

Nov. 21, 1967

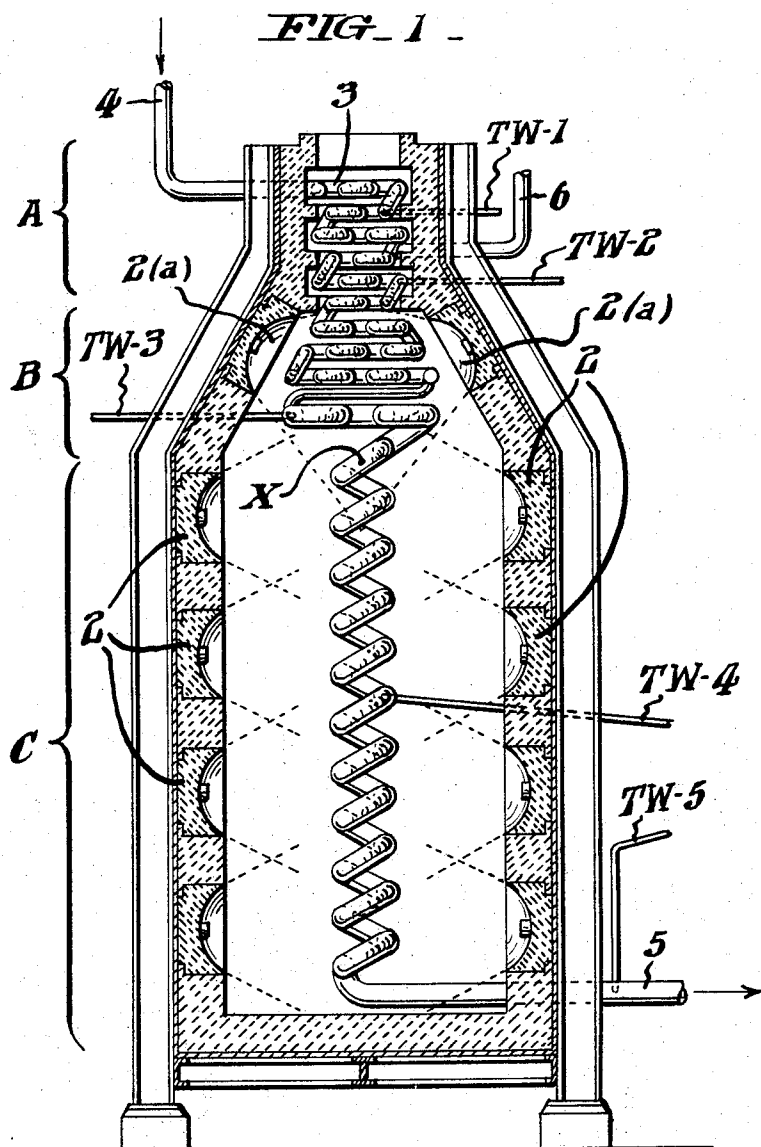
M. R. KITZEN

3,353,920

HIGH SEVERITY PYROLYSIS APPARATUS

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6 Sheets-Sheet 1



INVENTOR.
Maurice R. Kitzen,
BY
Paul & Paul
ATTORNEYS.

Nov. 21, 1967

M. R. KITZEN

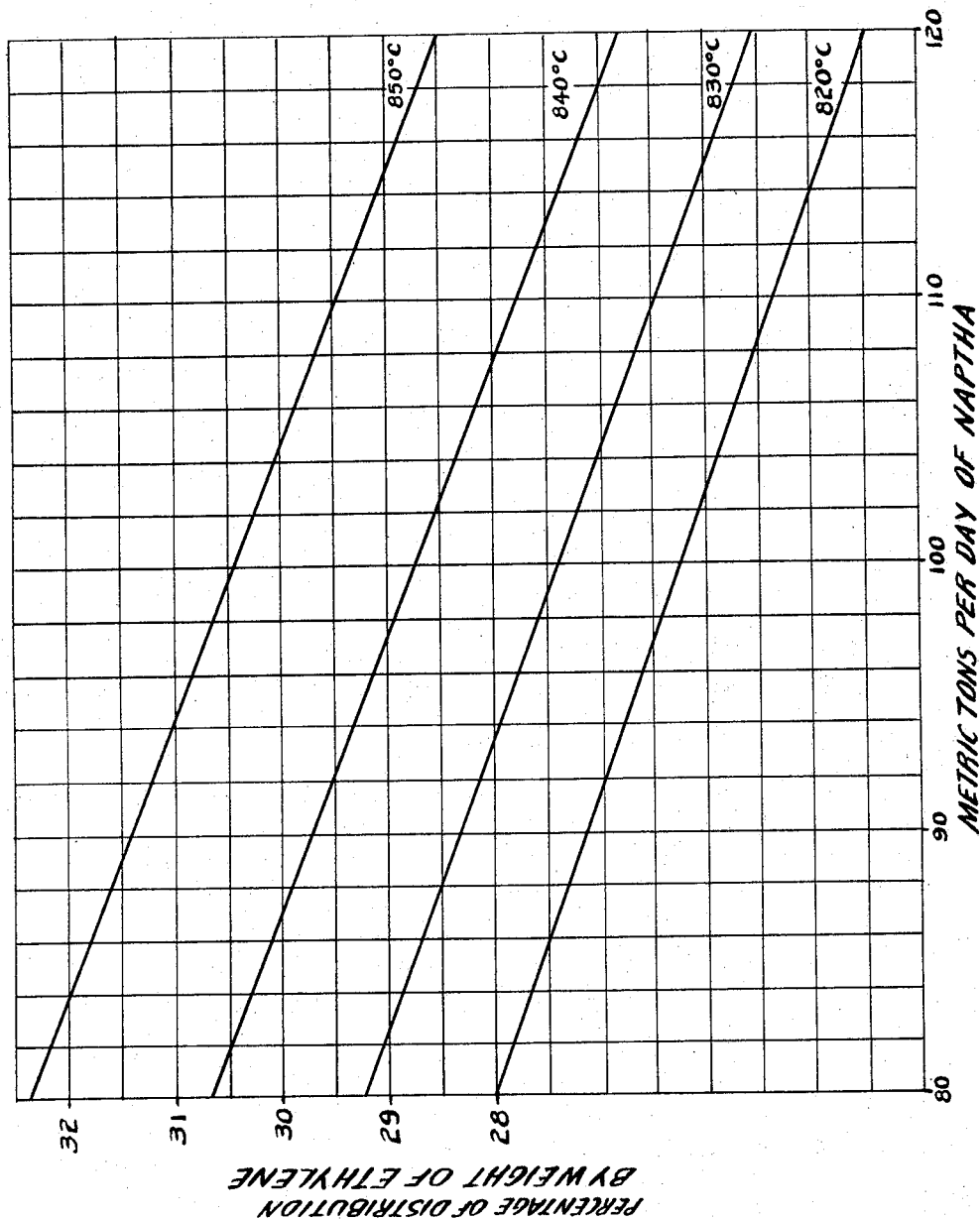
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FIG. 2 -



INVENTOR.
Maurice R. Kitzen,
BY
Paul & Paul
ATTORNEYS.

Nov. 21, 1967

M. R. KITZEN

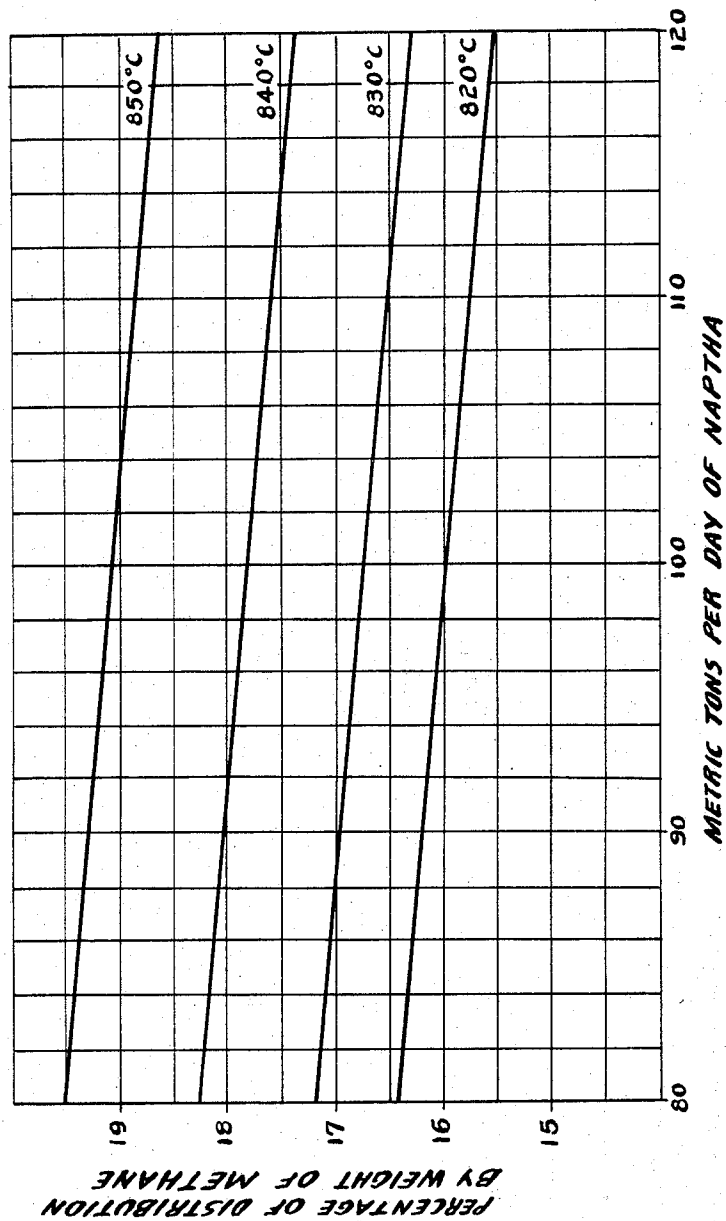
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FIG. 3 -



INVENTOR.

Maurice R. Kitzen,

BY

Paul & Paul
ATTORNEYS.

Nov. 21, 1967

M. R. KITZEN

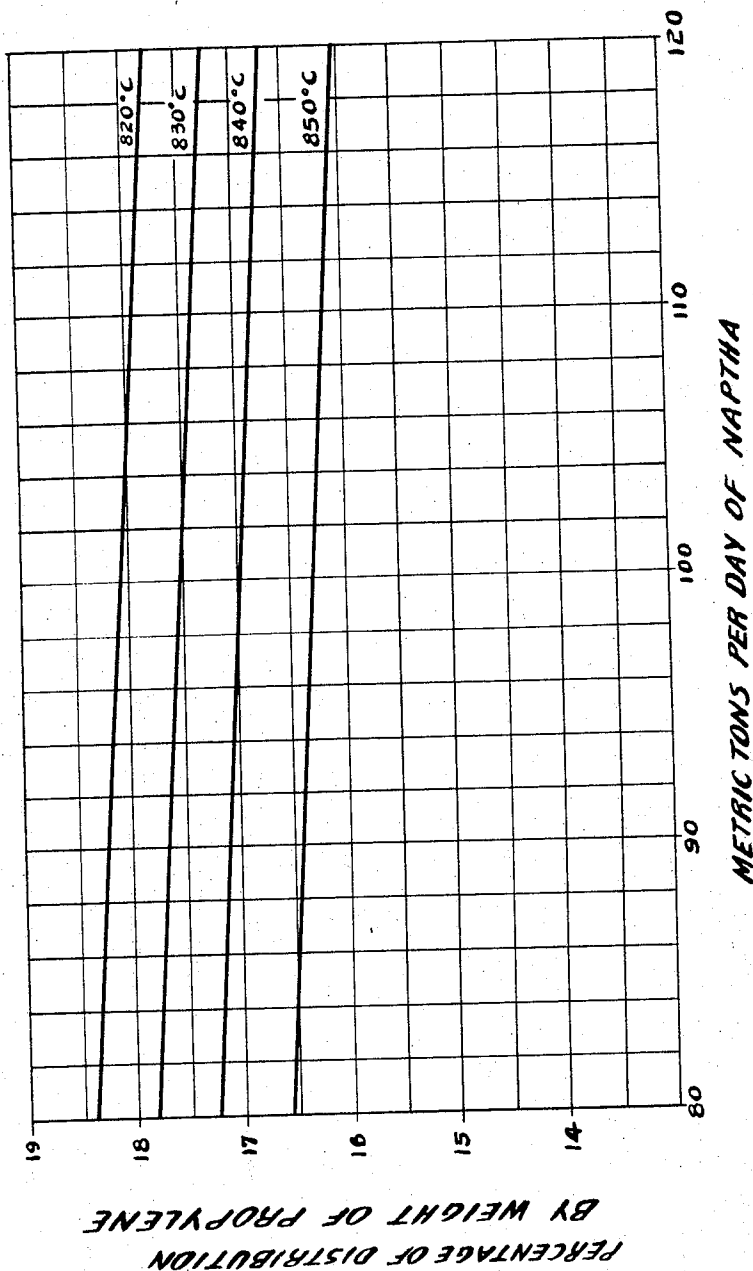
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FIG. 4-



INVENTOR.
Maurice R. Kitzen,
BY
Paul & Paul
ATTORNEYS.

Nov. 21, 1967

M. R. KITZEN

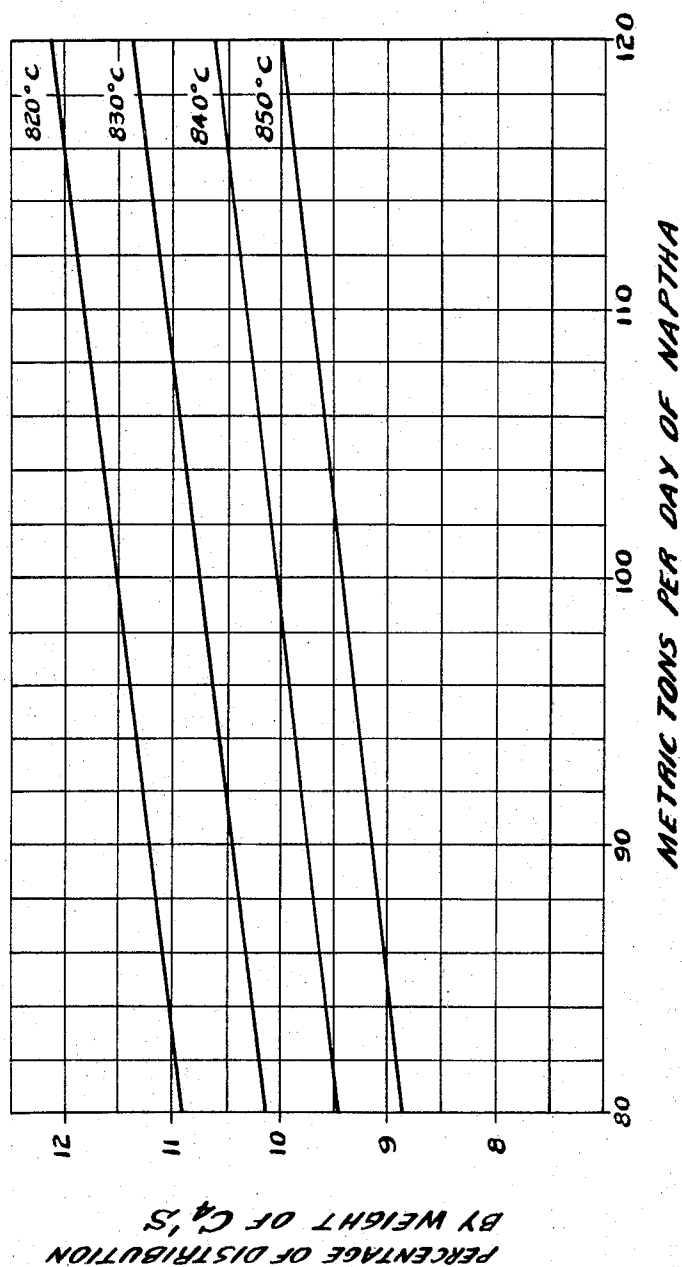
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HIGH SEVERITY PYROLYSIS APPARATUS

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FIG. 5



INVENTOR.
Maurice R. Kitzen,
BY
Paul & Paul
ATTORNEYS.

Nov. 21, 1967

M. R. KITZEN

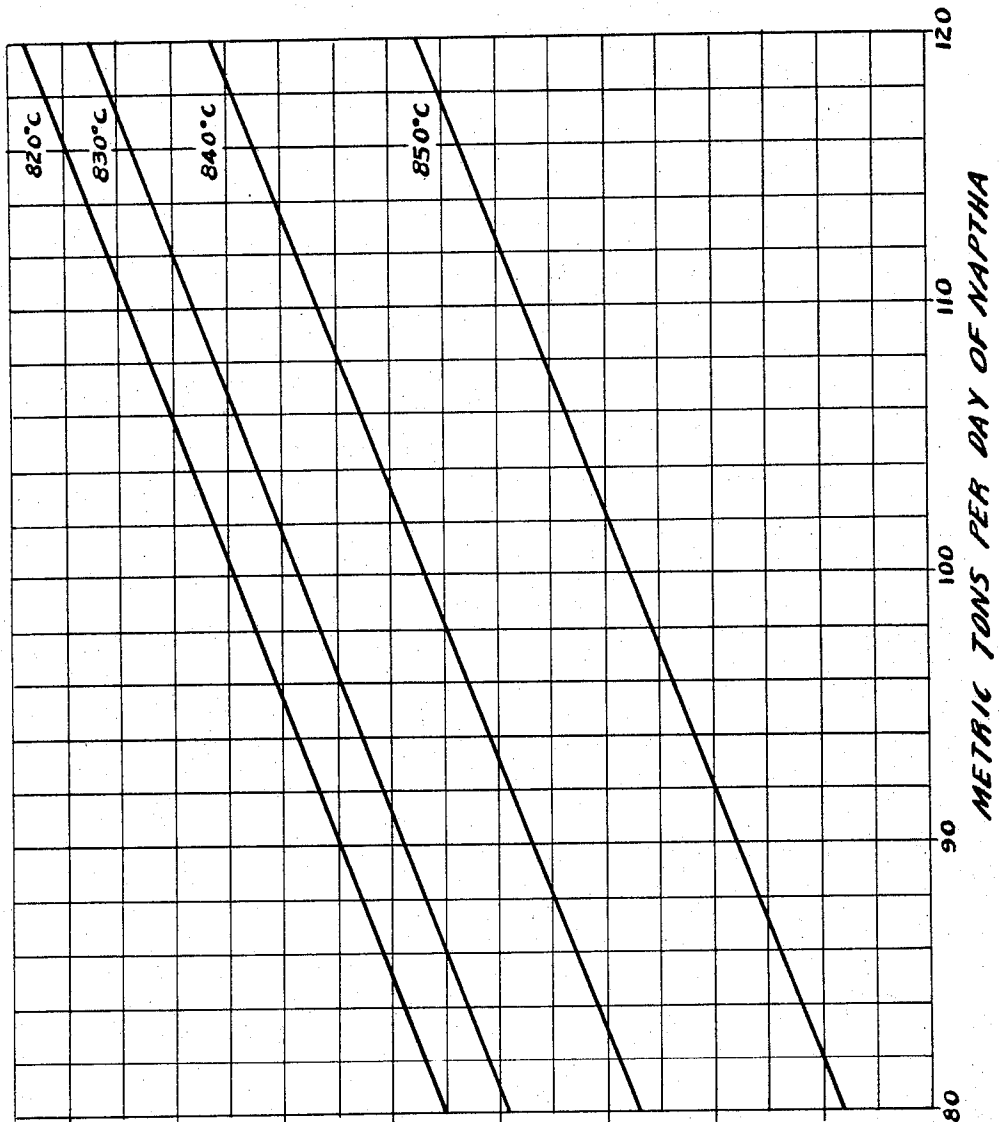
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HIGH SEVERITY PYROLYSIS APPARATUS

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FIG. 6 -



PERCENTAGE OF DISTRIBUTION
BY WEIGHT OF C₃'S AND ABOVE

INVENTOR.

Maurice R. Kitzen,

BY

Paul & Paul

ATTORNEYS.

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3,353,920

HIGH SEVERITY PYROLYSIS APPARATUS

Maurice R. Kitzen, Elkins Park, Pa., assignor to Selas Corporation of America, Dresher, Pa., a corporation of Pennsylvania

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1 Claim. (Cl. 23—277)

This invention relates to high severity pyrolysis and more particularly to a high severity hydrocarbon cracking apparatus.

Heretofore, conventional hydrocarbon cracking furnaces designed for the production of specific end products, such as ethylene, have involved operating conditions that allowed each of the fractionated components of the cracking process to reach substantially an equilibrium condition before recovery. In this manner, yields of particular products, such as ethylene, were established which were some function of the outlet temperature of the process apparatus. In practice the "equilibrium approach" has been used for the cracking of ethane to ethylene, for example.

The application of this theory, however, to the cracking of some heavier hydrocarbon cuts, such as various grades of naphtha, has posed serious problems which have not been successfully overcome prior to this invention. The cracking of naphtha using the equilibrium approach results in the production of a considerable number of hydrocarbon products existing simultaneously in equilibrium in the exit stream of the cracking unit. Expensive installations have therefore been required downstream of the cracking unit to separate and to refine these components. Subsequent cracking of individual components or groups of components was usually necessary to produce high yields of unsaturated low molecular weight hydrocarbons, such as ethylene.

In addition, the cracking of naphtha in this manner has posed difficult maintenance problems. When reactants are in the cracking unit long enough to achieve equilibrium conditions, considerable amounts of higher molecular weight residues are also formed. Under the cracking conditions these products have a tendency toward formation of coking residues; this has required frequent, expensive and time-consuming maintenance. While coking is a problem in any hydrocarbon cracking process, the coking encountered in the cracking of naphtha can be particularly serious.

It is therefore an object of this invention to provide a hydrocarbon cracking apparatus which is both efficient in terms of specific yields of various desired hydrocarbon products and operationally economical. It is a further object of this invention to provide a high severity pyrolysis apparatus for the production of unsaturated lower molecular weight hydrocarbons, such as ethylene.

Other objects and advantages of this invention will become apparent from the following disclosure.

It has been discovered that during hydrocarbon cracking the combination of a high operating temperature together with a greatly reduced residence time for the fluent reactant materials in the reaction zone results in the selective formation of high total yields of various desired products without an undue increase in coking and the elimination of expensive downstream separation equipment.

Referring now to the drawings:

FIG. 1 is a schematic illustration of one specific form of radiant furnace installation constructed for high severity pyrolysis according to this invention;

FIGS. 2-6 are graphic illustrations based on actual high severity pyrolysis runs showing the inter-relationship of the operating variables according to this invention.

Referring now to FIG. 1, the high temperature furnace, preferably equipped with gas-fired radiant heating burners

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as at 2, 2 (a) is fitted with serpentine coiled tubes 3 which permit the introduction of raw hydrocarbon material at 4 and emit the reaction products in a fluent stream at 5. For accurate control of the reaction temperatures the furnace is fitted with thermocouple-containing thermowells at various positions, TW-1, TW-2, TW-3, TW-4 and TW-5. In addition, at a predetermined position in the narrow neck of the furnace, steam is introduced into the coiled tubing through a tube 6.

The burners 2 (a) are connected to sources of fuel and combustion supporting medium such, for example, as fuel oil and air. Controls are provided (not shown and conventional per se) for selectively feeding oil plus air (for heating) or air alone (for cooling), and these connections may be as shown in the patent to Hess No. 2,638,879, for example.

In operation, a predetermined charge rate is established with a feed stock of naphtha, having an initial boiling point range from about 29° C. to about 33° C. and a final boiling point range from about 175° C. to about 205° C. The naphtha feed stock is diluted by steam introduced at 6 in Zone A. This step, combined with the other steps in the operation of the apparatus, reduces coking problems associated with the use of the relatively heavy feed stock, naphtha, and breaks up the naphtha into a fog-like mist thereby providing for more uniform heat absorption and additional control of crossover temperature.

As the feed stock, thus treated, progresses down through the heating coils and into Zone B, the temperature sensing devices TW-1 and TW-2 are utilized in conjunction with automatic controls (which are conventional per se and are therefore not shown) for adjusting the fuel-air ratio in the feed to the radiant burners 2, thereby producing close control of the heating of the feed stock under an extremely wide range of possible charging rates. Of utmost importance in the operation of the apparatus according to this invention is the close control of temperature in Zone B.

The location of thermowell TW-3 schematically represents the position where the temperature of the feed stock is carefully maintained at about 525° C. This temperature, hereinafter referred to as the crossover temperature, occurs at a predetermined point within Zone B, preferably at the transition from the small tubes in Zone B to the larger cross-sectioned serpentine coiled tubes shown entering Zone C. The effect of maintaining this crossover temperature upon this high severity pyrolysis process will hereinafter become apparent, when referring to the examples.

It will be understood that, by regulating the rate of heating or cooling supplied by the burners 2 (a), the location of the occurrence of the crossover temperature can be controlled. This is an important and advantageous feature of this invention.

The now fluent feed stock, upon entering Zone C, is severely heated in order quickly to reach a temperature in the range of from about 580° C. to 620° C. at approximately point X in FIG. 1, regardless of the charge rate used in the feed stock. This temperature is referred to as the incipient cracking temperature of the particular naphtha feed stock. The firebox temperature of Zone C is maintained in a temperature range of from about 1170° C. to about 1180° C. The term "residence time" refers to the time required for the fluent materials to travel from the approximate point of incipient cracking to the material outlet at the base of the furnace at 5.

The following examples show runs with various controlled outlet rates to illustrate how these factors can be varied to obtain different proportions of hydrocarbon products resulting from the use of the high severity pyrolysis apparatus of this invention.

FIGS. 2, 3, 4, 5 and 6 are graphs constructed from the data presented as indicated. During the collection of the following data variables such as the charge rate of the feed stock, the steam dilution rate, the crossover temperature and the outlet temperature were maintained at essentially constant values for each run. In the case of the various temperature values, the firing of the radiation burners in the different zones of the furnace was closely controlled so as to establish the desired heating curve. In this manner it was possible to record the effect of residence time alone on the yield distribution of the cracked components, especially ethylene, methane and propylene. By repeating the runs at different predetermined conditions the interrelationship of the residence time and the crossover and outlet temperatures can be graphically seen. In the table (see FIG. 2) the combination of short residence time (high charge rate) and high outlet temperature yields a large weight percentage of ethylene in the effluent outlet stream. The data indicate that within the limits of the graph the percentage distribution falls off as the charge rate becomes very large. It is important to note that all of the charge rates displayed on the graph are exceptionally high thereby producing residence times which are much smaller than any prior art process in this art. The significance of the particular graphic illustrations is in the unusual character of the phenomenon observed. While the percentage of desired components is decreasing and the percentage of undesired components is increasing the differences in the rates of charge are of a small enough relative order of magnitude to enable the operator of the apparatus to alter the distribution of products in the effluent stream thereby maximizing the yield of desired products and minimizing the yield of undesired products as a function of outlet temperature-charge rate interrelationship. This is a desirable improvement in that the percentage distribution of particular products does not have to depend on equilibrium conditions where only outlet temperatures can be used as a means of controlling the output product distributions of the particular cracking operation.

Table 1

Runs with a crossover temperature of approximately 525° C. and approximately 60% steam dilution using a light naphtha feed stock boiling from 35° C. to 110° C. while varying the outlet temperature as shown, were performed. The results were as follows:

	Charge rate in metric tons per day				
	120	110	100	90	80
Percent Ethylene at—					
850° C.....	28.5	29.5	30.4	31.4	32.4
840° C.....	26.8	27.8	28.75	29.7	30.65
830° C.....	25.55	26.5	27.4	28.35	29.25
820° C.....	24.5	25.35	26.25	27.1	28.0
Percent Methane at—					
850° C.....	18.6	18.18	19.05	19.25	19.5
840° C.....	17.35	17.55	17.8	18.0	18.25
830° C.....	16.25	16.5	16.7	16.95	17.2
820° C.....	15.5	15.7	15.95	16.2	16.4
Percent Propylene at—					
850° C.....	16.0	16.15	16.3	16.4	16.55
840° C.....	16.7	16.8	16.95	7.1	17.25
830° C.....	17.25	17.4	17.55	17.7	17.8
820° C.....	17.75	17.9	18.05	18.2	18.35
Percent C ₄ Compounds at—					
850° C.....	10.0	9.7	9.4	9.15	8.9
840° C.....	10.6	10.3	10.0	9.75	9.45
830° C.....	11.35	11.05	10.75	10.45	10.1
820° C.....	12.1	11.8	11.5	11.2	10.9
Percent of Compounds of C ₃ and above—					
850° C.....	18.7	17.7	16.75	15.75	14.8
840° C.....	20.6	19.6	8.65	17.65	16.7
830° C.....	21.75	20.8	19.8	18.9	17.9
820° C.....	22.35	21.4	20.4	19.45	18.5

Referring now to FIGS. 5 and 6, it is observed that the distribution of C₄ compounds and compounds of C₅

and above follow a pattern opposite to that obtained with compounds having three or less carbon atoms. In these cases the higher outlet temperatures yield relatively lower weight percentages of C₄, C₅ and heavier components. A selection of operating conditions can therefore be chosen which will significantly alter the distribution of both the desired and undesired end products. This factor gives the apparatus of the present invention a greater flexibility than it has previously been possible to achieve, particularly when cracking heavier hydrocarbon cuts.

In further explanation of the data in Table 1, both the data and the graphs of FIGS. 2, 3, 4, 5 and 6 show variable outlet temperatures compared to variable feed stock charge rate with other fixed experimental conditions. Rather than limiting these observations to the particular capacities of the experimental furnace used, the charge rate data was used for convenience here in place of the more conventional residence time characterization. This choice is purely arbitrary and does not affect the significance of the data. Residence time can easily be calculated for the particular furnace chosen for use in the high severity pyrolysis process of this invention. By definition, residence time is the length of time the fluent stream of reactant is exposed to a temperature at or above its incipient cracking temperature. In the case of naphtha, that temperature is about 1100° F. or about 600° C. By closely controlling the crossover temperature and the subsequent firebox temperature downstream of that point, an operator can determine very closely where the fluent stream has reached the incipient cracking temperature. Of course, consideration must be given also the thermodynamic characteristics of the particular cracking reactions taking place in the reaction tubes, as well as the increased velocity of the expanding fluent stream as the temperature increases. Using English units for convenience, specific velocity (pounds per second per square foot of cross-sectional area of the reaction tube) times specific volume (cubic feet of volume per pound or the reciprocal of density) equals the average linear velocity of the fluent reactant stream in feet per second. The total linear feet of tubing which is maintained above the incipient cracking temperature, divided by the average linear velocity will give the residence time. To calculate the above factors which include a weight term for simplicity and for convenience, the assumption has been made that the average molecular weight of the constituents in the fluent stream, including the steam, is equal to the molecular weight of the stream at the crossover temperature point plus the molecular weight at the outlet, divided by two.

Considering these calculations and applying them to the furnace used in these experiments with the firebox temperature maintained at about 2150° F. and maintaining a heat input of in the range of from about 15,000 to about 30,000 B.t.u. the actual residence times varied from about 0.6 second to about 1.25 seconds. These values were calculated on the basis of an arbitrarily imposed maximum linear velocity for the reactants of about 1200 feet per second.

In referring to the expression "actual residence time," it should be appreciated that the kinetics of the reactions, as well as the reactions themselves are very complex, and this term is therefore preferably, though rather arbitrarily, defined in the ultimate expression derived from the foregoing calculation.

On the basis of further information it has been discovered that the unique advantages of this invention can be achieved with residence times as low as 0.1 second as great as 1.5 seconds. Contrasting these findings with the prior art it has been determined that the prior art low severity processes as opposed to the conditions of this process had residence times of about 2.0 or more seconds. Since for the same furnace the residence time will be directly proportional to the furnace feed charge rate, when the crossover is controllable, the figures and data indicate

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that an increase in residence time at any given temperature will decrease the weight percent of certain products in the outlet stream and increase the weight percent of others. By choosing the proper operating conditions, the recovered weight percentage of a particular desired product, for example ethylene, can be maximized while minimizing certain other products, for example, compounds of C₄ and over. The advantage of this flexibility should readily be apparent. An alteration in the distribution of the end products which is made possible through the flexibility of the process according to this invention also works a very real advantage in reducing the cost of production of the specific fractions sought. By eliminating the need for a very large capital investment in separation equipment downstream of the furnace the production cost of ethylene is materially reduced. Further, the economic advantages of this invention can be measured by the reduction of percentage of compounds containing three carbons and lighter in the products which means reduction of compression costs for a given ethylene yield.

While this high severity pyrolysis apparatus has been described with particular reference to the production of ethylene from naphtha feed stocks, it will be readily apparent that other feed stocks can be utilized in the production of other desired hydrocarbon fractions by employing the teachings contained herein, and that equivalents may be substituted, parts reversed and certain features utilized independently of others, without departing from the spirit of the invention as defined in the appended claim.

The following is claimed:

In an apparatus for high severity cracking of a hydrocarbon including a furnace section having radiant heating means therein, and having tubing disposed in said furnace section to conduct said hydrocarbon material through said furnace section, said furnace tubing being disposed to receive heat from said radiant heating means, said apparatus having an exhaust section substantially free of radiant heat for exhausting the products of combustion and heat generated in said furnace section and having a preheat section disposed between said furnace section

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and said exhaust section, the combination which comprises: preheater tube means disposed in said exhaust section and said preheat section and connected to receive said hydrocarbons from their source and to introduce said hydrocarbons into said furnace tubing, steam tube means extending into said exhaust section and connected to said preheater tube means for introducing steam into said preheater tube means to form a hydrocarbon-steam mixture, radiant heating means located in said preheat section to transfer heat to said preheater tubing means to heat said hydrocarbon-steam mixture to a point above its incipient cracking temperature, control means comprising a temperature sensing means in said exhaust section coacting with said radiant heating means in said preheat section for controllably varying the location of said point of incipient cracking along said preheater tubing means, control means in said furnace section for controlling the temperature in said furnace section, and outlet means connected to said tubing in said furnace section for the products.

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