[0009] Another option involves using a fixed bed reactor media in the form of wagon wheels, Raschig rings, and other shapes having high void fractions ("high void" means typically 50% or higher void fraction). Reactors containing top layers of these media can hold more solids before reaching the pressure drop limit. These high void media, including high void/low activity catalysts (e.g. "active rings"), may be graded to provide systems achieving significantly longer pressure drop limited run lengths. "Low activity catalysts" are those catalysts with less than 5 wt% of the active catalytic metal. Some of the top bed grading media contains internal macro-porosity capable of capturing very fine particulates that can nonetheless agglomerate within the fixed bed reactor void space and cause pressure drop issues.

[0010] An internal bypass apparatus for fixed bed reactors is another option. The bypass can include pipes which allow a hydrotreater feed to bypass the fouled section of the reactor so that nothing runs through the fouled section. The pipes can be equipped with rupture disks that burst open when the pressure drop reaches a value just below the operating limit, thus extending run length.

[0011] Although the above pressure drop mitigation methods and equipment can be useful for hydroprocessing reactor feeds comprising bio-oils, additional methods more suitable for solid deposits characteristic of bio-oils are desirable.

SUMMARY

[0011a] In one aspect, there is provided a method comprising reducing a pressure drop across a hydroprocessing reactor having

a reactor feed and producing a hydroprocessing product, wherein:

the reactor feed comprises a bio-oil feed and a hydrocarbon diluent at a volumetric ratio of hydrocarbon diluent to bio-oil feed from about 1:1 to about 3:1;

reducing the pressure drop is performed after a rate of pressure drop increase in the hydroprocessing reactor is about 0.1 psi/hr;

reducing the pressure drop comprises

supplying a volumetric ratio of hydrocarbon diluent to bio-oil feed of at least about 10:1 to the reactor to generate a mass flux of at least about 1,000 lb/hr/ft^2;

and

re-establishing the volumetric ratio of hydrocarbon diluent to bio-oil feed from about 1:1 to about 3:1 once a rate of pressure drop decrease is below about 0.1 psi/hr.

[0012] In one ~~aspect~~embodiment, a method is provided comprising reducing a pressure drop across a hydroprocessing reactor having a reactor feed and producing a hydroprocessing product, where the reactor feed includes a bio-oil feed and a hydrocarbon diluent; and the step of reducing the pressure drop includes stopping or substantially reducing the bio-oil feed supplied to the hydroprocessing reactor and supplying the hydrocarbon diluent to the reactor to generate a mass flux of at least about 1,000 lb/hr/ft^2. In some embodiments, the mass flux is from about 1,000 lb/hr/ft^2 to about 10,000 lb/hr/ft^2. In some embodiments, the mass flux is at least about 2,000 lb/hr/ft^2. In some embodiments, the hydrocarbon diluent comprises the hydroprocessing product of the hydroprocessing reactor. In some embodiments, the bio-oil feed supplied to the reactor is substantially reduced.

[0013] In some embodiments, the reduction of the pressure drop is performed after 100 to 10,000 reactor volumes of bio-oil have been processed. In some embodiments, the reduction of the pressure drop is performed after the rate of ΔP increase is about 0.1 psi/hr. In some embodiments, the method is performed periodically. In some embodiments, the periodic reduction of the pressure drop is performed after about 2 days to about 12 months since either the start of hydroprocessing or the last reduction of pressure drop.

[0014] In some embodiments, substantially reducing the bio-oil feed includes supplying the hydrocarbon diluent to the hydroprocessing reactor at a volumetric ratio of at least 10:1 of hydrocarbon diluent to bio-oil. In some embodiments, substantially reducing the bio-oil feed includes supplying the hydrocarbon diluent to the hydroprocessing reactor at a volumetric ratio of at least 15:1 hydrocarbon diluent to bio-oil. In some embodiments, the hydrocarbon diluent is supplied at a temperature of about 400 °F to about 800 °F. In some embodiments, the hydrocarbon diluent has a boiling point range of about 300 °F to about
800 °F. In some embodiments, the step of reducing the pressure drop does not interrupt production of the hydroprocessing product.

[0015] In some embodiments, the bio-oil includes a lipid, a carboxylic acid, a plant oil, animal fat, algal oil, a distillate from the fermentation of sugars, a liquid fraction derived from the fast pyrolysis of biomass, or a mixture of any two or more thereof. In some embodiments, the plant oil or animal fat contains nitrogen, sulfur, or phosphorus from about 0.1 wppm to about 30,000 wppm. In some embodiments, the bio-oil comprises a liquid fraction from the fast pyrolysis of biomass. In some embodiments, the liquid fraction is derived from ground wood, ground switch grass, or combinations thereof.

[0016] In some embodiments, the hydroprocessing reactor comprises a graded bed. In some embodiments, the graded bed comprises high void and high macro-porosity media. In some embodiments, the graded bed comprises a catalyst that includes Co, Mo, Ni, Pt, Pd, Ru, W, NiMo, NiW, CoMo, or combinations of any two or more thereof. In some embodiments, the reactor feed further includes a hydrogen gas. In some embodiments, the hydroprocessing reactor performs at least some hydrodeoxygenation.

[0016a] In another aspect, there is provided a method comprising reducing a pressure drop across a hydroprocessing reactor having a reactor feed, wherein:

the hydroprocessing reactor produces a hydroprocessing product;

the reactor feed is at a temperature from about 550° F. to about 750° F. and is produced by at least combining

a bio-oil feed at a temperature of about 100° F. to about 350° F.; and

a recycled hydroprocessing product of the hydroprocessing reactor at a temperature of about 550° F. to about 800° F.;

wherein the volumetric ratio of recycled hydroprocessing product to bio-oil feed is from about 1:1 to about 3:1;

reducing the pressure drop is performed after the theoretical void fraction drops below 26% and comprises

supplying a volumetric ratio of recycled hydroprocessing product to bio-oil feed of at least about 10:1 to the reactor to generate a mass flux of at least about 2,000 lb/hr/ft^2; and

re-establishing the volumetric ratio of hydrocarbon diluent to bio-oil feed from about 1:1 to about 3:1 once a decrease in pressure drop is in the range from about 10% to about 99%.

[0016b] In yet another aspect, there is provided a method comprising reducing a pressure drop across a hydroprocessing reactor having a reactor feed and producing a hydroprocessing product, wherein:

the reactor feed comprises

a bio-oil feed and a hydrocarbon diluent at a volumetric ratio of hydrocarbon diluent to bio-oil feed from about 1:1 to about 3:1; and

the bio-oil comprises a plant oil, animal fat, or both;

reducing the pressure drop is performed after a rate of pressure drop increase in the hydroprocessing reactor is about 0.1 psi/hr;

reducing the pressure drop comprises

stopping the reactor feed to the hydroprocessing reactor and supplying the hydrocarbon diluent to the hydroprocessing reactor to generate a mass flux of about 1,000 lb/hr/ft^2 to about 10,000 lb/hr/ft^2; and

re-establishing the supply of reactor feed once a decrease in pressure drop is in the range from about 10% to about 99%.

[0017] In an ~~aspect~~embodiment, a method is provided that includes the step of reducing a pressure drop across a hydroprocessing reactor having a reactor feed, where the

~~WHAT IS CLAIMED IS:~~

1. A method comprising reducing a pressure drop across a hydroprocessing reactor having a reactor feed and producing a hydroprocessing product, wherein:

the reactor feed comprises a bio-oil feed and a hydrocarbon diluent; and

reducing the pressure drop comprises

stopping or substantially reducing the bio-oil feed supplied to the hydroprocessing reactor; and

supplying the hydrocarbon diluent to the reactor to generate a mass flux of at least about 1,000 lb/hr/ft^2.

2. The method of claim 1, wherein the mass flux is from about 1,000 lb/hr/ft^2 to about 10,000 lb/hr/ft^2.

3. The method of claim 1, wherein the mass flux is at least about 2,000 lb/hr/ft^2.

4. The method of claim 1, wherein the hydrocarbon diluent comprises the hydroprocessing product of the hydroprocessing reactor.

5. The method of claim 1, wherein the bio-oil feed supplied to the hydroprocessing reactor is substantially reduced.

6. The method of claim 1, wherein the reduction of the pressure drop is performed after 100 to 10,000 reactor volumes of bio-oil have been processed.

7. The method of claim 1, wherein the reduction of the pressure drop is performed after the rate of pressure drop increase is about 0.1 psi/hr.

8. The method of claim 1, wherein the reduction of the pressure drop is performed periodically.

9. The method of claim 8, wherein the periodic reduction of the pressure drop is performed after about 2 days to about 12 months since either the start of hydroprocessing or the last reduction of pressure drop.

10. The method of claim 1, wherein substantially reducing the bio-oil feed comprises supplying the hydrocarbon diluent to the hydroprocessing reactor at a volumetric ratio of at least 10:1 of hydrocarbon diluent to bio-oil.

11. The method of claim 1, wherein substantially reducing the bio-oil feed comprises supplying the hydrocarbon diluent to the hydroprocessing reactor at a volumetric ratio of at least 15:1 hydrocarbon diluent to bio-oil.

12. The method of claim 1, wherein the hydrocarbon diluent is supplied at a temperature of about 400 °F to about 800 °F.

13. The method of claim 1, wherein the hydrocarbon diluent has a boiling point range of about 300 °F to about 650 °F.

14. The method of claim 1, wherein the step of reducing the pressure drop does not interrupt production of the hydroprocessing product.

15. The method of claim 1, wherein the bio-oil comprises a lipid, a carboxylic acid, a plant oil, animal fat, algal oil, a distillate from the fermentation of sugars, or a liquid fraction derived from the fast pyrolysis of biomass.

16. The method of claim 15, wherein the plant oil, animal fat, or both, contains nitrogen, sulfur, or phosphorus from about 0.1 wppm to about 30,000 wppm.

17. The method of claim 1, wherein the bio-oil comprises a liquid fraction from the fast pyrolysis of biomass.

18. The method of claim 17, wherein the liquid fraction is derived from ground wood, ground switch grass, or combinations thereof.

19. The method of claim 1, wherein the hydroprocessing reactor comprises a graded bed.

20. The method of claim 19, wherein the graded bed comprises high void and high macro-porosity media.

21. The method of claim 20, wherein the graded bed comprises a catalyst comprising Co, Mo, Ni, Pt, Pd, Ru, W, NiMo, NiW, or CoMo.

~~22. The method of claim 1, wherein the reactor feed further comprises hydrogen gas.~~

23. The method of claim 1, wherein the hydroprocessing reactor performs at least some hydrodeoxygenation.

24. A method comprising reducing a pressure drop across a hydroprocessing reactor having a reactor feed, wherein:

the hydroprocessing reactor produces a hydroprocessing product;

the reactor feed is at a temperature from about 550 °F to about 750 °F and is produced by at least combining

a bio-oil feed at a temperature of about 100 °F to about 350 °F;

a recycled hydroprocessing product of the hydroprocessing reactor at a temperature of about 550 °F to about 800 °F;

reducing the pressure drop comprises

substantially reducing the bio-oil feed supplied to the reactor; and

supplying the recycled hydroprocessing product to the reactor to generate a mass flux of at least about 2,000 $lb/hr/ft^2$;

reducing the pressure drop is performed after the theoretical void fraction drops below 26 %.

WHAT IS CLAIMED IS:

1. A method comprising reducing a pressure drop across a hydroprocessing reactor having a reactor feed and producing a hydroprocessing product, wherein:

the reactor feed comprises a bio-oil feed and a hydrocarbon diluent at a volumetric ratio of hydrocarbon diluent to bio-oil feed from about 1:1 to about 3:1;

reducing the pressure drop is performed after a rate of pressure drop increase in the hydroprocessing reactor is about 0.1 psi/hr;

reducing the pressure drop comprises

supplying a volumetric ratio of hydrocarbon diluent to bio-oil feed of at least about 10:1 to the reactor to generate a mass flux of at least about 1,000 lb/hr/ft^2;

and

re-establishing the volumetric ratio of hydrocarbon diluent to bio-oil feed from about 1:1 to about 3:1 once a rate of pressure drop decrease is below about 0.1 psi/hr.

2. The method of claim 1, wherein the mass flux is from about 1,000 lb/hr/ft^2 to about 10,000 lb/hr/ft^2.

3. The method of claim 1, wherein the mass flux is at least about 2,000 lb/hr/ft^2.

4. The method of claim 1, wherein the hydrocarbon diluent comprises the hydroprocessing product of the hydroprocessing reactor.

5. The method of claim 1, wherein reducing the pressure drop comprises supplying the hydrocarbon diluent to the hydroprocessing reactor at a volumetric ratio of at least 15:1 hydrocarbon diluent to bio-oil.

6. The method of claim 1, wherein the hydrocarbon diluent is supplied at a temperature of about 400° F. to about 800° F.

7. The method of claim 1, wherein the hydrocarbon diluent has a boiling point of about 300°

F. to about 650° F.

8. The method of claim 1, wherein the bio-oil comprises a lipid, a carboxylic acid, a plant oil, animal fat, algal oil, a distillate from the fermentation of sugars, or a liquid fraction derived from the fast pyrolysis of biomass.

9. The method of claim 8, wherein the plant oil, animal fat, or both, contains nitrogen, sulfur, or phosphorus from about 0.1 wppm to about 30,000 wppm.

10. The method of claim 1, wherein the bio-oil comprises a liquid fraction from the fast pyrolysis of biomass.

11. The method of claim 10, wherein the liquid fraction is derived from ground wood, ground switch grass, or combinations thereof.

12. The method of claim 1, wherein the hydroprocessing reactor comprises a graded bed.

13. The method of claim 12, wherein the graded bed comprises high void and high macro-porosity media.

14. The method of claim 13, wherein the graded bed comprises a catalyst comprising Co, Mo, Ni, Pt, Pd, Ru, W, NiMo, NiW, or CoMo.

15. The method of claim 1, wherein the reactor feed further comprises hydrogen gas.

16. The method of claim 1, wherein the hydroprocessing reactor performs at least some hydrodeoxygenation.

17. A method comprising reducing a pressure drop across a hydroprocessing reactor having a reactor feed, wherein:

the hydroprocessing reactor produces a hydroprocessing product;

the reactor feed is at a temperature from about 550° F. to about 750° F. and is

produced by at least combining

a bio-oil feed at a temperature of about 100° F. to about 350° F.; and

a recycled hydroprocessing product of the hydroprocessing reactor at a temperature of about 550° F. to about 800° F.;

wherein the volumetric ratio of recycled hydroprocessing product to bio-oil feed is from about 1:1 to about 3:1;

reducing the pressure drop is performed after the theoretical void fraction drops below 26% and comprises

supplying a volumetric ratio of recycled hydroprocessing product to bio-oil feed of at least about 10:1 to the reactor to generate a mass flux of at least about 2,000 lb/hr/ft^2; and

re-establishing the volumetric ratio of hydrocarbon diluent to bio-oil feed from about 1:1 to about 3:1 once a decrease in pressure drop is in the range from about 10% to about 99%.

18. A method comprising reducing a pressure drop across a hydroprocessing reactor having a reactor feed and producing a hydroprocessing product, wherein:

the reactor feed comprises

a bio-oil feed and a hydrocarbon diluent at a volumetric ratio of hydrocarbon diluent to bio-oil feed from about 1:1 to about 3:1; and

the bio-oil comprises a plant oil, animal fat, or both;

reducing the pressure drop is performed after a rate of pressure drop increase in the hydroprocessing reactor is about 0.1 psi/hr;

reducing the pressure drop comprises

stopping the reactor feed to the hydroprocessing reactor and supplying the hydrocarbon diluent to the hydroprocessing reactor to generate a mass flux of about 1,000 lb/hr/ft^2 to about 10,000 lb/hr/ft^2; and

re-establishing the supply of reactor feed once a decrease in pressure drop is in the range from about 10% to about 99%.

19. The method of claim 18, wherein the hydrocarbon diluent comprises the hydroprocessing product of the hydroprocessing reactor.

20. The method of claim 18, wherein the hydrocarbon diluent is supplied at a temperature of about 400° F. to about 800° F. and has a boiling point of about 300° F. to about 650° F.

21. The method of claim 18, wherein the hydroprocessing reactor comprises a graded bed; and the graded bed comprises a NiMo catalyst, a CoMo catalyst, or a combination thereof.

22. The method of claim 18, wherein reducing the pressure drop comprises re-establishing the supply of reactor feed once the decrease in pressure drop is in the range from about 25% to about 80%.

23. The method of claim 18, wherein the mass flux is from about 2,000 lb/hr/ft^2 to about 10,000 lb/hr/ft^2.