

CATALYTIC REFORMING PROCESS AND SYSTEM FOR MAKING AROMATIC HYDROCARBONS**Cross-Reference to Related Applications**

[0001] This application is related to, and claims priority benefit from, U.S. Provisional Application Serial No. 62/720,802, filed August 21, 2018, entitled "CATALYTIC REFORMING PROCESS AND SYSTEM FOR MAKING AROMATIC HYDROCARBONS", herein incorporated by reference in its entirety.

Field of the Invention

[0002] A catalytic reforming process and system for producing aromatic hydrocarbons is disclosed. The process and system are useful in the petroleum and chemical processing industries in the catalytic reforming of hydrocarbon feedstocks to form aromatic hydrocarbons such as benzene.

Background of the Invention

[0003] The catalytic conversion of hydrocarbons into aromatic compounds, referred to as aromatization or naphtha reforming, is an important industrial process. Aromatization (reforming) reactions may include dehydrogenation, isomerization, dehydroisomerization, cyclization, dehydrocyclization, dealkylation and hydrocracking of a hydrocarbon feed stream, with each reaction type producing specific aromatic compounds. These reactions are generally conducted in one or more aromatization reactors containing one or more specific aromatization catalysts. Such catalysts may increase the reaction rates, production of desired aromatics, and/or throughput rates for certain desirable aromatic compounds.

[0004] The dehydrocyclization of linear hydrocarbon feeds, e.g., the formation of aromatic hydrocarbons such as benzene from naphtha or other paraffinic feed streams comprising C₆ to C₈ alkanes, is a commercially useful process. The process is usually practiced on a straight run naphtha fraction that has been hydrodesulfurized. Straight run naphtha is typically highly paraffinic but may contain significant amounts of naphthenes and minor amounts of aromatics or olefins. In a typical reforming process, the reactions include dehydrogenation, cyclization, isomerization, and hydrocracking. The dehydrogenation reactions will usually include the dehydroisomerization of alkylcyclopentanes to aromatics, the dehydrogenation of paraffins to olefins, the dehydrogenation of cyclohexanes to aromatics, and the dehydrocyclization of paraffins to aromatics. The aromatization of the n-paraffins to aromatics is generally considered to be important in fuels refining because of the high octane of the resulting aromatic product compared to the low octane ratings for n-paraffins. The isomerization reactions include isomerization of n-paraffins to isoparaffins and vice versa, and the isomerization of substituted five and six membered ring naphthenes. The hydrocracking reactions

include the hydrocracking of paraffins and hydrodesulfurization of any remaining sulfur present in the feedstock.

[0005] One such process was developed in the early 1980's, known as AROMAX[®] technology, and has been commercialized in a number of locations. Later developments in AROMAX[®] catalysts in the late 1990s also led to commercial deployments. Compared to other reforming technologies, AROMAX[®] technology is attractive for benzene and aromatics production, particularly from paraffinic feedstocks, such as hexanes through octanes. Despite such benefits and commercial activity, however, AROMAX[®] technology has not seen wide commercial acceptance, at least in part, due to limited market need for on-purpose benzene production where substantial benzene production as a process by-product may be available, and due to the comparative high capital cost of the technology. Such costs can be attributed to the number of furnaces and reactors required due to the large endothermic heat effects in reforming reactions and to the sensitivity of the reforming catalysts to sulfur poisoning, thereby necessitating extensive feed pre-treatment.

[0006] Reforming processes are described in the literature, including, e.g., U.S. Patent Nos. 6,063,264; 5,879,538; and 6,004,452, which detail the use of catalysts comprising L-zeolite for the catalytic reforming of feed hydrocarbons to form aromatics. Such catalysts are generally monofunctional, non-acidic catalysts comprising L-zeolite and a Group VIII metal and are well-documented in the patent literature, particularly in U.S. 5,879,538. A process and system for converting acyclic C₅ feedstock to non-aromatic, cyclic C₅ hydrocarbon is disclosed in U.S. Patent No. 9,914,678.

[0007] As with all chemical processes, the economics of a catalytic reforming process are affected by many factors, including capital cost, plant efficiency, and margin of the product. In catalytic reforming processes, the cost of the reforming plant and catalyst, the run-length of the catalyst and the throughput of the plant play an important role in determining the economics. Due to their commercial importance, an ongoing need therefore exists for improved processes and systems for the catalytic reforming of hydrocarbons.

Summary of the Invention

[0008] The present invention is directed to a process and system for forming aromatic hydrocarbons from a hydrocarbonaceous feed stream. One of the goals of the invention is to provide improvements to reforming processes and systems that lead to lower capital and operating costs for producing aromatic hydrocarbons. The process generally includes contacting the feed stream with a catalyst contained within the heater tubes of a reactor furnace, the catalyst being disposed on a substrate, and providing heat to the furnace heater tubes. The catalyst comprises a non-acidic catalyst effective to form aromatic hydrocarbons by catalytic reforming of the feed stream hydrocarbons, e.g., an L-zeolite catalyst, and the feed stream comprises a naphtha fraction, typically a naphtha feed stream having a predominately C₆ to C₈ content.

[0009] The invention is further directed to a system for the catalytic reforming of a hydrocarbonaceous feed stream to form aromatic hydrocarbons. The system generally comprises a reforming furnace reactor containing heater tubes with a catalyst contained within the heater tubes of the furnace, the catalyst being disposed on a substrate, and a heat source to provide heat to the furnace heater tubes for the catalytic reforming of the feed stream hydrocarbons to form aromatic hydrocarbons. The heat transfer to the center of the tube may be enhanced through heat-conducting inserts in the tube. As with the associated process, the catalyst comprises a non-acidic catalyst effective to form aromatic hydrocarbons by catalytic reforming of the feed stream hydrocarbons, e.g., an L-zeolite catalyst.

Brief Description of the Drawings

[0010] The scope of the invention is not limited by any representative figures accompanying this disclosure and is to be understood to be defined by the claims of the application.

[0011] FIG. 1 illustrates the temperature in the center of a reactor tube along the flow direction for cordierite monolith as described in an embodiment of the examples.

[0012] FIG. 2 illustrates the temperature in the center of a reactor tube along the flow direction for FeCrAl monolith as described in an embodiment of the examples.

Detailed Description

[0013] Although illustrative embodiments of one or more aspects are provided herein, the disclosed systems and/or processes may be implemented using any number of techniques. The disclosure is not limited to the illustrative or specific embodiments, drawings, and techniques illustrated herein, including the exemplary designs and embodiments illustrated and described herein, and may be modified within the scope of the appended claims along with their full scope of equivalents.

[0014] Unless otherwise indicated, the following terms, terminology, and definitions are applicable to this disclosure. If a term is used in this disclosure but is not specifically defined herein, the definition from the IUPAC Compendium of Chemical Terminology, 2nd ed (1997), may be applied, provided that definition does not conflict with any other disclosure or definition applied herein, or render indefinite or non-enabled any claim to which that definition is applied. To the extent that any definition or usage provided by any document incorporated herein by reference conflicts with the definition or usage provided herein, the definition or usage provided herein is to be understood to apply.

[0015] "Aromatization", "aromatizing", and "reforming" as used herein refer to the catalytic treatment of a hydrocarbon-containing feed stream to provide an aromatics-enriched product (i.e., a product comprising an aromatics content that is greater than in the feed stream).

[0016] An “aromatic” compound is a compound containing a cyclically conjugated double bond system that follows the Hückel $(4n+2)$ rule and contains $(4n+2)$ pi-electrons, where n is an integer from 1 to 5. Aromatic compounds include “arenes” (hydrocarbon aromatic compounds, e.g., benzene, toluene, and xylenes) and “heteroarenes” (heteroaromatic compounds formally derived from arenes by replacement of one or more methine ($-C=$) carbon atoms of the cyclically conjugated double bond system with a trivalent or divalent heteroatoms, in such a way as to maintain the continuous pi-electron system characteristic of an aromatic system and a number of out-of-plane pi-electrons corresponding to the Hückel rule $(4n+2)$). As disclosed herein, the term “substituted” may be used to describe an aromatic group, arene, or heteroarene, wherein a non-hydrogen moiety formally replaces a hydrogen atom in the compound, and is intended to be non-limiting, unless specified otherwise.

[0017] The term “support”, particularly as used in the term “catalyst support”, refers to conventional materials that are typically a solid with a high surface area, to which catalyst materials are affixed. The support may be inert or participate in the catalytic reactions, and may be porous or non-porous. Typical catalyst supports include various kinds of carbon, alumina, silica, and silica-alumina, e.g., amorphous silica aluminates, zeolites, alumina-boria, silica-alumina-magnesia, silica-alumina-titania and materials obtained by adding other zeolites and other complex oxides thereto. Supported catalysts are generally catalysts in which the active components, e.g., Group VIII and Group VIB metals or compounds thereof, are deposited on a carrier or the support.

[0018] “Molecular sieve” refers to a material having uniform pores of molecular dimensions within a framework structure, such that only certain molecules, depending on the type of molecular sieve, have access to the pore structure of the molecular sieve, while other molecules are excluded, e.g., due to molecular size and/or reactivity. Zeolites, crystalline aluminophosphates and crystalline silicoaluminophosphates are representative examples of molecular sieves. Non-limiting representative examples of silicoaluminophosphates include SAPO-11, SAPO-31, and SAPO-41.

[0019] “Zeolite” generally refers to an aluminosilicate having an open framework that allows for ion exchange and reversible dehydration. A large number of zeolites have been found to be suitable for catalysis of hydrocarbon reactions. Non-limiting representative examples include L-zeolite (also referred to as zeolite L), Y-zeolite (or zeolite Y), ultrastable Y zeolite or ultrastable zeolite Y (often abbreviated as USY zeolite), zeolite beta, ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-34, ZSM-35, ZSM-38, ZSM-48, ZSM-50, and ZSM-57. Zeolites may include other metal oxides in addition to the aluminosilicate, in the framework structure.

[0020] The term “substrate” as used herein, generally refers to materials that are not themselves typical catalyst supports, i.e., those various typical catalyst supports described hereinabove. For example, the term “substrate” is not intended to include zeolites, silica/alumina or other similar support materials. Such substrates are instead materials that are generally formed into appropriate structures

for use in the heater tubes of the reforming system and according to the process described herein.

While not limited thereto, such structures include, e.g., monolith forms such as honeycomb, cordierite, sinusoidal or other forms, foam structures such as metallic foam tubes, wire mesh screens oriented vertically or horizontally, or other forms such as extruded shapes, metallic coated/sheathed materials, and ceramic or metallic structures, including fiber, pellet, extrudate and other forms.

[0021] "Disposed on a substrate" means the catalyst, or another material or compound, is present on the substrate, either directly or indirectly with an intermediate layer, such as, e.g., a bonding agent or another coating. The method of disposing the catalyst or material on a substrate is not generally limited and may include the use of a coating process (e.g., a washcoat process), a process of direct synthesis or preparing the catalyst or material on the substrate, or any other technique that applies, contacts, or adheres the catalyst or material to the substrate.

[0022] "Group IIA" or "Group IIA metal" refers to beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), radium (Ra), and combinations thereof in any of elemental, compound, or ionic form.

[0023] "Group IIB" or "Group IIB metal" refers to zinc (Zn), cadmium (Cd), mercury (Hg), and combinations thereof in any of elemental, compound, or ionic form.

[0024] "Group IVA" or "Group IVA metal" refers to germanium (Ge), tin (Sn) or lead (Pb), and combinations thereof in any of elemental, compound, or ionic form.

[0025] "Group VIB" or "Group VIB metal" refers to chromium (Cr), molybdenum (Mo), tungsten (W), and combinations thereof in any of elemental, compound, or ionic form.

[0026] "Group VIII" or "Group VIII metal" refers to iron (Fe), cobalt (Co), nickel (Ni), ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir), platinum (Pt), and combinations thereof in any of elemental, compound, or ionic form.

[0027] "Hydrocarbonaceous", "hydrocarbon" and similar terms refer to a compound containing only carbon and hydrogen atoms. Other identifiers may be used to indicate the presence of particular groups, if any, in the hydrocarbon (e.g., halogenated hydrocarbon indicates the presence of one or more halogen atoms replacing an equivalent number of hydrogen atoms in the hydrocarbon).

[0028] The term "monofunctional" generally refers to "non-acidic" catalysts that do not have an acidic function in reforming reactions. Such catalysts are contrasted with conventional bifunctional reforming catalysts that have both an acidic function and a metallic function. The term "non-acidic" is understood in the art, particularly due to the contrast between monofunctional (non-acidic) reforming catalysts and bifunctional (acidic) reforming catalysts, and refers to catalysts characterized by an absence (or substantial absence) of accessible acid sites. The substantial absence of accessible acidic sites can be inferred from the reforming reaction products or determined by various analytical techniques well known in the art. For example, certain bands in O-H stretching region of infrared

spectrum of the catalyst can be used to measure the number of acid sites that are present. One method of achieving nonacidity is by incorporating alkali and/or alkaline earth metals in the L-zeolite, and preferably is achieved, along with other enhancement of the catalyst, by exchanging cations such as sodium and/or potassium from the synthesized L-zeolite using alkali or alkaline earth metals. Preferred alkali or alkaline earth metals for exchange include potassium and barium. According to one technique, a substantially non-acidic support material has a low (i.e., less than about 0.1) relative n-hexane cracking activity of the support compared to a standard silica/alumina catalyst, as determined in the Alpha Test described in U.S. 3,354,078 and in the journal "Catalysis," Vol. 4, p. 527 (1965); Vol. 6, p. 278 (1966); and Vol. 61, p. 395 (1980).

[0029] "Predominantly naphtha fraction" generally refers to a hydrocarbon composition that is predominantly comprised of a C₅ to C₉ fraction, and more particularly, where specified, a predominantly C₆ to C₈ fraction. The term "predominantly" is used in the normal sense, i.e., that fraction which is the largest (most) in the composition.

[0030] "LHSV" refers to "liquid hourly space velocity" and is a conventional term in reactor science and engineering meaning the ratio of liquid volume flow per hour to catalyst volume (hr⁻¹). In the case of substrate applications, catalyst volume refers to the washcoat volume. LHSV is inversely proportional to residence time.

[0031] The Periodic Table of the Elements refers to the version published by the CRC Press in the CRC Handbook of Chemistry and Physics, 88th Edition (2007-2008). The names for families of the elements in the Periodic Table are given here in the Chemical Abstracts Service (CAS) notation.

[0032] In this disclosure, while compositions and methods or processes are often described in terms of "comprising" various components or steps, the compositions and methods may also "consist essentially of" or "consist of" the various components or steps, unless stated otherwise.

[0033] The terms "a," "an," and "the" are intended to include plural alternatives, e.g., at least one. For instance, the disclosure of "a transition metal" or "an alkali metal" is meant to encompass one, or mixtures or combinations of more than one, transition metal or alkali metal, unless otherwise specified.

[0034] The present invention employs a reforming catalyst for the catalytic reforming of feed hydrocarbons to form aromatic hydrocarbons. Catalysts useful in the system and process of the invention are generally monofunctional catalysts comprising a Group VIII metal. Although suitable Group VIII metals include any single or combination of such metals that function effectively to form aromatic hydrocarbons, preferred metals comprise platinum, palladium, iridium and combinations thereof. Platinum is generally most preferred, either alone or in combination with one or more other Group VIII metals.

[0035] Preferred catalysts for use in the present invention comprise non-acidic L-zeolite catalysts, wherein exchangeable ions from the L-zeolite, such as sodium and/or potassium, have been exchanged

with alkali or alkaline earth metals. A particularly preferred catalyst is Pt Ba L-zeolite, wherein the L-zeolite has been exchanged using a barium containing solution. Combinations of catalysts may be used as well, particularly comprising such L-zeolite catalysts.

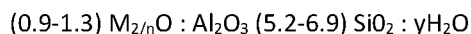
[0036] Catalysts suitable for use in the invention, and/or having features that are beneficial in forming aromatic hydrocarbons, as well as methods of making such catalysts, are described in more detail in the patent literature. See, e.g., U.S. Pat. Nos. 4,104,320; 4,424,311; 4,435,283; 4,447,316; 4,517,306; 4,456,527; 4,681,865; 5,091,351; 5,879,538; 6,004,452; 6,063,264; U.S. Pub. No. 2018/0170837A1; and EP Pub. Nos. 201856A, 403976, and 498182A. Details for L-zeolite catalysts as described in these patents are useful for the reforming catalyst of the present invention.

[0037] The Group VIII metal of the catalyst of the present invention is preferably a noble metal, such as platinum or palladium. Platinum is particularly preferred. Preferred amounts of platinum are 0.1 to 5 wt. %, more preferably 0.1 to 3 wt. %, and most preferably 0.3 to 1.5 wt. %, based on L-zeolite.

[0038] The alkaline earth metal used herein generally refer to the Group IIA elements beryllium, magnesium, calcium, strontium, barium, and radium, with barium, strontium and calcium preferred, and barium more preferred.

[0039] One method of making non-acidic L-zeolite catalyst is by incorporating alkali and/or alkaline earth metals in the L-zeolite, and is preferably achieved, along with other enhancement of the catalyst, by exchanging cations such as sodium and/or potassium from the synthesized L-zeolite using alkali or alkaline earth metals. Preferred alkali or alkaline earth metals for exchange include potassium and barium.

[0040] As used herein, the terms "L zeolite", "zeolite L" and "Type-L zeolite" are used synonymously to refer to LTL type zeolite. The L-zeolite component of the catalyst is described in published literature, such as U.S. Pat. No. 3,216,789 and 6,063,264. The chemical formula for L-zeolite may be represented as follows:



[0041] wherein M designates a cation, n represents the valence of M, and y may be any value from 0 to about 9. Zeolite L, its X-ray diffraction pattern, its properties, and method for its preparation are described in detail in U.S. Pat. No. 3,216,789. Zeolite L has been characterized in "Zeolite Molecular Sieves" by Donald W. Breck, John Wiley and Sons, 1974, (reprinted 1984) as having a framework comprising 18 tetrahedra unit cancrinite-type cages linked by double six rings in columns and cross-linked by single oxygen bridges to form planar 12-membered rings. The hydrocarbon sorption pores for L-zeolite are reportedly approximately 7 Å in diameter.

[0042] The various zeolites are generally defined in terms of their X-ray diffraction patterns. Several factors affect the X-ray diffraction pattern of a zeolite, including, e.g., temperature, pressure, crystal

size, impurities and type of cations present. As the crystal size of the type-L zeolite becomes smaller, the X-ray diffraction pattern becomes somewhat broader and less precise. Thus, the terms “L-zeolite” and “zeolite L” includes any of the various zeolites made of cancrinite cages having an X-ray diffraction pattern substantially the same as the X-ray diffraction patterns shown in U.S. Pat. No. 3,216,789. Type-L zeolites are conventionally synthesized in the potassium form, that is, in the theoretical formula previously given; most of the M cations are potassium. M cations are exchangeable so that a given L-zeolite, for example, a type-L zeolite in the potassium form, can be used to obtain type-L zeolites containing other cations by subjecting the L-zeolite to ion-exchange treatment in an aqueous solution of an appropriate salt or salts. However, it is difficult to exchange all the original cations, for example, potassium, since some cations in the zeolite are in sites that are difficult for the reagents to reach. Preferred L-zeolites for use in the present invention are those synthesized in the potassium form. Preferably, the potassium form L-zeolite is ion exchanged to replace a portion of the potassium, most preferably with an alkaline earth metal, barium being an especially preferred alkaline earth metal.

[0043] The AROMAX[®] reaction makes use of a mono-functional catalyst – platinum on L-zeolite. Any acidity in the L-zeolite is neutralized by ion exchange with an alkaline metal, such as Ba. First generation AROMAX[®] I catalyst is referred to as Pt/KL. L-zeolite facilitates the adsorption of n-hexane and suppression of coke formation resulting in a high catalyst stability. AROMAX[®] II is a subsequent generation of reforming catalysts that further improved AROMAX[®] I catalyst. These two catalysts both enable two classes of reactions: dehydrogenation (such as cyclohexane to benzene) and dehydrocyclization (n-hexane to Benzene). The dehydrogenation reaction is very fast and product yields are equilibrium limited (aromatics formation favored at high temperature and low pressure) whereas dehydrocyclization of paraffin to aromatic is moderately fast (with limitations being space velocity, diffusion and heat transfer).

[0044] A comparison of catalyst performance for AROMAX[®] I and II catalysts with conventional Pt on chlorided alumina type Rheniforming catalyst is shown in Table 1, illustrating the greater benzene and hydrogen yield differences between AROMAX[®] and conventional Pt/Al₂O₃ catalyst for an n-hexane feed. The data in Table 1 underscores the lower C₁-C₄ yield and particularly, the great difference in selectivity for aromatics over competing cracking products (C₁-C₄) for AROMAX[®] II catalyst relative to AROMAX[®] I and conventional reforming catalysts. The high benzene yield provided by AROMAX[®] catalysts is accompanied by a high yield of hydrogen and hydrogen purity and recovery tend to be high due to low C₁-C₄ yield.

Table 1¹

Yield ²	AROMAX [®] II (Pt/FKL)	AROMAX [®] I (Pt/KL)	Pt on Chlorided Alumina
Benzene	81.4	74.5	21.6
C7+	0.1	0.1	7.2
Aromatics			
Hydrogen	8.1	7.6	1.2
C1-C4	6.2	11.2	39.5
C5+	4.2	6.5	30.5
paraffinic			
Selectivity:			
Aromatics/ (C1-C4) Yield	13.1	6.6	0.73

¹reproduced from Fukunaga and Katsuno, Catal Surv Asia (2010), 14:96-102

²at 500 °C; 0.6 MPa, LHSV=2, and H₂/HC mole ratio = 5 for a pure n-hexane feed

[0045] At high LHSV, AROMAX[®] II catalyst selectivity for aromatics is improved compared with AROMAX[®] I (Table 2). AROMAX[®] II catalysts are therefore attractive since even if a portion of a normal paraffin feed remains unreacted due to high space velocity in the reactor, any unreacted feed (e.g., n-hexane) can be recycled rather than cracked into lighter hydrocarbons.

Table 2¹

Catalyst ²	AROMAX [®] II (Pt/FKL)	AROMAX [®] I (Pt/KL)
Conversion, wt%	14.2	2.2
Selectivity:		
Aromatics/(C1- C4) Yield	20.7	8.6

¹reproduced from Fukunaga and Katsuno, Catal Surv Asia (2010), 14:96-102

²at 480 °C; 0.6 MPa, LHSV=80, and H₂/HC mole ratio = 5 for a pure n-hexane feed

[0046] In an embodiment of the present invention, the catalyst is selected to have a low deactivation rate under reforming conditions. Preferably, the catalyst selected for use and the reaction

conditions are such that the catalyst deactivation rate is controlled to less than 0.04 °F per hour, more preferably to less than 0.03 °F, still more preferably to less than 0.02 °F, and most preferably to less than 0.01°F per hour, at an aromatics yield of 50 wt % (as described in US 6,063,264).

[0047] One aspect of the invention that distinguishes it from prior AROMAX® and other aromatics reforming systems and processes is the use of a substrate material and/or structure not previously used in such applications, wherein the catalyst is disposed on the substrate and contained within the heater tubes of a reactor furnace. Suitable substrates are generally of a comparatively large structural scale relative to typical catalyst supports or carriers for catalysts and do not include zeolites or other small scale supports as noted herein. While not necessarily limited thereto, such substrates may be in a form selected from extrudates or pellets, optionally wrapped in a metallic sheath and with periodic heat-conducting inserts to conduct wall heat to the center of the tube; or a ceramic or metal structure comprising fiber, monolith, foam, wire mesh or honeycomb forms; or a combination thereof. In some embodiments, the substrate comprises a ceramic or metal structure, or a combination thereof, and in associated aspects, the metal may be selected from iron, chromium, aluminum, nickel, or copper, or an alloy or a combination thereof. Inorganic materials such as cordierite, in the various forms described herein, are also suitable as substrate materials. In more particular aspects, the substrate may comprise a cordierite or metal monolith or wire mesh or entrapped metal fiber or eggshell pellet structure or a combination thereof. Such structures are generally known for use in catalytic reactors, e.g., as disclosed in U.S. Patent Nos. 5,318,757; 6,585,940; and 6,773,580.

[0048] The terms “monolithic” or “monolith” in relation to catalysts are known in the art and generally refer to a solid phase catalyst exhibiting substantially uniform structure or geometry throughout. Monolithic catalysts are usually provided as larger blocks of material, allowing easy and consistent orientation of geometric features when packed (such as into a reactor heater tube). Monolithic catalysts can have honeycomb-type or corrugated structure which is typically characterized by a regular, open cellular structure having a plurality of interconnecting pores and/or channels. The “geometry” or “geometric structure” of honeycomb-type catalysts refers to the structural features of the catalyst and describes material characteristics having some degree of uniformity throughout the material. Such characteristics can include, pore size, channel structure, channel diameter, cell density, wall thickness, void fraction, open frontal area (i.e., percentage of total surface area occupied by channels or void area), and the like. Monolithic catalysts having honeycomb-type or corrugated structure can also be referred to as “monoliths” “monolithic catalysts” and “honeycomb catalysts”.

[0049] Honeycomb-type catalysts can be made from any material capable of being extruded, whereas metal substrates are wrapped from foil. Catalytic materials can be disposed onto the honeycomb structure to vary catalytic activity for the reactions desired. Monolithic catalysts having honeycomb-type structure that are suitable for use in catalytic reforming can include any material

capable of forming a honeycomb-type substrate structure and providing a rigid honeycomb structural framework. Preferably, the substrate structure is stable at typical reforming and regeneration conditions. Such substrate materials may be inert or actively involved in catalytic reforming reactions. Suitable substrate materials include oxides of Si, Al, Ti, Zr, Mg and the like, and some substrate materials include ceramics, metals and/or zeolites. Besides Cordierite, ceramic substrates can include those with higher thermal conductivity, e.g., silicon carbide, aluminum nitride, boron carbide, and silicon nitride. Although not required, the substrate structure (honeycomb or other form) can support further catalytic or promoter materials suitable for naphtha reforming. For example, metals such as Pt, Pd, Ni, Re, Ir, Cu, Ni, Sn, Ge, other metals, and mixtures thereof, can be dispersed into or onto a supporting honeycomb substrate structure.

[0050] Examples of honeycomb catalysts and their preparation are numerous described throughout the art and illustrated, for example, in Parmaliana, et al., *Catalysis*, 1987, 43. According to some embodiments, L-zeolite and/or other reforming catalysts can be generally applied to supporting substrate structures by impregnation or coating. Preferably, the substrate is coated with the catalyst or wherein the catalyst is contained within the substrate. In particular, the catalyst may be coated on a suitable substrate monolith or can be formed as an extruded-type catalyst, but is preferably used in a catalyst coating. In one embodiment, the L-zeolite catalyst is coated on a flow-through monolith substrate (i.e., a honeycomb monolithic catalyst substrate structure with many small, parallel channels running axially through the entire part) or other monolith substrate. The catalyst may be coated (e.g., as a washcoat component) on a suitable monolith substrate, such as a metal or ceramic flow through monolith substrate or sintered metal or partial filter. Alternatively, the catalyst may be synthesized directly onto the substrate. The metal substrate may be pre-treated with acid wash to remove impurities and generate surface roughness. A primer coat may be first applied to the bare metal followed by the catalytic washcoat. The catalyst may be dip-coated multiple times until a desired washcoat thickness or adhesion is achieved.

[0051] Monoliths can be fabricated with a range of unit cell dimensions, wall thicknesses and heights. A standard monolith cell density (typically used in automotive applications) is in the range of 400 cells per square inch. Typical monolith wall thicknesses may range from 4/1000th to 12/1000th of an inch. A thin wall could refer to 4/1000th of an inch whereas a thick wall could refer to 12/1000th of an inch. Monoliths can be readily fabricated as 3 to 6 in. diameter cylinders with cylinder heights ranging from 6 to 12 inches. Catalyst washcoat(s) of varying thicknesses can be applied to the monolith and can range from 20 micron to 200 microns. The wash coating thickness for a particular application will depend of the strength of the adhesion and the thickness needed to meet a required catalyst volume. Providing the catalyst in the form of a 100 micron washcoat, as opposed to a 1/16 or 1/8 in. extrudate, is particularly appropriate for higher temperature endothermic reactions using precious metal catalysts

(as in this application) where heat diffusion to and from the catalyst to the bulk gas or mass diffusion through the zeolite pores control reaction rates, as opposed to kinetics.

[0052] Other suitable formed inorganic substrate materials and structures include ceramic or metal foams or porous wire mesh having open cell structures and microfibrinous structures, e.g., as described in U.S. Pub. No. 2011/0135543A1 and similar patent publications (Auburn Univ., Tatarchuk et al.) Porous wire mesh can be fabricated in a range of mesh sizes and wire diameters, ranging from 16 to 200 wires per inch with wire diameters ranging from 10 micron to 500 micron. While isotropic mesh screens are more common, they can also be fabricated as anisotropic, which can have unique heat transfer properties. The wire mesh may include multiple layers of plain-weave metallic wire mesh screen, to fit the diameter of the heater tube, with successive screen layers bonded or soldered to each other to improve thermal conductivity. Since the wire mesh is porous, the holes on successive mesh layers may be oriented to align or stagger the holes. Pressure drop and mixing effectiveness may need to be considered depending on the mesh layer configuration. While not required, the mesh layers can be compressed to fit more screen layers into the same overall height.

[0053] The reforming furnace reactor system generally comprises heater tubes with a catalyst contained within the heater tubes of the furnace, the catalyst being disposed on a substrate contained within the tubes. The heater tubes are typically made from a corrosion resistant material, preferably stainless steel or high Chromium steel such as 5 wt% or 9 wt % Chromium, and are optionally coated or treated with a corrosion or carburization inhibitor, preferably comprising an interior layer of tin. While any known furnace reactor tube configuration may be used, preferably the furnace comprises multiple parallel reactor tubes, e.g., in tube configurations such as those described in U.S. Pat. No. 6,063,264. Preferably the tubes are positioned vertically so feedstock enters from the top of the reactor tubes and product leaves with reactor effluent exiting the bottom of the reactor tubes. Although coiled or curved tubes may be used, the reactor tubes are typically straight rather than having a coiled or curved path through the furnace. The tubes may have a cross section that is circular, elliptical, rectangular, and/or other known shapes. While the tubes have a cross-sectional size to minimize cross-sectional radial temperature gradients, decreasing the cross-sectional size of the tubes increases the number of tubes required for a given production rate. Tube size is therefore advantageously set to minimize cross-sectional radial temperature gradients while also minimizing cost of construction. While not limited thereto, suitable cross-sectional tube diameters may be from about 2 to 8 in., preferably from about 2 to 6 in., and more preferably from about 3 to 6 in. Tube length may also be varied depending on process, operability (e.g., the use of structural substrates as compared with extrudates) and cost considerations. While not limited thereto, suitable lengths are generally in the range of about 20-50 ft, or 30-50 ft, or 40-50 ft. The heater tubes are typically sized for a feed stream flowrate through the

heater tubes at an LHSV between about 1 to 12 hr⁻¹, more particularly about 6 to 12 hr⁻¹, or about 8 to 12 hr⁻¹.

[0054] The tubes may be heated with any burner type known in the art such as ceiling or top-fired, wall or side-fired, terrace-fired, arbor or inverted arbor designs, and floor mounted burners. Preferably the burners are positioned to provide heat flux near the reactor tube inlet that is greater than heat flux near the exit of the reactor tubes. If the reactor tubes are vertically oriented, the burners are preferably positioned near the top inlet of the reactor tubes having flames burning in a downward direction along the length of the tubes. Orienting the burners near the top of the vertical reactor tube and firing downward provides heat flux near the reactor tube inlet (top) that is greater than the heat flux near the reactor tube outlet. Higher heating is desired near the reactor tube inlet to provide the heat of reaction and heat required to heat feedstock to the desired reaction temperature. Sufficient spacing should be provided between burners and tubes to prevent hot spots. Burners are typically arranged on both sides of the tubes and tubes may be typically separated by 0.25 to 2.0 tube diameters to provide uniform heating of the tubes.

[0055] Generally, less heat transfer is desired near the outlet of the heater tubes. To avoid higher temperatures that might promote undesired coking and/or cracking conditions, the reactor furnace may optionally also comprise one or more shields positioned to block at least a portion of the burner flame heat from an outlet portion of the tubes. If the reactor tubes are vertically oriented with a down-firing burner, at least one shield may be positioned to block a portion of flame radiation from a bottom portion of the reactor tube.

[0056] The heater tubes used in the invention contain the reforming catalyst disposed on a substrate and may further contain a thermal conductivity enhancer, or a radial mixing enhancer, or a combination thereof. For example, the tubes may comprise internal mixing structures positioned within the tubes to provide mixing in the radial direction. The mixing internal structures for radial mixing enhancement may be positioned within the substrate material or a portion thereof, or may be located within a bed of catalyst composition or in portions of the reactor tube separating two or more zones. The radial mixing enhancer may, e.g., comprise a static mixer, metal foam, wire mesh, metallic fibers, particles, pellets, or a combination thereof. Suitable additional mixing structures include fins or contours on the inside or outside of the tubes promoting heat transfer from the tube wall to the interior of the tube. The mixing enhancers may be positioned to provide heat transfer near the tube inlet that is greater than heat transfer near the outlet of the tubes. Examples of suitable internal structures include a plurality of baffles, sheds, trays, tubes, rods, fins, contours, and/or distributors, and the materials used may be metallic and/or ceramic. These internal structures may also be coated with catalyst. Preferred metals and ceramics are those having high thermal conductivity, e.g., including ceramics such as silicon carbide, aluminum nitride, boron carbide, and silicon nitride.

[0057] Suitable thermal conductivity enhancers include, e.g., wire mesh, metallic fibers, particles, foams, or pellets, or a combination thereof. Porous wire mesh screens may be used as a static mixer and thermal conductivity enhancer. It may be mounted vertically or horizontally inside the tube, in parallel or orthogonal to the flowing fluid. The porous screen may be coated with catalyst or used uncoated, merely as a heat exchanging cum mixing device. Interweaving wires in the wire mesh may be bonded to each other to enhance heat transfer. Successive layers of wire mesh screen may be bonded to each other in an inline or staggered fashion. A preferred orientation of the uncoated screen is to place it downstream of the monolith segment to enhance gas mixing and radial heat transfer. The frequency would depend of the magnitude of the radial temperature gradient, with higher frequency warranted in the top of the tube and lower frequency in the bottom of the tube. The wall thermal conductivity enhancer may comprise a metal sheath enclosing the substrate and draping the inside of the tube wall, preferably wherein the metal sheath comprises copper, and preferably wherein the metal sheath comprises metal, e.g., copper foil or copper fibers or copper mesh cloth. Generally, such metals may be selected from iron, chromium, aluminum, nickel, or copper, or an alloy or a combination thereof. As noted, the metal preferably comprises copper.

[0058] In general, the heater tubes and substrate contained therein provide operating conditions of a radial temperature gradient from the tube wall to the tube center of less than about 250°F, preferably less than about 200°F, or preferably less than about 100°F. Advantageously, the heater tubes may comprise an entry zone, a middle zone and an exit zone, the entry zone being from about 10-30% of the linear length of the tubes, the middle zone being about 40-80% of the linear length of the tubes, and the exit zone being from about 10-30% of the linear length of the tubes. The same or different substrates and catalyst compositions may be present in these zones. The design and selection of suitable substrates, catalysts and operating conditions may therefore provide: (a) an entry zone radial temperature gradient from the tube wall to the tube center of less than about 250°F, preferably less than about 200°F, or preferably less than about 150 °F; or (b) a middle zone radial temperature gradient from the tube wall to the tube center of less than about 200°F, preferably less than about 150°F, or preferably less than about 100°F; or (c) an exit zone radial temperature gradient from the tube wall to the tube center of less than about 150°F, preferably less than about 100°F, or preferably less than about 75°F; or a combination of (a), (b), or (c) thereof. While not limited thereto, the heater tubes may be sized for an overall furnace process-side pressure drop through the heater tubes of less than about 45 psig, or 35 psig or 25 psig.

[0059] In certain embodiments, the entry zone may comprise a metallic substrate having a low cell density with thick walls, wherein the substrate is coated with a relatively thick catalyst layer. The exit zone may similarly comprise a substrate having a high cell density with thin walls, such as a cordierite or metallic substrate, wherein the substrate is coated with a comparatively thin catalyst layer.

[0060] In general, any suitable process and system operation conditions may be used that are appropriate to form aromatics according to the invention. Such conditions are known in the art and include, e.g., reforming conditions using L-zeolite in the furnace reactor tubes with an catalyst volume LHSV of about 1 to 20 hr^{-1} , preferably about 1 to 15 hr^{-1} or 1 to 12 hr^{-1} , or more preferably about 2 to 12 hr^{-1} ; a hydrogen to hydrocarbon ratio (H_2 : HC) between about 0.5 and 3.0, preferably between about 0.5 and 2 or between about 0.5 and 1.5, or more preferably between about 1.0 and 1.5. Typical outlet operating conditions at Start of Run (SOR) of a heat exchange surface temperature for the reactants (interior temperature) may be between about 600°F and 960°F at the inlet and between 860°F and 960°F at the outlet, and, at End of Run (EOR), between about 600°F and 1025°F at the inlet and between 920°F and 1025°F at the outlet. EOR is the time at which the run is ended either due to a tube metallurgy operational limit or due to deactivation of the catalyst or due to undesirable hydrocracking reactions and is typically considered to be a point when the outlet temperature is no higher than 1025°F.

[0061] Typical feed stream conditions and characteristics associated with a predominantly naphtha feed stream for use in a reforming process are suitable for use in the process. In particular, the feed stream is predominantly comprised of a C_5 to C_9 fraction, and more particularly, a predominantly C_6 to C_8 fraction. In more specific embodiments, the feed stream C_6 to C_8 content is at least about 60 vol.%, or 70 vol.%, or 80 vol.%, or 90 vol.%, or 95 vol.%, or 98 vol.%, or 99 vol.%. The feed stream C_6 to C_7 content may further be at least about 60 vol.%, or 70 vol.%, or 80 vol.%, or 90 vol.%, or 95 vol.%, or 98 vol.%, or 99 vol.%. In another aspect, the feed stream sulfur content may be less than about 100 ppb, or 50 ppb sulfur or 30 ppb, or 20 ppb, or 10 ppb, or 5 ppb, or 2 ppb, or 1 ppb. The feed stream is also typically less than about 100 ppm water, or 50 ppm, or 30 ppm, or 20 ppm, or 10 ppm, or 5 ppm, or 2 ppm, or 1 ppm.

[0062] The reactor furnace may contain multiple bays or tube bundles with a common convection section in the middle such that the preheated (as in a feed/effluent heat exchanger) hydrocarbonaceous feed enters the common convection section, is further preheated and then passes to the feed inlet at the top of each of the tube bundles or multi-tubular bays. Such bays may be configured so that they are all operating in a naphtha reforming mode at the same time or in a partial operation mode, e.g., where one or more bays is operating in a naphtha reforming mode while one or more other bays is completely isolated and is operating in a catalyst regeneration mode.

[0063] The system may include a radial flow adiabatic reactor downstream of the multi-tubular reactor furnace for conducting non-endothermic or exothermic reactions. While hydrocracking or isomerization reactions are not particularly desirable in this particular aromatization application, in other naphtha reforming applications (e.g., fuels refining, where gasoline octane may be the target) some of the unreacted paraffins may be isomerized and hydrocracked to meet an octane rating. In such

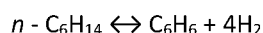
cases, it might be advantageous to add an adiabatic reactor, downstream of the multi-tubular furnace reactor, to facilitate the non-endothermic isomerization and hydrocracking reactions.

[0064] In order to obtain a more complete understanding of the present invention, the following examples illustrating certain aspects of the invention are set forth. It should be understood, however, that the invention is not limited in any way to the specific details of the examples.

Examples

[0065] The effects of tube ID, tube wall temperature, thermal conductivity of monolithic substrate, and the number of tubes required for a given feed throughput (LHSV), were evaluated through a simulation of axi-symmetric two-dimensional fluid flow, heat transfer, and chemical reaction modelling. Since every tube within the furnace reactor behaves essentially the same, only one tube was simulated. The feed gas mixture enters at the top of the tube at a known mass flow rate, which is the total throughput divided by the number of tubes. The product and unconverted reactant exits from the bottom end of the vertical tube.

[0066] The commercial Computational Fluid Dynamics (CFD) software ANSYS FLUENT version 19.0 was used to numerically simulate the flow through the tube and chemical reactions inside the tube. The modeling software offers a menu of options to model a particular application. The options selected and assumptions made for the simulation are described as follows. The tube, packed with monolithic blocks, was modeled by the pseudo-homogeneous reactor model. The monolithic block was modeled by the continuum approach and its effects on the gas flow was modeled by the ANSYS FLUENT porous zone function. Flow resistance coefficients of the substrate are anisotropic and were specified along the channel direction based on the substrate type, cell density, hydraulic diameter and flow resistance of the substrate. The flow resistance in the radial direction was assumed to be 1000 times that in the axial direction. The tube wall was modeled with constant temperature stationary wall boundary condition. A pressure-outlet boundary condition was set at the outlet. Realizable k-epsilon turbulence model with standard wall function was used. The pressure-velocity coupling formulation of SIMPLE algorithm was adopted and the second order upwind scheme was selected for solving the momentum and energy equations. A non-equilibrium thermal model for heat transfer between monolith substrate and the flow phase was selected with pseudo-transient solver. A mass-flow-inlet boundary condition with flat velocity profile and constant temperature was set at the inlet. An n-hexane and hydrogen mixture feed stream in a molar ratio of 1:1 was used. Only the reversible benzene formation reaction was modeled:



[0067] The rate equation for benzene formation from n-hexane was assumed to be a first order with respect to partial pressure of n-hexane. The reverse reaction was represented using the equilibrium constant, assuming a first order and fourth order reaction with respect to the partial

pressure of benzene and hydrogen, respectively. Kinetic parameters were taken from Nagamatsu et al (Sekiyu Gakkaishi, 44, (6), 351-359 (2001).

[0068] A catalyst washcoat containing 1 wt% Pt on KL-zeolite was coated on the monolith supports loaded inside the tubes of a multi-tubular reactor furnace. n-Hexane was fed at a flowrate of 35,000 Bbl/day and was aromatized according to the conditions shown in Tables 1 and 2 with tube ID of 4 inches and 4.921 inches respectively. Conversion of n-hexane, hydrogen production rate, n-hexane LHSV, and number of tubes required are shown in the following example tables for all cases simulated.

[0069] Higher thermal conductivity substrates require fewer tubes in a multi-tubular reactor furnace for the aromatization of n-hexane yielding 100 MMSCFD of hydrogen, resulting in a more compact furnace reactor. Notwithstanding axial flow through the tubes, the multi-tubular reactor furnace packed with monolith substrates compares favorably to radial flow adiabatic reactor system when it comes to total bed pressure drop.

Example 1 (Comparative)

[0070] A comparative example of an adiabatic multi-stage reactor system based on U.S. Patent No. 6,063,264 was simulated to provide a comparison with the invention using a multi-tubular furnace/reactor at LHSV=2 & H₂/HC ratio of 1:1. The catalyst was Pt on KL-zeolite processing a light naphtha feed predominantly comprising C₆ (n-Hexane) naphtha (C₅: 2%, C₆: 90%, C₇:8%). The catalyst volume was pro-rated from the original example to a 35000 bpsd hydrocarbon feed rate to facilitate the comparison. The modeled comparative adiabatic multi-tubular reactor system had six separate reactor vessels, with each reactor preceded by a feedstock fired heater. The simulation results are shown in Table 3, where "Total" refers to the combination of the six reactors.

Table 3. Process Conditions and Performance of Comparative Adiabatic Multi-Stage Reactor System

Process or Performance Condition	Reactor 1	Reactor 2	Reactor 3	Reactor 4	Reactor 5	Reactor 6	Total
Rx Inlet temperature, °F	945	950	955	960	965	970	
H ₂ /Hydrocarbon ratio	1:1	1:1	1:1	1:1	1:1	1:1	
Inlet pressure, psig							85
Outlet pressure, psig							45
Catalyst Volume required for 35000 bpd Hexane feed, ft ³	420	420	420	805	805	1225	4095
LHSV (based on catalyst volume), hr ⁻¹							2
Aromatics Yield, wt % (based on feed)							65.1

Example 2

[0071] The performance of a multi-tubular furnace/reactor with 4 in. ID tubes according to the invention was simulated using Cordierite, FeCrAl and Copper substrates, wash-coated with the same Platinum of KL-zeolite catalyst and processing a 100 % n-Hexane feed. The tube wall operating temperature range in this and subsequent examples refers to a typical operating range. The lower tube wall temperature is generally set by a minimum n-hexane conversion needed whereas the higher tube wall temperature is set by tube metallurgy and end-of-run (EOR) considerations. The simulation results are shown in Table 4.

Table 4. Process conditions and performance of Multi-tubular furnace/reactor with 4 in. ID tubes

Process or Performance Condition	Monolith Type					
	Cordierite	Cordierite	FeCrAl	FeCrAl	Copper	Copper
Inner Tube wall Operating Temperature Range, °F	970	1050	970	1050	970	1050
Inner Diameter of Tube, in.	4	4	4	4	4	4
Length of Tube, ft.	49.2	49.2	49.2	49.2	49.2	49.2
Monolith Size, cells per sq in.	400	400	400	400	400	400
Geometric surface area/tube, in ² /in ³	73.6	73.6	68.8	68.8	68.8	68.8
Monolith Solid thermal Conductivity, W/m. K	3	3	25	25	387	387
Washcoat Thickness, micron	100	100	100	100	100	100
Void Fraction	0.55	0.55	0.55	0.55	0.55	0.55
Composite Substrate Effective Thermal Conductivity, W/m. K	0.5	0.5	3	3	30	30
H ₂ /Hydrocarbon ratio	1:1	1:1	1:1	1:1	1:1	1:1
Feed inlet temperature, °F	930	930	930	930	930	930
Effluent outlet temperature, °F	875	928	893	946	928	1011
Inlet pressure, psig	55.7	56	62.1	63.7	63.3	65.4
Outlet pressure, psig	53.2	53.2	53.2	53.2	53.2	53.2
No of Heater tubes required	2200	2200	600	600	600	600
Total washcoat volume per tube, ft ³	1.237	1.237	1.108	1.108	1.108	1.108
Total catalyst volume, ft ³	2721.4	2721.4	664.8	664.8	664.8	664.8
Reactor Pressure drop, psi	2.5	2.8	8.9	10.5	10.1	12.2
Radial temp gradient @ L=6.6 ft	191	263	132	197	99	154
Radial temp gradient @ L=42.6 ft	174	233	106	151	56	65
LHSV (based on cat. volume), hr-1	3.0	3.0	12.3	12.3	12.3	12.3
Conversion, %	66%	78%	57%	77%	72%	96%
H ₂ production rate, MMSCFD	88	106	76	102	96	128

[0072] This example shows that substantially higher space velocities and lower catalyst volumes are achieved, resulting in platinum and catalyst savings and process intensification, when monoliths are deployed. It further shows that monolith-fitted tubes offer substantially lower reactor pressure drop compared to multi-stage radial flow adiabatic reactors. The results also show that the principal weakness of monoliths, particularly cordierite monoliths, is the large radial temperature gradient, particularly in the entry zone, resulting in low reaction temperatures at the center of the tube. This impacts platinum utilization and requires relatively higher catalyst volume.

Example 3

The performance of multi-tubular furnace/reactor with 5 in. ID tubes according to the invention was simulated using Cordierite, FeCrAl and Copper substrates, wash-coated with the Platinum on KL-zeolite catalyst and processing the same feed as in example 2. The simulation results are shown in Table 5.

Table 5. Process conditions and performance of multi-tubular furnace reactor with 5 in. ID tubes

Process or Performance Condition	Monolith Type					
	Cordierite	Cordierite	FeCrAl	FeCrAl	Copper	Copper
Inner Tube wall Operating Temperature Range, °F	970	1050	970	1050	970	1050
Inner Diameter of Tube, in.	4.92	4.92	4.92	4.92	4.92	4.92
Length of Tube, ft.	49.2	49.2	49.2	49.2	49.2	49.2
Monolith Size, cells per sq in.	400	400	400	400	400	400
Monolith Solid thermal Conductivity, W/m. K	3	3	25	25	387	387
Washcoat Thickness, micron	100	100	100	100	100	100
Void Fraction	0.55	0.55	0.55	0.55	0.55	0.55
Composite Substrate Effective Thermal Conductivity, W/m. K	0.5	0.5	3	3	30	30
H ₂ /Hydrocarbon ratio	1:1	1:1	1:1	1:1	1:1	1:1
Feed inlet temperature, °F	930	930	930	930	930	930
Effluent outlet temperature, °F	863	900	902	974	924	1012
Inlet pressure, psig	55.6	56	59.5	60.7	63.1	65.3
Outlet pressure, psig	53.2	53.2	53.2	53.2	53.2	53.2
No of Heater tubes required	1500	1500	600	600	400	400
Washcoat volume per tube, ft ³	1.933	1.933	1.731	1.731	1.731	1.731
Total catalyst volume, ft ³	2899.5	2899.5	1038.6	1038.6	692.4	692.4
Reactor Pressure drop, psi	2.4	2.8	6.3	7.5	9.9	12.1
Radial temp gradient @ L=6.6 ft	202	277	142	207	101	156
Radial temp gradient @ L=42.6 ft	186	243	108	146	58	68
LHSV (based on cat volume), hr ⁻¹	2.82	2.82	7.88	7.88	11.82	11.82
Conversion, %	69%	83%	69%	90%	72%	96%
H ₂ production rate, MMSCF	92	121	92	117	96	128

[0073] This example shows the performance using copper monolith benefits significantly from switching to 5 in. tubes, due to the higher substrate effective thermal conductivity, whereas the cordierite monoliths do not benefit. The number of tubes required can therefore be reduced from 600 to 400 tubes in the case of the copper monolith, resulting in a LHSV of 11.82 hr⁻¹ and a more compact

reactor furnace with 400 tubes. It should be noted that as tube diameter increases, the catalyst volume per tube goes up but the radial temperature gradient also generally widens, which may result in poorer utilization of Platinum in the center of the tube.

Example 4

[0074] The performance of multi-tubular furnace/reactor with thermal conductivity inserts according to the invention was simulated to investigate the reactor performance and the potential for moderating the large radial temperature gradient observed in the case of Cordierite and FeCrAl monoliths, particularly when deployed in 5 in. larger diameter tubes. Cordierite and FeCrAl substrates were used in the simulation, wash-coated with the same Platinum on KL-zeolite catalyst and processing the same feed as in examples 2-3. Wire mesh screens, oriented horizontally and perpendicular to the axial flow of gas, were situated after the monolith segments. As earlier described herein, such screens are intended to enhance static gas mixing and thermal conductivity, and reduce radial temperature gradients. The frequency of deployment of the copper wire mesh depends on the magnitude of the expected radial temperature gradient. The mesh screens were simulated as 1-inch length copper mesh wire pads between adjacent monolith blocks. The mesh pads were located at different spacings based on the distance from the tube entrance: in the first 1/3 section from the inlet, the pads were spaced every 6 inches of monolith segment; in the middle 1/3 section, the pads were spaced every 12 inches of monolith segment; and, in the bottom 1/3 segment, the pads were spaced every 18 inches of monolith segment. The simulation results are shown in Table 6.

Table 6. Process conditions and performance of multi-tubular furnace reactor with 5 in. ID tubes with thermal conductivity inserts

Process or Performance Condition	Monolith Type			
	Cordierite	Cordierite	FeCrAl	FeCrAl
Inner Tube wall Operating Temperature Range, °F	970	1050	970	1050
Inner Diameter of Tube, in.	4.92	4.92	4.92	4.92
Length of Tube, ft.	49.2	49.2	49.2	49.2
Monolith Size, cells per sq in.	400	400	400	400
Monolith Solid thermal Conductivity, W/m. K	3	3	25	25
Washcoat Thickness, micron	100	100	100	100
Void Fraction	0.55	0.55	0.55	0.55
Composite Substrate Effective Thermal Conductivity, W/m. K	0.5	0.5	3	3
Copper mesh wire section effective thermal conductivity, W/m.K	83	83	83	83
H ₂ /Hydrocarbon ratio	1:1	1:1	1:1	1:1
Feed inlet temperature, °F	930	930	930	930
Effluent outlet temperature, °F	898	984	908	985
Inlet pressure, psig	56.7	57.2	63.8	65.7
Outlet pressure, psig	53.2	53.2	53.2	53.2
No of Heater tubes required	1500	1500	600	600
Washcoat volume per tube, ft ³	1.933	1.933	1.731	1.731
Total catalyst volume, ft ³	2899.5	2899.5	1038.6	1038.6
Reactor Pressure drop, psi	3.5	4	10.6	12.5
Radial temp gradient @ L=6.6 ft	152	224	130	195
Radial temp gradient @ L=42.6 ft	124	150	95	121
LHSV based on cat volume, hr ⁻¹	2.82	2.82	7.88	7.88
Conversion, %	86%	98%	72%	94%
H ₂ production rate, MMSCFD	114	126	96	125

[0075] This example shows that thermal conductivity inserts, when deployed strategically through the length of the tubes, can reduce the radial temperature gradient by as much as 70 °F, thereby improving platinum utilization at the center of the tube, resulting in higher overall conversion. Figs. 1 and 2 further illustrate the simulation results for the monolith substrates of this example and show that significant reductions in the radial temperature gradient can be achieved using copper mesh screen thermal conductivity enhancer inserts. Cordierite monoliths benefit the most from the thermal

conductivity inserts compared to FeCrAl monoliths, because of the lower starting substrate thermal conductivity.

[0076] The above set of examples illustrate that the combination of catalyst substrate and thermal conductivity inserts, such as copper wire mesh pads, when deployed in the tubes of a furnace/reactor can substantially reduce catalyst volume compared to conventional multi-stage adiabatic reactor systems.

[0077] This invention makes all three monolith types viable for this application. Cordierite is the most widely deployed substrate in automotive exhaust control applications, followed by FeCrAl whereas copper has great heat-conducting ability but is not widely deployed.

[0078] In the above examples, numerous parameters, such as tube length, monolith cell density, washcoat thickness etc. were held constant across the set of examples to illustrate relative performance. In reality, many of these variables can be optimized for a given application to deliver superior overall performance. Also, the catalyst size, shape and activity can be graded in the each of the tubes over the length of the tube as the required heat flux, temperature and pressure drop vary through the tube as the reaction progresses.

[0079] The foregoing description of one or more embodiments of the invention, including the examples, is primarily for illustrative purposes, it being recognized that variations might be used which would still incorporate the essence of the invention. Reference should be made to the following claims in determining the scope of the invention.

[0080] For the purposes of U.S. patent practice, and in other patent offices where permitted, all patents and publications cited in the foregoing description of the invention are incorporated herein by reference to the extent that any information contained therein is consistent with and/or supplements the foregoing disclosure.

WHAT IS CLAIMED IS:

1. A process for forming aromatic hydrocarbons from a hydrocarbonaceous feed stream, comprising:
 - contacting the feed stream with a catalyst contained within the heater tubes of a reactor furnace, wherein
 - the catalyst comprises a Pt/FKL catalyst that is coated on a substrate selected from honeycomb monolith, preferably cordierite honeycomb monolith, sinusoidal metal monolith, or metallic open cell foam, or porous wire mesh, the catalyst being effective to form aromatic hydrocarbons by catalytic reforming of the feed stream hydrocarbons, and
 - the feed stream comprises a naphtha fraction having a predominately C₆ to C₈ content; and
 - providing heat to the furnace heater tubes for the catalytic reforming of the feed stream hydrocarbons to form aromatic hydrocarbons.
2. The process of claim 1, wherein the catalyst is made by a process comprising ion exchange with an alkaline earth metal, wherein the alkaline earth metal comprises barium.
3. The process of any one of claims 1-2, wherein the catalyst is treated with a halogen compound comprising fluorine, chlorine, or a mixture thereof.
4. The process of claim 1, wherein the substrate is wrapped in a metallic sheath.
5. The process of any one of claims 1-4, wherein the substrate is in a form selected from extrudates or pellets, optionally wrapped in a metallic sheath; or a structure comprising fiber, monolith, foam, porous wire mesh or honeycomb forms; or a combination thereof.
6. The process of claim 5, wherein the substrate comprises a ceramic or metal structure, wherein the metal is selected from iron, chromium, aluminum, nickel, or copper, or an alloy or a combination thereof.
7. The process of any one of claims 1-6, wherein the substrate comprises a cordierite or metal monolith or entrapped metal fiber or porous wire mesh or eggshell pellet structure or a combination thereof; or wherein the substrate is coated with the catalyst or wherein the catalyst is contained within the substrate.
8. The process of any one of claims 1-7, wherein the heater tubes further contain a thermal conductivity enhancer, or a radial mixing enhancer, or a combination thereof.

9. The process of claim 8, wherein the thermal conductivity enhancer is selected from metallic fibers, particles, foams, porous wire mesh, or pellets, or a combination thereof, or wherein the thermal conductivity enhancer comprises a metal sheath enclosing the substrate, preferably wherein the metal sheath comprises copper, and preferably wherein the metal sheath comprises copper foil or copper fibers or copper mesh cloth.
10. The process of any one of claims 8 or 9, wherein the thermal conductivity enhancer comprises metal foil or metal fibers or wires, wherein the metal is selected from iron, chromium, aluminum, nickel, or copper, or an alloy or a combination thereof, preferably wherein the metal comprises copper.
11. The process of any one of claims 8-20, wherein the radial mixing enhancer comprises a static mixer, metal foam, metallic fibers, particles, pellets, or a combination thereof.
12. The process of any one of claims 8-11, wherein the radial mixing enhancer and the thermal conductivity enhancer are the same or different, or wherein the radial mixing enhancer and the thermal conductivity enhancer are the same, or wherein the radial mixing enhancer and the thermal conductivity enhancer are different.
13. The process of any one of claims 8-12 wherein the porous wire mesh pad is composed of multiple layers of plain-weave metallic wire mesh laminate, with successive layers bonded or soldered to each other so that the holes are either aligned or staggered with the overall pad compressed, so as to fit more metal into a smaller height; or wherein the porous wire mesh pad is optionally wash-coated with catalyst; or wherein the porous wire mesh pad is optionally fabricated out of copper wire.
14. The process of any one of claims 1-13, wherein the radial temperature gradient from the tube wall to the tube center is less than about 250°F, preferably less than about 200°F, and preferably less than about 100°F.
15. The process of any one of claims 1-14, wherein the heater tubes comprise an entry zone, a middle zone and an exit zone, the entry zone being from about 10-30% of the linear length of the tubes, the middle zone being about 40-80% of the linear length of the tubes, and the exit zone being from about 10-30% of the linear length of the tubes.
16. The process of claim 15, wherein (a) the entry zone radial temperature gradient from the tube wall to the tube center is less than about 250°F, preferably less than about 200°F, or preferably less than about 150 °F; or (b) the middle zone radial temperature gradient from the tube wall to the tube

center is less than about 200°F, preferably less than about 150°F, or preferably less than about 100°F; or (c) the exit zone radial temperature gradient from the tube wall to the tube center is less than about 150 °F, preferably less than about 100 °F, or preferably less than about 75 °F; or a combination of (a), (b), or (c) thereof.

17. The process of any one of claims 1-16, wherein the overall furnace process-side pressure drop through the heater tubes is less than about 45 psig, or 35 psig or 25 psig.

18. The process of claim 19, wherein the entry zone comprises a cordierite or metallic substrate having a low cell density and thick walls, wherein the substrate is coated with a thick catalyst layer; and/or wherein the exit zone comprises a cordierite or metallic substrate having a high cell density and thin walls, wherein the substrate is coated with a thin catalyst layer.

19. The process of any one of claims 1-18, wherein the heater tubes are made from a corrosion resistant material, preferably stainless steel, optionally comprising 5 wt% or 9 wt% chromium, and are optionally coated or treated with a corrosion or carburization inhibitor, preferably comprising an interior layer of tin.

20. The process of any one of claims 1-19, wherein the heater comprises more than one tube bundle, so that at least one tube bundle may be isolated with the catalyst being regenerated while the other tube bundles are operating at any given time.

21. The process of any one of claims 1-20, wherein the feed stream C₆ to C₈ content is at least about 60 vol%, or 70 vol.%, or 80 vol.%, or 90 vol.%, or 95 vol.%, or 98 vol.%, or 99 vol.% or wherein the feed stream C₆ to C₇ content is at least about 60 vol%, or 70 vol.%, or 80 vol.%, or 90 vol.%, or 95 vol.%, or 98 vol.%, or 99 vol.%.

22. The process of any one of claims 1-21, wherein the feed stream comprises less than about 100 ppb, or 50 ppb sulfur or 30 ppb, or 20 ppb, or 10 ppb, or 5 ppb, or 2 ppb, or 1 ppb or wherein the feed stream comprises less than about 100 ppm water, or 50 ppm, or 30 ppm, or 20 ppm, or 10 ppm, or 5 ppm, or 2 ppm, or 1 ppm .

23. The process of any one of claims 1-22, wherein feed stream flowrate through the heater tubes is conducted at an LHSV between about 1 to 12 hr⁻¹, or about 6 to 12 hr⁻¹, or about 8 to 12 hr⁻¹; or wherein said process is operated at an H₂ to feed stream hydrocarbon mole ratio H₂:HC of between about 0.5 to 2, or about 0.5 to 1.5, or about 1.0 to 1.5.

24. A catalytic reforming system for forming aromatic hydrocarbons from a hydrocarbonaceous feed stream, comprising

a reforming furnace reactor containing heater tubes with a catalyst contained within the heater tubes of the furnace, wherein

the catalyst comprises a Pt/FKL catalyst that is coated on a substrate selected from honeycomb monolith, preferably cordierite honeycomb monolith, sinusoidal metal monolith, or metallic open cell foam, or porous wire mesh, the catalyst being effective to form aromatic hydrocarbons by catalytic reforming of feed stream hydrocarbons, and

a heat source to provide heat to the furnace heater tubes for the catalytic reforming of the feed stream hydrocarbons to form aromatic hydrocarbons.

25. The system of claim 24, wherein the catalyst is made by a process comprising ion exchange with an alkaline earth metal, wherein the alkaline earth metal comprises barium.

26. The system of any one of claims 24-25, wherein the catalyst is treated with a halogen compound selected from the group consisting of: fluorine, chlorine, and mixtures thereof.

27. The system of claim 24, wherein the substrate is wrapped in a metallic sheath.

28. The system of any one of claims 24-27, wherein the substrate is in a form selected from extrudates or pellets, optionally wrapped in a metallic sheath; or a structure comprising fiber, monolith, foam, porous wire mesh or honeycomb forms; or a combination thereof.

29. The system of claim 28, wherein the substrate comprises a ceramic or metal structure, wherein the metal is selected from iron, chromium, aluminum, nickel, or copper, or an alloy or a combination thereof.

30. The system of any one of claims 24-29, wherein the substrate comprises a cordierite or metal monolith or entrapped metal fiber or porous wire mesh or eggshell pellet structure or a combination thereof; or wherein the substrate is coated with the catalyst or wherein the catalyst is contained within the substrate.

31. The system of any one of claims 24-30, wherein the heater tubes further contain a thermal conductivity enhancer, or a radial mixing enhancer, or a combination thereof.

32. The system of claim 31, wherein the thermal conductivity enhancer is selected from metallic fibers, particles, foams, porous wire mesh or pellets, or a combination thereof, or wherein the

thermal conductivity enhancer comprises a metal sheath enclosing the substrate, preferably wherein the metal sheath comprises copper, and preferably wherein the metal sheath comprises copper foil or copper fibers or copper mesh cloth, and wherein the thermal conductivity enhancer is optionally washcoated with catalyst.

33. The system of any one of claims 31-32, wherein the thermal conductivity enhancer comprises metal foil or metal fibers or wires, wherein the metal is selected from iron, chromium, aluminum, nickel, or copper, or an alloy or a combination thereof, preferably wherein the metal comprises copper.

34. The system of any one of claims 31-33, wherein the radial mixing enhancer comprises a static mixer, metal foam, porous wire mesh, metallic fibers, particles, pellets, or a combination thereof.

35. The system of any one of claims 24-34, wherein the specifications for the heater tube and substrate contained therein provide operating conditions of a radial temperature gradient from the tube wall to the tube center of less than about 250°F, preferably less than about 200°F, or preferably less than about 100°F.

36. The system of any one of claims 24-35, wherein the heater tubes comprise an entry zone, a middle zone and an exit zone, the entry zone being from about 10-30% of the linear length of the tubes, the middle zone being about 40-80% of the linear length of the tubes, and the exit zone being from about 10-30% of the linear length of the tubes.

37. The system of claim 36, wherein the substrate is a monolith substrate divided into monolith block segments within each of the entry, middle, and exit zones.

38. The system of claim 37, wherein a porous wire mesh is inserted after every monolith block in the entry zone, after every two monolith blocks in the middle zone and every three monolith blocks in the exit zone.

39. The system of claim 38, wherein the specifications for the heater tube and substrate contained therein provide operating conditions of: (a) an entry zone radial temperature gradient from the tube wall to the tube center of less than about 250°F, preferably less than about 200°F, or preferably less than about 150 °F; or (b) a middle zone radial temperature gradient from the tube wall to the tube center of less than about 200°F, preferably less than about 150°F, or preferably less than about 100°F; or (c) an exit zone radial temperature gradient from the tube wall to the tube center of less than about 150°F, preferably less than about 100°F, or preferably less than about 75°F; or a combination of (a), (b), or (c) thereof.

40. The system of any one of claims 24-39, wherein the heater tubes are sized for an overall furnace process-side pressure drop through the heater tubes of less than about 45 psig, or 35 psig or 25 psig.
41. The system of claim 39, wherein the entry zone comprises a metallic substrate having a low cell density with thick walls, wherein the substrate is coated with a thick catalyst layer; or wherein the exit zone comprises a cordierite or metallic substrate having a high cell density with thin walls, wherein the substrate is coated with a thin catalyst layer.
42. The system of any one of claims 24-41, wherein the heater tubes are made from a corrosion resistant material, preferably stainless steel, optionally comprising 5 wt% or 9 wt% chromium, and are optionally coated or treated with a corrosion or carburization inhibitor, preferably comprising an interior layer of tin.
43. The system of any one of claims 24-42, further including a pre-heater, optionally comprising a convection section, for pre-heating the feed stream prior to entering the heater tubes.
44. The system of any one of claims 24-43, further including an adiabatic radial flow reactor downstream of the reactor furnace for conducting non-endothermic or exothermic reactions on the same Pt/FKL or other catalyst, prior to hydrogen recovery and product fractionation.
45. The system of any one of claims 24-44, where the reactor furnace comprises two multi-tubular bundles or bays with a common convection system in the middle, such that one bay may be on-stream and operating while the other bay is in a catalyst regeneration mode.