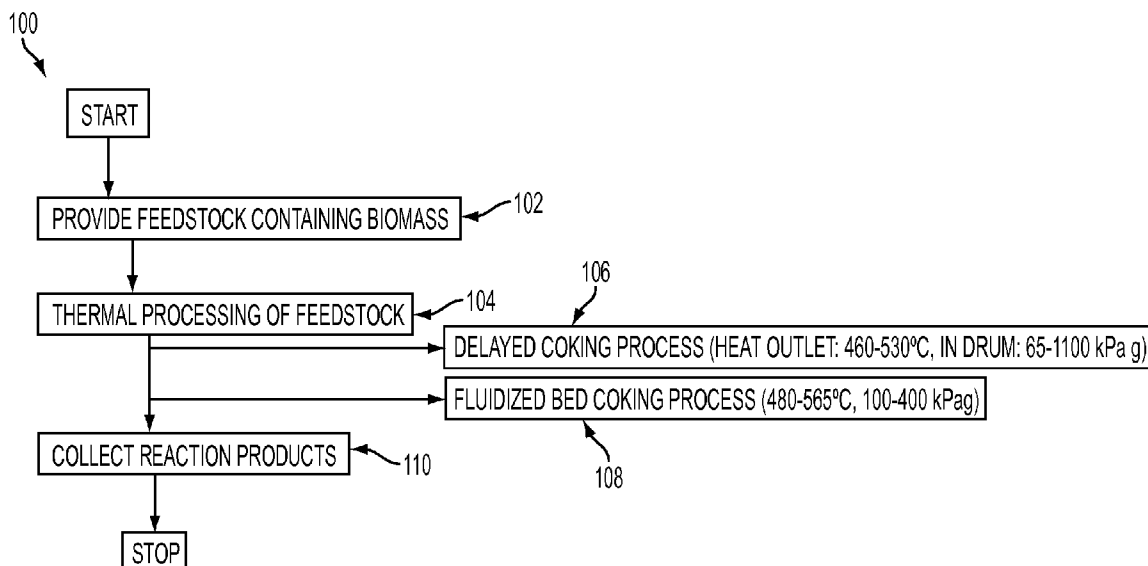




US 20120325641A1

(19) **United States**(12) **Patent Application Publication**
Elliott et al.(10) **Pub. No.: US 2012/0325641 A1**(43) **Pub. Date: Dec. 27, 2012**(54) **PYROLYSIS OF SOLID BIOMASS IN THE
PRODUCTION OF BIOFUELS****Publication Classification**(75) Inventors: **John Daniel Elliott**, Katy, TX (US);
David Allan Wedlake, Houston, TX
(US)(51) **Int. Cl.**
C10B 57/04 (2006.01)
C10B 55/10 (2006.01)(52) **U.S. Cl.** **201/23**(73) Assignee: **Foster Wheeler USA Corporation**,
Houston, TX (US)(57) **ABSTRACT**(21) Appl. No.: **13/531,506**(22) Filed: **Jun. 23, 2012****Related U.S. Application Data**(60) Provisional application No. 61/500,250, filed on Jun.
23, 2011.

The invention relates to the production of a biofuel from a feedstock that includes a solid biomass material such as lemna. A hydrocarbon feedstock is fed into the coking process and reaction products generated from the thermal process are collected. The invention further relates to the production of a coke product having an isotropic structure.



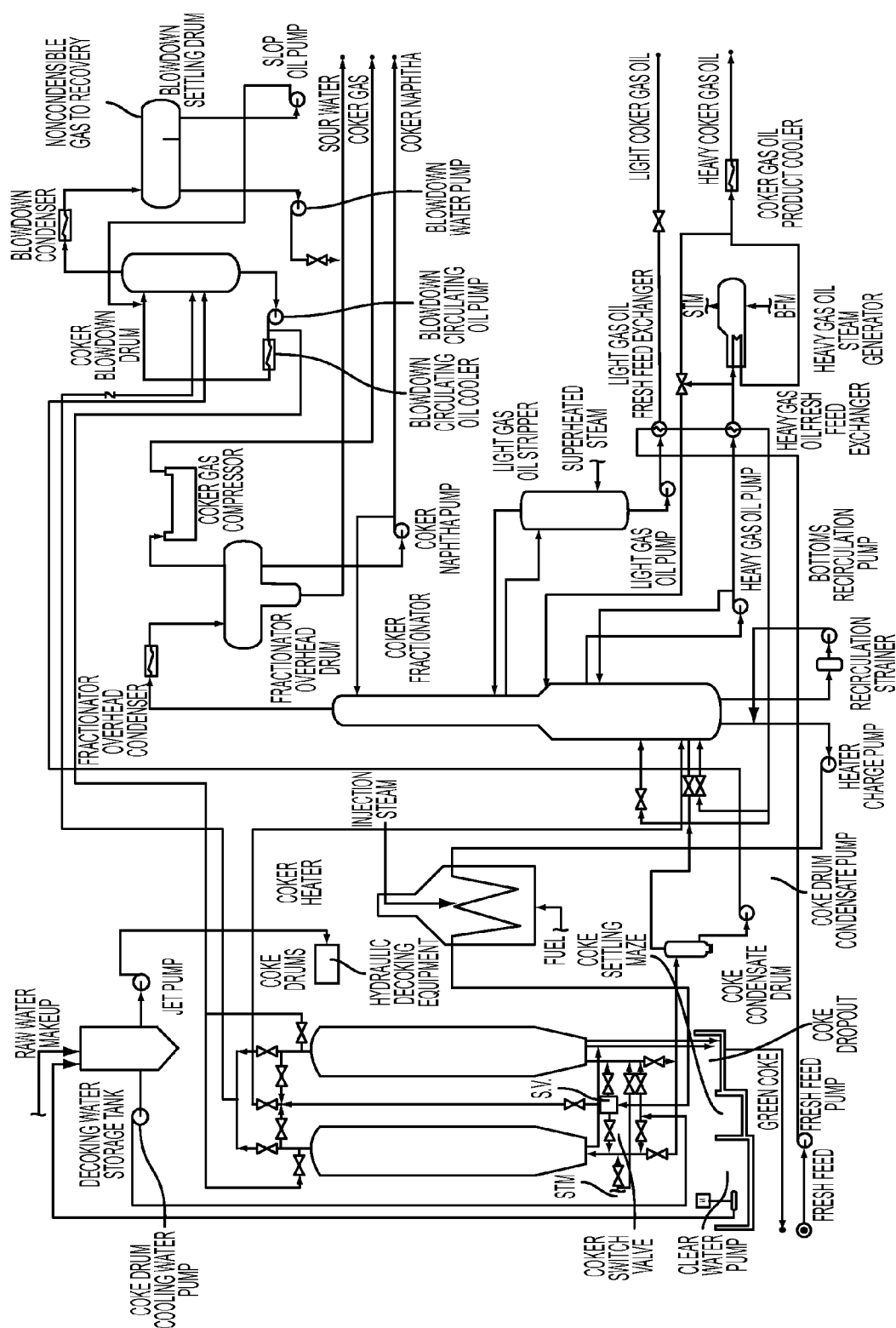


FIG. 1

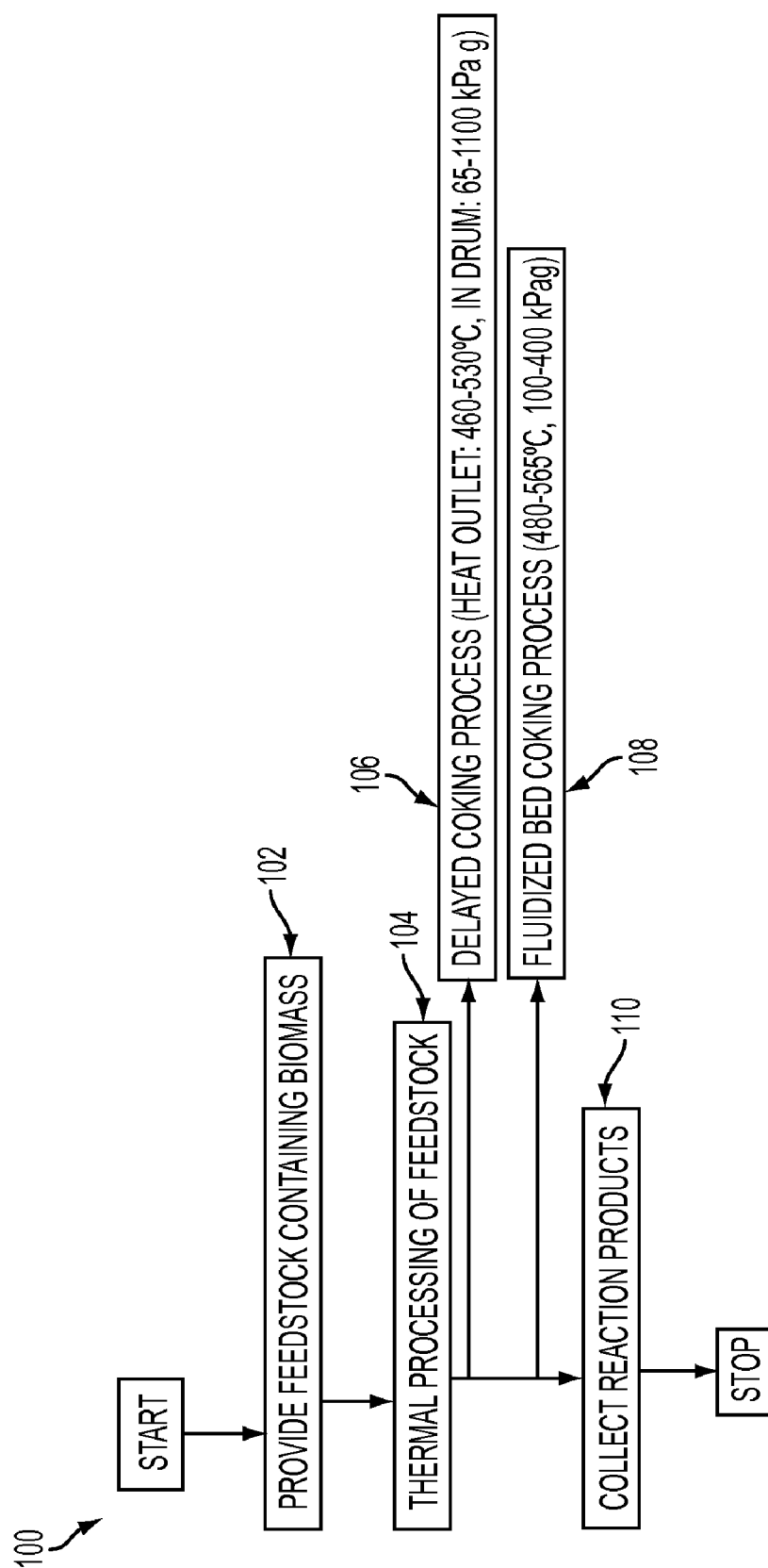


FIG. 2

PYROLYSIS OF SOLID BIOMASS IN THE PRODUCTION OF BIOFUELS

CROSS-REFERENCES TO RELATED APPLICATIONS

[0001] This Application claims the benefit under 35 U.S.C. §119(e) of U.S. Provisional Patent Application Ser. No. 61/500,250 filed Jun. 23, 2011, which is incorporated herein by reference in its entirety as if fully set forth herein.

FIELD OF THE INVENTION

[0002] The invention relates to the production of a biofuel composition from a feedstock that includes a solid biomass material.

BACKGROUND OF THE INVENTION

[0003] Rising costs and threats of shortages and supply interruptions have recently highlighted the need for alternative fuel sources to petroleum-based products. Biofuels have particularly been a focus for alternative fuels.

[0004] The present invention presents a process for the production of biofuels in a refinery thermal processing unit, by the co-processing of biomass together with distillates and residuals from a traditional refining process.

[0005] There are particular problems associated with producing fuels from any variety of renewable feedstocks namely achieving the desirable characteristics of a specific fuel. Accordingly, there is desired a process in which renewable type feedstocks can be effectively used to make high quality fuels.

SUMMARY OF THE INVENTION

[0006] The process for production of biofuel by delayed coking of a feedstock, according to an embodiment of the present invention is directed to the co-processing of a solid biomass with the fresh feed of hydrocarbon in a conventional delayed coking unit.

[0007] In an embodiment of the claimed invention, the feedstock of the conventional delayed coking unit comprises a feed of hydrocarbon such as petroleum residuals with or without distillates and a solid biomass material. In certain embodiments of the invention, the solid biomass material is derived from aquatic plants. For example, aquatic plants such as pre-processed or whole lemna serve as a rich source of lipids, carbohydrates, residual proteins, cellulose and other organic materials that have the potential to be converted to hydrocarbons. Pre-processing of lemna involves extraction of a protein rich stream prior to biomass conversion in a coker. Other sources of solid biomass material that may be used in embodiments of the invention include materials of vegetable origin such as saw grass, woody materials, oil seeds and materials of animal origin such as fats. Biomasses of various types and origins may be used in embodiments of the invention.

[0008] In certain embodiments of the invention, the solid biomass is mixed with hydrocarbon residue in varying proportions and the resultant slurry is coked in a delayed coker. The slurry can be formed in the fresh feed section of the unit or in the coke drum during the reaction stage. The percentage by volume of said amount of solid biomass relative to the fresh feed is in a range from 0.1% to 60%. The proportion of

biomass in the slurry can be increased depending upon the capacity of the coker unit and its ability to handle the biomass material.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] FIG. 1 shows a schematic diagram of a delayed coking process; and

[0010] FIG. 2 shows a flowchart of a process for processing of biomass in accordance with an exemplary embodiment of the invention.

DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS OF THE INVENTION

[0011] In an embodiment of the invention, a delayed coking process with a slurry comprising hydrocarbons and a solid biomass material is carried out in a delayed coker as set forth in FIG. 1, or other suitable refinery thermal processing unit, e.g. visbreaking or thermal cracking unit.

[0012] In an embodiment of the invention, a hydrocarbon feed is fed into the coking process through the bottom liquid pool of a coker fractionator. The fractionator serves as the point from where various liquid and gas products are withdrawn, for example fuel gas and LPG, light naphtha, heavy naphtha, light gas oil, medium gas oil and heavy gas oil. The bottom product from the coker fractionator is fed into a coker heater so that the reactions of thermal cracking can begin. The effluent from the coker heater is then sent to a coke drum, where the reactions of thermal cracking and coking or carbonization proceed to completion, producing coke and an effluent from the coke drum (coking vapor), composed of light hydrocarbons, which is sent to the coker fractionator. In certain embodiments, a portion of the condensed liquids may be recycled and pumped to the coker heater with the feed.

[0013] In an embodiment of the invention, the solid biomass material is mixed with a residual hydrocarbon feed and fed into a coker fractionator.

[0014] In another embodiment of the invention, the solid biomass material may be added directly in the coke drum during the reaction or quenching stage.

[0015] In another embodiment of the invention, the solid biomass material, preferably in slurry form, may be added directly in the coker heater feed line or directly into the coke drum with prior heating. In other embodiments of the invention, the solid biomass material may be added to the coker heater feed line without prior heating.

[0016] Slurried biomass may be heated in stages and flashed following low temperature heating to reduce the load of produced water and acidic hydrocarbons that would otherwise need to be dealt with in the main section of the coker fractionator, coker heater, coke drums, fractionator recovery systems and refinery waste systems.

[0017] The percentage by weight of the amount of solid biomass material relative to the remainder of the slurry is in a range from 0.1% to 60%. In an embodiment of the invention, a preferred weight on the amount of the solid biomass relative to the remainder of the slurry is in a range from 10% to 40%. In another embodiment of the invention, a preferred weight on the amount of the solid biomass relative to the remainder of the slurry is in a range from 20% to 40%. The proportion of biomass in the slurry can vary depending upon the capacity of the coker unit. A small capacity unit may be able to accommodate between 5 and 20 wt % of biomass in petroleum

residue, whereas a large capacity unit may be able to process between 40 and 50 wt % of solid biomass material in the slurry.

[0018] Since the biomass is introduced into the coker feed stream within the range of 0.1% to 60%, coking is carried out at normal temperatures and pressures. In a delayed coker, the heavy oil feed, e.g. vacuum residue is pumped to the coker heater at a pressure of about and preferably 300 to 4000 kPa (about 44 to 580 psig), where it is heated to a temperature from about 460° C. to about 530° C. It is then discharged into the coker drum where a lower pressure prevails to allow volatiles to be removed overhead, typically from 65 to 1100 kPa (about 10 to 58 psig) and preferably in the range of 100 to 300 kPa (about 10 to 160 psig). Typical operating temperatures of the drum top are between about 405° C. and 460° C.

[0019] An embodiment of the process of the invention is set forth in FIG. 2. The flowchart in FIG. 2 depicts a process for the pyrolysis of biomass. In a step of the described process, a feedstock containing biomass is provided (Step 102). In a subsequent step (Step 104), the feedstock is subjected to thermal processing. In certain embodiments of the invention, the thermal processing is carried out using a delayed coking process (Step 106). In other embodiments of the invention, the thermal processing is carried out using a fluidized bed coking process (Step 108).

[0020] When the delayed coking process is used (Step 106), in some embodiments of the invention, the feed stream is heated to a temperature of 460 to 530° C. at a pressure of 300 to 4000 kPa after which the heated stream is discharged into a delayed coker drum at a pressure of 65 to 1100 kPa and a top temperature of 405 to 460° C.

[0021] When the fluidized bed coking process is used in the thermal processing step (Step 108), the feed stream is discharged into a fluidized bed coking reactor at a pressure from atmospheric to 400 kPa and a temperature of 480 to 565° C.

[0022] The solid biomass typically starts to decompose at temperatures as low as 200° C. However, the stability of the solid biomass during the pyrolysis process is not compromised because the main reactions take place in the coke drum and are endothermic.

[0023] In an embodiment of the invention, the lower temperature biomass decomposition reactions produce reaction water and a number of potentially valuable chemical species including acetic acid.

[0024] The biomass decomposition reactions in the delayed coker at high temperatures in the coke drum impact the overall reacting mass. The inlet reacting material needs to be at a temperature sufficiently high to overcome the decomposition endothermic reaction of the biomass. This temperature is significantly higher than the temperature that would be needed in a conventional coker and is dependent on the amount of biomass in the feed blend. This has an impact not only on the operation but on the specification of heat transfer equipment, typically a fired heater, to supply a higher than normal enthalpy.

[0025] An embodiment of the invention is directed to an alternative configuration for co-processing biomass in a delayed coker, wherein a pre-reaction section that is either within or external to the coker. The use of a pre-reaction section either within or external to the coker would have the following advantages:

a. Remove a significant amount of reaction water from the coker operation, simplifying processing of resultant products.

b. It reduces the impact of the total enthalpy variance compared to non-biomass operations required in the coker.

c. Remove and recover water soluble acid components for the coker. The components could be recovered separately if deemed commercially attractive.

d. The segregation of the acid water from the other coker water streams simplifies corrosion and treatment of the normal water streams in and from the delayed coker.

e. The pre-reaction system can be configured a number of different ways. Some of these are: (1) Slurry with hot petroleum residue and flash off the water and light components using a simple vessel; and, (2) Slurry with hot petroleum residue and strip off the water and light components in a tower system.

Working Examples

[0026] The present invention will be understood and assessed more easily from the examples presented below. However, these examples are only to be regarded as being representative of the scope of the present invention and do not in any way limit the invention.

[0027] The dried lemma biomass that is used as a solid biomass material in certain embodiments of the invention, has the following composition (in wt %) as set forth in Table 1, which can vary depending on growth optimization and degree of pre-processing following protein extraction.

TABLE 1

Minerals	Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen
6.95	45.89	6.04	3.71	0.27	37.15

[0028] The lemma biomass is a light fluffy solid with a density of about 490 kg/m³. It may be pelletized for shipment to the refinery to minimize deliquescent water absorption and provides ease of handling with minimal dusting. The biomass contains lipids, carbohydrates, residual proteins, cellulose and other organic materials of little or no interest to a typical petroleum refiner except as to the potential to convert it to hydrocarbons and especially valuable liquid transportation fuels or chemical intermediates.

[0029] Hydrocarbons derived from mineral sources are composed mainly of organic compounds such as carbon and hydrogen with varying amounts of sulfurous and nitrogenous molecules and very minor amounts of oxygen, generally less than 0.5%, and metals. The biomass assay above compared to typical delayed coker petroleum residue feedstock shows very low sulfur, high nitrogen and metals plus very high oxygen content. The biomass carbon to hydrogen weight ratio (C:H) is 7.6 but it is only 52% by weight of the total. In comparison, a typical heavy petroleum residue fed to a commercial delayed coker might have a hydrogen content of 8.5 to 11 percent by weight with a C:H ratio on the order of 8.5 to 9.0. This ratio varies significantly by crude derivation and residue processing upstream of the delayed coker. By inspection, it can be expected that the yield of liquid hydrocarbons from converting biomass in a delayed coker will be lower than that obtained from conventional residue feeds. Furthermore, the conversion of complex biological organic solid compounds to non-condensable gases, liquids and coke (char) would be unique in a delayed coker and the reactions more complex than those encountered in conventional coking of petroleum liquid residues, even complex residues.

Example 1

[0030] The lemna biomass residue, following protein extraction, was co-processed with different petroleum residues in a delayed coker pilot plant to provide proof of principle of conversion of the biomass to liquids usable in a petroleum refinery and to determine information on how the reactions differ from conventional coking. This work was done in multiple runs each of which involved processing standard petroleum residues obtained from a commercial refineries as a baseline operations. On other runs the lemna biomass was mixed with the residue in varying proportions that the pilot plant equipment could handle and the resultant slurry was coked. Each run set was made with a fixed baseline residue which was also the slurried liquid vehicle. To maximize liquid yields each run was made at a low pressure of 15 psig and zero recycle, i.e. none. Feeds and products were analyzed. The results were subjected to review and analysis and the net yield structure from the biomass was determined by difference.

[0031] Slurry concentrations with 10 and 20% wt. biomass in petroleum residue were tested. This was the limit of the pilot plant capability. However in a commercial unit, depending on the capability of the unit, higher concentrations are possible up to 40 or 50% wt. or more.

[0032] Table 2 below shows the results of coking lemna biomass as a 10% blend with a light vacuum residue.

TABLE 2

Yield & Elemental Composition of Lemna Biomass Coking Products								
	wt %	Metals & Minerals	C	H	N	S	O	Total
Gas	24.66	0.00	28.22	0.00	0.00	0.00	71.78	100.00
Dissolved CO ₂	0.51	0.00	27.27	0.00	0.00	0.00	72.73	100.00
NH ₃	3.41	0.00	0.00	17.65	82.35	0.00	0.00	100.00
Reaction H ₂ O	17.34	0.00	0.00	11.11	0.00	0.00	88.89	100.00
H ₂ S	0.05	0.00	0.00	5.88	0.00	94.12	0.00	100.00
Liquid Product	31.83	Minimal	84.67	8.12	0.77	0.44	6.08	100.08
Coke	22.20	16.79	63.60	2.45	3.56	0.43	13.19	100.02
Total	100.00	3.73	48.17	5.66	3.85	0.28	38.35	100.03
Biomass Assay		3.60	47.54	6.26	3.85	0.28	38.49	100.00
Error		3.6%	1.3%	-9.5%	0.0%	0.5%	-0.4%	

[0033] The results on varying sets and with different vacuum residues being co-processed were similar. Variances in the totals are due to (1) "noise" in the yields, recoveries and analyses by difference; (2) reproducibility and repeatability of feed and product testing and (3) minor data reconciliation efforts by researchers.

[0034] The lemna biomass mixes well with petroleum vacuum residue. The biomass has a particle size averaging about 100 to about 150 microns and the bulk density is about 490 kg/m³. If the biomass is pelletized to provide environmentally low impact, more safe and convenient transportation, crushing and grinding would be used to produce the small particles for testing. Mixing will be improved by grinding to smaller particles, say 50 micron average size.

[0035] The principle of breakdown of solid biomass by coking to gas, liquid products and coke is demonstrated effectively, i.e. proof of principle. In particular liquid products for further processing in a petroleum refinery are produced at a substantial amount.

[0036] In an embodiment of the invention, the gas produced is nearly all CO₂ with minor amounts of hydrogen and light hydrocarbons (methane, ethane, ethene, etc).

[0037] In an embodiment of the invention, a high percentage of light gas, greater than 20%, is produced compared to the typical 8 to 10% that is common when coking neat petroleum residues. A high percentage of the biomass nitrogen content reacts to form ammonia.

[0038] The high relative oxygen content of the biomass relative to petroleum delayed coker feedstock is shown to react mainly to gas as CO₂ and water with a relatively high amount of oxygen in the coke. The liquid product has a high amount of oxygen relative to liquid product produced from coking petroleum residue feed. But the value is low compared to the total biomass oxygen content and when diluted in the operation with the liquid produced from the petroleum residue, the impact on other refinery processes such as hydrotreaters is mitigated.

Reactions

[0039] The oxygen reacting with coke forming components in the feed and resulting in higher oxygen content coke, making the coke more isotropic. This finding could be used by mixing limited, low biomass rates to improve the isotropic nature affecting friability and hardness of specialty anode coke. During the testing at mixtures of 10% and 20% by

weight biomass in petroleum residue we were able to significantly affect the physical coke structure. Coke produced without any biomass in the feed had a sponge texture consistent with good anode coke when a petroleum residue known for making anode coke was employed. The coke produced with 10% and 20% biomass in the feed blend was very dense, exhibited low porosity consistent with highly isotropic shot coke structure. This phenomenon is explained by the released biomass high content oxygen compounds reacting with the coke forming materials in the bio-tars and the petroleum residue.

[0040] Although the present invention has been described in its preferred embodiments and with representative examples, the basic concept guiding the present invention of a process for production of biofuels from the co-processing of biomass together with hydrocarbon feedstock in a delayed coking unit is described herein in a manner that would allow a person skilled in the art to put into practice variations, modifications, changes, adaptations and substitutions that are compatible with the subject matter treated here, though with-

out deviating from the spirit and scope of the present invention, as represented by the appended claims.

What is claimed is:

1. A process for production of biofuels by co-processing of biomass in a refinery thermal processing unit, comprising the steps of:

feeding a feed material to a thermal processing unit wherein the feed material comprises a mixture of hydrocarbons and a solid biomass material;
thermally processing the feed material; and
collecting reaction products generated from the thermal processing of the feed material.

2. The process of claim 1, wherein the solid biomass material is derived from a plant source, an animal source or an aquatic source.

3. The process of claim 2, wherein the aquatic source is an aquatic plant.

4. The process of claim 3, wherein the aquatic plant is lemna or derived as a solid residual from lemna following protein extraction.

5. The process of claim 1, wherein the hydrocarbons in the feed are petroleum residuals and distillates.

6. The process of claim 1, wherein the solid biomass material is present at a concentration of 10-20 wt %.

7. The process of claim 1, wherein the solid biomass material is present at a concentration of 40-50 wt %.

8. The process of claim 1, wherein the solid biomass material is present at a concentration of 0.1-60 wt %.

9. The process of claim 1, wherein the thermal processing unit is a delayed coker.

10. The process of claim 1, wherein the reaction products include carbon dioxide, ammonia and acetic acid.

11. The process of claim 4, wherein the lemna is preprocessed to remove protein prior to being introduced in the feed.

12. The process of claim 1 wherein the feed material is fed into a coker fractionator.

13. The process of claim 1 wherein the feed material is fed directly to the coke drum.

14. The process of claim 1 wherein the feed material is fed directly to a heater inlet.

15. The process of claim wherein the feed material is heated prior to being added to the thermal processing unit.

16. The process of claim 1 in which the thermal process is a delayed coking process.

17. The process of claim 1 in which the thermal process is a fluidized bed coking process.

18. The process of claim 14 in which the coking process is a delayed coking process in which the feed stream is heated to a temperature of 460 to 530° C. at a pressure of 300 to 4000 kPa after which the heated stream is discharged into a delayed coker drum at a pressure of 65 to 1100 kPa and a temperature of 400 to 475° C.

17. The process of claim 15 in which the coking process is a fluidized bed coking process in which the feed stream is discharged into a fluidized bed coking reactor at a pressure from atmospheric to 400 kPa and a temperature of 480 to 565° C.

18. A process for producing isotropic coke, comprising the steps of:

- a) combining a feed material comprising a mixture of hydrocarbons and a solid biomass material, and
- (b) subjecting the combined material to a thermal process to produce an isotropic coke.

19. The process of claim 18, wherein the isotropic coke exhibits low porosity.

20. The process of claim 18, wherein the solid biomass material is present in the feed material at 0.1% to 60% by weight.

* * * * *