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(54) **MEMBRANE METHOD OF REMOVING
OIL-SOLUBLE METALS FROM
HYDROCARBONS**

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(57) **ABSTRACT**

A method of removing an oil-soluble metal from a hydrocarbon feedstock comprises passing the hydrocarbon feedstock through a nanofiltration membrane or a reverse osmosis membrane to produce a permeate stream having at least a vanadium concentration less than an initial vanadium concentration in the hydrocarbon feedstock, and a retentate stream having at least a vanadium concentration greater than the initial vanadium concentration in the hydrocarbon feedstock.

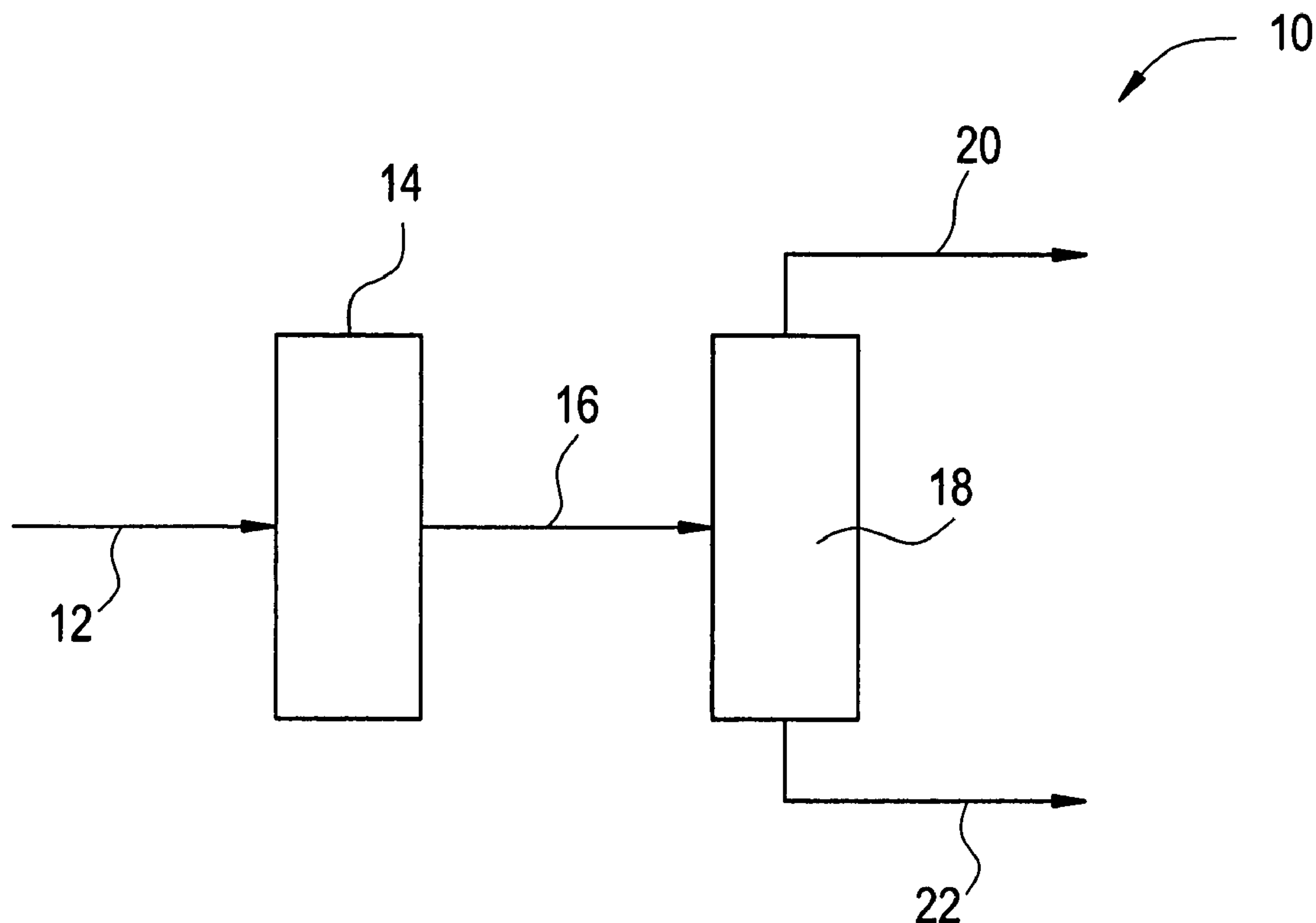


FIG. 1

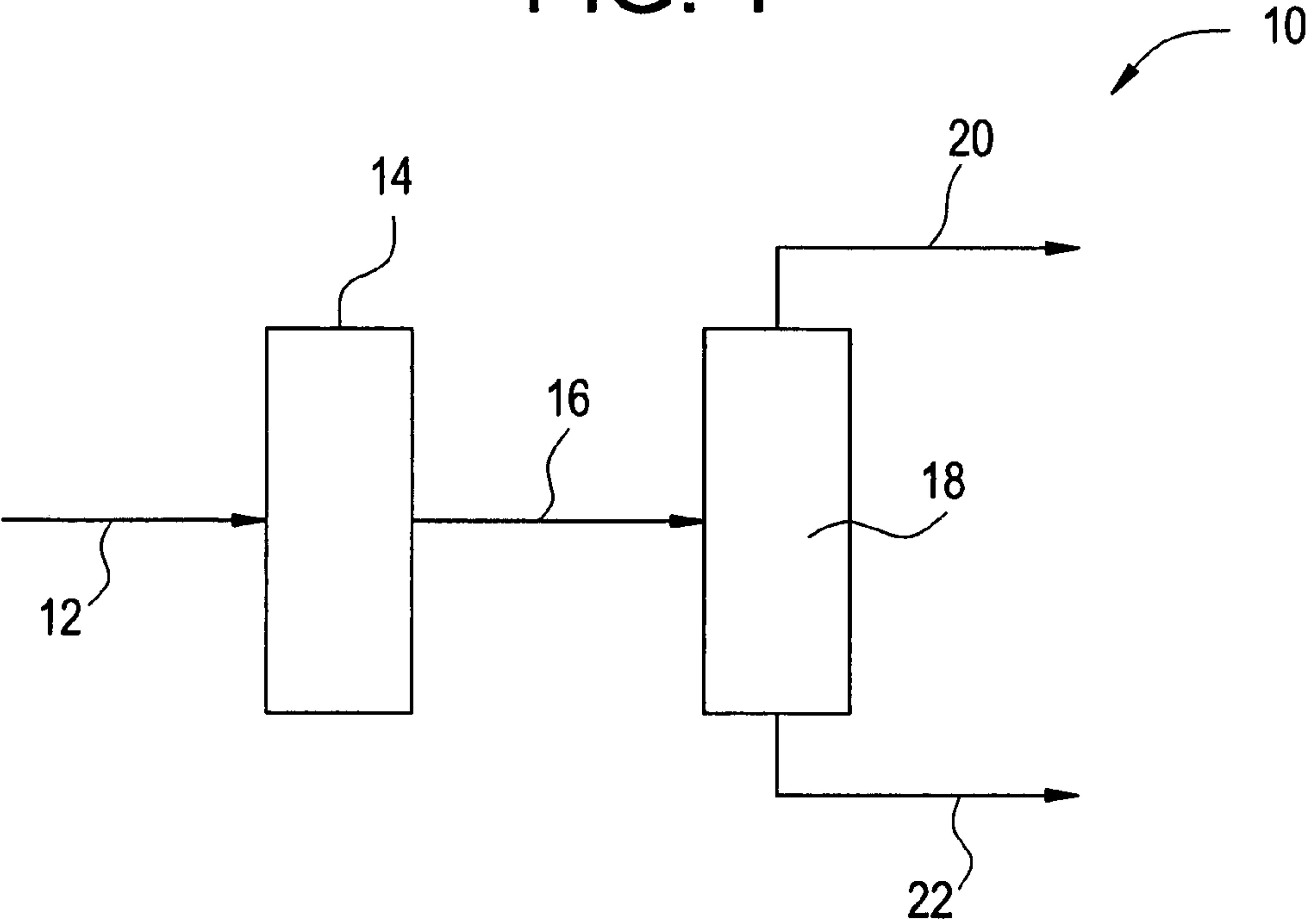


FIG. 2

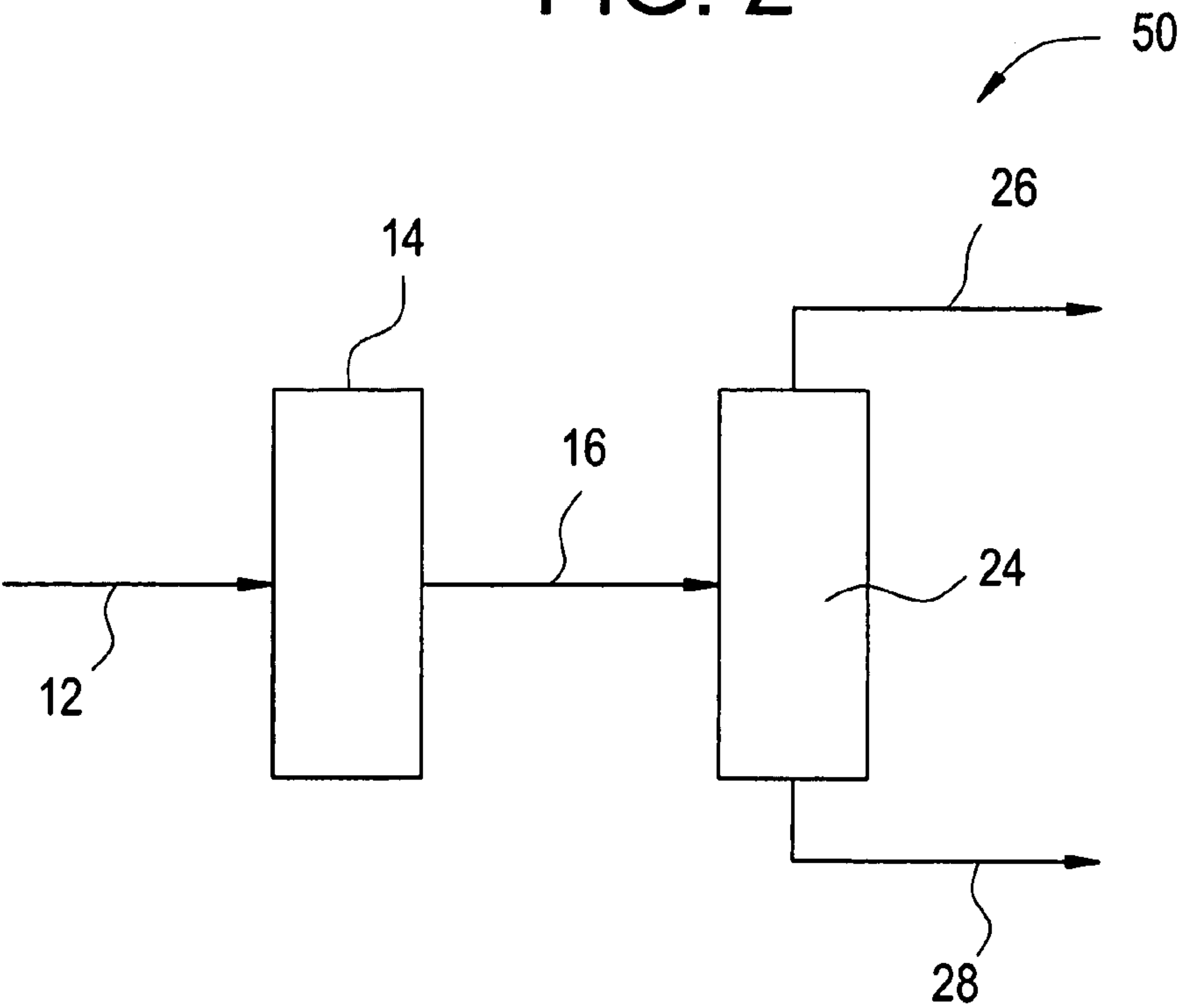


FIG. 3

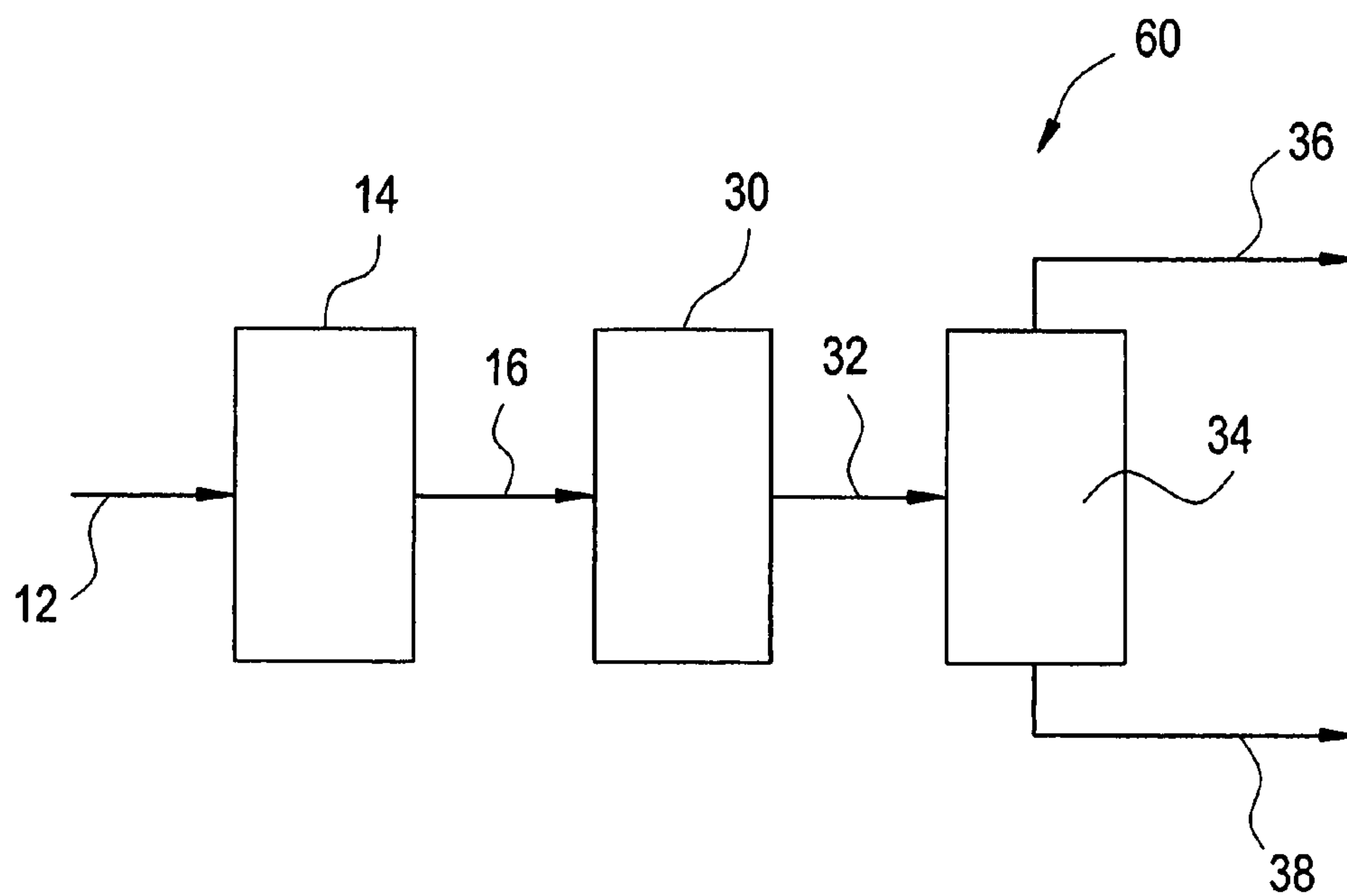
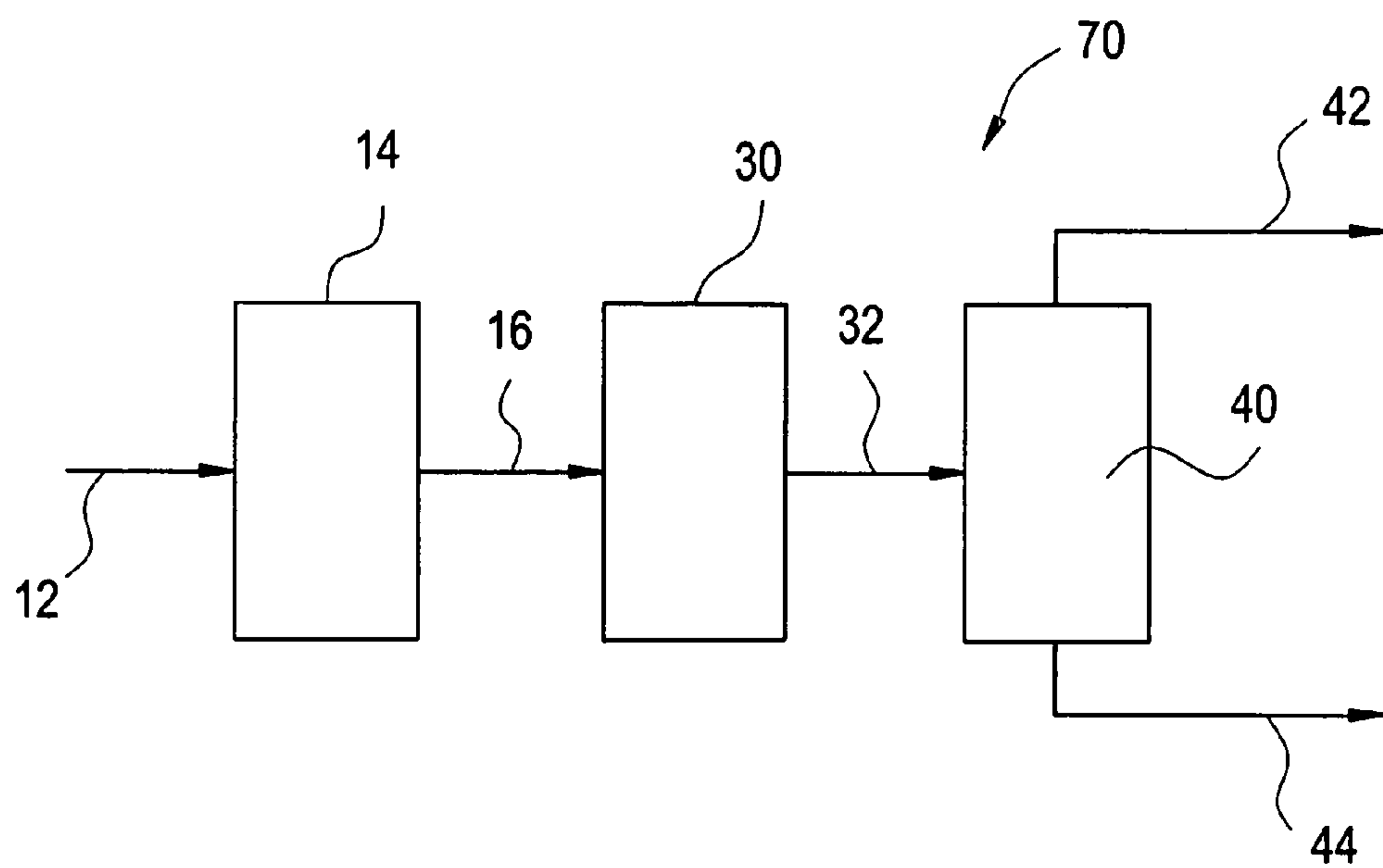


FIG. 4



MEMBRANE METHOD OF REMOVING OIL-SOLUBLE METALS FROM HYDROCARBONS

BACKGROUND

[0001] The present disclosure generally relates to methods of removing vanadium and other oil-soluble metals from hydrocarbons, and more particularly, to membrane methods of removing vanadium and other oil-soluble metals from hydrocarbons.

[0002] Various petroleum feedstocks and products, such as crude petroleum oils, heavy vacuum gas oils, shale oils, oils from bituminous sands, topped crudes, atmospheric or vacuum residual fractions, and residual-grade fuel oils contain varying amounts of non-metallic and metallic impurities. The non-metallic impurities usually include nitrogen, sulfur, and oxygen. The metallic impurities usually include nickel, vanadium, iron, sodium, copper, zinc, and arsenic. Most metallic impurities are present as inorganic sulfides, oxides, and water-soluble constituents, while the remainder is usually in the form of relatively thermally stable organo-metallic complexes such as metal porphyrins and derivatives thereof.

[0003] When combusted in a turbine, various inorganic impurities in the fuel (e.g., sodium-, potassium-, lead-, mercury-, and vanadium-containing compositions) can cause hot corrosion of the various parts of the turbine. While fuel washing, centrifuging, and the like can treat alkali metals, vanadium and other oil-soluble metals are chemically bound to fuel and cannot be removed by traditional methods. Vanadium is generally present in fuel in the form of oil-soluble porphyrins. These porphyrins decompose in the gas stream of the turbine to produce mainly vanadium pentoxide (V_2O_5). Vanadium pentoxide is particularly damaging to the various parts of the turbine, since it is in a liquid state at normal combustion temperatures of the turbine. Although several corrosion mechanisms can occur, one frequently observed manifestation is surface oxidation and/or pitting of the various turbine parts caused by low melting point (i.e., having a melting point lower than the operating temperatures to which they are exposed) ash deposits originating from these inorganic impurities in the fuel.

[0004] One approach to mitigate this so-called “hot corrosion” is to add a corrosion inhibitor to the fuel. Corrosion inhibitors generally function by reacting with a specific contaminant to produce a more benign species, such as a higher melting point non-corrosive ash deposit. Unfortunately, over extended periods of operation, these and other deposits can build up and partially block the flow of hot gas through the turbine. Once a threshold level of blockage has been attained, the deposits must be removed by a cleaning procedure, which in some instances necessitates the shut down of the turbine. Further, various corrosion inhibitors are also not suitable for some turbine applications. For example, use of magnesium as an inhibitor is not a solution for aero-derivative turbines, since it forms magnesium oxide at aero-derivative turbine operating temperatures.

[0005] Accordingly, a continual need exists for methods of removing oil-soluble metals such as vanadium from hydrocarbons.

BRIEF SUMMARY

[0006] Disclosed herein are membrane methods of removing vanadium and other oil-soluble metals from hydrocarbons.

[0007] In one embodiment, a method of removing an oil-soluble metal from a hydrocarbon feedstock, the method comprises passing the hydrocarbon feedstock through a nanofiltration membrane or a reverse osmosis membrane to produce a permeate stream having at least a vanadium concentration less than an initial vanadium concentration in the hydrocarbon feedstock, and a retentate stream having at least a vanadium concentration greater than the initial vanadium concentration in the hydrocarbon feedstock.

[0008] In one embodiment, a method of removing an oil-soluble metal from a hydrocarbon feedstock, the method comprises passing the hydrocarbon feedstock through a microfilter to produce a pre-filtered stream; passing the pre-filtered stream through an ultrafiltration membrane to produce an ultrafiltration stream; passing the ultrafiltration stream through a nanofiltration membrane or a reverse osmosis membrane to produce a permeate stream having at least a vanadium concentration less than an initial vanadium concentration in the hydrocarbon feedstock, and a retentate stream having at least a vanadium concentration greater than the initial vanadium concentration in the hydrocarbon feedstock.

[0009] The above described and other features are exemplified by the following Figures and detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] Referring to the exemplary drawings wherein like elements are numbered alike in the several Figures:

[0011] FIG. 1 is a schematic illustration of an embodiment of a method of removing vanadium from hydrocarbons;

[0012] FIG. 2 is a schematic illustration of an embodiment of a method of removing vanadium from hydrocarbons;

[0013] FIG. 3 is a schematic illustration of an embodiment of a method of removing vanadium from hydrocarbons; and

[0014] FIG. 4 is a schematic illustration of an embodiment of a method of removing vanadium from hydrocarbons; and

DETAILED DESCRIPTION

[0015] Disclosed herein are membrane methods of removing vanadium and other oil-soluble metals from hydrocarbons. For ease in discussion, reference is made hereinafter to only vanadium contaminants with the understanding that the methods discussed in this disclosure can be equally applicable to other oil-soluble metals (e.g., nickel). As will be discussed in greater detail, vanadium is removed from a hydrocarbon feedstock by passing the feedstock through a nanofiltration membrane or a reverse osmosis membrane.

[0016] In the descriptions that follow, an “upstream” direction refers to the direction from which the local flow is coming, while a “downstream” direction refers to the direction in which the local flow is traveling. In the most general sense, flow through the system tends to be from front to back, so the “upstream direction” will generally refer to a forward direction, while a “downstream direction” will refer to a rearward direction. The term “direct fluid communication” as used herein refers to a communication between a first point and a second point in a system that is uninterrupted by the presence of additional devices.

[0017] Referring to FIG. 1, an embodiment of a method of removing vanadium from a hydrocarbon feedstock, generally designated 10, is schematically illustrated. A hydrocarbon feedstock 12 is passed through a microfilter 14 to produce a pre-filtered stream 16. More specifically, the

microfilter **14** removes particulates and macromolecular contaminants having a particle size greater than 0.03 micrometers. Optionally, a vanadium porphyrin binding absorbent can be added to the hydrocarbon feedstock **12** prior to passing the hydrocarbon feedstock **12** through the microfilter **14**. The hydrocarbon feedstock **12** includes, but is not limited to, various petroleum feedstocks and products, such as crude petroleum oils, heavy vacuum gas oils, shale oils, oils from bituminous sands, topped crudes, atmospheric or vacuum residual fractions, and residual-grade fuel oils. In one embodiment, the hydrocarbon feedstock **12** includes crude oil. The initial vanadium concentration in the hydrocarbon feedstock **12** varies depending on the source of the feedstock (e.g., crude oil from North America, South America, Asia, and the like). For example, for some United States crude oils, the vanadium concentration is greater than or equal to 15 parts per million (ppm), whereas Venezuelan crudes average about 200 ppm.

[0018] The pre-filtered stream **16** is then passed through a nanofiltration membrane **18**. In one embodiment, the nanofiltration membrane **18** is disposed downstream of and in direct fluid communication with the microfilter **14**. The nanofiltration membrane **18** removes porphyrins, asphaltenes, and other heavy components from the pre-filtered stream **16**. More specifically, the nanofiltration membrane **18** is capable of removing molecular weight species having a molecular weight greater than or equal to about 200, specifically greater than or equal to about 300. Further, the nanofiltration membrane **18** has a sufficient flux and selectivity to separate a permeate stream **20** that is vanadium deficient from a retentate stream **22** that is vanadium enriched. The material of the nanofiltration membrane **18** varies depending on the application. Suitable materials include ceramics and polymers.

[0019] In one embodiment, suitable polymers for the nanofiltration membrane **18** include poly(acrylic acids), poly(acrylates), polyacetylenes, poly(vinyl acetates), polyacrylonitriles, polyamines, polyamides, polysulfonamides, polyethers, polyurethanes, polyimides, polyvinyl alcohols, polyesters, cellulose, cellulose esters, cellulose ethers, chitosan, chitin, elastomeric polymers, halogenated polymers, fluoroelastomers, polyvinyl halides, polyphosphazenes, polybenzimidazoles, poly(trimethylsilylpropyne), polysiloxanes, poly(dimethyl siloxanes), and copolymers blends thereof. These polymers can be physically or chemically cross-linked to further increase their solvent stability. In one embodiment, the polymer is solvent-stable at temperatures less than or equal to 200° C. The term “stable” is used through this disclosure to refer to a compound that has not undergone significant chemical changes to substantially impair the desired properties of the compound. Stability can be verified by various well-known techniques, which include, but are not limited to, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The term “solvent” refers to hydrocarbon compounds in feedstock **12** and various light hydrocarbon diluents that may optionally be present or added to the hydrocarbon feedstock **12**, which may be useful to reduce the viscosity of the hydrocarbon feedstock **12**.

[0020] Optionally, a catalyst can be disposed in physical communication with the nanofiltration membrane **18**. For example, a catalyst can be embedded in or disposed on a surface of the nanofiltration membrane **18**. The optional catalyst can act to destroy undesirable species within the

pre-filtered stream **16**. While catalysts vary depending on the desired applications, suitable catalysts include, but are not limited to, noble metals such as gold, silver, platinum, and palladium.

[0021] The permeate stream **20** is vanadium deficient, that is, the permeate stream **20** comprises a vanadium concentration that is lower than the initial vanadium concentration present in the hydrocarbon feedstock **12**. In one embodiment, the vanadium concentration in the permeate stream **20** is less than or equal to about 1 part per million (ppm), specifically less than or equal to about 0.2 ppm. Within this range, the vanadium concentration can be about 0.2 ppm to about 1 ppm. A resulting fuel produced from the permeate stream **20** is suitable for gas turbine applications, which includes aero-derivative turbine applications.

[0022] The retentate stream **22** is vanadium enriched, that is, the retentate stream **22** comprises a vanadium concentration that is higher than the initial vanadium concentration present in the hydrocarbon feedstock **12**. A resulting fuel produced from the retentate stream **22** is suitable for less-demanding applications when compared to aero-derivative turbine applications. For example, the fuel produced from the retentate stream **22** can be employed in marine applications, as boiler fuel, and the like. In other embodiments, the vanadium can be separated from the retentate stream for use in a variety of different applications. For example, vanadium can be employed as an alloying element in iron to enhance strength, toughness, and ductility.

[0023] Referring to FIG. 2, an embodiment of a method of removing vanadium from a hydrocarbon feedstock, generally designated **50**, is schematically illustrated. In this embodiment, the hydrocarbon feedstock **12** is passed through the microfilter **14** to produce the pre-filtered stream **16** in a manner as discussed above in relation to method **10**. Again, a vanadium porphyrin binding absorbent can optionally be added to the hydrocarbon feedstock **12** prior to passing the hydrocarbon feedstock **12** through the microfilter **14**. Suitable examples for the hydrocarbon feedstock **12** include, but are not limited to, those examples discussed above in relation to method **10**. In one embodiment, the hydrocarbon feedstock **12** includes a residual-grade fuel oil.

[0024] The pre-filtered stream **16** is then passed through a reverse osmosis (RO) membrane **24**. In one embodiment, the RO membrane **24** is disposed downstream of and in direct fluid communication with the microfilter **14**. The RO membrane **24** removes porphyrins, asphaltenes, and other heavy components from the pre-filtered stream **16**. More specifically, the RO membrane **24** is capable of removing molecular weight species having a molecular weight greater than or equal to about 100, specifically greater than or equal about 200. Further, the RO membrane **24** has a sufficient flux and selectivity to separate a permeate stream **26** that is vanadium deficient from a retentate stream **28** that is vanadium enriched. In one embodiment, the vanadium concentration in the permeate stream **26** is less than or equal to about 1 part per million (ppm), specifically less than or equal to about 0.2 ppm. Within this range, the vanadium concentration can be about 0.2 ppm to about 1 ppm. The material of the RO membrane **24** varies depending on the application and desired processing conditions (e.g. pressure).

[0025] In one embodiment, the RO membrane **24** comprises a polymer. Suitable polymers for the RO membrane **24** include those polymers discussed above in relation to nanofiltration membrane **18** (FIG. 1). In one embodiment,

the polymer is solvent-stable at temperatures less than or equal to 200° C. The RO membrane 24 is selected to withstand the pressure needed for reverse osmosis. Additionally, the RO membrane 24 may comprise an optional catalyst. For example, a catalyst can be embedded in or disposed on a surface of the RO membrane 24. The catalyst can act to destroy undesirable species within the pre-filtered stream 16. Suitable catalysts include, but are not limited to, those discussed above in relation to method 10.

[0026] Referring to FIG. 3, an embodiment of a method of removing vanadium from a hydrocarbon feedstock, generally designated 60, is schematically illustrated. In this embodiment, the hydrocarbon feedstock 12 is passed through a microfilter 14 to produce a pre-filtered stream 16 in a manner as discussed above in relation to method 50. The pre-filtered stream 16 is then passed through an ultrafiltration (UF) membrane 30 to produce a UF stream 32. In one embodiment, the UF membrane 30 is disposed downstream of and in fluid communication with microfilter 14, while also being disposed upstream of and in fluid communication with a reverse osmosis (RO) membrane 34. Further, in one embodiment, the UF membrane 30 is in direct fluid communication with the RO membrane 34. In yet other embodiments, the UF membrane 30 is disposed in direct fluid communication with the microfilter 14.

[0027] The UF membrane 30 is suited to remove asphaltene from the pre-filtered stream 16. More specifically, the UF membrane 30 is capable of removing molecular weight species having a molecular weight greater than or equal to about 1,000, specifically greater than or equal to about 10,000. Within this range, the number average molecular weight can be about 1,000 to about 500,000, specifically about 10,000 to about 100,000. The material of the UF membrane 30 varies depending on the application. Suitable materials include ceramics and polymers.

[0028] The UF stream 32 is then passed through the RO membrane 34. The RO membrane 34 removes residual porphyrins from the UF stream 32. The RO membrane 24 has a sufficient flux and selectivity to separate a permeate stream 36 that is vanadium deficient from a retentate stream 38 that is vanadium enriched. In one embodiment, the vanadium concentration in the permeate stream 36 is less than or equal to about 1 part per million (ppm), specifically less than or equal to 0.2 ppm. Within this range, the vanadium concentration can be about 0.2 ppm to about 1 ppm. The material of the RO membrane 34 varies depending on the application and desired processing conditions (e.g. pressure).

[0029] In one embodiment, the RO membrane 34 comprises a polymer. Suitable polymers include, but are not limited to, those discussed above in relation to RO membrane 24. Further, similar to RO membrane 24, in one embodiment, the polymer is solvent-stable at temperatures less than or equal to 200° C. The RO membrane 34 is selected to withstand the pressure needed for reverse osmosis. Additionally, the RO membrane 34 may comprise an optional catalyst. For example, a catalyst can be embedded in or disposed on a surface of the RO membrane 34. The catalyst can act to destroy undesirable species within the UF stream 32. Suitable catalysts include, but are not limited to, those discussed above in relation to method 10.

[0030] Referring to FIG. 4, an embodiment of a method of removing vanadium from a hydrocarbon feedstock, generally designated 70, is schematically illustrated. The embodi-

ment illustrated is a variation of method 60, wherein a nanofiltration membrane 40 may be employed instead of the RO membrane 34 discussed in method 60 (FIG. 3). In this embodiment, the hydrocarbon feedstock 12 is passed through the microfilter 14 to produce the pre-filtered stream 16 in a manner as discussed above in relation to method 50. The pre-filtered stream 16 is then passed through the ultrafiltration (UF) membrane 30 to produce the UF stream 32. [0031] The UF stream 32 is then passed through the nanofiltration membrane 40. The nanofiltration membrane 40 removes residual porphyrins from the UF stream 32. The nanofiltration membrane 40 has a sufficient flux and selectivity to separate a permeate stream 42 that is vanadium deficient from a retentate stream 44 that is vanadium enriched. In one embodiment, the vanadium concentration in the permeate stream 42 is less than or equal to about 1 part per million (ppm), specifically less than or equal to 0.2 ppm. Within this range, the vanadium concentration can be about 0.2 ppm to about 1 ppm. The material of the nanofiltration membrane 40 varies depending on the application. Suitable materials include ceramics and polymers.

[0032] In one embodiment, the nanofiltration membrane 40 comprises a polymer. Suitable polymers for the nanofiltration membrane 40 include, but are not limited to, those polymer discussed above in relation to nanofiltration membrane 18 (FIG. 1). In one embodiment, the polymer is solvent-stable at temperatures less than or equal to 100° C. Additionally, the nanofiltration membrane 40 may comprise an optional catalyst. For example, a catalyst can be embedded in or disposed on a surface of the nanofiltration membrane 40. The catalyst can act to destroy undesirable species within the UF stream 32. Suitable catalysts include, but are not limited to, those discussed above in relation to method 10.

[0033] Advantageously, the methods disclosed herein provide a cost effective way to remove vanadium from a hydrocarbon feedstock, thereby allowing the use of regional hydrocarbon feedstock that may have a relatively higher vanadium content compared other hydrocarbon feedstock. Further, the methods allow the use of cheap and heavy fraction of oil for marine applications and provide opportunities for simple and combined cycle turbine applications.

[0034] While the disclosure has been described with reference to an exemplary embodiment, it will be understood by those skilled in the art that various changes may be made and equivalents may be substituted for elements thereof without departing from the scope of the disclosure. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the disclosure without departing from the essential scope thereof. Therefore, it is intended that the disclosure not be limited to the particular embodiment disclosed as the best mode contemplated for carrying out this disclosure, but that the disclosure will include all embodiments falling within the scope of the appended claims.

What is claimed is:

1. A method of removing an oil-soluble metal from a hydrocarbon feedstock, the method comprising:
passing the hydrocarbon feedstock through a nanofiltration membrane or a reverse osmosis membrane to produce a permeate stream having at least a vanadium concentration less than an initial vanadium concentration in the hydrocarbon feedstock, and a retentate

stream having at least a vanadium concentration greater than the initial vanadium concentration in the hydrocarbon feedstock.

2. The method of claim 1, further comprising passing the hydrocarbon feedstock through a microfilter prior to passing the hydrocarbon feedstock through the nanofiltration membrane or the reverse osmosis membrane.

3. The method of claim 2, further comprising removing particulates having a particle size greater than 0.03 from the hydrocarbon feedstock using the microfilter.

4. The method of claim 1, wherein the vanadium concentration in the permeate is less than or equal to about 0.2 ppm.

5. The method of claim 1, further comprising passing the hydrocarbon feedstock through an ultrafiltration membrane prior to passing the hydrocarbon feedstock through the nanofiltration membrane or the reverse osmosis membrane, wherein the ultrafiltration membrane removes at least asphaltenes from the hydrocarbon feedstock and the nanofiltration membrane or the reverse osmosis membrane removes at least porphyrins from the hydrocarbon feedstock.

6. The method of claim 1, wherein the nanofiltration membrane or the reverse osmosis membrane comprises a polymer.

7. The method of claim 6, wherein the polymer is selected from the group consisting of poly(acrylic acids), poly(acrylates), polyacetylenes, poly(vinyl acetates), polyacrylonitriles, polyamines, polyamides, polysulfonamides, polyethers, polyurethanes, polyimides, polyvinyl alcohols, polyesters, cellulose, cellulose esters, cellulose ethers, chitosan, chitin, elastomeric polymers, halogenated polymers, fluoroelastomers, polyvinyl halides, polyphosphazenes, polybenzimidazoles, poly(trimethylsilylpropyne), polysiloxanes, poly(dimethyl siloxanes), and copolymers blends thereof.

8. The method of claim 1, further comprising diluting the hydrocarbon feedstock with a solvent to reduce viscosity of the hydrocarbon feedstock.

9. The method of claim 1, further comprising adding a vanadium porphyrin binding absorbent to the hydrocarbon feedstock.

10. A method of removing an oil-soluble metal from a hydrocarbon feedstock, the method comprising:

- passing the hydrocarbon feedstock through a microfilter to produce a pre-filtered stream;
- passing the pre-filtered stream through an ultrafiltration membrane to produce an ultrafiltration stream;
- passing the ultrafiltration stream through a nanofiltration membrane or a reverse osmosis membrane to produce

a permeate stream having at least a vanadium concentration less than an initial vanadium concentration in the hydrocarbon feedstock, and a retentate stream having at least a vanadium concentration greater than the initial vanadium concentration in the hydrocarbon feedstock.

11. The method of claim 10, wherein the ultrafiltration membrane removes at least asphaltenes from the pre-filtered stream.

12. The method of claim 10, wherein the nanofiltration membrane or the reverse osmosis membrane removes at least porphyrins from the ultrafiltration stream.

13. The method of claim 10, further comprising removing particulates having a particle size greater than 0.03 from the hydrocarbon feedstock using the microfilter.

14. The method of claim 10, wherein the vanadium concentration in the permeate is less than or equal to about 0.2 ppm.

15. The method of claim 10, wherein the nanofiltration membrane or the reverse osmosis membrane comprises a polymer.

16. The method of claim 15, wherein the polymer is selected from the group consisting of poly(acrylic acids), poly(acrylates), polyacetylenes, poly(vinyl acetates), polyacrylonitriles, polyamines, polyamides, polysulfonamides, polyethers, polyurethanes, polyimides, polyvinyl alcohols, polyesters, cellulose, cellulose esters, cellulose ethers, chitosan, chitin, elastomeric polymers, halogenated polymers, fluoroelastomers, polyvinyl halides, polyphosphazenes, polybenzimidazoles, poly(trimethylsilylpropyne), polysiloxanes, poly(dimethyl siloxanes), and copolymers blends thereof.

17. The method of claim 10, further comprising diluting the hydrocarbon feedstock with a solvent to reduce viscosity of the hydrocarbon feedstock.

18. The method of claim 10, further comprising adding a vanadium porphyrin binding absorbent to the hydrocarbon feedstock.

19. The method of claim 10, further comprising adding a vanadium porphyrin binding absorbent to the hydrocarbon feedstock prior to passing the hydrocarbon feedstock through the microfilter.

20. The method of claim 10, wherein the nanofiltration membrane or the reverse osmosis membrane comprises a catalyst.

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