



(51) International Patent Classification:

C10B 49/22 (2006.01) C10B 55/10 (2006.01)

C10B 53/02 (2006.01) C10J 3/46 (2006.01)

(21) International Application Number:

PCT/US2023/026190

(22) International Filing Date:

26 June 2023 (26.06.2023)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

63/356,722 29 June 2022 (29.06.2022) US

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(54) Title: CO-PROCESSING OF BIOMASS DURING FLUIDIZED COKING WITH GASIFICATION

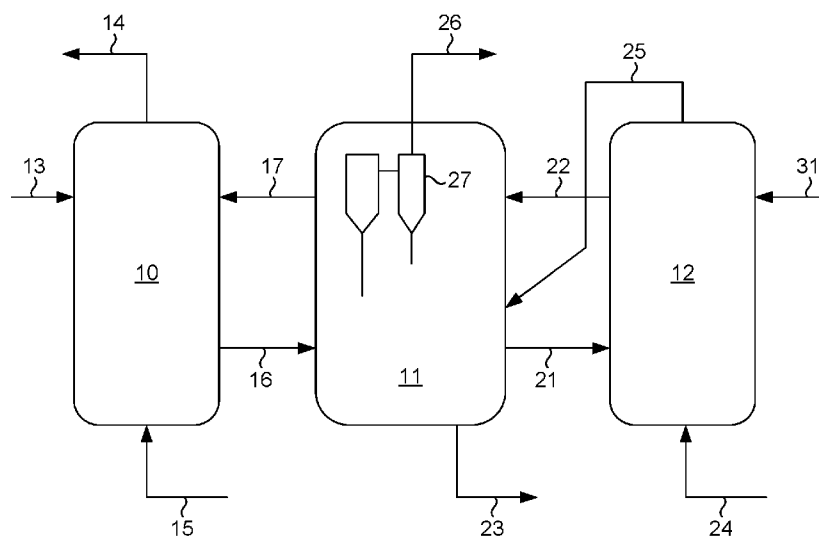


FIG. 1.

(57) Abstract: Systems and methods are provided for integrated coking and gasification of a biomass feed in a three-vessel fluidized coking system under co-processing conditions so that biomass is co-fed with a conventional and/or mineral coker feed, such as a feed containing resid or heavy crude oil. It has been discovered that co-processing of a biomass feed can unexpectedly increase the reaction rate for coking of the conventional / mineral coker feed. This unexpected increase in reaction rate can allow for modification of how the three-vessel fluidized coking reaction system is operated. The resulting modification in operating conditions can allow for production of a modified and/or improved product slate from the fluidized coker. The modifications in the product slate can include an increase in total liquid products as well as a decrease in micro carbon residue and/or n-heptane insolubles in the total liquid products.

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(81) **Designated States** (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, MG, MK, MN, MU, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) **Designated States** (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, CV, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SC, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, ME, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
- *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:

- *with international search report (Art. 21(3))*

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**CO-PROCESSING OF BIOMASS DURING FLUIDIZED COKING WITH
GASIFICATION****FIELD**

[0001] Systems and methods are provided for co-processing biomass in a reaction system
5 for performing fluidized coking and gasification, where the reaction system includes at least
one intervening reactor vessel for heat transfer between the fluidized coker and the gasifier.

BACKGROUND OF THE INVENTION

[0002] One area of focus for reducing net greenhouse gas emissions from energy
production, or more generally for production of carbon-based products, is to use biomass and/or
10 fractions derived from biomass as the source for at least part of the carbon in a fuel or other
carbon-based product. Because biomass removes CO₂ from the environment as it grows, the
net CO₂ generated by combustion of a fuel derived from biomass is offset by the CO₂ consumed
during the growth of the biomass.

[0003] Due to the difficulties in handling solid biomass in many types of refinery
15 equipment a common technique for processing biomass is to use an initial pyrolysis stage to
convert the biomass. Instead of having to build a dedicated pyrolysis reactor for handling
biomass, it would be desirable to use existing refinery facilities for processing of biomass. A
fluidized coker is an example of an existing refinery process that can potentially co-process
biomass.

[0004] Some types of fluidized coker reaction systems correspond to systems that use
20 three reaction vessels. The three reaction vessels correspond to a coker reactor, an intermediate
heater, and a gasifier. In this type of three reaction vessel configuration, instead of forming
CO₂ during the gasification process, the overhead gas can instead optionally correspond to a
gas stream that includes synthesis gas components. It would be desirable to develop improved
25 methods for co-processing biomass in such three-vessel fluidized reactor systems.

[0005] U.S. Patent Application Publication 2018/0118644 describes performing both
partial oxidation and pyrolysis of biomass within the same reactor environment, so that the heat
for the pyrolysis reaction can be generated in-situ by the partial oxidation.

[0006] U.S. Patent Application Publication 2005/0095183 describes a multi-stage
30 gasification system for conversion of biomass or municipal solid waste into a synthesis gas
product while reducing the amount of carbon char and/or tar in the product.

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[0007] U.S. Patent Application Publication 2019/0144756 describes methods for fluidized coking with increased liquids production.

SUMMARY OF THE INVENTION

[0008] In an aspect, a method for co-processing biomass in a fluidized coking system is provided. The method includes exposing a feed containing 1.0 wt% to 60 wt% of biomass and 40 wt% to 99 wt% of a mineral fraction having a T10 distillation point of 500°C or higher, to a fluidized bed of particles under fluidized coking conditions in a reactor vessel to form i) a coker effluent having a liquid portion, ii) char, coke, or a combination thereof, at least a portion of the char, coke, or combination thereof being deposited on the particles to form particles comprising deposited char, coke, or a combination thereof, and iii) additional hydrocarbons associated with the particles comprising deposited char, coke, or a combination thereof. The method further includes passing at least a portion of particles comprising deposited char, coke, or a combination thereof from the reactor vessel into a heater vessel. The at least a portion of particles comprising deposited char, coke or a combination thereof can contain 0.08 wt% or less of the associated additional hydrocarbons, relative to a weight of the feed. The method further includes mixing the at least a portion of the particles comprising deposited char, coke, or a combination thereof with a portion of partially gasified particles in the heater vessel to form a heated particle mixture. The method further includes passing a first portion of the heated particle mixture into the reactor vessel. The method further includes passing a second portion of the heated particle mixture into a gasification vessel. The method further includes introducing an oxygen-containing stream and steam into the gasification vessel. The method further includes exposing the second portion of the heated particle mixture to oxidation conditions in the gasification vessel to form a gas phase product, and partially gasified particles. Additionally, the method includes passing at least a portion of the partially gasified particles from the gasification vessel to the heater vessel. In some aspects, the liquid portion of the coker effluent can have a micro carbon residue content of 0.5 wt% or less, an n-heptane insolubles content of 0.5 wt% or less, or a combination thereof.

[0009] In another aspect, a liquid product is provided. The liquid product can be, for example, the liquid portion of a coker effluent. The liquid product includes 30 wt% to 50 wt% of naphtha boiling range components, 30 wt% to 50 wt% of heavy distillate boiling range components, 10 wt% to 25 wt% of light distillate boiling range components, and 5.0 wt% or less of vacuum resid boiling range components. Additionally, the liquid product can contain 0.9 wt% to 3.0 wt% of oxygen. Additionally, the liquid product can contain a) 0.05 wt% to 0.5

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wt% of micro carbon residue content, b) 0.05 wt% to 0.5 wt% of n-heptane insolubles, or c) a combination of a) and b).

BRIEF DESCRIPTION OF THE DRAWING

- 5 [0010] FIG. 1 shows an example of a fluidized bed coking system including a coker, a heater, and a gasifier.
- [0011] FIG. 2 shows results from pyrolysis of various feeds.
- [0012] FIG. 3 shows results from co-pyrolysis of cellulose with mineral resid and a comparison with predicted model results.
- 10 [0013] FIG. 4 shows results from co-pyrolysis of pine wood chips with a mineral resid at 530°C.
- [0014] FIG. 5 shows results from co-pyrolysis of pine wood chips with a mineral resid at 360°C.
- [0015] FIG. 6 shows the impact of increased reaction rate on hydrocarbon carry under in a three-vessel fluidized coking configuration.
- 15 [0016] FIG. 7 shows model product yield results that were generated from a fluidized coking process model at various temperatures.
- [0017] FIG. 8 shows modeled results for fluidized coking of resid alone versus co-processing of resid and biomass.
- [0018] FIG. 9 shows distillation profiles for total liquid products from fluidized coking of various feeds.
- 20 [0019] FIG. 10 shows additional analytical results for total liquid products from fluidized coking of various feeds.
- [0020] FIG. 11 shows Fourier-transform ion cyclotron resonance (FTICR-MS) analysis of the classes of compounds present in total liquid products from fluidized coking of various feeds.
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DETAILED DESCRIPTION OF THE INVENTION

- [0021] All numerical values within the detailed description and the claims herein are modified by “about” or “approximately” the indicated value, and take into account experimental error and variations that would be expected by a person having ordinary skill in the art.
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Overview

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[0022] In various aspects, systems and methods are provided for integrated coking and gasification of a biomass feed in a three-vessel fluidized coking system under co-processing conditions so that biomass is co-fed with a conventional and/or mineral coker feed, such as a feed containing resid or heavy crude oil. It has been discovered that co-processing of a biomass feed can unexpectedly increase the reaction rate for coking of the conventional / mineral coker feed. This unexpected increase in reaction rate can allow for modification of how the three-vessel fluidized coking reaction system is operated. The resulting modification in operating conditions can allow for production of a modified and/or improved product slate from the fluidized coker. The modifications in the product slate can include an increase in total liquid products as well as a decrease in micro carbon residue and/or n-heptane insolubles in the total liquid products. Additionally, co-processing of biomass with a conventional / mineral coker feed can result in a total liquid product with an unexpected composition with regard to the types of components present within the total liquid product.

[0023] It is noted that the term “gasification” is used herein to broadly cover conversion of biomass to CO and/or H₂ in varying ratios of CO to H₂, including partial burn conditions that result in CO production with a reduced or minimized amount of H₂ production (such as substantially no H₂ production).

[0024] During operation of a three-vessel fluidized coking system, the center vessel corresponds to a “heater” vessel that provides several functions. First, the heater vessel facilitates heat transfer between the gasifier vessel and the reactor vessel. In the heater, hot coke from the gasifier mixes with cold coke from the reactor. This results in moderately heated particles that can then be returned in part to the reactor to provide heat for the endothermic coking reaction. Additionally, the gas phase products generated in the gasifier are returned at least in part to the heater as part of the fluidizing gas for transferring hot coke back to the heater. These gases then exit from the three-vessel fluidized coking system from a heater outlet, such as a heater overhead outlet.

[0025] The heater vessel, however, also places some constraints on the operating conditions for the three-vessel fluidized coking system. For example, one of the constraints on operation is the need to fully cure coke formed in the reactor vessel prior to transferring the coke particles to the heater vessel. The primary reaction in the coking reactor vessel is a pyrolysis reaction that can occur relatively quickly under a variety of conditions. However, the combination of a) reaction temperature and b) residence time for coke particles within the reactor vessel is typically higher in severity than is required for only performing the coking reaction. Instead, the residence time and temperature within the coking vessel are selected at a

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higher severity level to allow for additional reaction of the “hydrocarbon carry under” (HCCU). The HCCU corresponds to hydrocarbons (coke precursors) that are entrained with the coke particles as the coke particles exit from the reactor. Such entrainment can include entrainment within pores in the coke particles, or entrainment in the flow of coke particles. If these additional hydrocarbons are still at least partially in the fluid phase when they enter the heater, the increased temperature in the heater can volatilize these hydrocarbons. The volatilized hydrocarbons can then deposit in the overhead exit of the heater, resulting in fouling and thereby decreasing the operating lifetime between cleaning cycles.

5 [0026] To maintain longer operating lifetime between maintenance events, the coking reactor is operated at combinations of fluidized bed temperature and coke particle residence time that are higher in severity than is required for simply performing pyrolysis. This allows for additional reaction of the HCCU hydrocarbons. The additional reaction allows for additional pyrolysis of the HCCU hydrocarbons, so that the amount of potentially volatile hydrocarbons exiting from the reactor is reduced or minimized. However, this also means that additional pyrolysis occurs for substantially the entire feed in the coking reactor.

10 [0027] In various aspects, by co-processing a sufficient amount of biomass with a conventional resid feed, the reaction severity within the reactor can be reduced. It is noted that the impact of the biomass is catalytic in nature, so that at least a portion of the benefit can be realized even at relatively low amounts of biomass in the feed. This can allow for improvements in the resulting product slate from fluidized coking. First, the net amount of liquid product can be increased while reducing the production of light ends and coke. Second, even though the liquid product includes an increased amount of heavier liquids (such as heavy coker gas oil), the amount of micro carbon residue and/or n-heptane insoluble in the liquid product can be reduced or minimized. The reduction in micro carbon residue and/or n-heptane insolubles is accompanied by more general changes in the composition of the liquid product when co-processing biomass. It is noted that the benefits of reduction in micro carbon residue and/or n-heptane insolubles are realized when performing co-processing of biomass with a mineral feed that contains a sufficient amount of micro carbon residue and/or n-heptane insolubles. Thus, this benefit is typically realized when co-processing biomass with mineral feeds that include a substantial portion of components with a boiling point of 500°C or above.

25 [0028] In some aspects, additional benefits from co-processing biomass with a mineral feedstock can be achieved for mineral feedstocks containing a sufficient amount of micro carbon residue (MCR) and/or n-heptane insolubles. In such aspects, a mineral portion of the feedstock for co-processing with biomass (such as a vacuum resid feedstock for co-processing)

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can have a micro carbon residue of 5.0 wt% or more, or 15 wt% or more, or 20 wt% or more, or 30 wt% or more, such as up to 50 wt% or possibly still higher. Additionally or alternately, a mineral portion of the feedstock for co-processing with biomass can have an n-heptane insolubles content of 5.0 wt% or more, or 10 wt% or more, or 15 wt% or more, or 20 wt% or more, or 30 wt% or more, such as up to 50 wt% or possibly still higher. After co-processing such a feedstock with biomass, the resulting total liquid product can have a micro carbon residue content of 0.5 wt% or less, or 0.2 wt% or less, or 0.1 wt% or less, such as down to substantially no micro carbon residue content (0.05 wt% or less). Additionally or alternately, after co-processing such a feedstock with biomass, the resulting total liquid product can have a content of n-heptane insolubles of 0.5 wt% or less, or 0.4 wt% or less, or 0.2 wt% or less, or 0.1 wt% or less, such as down to substantially no content of n-heptane insolubles (0.05 wt% or less). In contrast, typical coker liquid products (produces in the absence of a biomass co-feed) can contain 0.6 wt% or more, or 1.0 wt% or more, such as up to 5 wt% or more n-heptane insolubles or MCR.

[0029] In various aspects, the total liquid product can also have an unexpected content of oxygen and/or oxygenated components. In some aspects, the oxygen content of a co-processed total liquid product can be between 0.9 wt% to 3.0 wt%, or 0.9 wt% to 2.5 wt%. This is in contrast to a conventional total liquid product from processing of a mineral feed, which would be expected to have an oxygen content of less than 0.5 wt%. This is also different from a pyrolysis oil, which would be expected to have an oxygen content of well over 10 wt%. Additionally, it has been discovered that the oxygen content of a co-processed total liquid product is unexpectedly lower than the oxygen content that would be expected based on a weighted average of the feeds used for co-processing. The unexpected oxygen content also can be characterized based on the number of components / compounds in the total liquid product that include at least one oxygen atom. For a total liquid product from a conventional mineral feed, the content of oxygen-containing components would be expected to be less than 5.0 wt%. For a pyrolysis oil, more than 50 wt% of the compounds in the total liquid product would be expected to correspond to oxygen-containing components. By contrast, a co-processed total liquid product can contain between 10 wt% to 40 wt% of oxygen-containing components, or 10 wt% to 25 wt%, or 20 wt% to 40 wt%.

[0030] It is noted that the above benefits can be achieved while producing a total liquid product from co-processing of biomass and a mineral resid feedstock that includes 30 wt% to 50 wt% of naphtha boiling range components, 30 wt% to 50 wt% of heavy distillate boiling range components, 10 wt% to 25 wt% of light distillate boiling range components, and 5.0 wt%

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or less of vacuum resid boiling range components (such as down to substantially no vacuum resid boiling range components).

[0031] In addition to the above benefits related to an unexpected improvement in reaction rates within the coker reactor, a variety of additional features and/or benefits can be realized by using integrated pyrolysis and gasification to co-process biomass with a conventional feed for fluidized coking. One example of a benefit is a reduction in net greenhouse gas emissions. By integrating pyrolysis and gasification, the heat for pyrolysis can be provided by the heat generated during gasification. Because CO₂ was consumed by the biomass during the growth of the biomass, any CO₂ generated from gasification of the biomass represents no net addition of CO₂ to the environment. In aspects where co-processing is performed, the reduction in net CO₂ production can be proportional to the amount of biomass char that is gasified relative to the amount of conventional feed that is gasified.

[0032] Another benefit or feature can be related to synergies between the gasification conditions and the pyrolysis processing conditions. In various aspects, the gasification conditions can be selected so that partial oxidation of char is performed in the gasifier. Any coke generated by co-processing of a conventional feed in the reactor can also be exposed to the partial oxidation conditions. Operating the gasifier under partial oxidation conditions can allow a synthesis gas product to be recovered from the gas phase products of the gasifier. The synthesis gas product can be used as a fuel, or the synthesis gas product can be used as an input flow for the production of additional liquid products.

[0033] In aspects where the gasifier is operated under partial oxidation conditions, so that an increased amount of CO is produced, the amount of heat generated per carbon atom introduced into the gasifier will be lower than the heat that would be generated by performing full oxidation and converting substantially all carbon into CO₂. Due to this reduction in heat generated by the gasifier, there is an increased likelihood that maximizing the production of liquids in the pyrolysis reactor may result in production of insufficient amounts of coke and/or char to maintain heat balance in the integrated system. For a conventional pyrolysis process, the goal is to select process conditions that maximize liquid yield. By contrast, in some aspects, instead of maximizing the ratio of liquid products to char that is generated during pyrolysis, the relative amount of char production can be increased so that additional char is provided to the gasification process. In such aspects, the increased char production can allow sufficient char to be delivered to the gasifier to maintain heat balance and/or can reduce or minimize the amount of additional biomass (or other fuel) that is added as a supplemental fuel to the gasifier.

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[0034] In some aspects where integrated pyrolysis and gasification is performed, biomass can correspond to less than 50 wt% of the feed. In such aspects, the heat generated in the gasifier from partial oxidation can be sufficient to maintain heat balance while still operating at maximum liquid yield for the pyrolysis reaction. In other aspects, such as some aspects where biomass corresponds to 50 wt% to 60 wt% of the feed, the pyrolysis conditions can be selected to provide increased char production. Additionally or alternately, in some aspects where the char and/or coke generated during pyrolysis is not sufficient, additional biomass can be added to the gasifier in order to maintain heat balance.

[0035] In some aspects, additional particles can also be present in the reaction environment and/or can be added to the reaction environment. In a conventional fluidized coking process, coke particles are generated in the fluidized coking environment. The coke particles are partially gasified to provide heat, but the remaining mass of coke (in the form of particles) after the partial gasification can be sufficient to transport heat from the gasifier to the other reaction vessel(s) in the reaction system. However, in aspects where a sufficient amount of biomass is present in the feedstock, the mass of the char and/or coke that enters the gasifier may be relatively close to the amount of char and/or coke that is needed to maintain heat balance within the system. In such aspects, additional particles can be added to the system to act as a heat transfer particles, and to maintain the fluidized bed nature of the reaction environment in the reactor. In some aspects, relatively inert particles can be used, such as sand. In other aspects, at least a portion of the particles can correspond to a catalyst for catalyzing the pyrolysis reaction.

DEFINITIONS

[0036] In this discussion, some feeds, fractions, or products may be described based on a fraction that boils below or above a specified distillation point. For example, a 343°C-product corresponds to a product that substantially contains components with a boiling point (at standard temperature and pressure) of 343°C or less. Similarly, a 343°C+ product corresponds to a product that substantially contains components with a boiling point of 343°C or more. Substantially containing components within a boiling range is defined herein as containing 90 vol% or more of components within the boiling range, optionally 95 vol% or more, such as a product where all components are within the specified boiling range.

[0037] In this discussion, a liquid product is defined as a product that is substantially in the liquid phase at 20°C and ~100 kPa-a. Similarly, a gas product is defined as a product that is substantially in the gas phase at 20°C and ~100 kPa-a.

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[0038] In this discussion, reference may be made to conversion of a feedstock relative to a conversion temperature. Conversion relative to a temperature can be defined based on the portion of the feedstock that boils at greater than the conversion temperature. The amount of conversion during a process (or optionally across multiple processes) can correspond to the weight percentage of the feedstock converted from boiling above the conversion temperature to boiling below the conversion temperature. As an illustrative hypothetical example, consider a feedstock that includes 40 wt% of components that boil at 650°F (~343°C) or greater. By definition, the remaining 60 wt% of the feedstock boils at less than 650°F (~343°C). For such a feedstock, the amount of conversion relative to a conversion temperature of ~343°C would be based only on the 40 wt% that initially boils at ~343°C or greater. If such a feedstock could be exposed to a process with 30% conversion relative to a ~343°C conversion temperature, the resulting product would include 72 wt% of ~343°C- components and 28 wt% of ~343°C+ components.

[0039] As defined herein, the term “hydrocarbonaceous” includes compositions or fractions that contain hydrocarbons and hydrocarbon-like compounds that may contain heteroatoms typically found in petroleum or renewable oil fraction and/or that may be typically introduced during conventional processing of a petroleum fraction. Heteroatoms typically found in petroleum or renewable oil fractions include, but are not limited to, sulfur, nitrogen, phosphorous, and oxygen. Other types of atoms different from carbon and hydrogen that may be present in a hydrocarbonaceous fraction or composition can include alkali metals as well as trace transition metals (such as Ni, V, or Fe).

[0040] In this discussion, distillation points and/or distillation ranges can be determined according to ASTM D2887. In the event that a portion of a sample is not suitable for characterization using ASTM D2887, ASTM D7169 can be used instead.

[0041] In this discussion, the vacuum resid boiling range is defined as 538°C and above. It is noted that it is difficult to characterize the end boiling point for some vacuum resid fractions, but the portions of vacuum resid that are susceptible to distillation can have an end point of up to roughly 750°C. It is further noted that fractions composed primarily of vacuum resid often contain substantial amounts of lower boiling components. In this discussion, a vacuum resid boiling range fraction is a fraction that has a T10 distillation point of 480°C or higher (such as up to 600°C).

[0042] In this discussion, the naphtha boiling range is defined as 29°C to 221°C. The light distillate boiling range is defined as 221°C to 343°C. It is noted that the light distillate boiling range could also be referred to as the diesel boiling range. The heavy distillate boiling range is

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defined as 343°C to 538°C. It is noted that the heavy distillate boiling range could also be referred to as the vacuum gas oil boiling range.

[0043] Micro carbon residue can be determined according to ASTM D4530. The content of n-heptane insolubles in a sample can be determined according to ASTM D3279.

5 Feedstocks

[0044] In various aspects, biomass can be co-processed in a fluidized bed coking environment. The biomass can be co-processed with a feedstock not derived from biomass, such as a mineral feedstock, and/or a feedstock having a boiling range corresponding to the conventional boiling range for a fluidized coking feed. In some aspects, the biomass can
10 correspond to 1.0 wt% to 60 wt% of the feed for co-processing, or 1.0 wt% to 50 wt%, or 1.0 wt% to 35 wt%, or 10 wt% to 60 wt%, or 10 wt% to 50 wt%, or 10 wt% to 35 wt%, or 20 wt% to 60 wt% or 20 wt% to 50 wt%, or 30 wt% to 60 wt%, or 30 wt% to 50 wt%, or 50 wt% to 60 wt%.

[0045] The biomass used for a feed can be any convenient type of inedible lignocellulosic
15 biomass; that is, biomass that is composed primarily of cellulose, hemicellulose, lignin, or a combination thereof. Some forms of biomass can include direct forms of biomass, such as algae biomass and plant biomass. Examples of suitable biomass sources can include woody biomass and switchgrass.

[0046] In aspects where the biomass is introduced into the fluidized coking reactor at
20 least partially as solids, having a small particle size can facilitate transport of the solids into the reactor. Smaller particle size can potentially also contribute to achieving a desired level of conversion of the biomass. Thus, one or more optional physical processing steps can be used to prepare solid forms of biomass for conversion. To prepare solids for gasification, the solids can be crushed, chopped, ground, or otherwise physically processed to reduce the average
25 particle size to 3.0 cm or less, or 2.5 cm or less, or 2.0 cm or less, or 1.0 cm or less, such as down to 0.001 cm or possibly still smaller. For determining an average particle size, the particle size is defined as the diameter of the smallest bounding sphere that contains the particle.

[0047] Without being bound by any particular theory, it is believed that oxygenated
moieties derived from cellulose, lignin and hemicellulose within the biomass contribute to the
30 improved reaction rate when co-processing a mineral feed. In various aspects, the biomass for co-processing can have a cellulose content of 10 wt% or more (relative to a weight of the biomass), or 20 wt% or more, or 30 wt% or more, such as up to using biomass that is substantially composed of cellulose (e.g., a cotton ball or other biomass that contains up to 100 wt% cellulose). In such aspects, the lignin content of the biomass can optionally be less than

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35 wt%, or 30 wt% or less, such as down to having substantially no lignin content (1.0 wt% or less).

[0048] Biomass can be co-processed with one or more additional feedstocks, such as mineral feedstocks, based on the boiling range of the feed. The amount of the one or more additional feedstocks can correspond to 40 wt% to 99 wt% of the feed for co-processing, or 50 wt% to 99 wt%, or 65 wt% to 99 wt%, or 40 wt% to 90 wt%, or 50 wt% to 90 wt%, or 65 wt% to 90 wt%, or 40 wt% to 80 wt%, or 50 wt% to 80 wt%, or 40 wt% to 70 wt%. Conventionally, heavy oil feeds are typically used as feeds for fluidized coking processes. Thus, the heavy oil feed will typically be a heavy (high boiling) reduced petroleum crude; petroleum atmospheric distillation bottoms; petroleum vacuum distillation bottoms, or residuum; pitch; asphalt; bitumen; other heavy hydrocarbon residues; tar sand oil; shale oil; or even a coal slurry or coal liquefaction product such as coal liquefaction bottoms. Such feeds will typically have a Conradson Carbon Residue (ASTM D189-165) of at least 5 wt. %, generally from 5 to 50 wt. %. Preferably, the feed is a petroleum vacuum residuum. In some aspects, the one or more additional feedstocks can have a T10 distillation point (as determined according to ASTM D2887) 343°C or higher, or 400°C or higher, or 450°C or higher, or 500°C or higher, such as up to 600°C or possibly still higher.

[0049] A typical petroleum (mineral) chargestock suitable for processing in a fluidized bed coker can have a composition and properties within the ranges set forth below.

Table 1: Example of Coker Feedstock

Conradson Carbon	5 to 40	wt. %
API Gravity	−10 to 35°	
Boiling Point	340°C+ to 650°C+	
Sulfur	1.5 to 8	wt. %
Hydrogen	9 to 11	wt. %
Nitrogen	0.2 to 2	wt. %
Carbon	80 to 86	wt. %
Metals	1 to 2000	wppm

[0050] It is noted that still other components can be included in a feed for co-processing in a fluidized coker. In some aspects, 20 wt% or less of a feed for co-processing can correspond to components that are a) not biomass and/or derived from biomass and b) have a boiling point below 340°C, such as down to having substantially no components of this type.

Hydrocarbon Carry Under (HCCU)

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[0051] In various aspects, the improvement in reaction rates provided by co-processing lignocellulosic biomass under fluidized coking conditions can allow for changes in the target operating conditions for a feed, thereby allowing for production of a modified and/or improved product slate. This change is enabled in part by reducing the residence time required for full curing of coke precursors entrained in the coke exiting from the coker reactor vessel and passed into the heater vessel.

[0052] Hydrocarbon carry-under (HCCU) corresponds coke precursors that are not fully converted to a solid form prior to exiting from the coker reactor and entering the heater. Due to the higher temperatures in the heater, these coke precursors are volatilized and then deposit on cooler surfaces, such as the overhead exit from the heater. This results in coke formation in the overhead exit, eventually leading to constriction of the exit flow and requiring shut down to restore the flow path in the overhead exit to the original size. To avoid reduced length reaction cycles, the HCCU is maintained at a relatively low level by selecting sufficiently severe reaction conditions. In particular, relative to the average residence time for coke particles in the coker reactor vessel, higher temperatures are selected to maintain the HCCU at a sufficiently low level.

[0053] It has been discovered that co-processing of lignocellulosic biomass (that contains cellulose) in a fluidized coker can provide an increase in reaction rates within the coker reactor. This increase in reaction rates also increases the reaction rate for the curing process for coke precursors. Without being bound by any particular theory, it is believed that the increased reaction rates / increased curing rates are due to the creation of oxygen-containing radicals in the fluidized coking environment. It is believed that these oxygen radicals facilitate cracking of mineral portions of the feed within the fluidized coking environment. Additionally, it is believed that the oxygen radicals can also assist with conversion of some coke precursor compounds into compounds that instead form liquid products. Finally, it is believed that these oxygen radicals assist with the curing process for remaining coke precursors, so that HCCU is substantially reduced or minimized. As a result, the temperature in the fluidized bed of the coker reactor can be reduced while still maintaining a target level of HCCU. By reducing the temperature and/or based on the additional unexpected catalytic benefits of co-processing with biomass, a modified and/or improved product slate can be achieved.

[0054] The amount of HCCU during operation of a three-vessel fluidized coking system is typically maintained at a low level. In various aspects, by co-processing a mineral feedstock with biomass, the temperature and/or coke particle residence time in the coker reactor vessel can be reduced while still maintaining a low level of HCCU. In various aspects, the amount of

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HCCU during operation of a coker reactor vessel can correspond to 0.08 wt% of the input feed or less, or 0.06 wt% or less, such as down to having substantially no HCCU (0.005 wt% or less). The amount of HCCU can be characterized, for example, by sampling cold coke from the coke transfer line between the reactor and heater section of a commercial flexicoker during steady-state operations, and heat-treating the sampled material in an oxygen-free environment at temperatures that match those in the commercial unit's heater section. The wt% mass loss of volatilized material that is removed from the solid sample under these conditions corresponds to the HCCU.

Fluidized Coking System Operating Conditions

10 [0055] The feed for co-processing can be introduced into the fluidized coking reactor by any convenient method. One option is to form a slurry and/or solution of biomass in a conventional feed. As another option, biomass can be introduced separately from the co-feed(s) as a feedstock composed primarily of solids. In this type of aspect, a feed mechanism for delivery of solids such as a screw feeder can be used. The feed can be pre-heated prior to entering the reactor. For example, in aspects where a conventional co-feed is used to form a slurry, pre-heating can increase the temperature of the feed so that it is flowable and pumpable. The slurry can then be passed into the reactor toward the top of the reactor vessel through one or more slurry injection nozzles.

20 [0056] In various aspects, temperatures in the fluidized coking zone of the reactor can be in the range of 400°C to 550°C, or 400°C to 500°C. Pressures can be in the range of 120 kPag to 400 kPag (17 psig to 58 psig), and preferably 200 kPag to 350 kPag (29 psig to 51 psig).

25 [0057] The conditions in the fluidized coking zone can be selected so that a desired amount of conversion of the feedstock occurs in the fluidized bed reactor. The coking reaction and the amount of conversion can be selected to be similar to the values used in a conventional fluidized coking reaction. For example, the conditions can be selected to achieve at least 10 wt% conversion relative to 343°C (or 371°C), or at least 20 wt% conversion relative to 343°C (or 371°C), or at least 40 wt% conversion relative to 343°C (or 371°C), such as up to 80 wt% conversion or possibly still higher. In some aspects, the light hydrocarbon products of the coking (thermal cracking) reactions vaporize, mix with the fluidizing steam and pass upwardly through the dense phase of the fluidized bed into a dilute phase zone above the dense fluidized bed of coke particles. It is noted that in some aspects, other sweep gases such as CH₄, H₂, or other light gases may be used instead of at least a portion of the steam (such as up to in place of substantially all of the steam) to help control the conversion severity. In some configurations, this mixture of vaporized hydrocarbon products formed in the coking reactions flows upwardly

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through the dilute phase with the steam at superficial velocities of ~1 to 2 meters per second (~3 to 6 feet per second), entraining some fine solid particles of coke which are separated from the cracking vapors in the reactor cyclones as described above. The cracked hydrocarbon vapors pass out of the cyclones into the scrubbing section of the reactor and then to product
5 fractionation and recovery. The cracked hydrocarbon vapors can include one or more liquid products with a boiling range of 343°C or less. Examples of 343°C- liquid products include naphtha boiling range products and distillate boiling range products.

[0058] In some aspects, as the cracking process proceeds in the reactor, the coke, char, and/or other particles (such as optional sand particles) pass downwardly through the pyrolysis
10 zone, through the stripping zone, where occluded hydrocarbons are stripped off by the ascending current of fluidizing gas (steam). They then exit the coking reactor and are passed into the heating vessel.

[0059] The heating vessel receives particles from both the coker reactor vessel and from the gasification vessel. Particles arriving from the coker reactor correspond to “cold” particles,
15 while particles arriving from the gasification vessel correspond to “heated” particles. In the heater vessel, the particles mix resulting in transfer of heat from heated particles to cold particles. A portion of the particles are then sent to the coker reactor, while another portion of the particles are sent to the gasification reactor for further heating. A remaining portion of the particles can be withdrawn from the heater vessel. The removal of particles from the heater
20 vessel provides a mechanism for avoiding the build-up of metals within the fluidized coking system.

[0060] The combustion / oxidation products generated in the gasifier (such as synthesis gas components formed during partial oxidation) can serve as a fluidizing gas in the heater for mixing the particles.

[0061] Particles can exit from the heating vessel either by being passed into the coker reactor vessel or by being passed into the gasification reactor. The gasification reactor (gasifier)
25 which contains a fluidized bed of solid particles and which operates at a temperature higher than that of the reactor coking zone. In the gasifier, the coke particles are converted by reaction at the elevated temperature with steam and an oxygen-containing gas into a fuel gas comprising
30 primarily carbon monoxide and hydrogen.

[0062] The gasification zone is typically maintained at a high temperature ranging from 650°C to 1000°C, such as 850°C to 1000°C (1560°F to 1830°F) to maximize H₂/CO; or 650°C to 850°C to maximize CO; or 650°C to 760°C. The gasification zone can be maintained at a pressure ranging from 0 kPag to 1000 kPag (0 psig to 150 psig), preferably from 200 kPag to

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400 kPag (30 psig to 60 psig). Steam and an oxygen-containing gas are passed into the gasifier for reaction with the solid particles comprising coke deposited on them in the coking zone. Preferably, the oxygen-containing gas can have an oxygen content greater than air. Air can be used, but this increases the volume of nitrogen that will subsequently be separated from the gasifier products in order to recover synthesis gas. Alternatively, if the gasifier products are used as a fuel gas, the additional nitrogen from air reduces the concentration of fuel in the fuel gas. In some aspects, the gasification zone can be contained in a gasifier associated with the reactor, such as a gasifier from a fluidized coking system. In some aspects where a system similar to a fluid catalytic cracking system is used, the gasification zone can be contained in a “gasifier” that corresponds to a regenerator associated with a riser reactor.

[0063] In some aspects, the oxygen-containing gas can have a low nitrogen content, such as oxygen from an air separation unit or another oxygen stream including 95 vol% or more of oxygen, or 98 vol% or more, such as up to containing substantially only oxygen. In other aspects, the oxygen-containing gas can generally be enriched relative to air, such as having an oxygen content of 21 vol% or more, or 30 vol% or more, or 40 vol% or more, or 50 vol% or more, such as up to containing substantially only oxygen. In some aspects, the oxygen content can be 21 vol% to 50 vol%, or 21 vol% to 40 vol%, or 21 vol% to 30 vol%. Additionally or alternately, the N₂ content of the oxygen-containing gas can be 70 vol% or less, or 50 vol% or less, or 35 vol% or less, or 20 vol% or less, or 10 vol% or less, such as down to having substantially no content of N₂. In aspects where the oxygen-containing gas is enriched relative to air, it may be desirable to also introduce a diluent stream, to facilitate additional heat transport out of the gasifier. An example of a separate diluent stream can be recycled CO₂ and/or H₂S derived from the overhead gas produced by the gasifier. The amount of diluent can be selected by any convenient method. For example, the amount of diluent can be selected so that the amount of diluent replaces the weight of N₂ that would be present in the oxygen-containing stream if air was used as the oxygen-containing stream. As another example, the amount of diluent can be selected to allow for replacement of the same BTU value for heat removal that would be available if N₂ was present based on use of air as the oxygen-containing stream. These types of strategy examples can allow essentially the same or a similar temperature profile to be maintained in the gasifier relative to conventional operation. It is noted that if CO₂ is used as a diluent, this can increase the CO₂ concentration (and reduce the N₂ concentration) of the resulting flue or exhaust gas from the gasifier. This can facilitate performing carbon capture on the resulting flue or exhaust gas, or alternatively can facilitate performing carbon capture on another stream derived from the flue or exhaust gas.

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[0064] In the gasification zone the reaction between the coke and/or char and the steam and the oxygen-containing gas produces carbon monoxide-containing fuel gas and a partially gasified residual coke product. In some aspects, the fuel gas can further contain H₂, while in other aspects the fuel gas can include a reduced or minimized content of H₂, such as down to 5 containing substantially no H₂. Conditions in the gasifier are selected accordingly to generate these products. Steam, oxygen, and CO₂ (or other diluent gas) rates will depend upon the rate at which cold coke and/or char enters from the reactor. The amount of steam and oxygen can be selected so that the conditions in the gasifier correspond to partial oxidation conditions, in order to increase production of CO at the expense of CO₂. Generally, the conditions for partial 10 oxidation can correspond to conditions where the amount of oxygen in the environment is substantially below the stoichiometric amount that would be needed for complete combustion of the coke and/or char particles. The amount of steam can optionally also be substantially increased. By providing a substoichiometric amount of oxygen, insufficient oxidant is available to combust the available fuel. In some aspects, the flow rate of O₂ introduced into 15 the gasifier can correspond to 45% to 75% of the O₂ that would be required for complete combustion of all coke and char. Introducing extra steam can facilitate a water gas shift reaction, so that a portion of the CO produced by combustion is converted to H₂. This can assist with producing a target ratio of H₂ to CO in the resulting synthesis gas in the gasifier output stream.

20 [0065] The overhead gas product from the gasifier may contain entrained coke and/or char solids and these are removed by cyclones or other separation techniques in the gasifier section of the unit; cyclones may be internal cyclones in the main gasifier vessel itself or external in a separate, smaller vessel as described below. The overhead gas product is taken out as overhead from the gasifier cyclones. The resulting partly gasified solids are removed 25 from the gasifier and introduced directly into the coking zone of the coking reactor at a level in the dilute phase above the lower dense phase.

[0066] In some aspects, the partly gasified solid coke and/or char particles exiting from the gasifier may not be sufficient to transport the necessary amount of heat to the pyrolysis reaction. Additionally or alternately, the total content of coke and/or char particles in the 30 integrated reaction system may not be sufficient to maintain the desired fluidized bed condition in the pyrolysis reaction while also having particles present in the gasifier. In such aspects, additional particles can be added to the reaction system. Sand or other inert particles are one type of option.

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5 [0067] In aspects where gasification of the coke and/or char does not provide sufficient heat for the pyrolysis, additional fuel can be added the gasifier. In some aspects, a fuel such as methane or a mineral feed can be used. Preferably, the additional fuel can correspond to biomass or a fuel derived from biomass, so that any CO₂ generated in the gasifier corresponds to CO₂ generated from a fuel derived from a biological source.

10 [0068] An example of a fluidized coking system with an integrated gasifier is a Flexicoking™ system available from Exxon Mobil Corporation. In some aspects, the integrated process can allow for reduced or minimized production of inorganic nitrogen compounds by using oxygen from an air separation unit as the oxygen source for gasification. Although the amount of nitrogen introduced as a diluent into the gasification will be reduced, minimized, or eliminated, the integrated process can also allow for gasification of coke while reducing, minimizing, or eliminating production of slag or other glass-like substances in the gasifier. This can be achieved, for example, by recycling a portion of the CO₂ generated during gasification back to the gasifier. Additionally or alternately, other diluent compounds such as steam, CO, and/or inorganic compounds (such as inorganic compounds that are non-reactive in the gasifier environment) can be used as well.

20 [0069] One of the difficulties with using petroleum coke, coal, and/or heavy oils as a feed for gasification is that such feeds can potentially contain a relatively high percentage of transition metals, such as iron, nickel, and vanadium. During conventional operation of a gasifier, these transition metals are converted into a “slag” that tends to be corrosive for the internal structures of the gasifier. As a result, gasifiers can typically have relatively short operating lengths between shutdown events, such as operating lengths of roughly 3 months to 18 months. Biomass can include lower amounts of such metals, but the metals can still be present. Additionally, in some aspects, biomass can be co-processed with a conventional fluidized coking feed.

30 [0070] For an independently operated gasifier, frequent shutdown events may be acceptable. However, for a gasifier that is integrated to provide heat balance to another process, such as a fluidized bed coker, a short cycle length for the gasifier can force a short cycle length for the coker as well. In order to overcome this problem, a gasifier that is thermally integrated with a fluidized bed coking process and/or a pyrolysis process can be operated under conditions that reduce, minimize, or eliminate formation of slag.

[0071] One option for avoiding slag formation can be to use air as at least a major portion of the oxygen source for the gasifier that is integrated with the fluidized bed coking process. The additional nitrogen in air can provide a diluent for the gasifier environment that can reduce

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or minimize slag formation. Instead of forming a slag or other glassy type product containing metals, the metals in the coke can be retained in coke form and purged from the integrated system. This can allow the removal / disposition of the metals to be performed in a secondary device or location. By avoiding formation of the corrosive slag, the cycle length of the integrated coker and gasifier can be substantially improved. However, the additional nitrogen from using air as the oxygen-containing stream can dilute the overhead gas product from the gasifier, making it difficult to use the overhead gas as a fuel in a conventional burner. Alternatively, the additional nitrogen can increase the costs associated with recovering synthesis gas from the gasifier overhead product.

- 10 **[0072]** Instead of using air as the oxygen source, an oxygen-containing stream with an increased oxygen content can be used, such as an oxygen-containing stream generated by an air separation unit. While reducing the nitrogen content of the fuel gas can be beneficial, the nitrogen introduced into the gasifier also provided a benefit in the form of reducing or minimizing formation of slag or other glassy compounds in the gasifier. In order to maintain
- 15 a reduced or minimized level of slag formation (such as no slag formation), an alternative diluent can instead be introduced into the gasifier. In various aspects, the alternative diluent can correspond to CO₂, H₂S, steam, other inorganic compounds, or a combination thereof. Optionally, at least a portion of the alternative diluent can correspond to a recycle stream. The addition of steam and H₂S can also help reduce metal carburization and metal corrosion stemming from high carbon activity of the gasification product gases. This can help allow use of lower cost metallurgy. Although gasification is typically performed under conditions with a limited amount of oxygen present in the reaction environment, at least some CO₂ is typically formed by the gasification reaction. Additionally, the water-gas shift equilibrium for syngas can potentially favor additional formation of CO₂, depending on the temperature and the
- 25 relative concentrations of H₂, H₂O, CO, and CO₂. As a result, the overhead product formed in the gasifier can include a substantial portion of CO₂. This CO₂ formed in the gasifier environment can be separated out by any convenient method, such as by use of a monoethanol amine wash or another type of amine wash. Conveniently, an amine wash can also be suitable for removal of any H₂S that is formed during gasification (such as by reaction of H₂ with sulfur that is present in the coke). In some aspects, multiple amine regeneration steps can be used to
- 30 desorb CO₂ and H₂S rich streams separately, thus allowing for control over the amount of recycled CO₂ while also allowing for separate handling of H₂S. In some aspects, H₂S can be first removed using selective amine washing, such as a Flexsorb™ process, before using a more general amine wash for CO₂ separation. The pressure at which amine absorption of CO₂ takes

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place can be in the range of roughly 20 Psia to 1500 Psia (~140 kPa-a to 10.5 MPa-a) and it is optimized based on the overall configuration of the plant, including factors such as utilization of low pressure or high pressure CO shift reaction section and compression costs. At higher pressures the choice of amine or solvent for absorption of CO₂ expands, which can minimize cost and energy requirement of CO₂ absorption and desorption. At lower pressures amines like methylethylamine (MEA) can be preferred. At moderate pressures amines like methyldiethylamine (MDEA) can be preferred. At high pressures chemical solvents such as methanol can be preferred.

[0073] After separation of CO₂ and/or H₂S from the fuel gas, a portion of the CO₂ can be recycled back to the gasifier as a diluent to reduce or minimize formation of slag. In some aspects, the net concentration of O₂ in the oxygen stream introduced into the gasifier, after addition of any diluent and/or steam, can be 22 vol% to 60 vol% relative to the weight of the combined oxygen stream plus diluent and/or steam. In aspects where CO₂ is recycled, at least a portion of the H₂S present in a CO₂ stream can be removed prior to recycling the CO₂ stream to the gasifier. This can assist with maintaining conditions in the gasifier that allow the metals and/or ash content of coke to be removed from the gasifier as part of a coke purge, as opposed to forming a corrosive slag. Alternatively, a portion of the fuel gas after or before a H₂S adsorption (such as a Flexsorb unit) can be compressed and recycled back as the diluent stream.

[0074] By reducing or minimizing the content of N₂ in the fuel gas while also reducing or minimizing slag formation, the fuel gas generated by an integrated coker / gasifier can have a substantially increased content of synthesis gas. After removal of sulfur contaminants, water, and/or a majority of CO₂, the resulting overhead gas can correspond to 70 vol% to 99 vol% of H₂ and CO, or 80 vol% to 95 vol%, which are the components of synthesis gas for methanol production. This is a sufficient purity and/or a sufficiently high quality to potentially be valuable to use in synthesis of other compounds.

[0075] In various aspects, it is noted that the reaction conditions within the coker reactor vessel, the heater vessel, and the gasification vessel can be distinct from one another. The coker reactor vessel can operate at a temperature of 550°C or less. The heater vessel can operate at temperatures between 550°C and 700°C, with the temperature in the heater being higher than the temperature in the coker reactor by 50°C or more, or 100°C or more, such as up to 250°C or possibly still more. The gasifier can operate at temperatures of 650°C or higher in the presence of sufficient O₂ to perform partial oxidation. The temperature in the gasifier can be higher than the temperature in the heater by 50°C or more, or 100°C or more, such as up to 250°C or possibly still more.

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Example of Integrated Reaction Systems

[0076] FIG. 1 shows an example of a system including a gasifier that is thermally integrated with a fluidized bed coker with three reaction vessels: reactor, heater and gasifier. The unit comprises reactor section 10 with the pyrolysis zone and its associated stripping and scrubbing sections (not separately indicated), heater section 11 and gasifier section 12. The relationship of the pyrolysis zone, scrubbing zone and stripping zone in the reactor section is shown, for example, in U.S. Pat. No. 5,472,596, which describes those relationships in an aspect where the pyrolysis zone corresponds to a coking zone for a conventional feedstock. U.S. Pat. No. 5,472,594 is incorporated herein by reference for the limited purpose of further describing the relationships between the pyrolysis zone, the scrubbing zone, and stripping zone. A heavy oil feed is introduced into the unit by line 13 and pyrolyzed and/or cracked hydrocarbon product withdrawn through line 14. Fluidizing and stripping steam is supplied by line 15. Cold char, coke, and/or other particles (such as sand) for forming the fluidized bed are taken out from the stripping section at the base of reactor 10 by means of line 16 and passed to heater 11. The term "cold" as applied to the temperature of the withdrawn char / coke / particles is, of course, decidedly relative since it is well above ambient at the operating temperature of the stripping section. Hot char / coke / particles are circulated from heater 11 to reactor 10 through line 17. Char / coke / particles from heater 11 are transferred to gasifier 12 through line 21 and hot, partly gasified particles of char / coke / sand are circulated from the gasifier back to the heater through line 22. A portion of excess char / coke / particles can be withdrawn from the heater 11 by way of line 23. This can be beneficial, for example, for reducing or minimizing the accumulation of metals in the gasifier.

[0077] Gasifier 12 can be provided with its supply of steam and an oxygen-containing gas by line 24. The heated gasification product, including synthesis gas, can be taken from the gasifier to the heater through line 25. In some aspects, the oxygen-containing gas can correspond to air. In other aspects, instead of supplying air via a line 24 to the gasifier 12, a stream of oxygen with 55 vol% purity or more can be provided, such as an oxygen stream from an air separation unit. In such aspects, in addition to supplying a stream of oxygen, a stream of an additional diluent gas can be supplied by line 31. The additional diluent gas can correspond to, for example, CO₂ separated from the fuel gas generated during the gasification. The gasification product, including the synthesis gas, can be taken out from the unit through line 26 on the heater. Particle fines, such as char fines or coke fines, can be removed from the gasification product in heater cyclone system 27 comprising serially connected primary and secondary cyclones with diplegs which return the separated fines to the fluid bed in the heater.

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The gasification product from line 26 can then undergo further processing, such as separation of desired synthesis gas components from a remaining portion of the gasification product.

[0078] It is noted that in some optional aspects, heater cyclone system 27 can be located in a separate vessel (not shown) rather than in heater 11. In such aspects, line 26 can withdraw the gasification product from the separate vessel, and the line 23 for purging excess coke can correspond to a line transporting coke fines away from the separate vessel. These coke fines and/or other partially gasified coke particles that are vented from the heater (or the gasifier) can have an increased content of metals relative to the feedstock. For example, the weight percentage of metals in the coke particles vented from the system (relative to the weight of the vented particles) can be greater than the weight percent of metals in the feedstock (relative to the weight of the feedstock). In other words, the metals from the feedstock are concentrated in the vented coke particles. Since the gasifier conditions do not create slag, the vented coke particles correspond to the mechanism for removal of metals from the coker / gasifier environment. In some aspects, the metals can correspond to a combination of nickel, vanadium, and/or iron. Additionally or alternately, the gasifier conditions can cause substantially no deposition of metal oxides on the interior walls of the gasifier, such as deposition of less than 0.1 wt% of the metals present in the feedstock introduced into the coker / gasifier system, or less than 0.01 wt%.

[0079] In configurations such as FIG. 1, the system elements shown in the figure can be characterized based on fluid communication between the elements. For example, reactor section 10 is in direct fluid communication with heater 11. Reactor section 10 is also in indirect fluid communication with gasifier 12 via heater 11.

Example 1 – Coke Production, Partial Gasification, and Heat Balance

[0080] Coking is a type of pyrolysis. The conditions for fast pyrolysis can be similar to the conditions for fluidized coking. This can facilitate performing co-processing of biomass with a conventional fluidized coking feedstock in a fluidized coking reaction system.

[0081] Table 1 shows a comparison of typical compositions for coke produced during fluidized coking of a heavy oil mineral feed and char produced during fast pyrolysis of biomass.

Table 1 – Comparison of Char and Coke

Coke/Char Comp	Char from pyrolysis of Pine at 550°C		Gross Coke from Fluidized Coking of Mineral Feed at 530°C
C	86.9%	wt%	86.8%
H	3.4%		4%

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O	7.8%		0.8%
N	0.4%		1.5%
S	0%		6.7%
HHV	33.75	MJ/kg	36.4

[0082] As shown in Table 1, char from biomass is primarily composed of carbon, hydrogen, and oxygen. This is in contrast to the composition of coke from a heavy oil mineral feed, which is primarily composed of carbon, hydrogen, and sulfur. The compositions are otherwise similar, but the higher heating value of the coke is greater than the higher heating value of the char by roughly 10%. This means that under either complete or partial oxidation conditions, additional weight of char is needed to achieve the same heat during gasification as compared to coke.

[0083] Table 2 shows a comparison of operating conditions and products for operating a fluidized coking reaction system either for fluidized coking of a conventional heavy oil feedstock, or fast pyrolysis of biomass. The reaction system configuration for the values in Table 2 is similar to the configuration shown in FIG. 1. The fluidized coking values represent experimental data, while the pyrolysis values are a prediction based on public sources regarding yields from pyrolysis of biomass.

Table 2 – Comparison of Fluidized Coking Operation and Pyrolysis of Biomass in Fluidized Coking Reactor

	Fluidized Coking (mineral feed)	Pyrolysis (100% Biomass - Calculated)
T (dilute Phase)	530C	530C
P (Dilute Phase)	35 psia	35 psia
Feed Rate	46 kbd	5000 T/day
C5+ product rate (klb/hr)	360	330
Gas Phase Product (klb/hr)	95	50
Coke/Char Make (klb/hr)	165	60

[0084] In Table 2, the pyrolysis conditions were selected to be similar to fluidized coking conditions. The feed rate was selected so that the biomass heat of pyrolysis is equivalent to the heat of pyrolysis (coking) that was needed for the fluidized coking example. As shown in Table 2, the product yields for pyrolysis of biomass are generally lower, due in part to the fact that biomass pyrolysis also typically results in production of water, on the order of roughly 10 wt%

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of the total product. The weight ratio of char relative to the weight of gas phase products is also reduced for the biomass pyrolysis example.

[0085] It is noted that under partial gasification conditions, the weight of char produced by pyrolysis in Table 2 is not sufficient to provide the required heat for maintaining the pyrolysis reaction. One option for generating additional heat in the gasifier can be to add biomass directly to the gasifier. This can increase both the heat output and the output of synthesis gas generated in the gasifier. Additionally, by using biomass as the supplemental fuel in the gasifier, any CO₂ generated from gasification of the biomass will correspond to CO₂ derived from a biogenic source, thereby reducing or minimizing the net greenhouse gas emissions associated with the process.

[0086] The addition of biomass to the gasifier does not result in a substantial change in the composition of the overhead gas from a gasifier. To illustrate this, modeling calculations were performed for gasification of char from biomass in a gasifier. A second set of calculations were also performed where 20 wt% of the feed into the gasifier corresponded to biomass rather than char. In the calculations, air was used as the source of oxygen-containing gas. Table 3 shows the overhead gas compositions from the calculations.

Table 3 – Gasifier Overhead Product Gas Compositions

	100 % coke/char Feed (mol %)	80 % Coke/Char + 20 % Biomass (mol %)
H ₂	13.4	13.1
N ₂	49.9	50.0
CO	17.7	15.0
CO ₂	9.0	9.8
H ₂ O	9.4	11.6
H ₂ S	0.52	0.45
COS	0.03	0.02

[0087] As shown in Table 3, incorporating 20 wt% biomass into the input flows into the gasification reaction had only a modest impact on the overall product distribution. It appears that the biomass resulted in extra water being present in the gasifier environment, with a small reduction in the total content of carbon oxides.

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Example 2 – Increased Reaction Rate for Mineral Coking Feedstock During Biomass Co-Processing

[0088] In some aspects, solid biomass can be co-processed with a mineral resid feed portion under fluidized coking conditions, where the solid biomass corresponds to 1.0 wt% or more (or 10 wt% or more, or 20 wt% or more) of the combined feedstock and the mineral resid feed corresponds to 40 wt% or more (or 50 wt% or more) of the combined feedstock. In such aspects, it has been discovered that the presence of the biomass in the fluidized coking environment can increase the reaction rate for pyrolysis of the mineral resid portion of the combined feed. This can potentially allow for a variety of processing advantages, including (but not limited to) increasing product yield and reducing the reaction temperature during the fluidized coking.

[0089] The unexpectedly improved reaction rates for pyrolysis (such as coking) of mineral resid feed portions when co-processed with solid biomass is illustrated by a series of pyrolysis reactions that were performed on various combinations of biomass and mineral resid feeds. For the pyrolysis reactions involving the mineral resid feeds, the resid feed corresponded to a vacuum resid fraction with an MCR of 9.46 wt%, and n-heptane insolubles content of 1.1 wt%, and a T10 of 553°C. For the biomass, cellulose was used in some runs as the solid biomass, while other runs used pine wood chips. The biomass had an average particle size of roughly 0.5 mm. More generally, the biomass can have an average particle size of roughly 0.25 mm to 2500 mm, or 0.5 mm to 2.0 mm.

[0090] In a first set of runs, pyrolysis was performed on cellulose, mineral resid, and a mixture of 30 wt% cellulose and 70 wt% resid. The runs were performed in a thermogravimetric analysis (TGA) unit to allow for detailed measurement of a) temperature and b) weight loss from the feed during the pyrolysis reaction. In a TGA experiment, a solid and/or liquid sample is charged to a small (~50 mg), open pan, and this pan is secured within a temperature-controlled cell. The cell is purged of all oxygen using flowing nitrogen, and the temperature of the cell is raised rapidly to a target value. The temperature of the cell is maintained at this target value while nitrogen is flowed through the cell. During this process, the contents of the TGA pan are pyrolyzed, so that some or all of the sample cracks to lower molecular weight species, volatilizes, or both. The volatilized contents of the TGA pan are eluted from the cell in the nitrogen carrier gas, and the mass loss from the TGA pan is recorded by a gravimetric balance. This process is recorded in the form of a residual mass (normalized to 100%), versus time and the temperature of the cell. The weight loss represents the amount

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of feed converted from a solid to a fluid that is in the vapor phase under the pyrolysis conditions.

[0091] In the first set of runs, the target pyrolysis temperature was set to 400°C. However, because some time is required to heat the vessel to the target temperature, the pyrolysis reaction (for at least the cellulose) would start prior to reaching the target temperature of 400°C. To account for this, time was rescaled with temperature using a metric called Equivalent Residence Time (ERT; Equation 1):

$$[0092] \quad (1) \text{ ERT} = \int_0^t \exp\left(-\frac{E_{app}}{R} \left\{ \frac{1}{T(t)} - \frac{1}{T_{final}} \right\}\right) dt$$

[0093] In Equation 1, t is time, T is the absolute temperature of the TGA cell, T_{ref} is a reference temperature (e.g., 400°C), R is the gas constant, and E_{app} is an apparent activation energy chosen by the user (210 kJ/mol is typical for resid pyrolysis). ERT at temperature therefore allows for the TGA profile to be analyzed as though the process were occurring at constant temperature (similar to a continuous pyrolysis process like Flexicoking). In this discussion, the ERT temperature used for displaying data as a function of time will be specified.

[0094] FIG. 2 shows the results from pyrolysis of cellulose alone 310, and the resid feed alone 220. FIG. 2 is displayed based on ERT at 400°C. As shown in FIG. 2, pyrolysis of cellulose occurs rapidly at 400°C, with substantially all of the mass in the cellulose that is susceptible to conversion to a fluid being complete within roughly 2 minutes or less. By contrast, pyrolysis of the resid feed at 400°C take substantially longer, with some pyrolysis still occurring after roughly 55 minutes of time in the reactor. It is noted that both the cellulose pyrolysis residual mass curve 210 and the mineral resid pyrolysis residual mass curve 220 could be readily fit to a first-order reaction data model, as would be expected for a pyrolysis reaction.

[0095] A combined feed including 30 wt% cellulose and 70 wt% mineral resid was then pyrolyzed using the TGA reactor. FIG. 3 shows the results (displayed based on ERT at 400°C) from pyrolysis of the combined feed (curve 330), along with a model prediction of an expected residual mass curve 340. The model prediction of the expected residual mass curve 340 was determined based on an assumption of no interaction between the biomass and the mineral resid in the pyrolysis environment. The constants determined from model fitting of the individual cellulose and mineral resid pyrolysis runs were used in order to form this model prediction. As shown in FIG. 3, the measured pyrolysis residual mass curve 330 showed a substantially faster reaction than the reaction that was predicted by the (no interaction) model residual mass curve 340. The sharp difference between these curves demonstrates a synergy in reaction between

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the solid biomass (in this run, cellulose) and the mineral resid feeds. The difference in reaction rate between the (no interaction) model residual mass curve 340 and the measured residual mass curve 330 represents a roughly 2x increase in reaction rate.

[0096] A second set of runs were performed using similar procedures, but using pine wood chips, a whole form of biomass, rather than using cellulose. First, pyrolysis was performed on pine wood chips alone in the TGA reactor to allow for determination of constants for use in making model predictions. Pyrolysis was then performed on a mixture of 50 wt% pine wood chips and 50 wt% mineral resid at temperatures of 530°C (FIG. 4) and 360°C (FIG. 5).

[0097] As shown in FIG. 4, pyrolysis at 530°C of a mixed feed of pine wood chips and mineral resid resulted in a substantial increase in reaction rate for the resid, as evidenced by the difference in the measured residual mass curve 430 versus the (no interaction) model residual mass curve 440. A similar difference in the measured residual mass curve 530 and the (no interaction) model residual mass curve 540, as shown in FIG. 5. Based on the difference between the measured curves and the model curves, co-processing of solid biomass and mineral resid under pyrolysis conditions provides a roughly 2x increase in reaction rate relative to the expected value if there was no interaction between the reaction mechanisms for the pyrolysis of the co-feeds. This is an unexpected synergy based on co-processing of biomass and mineral feed under fluidized coking conditions.

[0098] The reaction rate benefit illustrated by the various residual mass curves in FIG. 3, FIG. 4, and FIG. 5 can be used in a variety of ways to improve the operation of a fluidized coking reaction system. For example, the increased reaction rate can allow for a reduction in temperature in the fluidized coking reactor while still maintaining a target conversion rate for the input feed. Reduced temperatures in a fluidized coking (or other pyrolysis) process generally result in increased liquid product yields.

Example 3 – Modified and/or Improved Fluidized Coking Based on Increased Reaction Rate

[0099] As illustrated in Example 2, co-processing of biomass with a mineral feedstock results in an increased reaction rate for the mineral feedstock portion of the feed under the fluidized coking conditions. The increased reaction rate can have a variety of impacts on the operation of the fluidized coking system and/or the resulting product slate.

[00100] One modification that can be enabled by increased reaction rate is a reduction in the processing severity within the coker reactor vessel while still achieving a target amount of HCCU during operation. FIG. 6 shows the impact of increased reaction rate on HCCU. FIG. 6 was generated based on a fluidized coking process model. The model is based on empirical

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data, and can provide yield predictions for the various products from fluidized coking based on changes in the modeled processing variables. In FIG. 6, the vertical axis shows the amount of HCCU that exits from the reactor and therefore would be passed into the heater of a three-vessel reaction system. The horizontal axis shows how increasing the reaction rate within the model (relative to the expected baseline value) modifies the HCCU.

[00101] As shown in FIG. 6, increasing the reaction rate for the reactions within a fluidized coking environment results in a decrease in HCCU. Based on the measurements in Example 2, it was calculated that co-processing of biomass could produce a factor of two increase in the reaction rate for the mineral portion of the feed. As shown in FIG. 6, increasing the reaction rate by a factor of 2 reduces the HCCU from an initial amount of 0.06 wt% down (for the expected reaction rate at the conditions) to having substantially no HCCU when the reaction rate is doubled.

[00102] Based on FIG. 6, co-processing of biomass can provide a substantial reduction in the amount of HCCU that is generated during fluidized coking relative to the HCCU that would be generated during processing of a mineral feed alone. Since fluidized coking is often constrained by the need to maintain a target level of HCCU, co-processing of biomass can allow for a reduction in severity for the conditions in the fluidized coking environment. For example, at roughly constant residence time for coke particles within the reactor vessel, a lower temperature can be used within the reactor while still achieving a target HCCU amount.

[00103] FIG. 7 illustrates an example of the benefits of reducing the temperature in the coking reactor. FIG. 7 shows model product yield results that were generated from the fluidized coking process model. In FIG. 7, modeled product yield results are shown for a resid feed as the temperature in the fluidized coking reactor is changed from 920°F (493°C) to 990°F (532°C). Based on the model, the difference in temperature between 493°C and 532°C roughly corresponds to the difference in operating temperature that could be achieved in a fluidized coking unit if the reaction rate for resid conversion is increased by a factor of two. In other words, the amount of HCCU generated at 532°C for processing the feed used in the model at the expected reaction rate is similar to the amount of HCCU generated at 493°C when the reaction rate is doubled. As illustrated in the modeled results shown in FIG. 7, reducing the temperature can reduce the yield of coke (751), light gases (753), and coker naphtha (755) while increasing the yield of light coker gas oil (757) and heavy coker gas oil (759). Thus, the temperature reduction enabled by an increase in reaction rate can provide a substantial shift in the nature of the product slate.

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[00104] FIG. 8 shows modeled results that illustrate how the change in product slate would appear when comparing processing of a resid feed alone versus co-processing the resid feed with solid biomass under fluidized coking conditions. In FIG. 8, estimated / modeled product yields are shown for fluidized coking of two types of feeds. The first feed corresponds to a model mineral resid. The second feed corresponds to a blend of 75 wt% of the model mineral resid with 25 wt% of model biomass particles.

[00105] To model the results, the product yield from the resid portion of each feed was modeled using the same methods used to generate the model yields shown in FIG. 7. For the biomass portion of the second feed, the product yields were modeled based on typical publicly reported values for fast pyrolysis of woody biomass at roughly 500°C.

[00106] In FIG. 8, the products generated from the model fluidized coking process are classified as coke, light gases, coker naphtha (KN), light coker gas oil (LKGO), and heavy coker gas oil (HKGO). The products shown represent products from processing of 622 klbs/hr of feed. The left hand solid bar for each product corresponds to the model yield prediction for the 100 wt% resid feed exposed to fluidized coking conditions at roughly 532°C. The right hand solid bar for each product corresponds to the model prediction for fluidized coking of the 75 wt% resid portion of the second feed at a temperature of 493°C. The box formed with dotted lines above the right hand solid bar for each product represents the additional estimated product yield contribution from fast pyrolysis of the 25 wt% of biomass.

[00107] As shown in the estimated yields in FIG. 8, by reducing the temperature and then adding back in the estimated yield from the biomass portion of the feed, co-processing of 25 wt% biomass with a resid feed can yield a product slate with reduced net yields of coke and light gases while providing a net increase in yield of coker naphtha and coker heavy gas oil. It is noted that the total liquid products shown in FIG. 8 correspond to roughly 40 wt% of naphtha boiling range components, roughly 40 wt% of heavy distillate boiling range components, and roughly 20 wt% of light distillate boiling range components.

Example 4 – Additional Product Characterization

[00108] To further characterize the benefits of co-processing of biomass and mineral feeds, additional characterization was performed on the liquid products generated from co-processing of mineral resid with 10 wt% biomass. For comparison, liquid products from fluidized coking of the mineral resid alone were also characterized. For the liquid products characterized in this example, the fluidized coking was performed at a reactor temperature of 400°C.

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[00109] Several types of characterization were performed on the total liquid products generated from the mineral feed and combined feed containing portions of both biomass and mineral feed. FIG. 9 shows SIMDIS (ASTM D2887) boiling point profiles for the resulting total liquid products. FIG. 10 shows analysis of sulfur, MCR, and n-heptane insolubles in the resulting total liquid products. FIG. 11 shows Fourier-transform ion cyclotron resonance (FTICR-MS) analysis of the classes of compounds present in the total liquid products. FIG. 12 shows two-dimensional gas chromatography (2D-GC) for the amounts of saturates, aromatics, and polar compounds present in the total liquid products.

[00110] FIG. 9 shows distillation profiles for the resulting total liquid products. Line 901 corresponds to the distillation profile for the co-processed product, while line 902 corresponds to the distillation profile from processing the mineral resid alone. As shown in FIG. 9, the total liquid product from co-processing 901 generally has a higher temperature distillation profile. It is believed that the higher temperature distillation profile reflects the unexpected chemistry occurring in the fluidized bed coking reactor when lignocellulosic biomass is co-processed. It is noted that due to differences in the type of mineral feed, the distillation profile in FIG. 9 is generally different from the distillation profile shown in FIG. 8. It is further noted that the co-processing of biomass changes the ratio of naphtha boiling range components to light distillate boiling range components that is generated by the process. The coker effluent from processing the mineral resid feed in FIG. 9 has a weight ratio of naphtha boiling range compounds to light distillate boiling range compounds of greater than 0.65, or greater than 0.70. By contrast, co-processing biomass that contains cellulose with the mineral resid feed allowed for production of an effluent with a weight ratio of naphtha boiling range compounds to light distillate boiling range compounds of 0.65 or less, or 0.62 or less, or 0.60 or less, such as down to 0.50 or possibly still lower.

[00111] FIG. 10 shows product analysis for the total liquid products, corresponding to sulfur content, micro carbon residue (MCR) content, and n-heptane insolubles content (abbreviated C7 Insol in FIG. 10). As shown in FIG. 10, there is a modest reduction in sulfur content between the co-processed product and the product from processing only the mineral feed. It is noted that the biomass has little or no sulfur content, so the lower sulfur content for the co-processed product in FIG. 10 may simply reflect the lower sulfur content in the combined biomass / resid feed prior to processing. For MCR and n-heptane insolubles, however, an additional synergistic effect is present. For the co-processed total liquid product, simple blending with biomass to dilute the initial concentration of MCR and n-heptane insoluble would, at best, result in a reduction in MCR to just over 0.5 wt% and a reduction in

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n-heptane insoluble to around 0.8 wt%. By contrast, as shown in FIG. 10, the MCR content and n-heptane insolubles content for the co-processed liquid product has been reduced to roughly 0.2 wt% or less, or 0.1 wt% or less. This is an unexpected improvement in product quality. It is believed that the catalytic interactions caused by oxygen radicals formed from the biomass reduces or minimizes the presence of coke precursors and/or other insolubles in the resulting total liquid product.

[00112] FIG. 11 shows FTICR-MS results from analysis of three products. One product corresponds to the total liquid product from fluidized coking of the mineral feed alone. A second product corresponds to the product from co-processing the mineral feed with biomass. The third product corresponds to FTICR-MS analysis of a representative pyrolysis oil formed by fast pyrolysis of a biomass feed.

[00113] Due to the high resolution of mass fragments in FTICR-MS, it is possible to make detailed assignments regarding the number and type of atoms different from carbon and hydrogen that are present in compounds within a sample. As shown in FIG. 11, the total liquid product from a conventional resid is primarily composed of hydrocarbons (greater than 40 wt%); compounds containing carbon, hydrogen, and 1 sulfur atom (roughly 25 – 30 wt%); and compounds containing carbon, hydrogen, and 1 nitrogen atom (roughly 10 – 15 wt%). The pyrolysis oil provides a substantially different profile, with the samples containing 5.0 wt% or less of hydrocarbons. Instead, the majority of compounds in the pyrolysis oil contain 4 oxygen atoms or more, with the single most common type of compound by weight corresponding to a compound containing carbon, hydrogen, and 12 oxygens. This illustrates that typical pyrolysis oils correspond to large hydrocarbonaceous compounds with multiple oxygen-containing functional groups. Typically, more than 50 wt% of the components in a conventional pyrolysis oil include at least one oxygen atom.

[00114] Unexpectedly, the FTICR-MS analysis of the product from co-processing biomass with the mineral resid feedstock does not resemble some sort of blend of the products from processing of biomass alone or mineral resid alone. The co-processing total liquid product does contain a substantial amount of hydrocarbons (15 – 20 wt%) and compounds containing carbon, hydrogen, and 1 sulfur (15 – 20 wt%). However, the compounds with large numbers of oxygen atoms are either not present or present in minimal amounts in the co-processed liquid product. Instead, the co-processed liquid product contains a substantial number of compounds composed of carbon, hydrogen, and 1 oxygen atom (roughly 10 wt%). The content of compounds including carbon, hydrogen, and 1 oxygen atom is approximately double the content found in the mineral resid liquid product. It is noted that the pyrolysis oil contained

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substantially no compounds containing carbon, hydrogen, and only 1 oxygen atom. Additionally, the co-processed liquid product contains roughly 5.0 wt% of compounds composed of carbon, hydrogen, and 3 oxygen atoms. This is higher than the content of such compounds in either the mineral resid liquid product or the pyrolysis oil.

5 **[00115]** Based on chromatographic characterizations of the liquid products, it is noted that coking of the mineral feed resulted in a total liquid product containing roughly 0.25 wt% oxygen in total. In contrast, the pyrolysis oil contained roughly 45 wt% or oxygen, as the pyrolysis oil contained relatively few components that did not contain at least one oxygen. However, co-processing of biomass with a mineral feed resulted in a total liquid product
10 containing about 1.2 wt% of oxygen. This is an increase in the total oxygen content of the total liquid products versus a pure mineral feed, but unexpectedly less by a substantial amount relative to the expected oxygen content based on a linear combination of independently generated mineral- and biomass-based products under similar conditions (4.7 wt%).

[00116] The nature of the FTICR-MS results illustrates that the total liquid product from
15 co-processing of biomass with a mineral resid is not simply an average of the products that would be generated individually. Instead, the FTICR-MS results show that interactions occur during reaction of the biomass and the mineral resid, resulting in formation of components in the co-processed total liquid product that would not be formed from processing either type of feedstock individually.

20 Additional Embodiments

[00117] Embodiment 1. A method for co-processing biomass in a fluidized coking system, comprising: exposing a feed comprising 1.0 wt% to 60 wt% of biomass and 40 wt% to 99 wt% of a mineral fraction having a T10 distillation point of 500°C or higher, to a fluidized bed of particles under fluidized coking conditions in a reactor vessel to form i) a coker effluent
25 comprising a liquid portion, ii) char, coke, or a combination thereof, at least a portion of the char, coke, or combination thereof being deposited on the particles to form particles comprising deposited char, coke, or a combination thereof, and iii) additional hydrocarbons associated with the particles comprising deposited char, coke, or a combination thereof; passing at least a portion of particles comprising deposited char, coke, or a combination thereof from the reactor
30 vessel into a heater vessel, the at least a portion of particles comprising deposited char, coke or a combination thereof comprising 0.08 wt% or less of the associated additional hydrocarbons, relative to a weight of the feed; mixing the at least a portion of the particles comprising deposited char, coke, or a combination thereof with a portion of partially gasified particles in the heater vessel to form a heated particle mixture; passing a first portion of the heated particle

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- mixture into the reactor vessel; passing a second portion of the heated particle mixture into a gasification vessel; introducing an oxygen-containing stream and steam into the gasification vessel; exposing the second portion of the heated particle mixture to oxidation conditions in the gasification vessel to form a gas phase product, and partially gasified particles; and passing
- 5 at least a portion of the partially gasified particles from the gasification vessel to the heater vessel, wherein the liquid portion of the coker effluent comprises a micro carbon residue content of 0.5 wt% or less, an n-heptane insolubles content of 0.5 wt% or less, or a combination thereof.
- [00118] Embodiment 2. The method of Embodiment 1, wherein the liquid portion of the
- 10 coker effluent comprises a micro carbon residue content of 0.4 wt% or less, an n-heptane insolubles content of 0.4 wt% or less, or a combination thereof.
- [00119] Embodiment 3. The method of any of the above embodiments, wherein the oxidation conditions comprise partial oxidation conditions to form a gas phase product comprising CO and CO₂.
- 15 [00120] Embodiment 4. The method of any of the above embodiments, wherein the gas phase product further comprises H₂.
- [00121] Embodiment 5. The method of any of the above embodiments, further comprising passing the gas phase product from the gasification vessel into the heater vessel, and exhausting at least a portion of the gas phase product from the heater vessel.
- 20 [00122] Embodiment 6. The method of any of the above embodiments, wherein the biomass comprises 20 wt% or more of cellulose, or wherein the biomass comprises 30 wt% or less of lignin, or a combination thereof.
- [00123] Embodiment 7. The method of any of the above embodiments, wherein the feed comprises 10 wt% to 60 wt% of biomass.
- 25 [00124] Embodiment 8. The method of any of the above embodiments, wherein the feed comprises 50 wt% to 60 wt% of biomass, or wherein the feed comprises 20 wt% or less of components with a boiling point of 350°C or less, or a combination thereof.
- [00125] Embodiment 9. The method of any of the above embodiments, wherein the oxidation conditions comprise exposing the second portion of particles to an oxygen-containing
- 30 stream comprising 45% to 75% of a stoichiometric amount of oxygen to combust the char, coke, or a combination thereof.
- [00126] Embodiment 10. The method of any of the above embodiments, wherein the liquid portion of the coker effluent comprises 0.9 wt% to 3.0 wt% of oxygen.

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[00127] Embodiment 11. A liquid portion of a coker effluent formed according to the method of any of Embodiments 1 to 10, the liquid portion of the coker effluent comprising: 30 wt% to 50 wt% of naphtha boiling range components; 30 wt% to 50 wt% of heavy distillate boiling range components; 10 wt% to 25 wt% of light distillate boiling range components; and
5 5.0 wt% or less of vacuum resid boiling range components, the liquid portion comprising 0.9 wt% to 3.0 wt% of oxygen, the liquid portion further comprising a) 0.05 wt% to 0.5 wt% of micro carbon residue content, b) 0.05 wt% to 0.5 wt% of n-heptane insolubles, or c) a combination of a) and b).

[00128] Embodiment 12. The liquid portion of a coker effluent of Embodiment 11,
10 wherein the liquid portion comprises 0.05 wt% to 0.4 wt% of micro carbon residue content, or wherein the liquid portion comprises 0.05 wt% to 0.4 wt% of n-heptane insoluble, or a combination thereof.

[00129] Embodiment 13. The liquid portion of a coker effluent of Embodiment 11,
15 wherein the liquid portion comprises 0.05 wt% to 0.2 wt% of micro carbon residue content, or wherein the liquid portion comprises 0.05 wt% to 0.2 wt% of n-heptane insoluble, or a combination thereof.

[00130] Embodiment 14. The liquid portion of a coker effluent of any of Embodiments 11 to 13, wherein the liquid portion comprises 10 wt% to 40 wt% of oxygenated components, or wherein the liquid portion comprises 0.9 wt% to 2.5 wt% of oxygen, or a combination thereof.

20 [00131] Embodiment 15. The liquid portion of a coker effluent of any of Embodiments 11 to 14, wherein the liquid portion comprises 1.0 wt% or less of vacuum resid boiling range components.

[00132] Additional Embodiment A. The method of any of Embodiments 1 – 10, wherein the liquid portion of the coker effluent comprises a weight ratio of naphtha boiling range components to light distillate boiling range components of 0.65 or less; or wherein the liquid
25 portion of the coker effluent comprises 30 wt% to 50 wt% of naphtha boiling range components, 30 wt% to 50 wt% of heavy distillate boiling range components, 10 wt% to 25 wt% of light distillate boiling range components; and 5.0 wt% or less of vacuum resid boiling range components.

30 [00133] When numerical lower limits and numerical upper limits are listed herein, ranges from any lower limit to any upper limit are contemplated. While the illustrative embodiments of the invention have been described with particularity, it will be understood that various other modifications will be apparent to and can be readily made by those skilled in the art without departing from the spirit and scope of the invention. Accordingly, it is not intended that the

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scope of the claims appended hereto be limited to the examples and descriptions set forth herein but rather that the claims be construed as encompassing all the features of patentable novelty which reside in the present invention, including all features which would be treated as equivalents thereof by those skilled in the art to which the invention pertains.

- 5 [00134] The present invention has been described above with reference to numerous embodiments and specific examples. Many variations will suggest themselves to those skilled in this art in light of the above detailed description. All such obvious variations are within the full intended scope of the appended claims.

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CLAIMS

1. A method for co-processing biomass in a fluidized coking system, comprising: exposing a feed comprising 1.0 wt% to 60 wt% of biomass and 40 wt% to 99 wt% of a mineral fraction having a T10 distillation point of 500°C or higher, to a fluidized bed of particles under fluidized coking conditions in a reactor vessel to form i) a coker effluent comprising a liquid portion, ii) char, coke, or a combination thereof, at least a portion of the char, coke, or combination thereof being deposited on the particles to form particles comprising deposited char, coke, or a combination thereof, and iii) additional hydrocarbons associated with the particles comprising deposited char, coke, or a combination thereof; passing at least a portion of particles comprising deposited char, coke, or a combination thereof from the reactor vessel into a heater vessel, the at least a portion of particles comprising deposited char, coke or a combination thereof comprising 0.08 wt% or less of the associated additional hydrocarbons, relative to a weight of the feed; mixing the at least a portion of the particles comprising deposited char, coke, or a combination thereof with a portion of partially gasified particles in the heater vessel to form a heated particle mixture; passing a first portion of the heated particle mixture into the reactor vessel; passing a second portion of the heated particle mixture into a gasification vessel; introducing an oxygen-containing stream and steam into the gasification vessel; exposing the second portion of the heated particle mixture to oxidation conditions in the gasification vessel to form a gas phase product, and partially gasified particles; and passing at least a portion of the partially gasified particles from the gasification vessel to the heater vessel, wherein the liquid portion of the coker effluent comprises a micro carbon residue content of 0.5 wt% or less, an n-heptane insolubles content of 0.5 wt% or less, or a combination thereof.
2. The method of claim 1, wherein the liquid portion of the coker effluent comprises a micro carbon residue content of 0.4 wt% or less, an n-heptane insolubles content of 0.4 wt% or less, or a combination thereof
3. The method of claim 1, wherein the oxidation conditions comprise partial oxidation conditions to form a gas phase product comprising CO and CO₂.
4. The method of claim 1, wherein the gas phase product further comprises H₂.

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5. The method of claim 1, further comprising passing the gas phase product from the gasification vessel into the heater vessel, and exhausting at least a portion of the gas phase product from the heater vessel.
6. The method of claim 1, wherein the biomass comprises 20 wt% or more of cellulose, or wherein the biomass comprises 30 wt% or less of lignin, or a combination thereof.
7. The method of claim 1, wherein the feed comprises 10 wt% to 60 wt% of biomass.
8. The method of claim 1, wherein the feed comprises 20 wt% or less of components with a boiling point of 350°C or less.
9. The method of claim 1, wherein the oxidation conditions comprise exposing the second portion of particles to an oxygen-containing stream comprising 45% to 75% of a stoichiometric amount of oxygen to combust the char, coke, or a combination thereof.
10. The method of claim 1, wherein the liquid portion of the coker effluent comprises a weight ratio of naphtha boiling range components to light distillate boiling range components of 0.65 or less; or wherein the liquid portion of the coker effluent comprises 30 wt% to 50 wt% of naphtha boiling range components, 30 wt% to 50 wt% of heavy distillate boiling range components, 10 wt% to 25 wt% of light distillate boiling range components; and 5.0 wt% or less of vacuum resid boiling range components.
11. The method of claim 1, wherein the liquid portion of the coker effluent comprises 0.9 wt% to 3.0 wt% of oxygen.
12. A liquid product comprising: 30 wt% to 50 wt% of naphtha boiling range components; 30 wt% to 50 wt% of heavy distillate boiling range components; 10 wt% to 25 wt% of light distillate boiling range components; and 5.0 wt% or less of vacuum resid boiling range components, the liquid product comprising 0.9 wt% to 3.0 wt% of oxygen, the liquid product further comprising a) 0.05 wt% to 0.5 wt% of micro carbon residue content, b) 0.05 wt% to 0.5 wt% of n-heptane insolubles, or c) a combination of a) and b).
13. The liquid product of claim 12, wherein the liquid product comprises 0.05 wt% to 0.4 wt% of micro carbon residue content.
14. The liquid product of claim 12, wherein the liquid product comprises 0.05 wt% to 0.4 wt% of n-heptane insolubles.

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15. The liquid product of claim 12, wherein the liquid product comprises 0.05 wt% to 0.2 wt% of micro carbon residue content.
16. The liquid product of claim 12, wherein the liquid product comprises 0.05 wt% to 0.2 wt% of n-heptane insolubles.
- 5 17. The liquid product of claim 12, wherein the liquid product comprises 10 wt% to 40 wt% of oxygenated components.
18. The liquid product of claim 12, wherein the liquid product comprises 15 wt% to 30 wt% of oxygenated components.
19. The liquid product of claim 12, wherein the liquid product comprises 1.0
10 wt% or less of vacuum resid boiling range components.
20. The liquid product of claim 12, wherein the liquid product comprises 0.9 wt% to 2.5 wt% of oxygen.

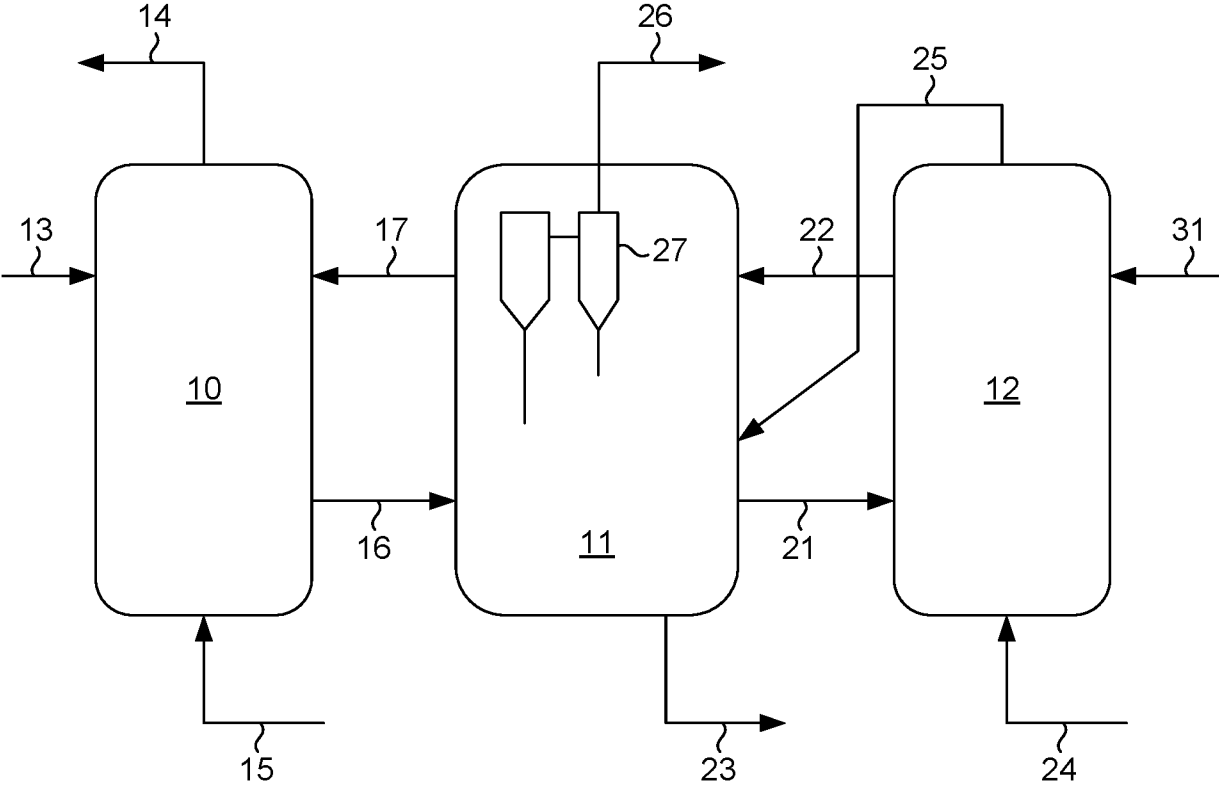


FIG. 1.

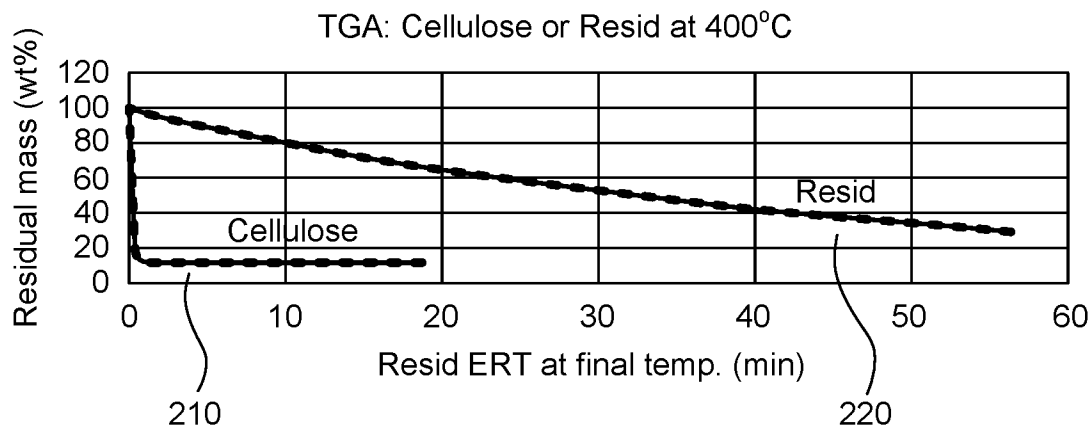


FIG. 2.

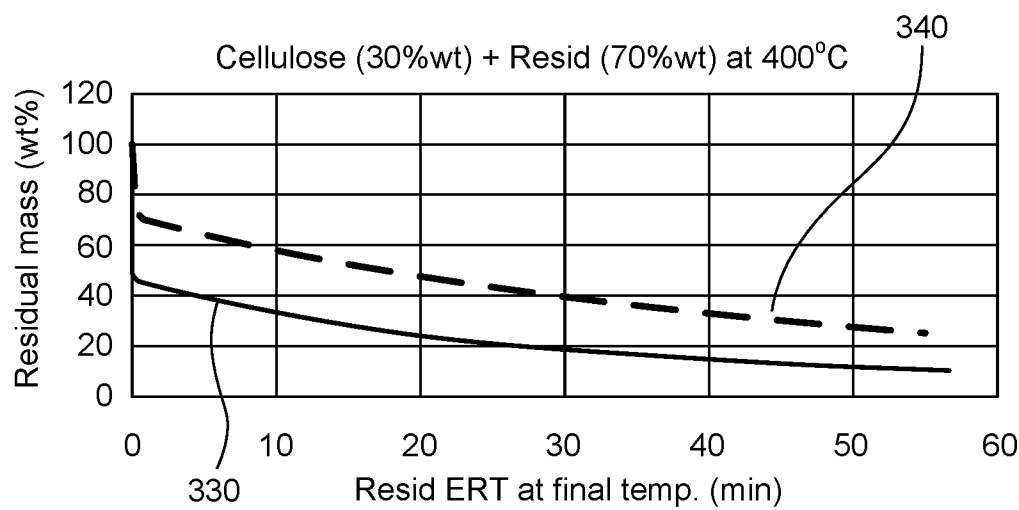


FIG. 3.

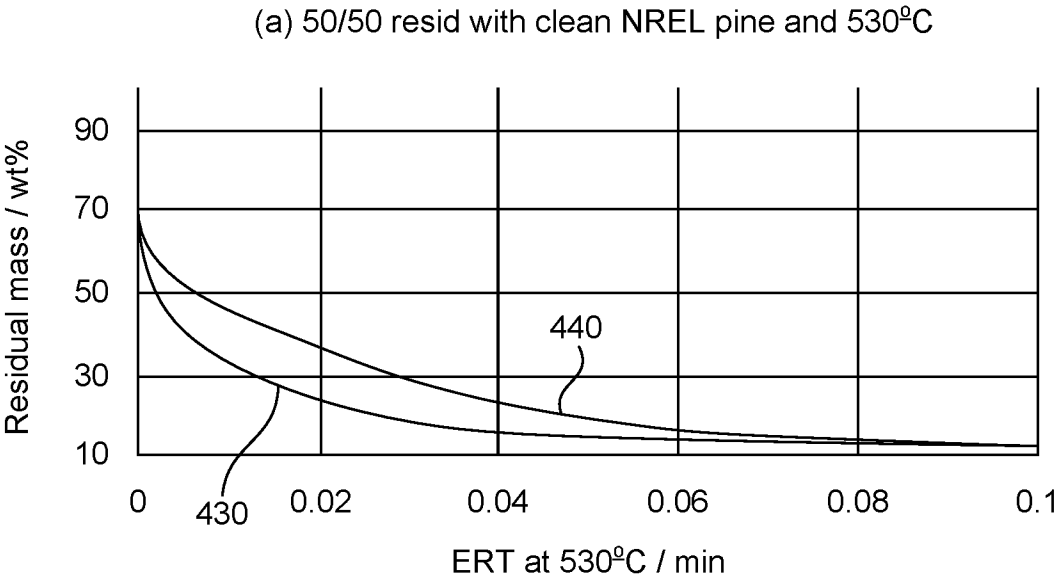


FIG. 4.

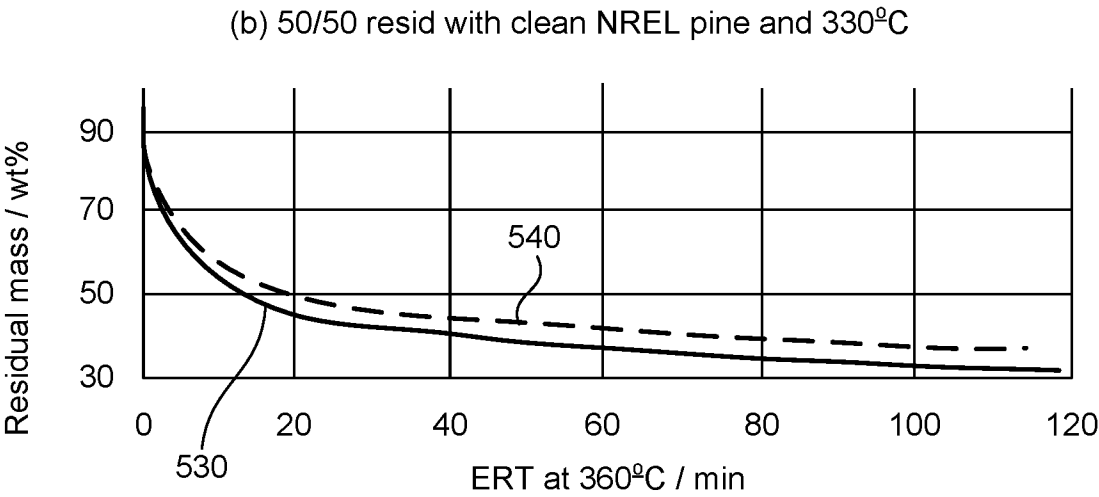


FIG. 5.

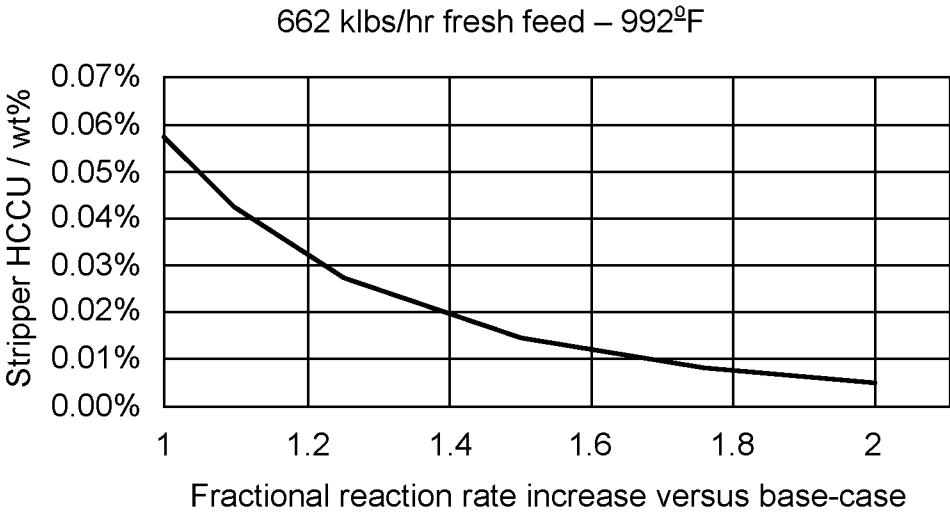


FIG. 6.

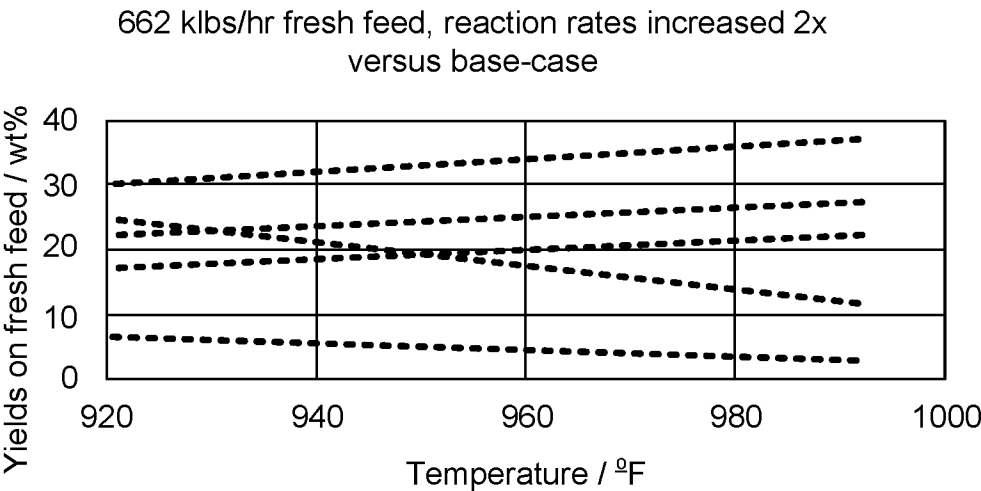


FIG. 7.

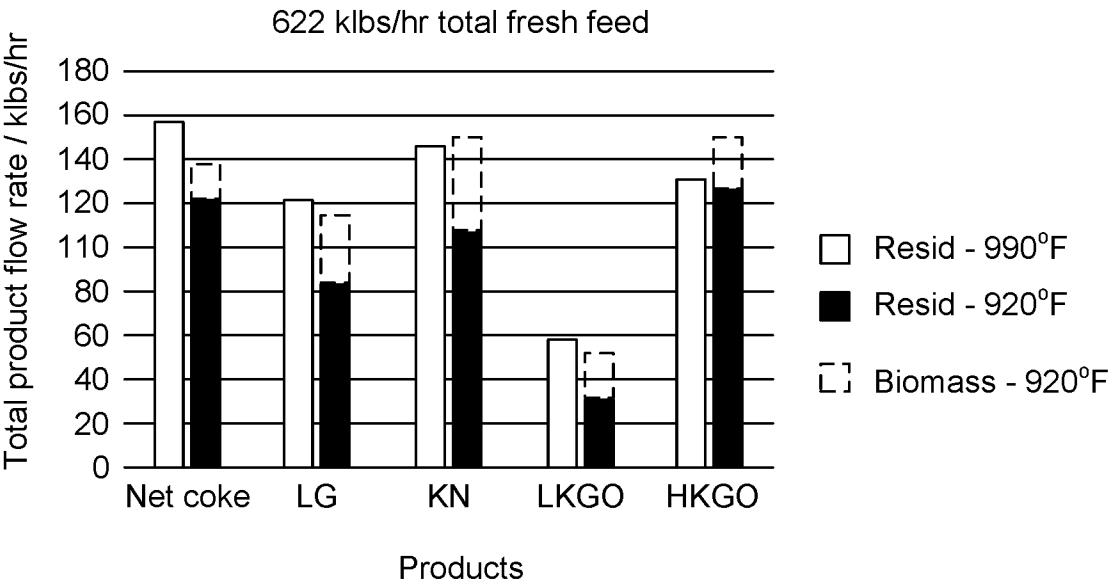


FIG. 8.

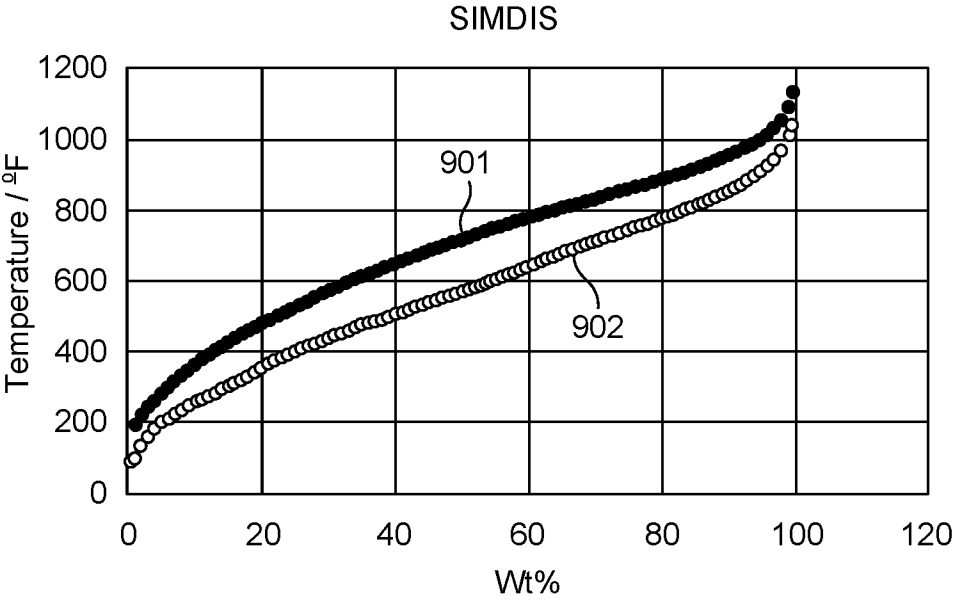


FIG. 9.

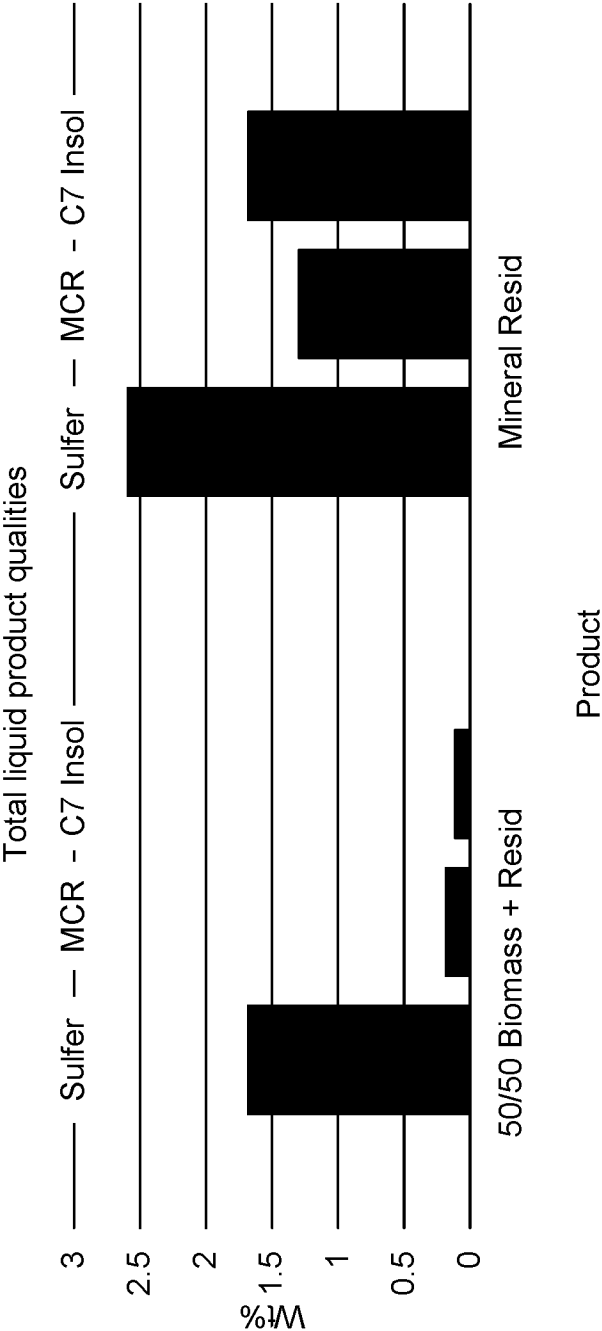


FIG. 10.

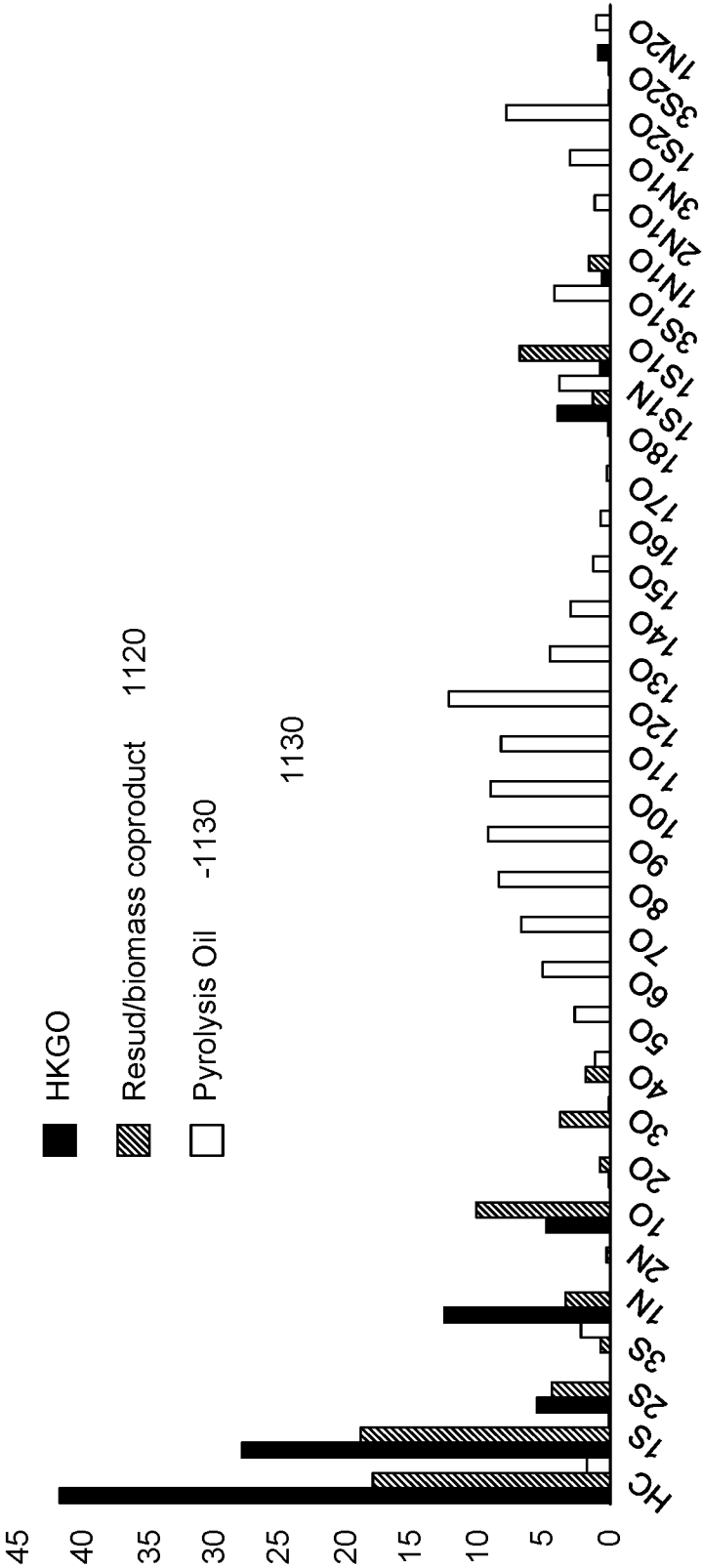


FIG. 11.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2023/026190

A. CLASSIFICATION OF SUBJECT MATTER INV. C10B49/22 C10B53/02 C10B55/10 C10J3/46 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C10B C10J Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2011/233042 A1 (SISKIN MICHAEL [US] ET AL) 29 September 2011 (2011-09-29)	1-20
Y	claims 1-20 paragraphs [0020], [0027], [0028], [0029]	1-20
Y	----- US 2020/063038 A1 (HARANDI MOHSEN N [US]) 27 February 2020 (2020-02-27) figure 2 claims 1-20 paragraphs [0041] - [0049]	1-20
A	----- US 2022/169928 A1 (XU XIAOCHUN [US] ET AL) 2 June 2022 (2022-06-02) table 2 ----- -/--	1-20
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
<p>* Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>		
Date of the actual completion of the international search 11 September 2023		Date of mailing of the international search report 21/09/2023
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Zuurdeeg, Boudewijn

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2023/026190

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

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