Claims

1. A method for upgrading a petroleum feedstock using a supercritical water petroleum upgrading system, the method comprising the steps of:

introducing the petroleum feedstock into the supercritical water petroleum upgrading system;

introducing a water stream into the supercritical water petroleum upgrading system;

introducing an auxiliary feed stream into the supercritical water petroleum upgrading system;

operating the supercritical water petroleum upgrading system such that a pressure and a temperature of the petroleum feedstock are increased to produce a pre-heated petroleum feedstock;

operating the supercritical water petroleum upgrading system such that a pressure and a temperature of the water stream are increased to produce a pre-heated water stream;

operating the supercritical water petroleum upgrading system such that the pre-heated petroleum feedstock and a portion of the pre-heated water combine to form a mixed petroleum feedstock;

operating the supercritical water petroleum upgrading system such that the auxiliary feed stream and a portion of the pre-heated water stream combine to form a pre-heated auxiliary feedstock;

operating the supercritical water petroleum upgrading system such that the mixed petroleum feedstock and the pre-heated auxiliary feedstock are introduced separately and simultaneously into a lower portion of an upflowing supercritical water reactor, where the pre-heated auxiliary feedstock is introduced into the upflowing reactor such

that a portion of a fluid contained within the upflowing reactor located proximate to the bottom of the upflowing reactor does not lack fluid momentum;

operating the upflowing supercritical water reactor such that the fluid contained within the upflowing reactor is maintained at a temperature equal to or greater than the critical temperature of water, at a pressure equal to or greater than the critical pressure of water, and is moving in a generally upwards direction, such that supercritical water forms from the introduced water in the fluid contained within the upflowing reactor;

operating the upflowing supercritical water reactor such that an upgraded and desulfurized petroleum product forms as the reaction product between the introduced pre-heated petroleum feedstock and the supercritical water in the fluid contained within the upflowing reactor;

operating the supercritical water petroleum upgrading system such that an upflowing reactor product fluid passes from an upper portion of the upflowing reactor, where the product fluid comprises the upgraded and desulfurized petroleum product, and where the amount of passing upflowing reactor product fluid is equivalent to the combined amount of the introduced mixed petroleum feedstock and the pre-heated auxiliary feedstock; and

operating the supercritical water petroleum upgrading system such that a gas-phase hydrocarbon product, the upgraded and desulfurized petroleum product and an aqueous-phase product are separately selectively separated from the upflowing reactor product fluid.

2. The method of claim 1 where the petroleum feedstock and the water are introduced such that a volumetric flow ratio of introduced water to introduced petroleum feedstock is maintained in a range of from 10:1 to 1:10 at standard conditions.

3. The method of claim 1 further comprising the step of operating the supercritical water petroleum upgrading system such that the pre-heated petroleum feedstock combined into the mixed petroleum feedstock has a temperature no greater than 150 °C, and a pressure equal to or greater than the critical pressure of water.

4. The method of claim 1 further comprising the step of operating the supercritical water petroleum upgrading system such that a volumetric flow ratio of the pre-heated auxiliary feedstock to the mixed petroleum feedstock at ambient temperature and at respective pressure conditions is in a range of from 2:1 to 1:1000 at standard conditions.

5. The method of claim 1 further comprising the step of operating the supercritical water petroleum upgrading system such that a temperature difference between the pre-heated auxiliary feedstock and the mixed petroleum feedstock is maintained in a range of from - 50 °C to 250 °C.

6. The method of claim 1 further comprising the step of operating the upflowing supercritical water reactor such that the temperature of the fluid within in the upflowing reactor is maintained in a range of from 380 °C to 600 °C.

7. The method of claim 1 further comprising the step of operating the supercritical water petroleum upgrading system such that the temperature difference between the upflowing reactor product fluid and the mixed petroleum feedstock is maintained in a range of from 50 °C to 300 °C and the pressure of the upflowing reactor product fluid is maintained in a range of from 3,200 psig to 6,000 psig.

8. The method of claim 1 where the pre-heated auxiliary feedstock is introduced into the upflowing supercritical water reactor such that the auxiliary fluid has a greater upward fluid velocity than the average superficial velocity of fluid in the reactor.

9. The method of claim 1 where the pre-heated auxiliary feedstock is introduced into the upflowing supercritical water reactor such that the fluid in the lower portion of the upflowing reactor is maintained in a turbulent fluid flow regime.

10. The method of claim 1 where the auxiliary feed stream comprises supercritical water.

11. The method of claim 10 where the auxiliary feed stream further comprises aromatic hydrocarbons, where the aromatic hydrocarbons are present in a range of from 1 weight percent (wt.%) to 75 wt.% of the auxiliary feed stream.

12. The method of claim 11 where the aromatic hydrocarbons consist essentially of toluene.

13. The method of claim 11 where the aromatic hydrocarbons comprise reformate from a naphtha reformer.

14. The method of claim 11 where the auxiliary feed stream further comprises a catalytic material, where the catalytic material is present in a range of from 100 ppm wt. to 1 wt.% of the auxiliary feed stream and consists of one to five active metals selected from the group consisting of iron, nickel, vanadium, molybdenum, chromium, manganese, cobalt, copper, zinc, tungsten, zirconium and titanium.

15. The method of claim 11 where the auxiliary feed stream further comprises a catalyst precursor, where the catalyst precursor is operable to convert into a catalytic material at the operating conditions of the upflowing supercritical water reactor, the catalyst precursor is present in a range of from 100 ppm wt. to 1 wt.% of the auxiliary feed stream and consists of one to five active metals selected from the group consisting of iron, nickel, vanadium, molybdenum, chromium, manganese, cobalt, copper, zinc, tungsten, zirconium and titanium.

16. The method of claim 11 where the auxiliary feed stream further comprises paraffinic sulfur, where the paraffinic sulfur is present in a range of from 0.05 wt.% to 1 wt.% of the auxiliary feed stream as calculated on a sulfur-only basis.

17. The method of claim 16 where the paraffinic sulfur is selected from the group consisting of thiol compounds having a carbon number in a range of from 1 to 8 and combinations thereof.

18. The method of claim 1 where the auxiliary feed stream comprises light hydrocarbons.

19. The method of claim 18 where the auxiliary feed stream further comprises paraffinic sulfur, where the paraffinic sulfur is present in a range of from 0.05 wt.% to 1 wt.% of the auxiliary feed stream as calculated on a sulfur-only basis and is selected from the group consisting of thiol compounds having a carbon number in a range of from 1 to 8 and combinations thereof.

20. The method of claim 1 further comprising the steps of:

operating the supercritical water petroleum upgrading system such that the upflowing reactor product fluid is introduced into an upper portion of a downflowing supercritical water reactor;

operating the downflowing supercritical water reactor such that a fluid contained in the downflowing reactor is maintained at a temperature and a pressure equal to or greater than the critical temperature and the critical pressure of water, respectively, and is moving in a generally downward direction; and

operating the supercritical water petroleum upgrading system such that a downflowing reactor product fluid passes from a lower portion of the downflowing supercritical water reactor,

where the amount of passing downflowing reactor product fluid is equivalent to the amount of introduced upflowing reactor product fluid;

where the step of operating the supercritical water petroleum upgrading system is such that the gas-phase hydrocarbon product, the upgraded and desulfurized petroleum product and the aqueous-phase product are produced through the separate selective separation of the downflowing reactor product fluid instead of the upflowing reactor product fluid; and

where the supercritical water petroleum upgrading system also includes the downflowing supercritical water reactor, where the downflowing reactor is fluidly coupled downstream of the upflowing supercritical water reactor and is operable to receive the upflowing reactor product fluid into the upper portion of the downflowing reactor.

21. The method of claim 20 further comprising the step of operating the downflowing supercritical water reactor such that the temperature of the fluid contained in the downflowing reactor is maintained at a temperature in a range of from 0 °C to 100 °C greater than the temperature of the fluid contained in the upflowing reactor.

22. The method of claim 1 further comprising the step of operating the supercritical water petroleum upgrading system such that the yield between the introduced petroleum feedstock and the upgraded and desulfurized petroleum product is equal to or greater than 92 percent by weight.

23. The method of claim 1 further comprising the step of operating the supercritical water petroleum upgrading system such that the difference in API gravity between the upgraded and desulfurized petroleum product and the introduced petroleum feedstock is equal to or greater than 8 degrees.

24. The method of claim 1 further comprising the step of operating the supercritical water petroleum upgrading system such that the upgraded and desulfurized petroleum product has less than 3 wt.% insoluble material.

25. The method of claim 1 where the pre-heated auxiliary feedstock is introduced to the upflowing reactor through multiple injection points such that the pre-heated auxiliary feedstock passes through a V-shaped false bottom.

26. A method for upgrading a petroleum feedstock using a supercritical water petroleum upgrading system, the method comprising the steps of:

introducing the petroleum feedstock into the supercritical water petroleum upgrading system;

introducing a water into the supercritical water petroleum upgrading system;

introducing an auxiliary feedstock into the supercritical water petroleum upgrading system,

where the auxiliary feedstock comprises supercritical water,

where the auxiliary feedstock further comprises aromatic hydrocarbons from a naphtha reformer, where the aromatic hydrocarbons from a naphtha reformer are present in a range of from 1 weight percent (wt.%) to 75 wt.% of the auxiliary feedstock;

operating the supercritical water petroleum upgrading system such that the petroleum feedstock and the water combine to form a mixed petroleum feedstock;

operating the supercritical water petroleum upgrading system such that the mixed petroleum feedstock and the auxiliary feedstock are introduced separately and simultaneously into a lower portion of an upflowing supercritical water reactor, where the auxiliary feedstock is introduced into the upflowing reactor such that a portion of a fluid contained within the upflowing reactor located proximate to the bottom of the upflowing reactor does not lack fluid momentum;

operating the upflowing supercritical water reactor such that the fluid contained within the upflowing reactor is maintained at a temperature equal to or greater than the critical temperature of water, at a pressure equal to or greater than the critical pressure of water, and is moving in a generally upwards direction, such that supercritical water forms from the introduced water in the fluid contained within the upflowing reactor;

operating the upflowing supercritical water reactor such that the upgraded and desulfurized petroleum product forms as the reaction product between the introduced petroleum feedstock and the supercritical water in the fluid contained within the upflowing reactor;

operating the supercritical water petroleum upgrading system such that an upflowing reactor product fluid passes from an upper portion of the upflowing reactor, where the product fluid comprises the upgraded and desulfurized petroleum product, and where the amount of passing upflowing reactor product fluid is equivalent to the combined amount of the introduced mixed petroleum feedstock and the auxiliary feedstock; and

operating the supercritical water petroleum upgrading system such that a gas-phase hydrocarbon product, the upgraded and desulfurized petroleum product and an aqueous-phase product are separately selectively separated from the upflowing reactor product fluid.

27. The method of claim 26 where the petroleum feedstock and the water are introduced such that a volumetric flow ratio of introduced water to introduced petroleum feedstock is maintained in a range of from 10:1 to 1:10 at standard conditions.

28. The method of claim 26 further comprising the step of operating the supercritical water petroleum upgrading system such that the petroleum feedstock combined into the mixed petroleum feedstock has a temperature no greater than 150 °C and a pressure equal to or greater than the critical pressure of water.

29. The method of claim 26 further comprising the step of operating the supercritical water petroleum upgrading system such that a volumetric flow ratio of the auxiliary feedstock to the mixed petroleum feedstock at ambient temperature and at respective pressure conditions is in a range of from 2:1 to 1:1000 at standard conditions.

30. The method of claim 26 further comprising the step of operating the supercritical water petroleum upgrading system such that a temperature difference between the auxiliary feedstock and the mixed petroleum feedstock is maintained in a range of from - 50 °C to 250 °C.

31. The method of claim 26 further comprising the step of operating the upflowing supercritical water reactor such that the temperature of the fluid within in the upflowing reactor is maintained in a range of from 380 °C to 600 °C.

32. The method of claim 26 further comprising the step of operating the supercritical water petroleum upgrading system such that the temperature difference between the upflowing reactor product fluid and the mixed petroleum feedstock is maintained in a range of from 50 °C to 300 °C and the pressure of the upflowing reactor product fluid is maintained in a range of from 3,200 psig to 6,000 psig.

33. The method of claim 26 where the auxiliary fluid is introduced into the upflowing supercritical water reactor such that the auxiliary fluid has a greater upward fluid velocity than the average superficial velocity of fluid in the reactor.

34. The method of claim 26 where the auxiliary fluid is introduced into the upflowing supercritical water reactor such that the fluid in the lower portion of the upflowing reactor is maintained in a turbulent fluid flow regime.

35. The method of claim 26 where the auxiliary feedstock further comprises a catalytic material, where the catalytic material is present in a range of from 100 ppm wt to 1 wt.% of the auxiliary feedstock and consists of one to five active metals selected from the group consisting of iron, nickel, vanadium, molybdenum, chromium, manganese, cobalt, copper, zinc, tungsten, zirconium and titanium.

36. The method of claim 26 where the auxiliary feedstock further comprises a catalyst precursor, where the catalyst precursor is operable to convert into a catalytic material at the operating conditions of the upflowing supercritical water reactor, the catalyst precursor is present in a range of from 100 ppm wt to 1 wt.% of the auxiliary feedstock and consists of one to five active metals selected from the group consisting of iron, nickel, vanadium, molybdenum, chromium, manganese, cobalt, copper, zinc, tungsten, zirconium and titanium.

37. The method of claim 26 where the paraffinic sulfur is selected from the group consisting of thiol compounds having a carbon number in a range of from 1 to 8 and combinations thereof.

38. The method of claim 26 where the auxiliary feedstock also comprises paraffinic sulfur, where the paraffinic sulfur is present in a range of from 0.05 wt.% to 1 wt.% of the auxiliary feedstock as calculated on a sulfur-only basis and is selected from the group consisting of thiol compounds having a carbon number in a range of from 1 to 8 and combinations thereof.

39. The method of claim 26 further comprising the step of operating the downflowing supercritical water reactor such that the temperature of the fluid contained in the downflowing reactor is maintained at a temperature in a range of from 0 °C to 100 °C greater than the temperature of the fluid contained in the upflowing reactor.

40. The method of claim 26 further comprising the step of operating the supercritical water petroleum upgrading system such that the yield between the introduced petroleum feedstock and the upgraded and desulfurized petroleum product is equal to or greater than 92 percent by weight.

41. The method of claim 26 further comprising the step of operating the supercritical water petroleum upgrading system such that the difference in API gravity between the upgraded and desulfurized petroleum product and the introduced petroleum feedstock is equal to or greater than 8 degrees.

42. The method of claim 26 further comprising the step of operating the supercritical water petroleum upgrading system such that such that the upgraded and desulfurized petroleum product has less than 3 wt.% insoluble material.

43. The method of claim 26 where the auxiliary feedstock is introduced to the upflowing reactor through multiple injection points such that the auxiliary feedstock passes through a V-shaped false bottom.

44. The method of claim 26 further comprising the steps of:

combining an auxiliary feed stream and a pre-heated water portion to form a pre-heated auxiliary feedstock; and

introducing the pre-heated auxiliary feedstock into the lower portion of the upflowing reactor.

45. A method for upgrading a petroleum feedstock using a supercritical water petroleum upgrading system, the method comprising the steps of:

introducing the petroleum feedstock into the supercritical water petroleum upgrading system;

introducing a water into the supercritical water petroleum upgrading system;

introducing an auxiliary feedstock into the supercritical water petroleum upgrading system;

operating the supercritical water petroleum upgrading system such that the petroleum feedstock and the water combine to form a mixed petroleum feedstock;

operating the supercritical water petroleum upgrading system such that the mixed petroleum feedstock and the auxiliary feedstock are introduced separately and simultaneously into a lower portion of an upflowing supercritical water reactor, where the auxiliary feedstock is introduced into the upflowing reactor through a V-shaped false bottom such that a portion of a fluid contained within the upflowing reactor located proximate to the bottom of the upflowing reactor does not lack fluid momentum such that heavy hydrocarbons in the fluid are carried upward in the upflowing reactor;

operating the upflowing supercritical water reactor such that the fluid contained within the upflowing reactor is maintained at a temperature equal to or greater than the critical temperature of water, at a pressure equal to or greater than the critical pressure of water, and is moving in a generally upwards direction, such that supercritical water forms from the introduced water in the fluid contained within the upflowing reactor;

operating the upflowing supercritical water reactor such that the upgraded and desulfurized petroleum product forms as the reaction product between the introduced petroleum feedstock and the supercritical water in the fluid contained within the upflowing reactor;

operating the supercritical water petroleum upgrading system such that an upflowing reactor product fluid passes from an upper portion of the upflowing reactor, where the product fluid comprises the upgraded and desulfurized petroleum product, and where the amount of passing upflowing reactor product fluid is equivalent to the combined amount of the introduced mixed petroleum feedstock and the auxiliary feedstock;

operating the supercritical water petroleum upgrading system such that a gas-phase hydrocarbon product, the upgraded and desulfurized petroleum product and an aqueous-phase product are separately selectively separated from the upflowing reactor product fluid;

operating the supercritical water petroleum upgrading system such that the upflowing reactor product fluid is introduced into an upper portion of a downflowing supercritical water reactor;

operating the downflowing supercritical water reactor such that a fluid contained in the downflowing reactor is maintained at a temperature and a pressure equal to or greater than the critical temperature and the critical pressure of water, respectively, and is moving in a generally downward direction; and

operating the supercritical water petroleum upgrading system such that a downflowing reactor product fluid passes from a lower portion of the downflowing supercritical water reactor,

where the amount of passing downflowing reactor product fluid is equivalent to the amount of introduced upflowing reactor product fluid;

where the step of operating the supercritical water petroleum upgrading system is such that the gas-phase hydrocarbon product, the upgraded and desulfurized petroleum product and the aqueous-phase product are produced through the separate selective separation of the downflowing reactor product fluid instead of the upflowing reactor product fluid; and

where the supercritical water petroleum upgrading system also includes the downflowing supercritical water reactor, where the downflowing reactor is fluidly coupled downstream of the upflowing supercritical water reactor and is operable to receive the upflowing reactor product fluid into the upper portion of the downflowing reactor.

46. The method of claim 45 where the petroleum feedstock and the water are introduced such that a volumetric flow ratio of introduced water to introduced petroleum feedstock is maintained in a range of from 10:1 to 1:10 at standard conditions.

47. The method of claim 45 further comprising the step of operating the supercritical water petroleum upgrading system such that the petroleum feedstock combined into the mixed

petroleum feedstock has a temperature no greater than 150 °C and a pressure equal to or greater than the critical pressure of water.

48. The method of claim 45 further comprising the step of operating the supercritical water petroleum upgrading system such that a volumetric flow ratio of the auxiliary feedstock to the mixed petroleum feedstock at ambient temperature and at respective pressure conditions is in a range of from 2:1 to 1:1000 at standard conditions.

49. The method of claim 45 further comprising the step of operating the supercritical water petroleum upgrading system such that a temperature difference between the auxiliary feedstock and the mixed petroleum feedstock is maintained in a range of from - 50 °C to 250 °C.

50. The method of claim 45 further comprising the step of operating the upflowing supercritical water reactor such that the temperature of the fluid within in the upflowing reactor is maintained in a range of from 380 °C to 600 °C.

51. The method of claim 45 further comprising the step of operating the supercritical water petroleum upgrading system such that the temperature difference between the upflowing reactor product fluid and the mixed petroleum feedstock is maintained in a range of from 50 °C to 300 °C and the pressure of the upflowing reactor product fluid is maintained in a range of from 3,200 psig to 6,000 psig.

52. The method of claim 45 where the auxiliary fluid is introduced into the upflowing supercritical water reactor such that the auxiliary fluid has a greater upward fluid velocity than the average superficial velocity of fluid in the reactor.

53. The method of claim 45 where the auxiliary fluid is introduced into the upflowing supercritical water reactor such that the fluid in the lower portion of the upflowing reactor is maintained in a turbulent fluid flow regime.

54. The method of claim 45 where the auxiliary feedstock comprises supercritical water.

55. The method of claim 54 where the auxiliary feedstock further comprises aromatic hydrocarbons, where the aromatic hydrocarbons are present in a range of from 1 weight percent (wt.%) to 75 wt.% of the auxiliary feedstock.

56. The method of claim 55 where the aromatic hydrocarbons consist essentially of toluene.

57. The method of claim 55 where the aromatic hydrocarbons comprise reformate from a naphtha reformer.

58. The method of claim 55 where the auxiliary feedstock further comprises a catalytic material, where the catalytic material is present in a range of from 100 ppm wt. to 1 wt.% of the auxiliary feedstock and consists of one to five active metals selected from the group consisting of iron, nickel, vanadium, molybdenum, chromium, manganese, cobalt, copper, zinc, tungsten, zirconium and titanium.

59. The method of claim 55 where the auxiliary feedstock further comprises a catalyst precursor, where the catalyst precursor is operable to convert into a catalytic material at the operating conditions of the upflowing supercritical water reactor, the catalyst precursor is present in a range of from 100 ppm wt. to 1 wt.% of the auxiliary feedstock and consists of one to five active metals selected from the group consisting of iron, nickel, vanadium, molybdenum, chromium, manganese, cobalt, copper, zinc, tungsten, zirconium and titanium.

60. The method of claim 55 where the auxiliary feedstock also comprises paraffinic sulfur, where the paraffinic sulfur is present in a range of from 0.05 wt.% to 1 wt.% of the auxiliary feedstock as calculated on a sulfur-only basis.

61. The method of claim 60 where the paraffinic sulfur is selected from the group consisting of thiol compounds having a carbon number in a range of from 1 to 8 and combinations thereof.

62. The method of claim 45 where the auxiliary feedstock comprises light hydrocarbons.

63. The method of claim 62 where the auxiliary feedstock also comprises paraffinic sulfur, where the paraffinic sulfur is present in a range of from 0.05 wt.% to 1 wt.% of the auxiliary feedstock as calculated on a sulfur-only basis and is selected from the group consisting of thiol compounds having a carbon number in a range of from 1 to 8 and combinations thereof.

64. The method of claim 63 further comprising the step of operating the downflowing supercritical water reactor such that the temperature of the fluid contained in the downflowing

reactor is maintained at a temperature in a range of from 0 °C to 100 °C greater than the temperature of the fluid contained in the upflowing reactor.

65. The method of claim 45 further comprising the step of operating the supercritical water petroleum upgrading system such that the yield between the introduced petroleum feedstock and the upgraded and desulfurized petroleum product is equal to or greater than 92 percent by weight.

66. The method of claim 45 further comprising the step of operating the supercritical water petroleum upgrading system such that the difference in API gravity between the upgraded and desulfurized petroleum product and the introduced petroleum feedstock is equal to or greater than 8 degrees.

67. The method of claim 45 further comprising the step of operating the supercritical water petroleum upgrading system such that such that the upgraded and desulfurized petroleum product has less than 3 wt.% insoluble material.

68. A method for upgrading a petroleum feedstock using a supercritical water petroleum upgrading system, the method comprising the steps of:

introducing the petroleum feedstock into the supercritical water petroleum upgrading system;

introducing a water into the supercritical water petroleum upgrading system;

introducing an auxiliary feedstock into the supercritical water petroleum upgrading system, where the auxiliary feedstock comprises light hydrocarbons;

operating the supercritical water petroleum upgrading system such that the petroleum feedstock and the water combine to form a mixed petroleum feedstock;

operating the supercritical water petroleum upgrading system such that the mixed petroleum feedstock and the auxiliary feedstock are introduced separately and simultaneously into a lower portion of an upflowing supercritical water reactor, where the auxiliary feedstock is introduced into the upflowing reactor through a V-shaped false bottom such that a portion of a fluid contained within the upflowing reactor located proximate to the bottom of the upflowing reactor does

not lack fluid momentum such that heavy hydrocarbons in the fluid are carried upward in the upflowing reactor;

operating the upflowing supercritical water reactor such that the fluid contained within the upflowing reactor is maintained at a temperature equal to or greater than the critical temperature of water, at a pressure equal to or greater than the critical pressure of water, and is moving in a generally upwards direction, such that supercritical water forms from the introduced water in the fluid contained within the upflowing reactor;

operating the upflowing supercritical water reactor such that an upgraded and desulfurized petroleum product forms as the reaction product between the introduced petroleum feedstock and the supercritical water in the fluid contained within the upflowing reactor;

operating the supercritical water petroleum upgrading system such that an upflowing reactor product fluid passes from an upper portion of the upflowing reactor, where the product fluid comprises the upgraded and desulfurized petroleum product, and where the amount of passing upflowing reactor product fluid is equivalent to the combined amount of the introduced mixed petroleum feedstock and the auxiliary feedstock; and

operating the supercritical water petroleum upgrading system such that a gas-phase hydrocarbon product, the upgraded and desulfurized petroleum product and an aqueous-phase product are separately selectively separated from the upflowing reactor product fluid.