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- (54) **INTEGRATION OF POLYMERIC WASTE CO-PROCESSING IN COKERS TO PRODUCE CIRCULAR CHEMICAL PRODUCTS FROM COKER GAS OIL**
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8, 2022.

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C10G 69/06 (2006.01)
C10G 69/12 (2006.01)
- (52) **U.S. Cl.**
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2400/20 (2013.01)
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(57) **ABSTRACT**

Systems and methods are provided for integration of poly-
meric waste co-processing in cokers to produce circular
chemical products from coker gas oil, including a method of
producing circular chemical products comprising: providing
a coker gas oil that is at least partially derived from
polymeric waste, wherein the coker gas oil has a paraffin
content of about 5 wt % to about 50 wt %, a sulfur content
of about 0.1 wt % to about 7 wt %, and a halide content of
about 0.1 wppm to about 5 wppm; and converting the coker
gas oil into at least a polymer.

22 Claims, 5 Drawing Sheets

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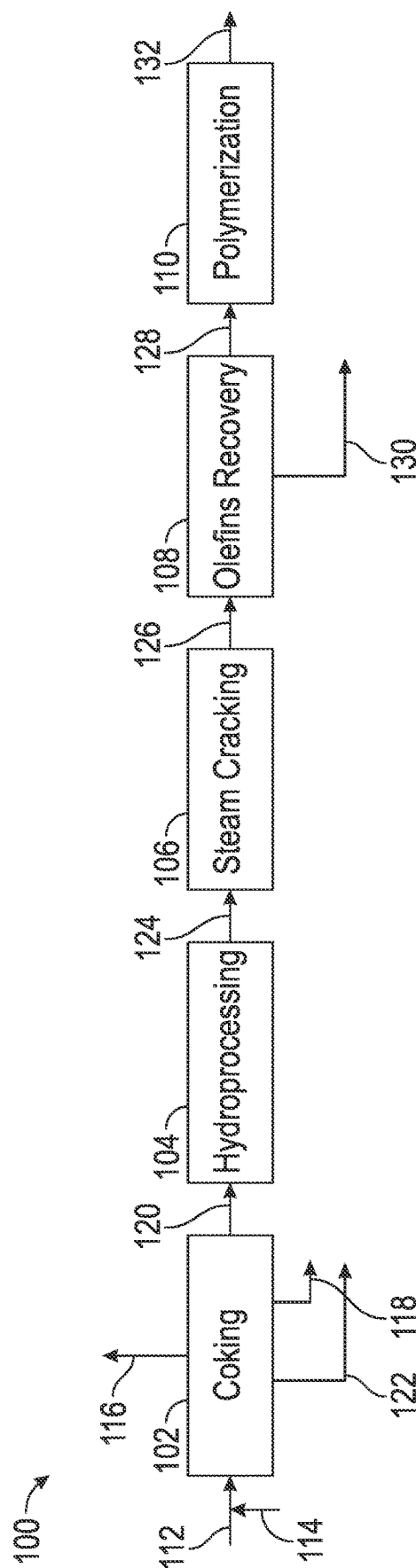


FIG. 1

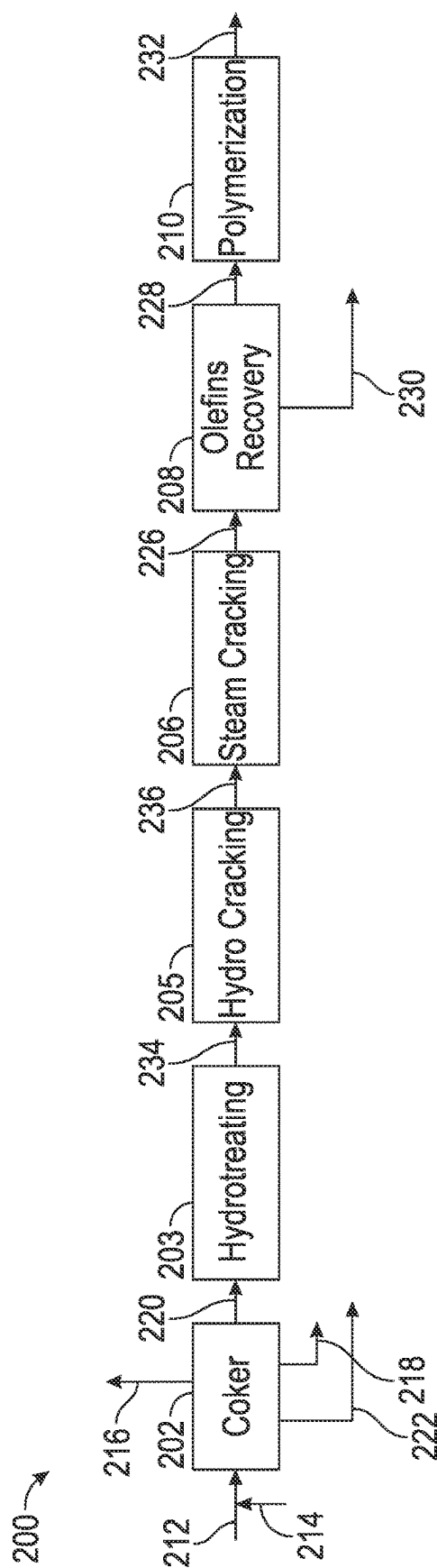


FIG. 2

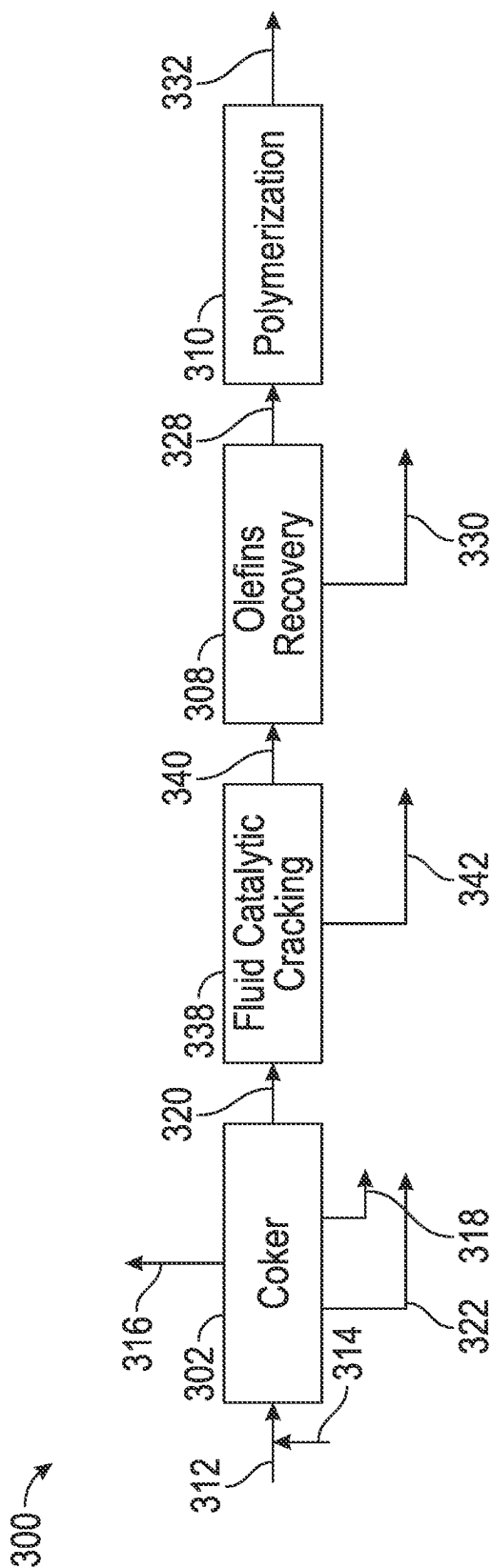


FIG. 3

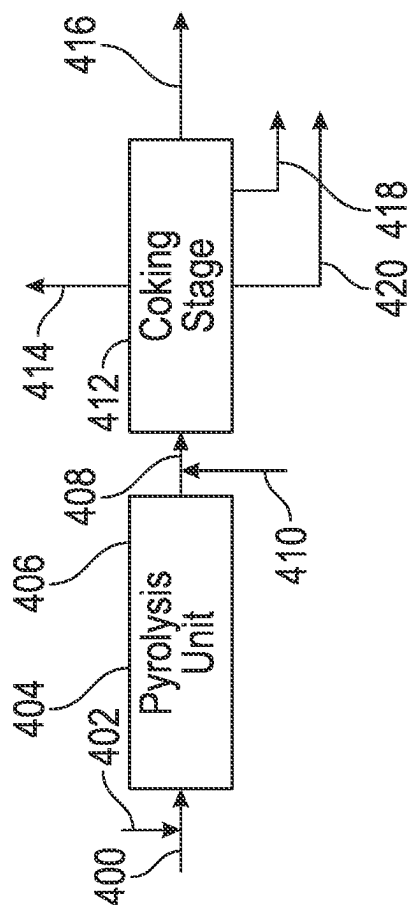


FIG. 4

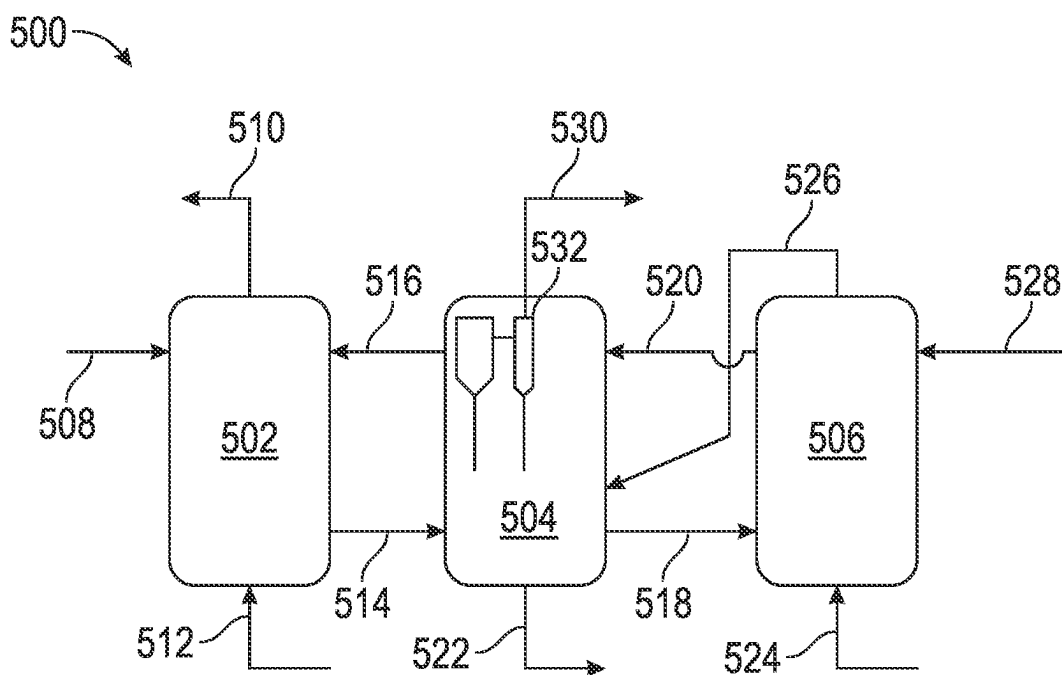


FIG. 5

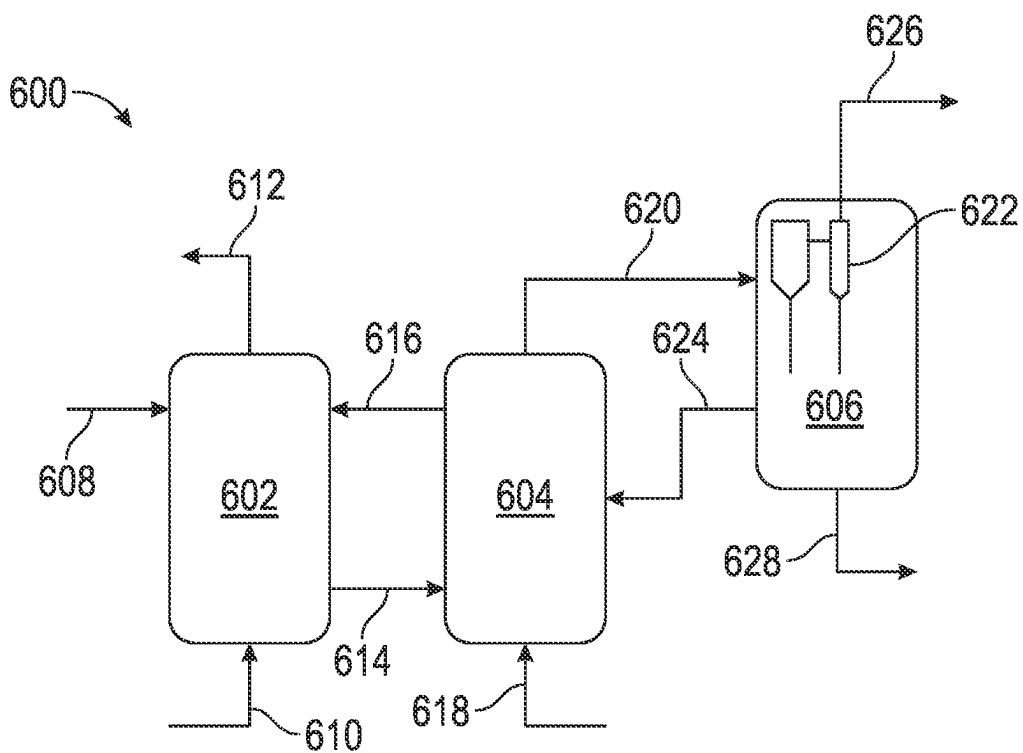


FIG. 6

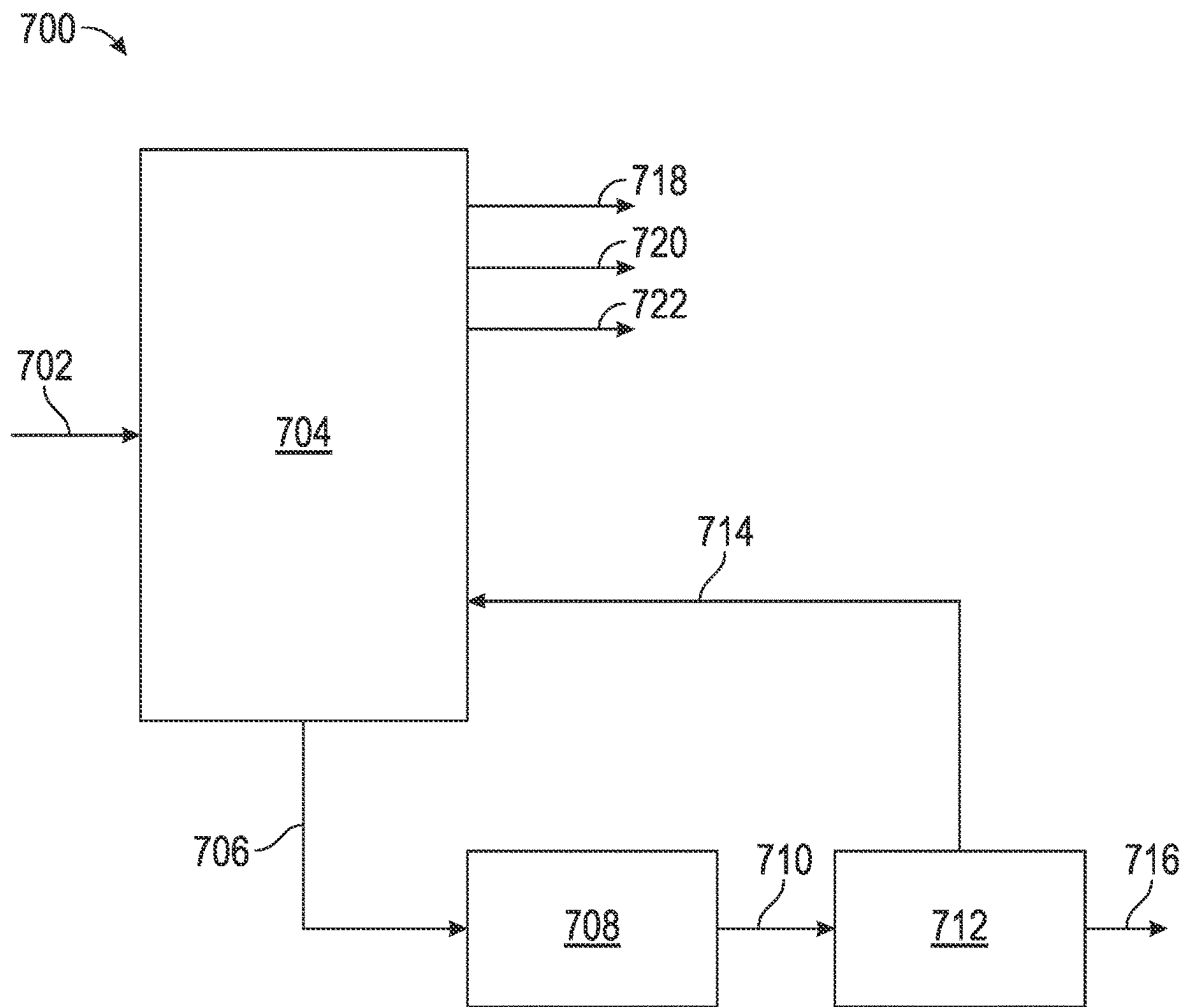


FIG. 7

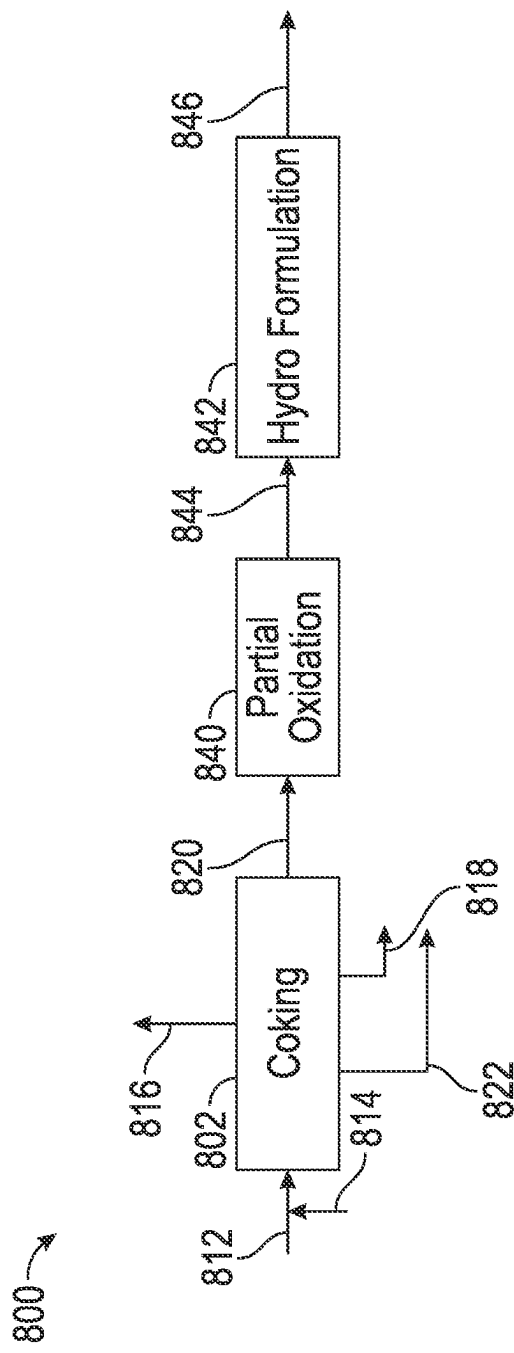


FIG. 8

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INTEGRATION OF POLYMERIC WASTE CO-PROCESSING IN COKERS TO PRODUCE CIRCULAR CHEMICAL PRODUCTS FROM COKER GAS OIL

CROSS REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of and priority to U.S. Provisional Application No. 63/374,946 filed Sep. 8, 2022, the disclosure of which is incorporated herein by reference.

FIELD

Systems and methods are provided for integration of polymeric waste co-processing in cokers to produce circular chemical products from coker gas oil.

BACKGROUND

Processing of polymeric waste is a subject of increasing importance. It is desirable to have a processing pathway that allows for production of circular chemical products. Specifically, it is desirable to produce circular chemical products through a processing pathway that includes polymeric waste recycling. Although dedicated processing systems could be used for polymeric waste recycling, such dedicated systems require substantial initial capital costs and a constant supply of waste feedstock. Thus, it is desirable to leverage an existing processing unit to be able to co-process polymeric waste into feedstock for production of circular chemical products.

SUMMARY

Disclosed herein is an example method of producing circular chemical products comprising: providing a coker gas oil that is at least partially derived from polymeric waste, wherein the coker gas oil has a paraffin content of about 5 wt % to about 50 wt %, a sulfur content of about 0.1 wt % to about 7 wt %, and a halide content of about 0.1 wppm to about 5 wppm; and converting the coker gas oil into at least a polymer.

Further disclosed herein is an example method of producing circular chemical products comprising: providing a coker gas oil that is at least partially derived from polymeric waste, wherein the coker gas oil has a paraffin content of about 5 wt % to about 50 wt %, a sulfur content of about 0.1 wt % to about 7 wt %, and a halide content of about 0.1 wppm to about 5 wppm; hydroprocessing at least a portion of the coker gas oil to form at least a hydroprocessing effluent; steam cracking at least a portion of the hydroprocessing effluent to form at least a steam cracking effluent; recovering olefins from the steam cracking effluent; and polymerizing at least a portion of the olefins to form at least polyolefins.

These and other features and attributes of the disclosed methods and systems of the present disclosure and their advantageous applications and/or uses will be apparent from the detailed description which follows.

BRIEF DESCRIPTION OF THE DRAWINGS

To assist those of ordinary skill in the relevant art in making and using the subject matter hereof, reference is made to the appended drawings, wherein:

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FIG. 1 is an illustrative depiction of an integrated process for production of circular chemical products from polymeric waste in accordance with certain embodiments of the present disclosure.

FIG. 2 is another illustrative depiction of an integrated process for production of circular chemical products from polymeric waste in accordance with certain embodiments of the present disclosure.

FIG. 3 is another illustrative depiction of an integrated process for production of circular chemical products from polymeric waste in accordance with certain embodiments of the present disclosure.

FIG. 4 is an illustrative depiction of a process for pyrolysis of polymeric waste followed by coking.

FIG. 5 is an illustrative depiction of a fluidized bed coking system including a coker, a heater, and a gasifier in accordance with certain embodiments of the present disclosure.

FIG. 6 is an illustrative depiction of a fluidized bed coking system including a coker and a gasifier in accordance with certain embodiments of the present disclosure.

FIG. 7 is an illustrative depiction of a delayed coking system including a coker and a fractionator in accordance with certain embodiments of the present disclosure.

FIG. 8 illustrates an example configuration for chemical recycling of polymeric waste.

DETAILED DESCRIPTION

In various embodiments, systems and methods are provided for chemical recycling of polymeric waste, such as plastic waste. In some embodiments, the polymeric waste is co-processed in a coker to produce coker products, including coker gas oil. Example embodiments further include includes production of circular chemical products from the coker gas oil that are at least partially derived from polymeric waste. In some embodiments, the circular products include circular olefins, which can be further processed to produce circular polyolefins.

Circular chemical products are chemical products derived from polymeric waste wherein the molecules of the chemical product can be attributed to the polymers in the polymeric waste, such as by crediting, allocating offsetting for other hydrocarbons, and/or substituting for other hydrocarbons in a mass or energy balance for a system. Circular chemical products include circular monomers, circular aromatics, and circular polymers, among others. Polymers that are certified for their circularity by third party certification may be referred to as certified circular. One example of such a certification is the mass balance chain of custody method set forth by the International Sustainability and Carbon Certification.

Coker gas oil is a coker effluent fraction that is formed in the coker with a T10 distillation point of 225° C. or higher and a T90 distillation point of 650° C. or less. Coker gas oil is a mixture of many different hydrocarbons, including paraffins, olefins, and aromatics. Coker gas oil can include hydrocarbons ranging from 8 carbon atoms to 70 carbon atoms. Coker gas oil is typically considered “heavy” if it has a boiling point range of 340° C. to 525° C. Coker gas oil is typically considered “light” if it has a boiling point range of 220° C. to 345° C. In some embodiments, coker gas oil is separated into light and heavy fractions.

Coker gas oil typically has a number of uses, including as a fuel that can be burned in a furnace or boiler for generation of energy. Coker gas oil can also be upgraded, for example, in a fluid catalytic cracking (“FCC”) unit. However, while coker gas oil can be used as an FCC feedstock, coker gas oil

typically presents challenges making it use as a feedstock for subsequent processing. For example, coker gas oil typically contains levels of sulfur that results in poor quality of resultant chemical products as well as posing challenges with process reliability. In addition, metals (e.g., lead, iron, and copper), aromatic content (e.g., multi-ring aromatics) and olefin content of the coker gas oil relative to paraffins also poses challenges to process reliability while also making chemical production less cost effective. Accordingly, coker gas oil typically must undergo extension pre-treatment, including hydrotreating, amine/caustic treatment, and/or water wash prior to chemical production, as well as fractionation for concentrating olefins prior to polymerization.

In one or more embodiments, the chemical products are produced from coker gas oil that is at least partially derived from polymeric waste. In some embodiments, the coker gas oil is produced by co-processing of polymeric waste with a conventional coker feedstock. Accordingly, at least a portion of the chemical products produced from the coker gas oil can be considered circular chemical products. Circular chemical products can have inherently higher value than chemical products produced from conventional coker gas oil, thus providing improved economics for chemical production from coker gas, oil for example, by having increased olefin content with reduced paraffin content, as well as lower aromatic content. In addition, the co-processing of the polymeric waste should also provide coker gas oil with reduced sulfur content. Advantageously, the reduction in sulfur and paraffin content from co-processing of polymeric waste should increase the value of coker gas oil for subsequent chemical production, for example, by reducing the extent of pre-treatment and/or fractionation that may be required.

In addition, processing of the coker gas oil that is at least partially derived from polymeric waste to form chemical products presents unique challenges. For example, coker gas oil from polymeric waste has increased halides as compared to conventional coker gas oil. The increased halide content is from halides present in the polymeric waste (e.g., polyvinyl chloride, polyvinylidene chloride, fire retardants, inks, dyes, fluoropolymer processing aids) that at least a portion of which ultimately end up in the coker gas. Additionally, the coker gas oil can also include increased levels of oxygen-containing compounds (e.g., ketones esters, acids, aldehydes, and combinations thereof) and nitrogen-containing compounds (e.g., pyrroles, pyridines, amines, amides, and combinations thereof) from coking of polymer waste. Accordingly, example embodiments include treatment of the coker gas oil for removal of these compounds, including halides, oxygen, and nitrogen.

Accordingly, present embodiments utilize the coker gas oil that is at least partially derived from polymeric waste as a feedstock for chemical production. This integration of a coker with chemical production allows the polymeric waste to be chemically recycled into chemical products, such as monomers (e.g., olefins), aromatics, polymers, synthetic elastomers and rubbers, plastic additives, epoxies, and resins, and specialty fluids, such as isopropyl alcohol, oxoalcohols, detergents, and lubricants.

Coker Gas Oil Integration

FIG. 1 illustrates an example configuration for chemical recycling of polymeric waste that includes an integrated process 100 for coking of polymeric waste with polymer production. As illustrated, the integrated process 100

includes a coking stage 102, a hydroprocessing stage 104, a steam cracking stage 106, an olefins recovery stage 108, and a polymerization stage 110.

In FIG. 1, a waste feedstock 112 and one or more conventional coking feedstocks 114 are fed into the coking stage 102. The waste feedstock 112 includes polymeric waste. The one or more conventional coking feedstocks 114 include, for example, a heavy oil with a T10 distillation point of 343° C. or greater, such as petroleum vacuum resid. Coking stage 102 corresponds to any suitable coking for coking the polymeric waste, including a delayed coker, a fluidized coker, flexicoker, or a combination thereof. In the coking stage 102, the combined feedstock of the waste feedstock 112 and the one or more conventional coking feedstocks 114 are processed to form at least a coking effluent. In the example shown in FIG. 1, the coking effluent can be separated to form a coker gas fraction 116 and a coker liquids fraction, which may be further separated, for example, into coker a naphtha fraction 118 and a coker gas oil fraction 120. In some embodiments, one or more of the fractions from the coking stage 102 may be combined. In some embodiments, one or more additional fractions may be produced in the coking stage 102. A coke product 122 also shown, but it should be understood that the coke product 122 is typically withdrawn from a coker separately from the coker effluent or gasified in a flexicoker, for example.

The coker gas oil fraction 120 that is at least partially derived from polymeric waste can then be passed into the hydroprocessing stage 104. Hydroprocessing stage 104 corresponds to any suitable process for hydroprocessing the coker gas oil, including hydrotreatment, hydrocracking, catalytic dewaxing and/or hydroisomerization, aromatic saturation. In some embodiments, hydroprocessing stage 104 corresponds to hydrotreatment of at least a portion of the coker gas oil fraction 120 that treatment of the coker gas oil with hydrogen in the presence of a hydroprocessing catalyst, for example at elevated temperatures and/or pressures. A number of different reactions can occur during hydrotreatment, including hydrodesulfurization, hydrodenitrogenation, and/or hydrogenation, among others.

Hydrotreatment can reduce halides, sulfur, and metal levels in the coker gas oil, as well as nitrogen- and oxygen-containing compounds, in addition to other impurities. In some embodiments, the coker gas oil fraction 120 is co-processed in the hydroprocessing stage 104 with one or more additional gas oils, which may be from different sources. In the example shown in FIG. 1, all of the coker gas oil fraction 120 from the coking stage 102 is passed into the hydroprocessing stage 104. In other embodiments, a portion of the coker gas oil fraction 120 from the coking stage 102 is used for another purpose with another portion of the coker gas oil fraction 120 passed to the hydroprocessing stage 104.

The hydroprocessing effluent 124 that is at least partially derived from polymeric waste can then be passed into the steam cracking stage 106. Steam cracking stage 106 corresponds to any suitable process for steam cracking saturated hydrocarbons into small hydrocarbons, including olefins such as ethylene, propylene, butylene (e.g., isobutylene), and butadiene, among others. For example, the hydroprocessing effluent 124 may be diluted with steam and heated to reaction temperatures for steam cracking. In some embodiments, the hydroprocessing effluent 124 from co-processing of the coker gas oil is co-processed in the steam cracking stage 106 with one or more additional steam cracking feeds. In the example shown in FIG. 1, all of the hydroprocessing effluent 124 from the hydroprocessing stage 104 is passed into the steam cracking stage 106. In

other embodiments, a portion of the hydroprocessing effluent **124** from the hydroprocessing stage **104** is used for another purpose with another portion of the hydroprocessing effluent **124** passed to the steam cracking stage **106**.

After the steam cracking stage **106**, the steam cracking effluent **126** that is at least partially derived from polymeric waste can then be passed into the olefins recovery stage **108**. In the example shown in FIG. 1, all of the steam cracking effluent **126** from the steam cracking stage **106** is passed into the olefins recovery stage **108**. In other embodiments, a portion of the steam cracking effluent **126** from the steam cracking stage **106** is used for another purpose with another portion of the steam cracking effluent **126** passed to the olefins recovery stage **108**. In some embodiments, the steam cracking effluent **126** (or portion thereof) may be treated, for example, to at least partially remove one or more components (e.g., halides, oxygen, nitrogen) before the olefins recovery stage **108**. In the olefins recovery stage **108**, olefins are separated from the steam cracking effluent **126** to form at least an olefins stream **128** and an additional product stream **130**. The olefins stream **128** does not necessarily include 100% olefins but should generally include a substantial portion of olefins, for example, 50 wt %, 60 wt %, 80 wt %, 90 wt %, 95 wt %, or more of olefins. Separation of the olefins from the steam cracking effluent **126** can occur in one or more vessels and/or one or more different operations. For example, the steam cracking effluent **126** can be fractionated or otherwise separated to form at least the olefins stream **128** and additional products stream **130**. At least a portion of the olefins separated from the steam cracking effluent **126** include circular olefins, such as circular ethylene, circular propylene, and circular butylene (e.g., circular butylene), and circular butadiene, among others. Circular olefins can be attributed, for example, to polymers in the polymeric waste. In some embodiments, the olefins stream **128** can be separated into one or more additional fractions, such as an ethylene fraction including circular ethylene, a butylene fraction including circular butylene, a propylene fraction including circular propylene, and/or a butadiene fraction including circular butadiene, among others. At least a portion of the products in the additional product stream **130** include circular products, such as aromatics, including benzene, toluene, xylene, and styrene. Additional circular products include, for example, cyclohexane, cyclopentadiene, and dicyclopentadiene. In some embodiments, the additional product stream **130** is separated into one or more fractions, such as an aromatics stream.

The olefins stream **128** from the olefins recovery stage **108** can then be passed to a polymerization stage **110** for production of chemical products, such as polymer products **132**. For example, an ethylene fraction, propylene fraction, and/or butylene fraction can be separately passed to a polymerization stage. Polymerization stage **110** corresponds to any suitable polymerization process for bonding two or more olefins, including chain growth propagation, step-growth, and condensation polymerization. The polymerization processes may be in the solution, slurry, or gas-phase, among others. In some embodiments, the polymer products **132** include polyolefins. At least a portion of the polymer products **132** produced in the polymerization stage **110** include circular polymers, such as circular polyethylene, circular polypropylene, circular polybutylene (e.g., circular polyisobutylene), circular polybutadiene, circular polyethylene terephthalate, circular polystyrene, circular polycarbonate, and circular polycaprolactam, among others. Circular polymers can be attributed, for example, to polymers in

the polymeric waste. In the example shown in FIG. 1, all of the olefins stream **128** from the olefins recovery stage **108** is passed into the polymerization stage **110**. In other embodiments, a portion of the olefins stream **128** from the olefins recovery stage **108** is used for another purpose with another portion of the olefins stream **128** passed to the polymerization stage **110**.

FIG. 2 illustrates another example configuration for chemical recycling of polymeric waste that includes an integrated process **200** for coking of polymeric waste with polymer production. The embodiment of FIG. 2 is similar to FIG. 1 except the integrated process **200** further includes a hydrotreating stage **203** and a hydrocracking stage **205**. As illustrated, the integrated process **200** includes a coking stage **202**, a hydrotreating stage **203**, a hydrocracking stage **205**, a steam cracking stage **206**, an olefins recovery stage **208**, and a polymerization stage **210**.

In FIG. 2, a waste feedstock **212** and one or more conventional coking feedstocks **214** are fed into the coking stage **202**. The waste feedstock **212** includes polymeric waste. The one or more conventional coking feedstocks **214** include, for example, a heavy oil with a T10 distillation point of 343° C. or greater, such as petroleum vacuum resid. Coking stage **202** corresponds to any suitable coking for coking the polymeric waste, including a delayed coker, a fluidized coker, flexicoker, or a combination thereof. In the coking stage **202**, the combined feedstock of the waste feedstock **212** and the one or more conventional coking feedstocks **214** are processed to form at least a coking effluent. In the example shown in FIG. 2, the coking effluent can be separated to form a coker gas fraction **216** and a coker liquids fraction, which may be further separated, for example, into coker a naphtha fraction **218** and a coker gas oil fraction **220**. In some embodiments, one or more of the fractions from the coking stage **202** may be combined. In some embodiments, one or more additional fractions may be produced in the coking stage **202**. A coke product **222** also shown, but it should be understood that the coke product **222** is typically withdrawn from a coker separately from the coker effluent or gasified in a flexicoker, for example.

The coker gas oil fraction **220** that is at least partially derived from polymeric waste can then be passed into the hydrotreating stage **203**. Any suitable technique for hydrotreatment may be used in accordance with one or more embodiments. In some embodiments, hydrotreatment of at least a portion of the coker gas oil fraction includes treatment of the coker gas oil with hydrogen in the presence of a hydrotreatment catalyst, for example at elevated temperatures and/or elevated pressures. A number of different reactions can occur during hydrotreatment, including hydrodesulfurization, hydrodenitrogenation, and/or hydrogenation, among others. Hydrotreatment can reduce sulfur and metal levels in the coker gas oil, as well as nitrogen- and oxygen-containing compounds. In the example shown in FIG. 2, all of the coker gas oil fraction **220** from the coking stage **202** is passed into the hydrotreating stage **203**. In other embodiments, a portion of the coker gas oil fraction **220** from the coking stage **202** is used for another purpose with another portion of the coker gas oil fraction **220** passed to the hydrotreating stage **203**.

The hydrotreated effluent **234** that is at least partially derived from polymeric waste can then be passed into the hydrocracking stage **205**. Hydrocracking generally includes treatment of the hydrotreated effluent **234** with hydrogen in the presence of a hydrocracking catalyst. In hydrocracking larger hydrocarbon molecules are broken down into smaller molecules, for example, by addition of hydrogen under

pressure and in the presence of a catalyst. Additional reactions can occur in hydrocracking including, for example, hydrodesulfurization, hydrodenitrogenation, and/or hydrogenation, among others. Hydrocracking can reduce sulfur and metal levels in the coker gas oil, as well as nitrogen- and oxygen-containing compounds, in addition to other impurities. In the example shown in FIG. 2, all of the hydrotreated effluent **234** from the hydrotreating stage **203** is passed into the hydrocracking stage **205**. In other embodiments, a portion of the hydrotreated effluent **234** from the hydrotreating stage **203** is used for another purpose with another portion of the hydrotreated effluent **234** passed to the hydrocracking stage **205**.

The hydrocracking effluent **236** from the hydrocracking stage **205** that is at least partially derived from polymeric waste can then be passed to the steam cracking stage **206**. Steam cracking stage **206** corresponds to any suitable process for steam cracking saturated hydrocarbons into small hydrocarbons, including olefins such as ethylene, propylene, butylene (e.g., isobutylene), and butadiene, among others. For example, the hydrocracking effluent **236** may be diluted with steam and heated to reaction temperatures for steam cracking. In the example shown in FIG. 2, all of the hydrocracking effluent **236** from the hydrocracking stage **205** is passed into the steam cracking stage **206**. In other embodiments, a portion of the hydrocracking stage **205** from the hydrocracking stage **205** is used for another purpose with another portion of the hydrocracking stage **205** passed to the steam cracking stage **206**.

After the steam cracking stage **206**, the steam cracking effluent **226** that is at least partially derived from polymeric waste can then be passed into the olefins recovery stage **208**. In the example shown in FIG. 2, all of the steam cracking effluent **226** from the steam cracking stage **206** is passed into the olefins recovery stage **208**. In other embodiments, a portion of the steam cracking effluent **226** from the steam cracking stage **206** is used for another purpose with another portion of the steam cracking effluent **226** passed to the olefins recovery stage **208**. In some embodiments, the steam cracking effluent **226** (or portion thereof) may be treated, for example, to at least partially remove one or more components (e.g., halides, oxygen, nitrogen) before the olefins recovery stage **208**. In the olefins recovery stage **208**, olefins are separated from the steam cracking effluent **226** to form at least an olefins stream **228** and an additional product stream **230**. The olefins stream **228** does not necessarily include 100% olefins but should generally include a substantial portion of olefins, for example, 50 wt %, 60 wt %, 80 wt %, 90 wt %, 95 wt %, or more of olefins. Separation of the olefins from the steam cracking effluent **226** can occur in one or more vessels and/or one or more different operations. For example, the steam cracking effluent **226** can be fractionated or otherwise separated to form at least the olefins stream **228** and additional products stream **230**. At least a portion of the olefins separated from the steam cracking effluent **226** include circular olefins, such as circular ethylene, circular propylene, and circular butylene (e.g., circular butylene), and circular butadiene, among others. Circular olefins can be attributed, for example, to polymers in the polymeric waste. In some embodiments, the olefins stream **228** can be separated into one or more additional fractions, such as an ethylene fraction including circular ethylene, a butylene fraction including circular butylene, a propylene fraction including circular propylene, and/or a butadiene fraction including circular butadiene, among others. At least a portion of the products in the additional product stream **230** include circular products,

such as aromatics, including benzene, toluene, xylene, and styrene. Additional circular products include, for example, cyclohexane, cyclopentadiene, and dicyclopentadiene. In some embodiments, the additional product stream **230** is separated into one or more fractions, such as an aromatics stream.

The olefins stream **228** from the olefins recovery stage **208** can then be passed to a polymerization stage **210** for production of chemical products, such as polymer products **232**. For example, an ethylene fraction, propylene fraction, and/or butylene fraction can be separately passed to a polymerization stage. Polymerization stage **210** corresponds to any suitable polymerization process for bonding two or more olefins, including chain growth propagation, step-growth, and condensation polymerization. The polymerization processes may be in the solution, slurry, or gas-phase, among others. In some embodiments, the polymer products **232** include polyolefins. At least a portion of the polymer products **232** produced in the polymerization stage **210** include circular polymers, such as circular polyethylene, circular polypropylene, circular polybutylene (e.g., circular polyisobutylene), circular polybutadiene, circular polyethylene terephthalate, circular polystyrene, circular polycarbonate, and circular polycaprolactam, among others. Circular polymers can be attributed, for example, to polymers in the polymeric waste. In the example shown in FIG. 2, all of the olefins stream **228** from the olefins recovery stage **208** is passed into the polymerization stage **210**. In other embodiments, a portion of the olefins stream **228** from the olefins recovery stage **208** is used for another purpose with another portion of the olefins stream **228** passed to the polymerization stage **210**.

FIG. 3 illustrates another example configuration for chemical recycling of polymeric waste that includes an integrated process **300** for coking of polymeric waste with polymer production. As illustrated, the integrated process **300** includes a coking stage **302**, a fluid catalytic cracking ("FCC") stage **338**, an olefins recovery stage **308**, and a polymerization stage **310**.

In FIG. 3, a waste feedstock **312** and one or more conventional coking feedstocks **314** are fed into the coking stage **302**. The waste feedstock **312** includes polymeric waste. The one or more conventional coking feedstocks **314** include, for example, a heavy oil with a T10 distillation point of 343° C. or greater, such as petroleum vacuum resid. Coking stage **302** corresponds to any suitable coking for coking the polymeric waste, including a delayed coker, a fluidized coker, flexicoker, or a combination thereof. In the coking stage **302**, the combined feedstock of the waste feedstock **312** and the one or more conventional coking feedstocks **314** are processed to form at least a coking effluent. In the example shown in FIG. 3, the coking effluent can be separated to form a coker gas fraction **316** and a coker liquids fraction, which may be further separated, for example, into a coker naphtha fraction **318** and a coker gas oil fraction **320**. In some embodiments, one or more of the fractions from the coking stage **302** may be combined. In some embodiments, one or more additional fractions may be produced in the coking stage **302**. A coke product **322** is also shown, but it should be understood that the coke product **322** is typically withdrawn from a coker separately from the coker effluent or gasified in a flexicoker, for example.

The coker gas oil fraction **320** that is at least partially derived from polymeric waste can then be passed into the FCC stage **338**. FCC stage **338** corresponds to any suitable process for fluid catalytic cracking of hydrocarbons into smaller hydrocarbons, including olefins such as ethylene,

propylene, butylene (e.g., isobutylene), and butadiene, among others. Fluid catalytic cracking includes, for example, heating of the feed of the coker gas oil fraction **320** and contacting the feed with a hot, powdered catalyst. The FCC stage **338** generates at least FCC gas **340** and FCC liquids **342**. The FCC gas **340** includes C₂-C₄ olefins, such as ethylene, propylene, and butylene. The FCC liquids includes hydrocarbons, such as, for example, a naphtha fraction and heavier hydrocarbons. In the example shown in FIG. 3, all of the coker gas oil fraction **320** from the coking stage **302** is passed into the FCC stage **338**. In other embodiments, a portion of the coker gas oil fraction **320** from the coking stage **302** is used for another purpose, such as fuel, with another portion of the coker gas oil fraction **320** passed to the FCC stage **338**.

After the FCC stage, the FCC gas **340** can be passed to an olefins recovery stage **308**. In the olefins recovery stage **308**, olefins are separated from the FCC gas **340** to form at least an olefins stream **328** and a paraffins stream **330**. It should be understood that separation of the olefins from the FCC gas **340** can occur in one or more vessels and/or one or more different operations. For example, the FCC gas **340** can be fractionated or otherwise separated to form at least the olefins stream **328** and paraffins stream **330**. At least a portion of the olefins separated from the FCC gas **340** include circular olefins, such as circular ethylene, circular propylene, and circular butylene (e.g., circular butylene), and circular butadiene, among others. Circular olefins can be attributed, for example, to polymers in the polymeric waste. In some embodiments, the olefins stream **328** can be separated into one or more additional fractions, such as an ethylene fraction including circular ethylene, a butylene fraction including circular butylene, a propylene fraction including circular propylene, and/or a butadiene fraction including circular butadiene, among others.

The olefins stream **328** from the olefins recovery stage **308** can then be passed to a polymerization stage **310** for production of chemical products, such as polymer products **332**. For example, an ethylene fraction, propylene fraction, and/or butylene fraction can be separately passed to a polymerization stage. Polymerization stage **310** corresponds to any suitable polymerization process for bonding two or more olefins, including chain growth propagation, step-growth, and condensation polymerization. The polymerization processes may be in the solution, slurry, or gas-phase, among others. In some embodiments, the polymer products **332** include polyolefins. At least a portion of the polymer products **332** produced in the polymerization stage **310** include circular polymers, such as circular polyethylene, circular polypropylene, circular polybutylene (e.g., circular polyisobutylene), circular polybutadiene, circular polyethylene terephthalate, circular polystyrene, circular polycarbonate, and circular polycaprolactam, among others. Circular polymers can be attributed, for example, to polymers in the polymeric waste. In the example shown in FIG. 3, all of the olefins stream **328** from the olefins recovery stage **308** is passed into the polymerization stage **310**. In other embodiments, a portion of the olefins stream **328** from the olefins recovery stage **308** is used for another purpose with another portion of the olefins stream **328** passed to the polymerization stage **310**.

FIG. 8 illustrates another example configuration for chemical recycling of polymeric waste that includes an integrated process **800** for coking of polymeric waste with polymer production. As illustrated, the integrated process **800** includes a coking stage **802**, a partial oxidation stage **840**, and a hydroformylation stage **842**.

In FIG. 8, a waste feedstock **812** and one or more conventional coking feedstocks **814** are fed into the coking stage **802**. The waste feedstock **812** includes polymeric waste. The one or more conventional coking feedstocks **814** include, for example, a heavy oil with a T10 distillation point of 343° C. or greater, such as petroleum vacuum resid. Coking stage **802** corresponds to any suitable coking for coking the polymeric waste, including a delayed coker, a fluidized coker, flexicoker, or a combination thereof. In the coking stage **802**, the combined feedstock of the waste feedstock **812** and the one or more conventional coking feedstocks **814** are processed to form at least a coking effluent. In the example shown in FIG. 8, the coking effluent can be separated to form a coker gas fraction **816** and a coker liquids fraction, which may be further separated, for example, into a coker naphtha fraction **818** and a coker gas oil fraction **820**. In some embodiments, one or more of the fractions from the coking stage **802** may be combined. In some embodiments, one or more additional fractions may be produced in the coking stage **802**. A coke product **822** is also shown, but it should be understood that the coke product **822** is typically withdrawn from a coker separately from the coker effluent or gasified in a flexicoker, for example.

The coker gas oil fraction **820** that is at least partially derived from polymeric waste can then be passed into the partial oxidation stage **840**. The partial oxidation stage **840** corresponds to any suitable process for partial oxidation including, for example, catalytic and thermal partial oxidation. In partial oxidation, the coker gas oil fraction **820** is partially combusted with oxygen to create a hydrogen-containing syngas. The oxidation effluent **844** generated in the partial oxidation stage **840** includes, for example, carbon monoxide and hydrogen. In some embodiments, the oxidation effluent includes carbon monoxide and hydrogen in an amount of at least 70 wt %, at least 80 wt %, or at least 90 wt %. In the example shown in FIG. 8, all of the coker gas oil fraction **820** from the coking stage **802** is passed into the partial oxidation stage **840**. In other embodiments, a portion of the coker gas oil fraction **820** from the coking stage **802** is used for another purpose, such as fuel, with another portion of the coker gas oil fraction **820** passed to the partial oxidation stage **840**.

After the partial oxidation stage **840**, the oxidation effluent **844** can be passed to a hydroformylation stage **842**. In the hydroformylation stage **842**, the oxidation effluent can be used for production of a variety of chemical products. In some embodiments, the syngas can be combined with olefins over a hydroformylation catalyst to produce oxo alcohols. A variety of chemical products and polymer precursors can also be produced, in some embodiments, from the syngas in the oxidation effluent **844** using the Fischer-Tropsch process. In some embodiments, oxidation effluent **844** is purified for hydrogen recovery. As illustrated, a product stream **846** is withdrawn from the hydroformylation stage **842**. Product stream **842** includes, for example, oxo alcohols. In the example shown in FIG. 8, all of the oxidation effluent **844** from the coking stage **302** is passed into the hydroformylation stage **842**. In other embodiments, a portion of the oxidation effluent **844** from the partial oxidation stage **840** is used for another purpose, such as fuel, with another portion of the oxidation effluent **844** passed to the hydroformylation stage **842**.

Coker Feed

In accordance with present embodiments, coking can be used to process a waste feedstock to produce coking products. In some embodiments, the waste feedstock is co-processed with a conventional coking feedstock.

The waste feedstock for coking can include or consist essentially of one or more types of polymers, such as polymers corresponding to plastic waste. The systems and methods described herein can be suitable for processing polymeric waste corresponding to a single type of polymer and/or polymeric waste corresponding to a plurality of polymers. In aspects where the waste feedstock consists essentially of polymers, the feedstock can include one or more types of polymers as well as any additives, modifiers, packaging dyes, and/or other components typically added to a polymer during and/or after formulation. The waste feedstock can further include components (e.g., paper) typically found in polymeric waste.

In some embodiments, the waste feedstock includes polymeric waste obtained from any source including, but not limited to, municipal, industrial, commercial or consumer sources. In some embodiments, the waste feedstock includes post-consumer use plastics. The polymeric waste further may include plastics obtained from a common source or from mixed sources, including mixed plastic waste obtained from municipal or regional sources and/or from waste streams of PET, HDPE, LDPE, LLDPE, polypropylene, and/or polystyrene. Furthermore, the waste feedstock may include thermoplastic elastomers and thermoset rubbers, such as from tires and other articles made from natural rubber, polybutadiene, styrene-butadiene, butyl rubber and EPDM.

Even further, examples of suitable waste feedstocks may include any of various used polymeric articles without limitation. Some examples of the many types of polymeric articles may include: films (including cast, blown, and otherwise), sheets, fibers, woven and nonwoven fabrics, furniture (e.g., garden furniture), sporting equipment, bottles, food and/or liquid storage containers, transparent and semi-transparent articles, toys, tubing and pipes, sheets, packaging, bags, sacks, coatings, caps, closures, crates, pallets, cups, non-food containers, pails, insulation, and/or medical devices. Further examples include industrial waste streams, such as linear alpha olefins and polypropylene heavy streams (e.g., >50 wt %). Further examples include automotive, aviation, boat and/or watercraft components (e.g., bumpers, grills, trim parts, dashboards, instrument panels and the like), wire and cable jacketing, agricultural films, geomembranes, playground equipment, and other such articles, whether blow molded, roto-molded, injection-molded, or the like. Any of the foregoing may include mixtures of polymeric and non-polymeric items (e.g., packaging or other articles may include inks, paperboards, papers, metal deposition layers, and the like). The ordinarily skilled artisan will appreciate that such polymeric articles may be made from any of various polymer and/or non-polymer materials, and that the polymer materials may vary widely (e.g., ethylene-based, propylene-based, butyl-based polymers, and/or polymers based on any C_2 to C_{40} or even higher olefins, and further including polymers based on any one or more types of monomers, e.g., C_2 to C_{40} α -olefin, di-olefin, cyclic olefin, etc. monomers). Common examples include ethylene, propylene, butylene, pentene, hexene, heptene, octene, and styrene; as well as multi-olefinic (including cyclic olefin) monomers such as ethylidene norbornene (ENB) and vinylidene norbornene (VNB) (including, e.g., when such cyclic olefins are used as comonomers, e.g., with ethylene monomers).

In various embodiments, the waste feedstock can include one or more nitrogen-containing polymers. Examples of nitrogen-containing polymers include polyamides (such as Nylon 6), polyurethanes, and polynitriles. The nitrogen-

containing polymers can correspond to 0.1 wt % to 25 wt % of the waste feedstock (relative to the weight of the waste feedstock), or 1.0 wt % to 25 wt %, or 5.0 wt % to 25 wt %, or 10 wt % to 25 wt %, or 1.0 wt % to 15 wt %, or 5.0 wt % to 15 wt %, or 1.0 wt % to 10 wt %. For example, nitrogen-containing polymers may be in the waste feedstock in an amount of 25 wt % or less, 10 wt % or less, 5 wt % or less, 1 wt % or less, or 0.1 wt % or less.

In some embodiments, the waste feedstock can include one or more chlorine-containing polymers. Examples of chlorine-containing polymers including PVC (polyvinyl chloride) and PVDC (polyvinylidene chloride). In some aspects, the chlorine-containing polymers can correspond to as 0.001 wt % to 15 wt % of the waste feedstock (relative to the weight of the waste feedstock), or 0.1 wt % to 15 wt %, or 1.0 wt % to 15 wt %, or 0.001 wt % to 10 wt %, or 0.1 wt % to 10 wt %, or 1.0 wt % to 10 wt %, or 0.001 wt % to 5.0 wt %, or 0.001 wt % to 1.0 wt %. For example, the chlorine-containing polymers may be in the waste feedstock in an amount of about 15 wt % or less, 10 wt % or less, 5 wt % or less, 1 wt % or less, or 0.1 wt % or less.

In some embodiments, the waste feedstock can include at least one of polyethylene and polypropylene. The polyethylene can correspond to any convenient type of polyethylene, such as high density or low-density versions of polyethylene. Similarly, any convenient type of polypropylene can be used. Additionally or alternately, the waste feedstock can include one or more of polystyrene, polyamide (e.g., nylon), polyethylene terephthalate, and ethylene vinyl acetate. Still other polyolefins can correspond to polymers (including co-polymers) of butadiene, isoprene, and isobutylene. In some embodiments, the polyethylene and polypropylene can be present in the mixture as a co-polymer of ethylene and propylene. More generally, the polyolefins can include co-polymers of various olefins, such as ethylene, propylene, butenes, hexenes, and/or any other olefins suitable for polymerization.

In this discussion, unless otherwise specified, weights of polymers in a feedstock correspond to weights relative to the total polymer content in the feedstock. Any additives and/or modifiers and/or other components included in a formulated polymer are included in this weight. However, the weight percentages described herein exclude any solvents or carriers that might optionally be used to facilitate transport of the polymer into the coker.

In some embodiments, the waste feedstock includes 0.01 wt % to 35 wt % of polystyrene, or 0.1 wt % to 35 wt %, or 1 wt % to 35 wt %, or 0.01 wt % to 20 wt %, or 0.1 wt % to 20 wt %, or 1 wt % to 20 wt %, or 10 wt % to 35 wt %, or 5 wt % to 20 wt %, or 0.01 wt % to 10 wt %, or 0.01 wt % to 1 wt %. In some embodiments, the waste feedstock can also include oxygen-containing polymers, such as polyterephthalates. It is noted that polyamides also contain oxygen as part of the polymer structure. In this discussion, a polymer that includes both oxygen and nitrogen as part of the repeat unit for forming the polymer is defined as a nitrogen-containing polymer for purposes of characterizing the waste feedstock.

In addition to polymers, a waste feedstock can include a variety of other components. Such other components can include additives, modifiers, packaging dyes, and/or other components typically added to a polymer during and/or after formulation. The waste feedstock can further include any components typically found in polymeric waste. Finally, the feedstock can further include a carrier fluid so that the waste feedstock to the cracking process corresponds to a solution or slurry of the polymeric waste.

In embodiments where the waste feedstock is introduced into the coking environment at least partially as solids, having a small particle size can facilitate transport of the solids and/or reduce the likelihood of incomplete conversion. In some embodiments, the waste feedstock includes polymeric waste having a median particle size to 0.01 mm to 50 mm, 0.01 mm to 25 mm, 0.01 mm to 10 mm, 1 mm to 50 mm, 1 mm to 25 mm, 1 mm to 10 mm, 5 mm, or 0.1 mm to 5 mm, or 0.01 mm to 3 mm, or 0.1 mm to 3 mm, or 0.01 mm to 3 mm, or 0.1 mm to 3 mm, or 1 mm to 3 mm. For determining a median particle size, the particle size is defined as the diameter of the smallest bounding sphere that contains the particle. Additionally or alternately, the polymeric waste in the waste feedstock can be melted and/or pelletized to improve the uniformity of the particle size of the plastic particles. In some embodiments, the polymeric waste has a maximum particles size of 10 mm or less, or 5 mm or less. Additionally or alternately, the polymeric waste can be provided in waste bail. In some embodiments, the waste bale is a composite bale.

It is noted that some types of polymeric waste can also include bio-derived components. For example, some types of plastic labels can include biogenic waste in the form of paper compounds. In some embodiments, 1 wt % to 25 wt % of the waste feedstock can correspond to bio-derived material. Such bio-derived material can also potentially contribute to the nitrogen and/or oxygen content of a waste feedstock.

Optionally, a carrier fluid can also be included in the waste feedstock to assist with introducing the polymeric waste into the cracking environment. For introduction into a cracking environment, it can be convenient for the feedstock to be in the form of a slurry. If a carrier fluid is used for transporting the waste feedstock, any suitable fluid can be used. Examples of suitable carrier fluids can include (but are not limited to) a wide range of petroleum or petrochemical products. For example, some suitable carrier fluids include crude oil, naphtha, kerosene, diesel, light or heavy cycle oils, catalytic slurry oil, and gas-oils. Other potential carrier fluids can correspond to naphthenic and/or aromatics solvents, such as toluene, benzene, methylnaphthalene, cyclohexane, methylcyclohexane, and mineral oil. Still other carrier fluids can correspond to refinery fractions, such as a gas oil fraction or naphtha fraction from a coker. As yet another example, a distillate and/or gas oil boiling range fraction can be used that generated by cracking of the waste feedstock, either alone or with an additional feedstock.

In various embodiments, coking is used to co-process a combined feedstock corresponding to a mixture of a conventional coking feedstock and a waste feedstock. In some embodiments, the conventional coking feedstock is used as the carrier fluid for the waste feedstock. The conventional coking feedstock can correspond to one or more types of petroleum and/or renewable feeds with a suitable boiling range for cracking, such as processing in a coker. The amount of waste feedstock in the combined feedstock can correspond to 1 wt % to 50 wt %, 3 wt % to 50 wt %, 10 wt % to 50 wt %, 25 wt % to 50 wt %, 1 wt % to 25 wt %, 1 wt % to 10 wt %, 1 wt % to 5 wt %, 1 wt % to 3 wt %, 3 wt % to 25 wt %, 10 wt % to 25 wt %, 3 wt % to 15 wt % by weight of the combined feedstock. The conventional coking feedstock can correspond to 50% to 99% by weight of the combined feedstock to the coker.

In some embodiments, the coking feedstock for co-processing with the waste feedstock can correspond to a conventional petroleum feedstock having a relatively high boiling fraction, such as a heavy oil feed. For example, the

coking feedstock portion of the feed can have a T10 distillation point of 343° C. or more, or 371° C. or more. In some embodiments, the coking feedstock has a T10 distillation point of 343° C. to 650° C. Examples of suitable heavy oils for inclusion in the coking feedstock include 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 wt % to 50 wt %. In some embodiments, the coking feedstock includes a petroleum vacuum residuum.

Some examples of conventional petroleum feedstock suitable for processing in a delayed coker or fluidized bed coker can have a composition and properties within the ranges set forth below in Table 1.

TABLE 1

Example 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

In addition to petroleum feedstocks, renewable feedstocks derived from biomass having a suitable boiling range can also be used as part of the cracking feed. Such renewable feedstocks include feedstocks with a T10 boiling point of 340° C. or more and a T90 boiling point of 600° C. or less. An example of a suitable renewable feedstock derived from biomass can be a cracking oil feedstock derived at least in part from biomass.

In some particular embodiments, the waste feedstock and the conventional coking feedstock (e.g., coker feedstock) are mixed to form a combined feedstock prior to entering the coking environment. In other embodiments, the waste feedstock and the conventional coking feedstock are separately introduced into the coking environment. More generally, however, any convenient method for introducing both the waste feedstock and the coking feedstock into the coking environment can be used.

Prior to being introduced into the coking environment, the feedstocks (optionally in the form of a combined feedstock) are pre-heated in accordance with one or more embodiments. Pre-heating the feedstocks in one or more heating stages can increase the temperature of the feedstocks to a mixing and storage temperature, to a temperature related to the cracking temperature, or to another convenient temperature.

In some embodiments, a portion of the pre-heating of a waste feedstock can be performed by mixing the waste feedstock with a coking feedstock in a mixing tank and heating the mixture in the mixing tank. For example, a waste feedstock and a coking feedstock can be mixed in a heated stirred tank for storage operating at 200° C. to 325° C., or 275° C. to 325° C. In some embodiments, tank agitation aids in uniform dispersal of the waste feedstock into resid and maintains slurry suspension. Heating in a mixing tank provides heat to the combined feedstock prior to introducing the

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combined feedstock into the cracking reaction environment. This can reduce or minimize additional cracking heat duty that would otherwise be required to heat the waste feedstock to thermal cracking temperatures. The mixed feedstock may be further heated and/or physically processed for particle size reduction prior to injection into the cracking reactor. The combined feedstock may be sized to provide particles with a maximum particle size, for example, of 5 mm or less, 2 mm or less, or 1 mm or less. In some embodiments, the particles are sized with milling equipment, such as a roller mill. In addition to heating, stripping of the combined waste feedstock and coking feedstock using a stripping gas can be performed in a mixing tank. Passing a stripping gas through the combined feedstock can assist with removing gases that are entrained in the combined feedstock.

In some embodiments, the waste feedstock is melted, for example, in an extruder. After extruding, the waste feedstock including melted polymeric waste can either be directly mixed with a conventional coking feedstock and/or a solvent, or the extruded plastic can be pelletized to form a desired particle size for the waste feedstock.

Still another option can be to mix the waste feedstock with the coking feedstock after the pre-heater furnace for the coker, in accordance with certain embodiments. In these embodiments, the coking feedstock can be heated to a higher temperature in the pre-heater, and then the waste feedstock can be added to the pre-heated coking feedstock to heat the waste feedstock.

Pyrolysis

In accordance with one or more embodiments, the waste feedstock is pyrolyzed to generate a pyrolysis oil that is then fed to the coking environment. In some embodiments, the waste feedstock is pyrolyzed with one or more additional feedstocks, such as rubber-containing feedstocks. In some embodiments, the pyrolysis oil at least partially derived from polymeric waste is co-processed in the coking environment with a conventional coking feedstock.

Pyrolysis is a technique of chemical recycling that includes thermal degradation of the pyrolysis feedstock to produce gas and liquid products, referred to as pyrolysis oil and a pyrolysis gas. Waste plastic pyrolysis units are distinct from coker units that have been specially designed to handle heavier feeds. In some embodiments, the waste feedstock may be heated in an environment free (or substantially free) of oxygen. For example, the pyrolysis may occur in an environment that includes about 5 weight percent oxygen or less, about 3 weight percent oxygen or less, about 1 weight percent oxygen or less, or about 0.5 weight percent oxygen or less. The pyrolysis products may depend on a number of factors, including, but not limited to, pyrolysis reactor temperature, pyrolysis reactor pressure, reactor residence time, feed type, feed quality, and process configuration.

A specific pyrolysis technique will now be described in more detail. In an example embodiment, a pyrolysis feedstock (e.g., a waste feedstock) may be provided, for example, in a granular, flake, or pellet form, and fed to a pyrolysis unit. In the pyrolysis unit, the waste feedstock may be melted to produce a molten liquid (e.g., molten plastic). For example, the polymeric waste may be melted in an extruder to a temperature of about 300° C. to about 320° C. The molten liquid may then be pyrolyzed in an environment free (or substantially free) of oxygen to produce pyrolysis gases. For example, the molten liquid may be heated in pyrolysis chamber to a higher temperature, such as 390° C. to about 550° C., while agitating. Long chain hydrocarbons (e.g., approximately 30 carbon atoms or longer) in the produced pyrolysis gases may then be condensed and further

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pyrolyzed for further thermal degradation while shorter chain hydrocarbons may exit in gaseous form. For example, the produced pyrolysis gases may be directed to a contactor for contact with a bank of condenser elements (e.g., plates) upon which the long chain hydrocarbons may condense. The long chain hydrocarbons may flow from the condenser back to the pyrolysis chamber. The pyrolysis gases including the shorter chain hydrocarbons may be distilled in a distillation column to provide pyrolysis gas and pyrolysis oil.

FIG. 4 illustrates an example configuration for pyrolyzing a waste feedstock followed by coking. In FIG. 4, a waste feedstock 400 and one or more optional feedstocks 402 are fed into the pyrolysis unit 404. The waste feedstock 400 includes polymeric waste, such as plastic waste. In the pyrolysis unit 404, the waste feedstock 400 containing the polymeric waste may be pyrolyzed to form at least a pyrolysis gas 406 and a pyrolysis oil 408. The pyrolysis unit 404 can include a variety of different equipment suitable for pyrolysis of polymeric waste, including but not limited to, reactors, extruders, tanks, vessels, valves, sensors, hoppers, conveyance systems, and piping, among others.

The pyrolysis oil 408 that is at least partially derived from polymeric waste is then passed into coking stage 412. Coking stage 412 corresponds to any suitable coking for coking the pyrolysis oil, including a delayed coker, a fluidized coker, or a combination thereof. As illustrated, a conventional coking feedstock 410 can also be fed into the coking stage 412 in accordance with one or more embodiments. In the coking stage 412, the combined feedstock of the pyrolysis oil 408 and the conventional coking feedstock 410 are processed to form at least a coking effluent. In the example shown in FIG. 4, the coking effluent can be separated to form a coker gas fraction 414, a coker naphtha fraction 416, and a coker gas oil fraction 418. A coke product 420 is also shown, but it should be understood that the coke product 420 is typically withdrawn from a coker separately from the coker effluent.

Coking

In accordance with one or more embodiments, the waste feedstock is coked, either alone or with a conventional coking feedstock, to produce more valuable coking products. In various aspects, co-processing can be performed by exposing the combined feedstock of waste feedstock and conventional coking feedstock to coking conditions.

Coking is a refining process that includes thermal cracking of longer chain molecules into shorter chain molecules with excess carbon left behind in the form of coke. Coking processes in modern refinery settings can typically be categorized as delayed coking or fluidized bed coking. In both processes, the feedstock is cracked to produce gas and liquid products, leaving behind coke. In delayed coking, the feedstock is heated and fed to a coking reactor (commonly referred to as a "coke drum") where the cracking takes place. To remove the coke, alternating drums can be used. In fluidized coking, the feedstock is head to the coking reactor where cracking takes place with coke transferred from the coking reactor to a heater as a fluidized solid.

The coking products produced from coking include a cracking effluent, which may include a gas, a liquid, or a mixture thereof. The cracking effluent can be fractionated or otherwise separated to form desirable product streams, such as coker gas (e.g., C₄ and lighter hydrocarbons), coker naphtha, and coker gas oil.

Coker gas is a coker effluent fraction that is formed in the coker with a T90 distillation point of 40° C. or less. Coker gas is a mixture of many different hydrocarbons, including paraffins, olefins, and aromatics. Coker gas can include

hydrocarbons ranging from 1 carbon atom to 5 carbon atoms. Coker gas can additionally include trace amounts of higher hydrocarbons (e.g., C_6), including benzene in gas. While coker gas is referred to a gas, it should be understood that the coker gas can be in liquid form, for example, depending on temperature and pressure, so long as the coker gas has a final boiling point of 100° C. or less.

Coker naphtha is a liquid coker effluent fraction that is formed in the coker with a T10 distillation point of 30° C. or higher and a T90 distillation point of 220° C. or less. Coker naphtha is a mixture of many different hydrocarbons, including paraffins, naphthenes, olefins, and aromatics. Coker naphthas can include hydrocarbons ranging from 4 carbon atoms to 12 carbon atoms.

Coker gas oil is a coker effluent fraction that is formed in the coker with a T10 distillation point of 225° C. or higher and a T90 distillation point of 650° C. or less. Coker gas oil is a mixture of many different hydrocarbons, including paraffins, olefins, and aromatics. Coker gas oil can include hydrocarbons ranging from 8 carbon atoms to 70 carbon atoms.

The coker gas oil at least partially derived from polymeric waste can have desirable reductions in certain components as compared to from a conventional hydrocarbon feedstock, such as decreases in sulfur and paraffin content. For example, the sulfur content of coker gas oil that is at least partially derived from polymeric waste can range from roughly 0.1 wt % to 7 wt %, for example, about 0.1 wt % to 5 wt % or from 0.1 wt % to 3 wt % or from 0.5 wt % to 2 wt %. By way of further example, the coker gas oil that is at least partially derived from polymeric waste can have a paraffin content of 5 wt % to 50 wt %. For example, a heavy coker gas oil can have a paraffin content of 10 wt % to 50 wt % while a light coker gas oil can have paraffin content of 5 wt % to 30 wt %. In addition, the coker gas can have desirable increases of other components, such as olefins. In some embodiments, the coker gas oil can include olefins in an amount of 10 wt % to 30 wt % or 15 wt % to 20 wt %.

In addition to a desirable decrease in paraffins and sulfur, the coker gas oil that is at least partially derived from polymeric waste can have increased levels of other components that can complicate subsequent chemical processing. Such components include halides, oxygen, and basic nitrogen, for example. The specific type and amount of these components depends, for example, on the particular polymeric waste used in forming the coker gas oil. For example, the coker gas oil at least partially derived from polymeric waste can include halides, such as chlorine, fluorine, and bromine, in amounts, for example, of 0.1 wppm to 50 wppm, or 0.1 wppm to 10 wppm, or 0.1 wppm to 5 wppm, or 1 wppm to 50 wppm, 1 wppm to 10 wppm, or 5 wppm to 50 wppm, or 5 wppm to 10 wppm, or 10 wppm to 100 wppm.

In some embodiments, the coker gas oil at least partially derived from polymeric waste can include nitrogen-containing compounds, such as pyrroles, pyridines, amines, amides, and combinations thereof. As compared to conventional coker gas oil, the coker gas oil at least partially derived from polymeric waste should have reductions in nitrogen-containing compounds. The nitrogen-containing compounds can be present at any level, depending for example, on the particular polymeric waste that was process, including a concentration of 100 wppm to 3,000 wppm.

The coking products further include coke. Because many polymeric wastes have relatively low sulfur content (as compared to a conventional coking feedstock), the cracking products have reduced sulfur content, in some embodiments, thus reducing the needed severity for any subsequent sulfur

removal processes, such as hydroprocessing. Coke produced in a coking process is typically a carbonaceous solid material of which a majority is carbon. Since the coke is produced from the co-processing of a conventional coking feedstock in the coker, it can also be referred to as petroleum coke or petcoke, in accordance with one or more embodiments. The coke yield typically is 20 wt % to 40 wt % of the combined coker feedstock. However, since polymeric wastes can have substantially higher atomic ratio of hydrogen to carbon, coking with a waste feedstock can produce a reduced or minimized amount of coke. The particular composition of the coke depends on a number of factors, including the particular coking process, such as a delayed coker or fluidized coker. Additional components in the coke include hydrogen, nitrogen, sulfur, and heavy metals, such as aluminum, boron, calcium, chromium cobalt, iron, manganese, magnesium, molybdenum, nickel, potassium, phosphorous, silicon, sodium, titanium, and/or vanadium. In some embodiments, the coke can include phosphorous in amount of 0 wppm to 1,000 wppm, 10 wppm to 1,000 wppm, or 100 wppm to 300 wppm.

Coking Conditions—Fluidized Coking

In accordance with one or more embodiments, polymeric waste can be processed in a fluidized coker. In some embodiments, the plastic waste is co-processed with a conventional coking feedstock. In various aspects, co-processing can be performed by exposing the combined feedstock of waste feedstock and conventional coking feedstock to fluidized coking conditions.

Fluidized coking is a petroleum refining process in which heavy petroleum feeds, typically the non-distillable residues (resids) from the fractionation of heavy oils are converted to lighter, more useful products by thermal decomposition (coking) at elevated reaction temperatures, typically 480° C. to 590° C., and in most cases from 500° C. to 550° C. Example heavy oils suitable for processing by the fluidized coking process include heavy atmospheric resids, petroleum vacuum distillation bottoms, aromatic extracts, asphalts, and bitumens from tar sands, tar pits and pitch lakes. In accordance with present embodiments, the plastic waste is processed in the fluidized coker either alone or in combination with a conventional coker feedstock.

Fluidized coking is carried out in a unit with a large reactor containing hot coke particles which are maintained in the fluidized condition at the required reaction temperature with steam injected at the bottom of the vessel with the average direction of movement of the coke particles being downwards through the bed. In particular embodiments, the combined feedstock is heated to a pumpable temperature, typically in the range of 350° C. to 400° C., mixed with atomizing steam, and fed through multiple feed nozzles arranged at several successive levels in the reactor. Steam is injected into a stripping section at the bottom of the reactor and passes upwards through the coke particles descending through the dense phase of the fluid bed in the main part of the reactor above the stripping section. Part of the feed liquid coats the coke particles in the fluidized bed and is subsequently cracked into layers of solid coke and lighter products which evolve as gas or vaporized liquid. The residence time of the feed in the coking zone (where temperatures are suitable for thermal cracking) is on the order of 1 second to 30 seconds. Reactor pressure is relatively low in order to favor vaporization of the hydrocarbon vapors which pass upwards from dense phase into dilute phase of the fluid bed in the coking zone and into cyclones at the top of the coking zone where most of the entrained solids are separated from the gas phase by centrifugal force in one or more cyclones

and returned to the dense fluidized bed by gravity through the cyclone diplegs. The mixture of steam and hydrocarbon vapors from the reactor is subsequently discharged from the cyclone gas outlets into a scrubber section in a plenum located above the coking zone and separated from it by a partition. It is quenched in the scrubber section by contact with liquid descending over sheds. A pump-around loop circulates condensed liquid to an external cooler and back to the top shed row of the scrubber section to provide cooling for the quench and condensation of the heaviest fraction of the liquid product. This heavy fraction is typically recycled to extinction by feeding back to the coking zone in the reactor.

During a fluidized coking process, the coking feedstock, pre-heated to a temperature at which it is flowable and pumpable, is introduced into the coking reactor towards the top of the reactor vessel through injection nozzles which are constructed to produce a spray of the feed into the bed of fluidized coke particles in the vessel. Temperatures in the coking zone of the reactor are typically in the range of 450° C. to 650° C. and pressures are kept at a relatively low level, typically in the range of 0 kPag to 700 kPag, and most usually from 35 kPag to 320 kPag, in order to facilitate fast drying of the coke particles, preventing the formation of sticky, adherent high molecular weight hydrocarbon deposits on the particles which could lead to reactor fouling. In some embodiments, the temperature in the coking zone can be 450° C. to 600° C., or 450° C. to 550° C. The conditions can be selected so that a desired amount of conversion of the feedstock occurs in the fluidized bed reactor. 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. 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. This mixture of vaporized hydrocarbon products formed in the coking reactions flows upwardly through the dilute phase with the steam at superficial velocities of roughly 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. In embodiments where steam is used as the fluidizing agent, the weight of steam introduced into the reactor can be selected relative to the weight of feedstock introduced into the reactor. For example, the mass flow rate of steam into the reactor can correspond to 6.0% of the mass flow rate of feedstock, or 8.0% or more, such as up to 10% or possibly still higher. The amount of steam can potentially be reduced if an activated light hydrocarbon stream is used as part of the stripping and/or fluidizing gas in the reactor. In such embodiments, the mass flow rate of steam can correspond to 6.0% of the mass flow rate of feedstock or less, or 5.0% or less, or 4.0% or less, or 3.0% or less. Optionally, in some embodiments, the mass flow rate of steam can be still lower, such as corresponding to 1.0% of the mass flow rate of feedstock or less, or 0.8% or less, or 0.6% or less, such as down to substantially all of the steam being replaced by the activated light hydrocarbon stream. The cracked hydrocarbon vapors pass out of the cyclones into the scrubbing section of the reactor and then to product fractionation and recovery.

In a general fluidized coking process, the coke particles formed in the coking zone pass downwards in the reactor

and leave the bottom of the reactor vessel through a stripper section where they are exposed to steam in order to remove occluded hydrocarbons. The solid coke from the reactor, consisting mainly of carbon with lesser amounts of hydrogen, sulfur, nitrogen, and traces of vanadium, nickel, iron, and other elements derived from the feed, passes through the stripper and out of the reactor vessel to a burner or heater where it is partly burned in a fluidized bed with air to raise its temperature from 480° C. to 700° C. to supply the heat required for the endothermic coking reactions, after which a portion of the hot coke particles is recirculated to the fluidized bed reaction zone to transfer the heat to the reactor and to act as nuclei for the coke formation. The balance is withdrawn as coke product. The net coke yield is only 65 percent of that produced by delayed coking.

For a coking process that includes a gasification zone, the cracking process proceeds in the reactor, the coke particles pass downwardly through the coking 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 pass to the gasification reactor (gasifier) 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 including carbon monoxide and hydrogen.

The gasification zone is typically maintained at a high temperature ranging from 850° C. to 1,000° C. and a pressure ranging from 0 kPag to 1000 kPag, preferably from 200 kPag to 400 kPag. Steam and an oxygen-containing gas are introduced to provide fluidization and an oxygen source for gasification. In some embodiments, the oxygen-containing gas can be air. In other embodiments, 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, are passed into the gasifier for reaction with the solid particles including coke deposited on them in the coking zone. In embodiments where the oxygen-containing gas has a low nitrogen content, a separate diluent stream, such as a recycled CO₂ or H₂S stream derived from the fuel gas produced by the gasifier, can also be passed into the gasifier.

In the gasification zone the reaction between the coke and the steam and the oxygen-containing gas produces a hydrogen and carbon monoxide-containing fuel gas and a partially gasified residual coke product. Conditions in the gasifier are selected accordingly to generate these products. Steam and oxygen rates (as well as any optional CO₂ rates) will depend upon the rate at which cold coke enters from the reactor and to a lesser extent upon the composition of the coke which, in turn will vary according to the composition of the heavy oil feed and the severity of the cracking conditions in the reactor with these being selected according to the feed and the range of liquid products which is required. In some embodiments, the fuel gas product from the gasifier contains entrained coke solids and these are removed by cyclones or other separation techniques in the gasifier section of the unit. Suitable cyclones include internal cyclones in the main gasifier vessel itself or external in a separate, smaller vessel as described below. The fuel gas product is taken out as overhead from the gasifier cyclones. The resulting partly gasified solids are removed 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.

In some embodiments, the coking conditions can be selected to provide a desired amount of conversion relative

to 343° C. Typically a desired amount of conversion can correspond to 10 wt % or more, or 50 wt % or more, or 80 wt % or more, such as up to substantially complete conversion of the feedstock relative to 343° C.

The volatile products from the coke drum are conducted away from the process for further processing. For example, volatiles can be conducted to a coker fractionator for distillation and recovery of coker gases, coker naphtha, light gas oil, and heavy gas oil. Such fractions can be used, usually, but not always, following upgrading, in the blending of fuel and lubricating oil products such as motor gasoline, motor diesel oil, fuel oil, and lubricating oil. Upgrading can include separations, heteroatom removal via hydrotreating and non-hydrotreating processes, de-aromatization, solvent extraction, and the like. The process is compatible with processes where at least a portion of the heavy coker gas oil present in the product stream introduced into the coker fractionator is captured for recycle and combined with the fresh feed (coker feed component), thereby forming the coker heater or coker furnace charge. The combined feedstock ratio ("CFR") is the volumetric ratio of furnace charge (fresh feed plus recycle oil) to fresh feed to the continuous fluidized coker operation. Fluidized coking operations typically employ recycles of 5 vol % to 35 vol % (CFRs of 1.05 to 1.35). In some embodiments, there can be no recycle and sometimes in special applications recycle can be up to 200%.

The Flexicoking™ process, developed by Exxon Research and Engineering Company, is a type of fluidized coking process that is operated in a unit including a reactor and a heater, but also including a gasifier for gasifying the coke product by reaction with an air/steam mixture to form a low heating value fuel gas. A stream of coke passes from the heater to the gasifier where all but a small fraction of the coke is gasified to a low-BTU gas (~120 BTU/standard cubic feet) by the addition of steam and air in a fluidized bed in an oxygen-deficient environment to form fuel gas including carbon monoxide and hydrogen. In a conventional Flexicoking™ configuration, the fuel gas product from the gasifier, containing entrained coke particles, is returned to the heater to provide most of the heat required for thermal cracking in the reactor with the balance of the reactor heat requirement supplied by combustion in the heater. A small amount of net coke (1 percent of feed) is withdrawn from the heater to purge the system of metals and ash. The liquid yield and properties are comparable to those from fluidized coking. The fuel gas product is withdrawn from the heater following separation in internal cyclones which return coke particles through their diplegs.

In this description, the term "Flexicoking" (trademark of ExxonMobil Research and Engineering Company) is used to designate a fluidized coking process in which heavy petroleum feeds are subjected to thermal cracking in a fluidized bed of heated solid particles to produce hydrocarbons of lower molecular weight and boiling point along with coke as a by-product which is deposited on the solid particles in the fluidized bed. References to fluidized cokers are intended to include conventional fluidized cokers as well as flexicokers. The resulting coke can then be converted to a fuel gas by contact at elevated temperature with steam and an oxygen-containing gas in a gasification reactor (gasifier). This type of configuration can more generally be referred to as an integration of fluidized bed coking with gasification. FIGS. 3 and 4 provide examples of fluidized coking reactors that include a gasifier.

FIG. 5 shows an example of a Flexicoker unit (i.e., a system including a gasifier that is thermally integrated with

a fluidized bed coker) with three reaction vessels: reactor, heater and gasifier. The coking system 500 includes coker reactor 502 with the coking zone and its associated stripping and scrubbing sections (not separately indicated), heater 504 and gasifier 506. A coking feedstock, which may be a waste feedstock (or combined feedstock of waste feedstock and conventional coking feedstock) is introduced into the coking system 500 by line 508 and coker effluent withdrawn through line 510. While FIG. 5, shows a combined feedstock, example embodiments also include separate introduction of the conventional coking feedstock and waste feedstock to the coker reactor 502. Fluidizing and stripping steam is supplied by line 512. Cold coke is taken out from the stripping section at the base of coker reactor 502 by means of line 514 and passed to heater 504. The term "cold" as applied to the temperature of the withdrawn coke is, of course, decidedly relative since it is well above ambient at the operating temperature of the stripping section. Hot coke is circulated from heater 504 to coker reactor 502 through line 516. Coke from heater 504 is transferred to gasifier 506 through line 518 and hot, partly gasified particles of coke are circulated from the gasifier back to the heater 504 through line 520. The excess coke is withdrawn from the heater 504 by way of line 522. In conventional configurations, gasifier 506 is provided with its supply of steam and air by line 524 and hot fuel gas is taken from the gasifier to the heater through line 526. In some alternative embodiments, instead of supplying air via a line 524 to the gasifier 506, a stream of oxygen with 95 vol % purity or more can be provided, such as an oxygen stream from an air separation unit. In such embodiments, in addition to supplying a stream of oxygen, a stream of an additional diluent gas can be supplied by line 528. The additional diluent gas can correspond to, for example, CO₂ separated from the fuel gas generated during the gasification. The fuel gas is taken out from the unit through line 530 on the heater; coke fines are removed from the fuel gas in heater cyclone system 532 including serially connected primary and secondary cyclones with diplegs which return the separated fines to the fluid bed in the heater. The fuel gas from line 530 can then undergo further processing. For example, in some embodiments, the fuel gas from line 530 can be passed into a separation stage for separation of CO₂ (and/or H₂S). This can result in a stream with an increased concentration of synthesis gas, which can then be passed into a conversion stage for conversion of synthesis gas to methanol.

It is noted that in some optional embodiments, heater cyclone system 532 can be located in a separate vessel (not shown) rather than in heater 504. In such aspects, line 530 can withdraw the fuel gas from the separate vessel, and the line 522 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 embodiments, 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% by weight of the metals present in the feedstock introduced into the coker/gasifier system, or less than 0.01% by weight.

In configurations such as FIG. 5, the system elements shown in the figure can be characterized based on fluid communication between the elements. For example, coker reactor 502 is in direct fluid communication with heater 504. Coker reactor 502 is also in indirect fluid communication with gasifier 506 via heater 504.

As an alternative, integration of a fluidized bed coker with a gasifier can also be accomplished without the use of an intermediate heater. In such alternative aspects, the cold coke from the reactor can be transferred directly to the gasifier. This transfer, in almost all cases, will be unequivocally direct with one end of the tubular transfer line connected to the coke outlet of the reactor and its other end connected to the coke inlet of the gasifier with no intervening reaction vessel, i.e., heater. The presence of devices other than the heater is not however to be excluded, e.g., inlets for lift gas etc. Similarly, while the hot, partly gasified coke particles from the gasifier are returned directly from the gasifier to the reactor this signifies only that there is to be no intervening heater as in the conventional three-vessel Flexi-coker™ but that other devices may be present between the gasifier and the reactor, e.g., gas lift inlets and outlets.

FIG. 6 shows an example of integration of a fluidized bed coker with a gasifier but without a separate heater vessel. In the configuration shown in FIG. 6, the cyclones for separating fuel gas from catalyst fines are located in a separate vessel. In other aspects, the cyclones can be included in a main gasifier vessel 604.

In the configuration shown in FIG. 6, the coker system 600 includes a coker reactor 602, main gasifier vessel 604 and a separator vessel 606. The coking feedstock is introduced into coker reactor 602 through line 608 and fluidizing/stripping gas through line 610; coker effluent is taken out through line 612. The coking feedstocks includes a waste feedstock with optional combination with a conventional coking feedstock (e.g., heavy oil feed). The waste feedstock can be separately introduced to the coker reactor 602 or introduced in combination with a conventional coking feedstock, for example. Cold, stripped coke is routed directly from coker reactor 602 to main gasifier vessel 604 by way of line 614 and hot coke returned to the reactor in line 616. Steam and oxygen are supplied through line 618. The flow of gas containing coke fines is routed to separator vessel 606 through line 620 which is connected to a gas outlet of the main gasifier vessel 604. The fines are separated from the gas flow in cyclone system 622 including serially connected primary and secondary cyclones with diplegs which return the separated fines to the separator vessel. The separated fines are then returned to the main gasifier vessel 604 through return line 624 and the fuel gas product taken out by way of line 626. Coke is purged from the separator through line 628. The fuel gas from line 626 can then undergo further processing for separation of CO₂ (and/or H₂S) and conversion of synthesis gas to methanol.

The coker and gasifier can be operated according to the parameters necessary for the required coking processes. Thus, the heavy oil feed in the coking feedstock 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 wt % to 50 wt %. In some embodiments, the coking feedstock is a petroleum vacuum residuum.

5 Coking Conditions—Delayed Coking

In particular embodiments, delayed coking is performed on a waste feedstock optionally combined with a conventional coking feedstock to produce liquid and vapor hydrocarbon products and coke. In various embodiments, the waste feedstock and optional conventional coking feedstock are exposed to delayed coking conditions.

Delayed coking is another coking process for the thermal conversion of heavy oils such as petroleum residua (also referred to as “resid”) to produce liquid and vapor hydrocarbon products and coke. In some embodiments, the conventional hydrocarbon feedstock includes resids from heavy and/or sour (high sulfur) crude oils. Delayed coking of the feedstock is carried out by converting part of the feedstock to more valuable hydrocarbon products. The resulting coke has value, depending on its grade, as a fuel (fuel grade coke), electrodes for aluminum manufacture (anode grade coke), etc.

Generally, a feedstock is pumped to a pre-heater where it is pre-heated, such as to a temperature from 480° C. to 520° C. The pre-heated feed is conducted to a coking reactor, typically a vertically oriented, insulated coker vessel, e.g., drum, through an inlet at the base of the drum. Pressure in the drum is usually relatively low, such as 100 kPa-g to 550 kPa-g, or 100 kPa-g to 240 kPa-g to allow volatiles to be removed overhead. Typical operating temperatures of the drum will be between roughly 400° C. to 445° C., but can be as high as 475° C. The hot feed thermally cracks over a period of time (the “coking time”) in the coke drum, liberating volatiles composed primarily of hydrocarbon products that continuously rise through the coke bed, which consists of channels, pores and pathways, and are collected overhead. The volatile products are conducted to a coker fractionator for distillation and recovery of coker gases, gasoline boiling range material such as coker naphtha, light gas oil, and heavy gas oil. In an embodiment, a portion of the heavy coker gas oil present in the product stream introduced into the coker fractionator can be captured for recycle and combined with the fresh feed (coker feed component), thereby forming the coker heater or coker furnace charge. In addition to the volatile products, the process also results in the accumulation of coke in the drum. When the coke drum is full of coke, the heated feed is switched to another drum and hydrocarbon vapors are purged from the coke drum with steam. The drum is then quenched with water to lower the temperature down to 95° C. to 150° C., after which the water is drained. When the draining step is complete, the drum is opened, and the coke is removed by drilling and/or cutting using high velocity water jets (“hydraulic decoking”).

FIG. 7 illustrates an example delayed coking system 700. In the illustrated embodiment, a feedstock 702 including a waste feedstock, which may be preheated, is fed into a coker fractionator 704. In some embodiments, the feedstock 702 further includes a conventional coking feedstock, which may alternatively be separately feed to the coker fractionator 704. In the illustrated embodiment, a fractionator effluent 706 including at least a portion of the waste feedstock and/or conventional coking feedstock is withdrawn from the coker fractionator 704 and fed to a coker furnace 708. From the coker furnace 708, the preheated effluent 710 including a preheated waste feedstock and/or preheated conventional coking feedstock is passed to a coking reactor 712, which includes, for example, a coking vessel or coking drum. The

preheated effluent **710** also includes, for example, tower bottoms (or recycle). The coking reactor **712** is operated at coking conditions such that the preheated waste feedstock/conventional coking feedstock thermally cracks over a period of time (the "coking time") in the coking reactor **712**, liberating volatiles composed primarily of hydrocarbon products that continuously rise through the coke bed, which consists of channels, pores and pathways, and are collected overhead as a coker of **714**, which is passed to the coker fractionator **704**. In the illustrated embodiment, the coker effluent **714** is separated in the coker fractionator **704** into various fractions, including, but not limited to, one or more of a coker gas fraction **718**, a coker naphtha fraction **720**, and a coker gas oil fraction **722**. It should be understood that separation of the coking products into various fractions can occur in one or more vessels and/or one or more different operations. As previously mentioned, coke is accumulated in the coking reactor **712** (e.g., coking vessel). A coke product **716** including coke is withdrawn from the coking reactor **712**.

Hydroprocessing of Coker Effluent Fractions

In various embodiments, at least a portion of a coker naphtha can be exposed to hydroprocessing conditions to reduce or minimize certain components, such as metals, organohalides, olefins, and/or sulfur-, nitrogen-, and oxygen-containing species, in the feed to subsequent chemical processing. In accordance with present embodiments, the coker naphtha is at least partially derived from plastic water. Such hydroprocessing can include, but is not limited to, hydrotreatment, hydrocracking, catalytic dewaxing and/or hydroisomerization, aromatic saturation.

In this discussion, hydroprocessing is defined as exposing an input flow to a hydroprocessing stage to a partial pressure of H_2 of 50 kPa or more (such as 3000 kPa) in the presence of a catalyst at a temperature of 150° C. to 450° C. Temperatures below 150° C. result in de minimis hydroprocessing activity, while temperatures greater than 450° C. primarily result in thermal cracking of hydrocarbon-like feeds.

Hydroprocessing (such as hydrotreating) is carried out in the presence of hydrogen. Hydrogen, contained in a hydrogen "treat gas," is provided to the reaction zone. For example, a hydrogen-containing stream is fed, injected, or otherwise introduced into a vessel, reaction zone, or hydroprocessing zone corresponding to the location of a hydroprocessing catalyst. Treat gas, as referred to herein, can be either pure hydrogen or a hydrogen-containing gas stream containing hydrogen in an amount that is sufficient for the intended reaction(s). Treat gas can optionally include one or more other gasses (e.g., nitrogen and light hydrocarbons such as methane) that do not adversely interfere with or affect either the reactions or the products. Impurities, such as H_2S and NH_3 are undesirable and can typically be removed from the treat gas to a sufficiently low level before conducting the treat gas to the reactor. In aspects where the treat gas stream can differ from a stream that substantially consists of hydrogen (i.e., at least 99 vol % hydrogen), the treat gas stream introduced into a reaction stage can contain at least 50 vol %, or at least 75 vol % hydrogen, or at least 90 vol % hydrogen.

During hydrotreatment, the coker naphtha can be contacted with a hydrotreating catalyst under effective hydrotreating conditions which can include temperatures in the range of 230° C. to 430° C.), or 285° C. to 400° C.); pressures in the range of 1.5 MPag to 20.8 MPag, or 2.9 MPag to 13.9 MPag; a liquid hourly space velocity (LHSV) of from 0.1 to 10 hr^{-1} , or 0.1 to 5 hr^{-1} ; and a hydrogen treat

gas rate of from 430 to 2600 Nm^3/m^3 , or 850 to 1700 Nm^3/m^3 . In some embodiments, hydrotreatment of coker naphtha can be performed at temperatures in the range of 230° C. to 375° C.), or 230° C. to 345° C.); pressures in the range of 1.5 MPag to 10.4 MPag, or 2.9 MPag to 6.9 MPag; a liquid hourly space velocity (LHSV) of from 0.1 to 10 hr^{-1} , or 0.1 to 5 hr^{-1} ; and a hydrogen treat gas rate of from 430 to 2600 Nm^3/m^3 , or 850 to 1700 Nm^3/m^3 .

Any convenient type of hydrotreating catalyst may be used, such as hydrotreating catalysts for naphtha hydrotreating, and/or for catalysts for hydrotreatment of wide cut fractions. The above hydrotreatment conditions cover a wide range of seventies.

The catalyst in a hydrotreatment stage can be a conventional hydrotreating catalyst, such as a catalyst composed of a Group VIB metal and/or a Group VIII metal on a support. Suitable metals include cobalt, nickel, molybdenum, tungsten, or combinations thereof. Preferred combinations of metals include nickel and molybdenum or nickel, cobalt, and molybdenum. Suitable supports include silica, silica-alumina, alumina, and titania.

Another hydroprocessing option is to expose coker naphtha (or at least a portion thereof) to catalytic dewaxing conditions. Exposing coker naphtha to catalytic dewaxing can be performed after hydrotreatment of the coker naphtha in a hydroprocessing stage, or the catalytic dewaxing can correspond to the first (and possibly only) type of hydroprocessing in a hydroprocessing stage. It is noted that many types of dewaxing catalysts involve noble metal catalysts. For such types of catalysts, performing hydrotreatment prior to dewaxing may be beneficial for improving the activity and/or operating lifetime of the dewaxing catalyst. For dewaxing catalysts that include non-noble metals and/or that are based primarily on cracking rather than isomerization, the dewaxing catalyst may be able to tolerate higher levels of sulfur and/or nitrogen while still providing dewaxing activity.

Process conditions in a catalytic dewaxing zone (in the presence of a dewaxing catalyst) can include a temperature of from 200° C. to 450° C., or 270° C. to 400° C., a hydrogen partial pressure of from 1.8 MPag to 34.6 MPag, or 4.8 MPag to 20.7 MPag, and a hydrogen treat gas rate of from 35.6 m^3/m^3 to 1781 m^3/m^3 , or 178 m^3/m^3 to 890.6 m^3/m^3 . The liquid hourly space velocity (LHSV) can be from 0.2 h^{-1} to 10 h^{-1} , such as from 0.5 h^{-1} to 5 h^{-1} and/or from 1 h^{-1} to 4 h^{-1} .

Still another hydroprocessing option can be to expose coker naphtha to a catalyst under aromatic saturation conditions/hydrofinishing conditions. Aromatic saturation conditions can include temperatures from 125° C. to 425° C., preferably 180° C. to 280° C., a hydrogen partial pressure from 3.4 MPa to 21 MPa), or 10 MPa to 17.5 MPa, and liquid hourly space velocity from 0.1 hr^{-1} to 5 hr^{-1} LHSV, preferably 0.5 hr^{-1} to 2.0 hr^{-1} .

Chemical Production

In accordance with one or more embodiments, the processing of the polymeric waste results in the production or recovery of chemical products. For example, coker naphtha from coking of polymeric waste can be processed to form chemical products. By way of further example, coker naphtha from coking of pyrolysis oil that is at least partially derived from polymeric waste can be processed to form chemical products.

In some embodiments, the coker gas oil includes one or more components that need to be removed and/or reduced in concentration prior to subsequent processing. For example, embodiments include treating the coker gas oil to remove at

least a portion of contaminants, including halides, acids, and sulfur species. Any of a variety of techniques may be used for treatment of the coker gas oil, including absorption, adsorption, hydroprocessing, filtration, and fractionation. Adsorption can be used for removal of specific contaminants, such as mercury. Examples of specific adsorption techniques include treatment beds, such as mercury beds. Absorption includes solid and liquid contacting methods such as water washing, amine gas treating, caustic treatment. Water washing includes, for example, contacting the coker gas oil with a water stream. Embodiments of hydroprocessing also may convert organic halides in the coker gas oil to inorganic acid. Neutralizing additives can then be added to the hydroprocessing effluent for neutralization of the produced inorganic acids. Filtration is used, for example, to remove solid particulates.

The chemical products produced from integration of co-processing of polymeric waste includes a variety of chemical products, including olefins (e.g., alpha-olefins), aromatics, oligomers, and polymers. A "polymer" has one or more repeating units that are the same or different. The term "polymer" as used herein includes oligomers (up to 75 repeating units) and larger polymers (greater than 75 repeating units). "Homopolymer" is a polymer having the same repeating unit. A "copolymer" is a polymer having two or more repeating units different from each other. A "terpolymer" is a polymer having three repeating units different from each other. "Different" is used to mean that the repeating units differ from each other by at least one atom or isomer. Therefore, the definition of the copolymer used herein includes a terpolymer and the like. The chemical products include or can be processed to form a number of desirable products, including: olefins, such as ethylene, propylene, butylene, butadiene, pentenes, C₅ olefins, and C₅ di-olefins, as well as longer olefins, such as hexene, nonene, and tetramer; aromatics, such as benzene, styrene, and toluene; cyclohexane; polymers, such as polyethylene, polypropylene, polystyrene, polyesters, poly-vinyl chloride; and divinyl chloride; synthetic elastomers and rubbers, such as styrene-butadiene rubber, ethylene-propylene-diene-rubbers, butyl rubbers, and halobutyl rubbers; plastic additives and modifiers, such as plasticizers; epoxies resins; and fluids with multiple applications, such as isopropyl alcohol, oxo-alcohols, glycols, detergents, and lubricants.

At least a portion of these chemical products may be circular chemical products that are attributable to the polymeric waste, such as determined by crediting, allocating, and/or offsetting or substituting for other hydrocarbons in a mass or energy balance for a system, such as in accordance with a third-party certification relating to circularity. At least a portion of these chemical products may be certified circular chemical products that are certified for their circularity by third party certification may be referred to as certified circular.

Various processes may be employed to integrate chemical production with coking. For example, coker naphtha received from coking may be converted in one or more of the following units: hydroprocessing units, such as hydrocracking and hydrotreating units; fluid catalytic cracking units; steam cracking units; catalytic reforming units; partial oxidation to synthetic gas; and/or isomerization. The chemical products may be directly produced by such processes or may be obtained by further processing, such as separation, treating, and/or cracking of an effluent of such processes. As an example, the chemical products may be obtained by processing of coker naphtha at least partially derived from polymeric waste. In addition, co-processing of polymeric

waste as a feed or co-feed into delayed or fluidized coking units (including FLEXICOKING™ units), may result in the attribution of the polymeric waste to chemical products (including olefins, polymers, or aromatics), such as determined by crediting, allocating, and/or offsetting or substituting for other hydrocarbons in a mass or energy balance for a system, such as in accordance with a third-party certification relating to circularity.

Accordingly, processes per various embodiments herein may further include obtaining olefins that have been produced or recovered from the processing of polymeric waste or olefins to which the processing of polymeric waste has been attributed, e.g., for employment in polymerization processes; and polymers of various embodiments described herein may include olefins that have been produced or recovered from the processing of polymeric waste or olefins to which the processing of polymeric waste has been attributed. As an example, at least a portion of the olefin content (e.g., employed in processes and/or included in compositions as described herein) may be from olefins that are produced or recovered directly from the processing of polymeric waste. Similarly, the processing of polymeric waste may be attributed to at least a portion of the olefins (e.g., employed in processes and/or included in compositions as described herein).

Additional Embodiments

Accordingly, the present disclosure may provide for the integration of polymeric waste co-processing in cokers to produce circular chemical products from coker gas. The methods and systems may include any of the various features disclosed herein, including one or more of the following statements.

Embodiment 1. A method of producing circular chemical products comprising: providing a coker gas oil that is at least partially derived from polymeric waste, wherein the coker gas oil has a paraffin content of about 5 wt % to about 50 wt %, a sulfur content of about 0.1 wt % to about 7 wt %, and a halide content of about 0.1 wppm to about 5 wppm; and converting the coker gas oil into at least a polymer.

Embodiment 2. The method of Embodiment 1, wherein the coker gas oil is derived from co-processing of polymeric waste and a heavy oil with a T10 distillation point of about 343° C. to about 575° C.

Embodiment 3. The method of Embodiment 1 or Embodiment 2, wherein providing the coker gas oil comprises: coking a feedstock comprising the polymeric waste and a heavy oil with a T10 distillation point of about 343° C. to about 575° C. to form at least a coker effluent and coke; and separating the coker gas oil from the coker effluent.

Embodiment 4. The method of Embodiment 3, wherein the polymeric waste comprises plastic waste.

Embodiment 5. The method of Embodiment 3 or Embodiment 4, wherein the heavy oil comprises petroleum vacuum resid.

Embodiment 6. The method of any of Embodiments 3 to 5, wherein the feedstock comprises the polymeric waste in an amount of about 0.1 wt % to about 25 wt %.

Embodiment 7. The method of any of Embodiments 3 to 6, wherein the coking comprises exposing the feedstock to delayed coking conditions.

Embodiment 8. The method of any of Embodiments 1 to 7, wherein providing the coker gas oil comprises pyrolyzing the polymeric waste to produce at least a pyrolysis oil and then coking at least the pyrolysis oil and a heavy oil with a T10 distillation point of about 343° C. to about 575° C.

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Embodiment 9. The method of any of Embodiments claims 1 to 8, wherein the polymeric waste comprises plastic waste.

Embodiment 10. The method of any of Embodiments 1 to 9, wherein at least a portion of the polymer is attributable to polymers in the polymeric waste.

Embodiment 11. The method of any of Embodiments 1 to 10, wherein the polymer comprises a circular polymer.

Embodiment 12. The method of any of Embodiments 1 to 11, wherein the polymer comprises a polymer that is certified circular in accordance with International Sustainability and Carbon Certification.

Embodiment 13. The method of any of Embodiments 1 to 12, further comprising treating the coker gas oil to reduce a concentration of one or more contaminants prior to the step of converting the coker gas oil.

Embodiment 14. The method of Embodiment 13, wherein the treating comprises hydroprocessing the coker gas oil.

Embodiment 15. The method of any of Embodiments 1 to 14, wherein the converting the coker gas oil into at least the polymer comprises recovering olefins from the coker gas oil; and polymerizing at least a portion of the olefins.

Embodiment 16. The method of any of Embodiments 1 to 14, wherein the converting the coker gas oil into at least the polymer comprises hydroprocessing at least a portion of the coker gas oil to form at least a hydroprocessing effluent, steam cracking at least a portion of the hydroprocessing effluent to form at least a steam cracking effluent; recovering olefins from the steam cracking effluent; and polymerizing at least a portion of the olefins.

Embodiment 17. The method of Embodiment 16, wherein the hydroprocessing comprises hydrotreating at least a portion of the coker gas oil to form at least a hydrotreating effluent; and hydrocracking at least a portion of the hydrotreating effluent to form at least the hydroprocessing effluent.

Embodiment 18. The method of any of Embodiments 1 to 14, wherein the converting the coker gas oil into at least the polymer comprises fluid catalytic cracking at least a portion of the coker gas oil to form at least a fluid catalytic cracking effluent; recovering olefins from at least a portion of the fluid catalytic cracking effluent; and polymerizing at least a portion of the olefins.

Embodiment 19. The method of any of Embodiments 1 to 14, wherein the converting the coker gas oil into at least the polymer comprises partially oxidizing at least a portion of the coker gas oil by at least combustion of the coker gas oil and an oxygen-containing gas to form at least an oxidation effluent comprising carbon monoxide and hydrogen; and reacting at least a portion of the oxidation effluent in the presence of olefins and a hydroformylation catalyst to form at least oxo alcohols.

Embodiment 20. A method of producing circular chemical products comprising: providing a coker gas oil that is at least partially derived from polymeric waste, wherein the coker gas oil has a paraffin content of about 5 wt % to about 50 wt %, a sulfur content of about 0.1 wt % to about 7 wt %, and a halide content of about 0.1 wppm to about 5 wppm; hydroprocessing at least a portion of the coker gas oil to form at least a hydroprocessing effluent; steam cracking at least a portion of the hydroprocessing effluent to form at

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least a steam cracking effluent; recovering olefins from the steam cracking effluent; and polymerizing at least a portion of the olefins to form at least polyolefins.

Embodiment 21. The method of Embodiment 20, wherein the hydroprocessing comprises hydrotreating at least a portion of the coker gas oil to form at least a hydrotreating effluent; and hydrocracking at least a portion of the hydrotreating effluent to form at least the hydroprocessing effluent.

Embodiment 22. The method of Embodiment 20 or Embodiment 21, further comprising coking a feedstock comprising the polymeric waste and a heavy oil with a T10 distillation point of about 343° C. to about 575° C. to form at least a coker effluent and coke; and separating the coker gas oil from the coker effluent.

To facilitate a better understanding of the present invention, the following examples of certain aspects of some embodiments are given. In no way should the following examples be read to limit, or define, the entire scope of the disclosure.

Example

In this example, a plastic feedstock and a petroleum vacuum resid were co-processed in a pilot-scale coking unit. Two tests were performed on the petroleum vacuum resid, identified as Tests 1 and 2 in the following tables. Six different plastic feedstocks were tested, identified as Plastic Feed A, Plastic Feed B, Plastic Feed C, Plastic Feed D, Plastic Feed E, and Plastic Feed F. Plastic Feed A was 100% linear low density polyethylene. Plastic Feed B was 100% polypropylene. Plastic Feed C was 100% high density polyethylene. Plastic Feed D was a plastic waste that included 12 wt % of polyvinylidene chloride with the remainder being polyethylene and ethyl vinyl acetate. Plastic Feed E was a plastic waste that included 10 wt % polyamide or nylon with the remainder being polyethylene, ethyl vinyl alcohol, and polyethylene terephthalate. Plastic Feed F was a plastic waste that included pellets of 100% low density polyethylene. The plastic feedstocks were provided in various forms including small granules, shreds (about 1-2 inches in length) or shreds with about 0.25 inches per side. The plastic feedstocks were processed into smaller grounds due to the size requirements and mixing capabilities of the pilot scale coking unit. The plastic feedstocks were fed into the pilot scale coking unit as a homogenous mixture with the petroleum vacuum resid after the plastic feedstock had been melted.

The pilot scale coking unit had the following operating conditions: (1) Pressure=15 psig; (2) Inlet Temperature=930° F. (500° C.); (3) Outlet Temperature=844° F. (avg) (450° C.); (4) Residence Time=5 hours). The compositional data for liquid product (coker effluent) from the pilot-scale coking unit for each test are provided below.

Table 1 provides the results for the comparative test with only the petroleum vacuum resid and no plastic feed, as well as Plastic Feeds A-C while Table 2 provides the results for Plastic Feeds D-F.

TABLE 2

Coker Liquid Effluent						
Test	1	2	3	4	5	6
Plastic	—	—	Plastic A: LLDPE	Plastic A: LLDPE	Plastic B: PP	Plastic C: HDPE
Plastic (wt %)	0	0	5	10	10	10
Density, g/ml (D4052)	0.868	0.865	0.871	0.8668	0.857	0.858
API (D4052)	31.4, 31.4	31.9	31.1, 30.8	31.5, 31.6	33.4	33.4
Kinematic Viscosity, 25° C. (mm ² /s)	7.299	7.293	22.720	62.200	6.596	3.634
Sulfur (wppm)	3980	2610	2870	2510	2430	2670
Nitrogen (wt %)	0.24	0.23	0.18	0.17	0.23	0.11
Hydrogen (wt %)	12.0	11.8	12.0	12.3	12.60	12.68
Oxygen (wt %)	0.43	0.41	0.31	0.29	0.29	0.35
Bromine Number (D1159 ASL Intertek)	40.2	27.8	39.8	40.3	33.7	29.1
Total Chlorine (wppm)	<1	12	<1	<1	7	5
Organic Chlorine (wppm)	<1	6	—	—	—	—
Total Fluorine (wppm)	<2	<1	<2	<2	<1	<1
1-Ring Aromatics (wt %)	20.0	21.3	21.4	21.9	—	22.7
2-Ring Aromatics (wt %)	10.4	10.1	9.9	9.6	—	8.9
3-Ring Aromatics (wt %)	9.5	10.7	9.0	8.7	—	9.6
Total Aromatics (wt %)	53.4	54.3	53.1	47.4	—	52.8
T10 Distillation Point (° C.)	158	138	150	147	134	143
T50 Distillation Point (° C.)	346	323	359	357	338	331
T90 Distillation Point (° C.)	492	458	508	503	491	472

TABLE 3

Coker Liquid Effluent (Contd.)					
Test	7	8	9	10	11
Plastic	Plastic D: PVdc, PE, EVA	Plastic E: PA, PE, EVOH, PET	Plastic E: PA, PE, EVOH, PET	Plastic F: LDPE	Plastic F: LDPE
Plastic (wt %)	5	5	10	5	7.5
Density, g/ml (D4052)	0.871	0.863	0.858	0.855	0.856
API (D4052)	30.9	32.3	33.3	33.8	33.7
Kinematic Viscosity, 50° C. (mm ² /s)	4.305	3.587	3.333	3.090	2.982
Sulfur (wppm)	2830	2580	2420	2410	2430
Nitrogen (wt %)	0.14	0.18	0.24	0.14	0.20
Hydrogen (wt %)	11.7	11.4	11.9	12.1	12.7
Oxygen (wt %)	0.37	0.39	0.45	0.29	0.32
Bromine Number (D1159 Intertek)	27.7	32.5	33.4	27.8	27.3
Total Chlorine (wppm)	300	39.43	55	7	9
Organic Chlorine (wppm)	290	—	50	—	—
Total Fluorine (wppm)	<1	<1	1	<1	<1
1-Ring Aromatics (wt %)	22.0	21.0	22.9	23.6	23.5
2-Ring Aromatics (wt %)	9.7	9.7	9.8	9.5	9.1
3-Ring Aromatics (wt %)	10.5	10.4	10.0	9.6	9.5
Total Aromatics (wt %)	55.0	53.3	55.8	53.1	54.2
T10 Distillation Point (° C.)	158	146	142	138	146
T50 Distillation Point (° C.)	346	338	334	323	331
T90 Distillation Point (° C.)	492	478	477	458	471

The coker effluent was fractionated to provide various fractions, including light and heavy coker gas oils. The compositional data for the light coker gas oil is provided in the tables below.

TABLE 4

Light Coker Gas Oil						
Test	1	2	3	4	5	6
Plastic	—	—	Plastic A: LLDPE	Plastic A: LLDPE	Plastic B: PP	Plastic C: HDPE
Plastic (wt %)	0	0	5	10	10	10
Density, g/ml (D4052)	0.855	0.855	0.852	0.847	0.848	0.848
Kinematic Viscosity, 40° C. (mm ² /s)	3.247	3.425	3.332	3.195	3.213	3.243
Sulfur (wppm)	3050	1840	1840	1660	1740	2380
Nitrogen (wppm)	744	604	553	<0.1	466	524
Hydrogen (wt %)	12.68	12.5	12.81	12.5	12.92	12.92
Oxygen (wt %)	0.26	0.18	0.17	0.18	0.32	0.27
Bromine Number (D1159 Intertek)	27.3	36.3	28.5	33.6	—	—
Total Chlorine (wppm)	<1	5.2, 5.1	3	<1	6	5
Total Fluorine (wppm)	<11	<1, <1	<1	<1	<1	<1
Paraffins (wt %)	14.7	15.4	15.9	16.5	15.5	18.7
1-Ring Aromatics (wt %)	19.5	18.5	17.8	17.3	18.3	18.7
2-Ring Aromatics (wt %)	7.0	6.6	6.5	6.5	6.2	6.5
3+Ring Aromatics (wt %)	5.6	4.2	4.5	5.5	3.7	3.5
Total Aromatics (wt %)	32.1	29.3	28.8	29.3	28.1	28.7
T10 Distillation Point (° C.)	217	236	232	231	234	236
T50 Distillation Point (° C.)	289	291	287	288	286	287
T90 Distillation Point (° C.)	355	340	336	343	278	331

TABLE 5

Light Coker Gas Oil (contd.)					
Test	7	8	9	10	11
Plastic	Plastic D: PVdc, PE, EVA	Plastic E: PA, PE, EVOH, PET	Plastic E: PA, PE, EVOH, PET	Plastic F: LDPE	Plastic F: LDPE
Plastic (wt %)	5	5	10	5	7.5
Density, g/ml (D4052)	0.854	0.854	0.854	0.852	0.846
Kinematic Viscosity, 40° C. (mm ² /s)	3.395	3.752	3.721	3.366	3.289
Sulfur (wppm)	1890	1750	1710	1810	1700
Nitrogen (wt %)	381	903	1748	600	564
Hydrogen (wt %)	12.76	12.78	12.79	12.87	12.88
Oxygen (wt %)	0.31	0.35	0.34	0.17	0.20
Bromine Number (D1159 Intertek)	27.6	27.2	26.7	34.6	26.1
Total Chlorine (wppm)	110	32, 31	49	2	2
Total Fluorine (wppm)	<1	<1, <1	<1	<1	<1
Paraffins (wt %)	15.6	15.7	16.0	—	—
1-Ring Aromatics (wt %)	18.8	18.6	17.8	—	—
2-Ring Aromatics (wt %)	6.9	6.7	6.6	—	—
3+Ring Aromatics (wt %)	4.7	4.8	4.8	—	—
Total Aromatics (wt %)	30.1	30.1	29.1	—	—
T10 Distillation Point (° C.)	235	233	234	233	232
T50 Distillation Point (° C.)	289	289	291	291	289
T90 Distillation Point (° C.)	343	341	347	356	342

The following summary table is provided to summarize the results from Tables 4 and 5 for the light coker gas oil. In the following tables, the co-processing results for Tests 3-11 are averaged for 5 wt % and 10 wt % plastic. Tests 1 and 2 are also averaged.

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TABLE 6

Light Coker Gas Oil Summary			
Test	1 & 2	CoProcessing	CoProcessing
Plastic (wt %)	0	5	10
Sulfur (wppm)	2445	1823	1873
Hydrogen (wt %)	12.4	12.6	12.6
Paraffins (wt %)	15.0	16.1	16.6
1-Ring Aromatics (wt %)	19.0	17.9	18.0
2-Ring Aromatics (wt %)	6.8	6.5	6.4
3+Ring Aromatics (wt %)	4.9	4.9	4.4
Total Aromatics (wt %)	30.7	29.3	28.8
Total Chlorine (wppm)	2.6	36.7	15.0
Total Fluorine (wppm)	<1	<1	<1

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The above table illustrates that coker gas oil at least partially derived from polymers, including plastic waste, has a different composition than conventional coker oil. As shown, the sulfur content in the coker gas oil from co-processing includes significantly less sulfur than Test 1 with no polymeric waste. In addition, the coker gas oil from co-processing of the polymers, including has an increase in hydrogen concentration and an increase in chlorine, with chlorine having a substantial increase from 2.6 wppm to 36.7 and 15.0 wppm, respectively. The compositional data for the heavy coker gas oil is provided in the tables below.

TABLE 7

Heavy Coker Gas Oil						
Test	1	2	2	3	4	5
Plastic	—	—	Plastic A: LLDPE	Plastic A: LLDPE	Plastic B: PP	Plastic C: HDPE
Plastic (wt %)	0	0	5	10	10	10
Density, g/ml (D4052)	0.950	0.930	0.930	0.919	0.927	0.916
Kinematic Viscosity, 100° C. (mm ² /s)	6.972	7.803	9.044	7.715	8.266	6.297
Sulfur (wppm)	6220	4000	4160	3720	3980	4820
Nitrogen (wppm)	2858	2943	2830	2410	2856	2758
Hydrogen (wt %)	11.69	—	11.86	12.04	11.88	12.16
Oxygen (wt %)	0.44	0.31	0.40	0.40	0.40	0.35
Bromine Number (D1159 Intertek)	19.5	30.1	17.0	19.2	—	—
Total Chlorine (wppm)	<1	2	<1	<1	<1	1
Total Fluorine (wppm)	<1	<1	<1	<1	<1	<1
1-Ring Aromatics (wt %)	21.8	24.1	23.2	22.7	25.5	27.0
2-Ring Aromatics (wt %)	10.4	10.2	9.7	9.7	10.1	9.2
3-Ring Aromatics (wt %)	9.9	11.7	9.2	9.2	11.9	10.5
4-Ring Aromatics (wt %)	14.7	15.3	17.2	13.6	14.0	14.0
T10 Distillation Point (° C.)	352	363	371	364	363	360
T50 Distillation Point (° C.)	425	433	449	444	436	424
T90 Distillation Point (° C.)	511	520	540	537	525	524

TABLE 8

Heavy Coker Gas Oil (contd.)					
Test	6	7	8	9	10
Plastic	Plastic D: PVdc, PE, EVA	Plastic E: PA, PE, EVOH, PET	Plastic E: PA, PE, EVOH, PET	Plastic F: LDPE	Plastic F: LDPE
Plastic (wt %)	5	5	10	5	7.5
Density, g/ml (D4052)	0.929	0.928	0.924	0.916	0.917
Kinematic Viscosity, 100° C. (mm ² /s)	7.755	7.381	7.060	5.608	6.105
Sulfur (wppm)	4300	3970	3740	3740	3710
Nitrogen (wt %)	2688	2907	3010	2630	2665
Hydrogen (wt %)	11.80	11.81	11.98	—	12.09
Oxygen (wt %)	0.38	1.59	0.33	0.27	0.32
Bromine Number (D1159 Intertek)	17.6	16.1	16.2	15.3	—
Total Chlorine (wppm)	18	8.7, 8.9	18	1	<2
Total Fluorine (wppm)	<1	<1, <1	<1	<1	<4
1-Ring Aromatics (wt %)	23.1	22.8	21.9	23.4	23.7
2-Ring Aromatics (wt %)	10.2	10.3	9.9	9.6	9.5
3-Ring Aromatics (wt %)	12.3	12.2	12.1	11.0	11.5
4-Ring Aromatics (wt %)	15.3	14.1	13.5	13.4	12.7
T10 Distillation Point (° C.)	362	365	362	347	356
T50 Distillation Point (° C.)	437	432	431	417	423
T90 Distillation Point (° C.)	537	513	515	494	516

The following summary table is provided to summarize the results from Tables 7 and 8 for the heavy coker gas oil. In the following tables, the co-processing results for Tests 3-11 are averaged for 5 wt % and 10 wt % plastic. Tests 1 and 2 are also averaged.

TABLE 9

Heavy Coker Gas Oil Summary			
Test	1 & 2	CoProcessing	CoProcessing
Plastic (wt %)	0	5	10
Sulfur (wppm)	5110	4043	4065
Hydrogen (wt %)	11.69	11.8	11.9
Paraffins (wt %)	22.9	34.9	35.1
1-Ring Aromatics (wt %)	10.3	23.1	24.2
2-Ring Aromatics (wt %)	10.8	9.9	9.7
3-Ring Aromatics (wt %)	15.0	11.2	10.9
4-Ring Aromatics (wt %)	17.9	15.0	13.8
Total Aromatics (wt %)	54.0	59.3	58.7
Total Chlorine (wppm)	1.0	7.0	4.8
Total Fluorine (wppm)	<1	<1	<1

The above table illustrates that coker gas oil at least partially derived from polymers, including plastic waste, has a different composition than conventional coker oil. As shown, the sulfur content in the coker gas oil from co-processing includes significantly less sulfur than Test 1 with no polymeric waste. In addition, the coker gas oil from co-processing of the polymers, including plastic waste, also includes less 2-ring, and 3+-ring aromatic, as well as having an increase in hydrogen concentration and decrease in aromatic concentration. The co-processed coker gas oil also includes an increase in chlorine, with chlorine having a substantial increase from <1 ppm to 7.0 and 4.8 wppm, respectively.

While the disclosure has been described with respect to a number of embodiments and examples, those skilled in the art, having benefit of this disclosure, will appreciate that other embodiments can be devised which do not depart from the scope and spirit of the disclosure as disclosed herein. Although individual embodiments are discussed, the present disclosure covers all combinations of all those embodiments.

While compositions, methods, and processes are described herein in terms of "including," "containing," "having," or "including" various components or steps, the compositions and methods can also "consist essentially of" or "consist of" the various components and steps. The phrases, unless otherwise specified, "consists essentially of" and "consisting essentially of" do not exclude the presence of other steps, elements, or materials, whether or not, specifically mentioned in this specification, so long as such steps, elements, or materials, do not affect the basic and novel characteristics of the disclosure, additionally, they do not exclude impurities and variances normally associated with the elements and materials used.

All numerical values within the detailed description are modified by "about" the indicated value, and take into account experimental error and variations that would be expected by a person having ordinary skill in the art.

Many alterations, modifications, and variations will be apparent to those skilled in the art in light of the foregoing description without departing from the spirit or scope of the present disclosure and that when numerical lower limits and numerical upper limits are listed herein, ranges from any lower limit to any upper limit are contemplated.

The invention claimed is:

1. A method of producing circular chemical products comprising:

providing a coker gas oil that is at least partially derived from polymeric waste, wherein the coker gas oil has a paraffin content of about 5 wt % to about 50 wt %, a sulfur content of about 0.1 wt % to about 7 wt %, and a halide content of about 0.1 wppm to about 5 wppm; and

converting the coker gas oil into at least a polymer.

2. The method of claim 1, wherein the coker gas oil is derived from co-processing of polymeric waste and a heavy oil with a T10 distillation point of about 343° C. to about 575° C.

3. The method of claim 1, wherein providing the coker gas oil comprises: coking a feedstock comprising the polymeric waste and a heavy oil with a T10 distillation point of about 343° C. to about 575° C. to form at least a coker effluent and coke; and separating the coker gas oil from the coker effluent.

4. The method of claim 3, wherein the polymeric waste comprises plastic waste.

5. The method of claim 3, wherein the heavy oil comprises petroleum vacuum resid.

6. The method of claim 3, wherein the feedstock comprises the polymeric waste in an amount of about 0.1 wt % to about 25 wt %.

7. The method of claim 3, wherein the coking comprises exposing the feedstock to delayed coking conditions.

8. The method of claim 1, wherein providing the coker gas oil comprises pyrolyzing the polymeric waste to produce at least a pyrolysis oil and then coking at least the pyrolysis oil and a heavy oil with a T10 distillation point of about 343° C. to about 575° C.

9. The method of claim 1, wherein the polymeric waste comprises plastic waste.

10. The method of claim 1, wherein at least a portion of the polymer is attributable to polymers in the polymeric waste.

11. The method of claim 1, wherein the polymer comprises a circular polymer.

12. The method of claim 1, wherein the polymer comprises a polymer that is certified circular in accordance with International Sustainability and Carbon Certification.

13. The method of claim 1, further comprising treating the coker gas oil to reduce a concentration of one or more contaminants prior to the step of converting the coker gas oil.

14. The method of claim 13, wherein the treating comprises hydroprocessing the coker gas oil.

15. The method of claim 1, wherein the converting the coker gas oil into at least the polymer comprises recovering olefins from the coker gas oil; and polymerizing at least a portion of the olefins.

16. The method of claim 1, wherein the converting the coker gas oil into at least the polymer comprises hydroprocessing at least a portion of the coker gas oil to form at least a hydroprocessing effluent, steam cracking at least a portion of the hydroprocessing effluent to form at least a steam cracking effluent; recovering olefins from the steam cracking effluent; and polymerizing at least a portion of the olefins.

17. The method of claim 16, wherein the hydroprocessing comprises hydrotreating at least a portion of the coker gas oil to form at least a hydrotreating effluent; and hydrocracking at least a portion of the hydrotreating effluent to form at least the hydroprocessing effluent.

18. The method of claim 1, wherein the converting the coker gas oil into at least the polymer comprises fluid

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catalytic cracking at least a portion of the coker gas oil to form at least a fluid catalytic cracking effluent; recovering olefins from at least a portion of the fluid catalytic cracking effluent; and polymerizing at least a portion of the olefins.

19. The method of claim 1, wherein the converting the coker gas oil into at least the polymer comprises partially oxidizing at least a portion of the coker gas oil by at least combustion of the coker gas oil and an oxygen-containing gas to form at least an oxidation effluent comprising carbon monoxide and hydrogen; and reacting at least a portion of the oxidation effluent in the presence of olefins and a hydroformylation catalyst to form at least oxo alcohols.

20. A method of producing circular chemical products comprising:

providing a coker gas oil that is at least partially derived from polymeric waste, wherein the coker gas oil has a paraffin content of about 5 wt % to about 50 wt %, a sulfur content of about 0.1 wt % to about 7 wt %, and a halide content of about 0.1 wppm to about 5 wppm;

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hydroprocessing at least a portion of the coker gas oil to form at least a hydroprocessing effluent;
steam cracking at least a portion of the hydroprocessing effluent to form at least a steam cracking effluent;
recovering olefins from the steam cracking effluent; and
polymerizing at least a portion of the olefins to form at least polyolefins.

21. The method of claim 20, wherein the hydroprocessing comprises hydrotreating at least a portion of the coker gas oil to form at least a hydrotreating effluent; and hydrocracking at least a portion of the hydrotreating effluent to form at least the hydroprocessing effluent.

22. The method of claim 20, further comprising coking a feedstock comprising the polymeric waste and a heavy oil with a T10 distillation point of about 343° C. to about 575° C. to form at least a coker effluent and coke; and separating the coker gas oil from the coker effluent.

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