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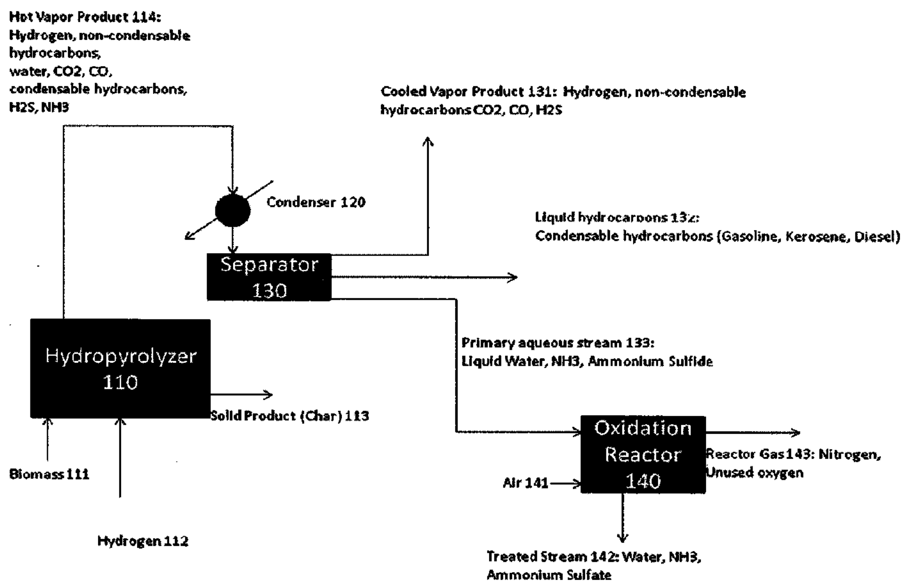
(54) Titre : ELIMINATION DU SULFURE D'HYDROGENE SOUS LA FORME DE SULFATE D'AMMONIUM DEPUIS LES VAPEURS D'UN PRODUIT D'HYDROPYROLYSE
(54) Title: REMOVAL OF HYDROGEN SULFIDE AS AMMONIUM SULFATE FROM HYDROPYROLYSIS PRODUCT VAPORS



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A system and method for processing biomass into hydrocarbon fuels that includes processing a biomass in a hydropyrolysis reactor resulting in hydrocarbon fuels and a process vapor stream and cooling the process vapor stream to a condensation temperature resulting in an aqueous stream. The aqueous stream is sent to a catalytic reactor where it is oxidized to obtain a product stream containing ammonia and ammonium sulfate. A resulting cooled product vapor stream includes non-condensable process vapors comprising H_2, CH_4, CO, $C0_2$, ammonia and hydrogen sulfide.

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(54) Title: REMOVAL OF HYDROGEN SULFIDE AS AMMONIUM SULFATE FROM HYDROPYROLYSIS PRODUCT VAPORS

(57) **Abstract**: A system and method for processing biomass into hydrocarbon fuels that includes processing a biomass in a hydropyrolysis reactor resulting in hydrocarbon fuels and a process vapor stream and cooling the process vapor stream to a condensation temperature resulting in an aqueous stream. The aqueous stream is sent to a catalytic reactor where it is oxidized to obtain a product stream containing ammonia and ammonium sulfate. A resulting cooled product vapor stream includes non-condensable process vapors comprising H_2, CH_4, CO, CO_2, ammonia and hydrogen sulfide.

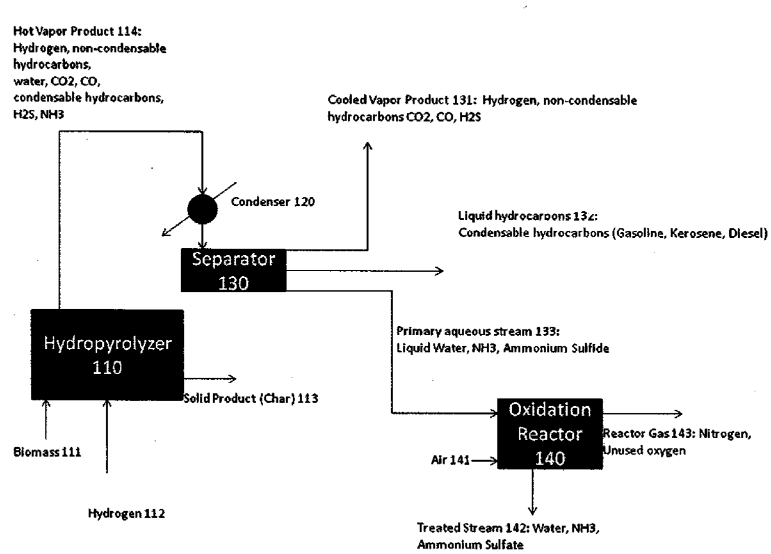

FIG. 1

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REMOVAL OF HYDROGEN SULFIDE AS AMMONIUM SULFATE FROM HYDROPYROLYSIS PRODUCT VAPORS

Field of the Invention

This invention relates to a process that removes hydrogen sulfide (H_2S) from product vapors exiting a hydropyrolysis reactor via reaction with ammonia (NH_3) to form ammonium sulfide. In addition, the process converts hydrogen sulfide to ammonium sulfate.

Description of Related Art

The process of the present invention relates to removal of H_2S from the effluent vapors exiting a hydropyrolysis reactor. Hydropyrolysis reactors are known in the art.

Commercially, H_2S is commonly removed from vapor streams via the Claus process, in a Claus plant. In the Claus Process, H_2S is oxidized to form sulfur dioxide (SO_2) and then the sulfur dioxide is reacted with more H_2S to produce water (H_2O) and elemental sulfur. The overall reaction is:

$$2\ H_2S + O_2 \rightarrow S_2 + 2\ H_2O$$

This process is well-known, and has been widely applied in the refining and reforming of petroleum products. However, the process is complex, and often involves multiple reaction steps. Moreover, the process can be most efficiently applied to streams containing 25% or more of H_2S, on a molecular basis. If streams containing ammonia, as well as H_2S are processed in a Claus plant, the ammonia is oxidized along with the H_2S. This is not desirable, because ammonia is a potentially-valuable reaction product of the hydropyrolysis process.

A significant portion of the product vapor stream from the hydropyrolysis reactor comprises water vapor and hydrocarbons with boiling points below 70 degrees Fahrenheit, at atmospheric pressure. The product vapor from the hydropyrolysis reactor must be cooled to ambient temperatures in order for liquid hydrocarbons to be recovered as a separate product stream. When the product vapor stream is cooled, water vapor in the product vapor stream condenses to form liquid water, and a significant fraction of any H_2S and any NH_3 in the product vapor stream go into solution in the liquid water. The resulting aqueous solution then contains ammonia and sulfide compounds.

Processes by which water-soluble sulfide compounds can be catalytically reacted with oxygen to form stable sulfate compounds are disclosed in Marinangeli et al., U.S. Patent 5,207,927 Gillespie, U.S. Patent 5,470,486. The approach taught by Marinangeli et al., involves passing an aqueous stream containing both the sulfide compound and oxygen over an appropriate oxidizing catalyst, under conditions wherein the pH of the solution is 9-12, and an oxygen-to-sulfur ratio greater than about 5 is maintained. The approach taught by Gillespie requires a pH greater than 12 and an oxygen-to-sulfur ratio greater than about 4 be maintained. Both approaches prefer metal phthalocynanines with Gillespie preferring the use of carbon supports. A product stream that is substantially free of sulfide compounds is thus obtained, since all sulfide compounds have been converted to sulfate compounds.

SUMMARY OF THE INVENTION

In the hydropyrolysis reactor of the process of the present invention, a biomass feedstock is converted into a stream containing the following:

1. Deoxygenated condensable hydrocarbons (with properties corresponding to those of gasoline, diesel and kerosene)
2. Non-condensable hydrocarbon vapors (such as methane, ethane, propane and butane),
3. Other non-condensable vapors (CO_2, CO, and hydrogen),
4. Water and species which are soluble in liquid water, such as ammonia (NH_3), and hydrogen sulfide (H_2S).

The NH_3 is present in the hydropyrolysis product stream due to the presence of nitrogen in the biomass feedstock. The H_2S is present in the hydropyrolysis stream due to the presence of sulfur in the biomass feedstock. The nitrogen and the sulfur in the feedstock react with hydrogen in the hydropyrolysis reactor to form NH_3 and H_2S, respectively.

It is one object of this invention to provide a method by which hydrogen sulfide can be removed from a product vapor stream, produced by the hydropyrolysis of biomass. Hydropyrolysis experiments, in the course of which biomass was deoxygenated and converted to products including hydrocarbons, have shown that the stream of vapor leaving the hydropyrolizer contains water vapor, NH_3, and H_2S, in proportions that make this product uniquely suited to a process in which the H_2S is combined with the NH_3 in an aqueous solution, and then oxidized to form ammonium sulfate. These experiments are original, and the concentrations of nitrogen and sulfur compounds in the vapor stream are unexpected and surprising. The experiments are described in detail in the examples presented below.

In order to carry out hydropyrolysis in the hydropyrolysis reactor associated with the present invention, some portion of the hydropyrolysis product stream from the reactor may be sent to a steam reformer, and there reacted with steam to produce hydrogen. Generally, it will be desirable to send some or all of the non-condensable hydrocarbon vapors, such as methane, ethane, butane, etc., to the reformer. The hydrogen thus obtained may then be introduced back into the hydropyrolysis reactor, so that hydropyrolysis can continue to be carried out. The need for a source of hydrogen, external to the hydropyrolysis process associated with the present invention, may thus be reduced or eliminated. Note that H_2S will be present in the product vapor stream from the hydropyrolysis process whenever sulfur is present in the feedstock, and the presence of the H_2S creates several problems.

The H_2S in the product vapor stream is highly toxic to humans. In addition, the H_2S can poison the catalysts involved in steam reforming of product vapors from the hydropyrolysis reactor. Moreover, the H_2S can be reacted with NH_3 to produce ammonium sulfide ($(NH_4)_2S$), and then oxidized to produce ammonium sulfate ($(NH_4)_2SO_4$), a product with considerable commercial value as a fertilizer.

The present invention describes a process which allows the H_2S and NH_3 contained in product vapor from hydropyrolysis of biomass to be captured in an aqueous stream. Biomass hydropyrolysis experiments have demonstrated that the hydropyrolysis process associated with the present invention produces a product stream that contains water vapor, H_2S, and NH_3 in particular quantities that make it possible to obtain the requisite conditions for H_2S removal via conversion to $(NH_4)_2SO_4$. Substantially all the H_2S captured in the aqueous stream is reacted with NH_3 to form $(NH_4)_2S$. In addition, a surplus of unreacted NH_3 is provided and dissolved in the aqueous stream, in order to increase the pH of the aqueous stream to approximately 12 or greater or lesser as required for subsequent conversion of $(NH_4)_2S$ to $(NH_4)_2SO_4$. The stream can then be reacted with oxygen in a thermal, non-catalytic conversion zone to substantially convert the dissolved $(NH_4)_2S$ to $(NH_4)_2SO_4$ and thiosulfate. The stream can be further contacted with oxygen and an oxidizing catalyst in accordance with the method disclosed in Gillespie, U.S. Patent 5,470,486 or, alternatively, the incoming aqueous stream can be reacted with oxygen, in the presence of an appropriate catalyst, in accordance with the method disclosed in the U.S. Patent 5,207,927 (Marinangeli, et al.). By employing either technology, within the ranges of pH, oxygen to sulfur mole ratio, pressure, temperature, and liquid hourly space velocities taught in these patents, an aqueous stream containing NH_3 and $(NH_4)_2SO_4$ is thereby obtained, and these compounds can then be recovered and sold as fertilizer. A variety of methods for obtaining ammonium sulfate from an aqueous stream containing ammonium sulfite and dissolved ammonia are currently in use and the examples cited above serve to illustrate that established technologies exist for effecting this conversion.

These ammonia-derived compounds that can be recovered and sold as fertilizer can be mixed with char produced by this process and pelletized to produce a product to provide fertilize and amend soils. Likewise these ammonia-derived compounds produced by this process that can be recovered and sold as fertilizer can also be mixed with char and other essential soil nutrients and minerals and pelletized to produce a product to provide improve, fertilize, and amend soils. It should also be obvious to one skilled in the art that these ammonia-derived compounds that incorporate char and other essential soil nutrients and minerals can be prepared in time-release formulations to avoid repetitive applications in an agricultural setting.

A stream of product vapor, from which substantially all the H_2S has been removed, is also obtained. This stream of vapor can then be handled in various ways, including use as a fuel to raise steam or directing it into a steam reformer.

BRIEF DESCRIPTION OF THE DRAWINGS

These and other objects and features of this invention will be better understood from the following detailed description taken in conjunction with the drawings wherein:

FIG. 1 shows a process flow diagram according to one preferred embodiment of this invention, in which H_2S is captured in a primary aqueous stream containing NH_3, and oxidized in a reactor to form $(NH_4)_2SO_4$.

FIG. 2 shows a process flow diagram according to one preferred embodiment of this invention, in which H_2S that still remains in the cooled vapor product stream is captured in a sorbent bed.

FIG. 3 shows a process flow diagram according to one preferred embodiment of this invention, in which the H_2S remaining in the cooled vapor product stream is captured and sent into the oxidation reactor along with the primary aqueous stream, promoting more complete overall conversion of H_2S to $(NH_4)_2SO_4$.

FIG. 4 shows a process flow diagram according to one preferred embodiment of this invention, in which the treated aqueous product stream, containing water, NH_3, and $(NH_4)_2SO_4$, is treated in a sour-gas stripper.

FIG. 5 shows a process flow diagram according to one preferred embodiment of this invention, in which a sour-water stripper removes NH_3 and H_2S from the primary aqueous stream prior to the introduction of the aqueous stream to the oxidation reactor.

FIG. 6 shows a process flow diagram according to one preferred embodiment of this invention, which incorporates both an H_2S removal unit, associated with the cooled vapor product stream, and a sour-water stripper upstream of the oxidation reactor.

DETAILED DESCRIPTION OF THE PRESENTLY PREFERRED EMBODIMENTS

FIGS. 1-6 show various preferred embodiments of the subject invention. FIG. 1 shows a process flow diagram, illustrating the simplest embodiment of the process of the present invention, in which H_2S is captured in a primary aqueous stream containing NH_3, and oxidized in a reactor to form $(NH_4)_2SO_4$. Product streams in this embodiment include a cooled vapor stream comprising primarily process vapors, and containing some H_2S, a liquid stream comprising primarily condensed hydrocarbons, a second vapor stream comprising primarily nitrogen and oxygen, and a treated aqueous stream comprising primarily water, NH_3, and $(NH_4)_2SO_4$.

FIG. 1 shows the first and most elementary embodiment of the process of the present invention. Biomass 111 and hydrogen 112 are introduced into a hydropyrolizer 110, which produces a solid, carbonaceous product 113 (referred to as char) and a product vapor stream 114. The solid product 113 comprises primarily carbonaceous residue, remaining after the hydropyrolysis of the biomass feedstock 111. The product vapor stream 114 leaves the hydropyrolizer 110 (which may comprise a single reactor, or multiple reactors in series) at a temperature that is characteristic of such hydropyrolytic processes, at a minimum, high enough that all constituents are maintained in a gaseous state. However, as is characteristic of such hydropyrolytic conversion processes, the temperature may also be significantly higher than this minimum. The product vapor stream 114 primarily comprises:

1. Deoxygenated condensable hydrocarbons (with properties corresponding to those of gasoline, diesel and kerosene)

2. Non-condensable hydrocarbon vapors (such as methane, ethane, propane and butane),
3. Other non-condensable vapors (CO_2, CO, and H_2),
4. Water and species which are soluble in liquid water, such as ammonia (NH_3), and hydrogen sulfide (H_2S).

The vapor stream is passed through a condenser 120, or other device, or other set of devices, wherein the temperature of the vapor stream is reduced to a point where substantially all the condensable hydrocarbons can be recovered as a liquid stream. At this point, three phases develop: A cooled vapor phase, a hydrocarbon phase, and an aqueous phase. The cooled product stream, containing all three phases, is sent to a separator 130, where the three phases can be split up into three separate streams.

The condensable hydrocarbon product stream 132 is preferably recovered at this point. The H_2S that was initially in the hot product vapor stream 114 is now divided, with some exiting the separator in the cooled vapor stream 131, and some in the primary aqueous stream 133. A trace of H_2S may also be present in the liquid hydrocarbon stream 132, but the solubility of the polar H_2S molecule in the liquid hydrocarbon stream is minimal.

The cooled vapor product stream 131 leaving the separator comprises primarily H2, non-condensable hydrocarbons, CO_2, CO, and H_2S. The cooled vapor product stream may also comprise ammonia.

The primary aqueous stream 133 leaving the separator comprises primarily water, NH_3, and ammonium sulfide ($(NH_4)_2S$). The $(NH_4)_2S$ in this stream is produced when the H_2S from the vapor stream enters the aqueous stream and reacts with NH_3, which is also in solution in the aqueous stream. It is an object of this invention to control the process of the invention in such a manner that the pH of the primary aqueous stream 133 is approximately 12, meaning that the concentration of NH_3 (as NH_4OH) in the stream is great enough to produce a strongly-basic solution. This is helpful, in part, to help stabilize the H2S and increase its solubility in the aqueous stream. It is also a preferred condition for the operation of the oxidation reactor 140, wherein the $(NH_4)_2S$ is oxidized to produce $(NH_4)_2SO_4$.

The primary aqueous stream 133 from the separator 130 is then introduced to an oxidation reactor 140, also referred to as a catalytic reactor herein. A stream of air 141 is also introduced to the oxidation reactor, in an amount sufficient to supply approximately 5 moles of oxygen for each mole of sulfur. After reaction at an appropriate temperature and pressure, in the presence of an appropriate catalyst, and for a sufficient residence time, the $(NH_4)_2S$ in the primary aqueous stream 133 is substantially completely oxidized.

In accordance with this first embodiment of the process of the present invention, a treated aqueous product stream 142 is preferably obtained from the oxidation reactor, including NH_3, liquid water, and $(NH_4)_2SO_4$. In addition, a reactor gas product stream 143 is obtained from the oxidation reactor, primarily comprising nitrogen and unused oxygen, and containing traces of NH_3 and water vapor. It will be noted that, in this first embodiment, a significant concentration of H_2S is still present in the cooled product vapor stream 131 exiting the separator unit 130.

FIG. 2 is a process flow diagram, illustrating an embodiment of the process of the present invention, in which H_2S that still remains in the cooled vapor product stream is captured in a sorbent bed. In this case, removal of the H_2S remaining in the cooled product vapor stream is substantially complete.

FIG. 2 illustrates a second embodiment of the process of the present invention. In this second embodiment an H_2S removal unit 250 has been added, downstream of the separator 230. The primary cooled vapor product stream 231 passes through the H_2S removal unit 250 (which may comprise a sorbent bed, liquid wash, or other similar apparatus). The H_2S in the primary cooled vapor product stream 231 is substantially completely removed from the primary cooled vapor product stream 231, and a secondary cooled vapor product stream 251 comprising primarily H_2, CO, CO_2, and non-condensable hydrocarbon vapors is obtained. This secondary stream may also comprise ammonia. In this embodiment, the H_2S is not recovered, and would, for example, be disposed of when the H_2S removal unit 250 is regenerated with H_2S-containing waste being appropriately discarded.

FIG. 3 illustrates a third embodiment of the process of the present invention. In this third embodiment, an H_2S removal unit 350 has been added, downstream of the separator 330, as in the second embodiment, described above. The primary cooled vapor product stream 331 passes through the H_2S removal unit 350 (which may comprise a reusable sorbent bed, amine scrubber, or some similar apparatus). The H_2S in the primary cooled vapor product stream 331 is substantially completely removed, and a secondary cooled vapor product stream 351 comprising primarily H_2, CO, CO_2, and non-condensable hydrocarbon vapors is obtained. However, in this third embodiment, the H_2S is recovered from the H_2S removal unit 350, in a stream 352 comprising primarily gaseous H_2S, and is sent to the oxidation reactor 340, along with the primary aqueous stream 333. In the oxidation reactor, the gaseous H_2S stream 352 is brought into contact with the primary aqueous stream 333 and an appropriate catalyst, and forms $(NH_4)_2S$, which is then oxidized to form $(NH_4)_2SO_4$. In this way, a secondary cooled product vapor stream 351, containing only trace amounts of H_2S, and comprising primarily H_2, non-condensable hydrocarbons, CO_2, and CO, is obtained. This secondary stream may also comprise ammonia. In addition, the overall conversion of H_2S is increased, and is higher than in the first embodiment of the process of the present invention, described above.

FIG. 4 illustrates a fourth embodiment of the process of the present invention. Ammonia (NH_3) is a potentially-valuable product, and is separated from the primary treated aqueous stream 442 leaving the oxidation reactor 440 in a sour-water stripper 460 in this fourth embodiment of the process of the present invention. This approach allows a gaseous stream 461 comprising primarily NH_3 to be recovered, while the water and $(NH_4)_2SO_4$ are recovered separately from the sour- water stripper in a secondary treated aqueous stream 462. $(NH_4)_2SO_4$ is highly water-soluble, and the aqueous solution of $(NH_4)_2SO_4$ has potential value as an agricultural fertilizer. If desired, this solution can be concentrated by further heating of the secondary treated aqueous stream 462, which could drive off some or all of the water in the stream.

FIG. 5 illustrates a fifth embodiment of the process of the present invention. This embodiment features a sour-water stripper 560 upstream of the oxidation reactor 540, which accepts the primary aqueous stream 533 from the separator. Water, NH_3 and H_2S, and any $(NH_4)_2S$ formed by the reaction of NH_3 and H_2S, are removed in the sour-water stripper 560, and leave the sour-water stripper as a gaseous stream 562. A stream of purified liquid water 561 is thereby produced. This purified water stream 561 is then available as a product stream. If desired, a portion of this purified water stream 561 can be brought back into contact with the gaseous stream 562 of NH_3 and H_2S from the sour-water stripper. In this case, the NH_3 and H_2S go back into solution in this portion of the liquid water stream 561, forming $(NH_4)_2S$, and this solution is then introduced into the oxidation reactor 540, for conversion to $(NH_4)_2SO_4$. However, preferably the purified water stream is not brought back into contact with the gaseous stream 562 and preferably, stream 562 is cooled as needed so that water in the stream is condensed and the NH_3 and H_2S in this stream go back into solution forming $(NH_4)_2S$, and this solution is then introduced into the oxidation reactor 540, for conversion to $(NH_4)_2SO_4$. This approach makes a stream of purified water 561 available, and creates a concentrated treated stream 542 of water, NH_3 and $(NH_4)_2SO_4$ at the outlet of the oxidation reactor 540.

FIG. 6 illustrates a sixth embodiment of the process of the present invention. This embodiment features a sour-water stripper 660 upstream of the oxidation reactor 640, which accepts the primary aqueous stream 633 from the separator 630. It also features an H_2S removal unit 650 downstream of the separator 630, as in the third embodiment described herein above. The primary cooled vapor product stream 631 passes through the H_2S removal unit 650 (which may comprise a sorbent bed, amine scrubber, or some similar apparatus). The H_2S in the primary cooled vapor product stream 631 is substantially completely removed and a secondary cooled product vapor stream 651 comprising primarily H_2, CO, CO_2, and non-condensable hydrocarbon vapors is obtained. This secondary stream may also comprise ammonia. As in the third embodiment, the H_2S is recovered, in a stream 652 comprising primarily gaseous H_2S, and is sent to the oxidation reactor 640.

As described herein above in the description of the fifth embodiment, dissolved NH_3 and H_2S, and any $(NH_4)_2S$ formed by the reaction of NH_3 and H_2S, are driven out of the primary aqueous stream 633 in the sour-water stripper 660. Water, NH_3 and H_2S, and any $(NH_4)_2S$ formed by the reaction of NH_3 and H_2S, are removed in the sour-water stripper 660, and leave the sour-water stripper as a gaseous stream 662. A stream of purified water 661 is thereby produced. This purified water stream 661 is then available as a product stream. If desired, a portion of this purified water stream 661 can be brought back into contact with the gaseous stream 662 of NH_3 and H_2S from the sour-water stripper. In this case, the NH_3 and H_2S go back into solution in this portion of the liquid water stream 661, forming $(NH_4)_2S$, and this solution is then introduced into the oxidation reactor 640, for conversion to $(NH_4)_2SO_4$. However, preferably the purified water stream is not brought back into contact with the gaseous stream 662 and preferably, stream 662 is cooled as needed so that water in the stream is condensed and the NH_3 and H_2S in this stream go back into solution forming $(NH_4)_2S$, and this solution is then introduced into the oxidation reactor 640, for conversion to $(NH_4)_2SO_4$. This approach makes a stream of purified water 661 available, and creates a concentrated treated stream 642 of water, NH_3 and $(NH_4)_2SO_4$ at the outlet of the oxidation reactor 540. The stream 652 of recovered H_2S from the H_2S removal unit is also introduced to the oxidation reactor.

This sixth embodiment of the process of the present invention makes a stream of purified water 661 available, and creates a concentrated treated stream 642 of water, NH_3 and $(NH_4)_2SO_4$ at the outlet of the oxidation reactor 640. It also provides a secondary stream of cooled vapor product 651 which may contain minute concentrations of H_2S, and promotes high overall conversion of H_2S to an $(NH_4)_2SO_4$ product.

The char produced from the hydropyrolysis of biomass (land and water based biomass, wastes from processes utilizing these materials), as well as plastics derived from biomass or petroleum has been found to be an essentially inert carbonaceous material, free of hydrocarbon contaminants that are toxic to humans or plants. It is one intent of this invention to combine the char produced from the hydropyrolysis of biomass or plastic with the ammonium sulfate recovered from this process to produce an agricultural fertilizer product, as a powder, granulated, or pelletized material that can both improve the quality of a soil for use as an agricultural substrate and provide a fertilizing component for the sustenance of lignocellulosic biomass.

EXAMPLES

A sample of wood with properties representative of those of most wood species was subjected to hydropyrolysis. The elemental composition of the wood is presented in Table A, below. The composition is presented on both an overall basis (which includes moisture and ash in the feedstock) and on a moisture- and ash-free (MAF) basis. As can be seen in Table A, small but significant quantities of nitrogen and sulfur were present in the wood.

The yield of hydropyrolysis products, obtained in the vapor stream leaving the experimental hydropyrolizer, is given in Table B. Not all of the nitrogen and sulfur initially present in the wood is ultimately found in the vapor stream from the hydropyrolizer. Some of the sulfur and some of the nitrogen are chemically bound up in the stream of solid product (comprising char and ash) from the hydropyrolizer. However, the experiment demonstrated that the yield of NH_3 in the primary product vapor stream constituted 0.18% of the mass of the feedstock, on an MAF basis. The yield of H_2S constituted 0.05% of the mass of the feedstock, on an MAF basis. It will be noted that the total masses in Table B add up to 104.83%. This is due to the fact that a given quantity of moisture and ash-free wood reacts with hydrogen in the hydropyrolysis process, and the resulting products have a greater total mass than the wood that was reacted.

As an example, one might assume that one kilogram of moisture-free, ash-free wood is subjected to hydropyrolysis. In this case, the vapor stream contains 1.8 grams of NH_3 and 0.5 grams of H_2S. Due to the different molar masses of NH_3 and H_2S, this equates to 0.106 moles of NH_3 and 0.014 moles of H_2S. The molar ratio of NH_3 to H_2S is therefore 7.4 to 1. In order to form $(NH_4)_2S$ in an aqueous solution, two moles of NH_3 are required for each mole of H_2S. The relative amounts of NH_3 and H_2S in the vapor stream leaving the hydropyrolysis reactor are more than adequate to react all the H_2S in the stream with NH_3, and produce an aqueous solution of $(NH_4)_2S$.

Further, the interaction with hydrogen in the hydropyrolysis process converts a significant fraction of the oxygen in the dry, ash-free wood into water vapor in the vapor stream leaving the hydropyrolysis process. Even if the feedstock is completely dry, there is still a significant formation of water during hydropyrolysis of the wood feedstock, and the amount of water produced is sufficient to substantially and completely dissolve all of the NH_3 and H_2S present in the hydropyrolysis product vapor stream.

While all or almost all of the NH_3 leaving the hydropyrolysis reactor ultimately goes into solution in the primary aqueous stream, the solubility of H_2S in aqueous solutions depends on a variety of factors, such as temperature, pressure, and pH of the solution. The NH_3 in solution in the primary aqueous stream will render the solution alkaline, and this will significantly increase the solubility of H_2S in the alkaline aqueous solution. H_2S and NH_3 react spontaneously in aqueous solution to form $(NH_4)_2S$, though the sulfide may be present in a dissociated form. However, not all the H_2S in the product vapor stream is likely to enter the primary aqueous stream when the process vapors are cooled. A cooled vapor stream, containing a significant concentration of H_2S, is still likely to result in practice. The various embodiments of the process of the present invention, described above, provide means by which this remaining concentration of H_2S can be removed from the cooled vapor stream, and, ultimately, reacted with NH_3 and oxygen to form $(NH_4)_2SO_4$.

In actual practice, the biomass feedstock conveyed into the hydropyrolizer will also contain some moisture, so the actual amount of water vapor in the heated vapor stream from the hydropyrolizer will contain significantly more water that would be the case if the feedstock were bone dry. This phenomenon assists in removal of H_2S from the cooled vapor stream, since the concentrations of NH_3 and H_2S in the primary aqueous stream will be even lower than they would be if the feedstock were completely dry, meaning that more H_2S can be stripped from the cooled vapor stream in the condenser and separator of the embodiments of the process of the present invention, described herein above. The solubility of $(NH_4)_2S$ in water is very high, and solutions of $(NH_4)_2S$ containing up to 52% by mass of $(NH_4)_2S$ appear to be commercially available.

Wood:	Initial Composition	Initial Composition, MAF Basis
% C (MF)	47.6	50.2
% H (MF)	5.7	6.0
% O (MF)	41.2	43.5
% N (MF)	0.2	0.2
% S (MF)	0.1	0.1
% ash (MF)	1.1	
% moisture	4.3	

Table A. Composition of Wood Feedstock

Wood Hydropyrolysis Hot Vapor Product Yield (MAF Basis):	Wt%
Gasoline	16
Diesel	10
Char	13
Water	36
CO	8.4
CO2	8.4
C1-C3	12.8
H2S	0.05
NH3	0.18

Table B. Yield of hot vapor products from hydropyrolysis of wood, on a moisture- and ash-free (MAF) basis

Not all biomass is equivalent, and a second feedstock, which differs significantly from wood in terms of mechanical properties, growth cycle, and composition, was also tested. This feedstock was corn stover. Corn stover includes residues of corn stalks and husks, left over after the nutritious parts of the plant have been harvested. The sample examined was typical of most types of corn stover generated during harvesting of corn. The composition of the corn stover sample is presented on both an overall basis (which includes moisture and ash in the feedstock) and on a moisture- and ash-free (MAF) basis in Table C. As can be seen in Table C, small but significant quantities of nitrogen and sulfur were present in the corn stover, as was the case with the wood feedstock. As can be seen from the table, the corn stover sample contained far more ash and far more moisture than did the sample of wood.

As with the wood feedstock, the ratio between hydrogen sulfide and ammonia in the hot product vapor leaving the corn stover hydropyrolysis process is very important. The hydropyrolysis product vapor composition of corn stover was found to be very similar to that of wood, on an MAF basis. The relevant values are shown in Table D. One significant difference between Tables B and D relates to the concentrations of NH_3 and H_2S in the product vapor. The molar ratio of NH_3 to H_2S in the product vapor, in the case of corn stover, is 15.2. Again, there is more than enough NH_3 present to react with the H_2S in the product vapor stream and form ammonium sulfide. As was the case with wood, there is more than sufficient water formed, during hydropyrolysis of corn stover, to completely dissolve any ammonium sulfide, and carry it in solution through the process of the present invention. It will be noted that the total masses in Table D add up to 106%. This is due to the fact that a given quantity of moisture and ash-free corn stover reacts with hydrogen in the hydropyrolysis process, and the resulting products have a greater total mass than the feedstock that was reacted.

Corn Stover:	Initial Composition	Initial Composition, MAF Basis
% C (MF)	38.0	50.7
% H (MF)	4.8	6.4
% O (MF)	31.2	41.6
% N (MF)	0.9	1.2
% S (MF)	0.1	0.2
% ash (MF)	8.3	
% moisture	20.0	

Table C. Composition of corn typical stover sample

Corn Stover Hydropyrolsyis Hot Vapor Product Yield (MAF Basis):	Wt%
Gasoline	15
Diesel	9
Char	15
Water	36
CO	8.4
CO2	8.4
C1-C3	13.8
H2S	0.12
NH3	0.92

Table D. Composition of effluent vapor, hydropyrolysis of typical corn stover, on MAF basis

While in the foregoing specification this invention has been described in relation to certain preferred embodiments thereof, and many details have been set forth for purpose of illustration, it will be apparent to those skilled in the art that the invention is susceptible to additional embodiments and that certain of the details described herein can be varied considerably without departing from the basic principles of the invention.

CLAIMS:

1. A method for processing biomass into hydrocarbon fuels comprising:

processing a biomass in a hydropyrolysis reactor resulting in char and a process vapor stream comprising hydrocarbons and water vapor;

cooling the process vapor stream to a condensation temperature resulting in a liquid hydrocarbon stream; a cooled product vapor stream comprising H_2, CH_4, CO, CO_2, and hydrogen sulfide; and an aqueous stream comprising ammonia and ammonium sulfide, wherein the ammonium sulfide in the aqueous stream is the reaction product of ammonia and hydrogen sulfide that is initially present in the process vapor stream and that condenses into the aqueous stream;

sending the aqueous stream to a catalytic reactor;

injecting air into the catalytic reactor to obtain an aqueous product stream containing ammonia and ammonium sulfate; and

removing hydrogen sulfide from the cooled product vapor stream.

2. The method of claim 1, wherein the cooled product vapor stream further comprises ammonia.

3. The method of claim 1 or 2, further comprising:

maintaining the aqueous stream comprising ammonium sulfide at a pH of approximately 9 to approximately 12 in said catalytic reactor, into which said air is injected at a ratio of greater than 5 atoms of oxygen for each atom of sulfur in the aqueous stream.

4. The method of any one of claims 1 to 3, further comprising:

sending the hydrogen sulfide, removed from the cooled product vapor stream, to the catalytic reactor, along with the aqueous stream comprising ammonium sulfide, to react with ammonia present in the aqueous stream and form additional ammonium sulfide for conversion to ammonium sulfate, thereby resulting in a high overall conversion of hydrogen sulfide to ammonium sulfate.

5. The method of any one of claims 1 to 4, further comprising:

treating the aqueous product stream leaving the catalytic reactor with a sour water stripper resulting in a gaseous stream comprising primarily ammonia and an aqueous stream comprising primarily water and ammonium sulfate.

6. The method of any one of claims 1 to 5, further comprising:

combining said char from the hydropyrolysis reactor with ammonium sulfate recovered from said aqueous product stream.

7. The method of claim 6, further comprising:

pelletizing said char, combined with said ammonium sulfate, to create a densified nutrient.

8. The method of claim 7, wherein said densified nutrient further comprises agricultural fertilizers.

9. A method for removal of sulfur from biomass conversion products comprising:

processing the biomass in a hydropyrolysis reactor, resulting in char and a heated process vapor stream containing hydrogen, water vapor, condensable hydrocarbon vapors, non-condensable hydrocarbon vapors, carbon monoxide and carbon dioxide;

cooling the heated process vapor stream to separate:

a liquid hydrocarbon stream;

an aqueous stream, containing water, ammonia, and ammonium sulfide, wherein the ammonium sulfide in the aqueous stream is the reaction product of ammonia and hydrogen sulfide that is initially present in the process vapor stream and that condenses into the aqueous stream; and

a cooled product vapor stream, containing non-condensable process vapors comprising H_2, CH_4, CO, CO_2, and hydrogen sulfide;

treating the aqueous stream with a sour water stripper, resulting in a purified liquid water stream and a solution comprising ammonium sulfide;

sending the solution comprising ammonium sulfide to a catalytic reactor, thereby oxidizing the ammonium sulfide over a catalyst to ammonium sulfate;

obtaining an aqueous product stream comprising ammonium sulfate; and

removing hydrogen sulfide from the cooled product vapor stream.

10. The method of claim 9, wherein the cooled product vapor stream further comprises ammonia.

11. The method of claim 9 or 10, further comprising the step of:

stripping ammonia from the aqueous product stream comprising ammonium sulfate to create a separate purified stream of gaseous ammonia.

12. The method of claim 11, further comprising the step of:

introducing the aqueous product stream comprising ammonium sulfate into a boiler to convert ammonium sulfate to crystallized ammonium sulfate and steam.

13. The method of claim 12, further comprising the step of:

obtaining crystallized ammonium sulfate from the aqueous product stream by evaporation of excess water and separation of the crystallized ammonium sulfate by filtration.

14. The method of claim 13, wherein the evaporation of excess water provides steam, and the method further comprises:

sending the steam to a steam reformer.

15. The method of claim 14, further comprising the step of:

sending the steam through a guard bed, upstream of the steam reformer, to remove trace H2S from the steam.

16. The method of any one of claims 13 to 15, further comprising the step of:

cooling the aqueous product stream, following the evaporation of the excess water and prior to separation of the crystallized ammonium sulfate by filtration.

17. The method of any one of claims 9 to 16, wherein the catalyst is monosulfonated cobalt phthalocynanine.

18. The method of any one of claims 9 to 17, further comprising:

combining the purified liquid water stream with the solution comprising ammonium sulfide, prior to oxidation in the catalytic reactor.

19. A hydropyrolysis process comprising:

introducing biomass and hydrogen into a hydropyrolyzer comprising one or more reactors;

heating and deoxygenating the biomass to provide a vapor product that exits the hydropyrolyzer at a temperature such that all constituents of the vapor product are maintained in the gaseous state, the vapor product comprising deoxygenated condensable hydrocarbons, non-condensable gases, and water;

cooling the vapor product to condense a liquid organic phase and a liquid aqueous phase which comprises ammonia (NH_3) and optionally at least one species of the vapor product which is/are solubilized in the liquid aqueous phase;

phase separating the liquid aqueous phase from the liquid organic phase; and

treating the liquid aqueous phase to obtain a gas phase NH_3 product or an aqueous NH_4OH product.

20. The process of claim 19, wherein the hydropyrolyzer comprises multiple reactors in series.

21. The process of claim 19 or claim 20, wherein the NH_3 and H_2S are first and second species of said at least one species of the vapor product, wherein said cooling of the vapor product condenses the liquid aqueous phase comprising an initial NH_3 amount and an initial H_2S amount, and wherein the solubilized NH_3 is present in the liquid aqueous phase as an excess amount that remains after reaction of said initial NH_3 amount with said initial H_2S amount to form $(NH_4)_2S$ in the liquid aqueous phase.

22. The process of claim 21, wherein treating the liquid aqueous phase comprises catalytically reacting the liquid aqueous phase with oxygen to substantially oxidize the $(NH_4)_2S$ to $(NH_4)_2SO_4$.

23. The process claim 19 or claim 20, further comprising separating, from the condensed organic and aqueous phases, a cooled vapor phase comprising the non-condensable gases, non-condensable hydrocarbons, and H_2S.

24. The process of claim 23, further comprising treating the cooled vapor phase to substantially remove the H_2S.

25. The process of claim 24, wherein treating the cooled vapor phase comprises contacting the cooled vapor phase with a bed of sorbent or with a liquid wash.

26. The process of claim 23, further comprising subjecting at least a portion of the cooled vapor phase to steam reforming, in order to generate hydrogen.

27. The process of claim 19 or claim 20, wherein the treating the aqueous phase comprises subjecting the liquid aqueous phase to sour water stripping to obtain the gas phase NH_3 product.

28. The process of claim 27,

wherein the NH_3 and H_2S are first and second species of said at least one species of the vapor product,

wherein said cooling the vapor product condenses the liquid aqueous phase comprising an initial NH_3 amount and an initial H_2S amount,

wherein the solubilized NH_3 is present in the liquid aqueous phase as an excess amount that remains after reaction of said initial NH_3 amount and said initial H_2S amount to form $(NH_4)_2S$ in the liquid aqueous phase, and

wherein a gas phase NH_3 product is obtained following reacting the liquid aqueous phase with oxygen to substantially oxidize the $(NH_4)_2S$ to $(NH_4)_2SO_4$, followed by subjecting the liquid aqueous phase to sour water stripping.

29. The process of claim 28, wherein reacting the liquid aqueous phase with oxygen is performed catalytically.

30. The process of claim 19 or claim 20,

wherein the NH_3 and H_2S are first and second species of said at least one species of the vapor product,

wherein said cooling the vapor product condenses the liquid aqueous phase comprising an initial NH_3 amount and an initial H_2S amount,

wherein solubilized NH_3 is present in the liquid aqueous phase as an excess amount that remains after reaction of said initial NH_3 amount and said initial H_2S amount to form $(NH_4)_2S$ in the liquid aqueous phase, and

wherein the aqueous NH_4OH product is obtained following reacting the liquid aqueous phase with oxygen to substantially oxidize the $(NH_4)_2S$ to $(NH_4)_2SO_4$.

31. The process of claim 19 or claim 20, wherein the biomass contains moisture that contributes to the liquid aqueous phase.

32. The process of claim 19 or claim 20, wherein the deoxygenated condensable hydrocarbons are substantially recovered in the liquid organic phase and comprise hydrocarbons having properties corresponding to gasoline, diesel, and/or kerosene.

33. The process of claim 19 or claim 20, wherein the biomass contains nitrogen (N) compounds and sulfur (S) compounds that, upon reaction with hydrogen that is introduced into said hydropyrolyzer, form both NH_3 and H_2S that are present in the vapor product, wherein an initial amount of NH_3 that is present in excess of that required to react with an initial amount of H_2S that is present, forms $(NH_4)_2S$.

34. The process of claim 19 or claim 20, wherein said vapor product comprises both the NH_3 and H_2S as first and second species of said at least one species of the vapor product and the liquid aqueous phase comprises more water than is sufficient to dissolve, into the liquid aqueous phase, $(NH_4)_2S$ that is formed by the reaction of the NH_3 with the H_2S.

35. A method for preparing an ammonia product, comprising:

processing biomass in a hydropyrolyzer to obtain solid char and a heated vapor product that exits the hydropyrolyzer at a temperature such that all constituents of the heated vapor product are maintained in the gaseous state, the heated vapor product comprising NH_3, H_2S, hydrogen, carbon monoxide, carbon dioxide, deoxygenated condensable hydrocarbons, and water vapor;

cooling the heated vapor product to condense, as separate liquid phases, an organic phase and an aqueous phase comprising NH_4OH that is formed from the dissolution of the NH_3 from the heated vapor product into the aqueous phase;

separating the liquid phases; and

obtaining the ammonia product as a gas phase NH_3 product or an aqueous NH_4OH product from treating of the aqueous phase.

36. The method of claim 35, wherein the aqueous phase further comprises $(NH_4)_2S$ that results from the dissolution, into the aqueous phase, of said NH_3 and said H_2S, upon said cooling of the heated vapor product, followed by reaction of a portion of said NH_3 with said H_2S in the aqueous phase.

37. The method of claim 35 or claim 36, wherein the hydropyrolyzer comprises multiple reactors in series.

38. The method of claim 35 or claim 36, wherein the ammonia product is a gas phase NH_3 product that is obtained by subjecting the aqueous phase to sour water stripping.

39. The method of claim 35 or claim 36, further comprising:

separating, from the liquid phases, a cooled vapor phase comprising non-condensable hydrocarbons, and

steam reforming at least a portion of the non-condensable hydrocarbons to generate hydrogen that is used for the processing of the biomass in the hydropyrolyzer.

40. A hydropyrolysis process comprising:

introducing a biomass feedstock and hydrogen into a hydropyrolyzer comprising one or more reactors, wherein sulfur is present in the biomass feedstock;

heating and deoxygenating the biomass to provide a vapor product that exits the hydropyrolyzer at a temperature such that all constituents of the vapor product are maintained in the gaseous state, the vapor product comprising deoxygenated condensable hydrocarbons, non-condensable hydrocarbons, H_2S, and water;

cooling the vapor product to obtain a condensed liquid organic phase, a condensed liquid aqueous phase, and a cooled vapor phase comprising at least a portion of the H_2S;

separating the condensed liquid organic phase, the condensed liquid aqueous phase, and the cooled vapor phase;

treating the cooled vapor phase to substantially remove the H_2S and obtain a treated vapor phase comprising at least a portion of the non-condensable hydrocarbons; and

subjecting the treated vapor phase to steam reforming, in order to generate reformed hydrogen from the non-condensable hydrocarbons.

41. The process of claim 40, wherein the hydropyrolyzer comprises multiple reactors in series.

42. The process of claim 40 or claim 41, wherein the step of treating comprises contacting the cooled vapor phase with a bed of sorbent or with a liquid wash.

43. The process of claim 40 or claim 41, further comprising recycling at least a portion of the reformed hydrogen to the hydropyrolyzer.

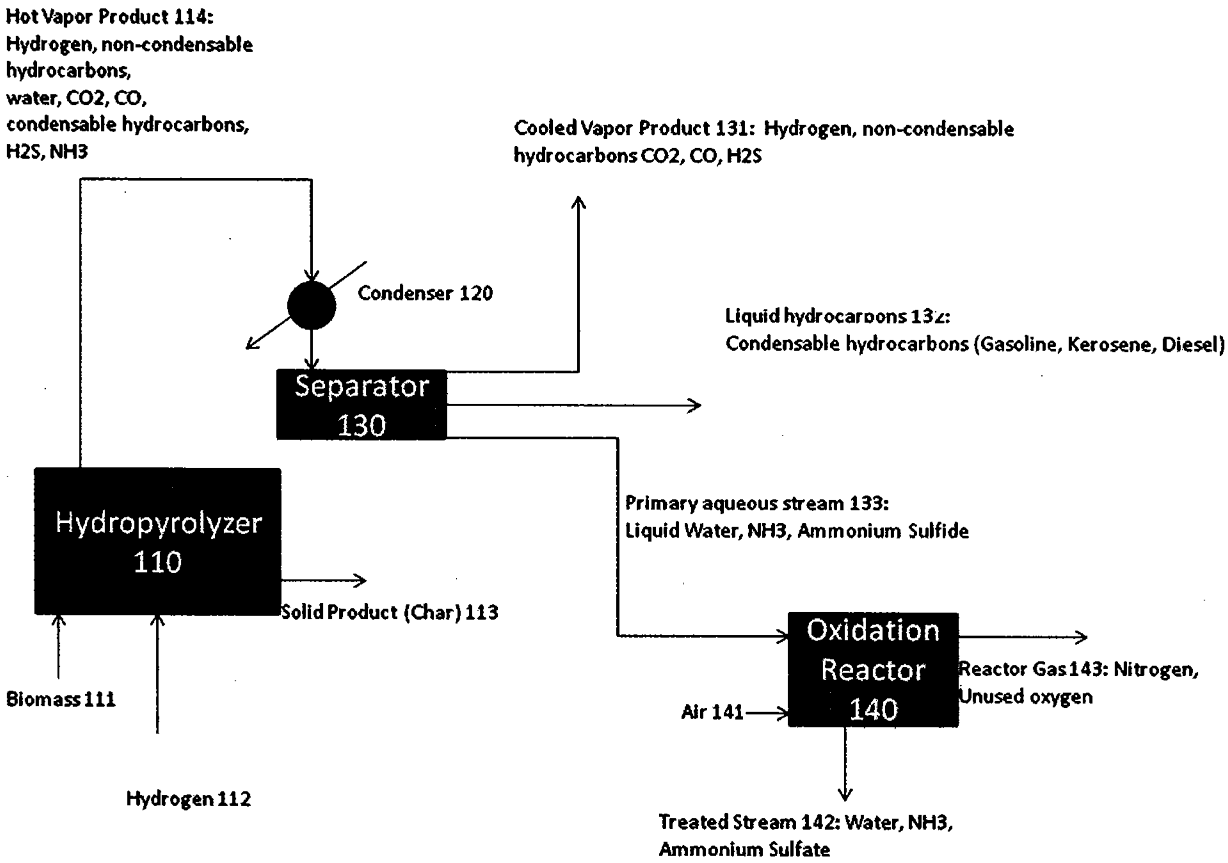

Hot Vapor Product 114:
Hydrogen, non-condensable hydrocarbons,
water, CO2, CO,
condensable hydrocarbons,
H2S, NH3
Cooled Vapor Product 131: Hydrogen, non-condensable hydrocarbons CO2, CO, H2S
Condenser 120
Liquid hydrocarbons 132:
Condensable hydrocarbons (Gasoline, Kerosene, Diesel)
Separator 130
Hydropyrolyzer 110
Primary aqueous stream 133:
Liquid Water, NH3, Ammonium Sulfide
Solid Product (Char) 113
Oxidation Reactor 140
Reactor Gas 143: Nitrogen, Unused oxygen
Biomass 111
Air 141
Hydrogen 112
Treated Stream 142: Water, NH3, Ammonium Sulfate

FIG. 1

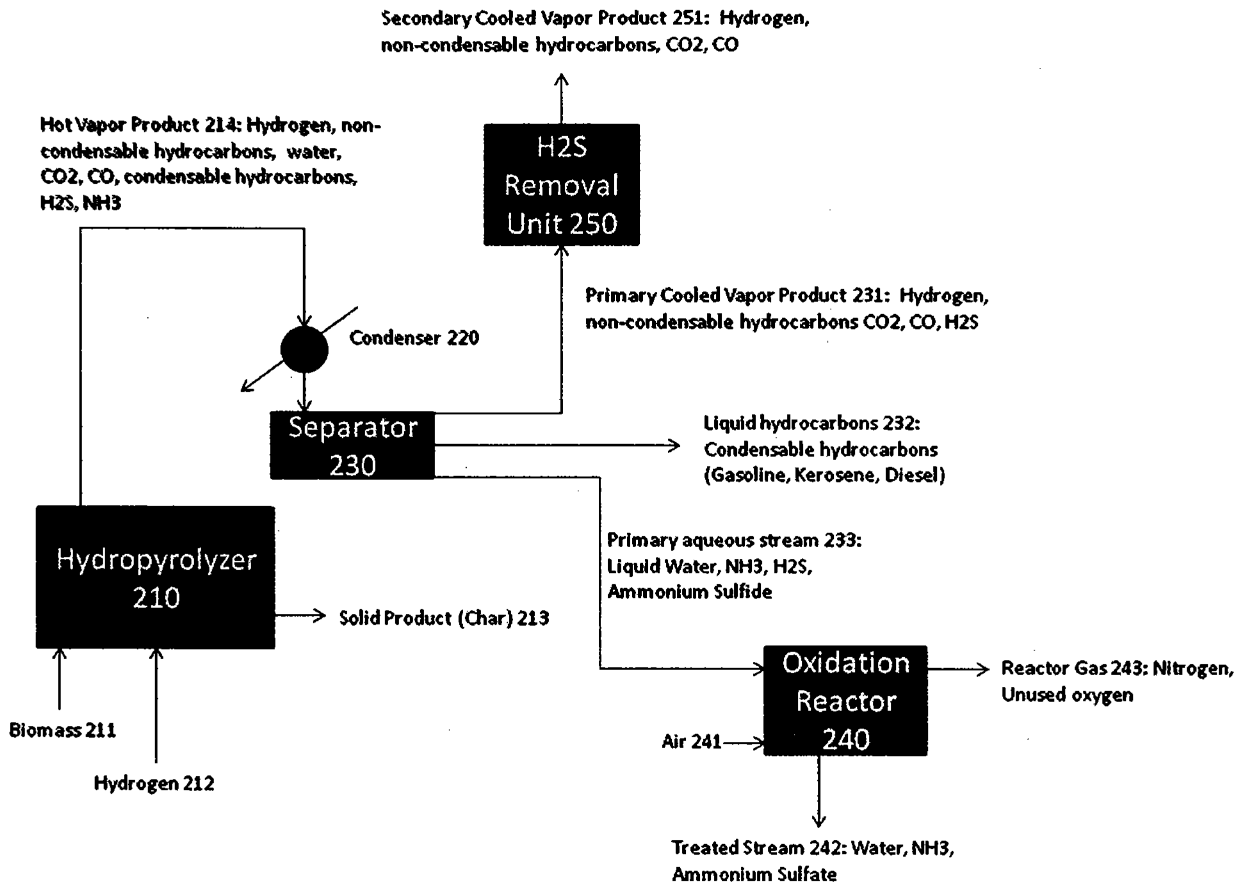

Secondary Cooled Vapor Product 251: Hydrogen, non-condensable hydrocarbons, CO2, CO
Hot Vapor Product 214: Hydrogen, non-condensable hydrocarbons, water, CO2, CO, condensable hydrocarbons, H2S, NH3
H2S Removal Unit 250
Primary Cooled Vapor Product 231: Hydrogen, non-condensable hydrocarbons CO2, CO, H2S
Condenser 220
Separator 230
Liquid hydrocarbons 232: Condensable hydrocarbons (Gasoline, Kerosene, Diesel)
Hydropyrolyzer 210
Primary aqueous stream 233: Liquid Water, NH3, H2S, Ammonium Sulfide
Solid Product (Char) 213
Oxidation Reactor 240
Reactor Gas 243: Nitrogen, Unused oxygen
Air 241
Biomass 211
Hydrogen 212
Treated Stream 242: Water, NH3, Ammonium Sulfate

FIG. 2

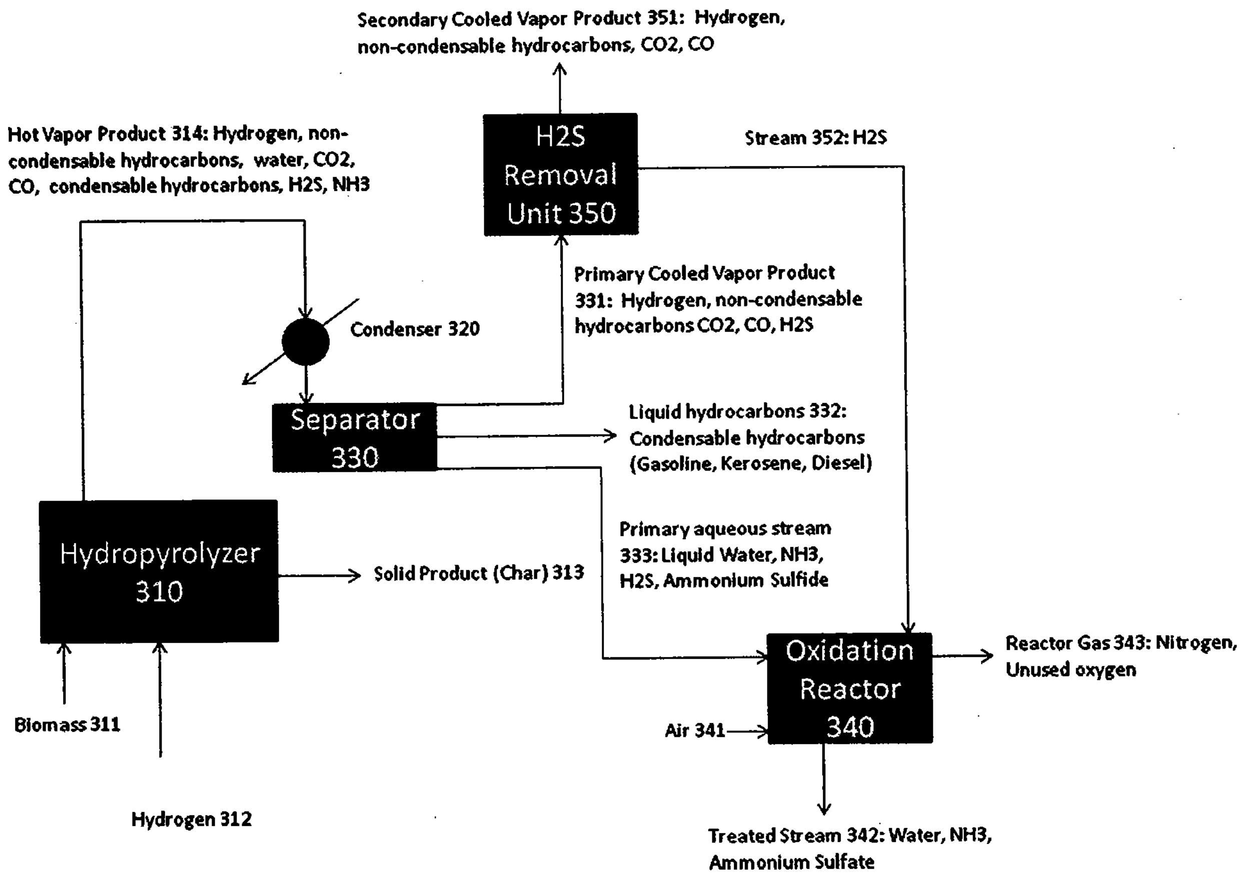

Secondary Cooled Vapor Product 351: Hydrogen, non-condensable hydrocarbons, CO2, CO
Hot Vapor Product 314: Hydrogen, non-condensable hydrocarbons, water, CO2, CO, condensable hydrocarbons, H2S, NH3
H2S Removal Unit 350
Stream 352: H2S
Primary Cooled Vapor Product 331: Hydrogen, non-condensable hydrocarbons CO2, CO, H2S
Condenser 320
Separator 330
Liquid hydrocarbons 332: Condensable hydrocarbons (Gasoline, Kerosene, Diesel)
Primary aqueous stream 333: Liquid Water, NH3, H2S, Ammonium Sulfide
Hydropyrolyzer 310
Solid Product (Char) 313
Oxidation Reactor 340
Reactor Gas 343: Nitrogen, Unused oxygen
Air 341
Biomass 311
Hydrogen 312
Treated Stream 342: Water, NH3, Ammonium Sulfate

FIG. 3

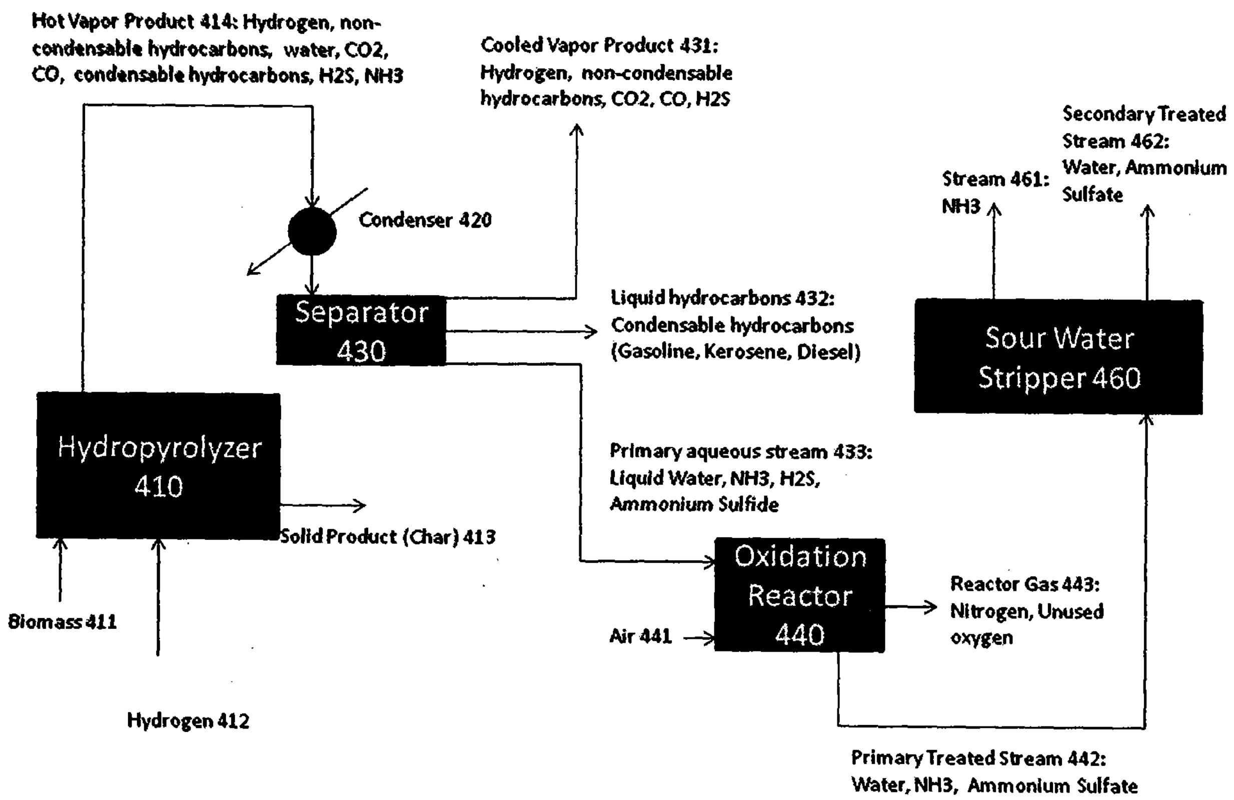

Hot Vapor Product 414: Hydrogen, non-condensable hydrocarbons, water, CO2, CO, condensable hydrocarbons, H2S, NH3
Cooled Vapor Product 431: Hydrogen, non-condensable hydrocarbons, CO2, CO, H2S
Condenser 420
Separator 430
Liquid hydrocarbons 432: Condensable hydrocarbons (Gasoline, Kerosene, Diesel)
Hydropyrolyzer 410
Solid Product (Char) 413
Biomass 411
Hydrogen 412
Primary aqueous stream 433: Liquid Water, NH3, H2S, Ammonium Sulfide
Oxidation Reactor 440
Air 441
Reactor Gas 443: Nitrogen, Unused oxygen
Primary Treated Stream 442: Water, NH3, Ammonium Sulfate
Sour Water Stripper 460
Stream 461: NH3
Secondary Treated Stream 462: Water, Ammonium Sulfate

FIG. 4

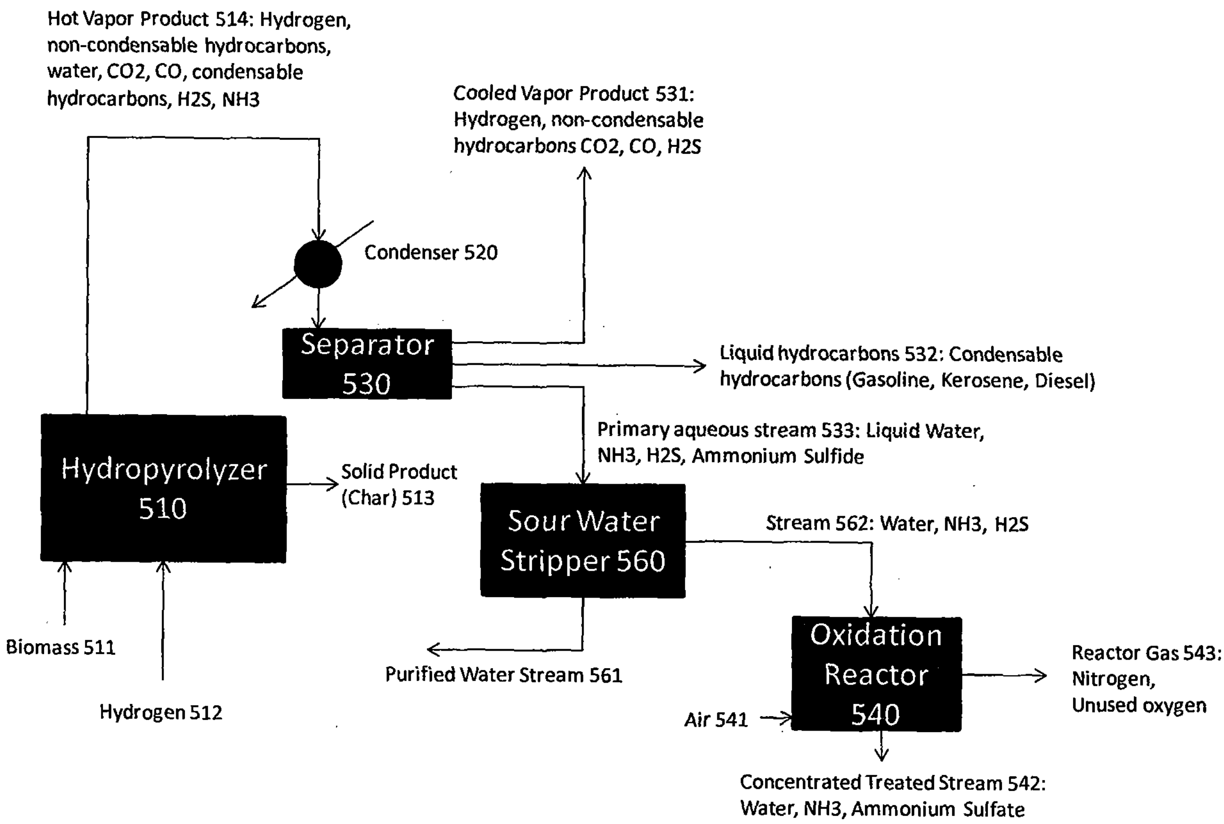

Hot Vapor Product 514: Hydrogen, non-condensable hydrocarbons, water, CO2, CO, condensable hydrocarbons, H2S, NH3
Cooled Vapor Product 531: Hydrogen, non-condensable hydrocarbons CO2, CO, H2S
Condenser 520
Separator 530
Liquid hydrocarbons 532: Condensable hydrocarbons (Gasoline, Kerosene, Diesel)
Primary aqueous stream 533: Liquid Water, NH3, H2S, Ammonium Sulfide
Hydropyrolyzer 510
Solid Product (Char) 513
Sour Water Stripper 560
Stream 562: Water, NH3, H2S
Oxidation Reactor 540
Reactor Gas 543: Nitrogen, Unused oxygen
Biomass 511
Purified Water Stream 561
Hydrogen 512
Air 541
Concentrated Treated Stream 542: Water, NH3, Ammonium Sulfate

FIG. 5

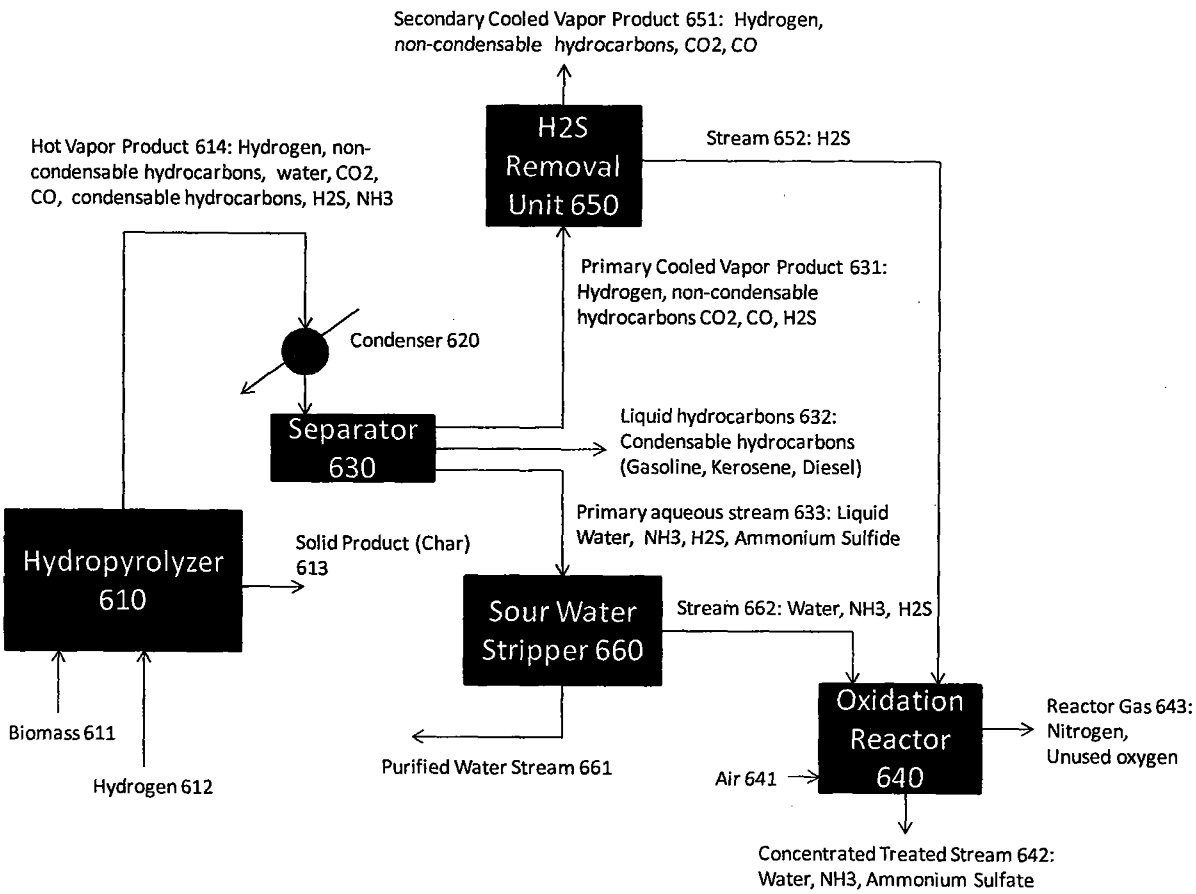
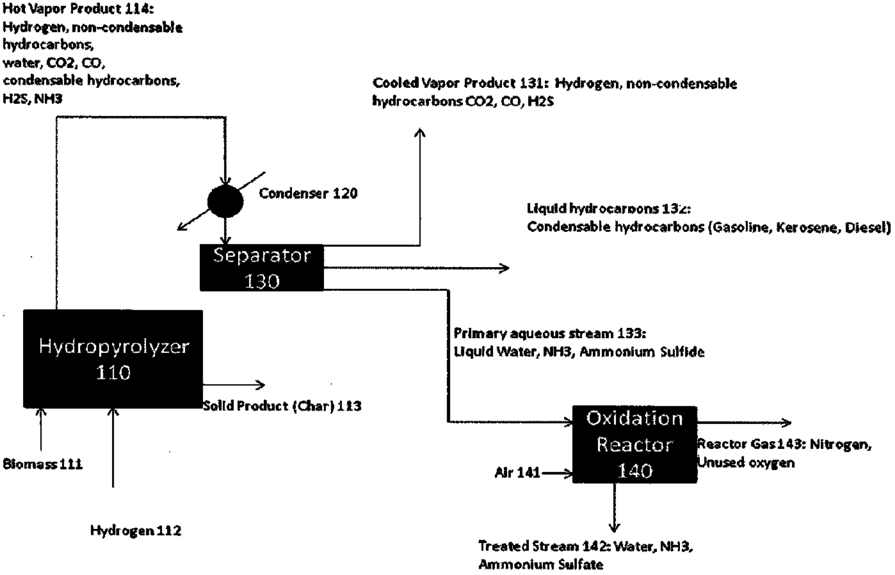

Secondary Cooled Vapor Product 651: Hydrogen, non-condensable hydrocarbons, CO2, CO
H2S Removal Unit 650
Stream 652: H2S
Hot Vapor Product 614: Hydrogen, non-condensable hydrocarbons, water, CO2, CO, condensable hydrocarbons, H2S, NH3
Primary Cooled Vapor Product 631: Hydrogen, non-condensable hydrocarbons CO2, CO, H2S
Condenser 620
Separator 630
Liquid hydrocarbons 632: Condensable hydrocarbons (Gasoline, Kerosene, Diesel)
Primary aqueous stream 633: Liquid Water, NH3, H2S, Ammonium Sulfide
Hydropyrolyzer 610
Solid Product (Char) 613
Sour Water Stripper 660
Stream 662: Water, NH3, H2S
Oxidation Reactor 640
Reactor Gas 643: Nitrogen, Unused oxygen
Biomass 611
Hydrogen 612
Purified Water Stream 661
Air 641
Concentrated Treated Stream 642: Water, NH3, Ammonium Sulfate

FIG. 6



Hot Vapor Product 114:
Hydrogen, non-condensable
hydrocarbons,
water, CO2, CO,
condensable hydrocarbons,
H2S, NH3
Cooled Vapor Product 131: Hydrogen, non-condensable
hydrocarbons CO2, CO, H2S
Condenser 120
Liquid hydrocarbons 132:
Condensable hydrocarbons (Gasoline, Kerosene, Diesel)
Separator
130
Primary aqueous stream 133:
Liquid Water, NH3, Ammonium Sulfide
Hydropyrolyzer
110
Solid Product (Char) 113
Oxidation
Reactor
140
Reactor Gas 143: Nitrogen,
Unused oxygen
Air 141
Biomass 111
Hydrogen 112
Treated Stream 142: Water, NH3,
Ammonium Sulfate