Dec. 4, 1945. D. K. FINLAYSON 2,390,244

CATALYTIC CONVERSION OF HYDROCARBONS

Filed July 31, 1941 2 Sheets-Sheet 1

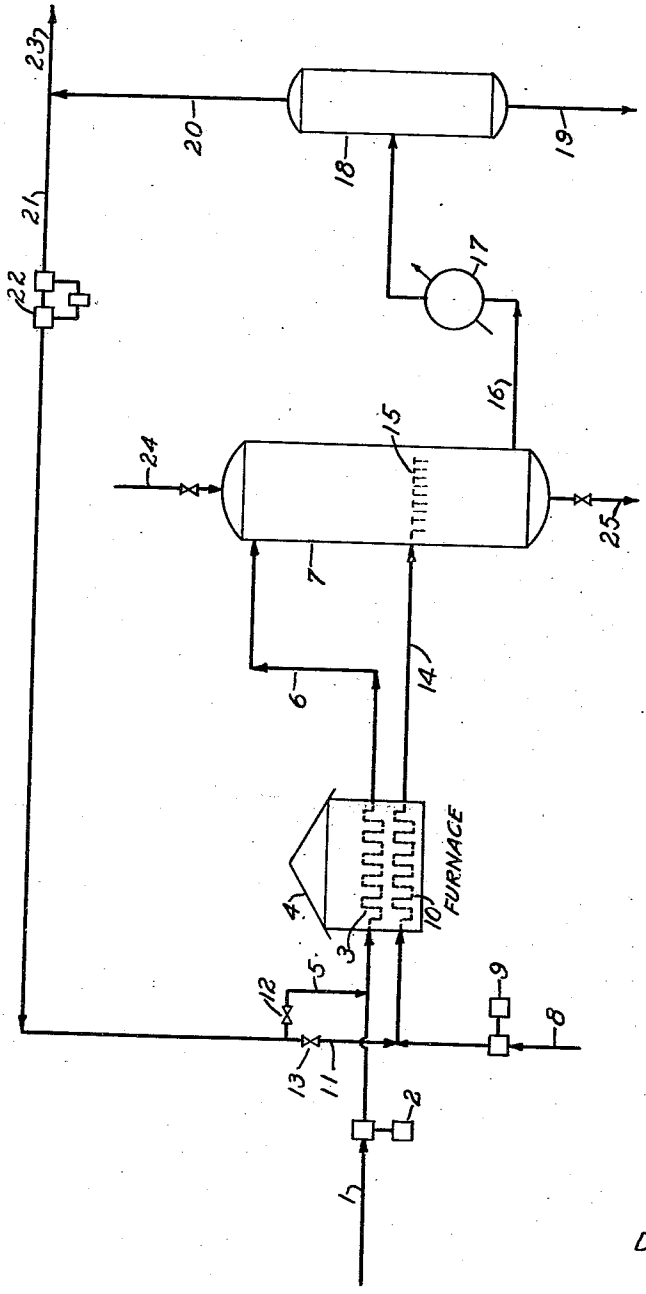


FIG. 1

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CATALYTIC CONVERSION OF HYDROCARBONS

Filed July 31, 1941 2 Sheets-Sheet 2

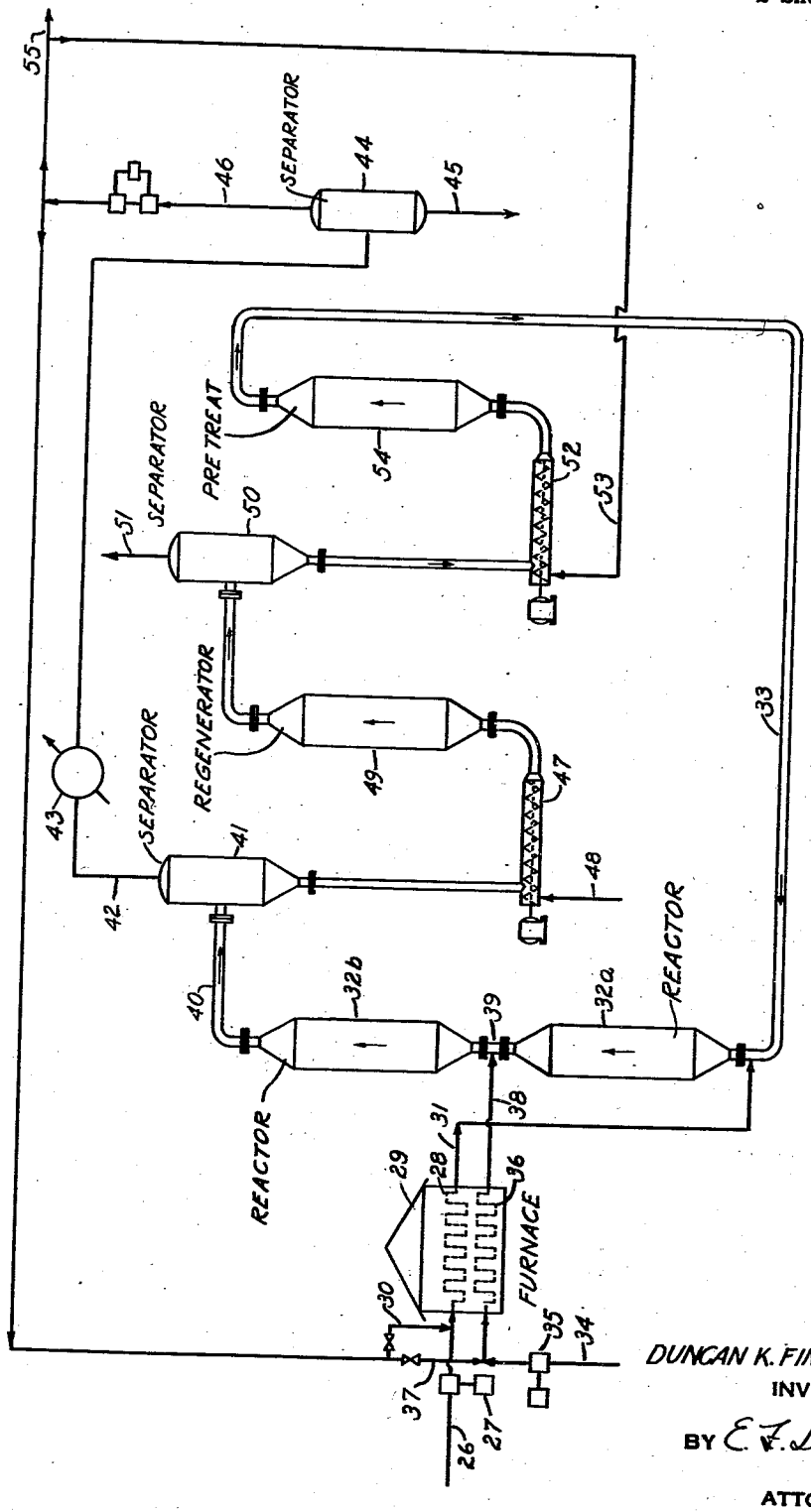


FIG-2

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UNITED STATES PATENT OFFICE

2,390,244

CATALYTIC CONVERSION OF HYDROCARBONS

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Application July 31, 1941, Serial No. 404,766

1 Claim. (Cl. 196—52)

My invention relates to the catalytic reforming of light distillate hydrocarbons and similar materials. Further, it relates to the catalytic dehydrogenation and aromatization of aliphatic and naphthenic hydrocarbons. More particularly, it comprises an improved unitary process for reacting two or more petroleum naphthas of different types.

An object of my invention is to convert light hydrocarbon distillates and similar materials into motor fuels of improved quality. Another object is to convert relatively low octane number naphthas into relatively high octane number aromatic type motor fuels by contacting said naphthas in the vapor phase with dehydrogenating and aromatizing catalysts in a reaction zone at elevated temperature and pressure. A further object is the provision of a method which permits more efficient processing of petroleum hydrocarbons. An important object of my invention is to provide a unitary method of reforming two or more different types of naphtha. Various other objects, advantages, and features of the invention will be readily apparent from the following description.

Many different types of naphtha feed stocks are available for catalytic reforming. The differences may be caused by varying geographical sources, varying processes from which the naphthas have been derived, or varying treatment to which they have been subjected. Classification of the naphthas is difficult because they are, for the most part, extremely complex mixtures of many types of hydrocarbon compounds. However, such terms as paraffinic, unsaturate, naphthenic, or aromatic as hereinafter employed in a relative sense are sufficiently definitive for one skilled in the art to apply them to the operation of the present invention. When it is desired to process two or more types of naphthas in a single catalytic reforming unit, the present practice is to combine these feeds and process the mixture as a single stream. This is not an entirely satisfactory procedure since the optimum reaction conditions to which one type of naphtha should be subjected are seldom the same as the optimum conditions for another type. These differences in preferred treatment arise from differences in such properties as refractoriness, coke forming tendencies, hydrogen producing tendencies, etc. I have discovered that the short-comings of the usual operation on a simple mixture can be substantially eliminated by the application of my invention wherein one type of naphtha is contacted with the catalysts at reaction conditions in a zone of sufficient magnitude to bring about a part of the desired reaction, and another type of naphtha is mixed with the now partly reacted first naphtha and the mixture contacted with the catalyst at reaction conditions in a zone of sufficient magnitude to complete the reaction of the first naphtha and bring about the desired reaction of the second naphtha. The invention can be easily applied to the processing of two, three, or more types of naphtha. For the sake of convenience the following examples of the application of my invention have been limited to cases involving only two types of naphtha.

It has been found in catalytic reforming that some hydrocarbons are more refractory than others. For example, predominately paraffinic hydrocarbon mixtures require more severe reaction conditions than predominately naphthenic hydrocarbon mixtures in order that a product of a given octane number be produced. It is therefore impossible to obtain the required extent of reaction on each type of hydrocarbon mixture when the usual method of operation is employed wherein both types are mixed and contacted with the catalyst together for the entire reaction. The practice of my invention makes it possible to obtain individual control of the extent of reaction of each type of hydrocarbon mixture by contacting one type alone for a portion of the reaction before adding the other type and completing the reaction on the combined streams. Thus it is possible to obtain the same or even a greater extent of reaction on a more refractory paraffinic naphtha by contacting it with the catalyst in the entire reaction space and contacting a less refractory naphthenic naphtha with the catalyst in only a portion of said reaction space.

In the dehydrogenation and aromatization of petroleum naphthas at elevated temperatures and pressures over suitable catalysts such as oxides of the sixth group of the periodic system, it is often advisable to carry out the reaction in the presence of a recycled gaseous product which is preferably rich in hydrogen in order to suppress coke formation on the catalyst and for other advantageous results. The purity of the hydrogen-containing gas recycled depends upon the purity and amount of hydrogen produced in the reaction, which in turn depends upon the type of naphtha being processed. An additional factor influencing the purity of the hydrogen-containing gas and thus the purity of the recycled hydrogen is the pressure in the reaction zone—lower pressures resulting in gases richer in hydrogen. It will be readily seen that compensation for the tendency of a naphtha to produce a gas which is too lean in hydrogen can be made by selection of a lower reaction pressure. The usual method of operation, wherein two or more naphthas are mixed and contacted with the catalyst throughout the entire reaction zone, does not allow the use of the optimum pressure on each of the different types of naphtha. This objection is overcome to a considerable extent by the practice of my invention wherein a first naphtha which tends to produce a gas rich in hydrogen (for example, a highly naphthenic naphtha) is

contacted with catalyst in an initial reaction zone at a relatively high pressure, and a second naphtha which tends to produce a gas relatively lean in hydrogen (for example, a highly cracked naphtha) is mixed with the now partly reacted first naphtha and the mixture contacted with catalyst in a second reaction zone maintained at a lower pressure than that maintained in said first zone.

In the catalytic reforming of petroleum naphthas a carbonaceous material is usually deposited on the catalyst, the amount of said deposit being proportional to the severity of the operating conditions and the extent of reaction. The necessary removal of the carbonaceous deposit is both difficult and expensive, and the amount of the deposit is therefore an important economic consideration. It has been found that those naphthas which are rich in unsaturate hydrocarbons, such as cracked naphthas, have a greater tendency to deposit carbonaceous material on the catalyst than the comparatively saturate hydrocarbons, such as virgin naphthas. In many instances, the magnitude of this carbonaceous deposit resulting from the cracked naphtha is the limiting factor as regards the severity of conditions which is allowable and the extent of reaction which is feasible in the usual method of operation wherein the relatively unsaturate feed is mixed with the saturate feed and the two contacted with the catalyst together. This situation is obviated by the practice of my invention wherein the virgin naphtha alone may be contacted with the catalyst for a portion of the reaction and the cracked naphtha subsequently added, thereby completing the reaction on the combined streams.

For convenience the present invention will be described in detail with respect to the catalytic dehydrogenation and aromatization of a virgin petroleum naphtha and an equal amount of cracked petroleum naphtha wherein it is desired to subject the cracked naphtha to less extensive reaction conditions than the virgin naphtha. However, it is to be understood that the invention is not limited thereto and is applicable generally to the field of catalytic reforming of light distillate hydrocarbons and similar materials.

In the accompanying drawings, forming a part of this specification—

Fig. 1 represents diagrammatically a simplified flow sheet of my improved system, the catalyst being maintained in fixed beds and regenerated in situ, and

Fig. 2 represents an alternate arrangement in which the catalyst in finely divided form continuously passes through the reaction zones.

Referring to Fig. 1 of the drawings, a virgin naphtha feed is introduced through line 1 by pump 2 into a heating coil 3 in furnace 4. A suitable amount of hydrogen-containing gas, preferably a recycle gas derived from the conversion products of the reaction, is introduced through line 5, added to the virgin feed in line 1, and passed through heating coil 3 therewith. Optionally the hydrogen-containing gas may be heated in a separate coil and added to the naphtha subsequent to the heater. After being vaporized and heated to a suitable temperature in coil 3, the mixture of hydrogen and virgin naphtha is passed by line 6 into catalyst tower 7 and through the catalyst bed contained therein.

A cracked naphtha feed is introduced through line 8 by pump 9 into heating coil 10 in furnace 4. A suitable portion of the hydrogen-containing gas may be introduced through line 11 and added to the cracked naphtha stream in line 8. The hydrogen-containing gas may be suitably proportioned between the virgin and the cracked naphtha streams by means of valves 12 and 13, or by closing valve 13 all of the gas may be added to the virgin naphtha stream. After being vaporized and heated to a suitable temperature in coil 10 the cracked naphtha is passed by line 14 into catalyst tower 7, suitable distributing means 15 being provided.

Catalyst tower 7 is filled with a dehydrogenating and aromatizing catalyst, for example, molybdenum oxide supported on activated alumina. The mixture of virgin naphtha and hydrogen-containing gas from line 6 is passed through tower 7 in contact with the catalyst through an initial zone of suitable size and under other operating conditions adapted to bring about a desired part of the reaction on the virgin naphtha before meeting the stream of cracked naphtha from line 14. The commingled streams of cracked naphtha and partly reacted virgin naphtha, together with the hydrogen-containing gas are then passed through the remainder of tower 7 in contact with the catalyst in a second zone of suitable size and under other operating conditions adapted to complete the reaction desired on the virgin naphtha stream and adapted to bring about the desired reaction on the cracked naphtha stream. The particular operating conditions employed in the various zones may suitably correspond to those disclosed in co-pending application, Serial No. 294,784, filed September 13, 1939.

Operating conditions suitably maintained in the first zone, wherein only the virgin naphtha is contacted with the catalyst, are illustrated by the following example of the conversion of a 42 octane number (C. F. R. M.) East Texas virgin naphtha having an initial boiling point of 250° F., an end point of 400° F., and an A. P. I. gravity of 50°:

Temperature — inlet of reactor (line 6) — ° F	1000
Temperature—end of first zone—° F	935
Pressure—lbs./sq. in. gage	250
Space velocity—vol. virgin naphtha/hr./vol. catalyst in first zone	1.2
Hydrogen gas recycle — cu. ft./bbl. virgin naphtha	2500
Length of each reaction period—hours	6

Operating conditions suitably maintained in the second zone, wherein both virgin and cracked naphtha are contacted with the catalyst, are illustrated by the following example of the conversion of a 62 octane number cracked naphtha having an initial boiling point of 220° F., an end point of 400° F., and an A. P. I. gravity of 49°:

Temperature—inlet of reactor (line 14) — ° F	1045
Temperature—combined streams—start of second zone (approx.)—° F	990
Temperature—outlet of reactor (line 16) — ° F	950
Pressure—lbs./sq. in. gage	245
Space velocity—vols. cracked naphtha/hr./vol. catalyst in second zone	0.6
Hydrogen gas recycle—cu. ft./bbl. cracked naphtha. (In addition to that with virgin naphtha)	2500
Length of each reaction period—hours	6

From tower 7 the reaction products are with-

drawn through line 16 and pass through cooler 17 into high pressure separator 18. This separator is maintained at such conditions of temperature and pressure that separation is obtained between the normally gaseous materials and the liquid reaction products. The normally gaseous materials comprise hydrogen and hydrocarbons of one to three carbon atoms. Preferably the separation is carried out under such conditions of temperature and pressure that the normally gaseous materials are relatively rich in hydrogen. The liquid reaction products are withdrawn from separator 18 by line 19 and passed to suitable stabilization or fractionation equipment, not shown. The hydrogen-containing gas is withdrawn from separator 18 by line 20. A suitable portion of this gas is recycled by line 21 and compressor 22 to the distribution valves 12 and 13 for introduction into the naphtha feed streams as previously described. The portion of the hydrogen-containing gas which is not desired for recycling is removed from the system by valved line 23 for further use or processing as desired.

During the course of the reaction a deactivating carbonaceous material is deposited on the catalyst. This deposit may be removed in many ways well known in the art—for example, by passing an oxygen-containing gas over the catalyst, provision for such regenerating gas being made by suitably valved lines 24 and 25. The operation of the unit may be made continuous by the provision of a plurality of reactors, one or more being used for reaction while others are being regenerated, purged, etc.

The reaction of the virgin naphtha in its passage through tower 7 is endothermic so that there is a temperature drop in the first zone between the inlet of line 6 and the inlet of the cracked naphtha from line 14 unless heat is supplied from an exterior source. This heat may be supplied by introducing the cracked naphtha from line 14 at a temperature substantially above the temperature dictated by the conversion requirements of the cracked naphtha alone. By thus raising the temperature of the mixture of virgin and cracked naphthas and the hydrogen-containing gas the heat content of the combined streams becomes sufficient to permit the reaction of such mixture without the endothermic nature of the reaction causing an excessively low temperature.

The tendency of a cracked naphtha to produce hydrogen is not so great as that of a virgin naphtha at substantially the same pressure because of the unsaturate nature of the former. It may, therefore, be desirable to operate the second zone, in which the mixture is reacted, at a somewhat lower pressure than the first zone. This may be brought about by suitable throttling means inserted between the zones, many methods of carrying out this pressure reduction being apparent to those skilled in the art. A preferred means of carrying out the pressure reduction would be to enclose each zone in separate towers with suitable valving or throttling means interposed.

The invention may also be carried out in a system in which the catalyst in finely divided or powdered form passes through the reaction zones. A simplified flow sheet of such a system is depicted in Fig. 2. The operation of my invention is now described in conjunction with Fig. 2, and for clarity of presentation a typical example is employed in which a cracked naphtha is injected into the reaction zone subsequent to the injection of a virgin naphtha stream. The virgin naphtha feed is introduced through line 26 by pump 27 into heating coil 28 in furnace 29. A suitable amount of hydrogen-containing gas is introduced through line 30, added to the virgin feed in line 26 and passed through heating coil 28 therewith. After being vaporized and heated to a suitable temperature in coil 28, the mixture of hydrogen and virgin naphtha is passed by line 31 to the base of reactor 32a where it is joined by a powdered catalyst—laden hydrogen-containing gas from line 33. This catalyst may suitably be a dehydrogenating and aromatizing catalyst, for example, molybdenum oxide supported on activated alumina. The catalyst, hydrogen-containing gas, and virgin naphtha pass up through reactor 32a, which is a first zone of suitable size and maintained under other operating conditions adapted to bring about a desired part of the reaction on the virgin naphtha. The proportions of reactor 32a are preferably selected so that the upward linear vapor velocities are relatively low, that is in the range of about 1 to 25 feet per second, and preferably in the range of about 1 to 5 feet per second. By regulating the velocity of the gases in the reactor the concentration of the catalyst within the reaction zone may be suitably maintained within the range of about 2 to 25 pounds of catalyst per cubic foot of reactor volume, and preferably within the range of about 6 to 16 pounds per cubic foot. The catalyst in the reaction zone is thereby maintained in a dense or "fluidized" phase. The linear vapor velocity and the catalyst concentration will depend upon such factors as the density, size and shape of the catalyst particles.

A cracked naphtha feed is introduced through line 34 by pump 35 into heating coil 36 in furnace 29. A suitable portion of the hydrogen-containing gas may be introduced through line 37 and added to the cracked stream in line 34. After being vaporized and heated to a suitable temperature in coil 36, the cracked naphtha is passed by line 38 into line 39 containing the stream of catalyst-bearing vapors of the mixture of hydrogen-containing gas and partly-reacted virgin naphtha. The commingled streams of cracked naphtha and partly reacted virgin naphtha together with the hydrogen-containing gas and the powdered catalyst are passed through the second reaction zone 32b, which zone is of suitable size and maintained under other operating conditions adapted to complete the reaction desired on the virgin naphtha stream and adapted to bring about the desired reaction on the cracked naphtha stream. The particular operating conditions employed in the various zones may suitably correspond to those disclosed in co-pending application, Serial No. 348,605, filed July 31, 1940.

The various reaction zones may be separated by a constricted area such as line 39 as shown, in which case there will be no internal recirculation of the "fluidized" catalyst between second zone 32b and first zone 32a. The reaction zones 32a and 32b may be incorporated in a single reactor without the constriction 39, and the vapors from line 38 may be injected with the use of suitable distribution means between the reaction zones. In the latter case, the powdered catalyst may be maintained in a "fluidized" bed with considerable internal recycle of catalyst. The second reaction zone is preferably of greater cross sectional area than the first zone in order to compensate for the greater volume of vapors passing

therethrough. As in the case of the fixed-bed operation, the invention as carried out in Fig. 2 may be operated with different conditions of temperature and pressure in the two reaction zones.

From reaction zone 32b the reaction products and catalyst are withdrawn by line 40 to suitable catalyst separating means 41. This separating means may comprise cyclone separators, Cottrell precipitators, or any apparatus of like function, all of which are well known in the art. From catalyst separating means 41 the reaction products are withdrawn through line 42 and pass through cooler 43 into high pressure separator 44 from which liquid reaction products are withdrawn by line 45 and normally gaseous materials are withdrawn by line 46.

The used catalyst in separating means 41 is partly deactivated by a deposit of carbonaceous material. This deposit may be removed by withdrawing the used catalyst from separating means 41 by pump 47 and passing said catalyst along with oxygen-containing gas from line 48 through regenerator 49 in which the necessary combustion takes place. The regenerated catalyst suspended in the regeneration flue gas then passes to catalyst separating means 50, the regeneration flue gas being removed by line 51.

It may be desirable to pretreat the regenerated catalyst with a hydrogen-containing gas prior to using said catalyst in the reaction zone. This is suitably carried out by removing the regenerated catalyst from catalyst-separating means 50 by means of pump 52 and passing said catalyst along with a hydrogen-containing gas from line 53 through catalyst pretreatment zone 54 which is maintained under the necessary operating conditions. From pretreatment zone 54 the catalyst-laden, hydrogen-containing gas is passed through line 33 to the reaction zone. By suitable piping means, not shown, a portion of the stream in line 33 may be injected into line 39 along with or close to the inlet of line 38. The hydrogen-containing gas in line 53 which is used for the catalyst pretreatment is preferably a recycle gas derived from the reaction products. The recycle gas is suitably proportioned among the virgin naphtha stream (line 30 to line 26), the cracked naphtha stream (line 37 to line 34), and the catalyst pretreatment (line 53 to pump 52). It may be found desirable to pass all of the recycle gas to the catalyst pretreatment zone 54. The net product hydrogen-containing gas is withdrawn through valved line 55.

For purposes of clarity the operation of my invention has been described in concrete examples with particular reference to the addition of a cracked naphtha to a reaction zone at a point subsequent to the partial reaction of a virgin naphtha. In certain instances, however, the points of introduction of the two naphtha streams may be reversed, in which case the initial portion of the reaction zone is maintained under preferred conditions for partially converting the cracked naphtha, and the subsequent portion of the reaction zone is maintained under preferred conditions for converting the combined streams. It is further apparent that the invention may be practiced with suitable modifications in many different ways and that it may be applied to naphthas and similar materials of many different types as heretofore described.

I claim:

The method of reforming by catalytic dehydrogenation two different types of naphtha, said types being based on substantial differences in operating conditions required to effect a given amount of dehydrogenation which comprises passing the first type of naphtha along with a finely divided or powdered catalyst through an initial reaction zone of sufficient volume to bring about part of the desired reaction, admixing the second type of naphtha with the partly reacted catalyst-bearing first naphtha, and passing the commingled naphthas through a second zone at a pressure lower than that maintained in the first zone of sufficient volume to complete the reaction of said first naphtha and simultaneously bring about the desired reaction of said second naphtha.

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