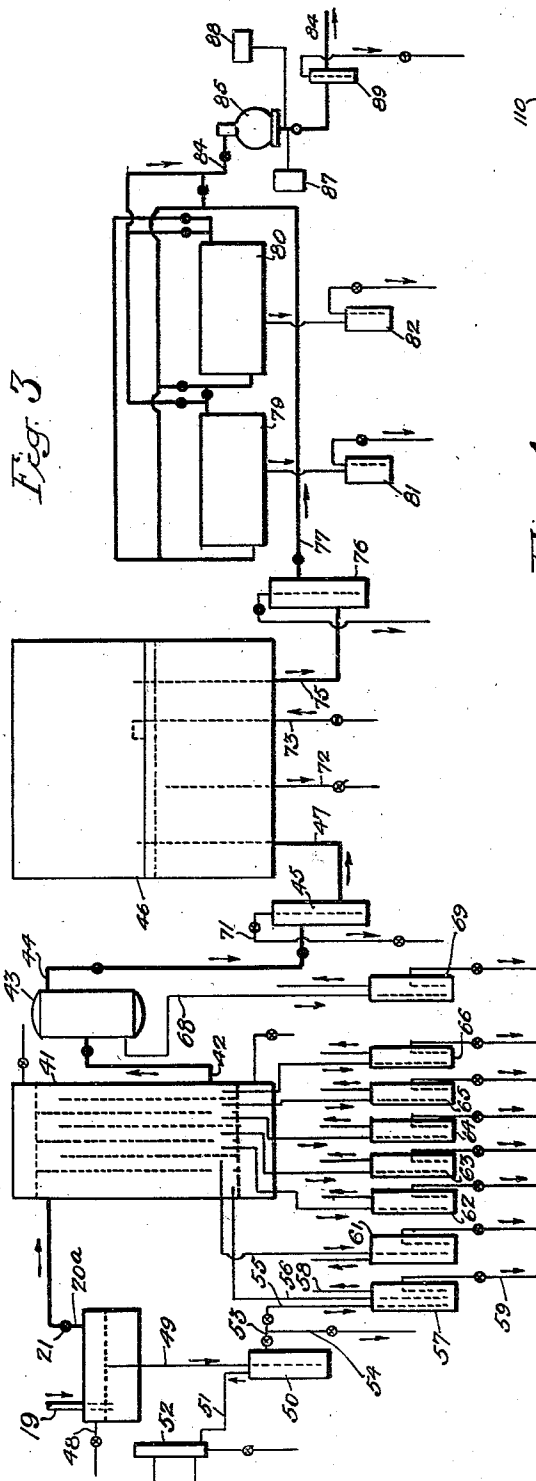
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PRODUCTION OF VALUABLE HYDROCARBONS

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3 Sheets-Sheet 3



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UNITED STATES PATENT OFFICE

2,383,772

PRODUCTION OF VALUABLE
HYDROCARBONS

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Application December 28, 1940, Serial No. 372,074

17 Claims. (Cl. 260-669)

This invention pertains generally to the production of valuable hydrocarbons from petroleum oil by pyrolysis and pertains particularly to the manufacture of relatively large quantities of alkylated and/or alkenated aromatic hydrocarbons and particularly aromatic resin-forming hydrocarbons by such petroleum oil pyrolysis.

By aromatic resin-forming hydrocarbons it is meant to include such compounds as styrene, methyl styrenes, and indene, and by alkylated and/or alkenated aromatic hydrocarbons it is meant to include in addition to aromatic resin-forming hydrocarbons, such compounds as toluene and xylenes. The invention also involves the production of non-aromatic resin-forming hydrocarbons such as isobutylene; the dienes, butadiene, cyclopentadiene, dicyclopentadiene, isoprene and piperylene, non-alkylated aromatic hydrocarbons such as benzene, naphthalene and anthracene, as well as other aromatic hydrocarbons boiling above 200° C. at atmospheric pressure and comprising dead oil and heavy tars.

Normally in the manufacture of oil gas, petroleum oil is pyrolytically decomposed at high temperatures and frequently under conditions of reduced partial pressures resulting from the presence of large volumes of other gases such as steam or water gas, the latter being a mixture of carbon monoxide and hydrogen. The products range all the way from hydrogen and normally gaseous hydrocarbons which are condensible with difficulty to materials of extremely low vapor pressure, such as the less volatile constituents of tar, for example, pitch. A considerable quantity of carbon may also be produced.

These prior art processes are conducted with either of two purposes in mind, namely, (1) the production of large volumes of combustible gas to be distributed as city gas, or (2) the production of motor fuel.

In both instances, the desideratum is to conduct the decomposition of the petroleum oil so as to avoid the production of large quantities of resin-forming hydrocarbons.

In the case of combustible gas for distribution, the presence of relatively large quantities of resin-forming hydrocarbons is highly undesirable since these hydrocarbons have a propensity to form resins throughout the gas distribution system and are responsible for the stoppage of gas

appliance valve orifices, causing the extinction of burners such as pilot burners and the malfunctioning of automatic appliances.

Likewise in the case of motor fuels, the presence of resin-forming hydrocarbons is highly undesirable because of their interference with the proper operation of internal combustion engines.

This invention as distinguished from the processes of the prior art is directed to the production of a relatively larger total quantity of the resin-forming hydrocarbons, particularly aromatic resin-forming hydrocarbons.

More particularly stated the invention comprises (1) the selection of a petroleum oil capable on controlled pyrolysis of producing relatively large yields of alkylated and/or alkenated aromatic hydrocarbons including relatively large yields of aromatic resin formers, and (2) the pyrolysis of said selected oil or a desired cut or cuts therefrom under controlled conditions to be set forth hereinafter.

It is found that the quantitative production of the individual above-mentioned alkylated and/or alkenated aromatic hydrocarbons including aromatic resin-forming hydrocarbons varies widely with the use of different petroleum oils, and that certain physical and chemical characteristics of a petroleum oil, or combinations of these characteristics, may be employed as indices to measure the ability of said petroleum oil to quantitatively produce these compounds under carefully controlled conditions of pyrolysis.

Still more particularly, a petroleum oil is selected which may be classed as predominantly naphthenic as determined by any one or more of a number of chosen methods of classification to be hereinafter more particularly set forth, for instance, by the method of classification described in Bureau of Mines Report of Investigations R. I. 3279.

In carrying out the invention the selected oil is pyrolytically decomposed in vapor phase and in an atmosphere diluted preferably with a readily condensible gas, such as steam, which is preferably present in sufficient quantity to materially reduce the partial pressures of the oil vapors. Preferably the steam is supplied in ratio of at least 2 parts of steam to 3 parts of oil by weight.

The use of water gas in large quantities as a

diluent is preferably avoided among other reasons, because of its relatively high concentration of hydrogen. Thus, we prefer to restrict the presence of any blue water gas to below 30 cubic feet per gallon of oil pyrolyzed and more preferably to below 20 cubic feet per gallon of oil pyrolyzed, said cubic feet being taken as if measured at a pressure of 760 mm. and a temperature of 60° F.

Generally speaking, the preferred operating conditions are of a cyclic character such as is characterized by the conventional cyclic gas making processes, although other types of operation including continuous are within the broad concept of the invention.

Also the process is preferably conducted with total pressures at atmospheric or near atmospheric pressure.

Additionally the environment of the oil pyrolysis is arranged so as to provide for "relatively homogeneous cracking." Homogeneous cracking is defined herein to embrace conditions such, for instance, as concentration of oil vapors, space velocity, turbulence, surface-volume relationships of the interior of the cracking vessel or vessels and character of heated surfaces which are such that in any given plane normal to the flow of materials, the materials throughout the plane have previously had substantially the same opportunity to be heated and to undergo the alternate decompositions and synthesis which comprises cracking and which progress toward products of greater thermal stability under the environment obtaining.

Other conditions being fixed, variation of any one of the following factors in the direction cited is considered to tend toward less homogeneity in the cracking operation: (1) decreased surface/volume ratio of the cracking vessels beyond the vaporizing zone; (2) reduced atomization of the oil; (3) increased impingement of oil on highly heated surfaces prior to vaporization; (4) increased concentration of the oil vapors; (5) decreased turbulence; and (6) increased space velocity except as effecting turbulence.

In addition to relative homogeneity of cracking which as defined would permit wide changes in cracking conditions during a cycle, it is preferred that the cracking conditions also be what is termed herein "relatively uniform" during the cycle.

In a cyclic operation in which oil cracking chambers are heated during a heating period and the stored heat utilized during the cracking period, the quantity of oil gas produced (and the yields of the desired products) per gallon of oil during any individual oil-cracking run will vary somewhat as the temperature of the cracking chambers decreases during said run. The degree of variation will depend among other factors, upon the length of the oil-cracking run, the oil and steam input rates, the presence or absence of supplementary heating during the run, the quantity of heat stored during the heating period and the character of the heat storage material.

Very large swings in oil gas production during a cycle are not preferred as any swing in oil gas production during a cycle necessitates a departure from the optimum conditions within the range of the swing and makes the cracking less uniform over the cycle.

In cyclic operation, other conditions being equal, swings in oil gas production during the cycle may be reduced by reducing temperature

swings during the cycle which is favored by use of a relatively short cycle and/or by the employment of highly conductive heat storage material.

Therefore, the environment of oil pyrolysis hereunder is advantageously arranged to provide not only relatively homogeneous cracking but also relatively uniform cracking.

A convenient measure of the homogeneity and uniformity of the cracking operation is the relation between the sulfonation residue and the free carbon in the condensate from the gas, as will hereinafter appear.

Sulfonation residue is a measure of the normally non-gaseous paraffines and naphthenes surviving the cracking operation, and hence, high sulfonation residue is an indication of light cracking. Free carbon, on the other hand, is an end product in the pyrolysis of hydrocarbons and, hence, high free carbon indicates severe cracking.

High sulfonation residue together with high free carbon indicates that both light and severe cracking have taken place during the cycle and, hence, is an indication either of great lack of homogeneity of cracking, or of great lack of uniformity of cracking, or both.

Inasmuch as the determinations of sulfonation residue and free carbon depend upon the methods of analysis employed, detailed descriptions of the analyses used herein will be given hereinafter and herein when the terms "sulfonation residue" and "free carbon" are employed, they refer to the determinations obtained by said methods of analysis or by equivalent methods.

The present invention includes in addition to relatively homogeneous cracking and relatively uniform cracking the adjustment of the oil pyrolyzing environment including such factors as (1) temperature, and (2) effective time of contact to obtain a desired intensity of cracking. "Intensity of cracking" is conveniently measured by the volume of "residual oil gas" produced per gallon of oil pyrolyzed, although any other suitable method may be employed or devised.

In accordance with this invention the oil pyrolyzing environment is such that per gallon of oil pyrolyzed the volume of "residual oil gas" produced is maintained between 40 and 65 cubic feet taken as if measured at a pressure of 760 mm. and a temperature of 60° F., and preferably between 45 and 60 cubic feet under the same conditions of pressure and temperature.

Other conditions being the same, increase in either (1) temperature or (2) effective time of contact, or both, increases the volume of "residual oil gas" per gallon of oil, and vice versa.

"Residual oil gas" is defined as the uncondensed final gas after removal of substantially all water vapor or after correction for the presence of water vapor, and after the removal of substantially all hydrogen sulfide or after the correction for the presence of hydrogen sulfide (unless the oil is low in sulfur content in which case the hydrogen sulfide is negligible for calculation of residual oil gas), and after removal of substantially all hydrocarbons having more than three carbon atoms, or after correction for the presence of such hydrocarbons having more than three carbon atoms, and after correction for the presence of gas not derived from the oil cracked such as air and combustion gases from fuel used for heating, and after correction for any water gas which may be present. Procedure for making such corrections will be set forth in detail hereinafter.

The oil gas remaining after the above removal of or correction for hydrocarbons having more than three carbon atoms and after correcting for the presence of gases other than oil gas will be referred to herein and in claims as "residual oil gas."

Various procedures for the control of temperature in cyclic gas-making sets are well understood by the skilled gas-maker. These include (1) adjustment of the length of the blast run; (2) adjustment of the rate of fuel consumption during the blast run; (3) adjustment of the length of the blast run with respect to the gas-making run or runs; (4) adjustment of the length of the purge or purges; (5) adjustment of the volume of steam or other gas used for purging; (6) adjustment of the length of the cycle; (7) the use of a reverse run or runs and the adjustment of their length; (8) the use of a reverse purge or purges; (9) the use of auxiliary heating means; (10) adjustment of the point of entry of secondary air and any tertiary air during the blast; and so forth.

Time of contact may be controlled by various factors, one of which is, of course, the dimensions including cross-sectional area, free space and length of the gas-making path of the set. In a given set the length of the gas-making path is more or less fixed and the same applies to the diameters of the various parts thereof such as the diameter of the interior of the carburetter, the diameter of the connection between the carburetter and the superheater, and the diameter of the superheater. With a given oil and steam rate the time of contact may be increased and decreased with increase and decrease respectively of the free space through which the vapors flow, for example, by adjusting the quantity and arrangement of the checkerbrick employed.

Time of contact may also be adjusted by adjusting the oil rate or the steam rate, or both as will be obvious since the larger the combined volume of the gases passing through the set the shorter the time of contact and vice versa.

The rate at which the oil is vaporized in the set, the rate at which the oil is cracked, and the degree to which the oil is cracked are also important factors.

Then too, the point or points of oil admission and the point or points of steam admission are to be considered.

Thus it will be seen that, although any exact mathematical determination of time of contact would be extremely involved, the control of the oil and steam rates, the control of the point or points of entry of oil and steam, and the control of the amount and arrangement of checkerbrick, each alone or in combination, affords to the skilled gas-maker a fairly flexible control of time of contact.

All such factors will be well understood by the skilled gas-maker, making it possible for him, upon becoming familiar with this invention, to readily adjust the operation of his set to yield "residual oil gas" within the ranges in volume specifically set forth above.

Provided conditions of (1) relatively homogeneous cracking and (2) relatively uniform cracking are maintained, the volume of "residual oil gas," as above defined per gallon of oil pyrolyzed is a dependable, convenient and substantially accurate yardstick of (3) the "intensity of cracking."

Since the intensity (or depth or degree) of cracking depends on many factors, such for in-

stance, as true temperature of the oil vapors and gas, the effective time of contact, the concentration of oil vapors, the presence of catalysts and possibly other environmental conditions, it is extremely difficult of measurement by any means available at the present time other than based upon the oil-gas produced. The true temperature, for example, may vary from the observed temperature according to some function of the factors influencing effective time of contact, which in turn may vary from calculated time of contact depending on functions of space velocity, turbulence and the surface-volume relationships of the cracking vessels. True temperature may also vary from observed temperature because of factors involving the pyrometers employed and their positions in relationship to the lining or other heat storage materials in the cracking vessels. It is obvious that many permutations of these factors may be made.

However, if the cracking is (1) relatively homogeneous and (2) relatively uniform, the volume of "residual oil gas" as above defined, is a measure which correlates these environmental factors and gives a convenient and accurate index of (3) the intensity of cracking.

It is as such an index that it is employed herein. The specific volumes of residual oil gas per gallon of oil recited have no utility per se except as a measure of a range of "intensity of cracking," just as certain heights of mercury in a thermometer may have no utility except as a measure of a range of temperatures.

If the cracking is not (1) "relatively homogeneous" and not (2) "relatively uniform," the volume of residual oil gas per gallon of oil pyrolyzed is not an accurate measure of (3) the "intensity of cracking" as the gas may then be composed of large portions of highly cracked material and large portions of lightly cracked material.

To summarize, broadly speaking our invention comprises pyrolyzing (1) a "selected oil" under conditions of (2) "relatively homogeneous cracking" and (3) "relatively uniform cracking," and with (4) the "intensity of cracking" such that (5) the "residual oil gas" falls within the range above given.

The "selected oil" is predominately naphthenic as defined by one or more of the means to be hereinafter more particularly described. "Relatively homogeneous cracking" conditions and "relatively uniform cracking" conditions are defined by the relationship between "sulfonation residue" and "free carbon," which relationship will also be hereinafter more particularly described and illustrated in the drawings. "Residual oil gas" determines the "intensity of cracking" and means for determining "residual oil gas" will also be hereinafter more particularly described.

For convenience, the invention will be further illustrated in connection with the drawings which form a part of this specification and which show a chart useful for determining the relationship between sulfonation residue and free carbon, and illustrate apparatus in which the invention may be conveniently performed, and in which:

Figure 1 shows an elevation partly in section, diagrammatically illustrating a cyclic gas-making set;

Figure 2 shows curves defining sulfonation residue-free carbon relationships; and

Figures 3 and 4 show a flow sheet illustrating the recovery of materials from the gas.

Referring to Figure 1—this figure illustrates diagrammatically apparatus in which the invention may be performed and comprises a cyclic gas-making set which may be conventional.

1 indicates a generator, 2 is a carburetter, 3 is a superheater, and 4 a wash box. The generator 1 is provided with a burner generally indicated at 5, with means for supplying fluid fuel such as tar, generally indicated at 6, and with means for supplying air for combustion of the fuel generally indicated at 7. The generator may be provided with secondary air supply means as at 8. 9 indicates checkerbrick arranged above the combustion space 10. 11, 12, and 13 are steam supply pipes.

The generator 1 is connected at its upper portion to the upper portion of the carburetter 2 by connection 14. The carburetter is illustrated as devoid of checkerbrick and is provided with oil supply means 15 provided with a nozzle 16 capable of finely atomizing the oil.

The carburetter 2 is connected at its base with the base of the superheater 3 by connection 17.

The superheater 3 is shown provided with the checkerbrick indicated conventionally at 18. Off-take 19 provided with valve 20 leads from the top of the superheater to the wash box 4, from whence connection 20a provided with valve 21 leads to condensate recovery equipment and a gas relief holder (not shown).

The superheater is further provided with a stack valve 22 and may be provided with a steam supply means such as steam pipe 23. Air supply means such as 24 may be provided for admitting tertiary air to the superheater.

The generator 1 may be provided with the gas offtake 25, provided with valve 26, and leading from the lower portion of the generator 1 to the wash box 4.

The refractory linings of the carburetter chamber and the superheater indicated at 27 and 28 respectively, as well as the checkerbrick such as in the superheater may if desired be of carborundum or other highly heat conductive material instead of the clay fire brick customarily employed for this purpose. The use of relatively highly heat conductive refractory material, an outstanding example of which is carborundum or silicon carbide, is especially advantageous from the standpoint of obtaining uniformity of cracking since among other things the swing in temperature during any given cycle is thus considerably reduced as compared to the swing when clay fire brick is used.

The carburetter may be provided with checkerbrick as well as the superheater. Checkerbrick in the carburetter if employed are preferably flued rather than staggered to decrease the percentage of liquid oil coming into contact with heated surfaces prior to vaporization. An empty carburetter functions very satisfactorily in this respect.

On the other hand, checkerbrick or its equivalent is definitely preferred in the superheater.

Thus it is preferred to provide a relatively low surface/volume ratio in the oil vaporizing zone and a relatively high surface/volume ratio in the cracking zone.

Other fluid fuel than tar may be employed for heating the generator 1, such for instance, as oil or gas. Further, the generator may be provided with a grate and solid fuel burned thereon for heating instead of fluid fuel, if desired.

Thermocouples such as the shielded thermocouples 29, 30, 31, 32 and 33 may be provided

at spaced intervals through the vaporizing and cracking chambers, their connections leading to temperature recorders (not shown).

An illustrative cycle of operation of the apparatus of Figure 1 will be given.

In operation of the apparatus of Figure 1, fluid fuel such as tar, oil or gas is admitted to the generator burner 5 and burned in the generator, with air supplied through pipe 7. Secondary air may be supplied through air supply pipe 8. The burning products pass from the generator to the carburetter 2 by way of connection 14 and thence through the carburetter to the superheater by way of connection 17. Tertiary air may be supplied through air supply means 24, if desired. The combustion products pass through the superheater and through the stack valve 22 to atmosphere or to a waste heat boiler (not shown). During this operation, the stack valve 22 is open and valve 26 is closed.

This operation, termed the blow, heats and stores heat in the checkerbrick and lining of the generator, the lining of the carburetter and the checkerbrick and lining of the superheater.

The tar may then be shut off and a short air purge made by air admitted through air supply means 7, followed by a short steam purge with steam supplied to the base of the generator as at 13. The purged products pass out of the set through the stack valve 22.

After the set is purged, and with the stack valve 22 closed, valve 26 closed, and valves 20 and 21 open, petroleum oil selected as previously and hereinafter further described, is admitted to the carburetter top and finely atomized by the nozzle 16 into the void space of the carburetter. Simultaneously, steam is admitted to the generator through the steam supply 13 in the generator base, heated in passage through the generator checkerbrick and passed into the carburetter top by way of connection 14. A portion or all of the steam may be admitted through the steam supply means 12 at the generator top above the checkerbrick, instead of through 13 at the bottom, and/or the temperature of the steam may be controlled by proportioning the quantities admitted to the two portions of the generator.

The oil is vaporized in the carburetter in the presence of the superheated steam from the generator, the quantity of steam being sufficient to materially reduce the partial pressure of the oil vapors.

The vaporized oil and steam pass down through the carburetter and into the superheater through connection 17. Some cracking may take place in the carburetter.

From the base of the superheater the vaporized oil, steam and partially cracked vapors pass upward through the superheater checkerbrick in which the desired pyrolysis is completed.

The reaction products and steam pass through connection 19, the wash box 4, and connection 20 to a relief holder (not shown) and thence through condensing or other apparatus (not shown) for the removal of the desired products from the gas.

After this operation, termed the run, the oil admission may be discontinued and the reaction products purged from the set by steam admitted to the generator, the reaction products being purged into the relief holder through the wash box.

The cycle may then be repeated. The above cycle is merely illustrative, it may be very greatly

modified. For instance, a back run with steam or steam and oil may be made during the cycle, with steam or steam and oil supplied through supply means 23. In such case, the stack valve 22 is closed, valve 20 is closed and valve 26 open. The steam or steam and oil vapors and reaction products pass reversely through the superheater, carburetter and generator and through connection 26 to the wash box and to the relief holder (not shown).

The fluid fuel burner as a means of providing heat during the blow is preferred, but recourse might be made to the use of a solid fuel bed as in the conventional water gas generator, with the difference that it is preferred not to pass any large quantity of water gas through the carburetter and superheater during the oil cracking period. Other means for superheating steam for the process might be then employed or saturated steam employed. The use of superheated steam, however, is preferred as it reduces the heating load on the carburetter.

During the blow, the operation is conducted to obtain the desired distribution of heat throughout the carburetter and superheater.

The following table will illustrate a typical swing in temperature at various points in a given set during a typical blow in the process of the invention. The temperatures were determined by the standard shielded type of thermocouple.

Table

Point in set	Temperature °F. start of blow	Temperature °F. end of blow
Carburetter top.....	1,405	1,685
Carburetter middle.....	1,415	1,665
Superheater base.....	1,455	1,545
Superheater middle.....	1,460	1,500
Superheater top.....	1,458	1,472

The temperature gradient throughout the set will vary with operating conditions and the nature and size of the set and the set lining and checkerbrick or other heat storage material.

In the case of set lining and other refractory material present, this is in a measure associated with the relative heat conductivity thereof. For instance, the substitution of refractory brick made of silicon carbide for refractory brick made of ordinary fire clay will shift the temperature gradient of the set and other conditions being equal will reduce the temperature swing throughout the cycle.

The temperature gradient naturally set up by the blow may be modified prior to the run by the injection of steam or other fluids to the top of the carburetter and/or the base and/or top of the superheater and/or to the generator. It may be employed to remove peak temperatures. Reference is made to copending application Serial Number 191,441, filed February 19, 1938, by Edwin L. Hall, now Patent 2,372,197, dated March 27, 1945.

The point or points of introduction of the oil may vary in different gas making equipment, from those chosen for illustration.

A carburetter devoid of checkerbrick is preferred for use in vaporizing the oil, but checkerbrick may be employed therein. The oil whether coming into contact with refractory surfaces in significant quantity or not is subjected to the temperatures of the carburetter and superheater with the steam and is decomposed in a manner essentially different from the decomposition of oil

when the principal object is gas making, or when the principal object is the production of motor fuel.

The temperatures given above are purely illustrative in character and the temperature conditions as well as other conditions governing pyrolysis of the oil will vary with different types of operation or equipment.

As previously pointed out, having selected a predominantly naphthenic oil, its pyrolysis is controlled by the gas maker, (modifying the interior of his set in accordance with the above observations if he finds it necessary or desirable), such that (1) the relationship between sulfonation residue and free carbon does not exceed certain maxima and (2) the residual oil gas falls within the range given. The relationship between sulfonation residue and free carbon determines (a) relatively homogeneous and (b) relatively uniform cracking conditions and the residual oil gas determines (c) the intensity of cracking.

Since determinations of sulfonation residue and free carbon may vary somewhat with the methods of analysis employed, detailed procedures of analyses for these respective factors will be given herein, it being understood that values for sulfonation residue and for free carbon as expressed in the claims are to be determined by these detailed procedures, or their equivalents for definitive purposes, and that other yardsticks might be devised for the same purpose without departing from the invention.

An overall sample of the tar (wet) resulting from the pyrolysis of a known quantity of oil and obtained by condensation from the resulting gas by bringing the gas down to a temperature of approximately 90° F. is heated in a batch in a stillpot with stirring and with some reflux of the heavier distillate until a dry residual tar having a viscosity of 1000 S. S. U. at 210° F. is obtained. It usually requires several hours to remove the water from the tar.

After separation of the water layer, if water is present, sulfonation residue is determined upon the hydrocarbon distillate obtained, and is expressed as per cent of the original oil by volume.

Free carbon is determined upon the dry residual tar and is expressed in per cent of the original oil by weight.

Free carbon determination is as follows.

Determination of free carbon

Free carbon is determined in the manner described in The Gas Chemists Handbook, 3rd edition, 1929, a publication of the American Gas Association, pages 425 and 426.

Sulfonation residue determination is as follows.

Determination of sulfonation residue

250 ml. sample of the above hydrocarbon distillate is shaken with 5% by volume (12.5 mls.) of 94% H₂SO₄ in a 500 ml. separatory funnel.

The acid is gradually and cautiously added and the temperature kept below 25° C. by immersing the funnel in ice water when necessary.

After the reaction is completed the contents of the flask are transferred in approximately equal portions to each of two small separatory funnels (150 ml. Squibb separatory funnels).

The acid-washed oil is then centrifuged in the smaller funnels for approximately five minutes at 500-600 R. P. M. using a laboratory centrifuge adapted to accommodate these funnels.

The acid sludge is run off slowly from each funnel into 200 mls. of ice water contained in a

beaker. The acid sludge will sink to the bottom of the beaker and disperse into the water when stirred. The first drop of oil will spread over the surface of the water showing that the end of sludge separation has been reached.

The contents remaining in the funnels are then washed with two successive portions of about 5% by volume of water, followed by centrifuging for two minutes at 500-600 R. P. M. and the separated wash water run off.

The oil is then washed with two successive portions of 5% by volume of 20% KOH solution followed by centrifuging for two minutes at 500-600 R. P. M. and separation of the alkaline solution.

A final wash of 5% by volume of water is made followed by centrifuging for two minutes at 500-600 R. P. M. and separation of the wash water.

The oil is dried by adding a few granules of 4-mesh anhydrous calcium chloride, and filtering, and the volume of dry oil measured.

100 mls. of the washed and dried oil are distilled in the following manner. The oil is put in a 200 ml. round bottom Pyrex boiling flask. The flask is then connected with a small Hempel distilling tube using a cork stopper. The top of the distilling tube is fitted with a two-hole cork stopper containing a thermometer (-5°C. to $+360^{\circ}\text{C.}$ in 1°C. intervals, 75 mm. immersion) and a draw-out capillary tube extending to the bottom of the flask. The purpose of the capillary tube is to admit a small stream of air during vacuum distillation for the purpose of preventing bumping.

The outlet of the Hempel distilling tube is connected to a Liebig condenser. The outlet of the condenser is connected to a Bogert distilling receiver. The pressure at which the vacuum distillation is conducted is regulated at the outlet of the Bogert receiver by means of a suitable type needle valve.

Any suitable vacuum pump may be used to reduce the pressure to 30 mm. mercury for the final distillation.

Distillation is made at two pressures—(a) oil boiling up to 160°C. is distilled off at atmospheric pressure, and (b) higher boiling fractions are distilled at 30 mm. mercury pressure and the distillation stopped when the temperature reaches 270°C.

If the material being distilled shows any of the characteristic signs of decomposition before the temperature of 270°C. is reached, the distillation is discontinued. The oil boiling up to 160°C. at atmospheric pressure is removed from the Bogert receiver before starting the vacuum distillation. Low pressure steam should be available for use in melting any naphthalene accumulations which may cause stoppages in the condenser tube.

The two distillates are mixed and the total volume recorded. Sulfonation residue tests are made on 10 ml. portions of the mixture in a Babcock milk testing bottle with 30 mls. of 100% H_2SO_4 added, followed by heating and shaking periods (six ten-minute heating periods at $98-100^{\circ}\text{C.}$, each of which is followed by a two-minute shaking period). Any unsulfonated oil is floated into the neck of the Babcock bottle with 94% H_2SO_4 where its volume is measured. This quantity of material expressed as a percentage by volume of the original oil is the per cent sulfonation residue employed herein.

Referring to Figure 2.

In this figure, per cent sulfonation residue as above determined and defined is plotted against

per cent free carbon as above determined and defined.

The area to the left and below curve A embraces the relations between sulfonation residue and free carbon defining relatively homogeneous and relatively uniform cracking conditions hereunder.

More preferably cracking conditions are selected to produce relationships between sulfonation residue and free carbon falling within the area to the left and below curve B.

Still more preferably cracking conditions are selected to produce relationships between sulfonation residue and free carbon falling within the area to the left and below curve C.

The area to the right and above curve A embraces relationships between sulfonation residue and free carbon which define relatively non-homogeneous and/or relatively non-uniform cracking conditions hereunder.

The formulae for curves A, B and C are as follows:

$$\text{Curve A} \text{ ----- } X^{2.3}(y-0.03)=0.05$$

$$\text{Curve B} \text{ ----- } X^{2.3}(y-0.03)=0.03$$

$$\text{Curve C} \text{ ----- } X^{2.3}(y-0.03)=0.01$$

in which

x =per cent free carbon as above described and defined

y =per cent sulfonation residue as above described and defined.

Moving to the right from the area to the left and below curve C, to the area between curves C and B and thence to the area between curves B and A, relationships of sulfonation residue and free carbon are encountered which progressively define less homogeneous and/or less uniform cracking conditions. To the right and above curve A, these relationships are such as to no longer define relatively homogeneous and relatively uniform cracking hereunder.

As previously stated the present invention includes adjusting the oil pyrolyzing environment including such factors as temperature, effective time of contact and concentration of oil vapors so that per gallon of oil the total volume of oil gas produced after the removal of substantially all water vapor, or after correction for the presence of water vapor; and after the removal of substantially all hydrogen sulfide, or after the correction for the presence of hydrogen sulfide (unless the oil is low in sulfur content, in which case the hydrogen sulfide is negligible for calculation of residual oil gas); and after removal of substantially all hydrocarbons having more than three carbon atoms, or after correction for the presence of hydrocarbons having more than three carbon atoms; and after correction for the presence of gas not derived from the oil cracked such as air, combustion gases from fuel used for heating and any water gas which may be present, is maintained between 40 and 65 cubic feet taken as if measured at a pressure of 760 mm. and a temperature of 60°F. , and preferably between 45 and 60 cubic feet under the same conditions of pressure and temperature.

The volume of residual oil gas may be calculated as follows:

Determination of residual oil gas

The gas may be metered and sampled at any convenient stage in its condensation and purification, preferably however after purification from H_2S . Water vapor is removed from a measured portion of the sample and the water vapor content of the gas calculated in per cent of the gas

by volume, according to methods set forth in the Gas Chemists Handbook, 3rd edition, 1929, a publication of the American Gas Association, or their equivalent. The dried portion of the sample may be analyzed by low temperature fractionation as by means of the well known Poddelniak gas analysis apparatus or its equivalent. This apparatus has been described in Industrial and Engineering Chemistry, analytical edition, March 15, April 15, and May 15, 1933, and its use in hydrocarbon gas analysis is very well known to those skilled in the art.

By the above means, the dried sample may be divided into four portions: (1) containing H_2 , N_2 , O_2 , CO , CO_2 , CH_4 , and any H_2S , CS_2 , HCN , SO_2 , NH_3 present, (2) containing C_2 hydrocarbons such as C_2H_4 and C_2H_6 , (3) containing C_3 hydrocarbons such as C_3H_6 and C_3H_8 , and (4) containing C_4 hydrocarbons and hydrocarbons of higher carbon content. The per cent by volume relationship of these portions to the original undried gas may be readily calculated.

Another measured portion of the original sample may be analyzed for H_2S according to methods described in the above mentioned Gas Chemists Handbook. From the analysis the percentage of H_2S by volume in the gas as metered may be readily calculated.

Portion 1 may be analyzed for H_2 , N_2 , O_2 , CO and CO_2 , by means of the well known Hempel apparatus or its equivalent by methods described in the above mentioned Gas Chemists Handbook or their equivalents which methods include the initial removal of H_2S and the percentage by volume of these constituents in the gas as metered calculated.

All of the N_2 , O_2 and a portion of the CO_2 are considered to be derived from air and combustion gases. The CO , the remainder of the CO_2 and a portion of the H_2 are considered to be derived from any water gas present. The remainder of the H_2 is considered to be part of the oil gas. The method of apportionment of the CO_2 between combustion gas and water gas and of the H_2 between water gas and oil gas is as follows:

$$\frac{\% N_2}{0.80} - (\% N_2 + \% O_2) = \% CO_2 \text{ in combustion gases} = \% CO_2 (C. G.)$$

$$\% \text{ air and combustion gases} = \% N_2 + \% O_2 + \% CO_2 (C. G.)$$

$$\% CO_2 - \% CO_2 (C. G.) = \% CO_2 \text{ in water gas} = \% CO_2 (W. G.)$$

$$2 \times \% CO_2 (W. G.) + \% CO = \% H_2 \text{ in water gas} = \% H_2 (W. G.)$$

$$\% \text{ water gas} = \% CO + \% H_2 (W. G.) + \% CO_2 (W. G.)$$

The above apportionment of CO_2 and H_2 is known to be approximate as the percentages of CO and CO_2 in water gas vary with the temperature of its generation. The approximation is however sufficiently accurate for the purpose of calculating the residual oil gas.

The CS_2 , SO_2 , HCN , and NH_3 contents of the gas may be assumed to be negligible in the calculation of the residual oil gas unless these materials are known to be present in significant quantities which is usually not the case.

If the gas be metered and sampled after the usual H_2S purification, the H_2S may be assumed to be negligible for this calculation also, as the usual H_2S purification removes practically all of the H_2S as well as HCN and SO_2 .

If the oil employed is not high in sulphur content, the H_2S may be negligible for the calculation of residual oil gas even before H_2S purification.

When employing low sulphur oils the H_2S content of the gas prior to H_2S purification may be of the order of 50 grains per 100 cu. ft., equivalent

to approximately .08% by volume, which would be insignificant.

If a high sulfur oil is employed the H_2S content of the gas prior to H_2S removal might not be negligible in the calculation of residual oil gas and therefore if the gas be metered and sampled prior to H_2S purification, the H_2S content should be determined and the volume of H_2S deducted in calculating the residual oil gas.

From the volume of total gas in cubic feet as metered and the volume of oil pyrolyzed in its manufacture, in gallons, the cubic feet of total gas per gallon of oil under the pressure and temperature conditions of metering may be readily calculated. The volume of total gas per gallon of oil is for convenience called V_1 .

$$V_1 \times \% \text{ air and combustion gases} = \text{cubic feet of air and combustion gases per gallon of oil} = V_2$$

$$V_1 \times \% \text{ of water gas} = \text{cubic feet of water gas per gallon of oil} = V_3$$

$$V_1 \times \% C_4 \text{ hydrocarbons and higher} = \text{cubic feet of } C_4 \text{ hydrocarbons and higher per gallon of oil} = V_4$$

$$V_1 \times \% \text{ water vapor} = \text{cubic feet of water vapor per gallon of oil} = V_5$$

$$V_1 \times \% H_2S = \text{cubic feet of } H_2S \text{ per gallon of oil} = V_6$$

$$V_1 - (V_2 + V_3 + V_4 + V_5 + V_6) = \text{cubic feet of residual oil gas per gallon of oil under the pressure and temperature conditions of metering} = V_7$$

If P = gas pressure as metered in mm. Hg and T = gas temperature as metered in °F. absolute.

$$V_7 \times \frac{P}{760} \times \frac{519.6}{T} = \text{residual oil gas in cubic feet per gallon of oil at a pressure of 760 mm. and a temperature of 60° F.}$$

If the gas is metered and analyzed after the usual H_2S purification V_6 need not be deducted or calculated.

If the gas be metered and analyzed after condensation of substantially all of the C_4 hydrocarbons, the volume V_4 will be very small and the volume of water vapor V_5 will be negligible, and both may, under such circumstances, be neglected without introducing substantial error.

For purposes of calculating residual oil gas, a sharp separation between hydrocarbons of three carbon atoms and hydrocarbons of four carbon atoms is not found to be essential, since even if a fair percentage of the hydrocarbons of four carbon atoms is left in the gas the total volume of residual oil gas is not greatly increased.

Due to the difficulty of condensing hydrocarbons of three carbon atoms or lower, no large portions of these hydrocarbons will ordinarily condense along with the hydrocarbons of four carbon atoms and higher.

As an example of homogeneous and uniform cracking the following is given:

Example 1

A cyclic cracking operation was carried on in a three shell set connected in series similar to that diagrammatically illustrated in Figure 1. The carburetter and superheater were 2' 9" in internal diameter. The carburetter was approximately 9' 5" long inside and the superheater was approximately 16' 9" long inside, they were connected at their bases by a connection 1' 0" internal diameter and 2' 6" long. Both carburetter and superheater were lined with Carborundum refractory brick. The carburetter was devoid of checkerbrick. The superheater was provided with 29 courses of Carborundum checkerbrick of standard size 4½" x 9" x 2½" set edgewise 3" apart with alternate courses in staggered relationship.

The cycle length was 3 minutes, 45% of which was occupied in heating and 33% by the oil admission period, the remaining portions of the

cycle were devoted to purges of combustion products and of oil gas.

The oil selected in accordance with this invention, was a Texas coastal crude oil from the Placedo field, a number 7 oil according to the Bureau of Mines Index to be hereinafter more particularly described, and having a Conradson carbon content below 4%. The oil was admitted to the carburetter top during the run at a rate of 4.02 gals. per minute with steam (heated in the generator) at a rate of 30.6 lbs. per minute.

The maximum and minimum and average temperatures as observed by shielded thermocouples at spaced intervals through the set were as follows:

	Maximum	Minimum	Swing	Average
	°F.	°F.	°F.	°F.
Carburetter top.....	1,685	1,405	280	1,545
Carburetter middle.....	1,665	1,415	250	1,540
Superheater base.....	1,535	1,465	70	1,500
Superheater middle.....	1,500	1,460	40	1,480
Superheater top.....	1,472.5	1,457.5	15	1,465
Ave. set temp.....				1,512

The yield of residual oil gas per gallon of oil was 52.1 cubic feet. The sulfonation residue, determined as above described was less than 0.03%. The free carbon, determined as above described, was 0.19%.

The relationship between sulfonation residue and free carbon is expressed by the point F in Figure 2.

As an example of non-homogeneous cracking the following may be given:

Example 2

A cyclic cracking operation was carried on in a three shell set, connected in series in a similar manner as the shells of a three shell carburetted water gas set. The carburetter and superheater were 2' 9" in internal diameter lined with Carborundum brick and both were devoid of checker-brick. The carburetter was approximately 9' 5" long inside and the superheater approximately 23' 6" long inside. The surface/volume ratio of the superheater in sq. ft./cu. ft. was approximately 1.6 as compared to 12.4 in the checkered portion of the superheater in Example 1.

The carburetter and superheater were heated during the heating period by tar burned in the generator, the resultant products passing through the carburetter and superheater.

During the cracking period oil was atomized into the top of the carburetter in the presence of steam which was heated in the generator and passed thence into the carburetter top. The oil was vaporized in the carburetter and the cracking of the oil vapors initiated therein. The mixture of steam, oil vapors and some oil gas resulting from the cracking passed from the carburetter to the superheater for further cracking of the oil constituents and thence to apparatus for the condensation of hydrocarbons of 4 carbon atoms and higher.

The cycle length was 3 minutes of which 45% was occupied in heating, 33% in the oil admission period and the remainder in purges of the apparatus of blast products and of oil gas.

The oil was a Texas Coastal Crude oil from the Placedo field, a No. 7 oil according to the Bureau of Mines Classification, to be hereinafter more particularly described, and having a Conradson carbon content of less than 4%. It was admitted at a rate of 3.96 gals. per minute, and

steam was admitted with the oil at a rate of 30.6 lbs. per minute.

The maximum and minimum temperatures through the cycle as observed by shielded thermocouples at spaced intervals through the carburetter and superheater were as follows:

	Maximum	Minimum	Swing	Average
	°F.	°F.	°F.	°F.
Carburetter top.....	1,925	1,595	350	1,760
Carburetter middle.....	1,895	1,505	390	1,700
Superheater base.....	1,670	1,480	190	1,575
Superheater middle.....	1,602.5	1,497.5	104	1,550
Superheater ext.....	1,537.5	1,512.5	65	1,550
Ave. set temp.....				1,615

The residual oil gas yield was 57 cubic feet per gallon of oil. The sulfonation residue determined as above described was 0.18. The percent free carbon determined as above described was 1.19. This relationship of sulfonation residue and free carbon is expressed by the point D in Figure 2.

Example 3

An operation similar to that of Example 2 was performed at lower temperatures, with set conditions other than temperature, oil and steam input, cycle length and subdivision remaining the same.

The observed temperatures at the same portions of the set were as follows:

	Maximum	Minimum	Swing	Average
Carburetter top.....	1,562.5	1,557.5	305	1,710
Carburetter middle.....	1,532.5	1,467.5	365	1,650
Superheater base.....	1,615	1,435	180	1,525
Superheater 9' 2" from bottom.....	1,582.5	1,437.5	145	1,510
Superheater 12' 11" from bottom.....	1,540	1,460	100	1,490
Superheater top.....	1,517.5	1,462.5	65	1,485
Average set temperature.....				1,581

The yield of residual oil gas was 50.3 cubic ft./gal. of oil. The sulfonation residue, determined as above described, was 0.36%. The free carbon, determined as above described, was 0.65%.

The relationship between sulfonation residue and free carbon is expressed by the point E in Figure 2.

In Example 1 the total yield of the more desirable products was not only higher than in Examples 2 and 3 but individual products were of markedly higher quality.

For example, the total yield of certain very desirable aromatic resin-forming hydrocarbons, namely, styrene, methyl styrene, and indene, was 27.7 pounds per 100 gallons of oil in Example 1; 20 pounds per 100 gallons of oil in Example 2; and 19.1 pounds per 100 gallons of oil in Example 3. In Example 1 these materials were in a form in which they could be readily purified for the production of high quality resins, whereas in Examples 2 and 3 considerable contamination of an extremely difficultly removable nature was present which destroyed the quality of the resins produced particularly in the case of styrene.

The total recovery of certain very desirable non-aromatic resin-forming hydrocarbons, namely, cyclopentadiene, butadiene, isoprene and perylene, was 26.4 pounds per 100 gallons of oil in the case of Example 1; 12.9 pounds per 100 gallons of oil in the case of Example 2; and 24.2 pounds per 100 gallons of oil in the case of Example 3. Thus the yield in Example 1 was substantially twice that in Example 2 and somewhat larger than that in Example 3. In Examples 2

and 3 these materials were obtained in considerably lower concentration in the condensate, there being present a considerably larger quantity of similarly boiling materials. This introduced a problem of separation of a magnitude much greater than that in the case of Example 1.

Thus the recovery of indene, methyl styrene, styrene, cyclopentadiene, piperylene, isoprene and butadiene totaled 54.1 pounds per 100 gallons of oil in Example 1 as against 32.9 pounds in Example 2 and 43.3 pounds in Example 3. Furthermore, the products in Example 1 were generally of very much higher quality which is an extremely important consideration when dealing with raw materials to be employed in resin production.

Referring now to the lower boiling saturated aromatics, namely, benzene, toluene and solvent naphtha, the total yield in Example 1 was 105.9 pounds per 100 gallons of oil; 104.6 pounds per 100 gallons of oil in Example 2 and 101.5 pounds per 100 gallons of oil in Example 3. While the yield in Example 1 was not particularly greater, these materials were considerably less contaminated. For example, the toluene obtained in Example 1 was readily purified for nitration purposes, whereas the toluene obtained in Examples 2 and 3 was industrially unsuitable for nitration purposes.

From the foregoing comparisons the outstanding advantages of the invention become readily apparent.

Due at least in part to the different thermal stabilities of the various products, it has not been found that any one set of operating conditions results in maximum production of all of the several products.

However, within the range of residual oil gas set forth, will be found the peak yields of styrene, the peak yield of toluene, the peak sum of the yields of toluene, solvent naphtha, styrene, methyl styrenes and indene, the peak sum of the yields of styrene, methyl styrenes and indene, the peak sum of the yields of styrene and cyclopentadiene.

Within the preferred range of residual oil gas set forth good yields of benzene, naphthalene, other saturated and unsaturated aromatic compounds contained in dead oil and residual tar, and of butadiene, isoprene, and piperylene may also be secured.

Higher yields of benzene and naphthalene and residual tar may be secured beyond the range of residual oil gas set forth on the high side, but accompanied by reduced yields of styrene, indene and toluene, low yields of methyl styrene, solvent naphtha and dead oil, and very low yields of the dienes particularly butadiene, isoprene and piperylene. The styrene may also be contaminated by relatively large quantities of phenyl acetylene.

Higher yields of solvent naphtha, methyl styrene, the dienes, and dead oil may be secured beyond the range of residual oil gas set forth on the low side. The solvent naphtha, benzene and toluene in such case are contaminated with relatively large quantities of olefines boiling within their boiling ranges and the dienes are in relatively low concentration among other C₄ and C₅ products.

Referring now more particularly to the character of the oil pyrolyzed, as previously stated, this comprises crude petroleum oils or a suitable cut or cuts from crude petroleum oils which may be classed as predominately naphthenic as determined by any one or more or a number of chosen methods of classification which will now be more particularly set forth.

Oil classification

In the classification of a crude oil in accordance with the Bureau of Mines method disclosed in Bureau of Mines Report of Investigations R. I. 3279, previously referred to, a given petroleum oil is subjected to fractional distillation and two cuts are collected, the first having a boiling range between 250° and 275° C. at atmospheric pressure, and the second having a boiling range between 275° and 300° C. at 40 mm. absolute pressure.

For convenience of identification, the lower boiling fraction is referred to as key fraction 1 and the higher boiling fraction is referred to as key fraction 2.

From the API gravities of these key fractions, the classification of the original oil is made as follows:

If the API gravity of key fraction 1 is 33 or below 33, the fraction is classified as naphthenic; if it is between 33 and 40 the fraction is classified as intermediate; and if it is 40 or above 40 the fraction is classified as paraffinic.

If the API gravity of key fraction 2 is 20 or below 20, the fraction is classified as naphthenic; if it is between 20 and 30 the fraction is classified as intermediate; and if it is 30 or above 30 the fraction is classified as paraffinic.

As a result of the foregoing classifications of the key fractions, the original oil is given one of seven classifications as follows:

If both key fractions are paraffinic, the original oil falls in class 1. If key fraction 1 is paraffinic and key fraction 2 is intermediate, the original oil falls in class 2.

If key fraction 1 is intermediate and key fraction 2 is paraffinic the original oil falls in class 3.

If both key fractions are intermediate, the original oil falls in class 4.

If key fraction 1 is intermediate and key fraction 2 is naphthenic the original oil falls in class 5.

If key fraction 1 is naphthenic and key fraction 2 is intermediate the original oil falls in class 6.

If both key fractions are naphthenic, the original oil falls in class 7.

Based upon the foregoing classification in accordance with the present invention, we employ oils falling within the classes 5 to 7 inclusive, or desired cuts from such oils; with class 7 oils or a desired cut or cuts therefrom preferred, provided, however, that in the case of any oil selected whether a crude or a cut, the Conradson carbon of the oil does not exceed approximately 7% and preferably does not exceed approximately 4%.

The test for Conradson carbon has been standardized under the American Society of Testing Materials Designation D189-36 and "Conradson carbon" as used herein is that Conradson carbon determined under such procedure.

The percentage of Conradson carbon is an indirect measure of the tendency of an oil to form carbon and hydrogen on pyrolysis instead of the valuable hydrocarbons desired.

Other things being equal in the pyrolysis of a crude oil, it is sometimes preferred to employ a crude oil having a relatively narrow boiling range for the bulk of the oil being pyrolyzed with considerable material boiling between and/or close to key fractions 1 and 2 of said crude oil.

A further method of selecting the petroleum oil for pyrolysis hereunder is by means of an evaluation factor which we term "evaluation factor B. D. D." and which is a function of the average boiling point, the density and the mean dispersion of the oil.

Specifically, this evaluation factor is a product function of two factors—factor I and factor II.

$$\text{Factor I} = 156 - 492 \left(\log_{10} \frac{\text{Average boiling point } ^\circ\text{F.} - 114}{d \cdot 20/4 \times 10^3 - 70.7} \right)$$

$$\text{Factor II} = 1004 \left(\sin \arctan \frac{\text{Average boiling point } ^\circ\text{F.} - 180}{H_F - c \times 10^4 - 65} \right) - 906$$

$$\text{Evaluation factor B. D. D.} = \text{Factor I} \times \text{Factor II} \times 10^{-4} =$$

$$\left[156 - 492 \left(\log_{10} \frac{\text{Average boiling point } ^\circ\text{F.} - 114}{d \cdot 20/4 \times 10^3 - 70.7} \right) \right]$$

$$\left[1004 \left(\sin \arctan \frac{\text{Average boiling point } ^\circ\text{F.} - 180}{H_F - c \times 10^4 - 65} \right) - 906 \right] \times 10^{-4}$$

The "Average boiling point" employed is determined by making a modified straight run Engler distillation of the oil and observing the temperatures at which 15%, 30%, 50%, 70% and 85% by volume of the oil is taken off as vapor. The arithmetical average of these temperatures in $^\circ\text{F.}$ is the average boiling point.

The general distillation procedure is that described in Gas Chemists Handbook 3rd edition 1929—pages 74 to 78 with the following exceptions.

The apparatus described is employed except that for the thermometer described there is substituted an A. S. T. M. general purpose thermometer (20° – 760°F.) 3 inches immersion.

The procedure described is modified so that the determinations are made on a volume basis and temperatures are read at which 15%, 30%, 50%, 70% and 85% of the material is distilled over. Separation of cuts, determinations of their specific gravity, and coking determinations are unnecessary.

The preheating period should be not less than 10 minutes nor more than 20 minutes, higher boiling oils having the longer preheating.

The rate of distillation is carefully adjusted, by the needle valve on the burner, to 4 cc. per minute and this rate is maintained unless a slight drop in temperature accompanies a rate increase. (This will not usually occur below 500°F. and its occurrence indicates undesirable liquid phase cracking.) In this event, the heating is increased so that the thermometer is returned to its previous reading regardless of the rate. If the rate then decreases with constant increase in temperature, it is permitted to do so until a rate of 4 cc./min. is again reached. If the rate does not so decrease, the distillation is continued in such manner that the temperature constantly rises.

As before stated the arithmetical average of the five temperature readings is employed as the average boiling point.

The density d $20/4$ is determined by employing a Sprengel pycnometer. It is defined as the ratio of the weight in air of 5 cc. of oil at 20°C. to the weight in air of 5 cc. of water at 4°C.

The mean dispersion $H_F - c$ is defined as the difference between the refractive index of the oil as determined with the F spectral line and the refractive index of the oil as determined with the C spectral line, employing a refractometer of the Abbe type.

Evaluation factor B. D. D. is a convenient measure of the ability of a petroleum oil to produce alkylated aromatic hydrocarbons such as solvent naphtha and toluene and aromatic resin formers such as styrene, methyl styrene and indene.

It has the advantage of applying to cuts from crude petroleum oils as well as the crudes, except such cuts as residuums too dark to permit the determination of the mean dispersion, and

residuums too heavy to permit the above determination of the average boiling point. Such residuums give very low yields of the desired products on pyrolysis.

This factor has been found to correlate very well the yields of styrene, aromatic resin formers, and aromatic resin formers plus toluene plus solvent naphtha, obtained in a large number of pyrolyses of petroleum crudes ranging from Bureau of Mines class 1 to Bureau of Mines class 7 oils inclusive, and also yields of such products and product groups obtained in the pyrolysis of cuts of such oils.

When $(H_F - c \times 10^4)$ is less than 65 it is assumed to be 65, so that the maximum value of factor II is 98.0 and so that negative values do not occur. Evaluation factor B. D. D. may be calculated directly from the formula or if desired it may be calculated by constructing nomograms (not shown) expressing the equations of factors I and II.

A large number of crude oils ranging from Bureau of Mines class 1 oils to Bureau of Mines class 7 oils inclusive and cuts from certain of the crudes on examination gave evaluation factors B. D. D. ranging from 49.5 to 87.7, with factor I ranging from 39.0 to 93.0 and factor II ranging from 57.3 to 98.0.

The formulae for evaluation B. D. D. were empirically derived from petroleum oil characteristics and the results of petroleum oil pyrolysis. They are not intended to apply to the pyrolysis of individual pure hydrocarbons. However, a fair relation between the yields of certain alkylated aromatic compounds is obtained even when the petroleum oil has had added to its quantities of benzene, for example 25% by volume.

In accordance with the present invention, there is selected for pyrolysis hereunder, crude petroleum oils or cuts from such oils having evaluation factors B. D. D. above 68 and preferably above 74.

If a given set is operated to crack (1) a petroleum oil selected as herein set forth, (2) relatively homogeneously and (3) relatively uniformly as herein defined, and (4) if the production of residual oil gas is held between the approximate limits above given, a substantially larger quantity of alkylated and alkenated aromatic hydrocarbons including a substantially larger quantity of aromatic resin-forming hydrocarbons, together with substantial quantities of other unsaturated resin-forming hydrocarbons and of saturated aromatic hydrocarbons are produced, and with a substantial reduction of paraffines and non-aromatic olefines boiling with the ranges of the saturated aromatic hydrocarbons.

In discussing the selection of petroleum oil for pyrolysis, it has been stated that a crude oil having the desired characteristics or a desired cut therefrom is employed. Heavy residuums unmixed with lighter cuts are preferably excluded.

The removal from the gas of hydrocarbons by condensation may be accomplished by any suitable means.

Generally speaking, there are four tools available for this purpose, namely, refrigeration, compression, absorption, such as in a scrubbing oil, and adsorption, such as on activated carbon. These may be used singly or in any desired combination.

Means for recovering valuable hydrocarbons from the gas produced is illustrated in Figures

3 and 4 which figures when arranged end to end comprise a continuous flow sheet.

At the extreme left of Figure 3 is shown line 19 and wash box 4 together with gas outlet 20a and valve 21 of Figure 1.

As illustrated, outlet 20a leads to a multi-pass condenser 41 which may be of any suitable design. Condenser 41 is shown with a gas outlet 42 which leads to a gas cleaner 43 of any suitable design for the removal of entrained tar. Outlet 44 from gas cleaner 43 leads through drip pot 45 of any suitable design and into relief holder 46 through vertical pipe 47.

Wash box 4 is provided with a water supply 48 and tar overflow 49 which leads to tar seal pot 50 to which as illustrated is connected a vapor outlet 51 leading to a condenser 52 for the recovery of any vaporized material.

Tar flows from seal pot 50 through outlet 53 and may be drawn off separately through line 54 or may be combined through line 55 with the tar from the first vertical pass of condenser 41 which latter tar drains through line 56 into seal pot 57 with which line 55 connects. Seal pot 57 is provided with a vapor outlet 58 which may lead to a condenser (not shown) and with a tar outlet 59.

Additional seal pots 61, 62, 63, 64, 65 and 66 have been illustrated, each connected to a separate vertical pass of condenser 41 for the withdrawal of tar. Each of the seal pots may be constructed similarly to seal pot 57 including a vapor outlet with a condenser (not shown) and a tar outlet.

Gas cleaner 43 is also shown with a tar outlet 68 leading to seal pot 69 which also may be similar to seal pot 57.

The particular arrangement of seal pots 50, 57, 61, 62, 63, 64, 65, 66 and 69, each of which is provided with a separate tar outlet makes it possible to separately process the tar condensed at various points, if desired, or to combine the separate bodies of tar in any desired manner prior to processing. For example, the tar flowing from seal pots 50, 57 and 61 might be combined to form heavy tar, and the tar flowing from seal pots 62, 63, 64, 65, and 66 might be combined to form light tar.

It will be understood, of course, that any other suitable construction or arrangement or method of collecting tar might be substituted.

As illustrated, the condensate collected in drip pot 45 is drawn off through outlet 71 and since it is usually non-tarry in nature, if desired, it may be combined with the light oil or otherwise processed, as desired.

Hydrocarbons also may condense within the relief holder 46 and if so are skimmed off of the top of the water through drain 72. This condensate is usually non-tarry in nature and is of the nature of light oil. Therefore, if desired, it may be combined, for example, with similar or lighter condensate and processed therewith.

Relief holder 46 is illustrated with the conventional water inlet 73 for replacing water losses from the tank thereof.

Relief holder 46 is shown with gas outlet 75 which leads through drip pot 76 and line 77 to the gas purifier system illustrated generally at 78 and more specifically as containing iron oxide boxes 79 and 80, although it is to be understood that any suitable gas purifier system may be substituted. The connections to the purifier boxes 79 and 80 are conventional and will, therefore, not be more particularly described.

Purifier boxes 79 and 80 are illustrated with drip pots 81 and 82 respectively for the collection and removal of condensate.

Outlet 84 from the purifier system 78 leads through gas meter 85 and past thermocouple junction 86 which is connected to pyrometer 87 for measuring the gas temperature. Gas pressure gauge 88 is also provided.

The purpose of meter 85, pyrometer 87 and pressure gauge 88 is to furnish data for calculating the volume of gas flowing through outlet 84.

If "residual oil gas" is to be calculated from this data a sample of the gas for analysis should be taken at this point.

Since condensation may occur in outlet 84, a drip pot 89 is illustrated in this outlet. It is to be understood that a drip pot or drip pots may be placed at any other point or points in the system for the collection and removal of condensate.

As illustrated, outlet 84 leads to compressor 91 driven by a prime mover 92, the gas passing through compressor 91, then through after-cooler 93, through a second compressor 94, after-cooler 95, a third compressor 96, after-cooler 97, and through line 98 to a scrubbing tower 99. Each of the after-coolers 93, 95 and 97 is illustrated as provided with condensate drains 101, 102, and 103 respectively which as illustrated are connected to a common line 104 to be referred to again hereinafter. The after-coolers may be of any suitable design and operation.

Each of the compressors 94 and 96 is also illustrated as driven by a prime mover 92.

Any other means may be provided for raising the pressure of the gas and for abstracting heat therefrom for the purpose of producing condensate.

Generally speaking, the pressure in the system from wash box 4 to and through outlet 84 is conveniently slightly above atmospheric. The pressure in outlet 98 may be as desired, for example, in the particular system illustrated conveniently of the order of from 200 to 225 lbs. per square inch absolute.

The temperature of the gas in outlet 84 may be conveniently maintained at any desired level such as between 85 and 100° F. Reference is made to copending application, Serial No. 301,330, filed October 26, 1939, now Patent 2,379,518, dated July 3, 1945. The temperature of the gas in outlet 98 may also be as desired, for example, conveniently of the order of from 85 to 100° F.

As illustrated outlet 98 is connected to the bottom of scrubber 99, the gas passing up through scrubber 99 countercurrently to a liquid gas-scrubbing medium of considerably lower vapor pressure such as a scrubbing oil. The scrubbing medium enters scrubber 99 through line 105 which leads from the bottom of stripping tower 114 through cooler 106 to the top of scrubber 99. The proportion of scrubbing oil to gas and the temperature of the scrubbing oil is conveniently regulated so that the effluent gas leaving scrubber 99 through outlet 107 contains for the most part only those hydrocarbons and other gas constituents which it is not desired to condense. For example, the effluent gas may contain hydrocarbons for the most part of less than 4 carbon atoms. However, as previously pointed out a sharp separation between hydrocarbons of 3 and 4 carbon atoms for the purpose of calculating "residual oil gas" using as a sample this effluent gas is not an indispensable essential.

The effluent gas is led through gas meter 108, past thermocouple junction 109 leading to pyrometer 110, and past pressure gauge 111. A purpose of meter 108, pyrometer 110 and pressure gauge 111 is to determine the volume of effluent gas for purposes of calculating "residual oil gas," provided "residual oil gas" is calculated from the analysis of gas sampled at this point.

It will of course be understood that even though a substantial portion of hydrocarbons of less than 4 carbon atoms were condensed it would, nevertheless, be possible to calculate "residual oil gas" as herein defined, by adding to the "residual oil gas" as determined from the sample a volume to compensate for such condensation.

Returning to scrubber 99, scrubbing medium containing condensate is withdrawn through line 113, through heater 125, and fed to the top of stripper 114 in which condensate scrubbed from the gas in scrubber 99 is stripped from the scrubbing medium such as with the aid of live superheated steam introduced through line 112. The stripped material is taken overhead through line 115 to and through condenser 116 which leads to decanter 117 and the scrubbing medium is returned through line 105 and cooler 106 to scrubber 99, any makeup being added as required.

Decanter 117 is conveniently provided for the separation of condensed water and of any gas remaining uncondensed after passing through condenser 116. Uncondensed gas is led through line 118 back to line 24 and is thus recycled through the compressors.

Line 104 conveniently leads to decanter 117 in which condensate from after-coolers 93, 95 and 97 is combined with condensate from condenser 116.

Any water collecting in decanter 117 is drained off through line 119, and hydrocarbon condensate is drained off through line 120 into fractionating tower 121. A separation is made between higher and lower boiling hydrocarbon components in tower 121, for example, between hydrocarbons of 6 carbon atoms and higher which are taken off in the liquid phase at the bottom through line 122, and hydrocarbons of less than 6 carbon atoms which are taken off in the vapor phase through line 123. The latter are condensed, a part returned to tower 121 as reflux, and the rest lead to fractionating tower 124 in which a separation is made between hydrocarbons of 5 carbon atoms and higher which are taken off in the liquid phase through line 126, and hydrocarbons of less than 5 carbon atoms which are taken off in the vapor phase through line 127. The latter are condensed, a part returned to tower 124 as reflux, and the rest lead to suitable apparatus for the recovery of hydrocarbons with 4 carbon atoms (not shown).

The unsaturated hydrocarbons of 5 carbon atoms, namely, isoprene, piperylene, and cyclopentadiene may be separated from each other by any available means such as by the processes described and claimed in Patent 2,211,038 granted August 13, 1940, to Alger L. Ward and in copending application Serial Number 342,910, filed June 28, 1940, by Alger L. Ward.

The unsaturated hydrocarbons of 4 carbon atoms, namely, butadiene and the butylenes may also be separated from each other by any available means such as by the processes described in the literature including granted patents.

The tar is processed for the recovery of light oil, dead oil and residual tar therefrom, either in a single combined body or in any selected por-

tions according to the method of collection. Since steam is usually used in the pyrolysis of the oil, and since the resulting gas passes through the wash box 4 which contains water, the tar is usually collected in the form of an emulsion. This emulsion is usually broken during the treatment for the recovery of light oil, dead oil and residual tar.

Any means may be employed for the recovery of light oil, dead oil and residual tar from the original tar, such as the conventional tar dehydration procedure using batch distillation followed by fractionation of the distillate into light oil and dead oil. However, it is preferred to use more refined processes such as the process described in copending application Serial Number 342,735, filed June 27, 1940, by Edwin L. Hall and Howard R. Batchelder, now Patent 2,366,899 dated January 9, 1945, and Serial Number 353,034, filed August 17, 1940, by Howard R. Batchelder.

The condensate collected from the various drip pots and from the holder 46 is usually not in the form of an emulsion, and the various valuable hydrocarbons are recovered therefrom usually by distillation. If desired, the condensate drained from the various drip pots and from holder 46 may be combined with the condensate fed to tower 121. On the other hand, this material may be combined with the light oil separated from the original tar and processed therewith.

Light oil recovered from the tar, and the condensate from the drip pots, and the holder, and the heavier hydrocarbon material separated in tower 121 are sources for benzene, alkylated benzenes such as toluene and the xylenes, for resin forming unsaturated hydrocarbons such as styrene, the methyl styrenes, dicyclopentadiene and indene as well as other valuable hydrocarbon material. Separations between these various hydrocarbons may be made by resorting to fractional distillation or other means to obtain relatively pure products or fractions in which the individual hydrocarbons specifically mentioned are concentrated.

Thus styrene may be separated in relatively pure form by special processing or by distillation into concentrated fractions which are preferably of at least approximately 30% concentration, since below this concentration serious contamination is present. Concentrations as high as approximately 60% or higher are obtainable by distillation and are especially preferred.

With indene the lower concentration is preferably at least approximately 50% and the higher concentration is at least approximately 80%.

With the methyl styrenes as a group the respective percentages are approximately the same as with styrene, and with dicyclopentadiene the respective percentages are approximately the same as with indene.

In addition to high quality resin-forming unsaturated hydrocarbons, the light oil produced by the process described and claimed herein yields high quality benzene, toluene and solvent naphtha especially within the preferred range of "residual oil gas" production.

Butadiene is concentrated in a fraction preferably of at least approximately 35% and especially of at least 50%.

The C₅ diolefines, namely, isoprene, piperylene and cyclopentadiene, some of the latter in the form of its dimer dicyclopentadiene, which may be formed in the separation, are preferably sep-

arated by fractional distillation or otherwise, in a fraction of at least 30% concentration.

Benzene, a substantial quantity of toluene, some styrene and xylenes are recovered from the material removed through line 122. There is also some material of 5 carbon atoms and some dicyclopentadiene recovered from this material.

A substantial quantity of isoprene, piperylene, cyclopentadiene and dicyclopentadiene (the latter formed during the processing), and some benzene and a small quantity of C₄ hydrocarbons are removed from the material withdrawn through line 126.

A substantial quantity of C₄ hydrocarbons some C₃ and C₂ hydrocarbons and a small quantity of C₅ and C₁ hydrocarbons are recovered from the material withdrawn through line 127. The quantity of hydrocarbons present of less than 4 carbon atoms in this material should be considered in the calculation of "residual oil gas."

The dead oil depending upon the method of separation from the original tar may contain an unusually high percentage of very valuable aromatic resin-forming material which is extremely unusual. The dead oil also contains a large number of saturated hydrocarbons for example naphthalene, substituted naphthalene, anthracene, etc.

A high grade of residual tar is obtained, useful for the various purposes to which material of this type is put.

It will be understood, however, that the particular description with respect to the removal of valuable hydrocarbons from the gas and their separation is for the purposes of illustration and that any other suitable system for this purpose might be substituted.

It is to be understood that if desired other materials may be added to the oil pyrolyzing environment in addition to the selected petroleum oil. For example, other hydrocarbon materials such as benzene, toluene, xylene and solvent naphtha may be added.

As an illustration the addition of benzene to the oil cracking environment as described and claimed in copending application Serial Number 220,649, filed July 22, 1938, by Newcomb K. Chaney (now Patent Number 2,226,531, dated December 31, 1940), is particularly beneficial when relatively large yields of certain resin-forming unsaturated hydrocarbons such as styrene is desired.

Materials of this character may be added to the oil cracking environment at any desired point such as at the point of introduction of the petroleum oil, or at any other desired point or points such as directly into the zone of major cracking.

The additive need not be a pure substance but may comprise for example benzol, toluol, xylol, solvent naphtha or any other portion of light oil or even overall light oil itself.

However particularly advantageous results are obtained when benzene itself or a fraction containing a substantial quantity of benzene such as a fraction preponderantly of benzene is used.

In view of equilibrium considerations there is a particular advantage in separating these products from the condensate produced and recycling them to the oil pyrolyzing environment in which they were produced. Thus for example, benzol may be separated from the condensate and recycled back to the set in which the benzol was originally produced.

Any suitable quantity of such material may be added as for example, up to 25% to 50% of benzene by volume of oil pyrolyzed.

When making any such aromatic hydrocarbon additions which preferably are restricted to materials which for the most part boil below 200° C., "residual oil gas" for convenience may be calculated as previously described, namely on the basis of petroleum oil pyrolyzed, with no deduction being made for any material of less than four carbon atoms which might be derived from the additive.

However, to the top of the range of residual oil gas is added 1 cubic foot of gas for each 3% of additive by volume of petroleum oil pyrolyzed with 75 cubic feet of residual oil gas per gallon of petroleum oil pyrolyzed as a top limit regardless of the amount of additive employed.

Thus the widest range when using aromatic hydrocarbon additive and this method of calculation is from 40 to 75 cubic feet of "residual oil gas" per gallon of petroleum oil pyrolyzed, with from 45 to 65 cubic feet of "residual oil gas" preferred.

According to another method of calculation designed to bring these operations within the broad range of residual oil gas employed as limits when no additive is employed, namely 40 to 65 cubic feet per gallon of petroleum oil pyrolyzed no subtraction is made for the presence of aromatic hydrocarbon additive when the "residual oil gas" calculated as herein described is between 40 and 65 cubic feet per gallon of petroleum oil pyrolyzed, but a subtraction up to 10 cubic feet is made from the residual oil gas to bring the residual oil gas within the limits of from 40 to 65 cubic feet if on calculation as herein set forth the "residual oil gas" exceeds 65 cubic feet.

While the invention has been more particularly described in connection with more or less conventional apparatus, it is to be understood that this is by way of illustration and that in its broad phases the invention may be employed with any suitable type of apparatus.

Additionally, while the invention has been described primarily in connection with the decomposition of a selected petroleum oil by pyrolysis, it is conceivable that pyrolysis may be supplemented by other means for decomposing the oil of which catalysis is an example. In fact even in conventional gas making processes catalysis may unavoidably play a part in view of the heterogeneous character of the reactions involved and the possibility of many different materials being present. Thus, a combination of temperature and catalyst is within the purview of the invention in its broadest aspects.

Therefore, changes, omissions, additions, substitutions, and/or modifications might be made within the scope of the claims without departing from the spirit of the invention.

We claim:

1. A process for the production in relatively high proportion and in good quality of resin-forming unsaturated aromatic hydrocarbons including resin-forming unsaturated aromatic hydrocarbons boiling above 200° C. and of other aromatic hydrocarbons in good quality, which comprises pyrolyzing a petroleum oil selected from the group consisting of petroleum oils of below 7% in Conradson carbon and falling within the classifications of from 5 to 7 inclusive as determined by the Bureau of Mines Index and fractions from said petroleum oils, and conducting said pyrolysis in vapor phase with an inten-

sity of cracking such that the volume of residual oil gas produced per gallon of petroleum oil pyrolyzed falls within the range of from 40 to 65 cubic feet taken as if measured at a pressure of 760 mm. and at a temperature of 60° F., and under conditions such that the relationship between the sulfonation residue and the free carbon obtained is within the sulfonation residue-free carbon relationships lying to the left of and below the curve defined by the equation

$$X^{2.3}(Y-0.03)=0.05$$

in which X and Y are respectively rectangular coordinates of free carbon expressed in percent by weight of the original oil pyrolyzed and of sulfonation residue expressed in percent by volume of the original oil pyrolyzed.

2. A process for the production in relatively high proportion and in good quality of resin-forming unsaturated aromatic hydrocarbons including resin-forming unsaturated aromatic hydrocarbons boiling above 200° C. and of other aromatic hydrocarbons in good quality, which comprises pyrolyzing a crude petroleum oil of below 4% in Conradson carbon and falling within the classification 7 as determined by the Bureau of Mines Index, and conducting said pyrolysis in vapor phase in the presence of a substantial proportion of steam and with an intensity of cracking such that the volume of residual oil gas produced per gallon of petroleum oil pyrolyzed falls within the range of from 40 to 65 cubic feet taken as if measured at a pressure of 760 mm. and at a temperature of 60° F., and under conditions such that the relationship between the sulfonation residue and the free carbon obtained is within the sulfonation residue-free carbon relationships lying to the left of and below the curve defined by the equation $X^{2.3}(Y-0.03)=0.05$ in which X and Y are respectively rectangular coordinates of free carbon expressed in percent by weight of the original oil pyrolyzed and of sulfonation residue expressed in percent by volume of the original oil pyrolyzed.

3. A process for the production in relatively high proportion and in good quality of resin-forming unsaturated aromatic hydrocarbons including resin-forming unsaturated aromatic hydrocarbons boiling above 200° C. and of other aromatic hydrocarbons in good quality which comprises pyrolyzing a fraction separated from a petroleum oil of less than 4% in Conradson carbon and falling within the classification 7 as determined by the Bureau of Mines Index, and conducting said pyrolysis in vapor phase in the presence of a substantial proportion of steam and with an intensity of cracking such that the volume of residual oil gas produced per gallon of petroleum oil pyrolyzed falls within the range of from 40 to 65 cubic feet taken as if measured at a pressure of 760 mm. and at a temperature of 60° F., and under conditions such that the relationship between the sulfonation residue and the free carbon obtained is within the sulfonation residue-free carbon relationships lying to the left of and below the curve defined by the equation $X^{2.3}(Y-0.03)=0.05$ in which X and Y are respectively rectangular coordinates of free carbon expressed in percent by weight of the original oil pyrolyzed and of sulfonation residue expressed in percent by volume of the original oil pyrolyzed.

4. A process for the production in relatively high proportion and in good quality of resin-forming unsaturated aromatic hydrocarbons including resin-forming unsaturated aromatic hydrocarbons boiling above 200° C. and of other aromatic hydrocarbons in good quality which comprises pyrolyzing a petroleum oil of below 7% in Conradson carbon and falling within the classification of from 5 to 7 inclusive as determined by the Bureau of Mines Index, and conducting said pyrolysis in vapor phase in the presence of a substantial proportion of steam and at a total pressure near atmospheric and with an intensity of cracking such that the volume of residual oil gas produced per gallon of petroleum oil pyrolyzed falls within the range of from 40 to 65 cubic feet taken as if measured at a pressure of 760 mm. and at a temperature of 60° F., and under conditions such that the relationship between the sulfonation residue and the free carbon obtained is within the sulfonation residue-free carbon relationships lying to the left of and below the curve defined by the equation $X^{2.3}(Y-0.03)=0.05$ in which X and Y are respectively rectangular coordinates of free carbon expressed in percent by weight of the original oil pyrolyzed and of sulfonation residue expressed in percent by volume of the original oil pyrolyzed.

5. A process for the production in relatively high proportion and in good quality of resin-forming unsaturated aromatic hydrocarbons including resin-forming unsaturated aromatic hydrocarbons boiling above 200° C. and of other aromatic hydrocarbons in good quality which comprises pyrolyzing in vapor phase a petroleum oil having an average boiling point-density-mean dispersion evaluation factor above 68 as determined by the formula:

Evaluation factor =

$$\left[\frac{156-492 \left(\log \log \frac{\text{Average boiling point } ^\circ\text{F.}-114}{d \cdot 20/4 \times 10^2 - 70.7} \right)}{1004 \left(\sin. \arctan. \frac{\text{Average boiling point } ^\circ\text{F.}-160}{H_F - C \times 10^4 - 65} \right) - 906 \right] \times 10^{-4}$$

in which $d \cdot 20/4$ is the density of the oil at 20° C. as compared with water at 4° C. and $H_F - C$ is the mean dispersion of the oil employing the F and C spectral lines, conducting said pyrolysis in the presence of a substantial proportion of diluent gas under conditions such that the volume of residual oil gas produced per gallon of petroleum oil pyrolyzed falls within the range of from 40 to 65 cubic feet taken as if measured at a pressure of 760 mm. and at a temperature of 60° F., and such that the relationship between the sulfonation residue and the free carbon obtained is within the sulfonation residue-free carbon relationships lying to the left of and below the curve defined by the equation $X^{2.3}(Y-0.03)=0.05$ in which X and Y are respectively rectangular coordinates of free carbon expressed in percent by weight of the original oil pyrolyzed and of sulfonation residue expressed in percent by volume of the original oil pyrolyzed.

6. A process for the production in relatively high proportion and in good quality of resin-forming unsaturated aromatic hydrocarbons including resin-forming unsaturated aromatic hydrocarbons boiling above 200° C. and of other aromatic hydrocarbons in good quality which comprises pyrolyzing in vapor phase a petroleum oil having an average boiling point-density-mean dispersion evaluation factor above 68 as determined by the formula:

$$\left[\frac{156-492 \left(\log \log \frac{\text{Average boiling point } ^\circ\text{F.}-114}{d \cdot 20/4 \times 10^2 - 70.7} \right)}{1004 \left(\sin. \arctan. \frac{\text{Average boiling point } ^\circ\text{F.}-160}{H_F - C \times 10^4 - 65} \right) - 906 \right] \times 10^{-4}$$

in which $d_{20/4}$ is the density of the oil at 20° C. as compared with water at 4° C. and H_F-c is the mean dispersion of the oil employing the F and C spectral lines, conducting said pyrolysis in the presence of a substantial proportion of steam and in the absence of more than 30 cubic feet of blue water gas per gallon of petroleum oil pyrolyzed, said cubic feet of blue water gas taken as if measured at a pressure of 760 mm. and at a temperature of 60° F., said pyrolysis also being conducted under conditions such that the volume of residual oil gas produced per gallon of petroleum oil pyrolyzed falls within the range of from 40 to 65 cubic feet taken as if measured at a pressure of 760 mm. and at a temperature of 60° F., and such that the relationship between the sulfonation residue and the free carbon obtained is within the sulfonation residue-free carbon relationships lying to the left of and below the curve defined by the equation $X^{2.3}(Y-0.03)=0.03$ in which X and Y are respectively rectangular coordinates of free carbon expressed in percent by weight of the original oil pyrolyzed and of sulfonation residue expressed in percent by volume of the original oil pyrolyzed.

7. A process for the production in relatively high proportion and in good quality of resin-forming unsaturated aromatic hydrocarbons including resin-forming unsaturated aromatic hydrocarbons boiling above 200° C. and of other aromatic hydrocarbons in good quality which comprises pyrolyzing in vapor phase a petroleum oil having an average boiling point-density-mean dispersion evaluation factor above 74 as determined by the formula:

Evaluation factor=

$$\left[156-492 \left(\log \log \frac{\text{Average boiling point } ^\circ\text{F.}-114}{d_{20/4} \times 10^2 - 70.7} \right) \right]$$

$$\left[1004 \left(\text{Sin. arc Tan.} \frac{\text{Average boiling point } ^\circ\text{F.}-160}{H_F-c \times 10^4 - 65} \right) - 906 \right] \times 10^{-2}$$

in which $d_{20/4}$ is the density of the oil at 20° C. as compared with water at 4° C. and H_F-c is the mean dispersion of the oil employing the F and C spectral lines, conducting said pyrolysis in the presence of a substantial proportion of steam while restricting any blue water gas present to less than approximately 20 cubic feet per gallon of petroleum oil pyrolyzed, said cubic feet of blue water gas taken as if measured at a pressure of 760 mm. and at a temperature of 60° F., and also conducting said pyrolysis under conditions such that the volume of residual oil gas produced per gallon of petroleum oil pyrolyzed falls within the range of from 45 to 65 cubic feet taken as if measured at a pressure of 760 mm. and at a temperature of 60° F., and such that the relationship between the sulfonation residue and the free carbon obtained is within the sulfonation residue-free carbon relationships lying to the left of and below the curve defined by the equation $X^{2.3}(Y-0.03)=0.01$ in which X and Y are respectively rectangular coordinates of free carbon expressed in percent by weight of the original oil pyrolyzed and of sulfonation residue expressed in percent by volume of the original oil pyrolyzed.

8. In a cyclic process for the manufacture in relatively high proportion and in good quality of resin-forming unsaturated aromatic hydrocarbons including resin-forming unsaturated aromatic hydrocarbons boiling above 200° C. and of other aromatic hydrocarbons in good quality in which in one portion of the cycle heat is stored in a gas-making path by the passage of hot blast gas

therethrough in contact with the surface of heat storage material arranged therein and in another portion of the cycle the stored heat is employed to pyrolyze petroleum oil passed through said gas-making path and over said heated surface, the steps of pyrolyzing in said gas-making path a petroleum oil having an average boiling point-density-mean dispersion evaluation factor above 68 as determined by the formula:

10 Evaluation factor=

$$\left[156-492 \left(\log \log \frac{\text{Average boiling point } ^\circ\text{F.}-114}{d_{20/4} \times 10^2 - 70.7} \right) \right]$$

$$\left[1004 \left(\text{Sin. arc Tan.} \frac{\text{Average boiling point } ^\circ\text{F.}-160}{H_F-c \times 10^4 - 65} \right) - 906 \right] \times 10^{-2}$$

15 in which $d_{20/4}$ is the density of the oil at 20° C. as compared with water at 4° C. and H_F-c is the mean dispersion of the oil employing the F and C spectral lines, and conducting said pyrolysis under conditions such that the volume of residual oil gas produced per gallon of petroleum oil pyrolyzed falls within the range of from 40 to 65 cubic feet taken as if measured at a pressure of 760 mm. and at a temperature of 60° F., and such that the relationship between the sulfonation residue and the free carbon obtained is within the sulfonation residue-free carbon relationships lying to the left of and below the curve defined by the equation $X^{2.3}(Y-0.03)=0.05$ in which X and Y are respectively rectangular coordinates of free carbon expressed in percent by weight of the original oil pyrolyzed and of sulfonation residue expressed in percent by volume of the original oil pyrolyzed.

30 9. In a cyclic process for the manufacture in relatively high proportion and in good quality of resin-forming unsaturated aromatic hydrocarbons including resin-forming unsaturated aromatic hydrocarbons boiling above 200° C. and of other aromatic hydrocarbons in good quality in which in one portion of the cycle heat is stored in a gas-making path by the passage of hot blast gas therethrough in contact with the surface of heat storage material arranged therein and in another portion of the cycle the stored heat is employed in the vapor phase pyrolysis of petroleum oil passed through said gas-making path, the steps of pyrolyzing in said gas-making path a petroleum oil having an average boiling point-density-mean dispersion evaluation factor above 68 as determined by the formula:

Evaluation factor=

$$\left[156-492 \left(\log \log \frac{\text{Average boiling point } ^\circ\text{F.}-114}{d_{20/4} \times 10^2 - 70.7} \right) \right]$$

$$\left[1004 \left(\text{Sin. arc Tan.} \frac{\text{Average boiling point } ^\circ\text{F.}-160}{H_F-c \times 10^4 - 65} \right) - 906 \right] \times 10^{-2}$$

75 in which $d_{20/4}$ is the density of the oil at 20° C. as compared with water at 4° C. and H_F-c is the mean dispersion of the oil employing the F and C spectral lines, conducting said pyrolysis in the presence of a substantial proportion of the steam while restricting the presence of any blue water gas to less than 30 cubic feet per gallon of oil pyrolyzed, said cubic feet of blue water gas taken as if measured at a pressure of 760 mm. and at a temperature of 60° F., and also conducting said pyrolysis under conditions such that the volume of residual oil gas produced per gallon of petroleum oil pyrolyzed falls within the range of from 40 to 65 cubic feet taken as if measured at a pressure of 760 mm. and at a temperature of 60° F., and such that the relationship between the sulfonation residue and the free carbon obtained is

within the sulfonation residue-free carbon relationships lying to the left of and below the curve defined by the equation $X^{2.3}(Y-0.03)=0.05$ in which X and Y are respectively rectangular coordinates of free carbon expressed in percent by weight of the original oil pyrolyzed and of sulfonation residue expressed in percent by volume of the original oil pyrolyzed.

10. In a cyclic process for the manufacture in relatively high proportion and in good quality of resin-forming unsaturated aromatic hydrocarbons including resin-forming unsaturated aromatic hydrocarbons boiling above 200° C. and of other aromatic hydrocarbons in good quality in which in one portion of the cycle heat is stored in a gas-making path by the passage of burning blast gas therethrough in contact with the surface of heat storage material of silicon carbide arranged therein and in another portion of the cycle the stored heat is employed in the vapor phase pyrolysis of petroleum oil passed through said gas-making path and over said heated surface, the steps of pyrolyzing in said gas-making path a petroleum oil having an average boiling point-density-means dispersion evaluation factor above 68 as determined by the formula:

Evaluation factor=

$$\left[156-492 \left(\log \log \frac{\text{Average boiling point } ^\circ\text{F.}-114}{d \ 20/4 \times 10^3 - 70.7} \right) \right] \\ \left[1004 \left(\text{Sin. arc Tan.} \frac{\text{Average boiling point } ^\circ\text{F.}-160}{H_F-c \times 10^4 - 65} \right) - 906 \right] \times 10^{-1}$$

in which $d \ 20/4$ is the density of the oil at 20° C. as compared with water at 4° C. and H_F-c is the mean dispersion of the oil employing the F and C spectral lines, conducting said pyrolysis at a total pressure near atmospheric in the presence of at least 2 parts of steam to 3 parts of oil pyrolyzed by weight while restricting the presence of any blue water gas to less than 30 cubic feet per gallon of oil pyrolyzed, said cubic feet of blue water gas taken as if measured at a pressure of 760 mm. and at a temperature of 60° F., and also conducting said pyrolysis under conditions such that the volume of residual oil gas produced per gallon of petroleum oil pyrolyzed falls within the range of from 40 to 65 cubic feet taken as if measured at a pressure of 760 mm. and at a temperature of 60° F., and such that the relationship between the sulfonation residue and the free carbon obtained is within the sulfonation residue-free carbon relationships lying to the left of and below the curve defined by the equation $X^{2.3}(Y-0.03)=0.03$ in which X and Y are respectively rectangular coordinates of free carbon expressed in percent by weight of the original oil pyrolyzed and of sulfonation residue expressed in percent by volume of the original oil pyrolyzed.

11. In a cyclic process for the manufacture in relatively high proportion and in good quality of resin-forming unsaturated aromatic hydrocarbons including resin-forming unsaturated aromatic hydrocarbons boiling above 200 C. and of other aromatic hydrocarbons in good quality in which in one portion of the cycle heat is stored in a gas-making path by the passage of hot blast gas therethrough in contact with the surface of heat storage material arranged therein of considerably higher heat conductivity than fire clay brick and in another portion of the cycle the stored heat is employed in the vapor phase pyrolysis of petroleum oil passed through said gas-making path, the steps comprising pyrolyzing in

said gas-making path a petroleum oil having an average boiling point-density-mean dispersion evaluation factor above 74 as determined by the formula:

5 Evaluation factor=

$$\left[156-492 \left(\log \log \frac{\text{Average boiling point } ^\circ\text{F.}-114}{d \ 20/4 \times 10^3 - 70.7} \right) \right] \\ \left[1004 \left(\text{Sin. arc Tan.} \frac{\text{Average boiling point } ^\circ\text{F.}-160}{H_F-c \times 10^4 - 65} \right) - 906 \right] \times 10^{-1}$$

in which $d \ 20/4$ is the density of the oil at 20° C. as compared with water at 4° C. and H_F-c is the mean dispersion of the oil employing the F and C spectral lines, conducting said pyrolysis in the presence of at least 2 parts of steam to 3 parts by weight of petroleum oil pyrolyzed while restricting the presence of any blue water gas to less than 20 cubic feet per gallon of oil pyrolyzed, said cubic feet of blue water gas taken as if measured at a pressure of 760 mm. and at a temperature of 60° F., and also conducting said pyrolysis under conditions such that the volume of residual oil gas produced per gallon of petroleum oil pyrolyzed falls within the range of from 45 to 65 cubic feet taken as if measured at a pressure of 760 mm. and at a temperature of 60° F., and such that the relationship between the sulfonation residue and the free carbon obtained is within the sulfonation residue-free carbon relationships lying to the left of and below the curve defined by the equation $X^{2.3}(Y-0.03)=0.01$ in which X and Y are respectively rectangular coordinates of free carbon expressed in percent by weight of the original oil pyrolyzed and of sulfonation residue expressed in percent by volume of the original oil pyrolyzed.

12. In a cyclic process for the manufacture in relatively high proportion and in good quality of resin-forming unsaturated aromatic hydrocarbons including resin-forming unsaturated aromatic hydrocarbons boiling above 200° C. and of other aromatic hydrocarbons in good quality in which in one portion of the cycle heat is stored in a gas-making path by the passage of hot blast gas therethrough in contact with the surface of heat storage material arranged therein of considerably higher heat conductivity than that of fire clay brick and in another portion of the cycle the stored heat is employed in the vapor phase pyrolysis of petroleum oil passed through said gas-making path, the steps of vaporizing in atomized condition in a portion of said gas-making path having a relatively high ratio of volume to surface and thereafter pyrolyzing in a succeeding portion of said gas-making path having a considerably lower ratio of volume to surface a petroleum oil having an average boiling point-density-mean dispersion evaluation factor above 68 as determined by the formula:

Evaluation factor=

$$\left[156-492 \left(\log \log \frac{\text{Average boiling point } ^\circ\text{F.}-114}{d \ 20/4 \times 10^3 - 70.7} \right) \right] \\ \left[1004 \left(\text{Sin. arc Tan.} \frac{\text{Average boiling point } ^\circ\text{F.}-160}{H_F-c \times 10^4 - 65} \right) - 906 \right] \times 10^{-1}$$

in which $d \ 20/4$ is the density of the oil at 20° C. as compared with water at 4° C. and H_F-c is the mean dispersion of the oil employing the F and C spectral lines, conducting said pyrolysis in the presence of at least 2 parts of steam to 3 parts by weight of petroleum oil pyrolyzed while restricting the presence of any blue water gas to

less than 30 cubic feet per gallon of oil pyrolyzed, said cubic feet of blue water gas taken as if measured at a pressure of 760 mm. and at a temperature of 60° F., and also conducting said pyrolysis under conditions such that the volume of residual oil gas produced per gallon of petroleum oil pyrolyzed falls within the range of from 40 to 65 cubic feet taken as if measured at a pressure of 760 mm. and at a temperature of 60° F., and such that the relationship between the sulfonation residue and the free carbon obtained is within the sulfonation residue-free carbon relationships lying to the left of and below the curve defined by the equation $X^{2.3}(Y-0.03)=0.03$ in which X and Y are respectively rectangular coordinates of free carbon expressed in percent by weight of the original oil pyrolyzed and of sulfonation residue expressed in percent by volume of the original oil pyrolyzed.

13. In a cyclic process for the manufacture in relatively high proportion and in good quality of resin-forming unsaturated aromatic hydrocarbons including resin-forming unsaturated aromatic hydrocarbons boiling above 200° C. and of other aromatic hydrocarbons in good quality in which in one portion of the cycle heat is stored in a gas-making path by the passage of hot blast gas therethrough in contact with the surface of heat storage material of silicon carbide arranged therein and in another portion of the cycle the stored heat is employed in the vapor phase pyrolysis of petroleum oil passed through said gas-making path and over said heated surface, the steps of pyrolyzing in said gas-making path a petroleum oil having an average boiling point-density-mean dispersion evaluation factor above 74 as determined by the formula:

Evaluation factor =

$$\left[156 - 492 \left(\log \log \frac{\text{Average boiling point } ^\circ\text{F.} - 114}{d \cdot 20/4 \times 10^4 - 70.7} \right) \right] \\ \left[1004 \left(\text{Sin. arc Tan.} \frac{\text{Average boiling point } ^\circ\text{F.} - 160}{H_F - c \times 10^4 - 65} \right) - 906 \right] \times 10^{-4}$$

in which $d \cdot 20/4$ is the density of the oil at 20° C. as compared with water at 4° C. and $H_F - c$ is the mean dispersion of the oil employing the F and C spectral lines, conducting said pyrolysis in the presence of a substantial proportion of steam under conditions such that the volume of residual oil gas produced per gallon of petroleum oil pyrolyzed falls within the range of from 45 to 65 cubic feet taken as if measured at a pressure of 760 mm. and at a temperature of 60° F., and such that the relationship between the sulfonation residue and the free carbon obtained is within the sulfonation residue-free carbon relationships lying to the left of and below the curve defined by the equation $X^{2.3}(Y-0.03)=0.03$ in which X and Y are respectively rectangular coordinates of free carbon expressed in percent by weight of the original oil pyrolyzed and of sulfonation residue expressed in percent by volume of the original oil pyrolyzed.

14. A process for the production in relatively high proportion and in good quality of resin-forming unsaturated aromatic hydrocarbons including resin-forming unsaturated aromatic hydrocarbons boiling above 200° C. and non-resin-forming aromatic hydrocarbons in good quality which comprises pyrolyzing in vapor phase in the presence of added benzene and in the presence of a substantial proportion of steam a petroleum oil having an average boiling point-density-

mean dispersion evaluation factor above 68 as determined by the formula:

Evaluation factor =

$$\left[156 - 492 \left(\log \log \frac{\text{Average boiling point } ^\circ\text{F.} - 114}{d \cdot 20/4 \times 10^4 - 70.7} \right) \right] \\ \left[1004 \left(\text{Sin. arc Tan.} \frac{\text{Average boiling point } ^\circ\text{F.} - 160}{H_F - c \times 10^4 - 65} \right) - 906 \right] \times 10^{-4}$$

in which $d \cdot 20/4$ is the density of the oil at 20° C. as compared with water at 4° C. and $H_F - c$ is the mean dispersion of the oil employing the F and C spectral lines, conducting said pyrolysis under conditions such that the volume of residual oil gas produced per gallon of petroleum oil pyrolyzed falls within the range of from 40 to 65 cubic feet taken as if measured at a pressure of 760 mm. and a temperature of 60° F., and such that the relationship between the sulfonation residue and the free carbon obtained is within the sulfonation residue-free carbon relationships lying to the left of and below the curve defined by the equation $X^{2.3}(Y-0.03)=0.05$ in which X and Y are respectively rectangular coordinates of free carbon expressed in percent by weight of the original oil pyrolyzed and of sulfonation residue expressed in percent by volume of the original oil pyrolyzed.

15. A process for the production in relatively high proportion and in good quality of resin-forming unsaturated aromatic hydrocarbons including resin-forming aromatic hydrocarbons boiling above 200° C. and of other aromatic hydrocarbons in good quality, which comprises pyrolyzing a petroleum oil selected from the group consisting of petroleum oils of below 7% in Conradson carbon and falling within the classifications of from 5 to 7 inclusive as determined by the Bureau of Mines Index and fractions from said petroleum oils, conducting said pyrolysis in vapor phase with an intensity of cracking such that the volume of residual oil gas produced per gallon of petroleum oil pyrolyzed falls within the range of from 45 to 65 cubic feet taken as if measured at a pressure of 760 mm. and at a temperature of 60° F., and under conditions such that the relationship between the sulfonation residue and the free carbon obtained is within the sulfonation residue-free carbon relationships lying to the left of and below the curve defined by the equation $X^{2.3}(Y-0.03)=0.05$ in which X and Y are respectively rectangular coordinates of free carbon expressed in percent by weight of the original oil pyrolyzed and of sulfonation residue expressed in percent by volume of the original oil pyrolyzed, condensing hydrocarbons including said resin-forming aromatic hydrocarbon material boiling above 200° C. from the gas resulting from said pyrolysis, and recovering from the resulting condensate a dead oil fraction in which said resin-forming aromatic hydrocarbon material boiling above 200° C. is concentrated.

16. A process for the production in relatively high proportion and in good quality of resin-forming unsaturated aromatic hydrocarbons including resin-forming unsaturated aromatic hydrocarbons boiling above 200° C. and alkenated aromatic hydrocarbons and of other aromatic hydrocarbons in good quality, which comprises pyrolyzing a petroleum oil selected from the group consisting of petroleum oils of below 7% in Conradson carbon and falling within the classifications of from 5 to 7 inclusive as determined by the Bureau of Mines Index and fractions from said petroleum oils, conducting said pyrolysis in vapor phase with an intensity of cracking such that the

volume of residual oil gas produced per gallon of petroleum oil pyrolyzed falls within the range of from 45 to 65 cubic feet taken as if measured at a pressure of 760 mm. and at a temperature of 60° F., and under conditions such that the relationship between the sulfonation residue and the free carbon obtained is within the sulfonation residue-free carbon relationships lying to the left of and below the curve defined by the equation

$$X^{2.3}(Y-0.03) = 0.05$$

in which X and Y are respectively rectangular coordinates of free carbon expressed in percent by weight of the original oil pyrolyzed and of sulfonation residue expressed in percent by volume of the original oil pyrolyzed, condensing hydrocarbons including said alkenated aromatic hydrocarbons from the gas resulting from said pyrolysis, and recovering from the resulting condensate a fraction in which alkenated aromatic hydrocarbon material is concentrated.

17. In a cyclic process for the manufacture in relatively high proportion and in good quality of resin-forming unsaturated aromatic hydrocarbons including resin-forming unsaturated aromatic hydrocarbons boiling above 200° C. and alkenated aromatic hydrocarbons and of other aromatic hydrocarbons in good quality in which in one portion of the cycle heat is stored in a gas-making path by the passage of hot blast gas therethrough in contact with the surface of heat storage material arranged therein of considerably greater heat conductivity than fire clay brick and in another portion of the cycle the stored heat is employed in the vapor phase pyrolysis of petroleum oil passed through said gas-making path and over said heated surface, the steps of pyrolyzing in said gas-making path a petroleum oil having an average boiling point-density-mean dispersion

evaluation factor above 68 as determined by the formula:

Evaluation factor =

$$\left[156 - 492 \left(\log \log \frac{\text{Average boiling point } ^\circ\text{F.} - 114}{d \cdot 20/4 \times 10^3 - 70.7} \right) \right] \left[1004 \left(\sin. \text{arc Tan.} \frac{\text{Average boiling point } ^\circ\text{F.} - 160}{Hr-c \times 10^4 - 65} \right) - 906 \right] \times 10^{-1}$$

in which $d \cdot 20/4$ is the density of the oil at 20° C. as compared with water at 4° C. and $Hr-c$ is the mean dispersion of the oil employing the F and C spectral lines, conducting said pyrolysis at a total pressure near atmospheric in the presence of a substantial proportion of steam under conditions such that the volume of residual oil gas produced per gallon of petroleum oil pyrolyzed falls within the range of from 40 to 65 cubic feet taken as if measured at a pressure of 760 mm. and at a temperature of 60° F., and such that the relationship between the sulfonation residue and the free carbon obtained is within the sulfonation residue-free carbon relationships lying to the left of and below the curve defined by the equation

$$X^{2.3}(Y-0.03) = 0.05$$

in which X and Y are respectively rectangular coordinates of free carbon expressed in percent by weight of the original oil pyrolyzed and of sulfonation residue expressed in percent by volume of the original oil pyrolyzed, condensing hydrocarbons including alkenated aromatic hydrocarbons from the gas resulting from said pyrolysis, and recovering from the resulting condensate a fraction in which resin-forming alkenated aromatic hydrocarbon material is concentrated.

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