CLAIMS

1. A method of producing a hydrocarbon raffinate having reduced levels of heteroatom compounds and 2-4 cycle polynuclear aromatic hydrocarbons, the method comprising:

providing a hydrocarbon feedstock containing crude oil fractions with a boiling point range of from about 165 °C to about 430 °C, the crude oil fractions comprising heteroatom compounds and 2-4 cycle polynuclear aromatic hydrocarbons;

extracting at least a portion of the heteroatom compounds from the hydrocarbon feedstock with a tunable solvent in at least one extraction vessel of a heteroatom extraction system to form a heteroatom-compound rich stream containing heteroatom compounds and a heteroatom-compound lean stream containing the 2-4 cycle polynuclear aromatic hydrocarbons, the tunable solvent comprising an ionic liquid formed from pressurized carbon dioxide and water, wherein the temperature of the tunable solvent is from greater than the critical temperature of carbon dioxide to about 150°C; and

extracting the 2-4 cycle polynuclear aromatic hydrocarbons from the heteroatom-compound lean stream with a solvent system to form the hydrocarbon raffinate, the solvent system comprising an aprotic solvent.

2. The method of claim 1, wherein extracting at least a portion of the heteroatom compounds from the hydrocarbon feedstock comprises:

extracting from the hydrocarbon feedstock a first portion of the heteroatom compounds having a first polarity to form a first feed stream, the first portion of the heteroatom compounds being extracted in a first extraction vessel of the heteroatom extraction system operating at a first pressure;

extracting from the first feed stream a second portion of the heteroatom compounds having a second polarity lower than the first polarity to form a second feed stream, the second portion of the heteroatom compounds being extracted in a second extraction vessel of the heteroatom extraction system operating at a second pressure higher than the first pressure after extracting the first portion of the heteroatom compounds; and

extracting from the second feed stream a third portion of the heteroatom compounds having a third polarity lower than the second polarity to form the heteroatom-compound lean stream, the third portion of the heteroatom compounds being extracted in a third extraction vessel of the heteroatom extraction system operating at a third pressure greater than ~~the first pressure and~~ the second pressure after extracting the second portion of the heteroatom compounds.

3. The method of claim 1, wherein at least 99% of the heteroatom compounds by weight from the hydrocarbon feedstock are extracted into the heteroatom-compound rich stream.

4. The method of claim 1, wherein the aprotic solvent is chosen from *N*-methylpyrrolidone, dimethylsulfoxide, and aromatic compounds.

5. The method of claim 1, wherein the aprotic solvent is chosen from *N*-methylpyrrolidone, dimethylsulfoxide, and aromatic compounds and the solvent system further comprises a protic co-solvent.

6. A method for extracting heteroatom compounds and 2-4 cycle polynuclear aromatic hydrocarbons from a hydrocarbon feedstock containing the heteroatom compounds and the 2-4 cycle polynuclear aromatic hydrocarbons, the method comprising:

extracting at least one targeted portion of the heteroatom compounds from the hydrocarbon feedstock with an aqueous solvent comprising an ionic liquid formed from pressurized carbon dioxide and water, wherein the temperature of the aqueous solvent is from greater than the critical temperature of carbon dioxide to about 150°C;

transferring to a PAH extractor a heteroatom-lean stream containing the 2-4 cycle polynuclear aromatic hydrocarbons after all targeted portions of the heteroatom compounds have been extracted from the hydrocarbon feedstock; and

extracting the 2-4 cycle polynuclear aromatic hydrocarbons from the heteroatom-lean stream in the PAH extractor with a solvent system comprising an aprotic solvent.

7. The method of claim 6, wherein extracting at least one targeted portion of the heteroatom compounds from the hydrocarbon feedstock comprises:

extracting a first targeted portion of the heteroatom compounds having a first polarity in a first extraction vessel operating at a first pressure;

extracting a second targeted portion of the heteroatom compounds in a second extraction vessel after extracting the first portion, the second extraction vessel operating at a second pressure greater than the first pressure, the second portion of the heteroatom compounds having a second polarity that is lower than the first polarity; and

extracting a third targeted portion of the heteroatom compounds in a third extraction vessel after extracting the second portion of the heteroatom compounds, the third extraction vessel operating at a third pressure greater than ~~the first pressure and~~ the second pressure, the third portion of the heteroatom compounds having a third polarity lower that is lower than the second polarity.

8. The method of claim 6, wherein the extraction of each targeted portion of the heteroatom compounds from the hydrocarbon feedstock comprises:

feeding into an extraction vessel separately or as a mixture:

the hydrocarbon feedstock or a feed stream derived from the hydrocarbon feedstock; and

the aqueous solvent,

whereby the combination of the hydrocarbon feedstock or the feed stream with the aqueous solvent in the extraction vessel forms an extraction mixture;

tuning the aqueous solvent to selectively form solvent complexes with the targeted portion of the heteroatom compounds in the extraction mixture, whereby the extraction mixture separates into at least a heteroatom-compound rich phase and a heteroatom-compound lean phase, the heteroatom-compound rich phase containing the solvent complexes;

removing the heteroatom-compound lean phase from the extraction vessel as a heteroatom-compound lean stream;

removing the heteroatom-compound rich phase from the extraction vessel as a heteroatom-compound rich stream; and

optionally transferring the heteroatom-compound lean stream from the extraction vessel as a feed stream derived from the hydrocarbon feedstock to an additional extraction vessel for extraction of an additional targeted portion of heteroatom compounds from the feed stream.

9. The method of claim 8, wherein tuning the aqueous solvent system comprises:

establishing an extraction pressure and an extraction temperature of the extraction mixture in the extraction vessel that together tune the aqueous solvent to selectively form a solvent complex with the targeted portion of the heteroatom compounds, wherein the extraction pressure is from 2 bar to 300 bar and the extraction temperature of the extraction mixture is from greater than the critical temperature of carbon dioxide to about 150 °C.

10. The method of claim 8, wherein at least two targeted portions of the heteroatom compounds are removed from the hydrocarbon feedstock, and extracting each targeted portion of the heteroatom compounds from the hydrocarbon feedstock further comprises:

transferring the heteroatom-compound rich stream to a respective ejector vessel;

depressurizing the respective ejector vessel to decrease the solubility of the heteroatom compounds in the aqueous solvent and eject a mixture of heteroatom compounds from the aqueous solvent; and

separating the mixture of heteroatom compounds from the aqueous solvent to form a heteroatom-compound recovery stream.

11. The method of claim 10, further comprising:

transferring the heteroatom-compound recovery stream to a heteroatom-compound fractionator;

fractionating the mixture of heteroatom compounds in the heteroatom-compound recovery stream in the fractionator into multiple heteroatom-compound solute fractions; and

recovering heteroatom compounds from the heteroatom-compound solute fractions.

12. The method of claim 8, wherein:

extracting at least one targeted portion of the heteroatom compounds from the hydrocarbon feedstock comprises extracting one targeted portion of the heteroatom compounds from the hydrocarbon feedstock, the one targeted portion of the heteroatom compounds comprising greater than 90% by weight of the heteroatom compounds present in the hydrocarbon feedstock.

13. The method of claim 12, further comprising:

extracting at least one targeted portion of the heteroatom compounds from a PAH-lean heteroatom-compound rich stream, wherein the PAH-lean heteroatom-compound rich stream is the heteroatom-compound rich stream formed during extraction of the one targeted portion of the heteroatom compounds from the hydrocarbon feedstock.

14. The method of claim 13, wherein the extraction of each targeted portion of the heteroatom compounds from the PAH-lean heteroatom-compound rich stream comprises:

feeding into an extraction vessel separately or as a mixture:

the PAH-lean heteroatom-compound rich stream or a feed stream derived from the PAH-lean heteroatom-compound rich stream; and

an aqueous solvent comprising an ionic liquid formed from pressurized carbon dioxide and water,

whereby the combination of the aqueous solvent and the PAH-lean heteroatom-compound rich stream or the aqueous solvents and~~hydrocarbon feedstock or~~ the feed stream derived from the PAH-lean heteroatom-compound rich stream~~with the aqueous solvent~~ forms an extraction mixture;

tuning the aqueous solvent to selectively form solvent complexes with the targeted portion of the heteroatom compounds in the extraction mixture, whereby the extraction mixture separates into at least a heteroatom-compound rich phase and a

heteroatom-compound lean phase, the heteroatom-compound rich phase containing the solvent complexes;

removing the heteroatom-compound lean phase from the extraction vessel as a heteroatom-compound lean stream;

removing the heteroatom-compound rich phase from the extraction vessel as a heteroatom-compound rich stream; and

optionally transferring the heteroatom-compound lean stream from the extraction vessel as a feed stream derived from the PAH-lean heteroatom-compound rich stream to an additional extraction vessel for extraction of an additional targeted portion of heteroatom compounds from the feed stream.

15. The method of claim 13, wherein extracting at least one targeted portion of the heteroatom compounds from the PAH-lean heteroatom-compound rich stream comprises:

extracting a first targeted portion of the heteroatom compounds having a first polarity in a first extraction vessel operating at a first pressure;

extracting a second targeted portion of the heteroatom compounds in a second extraction vessel after extracting the first portion, the second extraction vessel operating at a second pressure greater than the first pressure, the second portion of the heteroatom compounds having a second polarity that is lower than the first polarity; and

extracting a third targeted portion of the heteroatom compounds in a third extraction vessel after extracting the second portion of the heteroatom compounds, the third extraction vessel operating at a third pressure greater than the first pressure and the second pressure, the third portion of the heteroatom compounds having a third polarity lower that is lower than the first polarity.

16. The method of claim 13, wherein extracting each targeted portion of the heteroatom compounds from the PAH-lean heteroatom-compound rich stream further comprises:

transferring each heteroatom-compound rich phase to a respective ejector vessel;

depressurizing the ejector vessel to decrease the solubility of the heteroatom compounds in the aqueous solvent and eject a mixture of heteroatom compounds from the aqueous solvent; and

separating the mixture of heteroatom compounds from the aqueous solvent to form a heteroatom-compound recovery stream.

17. The method of claim 16, further comprising:

transferring the heteroatom-compound recovery stream to a heteroatom-compound fractionator;

separating the mixture of heteroatom compounds in the heteroatom-compound recovery stream in the fractionator into multiple heteroatom-compound solute fractions; and

recovering heteroatom compounds from the heteroatom-compound solute fractions.

18. The method of claim 6, wherein extracting the 2-4 cycle polynuclear aromatic hydrocarbons comprises:

combining the heteroatom-compound lean phase with the solvent system in the PAH extractor, whereby the heteroatom-compound lean phase separates into a PAH-rich phase and a PAH-lean phase, the PAH-rich phase comprising a mixture of polynuclear aromatic hydrocarbons;

removing the PAH-rich phase from the PAH extractor as a PAH recovery stream; and

removing the PAH-lean phase from the PAH extractor as a lean raffinate.

19. The method of claim 18, further comprising:

transferring the PAH recovery stream to a PAH fractionator;

separating the mixture of polynuclear aromatic hydrocarbons in the PAH recovery stream in the PAH fractionator into multiple PAH solute fractions; and

recovering polynuclear aromatic hydrocarbons from the PAH solute fractions.

20. The method of claim 6, wherein:

the heteroatom compounds comprise pyrrole, pyridine, quinoline, carbazole, indole, nickel tetraphenylporphyrin, vanadyl tetraphenylporphyrin, thiophene, benzothiophene, dibenzothiophene, 7,8,9,10-tetrahydro-benzo[b]naphtho[2,3-d] thiophene, or combinations thereof; and

the 2-4 cycle polynuclear aromatic hydrocarbons comprise benzanthracenes, naphthalenes, anthracenes, pyrenes, phenanthrenes, tetracenes, or combinations thereof.