

PROCESS TO SEPARATE ALKALI METAL SALTS FROM ALKALI METAL REACTED HYDROCARBONS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Provisional Application No. 61/812,057, filed April 15, 2013. This application is a continuation-in-part of U.S. Patent Application Serial No. 13/753,918, filed January 30, 2013, entitled “PROCESS FOR DESULFURIZING PETROLEUM FEEDSTOCKS”, which application claims the benefit of U.S. Provisional Patent Application Serial No. 61/594,846, filed February 3, 2012. This application is also a continuation-in-part of U.S. Patent Application Serial No. 12/916,984, filed November 1, 2010, entitled “UPGRADING OF PETROLEUM OIL FEEDSTOCKS USING ALKALI METALS AND HYDROCARBONS”, which application claims the benefit of U.S. Provisional Patent Application Serial No. 61/257,369, filed November 2, 2009, entitled “UPGRADING OF PETROLEUM OIL FEEDSTOCKS USING ALKALI METALS AND HYDROCARBONS”.

FIELD OF THE INVENTION

[0002] The present invention relates to a process for removing nitrogen, sulfur, and heavy metals from sulfur-, nitrogen-, and metal-bearing shale oil, bitumen, heavy oil, or refinery streams using an alkali metal. More particularly, the invention relates to a process to facilitate separation of alkali metal compounds and reduced heavy metals from alkali metal reacted hydrocarbons.

BACKGROUND OF THE INVENTION

[0003] U.S. Patent Application Serial No. 13/753,918 has been published as United States Patent Application Publication No. 2013/0140217. The reader is presumed to be familiar with the disclosure of this published application. This published application will be referred to herein as the “‘918 application.”

[0004] U.S. Patent Application Serial No. 12/916,984 has been published as United States Patent Application Publication No. 2011/0100874. The reader is presumed to be familiar with the disclosure of this published application. This published application will be referred to herein as the “‘984 application.”

[0005] U.S. Patent No. 8,088,270 relates to a “Process For Recovering Alkali Metals And Sulfur From Alkali Metal Sulfides And PolySulfides.” The reader is presumed to be familiar with the disclosure of this published patent. This published patent will be referred to herein as the “’270 patent.”

[0006] The demand for energy and the hydrocarbons from which that energy is derived is continually rising. The hydrocarbon raw materials used to provide this energy, however, can contain difficult to remove sulfur and metals that hinder their usage. Sulfur can cause air pollution, and can poison catalysts designed to remove hydrocarbons and nitrogen oxide from motor vehicle exhaust. Similarly, heavy metals contained in the hydrocarbon stream can poison catalysts typically utilized for removal of sulfur.

[0007] Extensive reserves of shale oil exist in the U.S. that will increasingly play a role in meeting U.S. energy needs. Over 1 trillion barrel reserves lay in a relatively small area known as the Green River Formation located in Colorado, Utah, and Wyoming. As the price of crude oil rises, these shale oil resources become more attractive. However, technical issues surrounding this shale oil remain to be solved. For example, this shale oil has a relatively high amount of nitrogen contained therein (in addition to high levels of heavy metals and sulfur). Shale oil characteristically is high in nitrogen, sulfur, and heavy metals which makes subsequent hydrotreating difficult. It is known that nitrogen is typically around 2% and sulfur around 1% in most samples of shale oil. Heavy metals may also present. Heavy metals contained in shale oil pose a large problem to upgraders trying to upgrade this shale oil for commercial use. For example, sulfur and nitrogen typically are removed from the shale oil via hydrotreating at elevated temperatures and pressures using catalysts such as Co–Mo/Al₂O₃ or Ni–Mo/Al₂O₃. However, such catalysts are deactivated (poisoned) by the presence of heavy metals as the heavy metals operate to mask the catalysts.

[0008] Another example of a source of hydrocarbon fuel where the removal of sulfur poses a problem is in bitumen existing in ample quantities in Alberta, Canada and heavy oils such as in Venezuela. In order to remove sufficient sulfur from the bitumen for it to be useful as an energy resource, excessive hydrogen must be introduced under extreme conditions, which creates an inefficient and economically undesirable process.

[0009] Over the last several years, sodium has been recognized as being effective for the treatment of high-sulfur petroleum oil distillate, crude, heavy oil, bitumen, and shale oil. Sodium is capable of reacting with the oil and its contaminants to dramatically reduce the sulfur, nitrogen, and metal content through the formation of sodium sulfide compounds

states, it is necessary to separate these products from the hydrocarbon materials. In many cases, a gravimetric separation, such as centrifugation or filtering, can separate the organic, upgraded oil, from the salt phase, metallic phase, and organic solids which may be formed.

[0019] Once the alkali metal compounds are separated from the hydrocarbon feedstock, sulfur and metals are substantially removed, and nitrogen is moderately removed. Also, both viscosity and density are reduced (API gravity is increased). Bitumen or heavy oil would be considered synthetic crude oil (SCO) and can be shipped via pipeline for further refining. Similarly, shale oil will have been considerably upgraded after such processing. Subsequent refining will be easier since the troublesome metals have been removed.

[0020] However, for some hydrocarbon feedstocks, gravimetric separation it is not possible without further processing. For example, the inventors have observed that certain hydrocarbon feedstocks that contain a heavy fraction of hydrocarbons, upon processing with an alkali metal produce a mixture of alkali metal compounds and reduced heavy metals that could not be separated from the upgraded hydrocarbon materials through conventional gravimetric separation.

[0021] It is an object of the present invention to provide a process to facilitate separation of alkali metal compounds, such as alkali metal sulfides and nitrides, and reduced heavy metals from alkali metal reacted hydrocarbons.

BRIEF SUMMARY

[0022] The present disclosure provides a process to facilitate separation of alkali metal compounds and reduced heavy metals from alkali metal reacted hydrocarbons.

[0022a] One aspect of the present invention relates to a process to facilitate separation of alkali metal salts from alkali metal reacted hydrocarbons comprising: reacting molten alkali metal, hydrogen and a quantity of a hydrocarbon feedstock having at least one heavy fraction to provide a mixture comprising alkali metal salts and alkali metal reacted hydrocarbons; heating the mixture in a holding vessel that is not the reactor to a temperature in the range from about 350°C to 400°C; mechanically mixing the mixture during the heating step, wherein the mixture is heated and mechanically mixed for a time period over 15 minutes; separating gravimetrically the alkali metal salts from the alkali metal reacted hydrocarbons.

[0022b] Also disclosed is a process to facilitate separation of sodium sulfide from sodium-reacted hydrocarbons comprising: reacting molten sodium, hydrogen gas or dissolved liquid hydrogen and a quantity of a hydrocarbon feedstock having at least one heavy fraction to provide a mixture comprising sodium sulfide and sodium-reacted hydrocarbons; heating the mixture to a temperature in the range from about 350°C to 400°C; mechanically mixing the mixture during the heating step; and separating gravimetrically the sodium sulfide from the sodium-reacted hydrocarbons.

[0022c] Yet another aspect relates to a process of upgrading a hydrocarbon feedstock comprising: obtaining a quantity of hydrocarbon feedstock having at least one heavy fraction, the hydrocarbon feedstock comprising at least one carbon atom and a sulfur heteroatom and/or one or more heavy metals; reacting the quantity of the hydrocarbon feedstock with a molten alkali metal and hydrogen gas to produce an upgraded hydrocarbon feedstock, wherein the alkali metal reacts with the sulfur heteroatom and/or the one or more heavy metals to form one or more inorganic products comprising alkali metal sulfide and/or alkali metal polysulfides and reduced heavy metals, and heating the mixture of inorganic products and the upgraded hydrocarbon feedstock to a temperature in the range from about 350°C to 400°C; mechanically mixing the mixture during the heating step; and gravimetrically separating the inorganic products from the upgraded hydrocarbon feedstock.

CLAIMS:

1. A process to facilitate separation of alkali metal salts from alkali metal reacted hydrocarbons comprising:

reacting molten alkali metal, hydrogen and a quantity of a hydrocarbon feedstock having at least one heavy fraction to provide a mixture comprising alkali metal salts and alkali metal reacted hydrocarbons;

heating said mixture in a holding vessel that is not the reactor to a temperature in the range from about 350°C to 400°C;

mechanically mixing the mixture during the heating step; and separating gravimetrically the alkali metal salts from the alkali metal reacted hydrocarbons.

2. The process according to claim 1, wherein the mixture is heated to a temperature of about 375°C ± 10°C.

3. The process according to claim 1, wherein the mixture is heated and mechanically mixed for a time period of over 30 minutes.

4. The process according to claim 1, wherein the mixture is heated and mechanically mixed for a time period of at least 1 hour.

5. The process according to claim 1, wherein the mixture is heated and mechanically mixed for a time period between about 1 and 2 hours.

6. The process according to claim 1, wherein the quantity of a hydrocarbon feedstock comprises bitumen, heavy oil, or a refinery stream containing a heavy fraction.

7. The process according to claim 1, further comprising the step of adding a portion of the separated alkali metal salts to the mixture of alkali metal salts and alkali metal reacted hydrocarbons prior to heating.

8. The process according to claim 1, further comprising the step of adding a portion of the separated alkali metal salts to the hydrocarbon feedstock prior to reacting with the alkali metal.

9. The process according to claim 1, wherein the alkali metal is sodium, the alkali metal salts

comprise sodium sulfide and/or sodium polysulfide and the alkali metal reacted hydrocarbons comprise sodium-reacted hydrocarbons.

10. The process according to claim 9, wherein the mixture is heated to a temperature of about $375^{\circ}\text{C} \pm 10^{\circ}\text{C}$.
11. The process according to claim 9, wherein the mixture is heated and mechanically mixed for a time period of over 30 minutes.
12. The process according to claim 9, wherein the mixture is heated and mechanically mixed for a time period of at least 1 hour.
13. The process according to claim 9, wherein the mixture is heated and mechanically mixed for a time period between about 1 and 2 hours.
14. The process according to claim 9, wherein the quantity of a hydrocarbon feedstock comprises bitumen, heavy oil, or a refinery stream containing a heavy fraction.
15. The process according to claim 9, further comprising the step of adding a portion of the separated sodium sulfide salts to the mixture of sodium salts and sodium-reacted hydrocarbons prior to heating.
16. The process according to claim 9, further comprising the step of adding a portion of the separated sodium sulfide salts to the hydrocarbon feedstock prior to reacting with the sodium.
17. A process of upgrading a hydrocarbon feedstock comprising:
obtaining a quantity of hydrocarbon feedstock having at least one heavy fraction, the hydrocarbon feedstock comprising at least one carbon atom and a sulfur heteroatom and/or one or more heavy metals;
reacting the quantity of the hydrocarbon feedstock with a molten alkali metal and an hydrogen gas to produce an upgraded hydrocarbon feedstock, wherein the alkali metal reacts with the sulfur heteroatom and/or the one or more heavy metals to form one or more inorganic products comprising alkali metal sulfide and/or alkali metal polysulfides and reduced heavy metals, and
heating the mixture of inorganic products and the upgraded hydrocarbon feedstock to a temperature in the range from about 350°C to 400°C ;
mechanically mixing the mixture during the heating step; and
gravimetrically separating the inorganic products from the upgraded hydrocarbon feedstock.
18. The process according to claim 17, wherein the quantity of hydrocarbon feedstock comprises bitumen, heavy oil, or a refinery stream containing a heavy fraction.

19. The process according to claim 17, further comprising the step of adding a portion of the separated inorganic products to the mixture of inorganic products and the upgraded hydrocarbon prior to heating.

20. The process according to claim 17, further comprising the step of adding a portion of the separated inorganic products to the hydrocarbon feedstock prior to reacting with the alkali metal.

21. The process according to claim 9, wherein the hydrogen comprises hydrogen gas and/or hydrogen dissolved in liquid.