Aug. 31, 1937. R. PYZEL 2,091,375

TREATMENT OF HYDROCARBON OILS

Filed Feb. 29, 1936 3 Sheets-Sheet 1

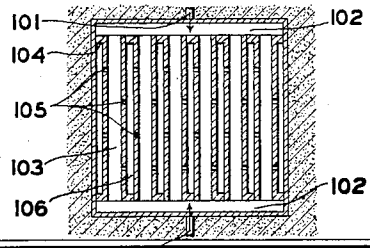


FIG. 2

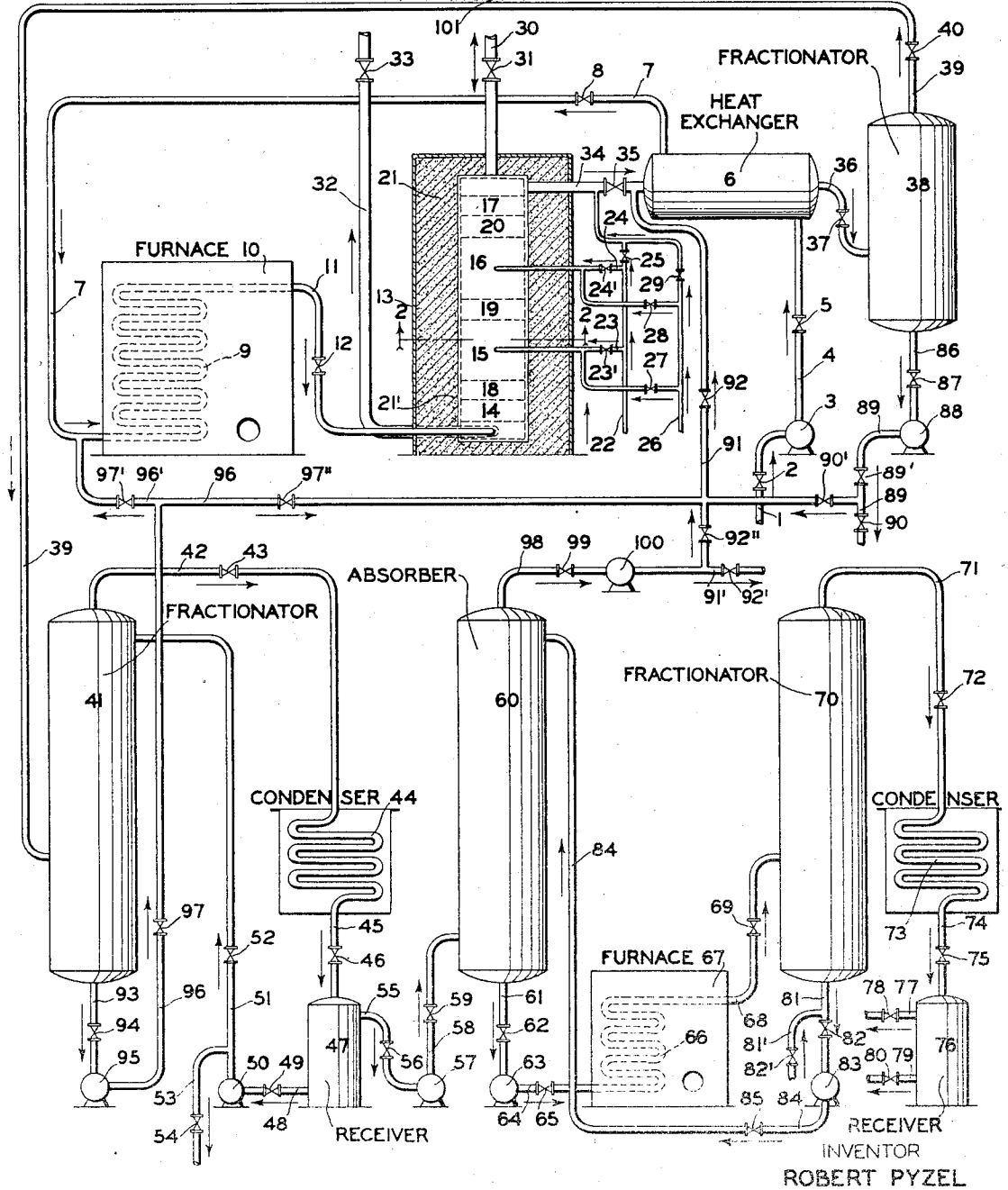


FIG. 1

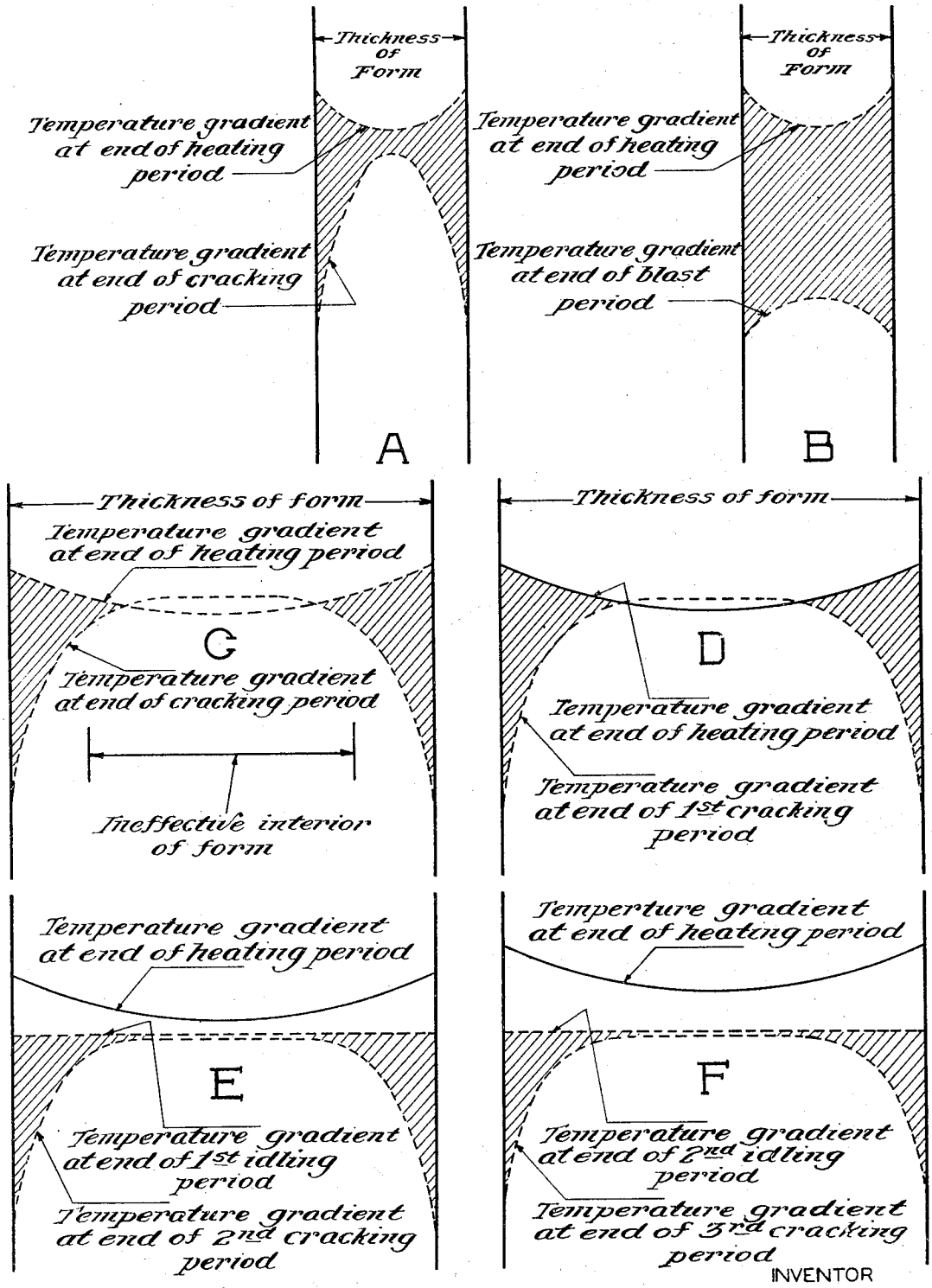
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TREATMENT OF HYDROCARBON OILS

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FIG. 3.



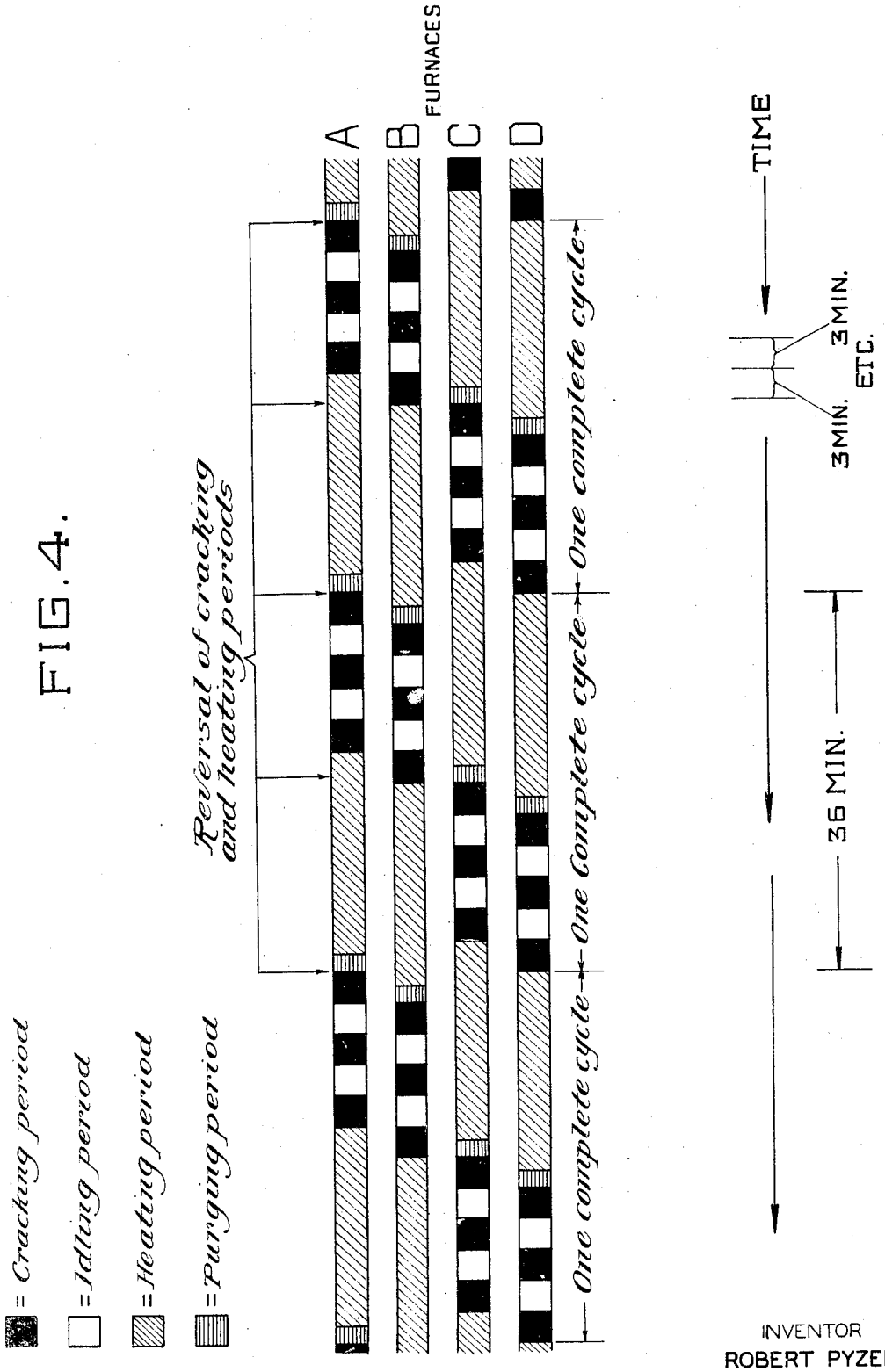
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TREATMENT OF HYDROCARBON OILS

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FIG. 4.



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UNITED STATES PATENT OFFICE

2,091,375

TREATMENT OF HYDROCARBON OILS

Robert Pyzel, Chicago, Ill., assignor to Universal Oil Products Company, Chicago, Ill., a corporation of Delaware

Application February 29, 1936, Serial No. 66,320

3 Claims. (Cl. 196—47)

This invention relates particularly to the treatment of lower boiling distillates produced in the refining of petroleum such as kerosene, naphtha or gas oil fractions produced either in the primary non-cracking distillation of crude petroleums or incidental to cracking processes.

In a more specific sense, the invention is concerned with the pyrolytic decomposition of such distillates under particular conditions of operation which have been found to yield large quantities of unsaturated or olefinic hydrocarbons, both gaseous and liquid; the liquid hydrocarbons boiling within the range of commercial gasoline say up to 400° F. being of superior antiknock value.

The present process is readily distinguishable from commonly employed pyrolytic or cracking processes in the employment of somewhat higher temperatures, considerably lower pressures, and much shorter time factors. In ordinary cracking processes conducted upon petroleum fractions of both a distillate and residual character for the production of maximum yields of gasoline, it is current practice to employ temperatures within the approximate range of 850 to 1000° F., pressures from 100 to 1000 pounds per square inch above atmospheric and a long time factor, the last resulting from the employment of cracking coils of considerable length and/or large vaporizing or reaction chambers following the heating elements. Such conditions of operation are generally conducive to the formation of large yields of low boiling liquid hydrocarbons of a character suitable for use as motor fuel, since due to the long time factor an equilibrium is approached corresponding to the temperature and pressure employed and a certain amount of secondary polymerization and condensation reactions take place following the primary reactions of decomposition.

In contradistinction to these conditions of operation the present process limits the decomposition reactions substantially to the primary reactions of decomposition so that equilibria corresponding to the temperatures and pressures as ordinarily employed are not reached, and the secondary polymerization reactions are obviated.

In one specific embodiment, the invention comprises vaporizing liquid hydrocarbon oil mixtures without substantial decomposition thereof and subjecting the vapors to pyrolysis at temperatures of from approximately 1500 to 1700° F. under subatmospheric pressures and for times less than 0.05 second.

It will be obvious to those skilled in the art of cracking hydrocarbons to produce lower boiling products that the present process may be conducted in various types of apparatus in which the various inter-connected elements are suitably proportioned to take care of charging stocks of somewhat varying character, along with different rates of flow and extent of cracking. Without unduly limiting the scope of the invention, the operation of the process will be described in connection with a particular type of apparatus which has been found to give satisfactory operation and good yields of desired products. To assist in this description the attached drawings have been provided, Fig. 1 of which shows partly in side elevation and partly in section, a general arrangement of an apparatus which may be used, while Fig. 2 is a cross sectional plan view of a portion of the apparatus taken along a plane indicated by the line 2—2 in Fig. 1. Fig. 2 merely indicates one arrangement and type of refractory filler which may be used for accomplishing the operation at the desired low time factors. Fig. 3 which includes graphs A, B, C, D, E and F shows by means of curves and shaded sections the temperature conditions obtaining in pieces of filling material at different stages of operation. In these figures the vertical coordinate is the temperature, which, however, is not shown as an exact scale but only schematically. Fig. 4 is a representation by means of a legended chart of the multiple furnace type of operation which superimposes the periods and the cycle of operations to show that continuous operations may be conducted with a minimum of manipulation. Figs. 3 and 4 will be used in a separate portion of the description which will follow the description of a single furnace operation given in connection with Figs. 1 and 2.

Referring to Fig. 1 of the drawings the principal units of the plant are seen to be a vaporizing element 9 and a cracking element 13 followed by suitable equipment for fractionating and recovering the products, utilizing the heat of the cracked vapors to preheat charging oil and an absorption plant to insure effective recovery of liquefiable vapors from fixed gases. Cracking element 13 is of special design and construction to make possible the use of relatively high temperatures for comparatively brief time intervals and will be later described in more complete detail.

In the operation of the process, a charging stock such as gas oil or kerosene distillate, for example, is admitted to the plant by way of charging line 1 and valve 2, to pump 3 and discharged therefrom by way of line 4 and valve 5

through a heat exchanger 6. While the pressure in the vaporizer, the main cracking element, and a portion of the subsequent cracking equipment is less than atmospheric, it is usually better to maintain some pressure on the charging oil during its passage through the heat exchanger to lessen the possibility of leaks. This may be accomplished by suitable manipulation of control valve 8 in raw oil discharge line 7 from the heat exchanger which leads to the vaporizing element 9 suitably disposed in a furnace setting 10. The vaporizing element may conveniently be a multiplicity of serially connected tubes or any other conventional form of heater commonly employed in refining processes.

The temperature and absolute pressure of the heated vapors which leave coil 9 by way of line 11 and valve 12, are preferably about 900° F. and 100 to 200 millimeters of mercury, respectively.

Cracking element 13 is essentially a regenerative type furnace containing refractory filling material (such as carborundum forms, for example, or other material capable of withstanding high temperatures) which is alternately heated to a suitable temperature and then employed to impart sufficient heat to the oil vapors supplied to their zone to effect the desired pyrolysis thereof. In the drawings 15 and 16 indicate sections of the heater filled with special refractory forms heated by surface combustion during the heating period. A sectional plan view of this portion of the furnace is illustrated in Fig. 2. Sections 14 and 17 indicate extra sections of refractory material, preferably in lattice arrangement, which store additional heat recovered from the combustion gases produced in sections 15 and 16. The portion of the furnace indicated at 18, 19 and 20 represent intervening free spaces. Depending upon the time factor found best in different cases, one or any desired number of the surface-combustion sections 15 and 16 or the refractory filler sections 17 and 18 may be employed. Where very short time factors of the order of 0.005 sec. are used, a single surface combustion section may be sufficient.

Referring to Fig. 2, which represents a section of the combustion zones 15 and 16, a pre-formed mixture of combustible gas and air is admitted through lines 101 on opposite sides of the furnace and the mixture first enters distributor spaces 102, flowing thence through openings 103 which pass through the center of the forms. These forms are spaced a definite distance apart by lugs 104 and contain perforations 105 through which the pre-formed combustion mixture passes to burn in spaces 106 between the forms. By proper regulation of the proportion of fuel to air, and proper proportioning of the size and number of perforations 105, combustion is controlled to take place on the surface of the forms within spaces 106 without deposition of carbon, the forms being thereby heated to the high temperature required for the subsequent cracking of admitted oil vapors which are passed through the spaces 106 under a predetermined time condition.

The use of relatively large forms as filler in regenerative furnaces with resultant higher heat capacity makes possible a considerable extension of the cracking period since as will be later more fully disclosed it is possible to alternate the cracking of the oil vapors with idling periods which permit the flow of interior heat to the surface of the forms so that they are again at a sufficiently high temperature to effect the desired type of cracking.

When heating the refractories to store heat necessary for cracking oil vapors, the resulting combustion gases may, if desired, be caused to pass both ways out of the cracking section, that is, some may be released upwardly through line 30 and valve 31 and the remainder downwardly through line 32 and valve 33. In the drawings line 22 is a header for gaseous fuel (such as for example the fixed gases from the process) and valves 23' and 24' in lines 23 and 24 control the admission of regulated amounts of gas to combustion zones 15 and 16 as desired. Line 26 is for the admission of controlled amounts of air to the gas lines so that the preferred pre-formed combustible mixture of air and gaseous fuel is admitted to the combustion spaces to insure the surface combustion on the filling material. Valves 27, 28, and 29 are provided to permit control over the quantity of air admitted at various points. This type of combustion provides a high temperature and a uniform distribution of heat so that there are no large temperature gradients in the sections of filling material. Furthermore, the combustion may be controlled so that any carbon or carbonaceous residue left on the refractory filler from the cracking step is burned off, leaving a clean surface for the cracking operation. To further assist in the heating period, and particularly in bringing the furnace up to a temperature sufficient for instigating surface combustion, ordinary combustion gases, such as, for example, those from the vaporizing furnace 10, may be admitted to the cracking furnace by way of line 30 containing valve 31 to flow downwardly therethrough. Valves 31 in line 30 and 33 in line 32 are ordinarily of high temperature-resistant material and/or special construction to insure their tightness since they are exposed to relatively high temperatures during the combustion periods and must allow no leakage of air or other gases into the furnace during the cracking period. When the flow through the cracking element is reversed upon the admission of oil vapors, valve 31 may be opened until residual products of combustion from the heating period are swept out, to avoid dilution of the cracked vapors with these gases in subsequent portions of equipment.

The cracking zone is preferably enclosed in a jacket 21' of high temperature metallic alloy or the like, which in turn is surrounded by heavy insulating or lagging 21.

In the furnace, as shown, vaporized oil is admitted from line 11 through valve 12 and passes upwardly through heated refractory sections 14, 15, 16 and 17 leaving the cracking zone through line 34 containing control valve 35. In the case of gas oil and kerosene distillates boiling in the approximate range of 400–750° F., satisfactory results in respect to olefin production have been obtained using temperatures of from 1500–1700° F. for relatively short times. To successfully eliminate secondary polymerization reactions among the cracked products, it is desirable to quickly cool or "quench" them, and this may be accomplished, for example, by admitting any one or more of several of the intermediate and final products of the process to line 34 by way of line 91 containing control valve 92. The particular quenching media and the details of their production and recirculation will be taken up in proper sequence. The temperature is preferably reduced to some point below 1000° F. before the cracked

products enter heat exchanger 6. It is to be understood that a plurality of cracking units such as the regenerative type described may be alternately operated and heated preparatory to further operation although only one such unit is shown in the drawings. Such operation is generally imperative if the process is to be made continuous, since normally the alternate blasting and cracking cycles are relatively short and the stream of oil vapors to be cracked must be frequently diverted to freshly heated units. In some units of this character the time of blasting is approximately 5 minutes, while the time that the heated filling material may be used to crack entering oil vapors is of the order of 3 minutes. Such short times are usually necessitated by the fact that best results are obtained only when there is a fairly accurate control of both temperature and time of exposure thereto. Obviously, mechanical controls may be provided which shift the necessary valve settings on a time basis to reverse the flow through the cracking units. Devices of this character are fairly well known in the cracking art, and since they constitute no special feature of the present invention, they are not illustrated or described in detail.

The cracked products supplied to heat exchanger 6 serve to preheat the charging stock for the process by indirect heat exchange therewith in this zone, as previously mentioned, following which the partially cooled products pass through line 36 and valve 37, to a primary separator or fractionator 38, which is provided to permit dropping out any heavy tarry material which is withdrawn through line 86 and valve 87 to a pump 88 which discharges through line 89 and thence either through line 89' and valve 90' to quenching line 91 or through valve 90 in line 89 to cooling and storage or elsewhere as desired. The amount of residual tar used at this point for quenching will be inversely proportional to its coking tendencies.

The vapors and fixed gases from separator 38 pass through line 39 containing control valve 40 and enter a more efficient fractionator 41, which is of suitable design and capacity for production of an overhead comprising only gasoline boiling range constituents, while leaving heavier intermediate products as a bottom reflux which may be recycled along with the fresh feed for further conversion or used as quenching material. Thus the bottom refluxes from fractionator 41 are withdrawn through line 93 containing control valve 94 and pumped by pump 95 which discharges through line 96 containing control valve 97 either to quenching line 91 by way of line 96 containing control valve 97'' or to raw oil line 7 by way of branch line 96' containing control valve 97'.

Vapors and fixed gases pass through overhead vapor line 42 containing control valve 43, through condenser 44 (which may be operated at lower than atmospheric temperature) and then through rundown line 45 containing control valve 46 to receiver 47. The liquid accumulating at this point, while preferably containing no constituents boiling higher than the end point of ordinary gasoline, may yet not contain certain of the lighter ends of the liquid products since the plant is still under vacuum up to this point. The complete recovery of the vapors of non-liquid products is accomplished in the subsequent absorption plant to be presently described. Liquid products are removed by way of line 48 containing control valve 49 to pump 50 which discharges through line 51 containing control valve 52 to the top of the fractionator to control the boiling range of effluent vapors or through branch line 53 containing control valve 54 to ultimate storage, where it is mixed with further recovered liquid material from receiver 76.

To recover normally liquid products, use is made of the ordinary cyclic absorption plant hook-up. Thus the gas from receiver 47 which may be quite rich in gasoline vapors passes through line 55 containing control valve 56 to pump 57 which discharges through line 58 containing control valve 59 and admits the gas-vapor mixture under a moderate superatmospheric pressure to the bottom portion of an absorption tower 60 to pass upwardly therethrough counter-current to a descending flow of absorber oil. The fixed gases at this point pass through line 98 containing control valve 99 to a pump 100 which discharges the gases either into quenching line 91 through valve 92'' or to storage through line 91' containing control valve 92'.

The absorber oil containing liquid gasoline fractions and some dissolved gases passes through line 61 containing control valve 62 to pump 63 which discharges through line 64 containing control valve 65 through a heating element 66 disposed to receive heat from a furnace 67, so that the temperature of the mixture may be raised sufficiently to volatilize absorbed hydrocarbons, the heated materials passing through line 68 containing control valve 69 to fractionator 70, which permits the vaporization and fractionation and ultimate recovery of the gasoline constituents and dissolved hydrocarbon gases. The overhead vapors from fractionator 70 pass through vapor line 71 containing control valve 72 and the liquefiable constituents are condensed during passage through condenser 73 to flow along with uncondensed gases through rundown line 74 containing control valve 75 to a final receiver 76 having a fixed gas release line 77 containing control valve 78 and liquid draw line 79 containing control valve 80. The fixed gases withdrawn at this point may be passed to the same storage as those from line 91', and the liquids are preferably blended with those from line 53.

The absorber oil, stripped of its light constituents, then passes through line 81 containing control valve 82 to recirculating pump 83 which discharges the oil (with cooling if necessary) through line 84 containing control valve 85 back to the top of absorbing tower 60 to repeat its cycle. Line 81' containing control valve 82' is indicated for the admission of absorbent either originally or for makeup purposes.

The foregoing description will indicate in a general way the type of cracking process comprised within the scope of the present invention. However, from a practical standpoint, it is imperative that operations be made continuous and that the shifting from heating to cracking periods and vice versa be minimized. In order to still more clearly designate the character of the invention the succeeding paragraphs will be devoted to a description of certain practical operating features which possess novelty in the present connection.

One novel feature consists in the use of alternate "idling" periods in the cracking period wherein the heat in refractory fillers following the heating period is utilized to crack oil vapors. As oil vapors pass over a refractory form at the rapid rates characteristic of the present invention, heat is abstracted at such a rate that the surface of the form is cooled below a desired

cracking temperature while the interior of the form is still at a considerably high temperature due to the poor heat conductivity of refractory materials. In connection with the present process therefore, it is proposed that instead of reheating the forms when the surface temperature has fallen below a given point, the flow of the oil vapors be halted until the surface has been returned to its previous high temperature by heat coming from the interior of the form. The flow of the oil vapors is then resumed and the cycle repeated until it is no longer possible to restore the surface temperature to a point above that desired for the cracking.

Fig. 3, A and B indicate diagrammatically the temperature gradients in forms of moderate size at the end of a cracking period in which the form has been used to heat oil vapors and at the end of the combustion or blasting period when the form has been brought up to an optimum temperature for use. It will be seen that the difference in temperature from the surface to the interior of the form is much greater at the end of the cracking period than at the end of the blasting period.

Fig. 3, C, D, E and F show the temperature gradients which will obtain in forms of larger size when idling periods are used to permit flow of heat from the interior to the surface of the forms. It will be observed that at the end of the idling periods, the curve indicating the temperature gradient has flattened out, that the difference in temperature between the exterior and the interior of the forms decreases after successive cracking periods and that the absolute surface temperature is lower. Conditions such as the size of the form, the permissible temperature range of cracking, the type of the oil vapors cracked and their rate of flow will determine in general both the absolute and relative time intervals which are best for these alternate cracking and idling periods.

In Fig. 4 the various periods of operation when using four furnaces in parallel and the aforementioned idling periods are indicated. The relative length of the periods is approximated from practice and it will be seen that cracking is taking place in some one of the furnaces at all times. The diagram also indicates that in the case of four furnaces they may be operated in a double parallel sense since two furnaces alternate between themselves in cracking and idling periods, involving merely a shift of the oil vapors from one furnace to the other while the other two furnaces are being purged of residual gases and heated by blasting or surface combustion to permit their further use in cracking oil vapors. The use of various types of furnaces and heaters in parallel connection to permit continuous operation along with the various manifolds and valves necessary are generally well known in the art and consequently have not been specifically indicated in the drawings. The use of the "idling" periods described and the double parallel operation is the feature characteristic of the present invention.

Owing to the evident possibility of varying charging oil, conditions of operation and type of plant construction, it is readily understood that numerous instances of operating results might be adduced in support of the commercial value of the present invention. However, the following example will be sufficient to indicate commercial value.

The charging stock used in a series of test runs to determine the best operating conditions was a Mid-Continent product having the following characteristics:

Gravity, °A. P. I. @ 60° F.	32.7
Specific gravity @ 60° F.	0.862

Engler distillation

I. B. P., °F.	446
10%	503
20	525
30	538
40	551
50	562
60	574
70	589
80	602
90	623
E. P., °F. (98.0%)	684

The following table shows the results obtained in three runs and indicates that the best conditions considering both the olefin content of the fixed gases and the anti-knock value of the liquid products were those shown in run No. 2.

Charging stock	Mid-Continent gas oil		
Run No.	1	2	3
Products: % by Wt. to charge			
distillate	18	22.5	32.0
Gases:			
Butylene	1.6	0.0	2.5
Butadiene	5.8	7.8	6.6
Butane			
Propylene	12.8	17.0	13.9
Propane			
Ethylene	14.2	17.8	13.6
Ethane			
Methane			
H_2	0.6	1.1	0.5
N_2	5.0	1.4	2.5
Paraffin	8.1	13.4	8.4
Coke and unaccounted losses	34.0	19.0	20.0
Total olefins	34.4	42.6	36.6
Octane number of gasoline, motor method	104	108	103
Reaction time, sec.	0.016	0.0105	0.012
Temp. °F. of reactor	1400–1290	1600–1420	1320–1220
Pressure, mm. of Hg. absolute	100	110	110

The figures given under "Temperature °F. of reactor" indicate the range which was obtained during the admission of oil vapors.

As a rule the olefinic gas mixtures produced by the present process may be utilized directly in various polymerization, condensation and alkylation reactions, with catalysts suitable for accelerating the different types of reactions involved.

The character of the invention and its utility as a branch of the cracking art is evident from the preceding specification and single instance of results obtained by its use, although neither section is to be construed as unduly limiting its generally broad scope.

I claim as my invention:

1. In a process for the pyrolytic conversion of hydrocarbons employing a regenerative type heater wherein said hydrocarbons are passed over the surfaces of previously heated refractory materials and wherein the rate of heat transfer from the hot refractory surfaces to said hydrocarbons is greater than the rate of heat transfer from the interior of said refractory materials to their external surfaces, the improved method of operation which comprises periodically stopping the flow of hydrocarbons over said refractory surfaces for a sufficient length of time to permit reheating of the surfaces by the trans-

fer of heat thereto from the interior of the refractory material, and subsequently re-establishing the flow of said hydrocarbons to be cracked over the reheated refractory surfaces.

2. A process as claimed in claim 1 characterized in that a plurality of such regenerative type heaters is employed and each heater is subjected to alternate periods of intermittent operation and regeneration and wherein a continuous stream of hydrocarbons to be cracked is alternately passed through and diverted from each heater in such a manner that said stream of hydrocarbons is continuously subjected to conversion in at least one of said heaters.

3. In a process for the pyrolytic conversion of hydrocarbons employing a plurality of alternately operated heaters which are preconditioned by storing heat within refractory materials contained therein and then utilized to heat said hydrocarbons by passing the latter therethrough in contact with the previously heated refractory materials, the improved method of operation which comprises first passing a stream of the hydrocarbons to be heated through a previously conditioned heater to subject the hydrocarbons to heating for a relatively short time at a rate greater than the rate of heat transfer from the interior of the refractory materials to the surface thereof in contact with the hydrocarbons, then diverting the stream of hydrocarbons to a second previously conditioned heater wherein they are again subjected to such high rates of heating for a relatively short time during which the first heater is allowed to idle and the temperature of the contact surface of the refractories in the first heater is materially increased by heat conducted thereto from the interior of the refractory materials, then diverting the stream of hydrocarbons from the second heater back to the first heater and allowing the second heater to idle, in the manner above described, while the stream of hydrocarbons is again subjected to high rates of heating for a relatively short time in the first heater, thence diverting the stream of hydrocarbons back to the second heater and continuing such alternate operation and idling of the first and second heaters until they require reconditioning to store additional heat in the refractory materials, preconditioning a third and a fourth heater during the periods of alternate operation and idling of the first and second heaters, diverting the stream of hydrocarbons to the third heater when the second heater requires reconditioning, alternately operating and idling the third and fourth heaters, in the manner previously described, while the first and second heaters are being reconditioned and alternately operating, idling and preconditioning each of the heaters in such sequence that the stream of hydrocarbons is continuously subjected to said high rates of heating.

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