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N. B. KING

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DEHYDROGENATION OF ALKYL AROMATIC COMPOUNDS IN  
THE PRESENCE OF NICKEL-BEARING ALLOY STEELS

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2 Sheets-Sheet 1

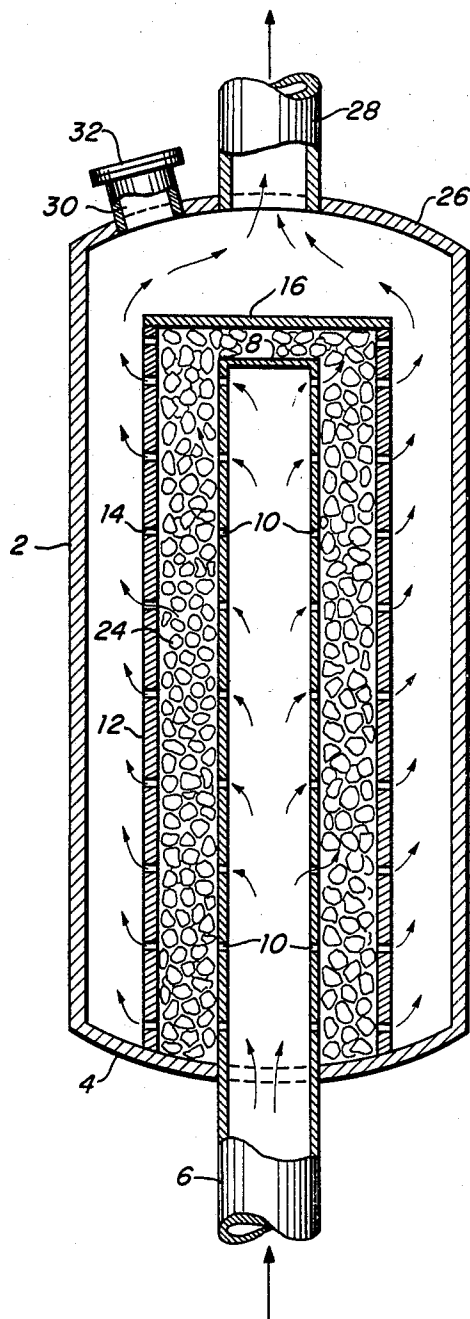


FIG. 1.

NORMAN B. KING  
INVENTOR.

BY  
*Schiller and Pankovic*

ATTORNEYS

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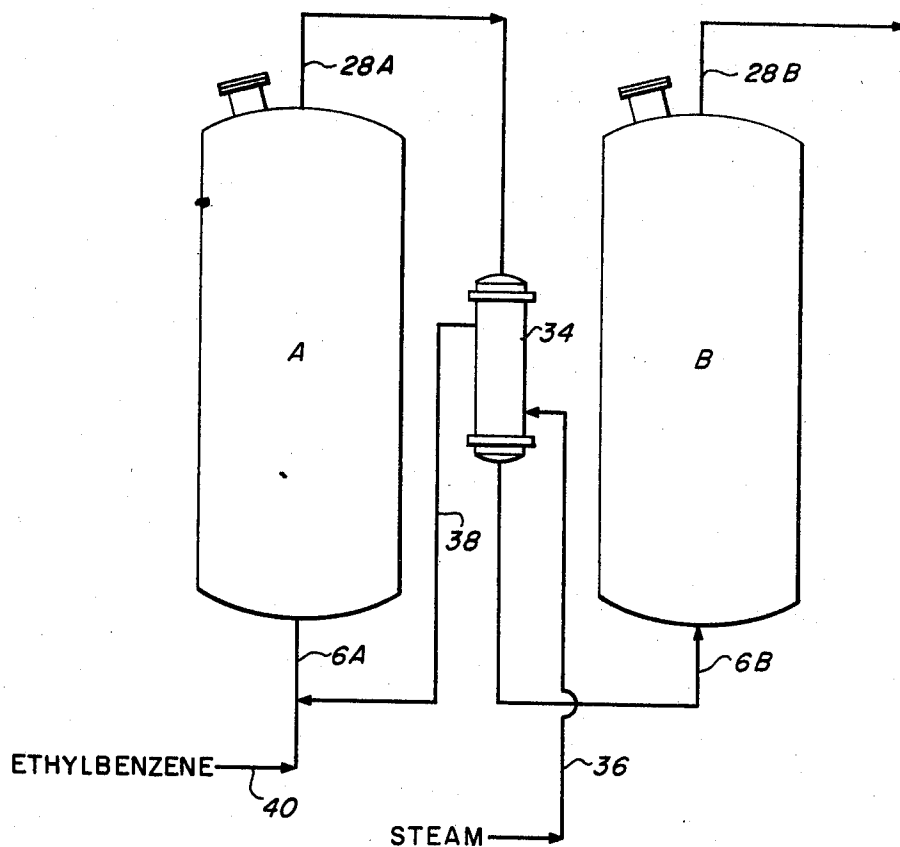


FIG. 2.

NORMAN B. KING  
INVENTOR.

BY

*Schiller & Pandisco*

ATTORNEYS

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## DEHYDROGENATION OF ALKYL AROMATIC COMPOUNDS IN THE PRESENCE OF NICKEL-BEARING ALLOY STEELS

Norman B. King, Wayland, Mass., assignor, by mesne assignments, to The Badger Company, Inc., Cambridge, Mass., a corporation of Delaware

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19 Claims

### ABSTRACT OF THE DISCLOSURE

Dehydrogenation of alkyl aromatic compounds involving reactors constructed in part of nickel-bearing alloy steels and in part of nickel-free alloy steels.

The present invention relates to dehydrogenation of alkyl aromatic hydrocarbons and more particularly to the conversion of ethylbenzene to styrene.

Styrene is a well known commercially available material having a wide variety of uses, including manufacture of polystyrene plastics, styrene-butadiene latex and other polymer products. It is most commonly made by catalytically dehydrogenating ethylbenzene. As conventionally practiced liquid ethylbenzene feed is vaporized, superheated, and passed together with superheated steam through a dehydrogenation reactor containing a bed of suitable catalyst. This dehydrogenation reaction is highly endothermic and the considerable drop in temperature which accompanies the reaction has the effect of limiting the yield. Yield refers to the ratio of moles of styrene appearing in the product, multiplied by 100, to the moles of ethylbenzene entering the reactor. To offset the aforesaid temperature drop and thereby achieve a suitable yield, sufficient heat is supplied directly or indirectly to the reactants or the dehydrogenation equipment to maintain the temperature of the mixture in the region of 550 to 660° C.

Heretofore it has been the practice to construct the dehydrogenation reactors of alloy steels having substantially little or no nickel content. This practice has been predicated on the ground that the presence of nickel promotes cracking of the hydrocarbon feed to undesirable products and results in carbon formation, reduced styrene yield, catalyst deactivation, and possible plugging of the catalyst system. However, the use of non-nickel alloy steels has resulted in more expensive dehydrogenation equipment because the allowable design stresses for such steels are relatively low at the high temperatures involved in the process. In particular the pressure-containing shells of the reactors require large design thicknesses which, coupled with the poor mechanical properties of nickel-free alloy steels, makes fabrication difficult and greatly increases equipment cost. A further problem with non-nickel containing alloy steels is that they tend to undergo metallurgical changes when subjected to substantial temperature changes, e.g., when the equipment is cooled down.

The general object of the invention is to provide a substantial improvement in the art of dehydrogenating alkyl aromatic hydrocarbons.

A further object of this invention is to provide a new method and apparatus for the dehydrogenation of alkyl aromatic hydrocarbons such as ethylbenzene whereby the foregoing disadvantages are overcome.

A more specific object of the invention is to provide

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new and improved reactors for dehydrogenating alkylated aromatic hydrocarbons, notably ethylbenzene, that are characterized by high through-put at relatively low pressure drops, even distribution of reactants, high yields, greater strength, relatively little or no metallurgical deformation resulting from substantial changes in temperature, and lower cost of construction.

According to this invention, dehydrogenation is effected in one or more reaction zones each comprising a reactor designed so that all but a selected section thereof in which the initial reaction occurs is made of nickel bearing alloy steels. This selected initial reaction section is fabricated of non-nickel bearing steels. The use of low allowable stress non-nickel bearing steels in the initial reaction section is feasible since it is not a pressure-containing part of the reaction vessel. This design is predicated on the discovery that cracking into undesired side products, substantial carbon formation and other harmful effects on the dehydrogenation system will occur only if the hot unreacted alkyl aromatic compounds contact nickel bearing steels while unmixed with steam or only partially mixed with steam. More specifically this design is derived from the discovery that the usual harmful effects are avoided if contact with the nickel bearing steels occurs after the alkyl aromatic feed and steam have been mixed and the dehydrogenation reaction has started and proceeded sufficiently to release hydrogen gas as one of the reaction products.

The foregoing objects and advantages are better appreciated and the invention better understood by the specific details presented below which are to be considered together with the accompanying drawing, wherein:

FIG. 1 is a sectional view of a preferred form of a reactor constructed in accordance with the invention; and

FIG. 2 is a schematic flow diagram of one illustrated embodiment of the novel process.

Turning now to FIG. 1, the reactor comprises a cylindrical outer pressure shell 2 fabricated of a suitable nickel-bearing alloy steel, e.g., series 300 austenitic stainless steels. The bottom head 4 of shell 2 is provided with an opening in which is mounted an inlet pipe 6 made of a non-nickel alloy steel, e.g., a series 400 stainless steel. The inner end of pipe 6 is closed off by an end head 8 which also is made of the same non-nickel stainless steel. That portion of pipe 6 located within shell 2 is provided with a multitude of holes 10 sized to permit optimum flow of the fluid reactants which are supplied to the reactor via conduits (not shown) connected to pipe 6.

The pipe 6 is surrounded by a concentrically disposed cylindrical wall 12 which also is provided with a multitude of holes 14 sized to permit optimum flow of reactants and reaction products. The bottom end of wall 12 is secured to the bottom head 4 of shell 2. The upper end of wall 12 is secured to a head plate 16. Head plate 16 which covers wall 12 is imperforate. Wall 12 and plate 16 both may be made of the same nickel-bearing alloy steel used to fabricate shell 2.

With this construction the wall 12, pipe 6, and that portion of bottom head 4 extending between pipe 6 and wall 12 together form a large volume chamber that contains a bed of a suitable catalyst 24 in particle form. In this connection it is to be appreciated that the relative sizes of the catalyst particles and the holes in pipe 6 and wall 12 are such that the particles cannot pass through the holes; alternatively the holes 10 and 14 may be substantially larger than the catalyst particles but covered with a fine mesh screen having openings smaller than the catalyst particles. The upper end head 26 of shell

2 has an outlet port fitted with a pipe 28 which serves to deliver the reactor effluent to associated process equipment, e.g., another reactor or a product recovery stage.

It is to be appreciated that FIG. 1 is directed to the essential aspects of the reactor design and that in practice the reactor may embody various conventional features and details of construction. For example, the reactor may be fitted with one or more manholes permitting access to its interior for inspection and maintenance purposes. Thus, FIG. 1 shows the upper end head 26 fitted with a manhole pipe 30 having a removable cover 32.

It also is to be understood that any one or a combination of a number of nickel-containing alloys and stainless steels may be used for the reactor walls and heads. By way of example, but not limitation; such parts of the reactor may be made of one or more of the following: Type 302, 304, 321 and 325 stainless steels. Similarly, the inlet pipe 6 may be made of any one of a variety of non-nickel alloy steels.

With a reactor designed generally as illustrated in FIG. 1 and as above described, all reactant feed mixing is completed and initial reaction occurs in the internal central pipe 6. Since this pipe is made of non-nickel steel, it is unaffected by the reactants and will produce no side cracking or other harmful effects on the dehydrogenation reaction if the steam and alkyl aromatic feed are not completely mixed as is true just after the reactants are introduced thereto. The initial dehydrogenation reaction occurring in pipe 6 releases hydrogen gas as one of its products. The initial reaction products and the unreacted reactants produce no significant degree of cracking and little or no carbon formation when brought into contact with the nickel-containing wall 12, plate 16, or shell 2.

Reference now is had to FIG. 2 which is a schematic flow diagram of one illustrative embodiment of the novel process directed to conversion of ethylbenzene to styrene. This illustrative embodiment employs two reactors A and B with the outlet pipe 28A of reactor A connected to the inlet pipe 6B of reactor B through a heat exchanger 34. The heat exchanger 34 and the inter-connecting pipes 28A and 6B may be constructed of nickel containing alloy steels. Steam, preferably superheated, is introduced via a pipe 36 to the outer section of heat exchanger 34 and, after heat exchange with the effluent of reactor A, it passes via a conduit 38 to the inlet pipe 6A where it is mixed with ethylbenzene feed supplied by a feed pipe 40. The final product mix leaves reactor B via its outlet pipe 28B and is introduced into a conventional product recovery system (not shown) where styrene is separated from the other reaction products and recovered.

In this system of FIG. 2, the conversion of ethylbenzene to styrene is effected in both reactors, with the effluent from reactor A (comprising styrene, ethylbenzene and steam) being heated to a desirable temperature by heat exchange with the steam supplied by pipe 36. This indirect heating is simple and offers the advantage that the same steam used to heat the effluent of reactor A is that employed in the dehydrogenation reaction.

The quantity of steam fed to reactor A depends upon the particular alkylated aromatic hydrocarbon making up the feed stock. In the case of ethylbenzene, conversion to styrene with a yield of 50-60% requires about 10-20 moles of steam per mole of ethylbenzene. The operating temperatures are not narrowly critical but can vary over a moderate range. Thus, the ethylbenzene-steam mixture fed to reactor A may be within the range of 580° C. to 660° C. while the effluent from reactor A has a temperature of about 550-610° C. In passing through exchanger 34 the effluent from reactor A may be reheated to the identical temperature as the reactant mixture delivered by inlet pipe 6A or to a higher or lower temperature. Preferably the entering temperature of the hydrocarbon-steam mixture fed to reactor B is about the same as that for reactor A.

Substantially any well-known dehydrogenation catalyst may be used for dehydrogenation of alkyl aromatic hydrocarbons according to this invention. These include ferric oxide-potassium oxide, magnesium oxide-ferrous oxide-potassium carbonate, and alumina-silica-nickel catalysts. These catalysts are arranged in beds having a height to depth ratio (the depth is measured from the central pipe 6 to the cylindrical wall 12) ranging from about 5:1 to about 40:1, with the preferred ratio being about 10:1.

The following example serves to illustrate the preferred mode of producing styrene from ethylbenzene according to this invention.

#### EXAMPLE

Two reactors designed as described above are coupled together in the manner illustrated in FIG. 2. Each reactor has a catalyst bed with a height to depth ratio of about 10:1. The catalyst is a promoted iron oxide type having an average particle size of  $\frac{1}{8}$  inch. Ethylbenzene and steam are delivered to reactor A at the relative rates of 72.6 and 220 pounds per hour respectively. The ethylbenzene delivered via pipe 40 has a temperature of about 550° C. while the steam fed via pipe 36 has a temperature of about 682.5° C. The steam-ethylbenzene mixture has a temperature of about 642° C. as it enters reactor A. The effluent withdrawn from reactor A has a temperature of about 595° C., but due to reheating in exchanger 34, it has a temperature of about 640° C. when it enters reactor B. The effluent from the second reactor is withdrawn at a temperature of about 617.5° C. This effluent is then fed to a conventional recovery system where styrene is recovered.

In this two stage system, the ethylbenzene feed is partially dehydrogenated to styrene upon contact with the fixed catalyst bed in reactor A and additional dehydrogenation occurs when the effluent from reactor A passes through the catalyst bed in reactor B. The overall conversion to styrene i.e., the ratio, multiplied by 100, of the moles of ethylbenzene converted to styrene in both reactors to the moles of ethylbenzene fed to reactor A, is in excess of 50%.

It is to be appreciated that this invention is not limited to styrene but embraces the dehydrogenation of other alkylated aromatic hydrocarbons such as isopropylbenzene, diethylbenzene, etc. to produce different vinyl substituted aromatic hydrocarbons. Furthermore the number of reactors that may be employed is variable and more than two reactors may be employed in a system provided provision is made for heating between stages. Where more than two reactors are used the temperature of the steam initially introduced into the system is adjusted to provide the desired degree of temperature rise for the effluent passing from one reactor to another. As a practical matter, the total number of reactors is determined by the economy of the process.

With reactors designed as herein described, the hydrocarbon and the steam may be premixed before introduction to the pipe 6 of reactor A or may be mixed within the pipe as in the preferred embodiment. If the steam and hydrocarbon are premixed before delivery to pipe 6, then the entire reactor A including pipe 6 may be made of nickel bearing stainless steel. However, this alternative procedure is less desirable since it produces a somewhat smaller yield. It is believed obvious that, in either case, the subsequent stage reactors, e.g. reactor B, may be made wholly of nickel bearing steels. It also is contemplated that the flow of gases through the reactors may be reversed. More specifically, it is contemplated that the hydrocarbon and steam may be premixed and then fed through pipe 28 into the space surrounding the catalyst bed, passed through the catalyst bed, and then withdrawn through pipe 6. This mode of operation is feasible and will not result in substantial carbon formation or undesired side products due to cracking since it is predicated on the hydrocarbon and steam being fully premixed before com-

ing into contact with the nickel-bearing steels of the reactor. It is to be understood also that reactor may be designed so that the inlet pipe 6 is at the top and the outlet 28 is at the bottom, in which case the system shown in FIG. 2 would be modified to provide for downward rather than upward flow of reactants and reaction products.

A dehydrogenation reactor designed as herein described and illustrated offers several advantages. For one thing it is a radial flow system offering high through-put with a relatively low pressure drop (about  $\frac{1}{2}$ –1 pound per square inch per reactor) between the internal pipe 6 and the outer shell 2. Hence the inner pipe 6 is not a pressure containing member and the stresses to which it is subjected are well within the allowable limits for non-nickel austenitic stainless steels. On the other hand, the higher allowable stress limits and greater ductility of the nickel bearing steels used to fabricate the shell and interior wall 12 make possible larger diameter equipment and greater flexibility in details of design (with consequent capital cost savings) than are possible if nickel-free alloy steels are used for the same parts.

As used herein the terms "nickel-free alloy steel" and "non-nickel alloy steels" means alloy steels that are substantially free of nickel or have a nickel content no greater than 0.75%.

Other modifications and variations of the process and apparatus herein described will be apparent to persons skilled in the art. Therefore, the invention should be considered as including all modifications, variations and alternative forms falling within the scope of the appended claims.

#### I claim:

1. In a process for dehydrogenation of an alkyl aromatic hydrocarbon feed in the presence of steam which comprises passing a mixture of said hydrocarbon and steam through a reactor having an outer shell formed of a nickel-bearing alloy steel and a catalytic dehydrogenation zone within said shell, the improvement which comprises mixing said hydrocarbon feed and steam in a chamber within said reactor constructed of a non-nickel alloy steel, dehydrogenating part of said hydrocarbon feed in said chamber, and passing the resulting mixture of hydrocarbon feed, steam, and dehydrogenation products through said catalytic dehydrogenation zone so as to further dehydrogenate said hydrocarbon feed.

2. The process of claim 1 wherein the effluent of said reactor is passed through a second reactor having a second catalytic dehydrogenation zone so that the dehydrogenation of said feed is effected in both reactors.

3. The process of claim 1 wherein said hydrocarbon feed is essentially ethylbenzene.

4. The process of claim 3 wherein 10–20 moles of steam are supplied for each mole of ethylbenzene.

5. The process of claim 3 wherein the mixture of hydrocarbon feed and steam is at a temperature in the range of 580–660° C. in said chamber.

6. The process of claim 2 wherein said hydrocarbon feed comprises ethylbenzene and said effluent is heated to a temperature of about 550–610° C. before it passes to said second reactor.

7. The process of claim 6 wherein said effluent is heated by indirect exchange of heat from said steam.

8. A process for dehydrogenating an alkyl aromatic hydrocarbon which comprises the steps of pre-mixing said hydrocarbon with steam, introducing the mixture into one end of a nickel-bearing alloy steel reactor containing a bed of dehydrogenation catalyst disposed between two concentric chambers, passing said mixture radially through said bed from one chamber to the other, and removing the products of reaction and the unreacted portion of said mixture from the opposite end of said reactor.

9. A dehydrogenation reactor comprising a closed shell having an outlet at one end, an inlet pipe extending into said shell from the end opposite said one end, and means in said shell defining a catalytic dehydrogenation zone surrounding said inlet pipe in the path of reactants

flowing from said inlet pipe to said outlet, said shell being formed of high allowable stress steel and said pipe being formed of a non-nickel alloy steel.

10. Apparatus adapted for dehydrogenation of alkyl aromatic hydrocarbons comprising a closed shell having an outlet at one end, an inlet pipe extending into said shell from the end opposite said one end, mechanical means within said shell defining a chamber surrounding said pipe and communicating with said inlet pipe and said outlet, and a dehydrogenation catalyst within said chamber, said shell and said mechanical means being made of nickel-bearing alloy steels and said inlet pipe being made of a non-nickel alloy steel.

11. Apparatus as defined by claim 10 wherein said pipe is provided with orifices that permit radial flow of reactants through said chamber.

12. Apparatus as defined by claim 10 wherein the ratio between the length of said chamber measured along the longitudinal axis of said shell and the depth of said chamber measured radially from said inlet pipe is in the range of 5:1 to 40:1.

13. A system for dehydrogenating alkyl aromatic hydrocarbons comprising two reactors as defined by claim 10, means for introducing a mixture of steam and an alkyl aromatic hydrocarbon to the inlet pipe of one reactor, and means connected between the outlet of said one reactor and the inlet pipe of the other reactor for delivering the effluent from said one reactor to the other reactor so that the alkyl aromatic hydrocarbon undergoes dehydrogenation in both reactors.

14. A process for dehydrogenating an alkyl aromatic hydrocarbon comprising intimately mixing said hydrocarbon with steam and initiating dehydrogenation of said hydrocarbon in a first chamber of a reactor where the hydrocarbon-contacting surfaces thereof are a non-nickel alloy steel, passing the mixture of hydrocarbon and steam and the products of initial dehydrogenation to a second chamber of said reactor which contains a dehydrogenation catalyst and where at least in part the hydrocarbon-contacting surfaces thereof are a nickel-bearing alloy steel, further dehydrogenating said hydrocarbon in said second chamber under the influence of said catalyst, and collecting the products of the dehydrogenation reaction from said second chamber.

15. The process of claim 14 wherein said non-nickel alloy steel is a 400 series stainless steel and said nickel-bearing steel is a 300 series stainless steel.

16. The process of claim 14 wherein said chambers are in concentric relation to each other, and further wherein the flow of hydrocarbon, steam and the products of initial dehydrogenation is substantially in a radial direction through said second chamber.

17. The process of claim 14 wherein said hydrocarbon and steam are passed to said second chamber only after the initial dehydrogenation reaction has proceeded sufficiently to release hydrogen gas as one of its products.

18. A process for dehydrogenating an alkyl aromatic hydrocarbon using a reactor having a first chamber in which its hydrocarbon-contacting surfaces are a non-nickel alloy steel and a second chamber in which its hydrocarbon-contacting surfaces at least in part are of a nickel-bearing alloy steel, said second chamber containing a dehydrogenation catalyst, comprising mixing said hydrocarbon and steam in said first chamber under conditions such that dehydrogenation of said hydrocarbon is initiated in said first chamber, passing the resulting mixture of hydrocarbon, steam and initial dehydrogenation reaction products to said second chamber under conditions such that further dehydrogenation of said hydrocarbon is catalyzed by said catalyst, and collecting the products of reaction from said second chamber.

19. In a method of performing a high temperature dehydrogenation reaction wherein a hydrocarbon feed is subjected to a temperature at which formation of carbon is promoted if the hydrocarbon feed is contacted

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with a nickel-containing alloy steel, the improvement comprising supplying said hydrocarbon feed and steam to a reactor having an outer pressure shell made of a nickel-bearing steel, mixing said hydrocarbon feed with steam in a first chamber of said reactor in which the surfaces thereof exposed to said feed are made of a non-nickel alloy steel, said mixing being effected under conditions such that part of said feed is dehydrogenated, passing the resulting mixture of hydrocarbon feed, steam and dehydrogenation products from said chamber through a catalytic reaction zone in said reactor and further dehydrogenating said feed in said zone under the influence of said catalyst, and collecting the products of dehydrogenation from said reactor.

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DELBERT E. GANTZ, Primary Examiner

C. R. DAVIS, Assistant Examiner

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