

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 is disposed on a substrate and comprises a non-acidic catalyst 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 a monofunctional catalyst comprising a Group VIII metal.
3. The process of claim 2, wherein the Group VIII metal comprises platinum.
4. The process of any one of claims 1-3, wherein the catalyst comprises L-zeolite or a combination of L-zeolite with another catalyst.
5. The process of claim 3, wherein the platinum is impregnated on L-zeolite or a combination of L-zeolite with another catalyst.
6. The process of any one of claims 1-5, wherein the catalyst is made by a process comprising ion exchange with an alkaline earth metal.
7. The process of claim 6, wherein the alkaline earth metal comprises barium.
8. The process of any one of claims 1-7, wherein the catalyst is treated with a halogen compound.
9. The process of claim 8, wherein the halogen compound comprises fluorine, chlorine, or a mixture thereof.
10. The process of any one of claims 1-9, wherein the catalyst comprises a Pt/FKL catalyst.
11. The process of claim 10, wherein the Pt/FKL catalyst 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 and wherein the substrate is optionally wrapped in a metallic sheath.
12. The process of any one of claims 1-11, wherein the catalyst deactivation rate is less than about 0.04 °F/hr, or less than about 0.02 °F/hr, or less than about 0.01 °F/hr, or less than about 0.005 °F/hr.

13. The process of any one of claims 1-12, 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.
14. The process of claim 13, wherein the substrate comprises a ceramic or metal structure.
15. The process of claim 14, wherein the metal is selected from iron, chromium, aluminum, nickel, or copper, or an alloy or a combination thereof.
16. The process of any one of claims 1-15, 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.
17. The process of any one of claims 1-16, wherein the substrate is coated with the catalyst or wherein the catalyst is contained within the substrate.
18. The process of any one of claims 1-17, wherein the heater tubes further contain a thermal conductivity enhancer, or a radial mixing enhancer, or a combination thereof.
19. The process of claim 18, 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.
20. The process of any one of claims 18 or 19, 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.
21. The process of any one of claims 18-20, wherein the radial mixing enhancer comprises a static mixer, metal foam, metallic fibers, particles, pellets, or a combination thereof.
22. The process of any one of claims 18-21, 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.
23. The process of any one of claims 18-22 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 not.

24. The process of any one of claims 18-23 wherein the porous wire mesh pad may be wash-coated with catalyst or not.

25. The process of any one of claims 18-23 wherein the porous wire mesh pad may preferably be fabricated out of copper wire.

26. The process of any one of claims 1-25, 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.

27. The process of any one of claims 1-26, 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.

28. The process of claim 27, 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.

29. The process of any one of claims 1-28, wherein the overall furnace process-side pressure drop through the heater tubes is less than about 45 psig, or 35 psig or 25 psig.

30. The process of claim 27, 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.

31. The process of claim 27, 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.

32. The process of any one of claims 1-31, wherein the furnace is top-fired, side-fired, or terrace-fired, or an arbor or inverted-arbor design.

33. The process of claim 32, wherein the furnace is top-fired with alternate rows of vertical heater tubes and top-mounted burners.

34. The process of claim 33, wherein the heater tube feed stream inlet is located at the top of the heater tubes.
35. The process of any one of claims 1-34, wherein the heater tubes have an inside diameter between about 3 in. and 6 in. (7.6 cm to 15.2 cm).
36. The process of any one of claims 1-35, 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.
37. The process of any one of claims 1-36, wherein the feed stream is pre-heated prior to entering the heater tubes, such as in a convection section.
38. The process of any one of claims 1-37, 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.
39. The process of any one of claims 1-38, 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.%.
40. The process of any one of claims 1-39, 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.%.
41. The process of any one of claims 1-40, 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.
42. The process of any one of claims 1-41, 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.
43. The process of any one of claims 1-42, 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.
44. The process of any one of claims 1-43, wherein 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.
45. 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 is disposed on a substrate contained within the heater tubes and the catalyst comprises a non-acidic catalyst 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.

46. The system of claim 45, wherein the catalyst is a monofunctional catalyst comprising a Group VIII metal.

47. The system of claim 46, wherein the Group VIII metal comprises platinum.

48. The system of any one of claims 45-47, wherein the catalyst comprises L-zeolite or a combination of L-zeolite with another catalyst.

49. The system of claim 48, wherein the platinum is impregnated on L-zeolite or a combination of L-zeolite with another catalyst.

50. The system of any one of claims 45-49, wherein the catalyst is made by a process comprising ion exchange with an alkaline earth metal.

51. The system of claim 50, wherein the alkaline earth metal comprises barium.

52. The system of any one of claims 45-51, wherein the catalyst is treated with a halogen compound.

53. The system of claim 52, wherein the halogen compound comprises fluorine, chlorine, or a mixture thereof.

54. The system of any one of claims 45-53, wherein the catalyst comprises a Pt/FKL catalyst.

55. The system of claim 54, wherein the Pt/FKL catalyst 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 and wherein the substrate is optionally wrapped in a metallic sheath.

56. The system of any one of claims 45-55, wherein the catalyst deactivation rate is less than about 0.04 °F/hr, or less than about 0.02 °F/hr, or less than about 0.01 °F/hr, or less than about 0.005 °F/hr.

57. The system of any one of claims 45-56, 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.

58. The system of claim 57, wherein the substrate comprises a ceramic or metal structure.
59. The system of claim 58, wherein the metal is selected from iron, chromium, aluminum, nickel, or copper, or an alloy or a combination thereof.
60. The system of any one of claims 45-59, 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.
61. The system of any one of claims 45-60, wherein the substrate is coated with the catalyst or wherein the catalyst is contained within the substrate.
62. The system of any one of claims 45-61, wherein the heater tubes further contain a thermal conductivity enhancer, or a radial mixing enhancer, or a combination thereof.
63. The system of claim 62, 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.
64. The system of any one of claims 62-63, 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.
65. The system of any one of claims 62-64, wherein the radial mixing enhancer comprises a static mixer, metal foam, porous wire mesh, metallic fibers, particles, pellets, or a combination thereof.
66. The system of any one of claims 45-65, 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.
67. The system of any one of claims 45-66, 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.

68. The system of claim 67, wherein the substrate is a monolith substrate divided into monolith block segments within each of the entry, middle, and exit zones.
69. The system of claim 68, 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.
70. The system of claim 69, 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.
71. The system of any one of claims 45-70, 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.
72. The system of claim 70, 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.
73. The system of claim 70, 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.
74. The system of any one of claims 45-73, wherein the furnace is top-fired, side-fired, or terrace-fired, or an arbor or inverted-arbor design.
75. The system of claim 74, wherein the furnace is top-fired with alternate rows of vertical heater tubes and top-mounted burners.
76. The system of claim 75, wherein the heater tube feed stream inlet is located at the top of the heater tubes.
77. The system of any one of claims 45-76, wherein the heater tubes have a diameter between about 3 in. and 6 in.
78. The system of any one of claims 45-77, 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.

79. The system of any one of claims 45-78, further including a pre-heater, optionally comprising a convection section, for pre-heating the feed stream prior to entering the heater tubes.

80. The system of any one of claims 45-79, 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.

81. The system of any one of claims 45-80, 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.

82. The system of any one of claims 45-81, wherein heater tubes are sized for a feed stream flowrate through the heater tubes at an LHSV, based on catalyst volume, between about 1 to 12 hr⁻¹, or about 6 to 12 hr⁻¹, or about 8 to 12 hr⁻¹.