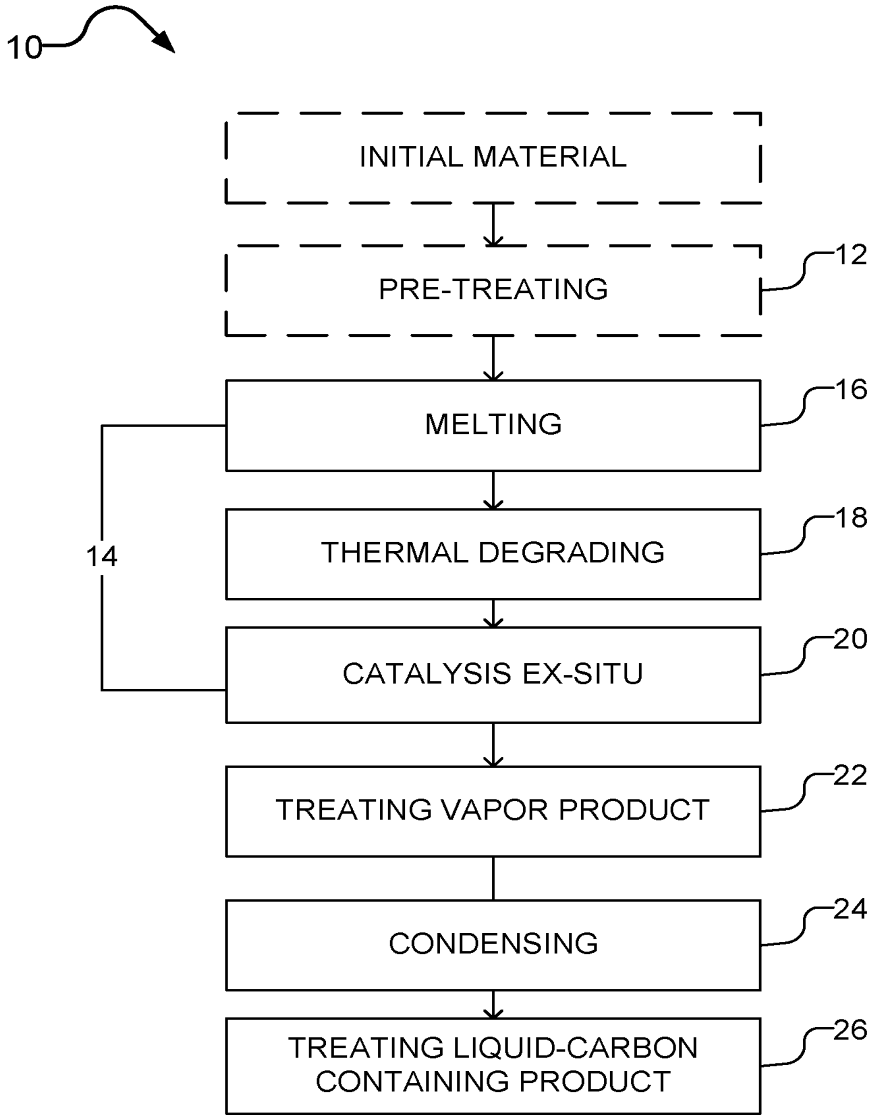

10
INITIAL MATERIAL
PRE-TREATING
12
MELTING
16
THERMAL DEGRADING
18
14
CATALYSIS EX-SITU
20
TREATING VAPOR PRODUCT
22
CONDENSING
24
TREATING LIQUID-CARBON CONTAINING PRODUCT
26

FIG. 1

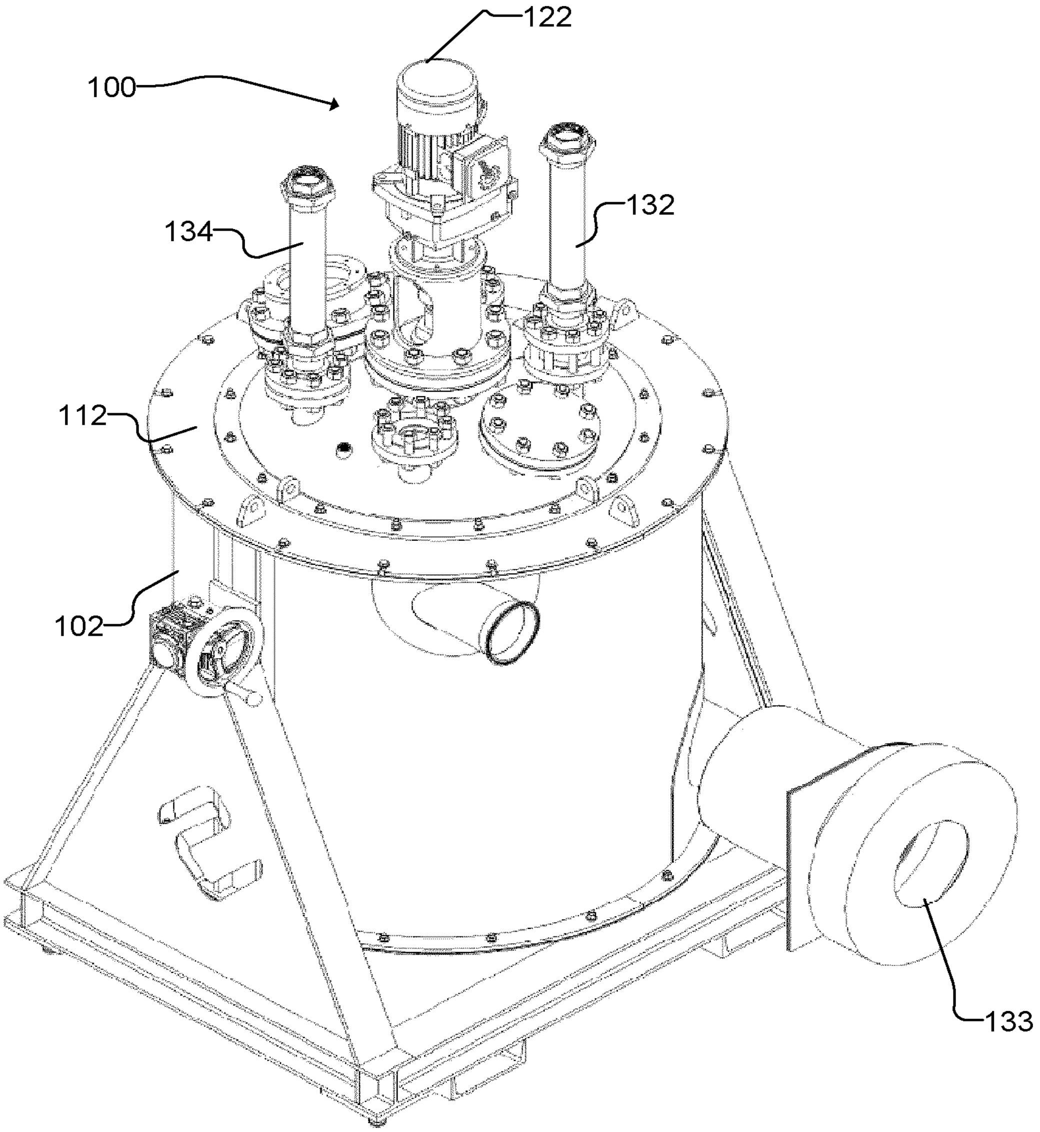


FIG. 2

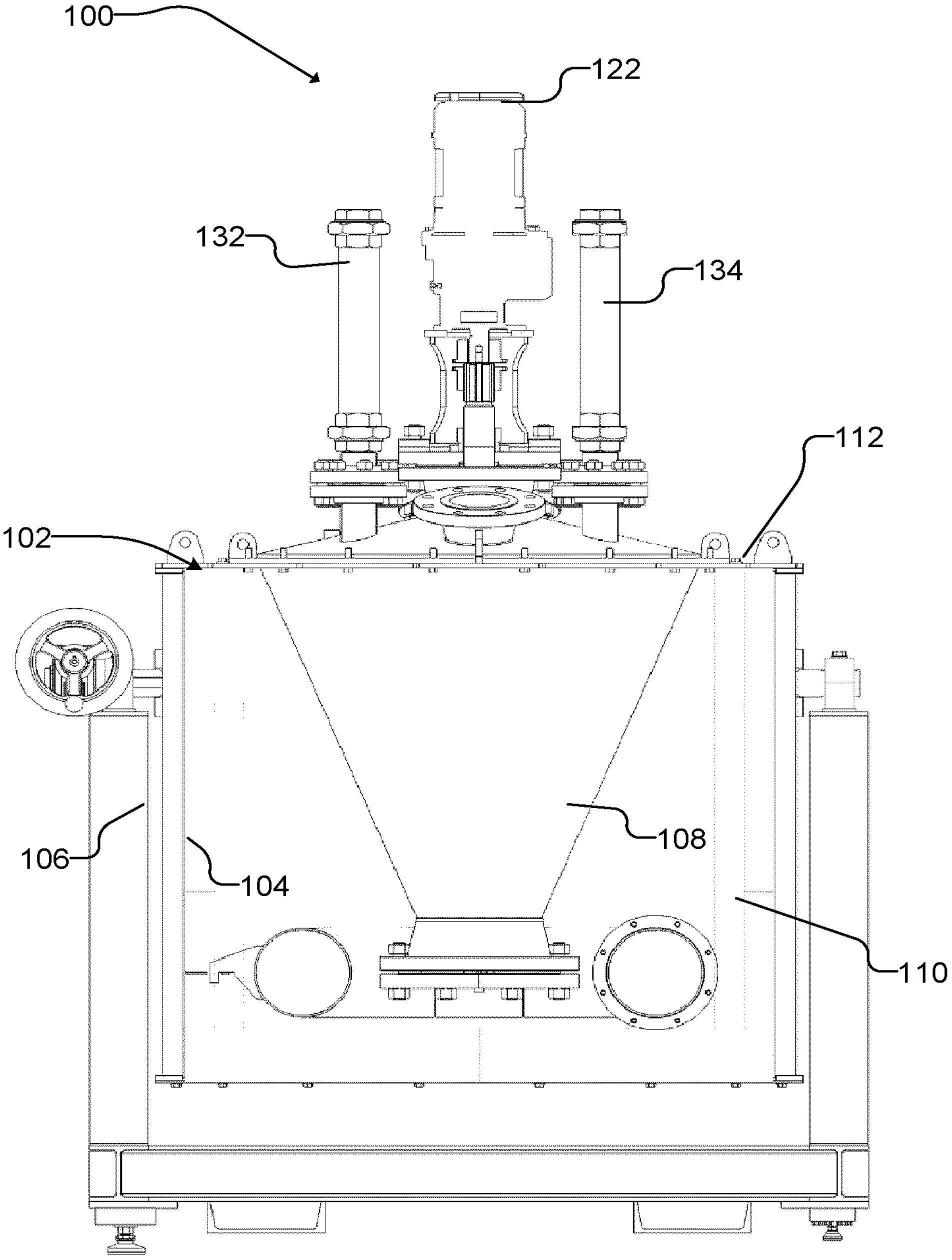
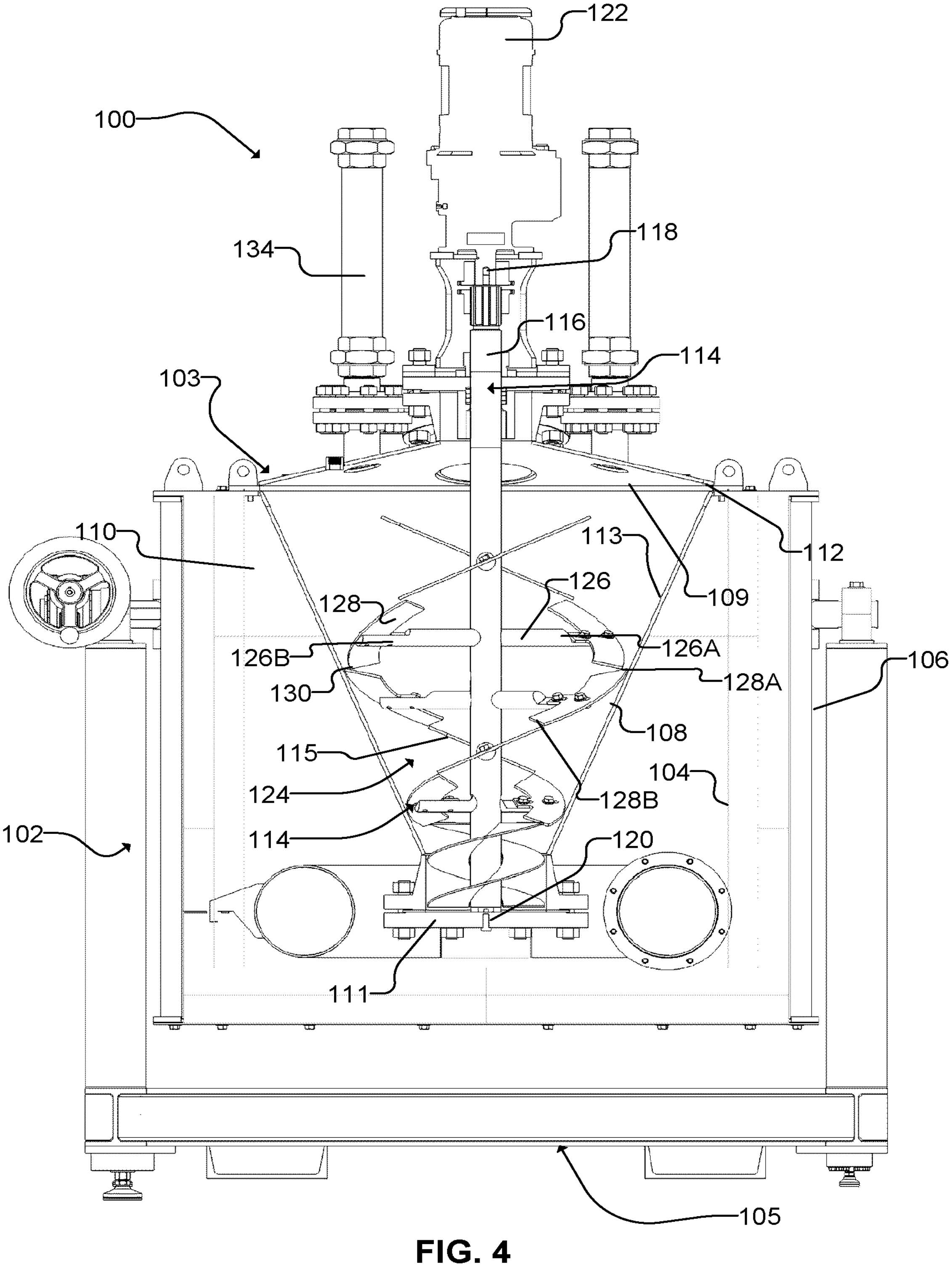


FIG. 3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126B
126A
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128A
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108
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128B
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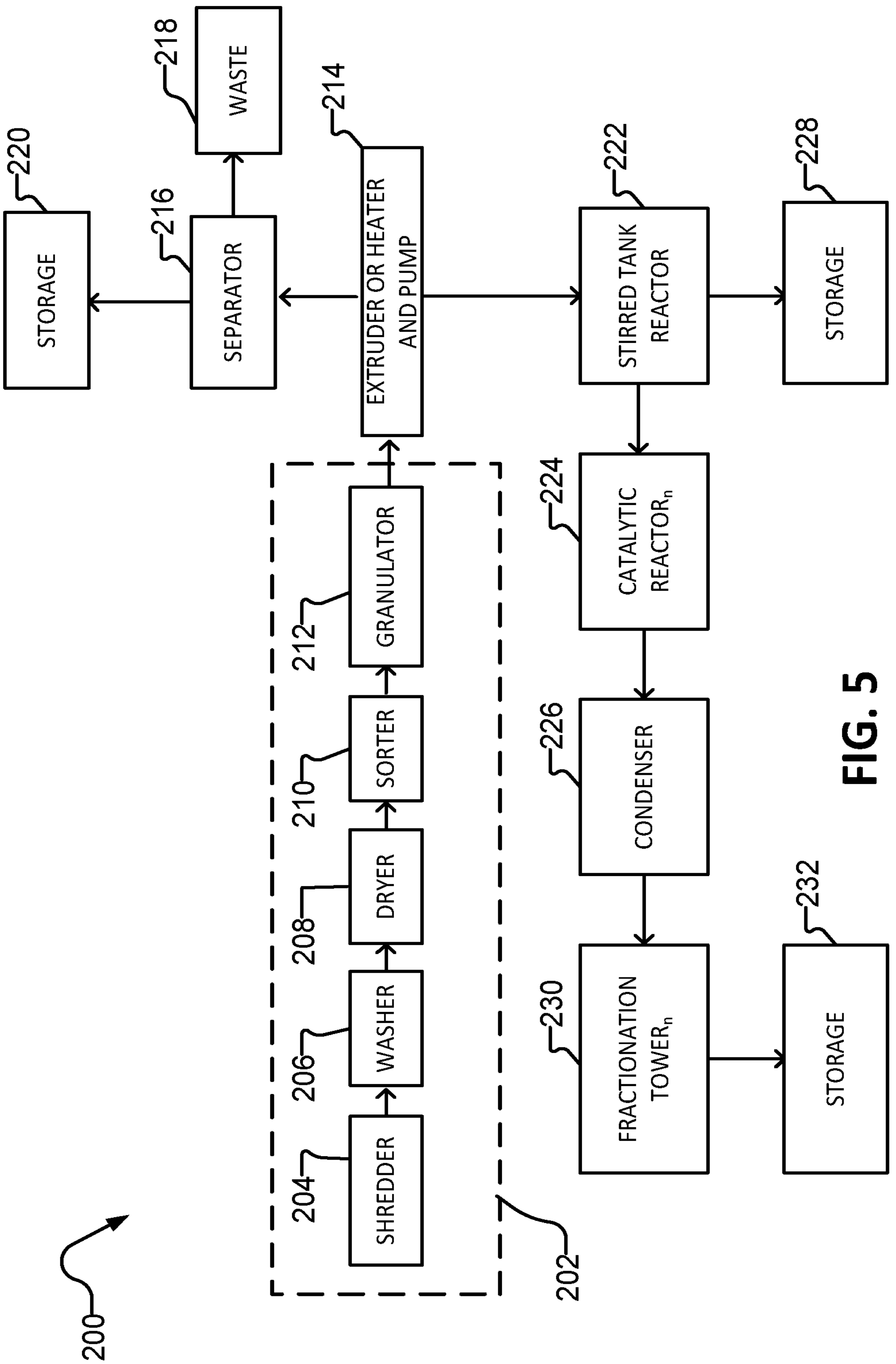
FIG. 4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202
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SHREDDER
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WASHER
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DRYER
210
SORTER
212
GRANULATOR
214
EXTRUDER OR HEATER AND PUMP
216
SEPARATOR
218
WASTE
220
STORAGE
222
STIRRED TANK REACTOR
224
CATALYTIC REACTOR$_n$
226
CONDENSER
228
STORAGE
230
FRACTIONATION TOWER$_n$
232
STORAGE

FIG. 5

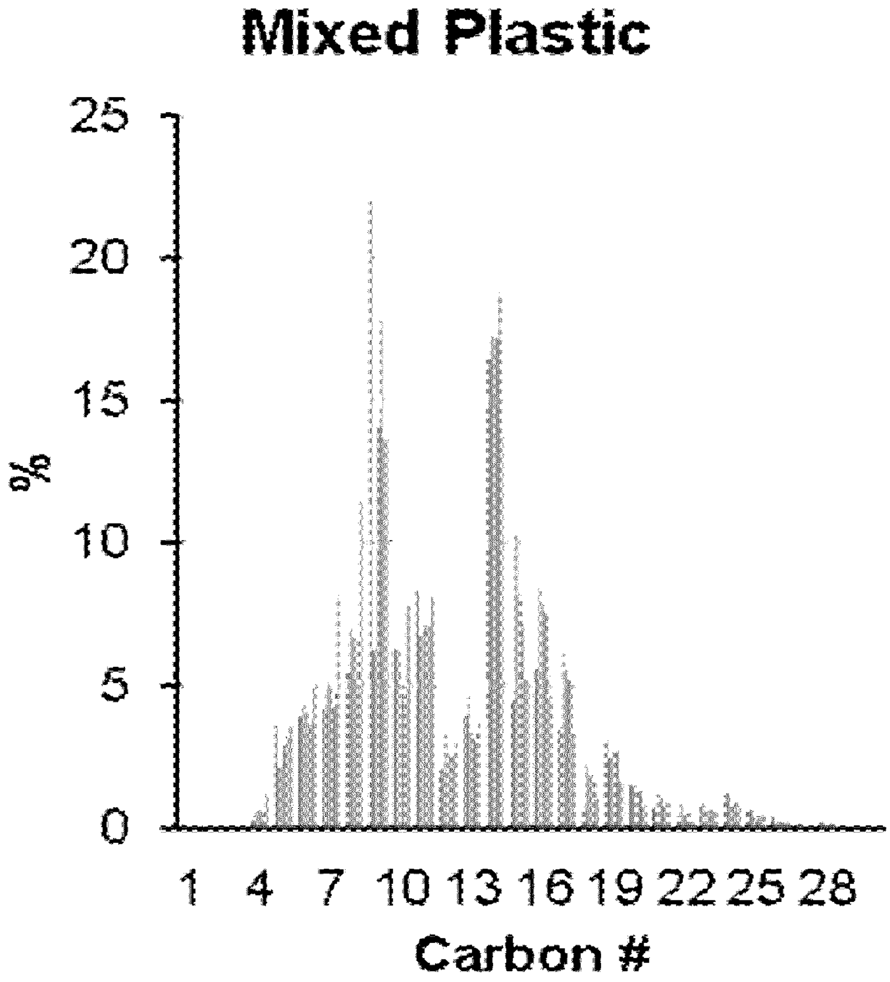

FIG. 6

PROCESSES AND SYSTEMS FOR CONVERTING POLYMERIC MATERIALS TO CARBON-CONTAINING PRODUCTS

Cross-Reference to Related Applications

[0001] This application claims priority from US application No. 63/485,284 filed 16 February 2023 and entitled PROCESSES AND SYSTEMS FOR CONVERTING POLYMERIC MATERIALS TO CARBON-CONTAINING PRODUCTS which is hereby incorporated herein by reference for all purposes. For purposes of the United States of America, this application claims the benefit under 35 U.S.C. §119 of US application No. 63/485,284 filed 16 February 2023 and entitled PROCESSES AND SYSTEMS FOR CONVERTING POLYMERIC MATERIALS TO CARBON-CONTAINING PRODUCTS which is hereby incorporated herein by reference for all purposes.

Field of the Invention

[0002] The invention pertains to systems and processes for converting polymeric materials to carbon-containing products.

Background of the Invention

[0003] It is known in the art to convert polymeric materials, such as plastic-based polymeric materials, to hydrocarbon-containing products, in particular, liquid carbon-containing products. It is desirable to provide an energy efficient and cost effective process and system for converting polymeric materials to liquid carbon-containing products. One particular application of the present invention is directed to an improved process and system for converting plastic wastes into liquid carbon-containing products such as hydrocarbon condensates.

Summary

[0004] One aspect of the invention provides a process for converting polymeric materials to carbon-containing products. The process may comprise optionally pre-treating an initial material such as plastics waste by one or more of shredding, washing, drying, sorting and granulating. The pre-treating of initial material may produce a feedstock that is suitable for participating in a pyrolysis process. In some embodiments, the pyrolysis process comprises three steps. The first step of the pyrolysis process may comprise heating the feedstock to a first temperature, thereby melting the feedstock into a molten form. The second step of the pyrolysis process may comprise thermally degrading the polymeric materials in the molten feedstock by heating the molten feedstock to a second temperature, thereby producing a vapor fraction. The third step of the pyrolysis process may comprise contacting the vapor fraction with a catalyst to form a vapor product comprising carbon-containing materials. The contacting of the vapor fraction with the catalyst may be performed ex-situ (also referred to herein as "ex-situ catalysis"), i.e., in one or more catalytic reactor arranged downstream of the reactor within which the first and second steps of the pyrolysis are performed.

[0005] In some embodiments, the first and/or second steps of the pyrolysis process further comprises supplying a catalyst to the feedstock. In such embodiments, the catalysis is performed in-situ, i.e., in the reactor within which the first and second steps of the pyrolysis are performed.

[0006] In some embodiments, the method comprises combining ex-situ and in-situ catalysis. In such embodiments, the catalyst is supplied to the feedstock in the first and/or second steps of the pyrolysis process. The vapor fraction, generated from the second step of the pyrolysis, is additionally contacted with the catalyst to form a vapor product in the third step of the pyrolysis process.

[0007] In some embodiments, the catalyst comprises a plurality of compounds. The catalyst may comprise a blend of different types of compounds. In some embodiments, the catalyst comprises a guard bed catalyst, and one or more cracking catalysts.

[0008] In some embodiments in which the pyrolysis process comprises ex-situ and in-situ catalysis, the catalyst selected for use in the in-situ catalysis is different from the catalyst selected for use in the ex-situ catalysis. In some embodiments, the catalyst selected for use in the ex-situ catalysis comprises 2 to 5 different types of compounds, and in some embodiments, 2 to 4, and in some embodiments, 2 to 3. In some embodiments, one compound is selected for use as the catalyst in the in-situ catalysis.

[0009] The compounds selected for use in the ex-situ catalysis may be immobilized in a respective one of a catalytic reactor.

[0010] In some embodiments, the process comprises treating the vapor product downstream of the pyrolysis process. The vapor product may be condensed by cooling the product to a fourth temperature. The condensing of the vapor product may separate the condensable vapor (which may contain a liquid carbon-containing product) from the non-condensable vapor. The liquid carbon-containing product may be further treated to yield a desirable product, such as a hydrocarbon condensate product which meets condensate specifications.

[0011] Another aspect of the invention provides an apparatus for thermally degrading polymeric materials in the molten feedstock. The apparatus may comprise a reactor tank having an inner wall and an outer wall surrounding the inner wall, an inner chamber disposed within the reactor tank dimensioned to receive the polymeric materials, a rotatable shaft disposed within the inner chamber, a plurality of mixing members disposed around the rotatable shaft, arranged to mix the polymeric materials received in the inner chamber, a vapor outlet arranged for flowing a vapor product out of the inner chamber, and means for supplying heat to the reactor tank. In some embodiments, the inner chamber comprises a conical shape. In some embodiments, the means for supplying heat to the reactor tank comprises a molten salt bath operatively connected to the reactor tank arranged to circulate molten salt between the inner and outer walls of the reactor tank. In some embodiments, the means for supplying heat comprises circulating flue gas and/or superheated steam between the inner and outer walls of the reactor tank. In some embodiments, the means for supplying heat comprises an electrical heating means. In such embodiments, an electrical power source is configured to supply heat to the electrical heating means.

[0012] Another aspect of the invention provides a system for converting polymeric materials to carbon-containing products.

[0013] Further aspects of the invention and features of specific embodiments of the invention are described below.

Brief Description of the Drawings

[0014] Exemplary embodiments are illustrated in referenced figures of the drawings. It is intended that the embodiments and figures disclosed herein are to be considered illustrative rather than restrictive.

[0015] Figure 1 is a flow chart showing the steps of a process for converting polymeric materials to carbon-containing products according to an example embodiment of the invention.

[0016] Figure 2 is perspective view of an apparatus for the thermal degradation of polymeric materials according to an example embodiment of the invention.

[0017] Figure 3 is an elevational, partly cutaway, view of the apparatus of Figure 2.

[0018] Figure 4 is an elevational, partly cutaway, view of the apparatus of Figure 2 showing the plurality of mixing members disposed inside the inner chamber of the apparatus.

[0019] Figure 5 is a schematic flow diagram illustrating a system for converting polymeric materials to carbon-containing products according to an example embodiment of the invention.

[0020] Figure 6 is a plot illustrating the carbon number distribution of the carbon-containing products obtained from pyrolyzing mixed plastics using an apparatus of the type illustrated in Figures 2-4.

Detailed Description

[0021] The invention provides systems, apparatuses, and processes for converting polymeric materials to carbon-containing products. In some embodiments, the process comprises a pyrolysis process. As used herein, “pyrolysis” refers to a thermal process adapted to break down materials into smaller constituent materials in the absence of oxygen, or in low oxygen conditions. One particular application of the invention is in the field of plastic waste. The plastic waste may comprise mixed plastics. Some example embodiments of the invention pertain to converting plastic wastes into hydrocarbon condensates. “Hydrocarbon condensates” may be composed of a blend of liquid hydrocarbon fractions. In some embodiments, the blend of liquid hydrocarbon fraction substantially contains C2-C30 hydrocarbons. In some embodiments, more than about 75% to about 90% of the blend of liquid hydrocarbon fraction contains C2-C7 hydrocarbons.

[0022] In some embodiments, the hydrocarbon condensates produced from the systems, apparatuses, and processes of the present invention are free of sulfur. The hydrocarbon condensates may be processed downstream to produce fuel. For example, in some embodiments, the hydrocarbon condensates may be used as a diluent to blend into heavier crudes such as heavy oils and/or bitumen. In some embodiments, the condensates may be fractionated. The fractionated liquid condensate may be fed to a cracking furnace. The systems, apparatuses, and processes of the present invention thus advantageously allow for recycling and upcycling of plastics.

Example Methods of Converting Polymeric Materials to Carbon-Containing Products

[0023] Referring to Figure 1, in one embodiment, the process 10 for converting polymeric materials to carbon-containing products begins with pre-treating an initial material containing the polymeric materials to convert the initial material into a feedstock that is suitable to undergo a pyrolysis process (block 12). The initial material may be pre-treated by subjecting the material to one or more mechanical and/or physical and/or chemical treatments. However, the pre-treating step is not mandatory. The initial material may be in a form that is suitable as a feedstock to undergo a pyrolysis process directly.

[0024] In some embodiments, the initial material is pre-treated to reduce the size of the material. The size of the initial material may be reduced using any suitable size reduction methods, including but not limited to, cutting, shredding, grinding, chopping, crushing, and/or granulating, etc. In some embodiments, reducing the size of the initial material comprises using a combination of different size reduction methods. In some example embodiments, reducing the size of the initial material comprises shredding the material into particles, followed by granulating the shredded particles to form granules or beads before being subjected to a pyrolysis process. In some embodiments, the average particle size of the feedstock has a diameter in the range of from about 6 mm to about 25 mm.

[0025] In some embodiments, the initial material is pre-treated by washing the material.

The initial material may be washed by water, or by any other suitable washing solution optionally comprising caustic agents and/or detergents. The initial material may be washed to remove dirt, impurities, and/or unwanted organic and/or inorganic contaminants such as minerals, food residue, soil, sand, and gravel. The washed feedstock may be dried by any suitable drying methods including but not limited to air drying, heat drying, microwave drying, oven drying, etc. In some example embodiments, the washed feedstock is dried by hot air drying methods. In some example embodiments, the hot air is sourced from waste heat produced from reactions occurring in downstream processes, such as from the pyrolysis process or one or more post-pyrolysis processes. The waste heat may be captured by a heat exchanger. The energy from the waste heat may be used to heat the air for supplying to the washed feedstock to air dry the feedstock.

[0026] In some embodiments, the initial material may be washed by suitable dry-cleaning methods, such as mechanical cleaning with compressed air, scrapping, and fluidized sand bed.

[0027] In some embodiments, the initial material is pre-treated by sorting in order to create an initial material which substantially comprises the desired material(s) for downstream processing. The feedstock may be sorted to remove foreign materials, including materials that are not suitable or desirable for pyrolysis. Foreign materials may be removed by any suitable sorting methods, including but not limited to, manual sorting, gravity sorting, sink-float sorting, magnetic sorting of metals, sensor-based sorting, etc.

[0028] In some embodiments, the feedstock is directly supplied to a pyrolysis process. In such embodiments, the feedstock is in a form (e.g., purity, size, and moisture level) that is suitable for processing by pyrolysis.

[0029] In one example embodiment, the initial material comprises mixed plastic waste. The plastic waste may be in the form of bales. The plastic waste may be pretreated by a combination of shredding, washing, drying, sorting and granulating. In some embodiments, the plastic bales are first shredded into particles. The particles may then be washed by water to reduce organic and inorganic contamination. The washed particles may be air dried. The dried plastic may be sorted to remove foreign and undesirable materials. In some embodiments, the foreign and undesirable materials are metals. In some embodiments, the desired materials for processing comprise mixed plastics, such as mixed plastic waste. The mixed plastic waste may include for example high density polyethylene (HDPE), low density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET), and PVC. The sorted particles may be granulated to form granules. The granules may be stored in storage. Alternatively, the granules may be supplied directly to the pyrolysis process as a feedstock.

[0030] In some embodiments, the feedstock is free of PVC. In some embodiments, the feedstock comprises PVC. The unwanted chlorides emitted from the PVC may be eliminated in downstream steps in the pyrolysis process, for example in the step of melting of the feedstock and/or ex-situ catalysis.

[0031] Referring to Figure 1, the feedstock undergoes a pyrolysis process (block 14). The pyrolysis process is performed in the absence or in low oxygen environment . In some embodiments, the pyrolysis process comprises three steps. The first step of the pyrolysis process (block 16) comprises heating the feedstock to a first temperature, melting the feedstock into a molten form. In some example embodiments, the feedstock is melted by an extrusion process. In some example embodiments, the extrusion process comprises feeding the feedstock through a heated barrel, within which the feedstock gradually melts into its molten form. In some embodiments, a rotatable screw may be arranged within the barrel configured to convey the feedstock through a longitudinal length of the barrel from an input end to an output end. In some example embodiments, the feedstock is melted in a heated hopper and/or pumped through a rotatable screw.

[0032] In some embodiments, the first temperature is in the range of from about 100°C to about 500°C, or in some embodiments, from about 250°C to about 450°C.

[0033] In some embodiments, the feedstock residence time is in the range of from about 15 minutes to about 2 hours, and in some embodiments, about 30 minutes to about 1 hour.

[0034] In some embodiments, the melting of the feedstock extracts vapor from the feedstock. In some example embodiments in which the melting of the feedstock is performed by an extrusion process, the extracted vapor flows out of the barrel during the extrusion process through a vent arranged at a point along the length of the barrel. In some embodiments, the extracted vapor is separated from the feedstock in a downstream separation step. For example, a separator may be arranged downstream of the extruder or the heated hopper and pump. The separator may be adapted to separate unwanted vapor from the desired vapor product. In some example embodiments, the unwanted vapor is hydrogen chloride (HCl) fumes, or hydrochloric acid. Hydrogen chloride gas may be released from the melting of PVC, if such type of plastic material is present in the feedstock.

[0035] In one example embodiment, the separation step comprises treating the vapor collected from the melting step with a suitable scrubber. In some example embodiments, the unwanted vapor is hydrogen chloride (HCl). In such embodiments, the scrubber comprises sodium carbonate (soda ash) and/or calcium carbonate (limestone).

[0036] The separated vapor comprising the desired vapor may be collected, and directly used, or optionally further treated and/or processed downstream of the melting process.

[0037] In some embodiments, the second step of the pyrolysis process (block 18) comprises thermally degrading the polymeric materials in the molten feedstock. Thermal degradation of the polymeric materials decomposes the polymer chains into one or more decomposed materials. The polymeric materials may undergo one or more of depolymerization, dehydration, decarbonylation, decarboxylation, deoxygenation, oligomerization, and aromatization during the thermal degradation process. The one or more decomposed materials include monomers, liquid and/or gaseous hydrocarbons, and/or intermediate compounds and/or syngas comprising one or more of hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), and nitrogen (N_2), and/or other saturated and/or unsaturated hydrocarbons, and/or water. In some embodiments, the majority of the hydrocarbons produced from the degradation of the polymeric materials in the molten feedstock are hydrocarbons with carbon numbers in the range of from about 1 to about 6. “Majority” refers to a value greater than about 60%, and in some embodiments, greater than about 70%, and in some embodiments, greater than about 80%, and in some embodiments, greater than about 90%.

[0038] The thermal degradation of the polymeric materials may comprise heating the molten feedstock to a second temperature. In some embodiments, the thermal degradation of the polymeric materials comprises subjecting the molten feedstock to a pressure. The thermal degradation of the polymeric materials may comprise occasionally, or continuously, stirring the molten feedstock.

[0039] In some embodiments, the heating of the polymeric materials to the second temperature comprises heating the polymeric materials with salt bath heating. In such embodiment, salt is heated to yield a molten form in a salt bath heater. The molten salt may then be supplied to heat the polymeric materials. In some embodiments, the thermal degradation of the polymer is performed in a reactor. The molten salt may be supplied from the salt bath heater to the reactor, circulating between inner and outer walls thereof. The molten salt, when cooled, may be returned to the salt bath heater.

[0040] In some embodiments, the heating of the polymeric materials to the second temperature comprises heating the materials with superheated steam and/or flue gas.

[0041] In some embodiments, a hot inert gas (e.g., N_2 gas) and/or flue gas is supplied to contact the polymeric materials. The hot inert gas and/or flue gas may for example flow within the reactor as bubbles, which facilitates to increase heat and mass transfer in the thermal pyrolysis process.

[0042] In some embodiments, the thermal degradation of the polymeric materials is performed in a stirred tank reactor. Figure 2 illustrates an example stirred tank reactor that is suitable for use in the thermal degradation process, which will be discussed in detail in the following section.

[0043] In some embodiments, the second temperature (i.e., temperature at which the molten feedstock heated to thermally degrade the polymeric materials) is greater than the first temperature (i.e., temperature at which the feedstock is heated to melt the feedstock). In some embodiments, the second temperature is in the range of from about 300°C to 600°C. In some embodiments, the second temperature is in the range of from about 350°C to 450°C.

[0044] In some embodiments, the molten feedstock is subjected to a pressure in the range of from about 1 to about 30 pounds per square gauge (psig). In some embodiments, the molten feedstock is subjected to a pressure in the range of from about 3 to about 20 psig. In some embodiments, the molten feedstock is subjected to a pressure in the range of from about 5 to about 10 psig.

[0045] In some embodiments, the molten feedstock residence time is in the range of from about 15 minutes to about 2 hours, and in some embodiments, about 30 minutes to about 1 hour.

[0046] In some embodiments, the thermal degradation of the polymeric materials produces solid residues. The solid residues may be occasionally, or continuously removed during the thermal degradation process. The collected solid residues may be processed downstream of the thermal degradation process to form useful materials. In some example embodiments, the initial material comprises mixed plastic waste. In such embodiments, the solid residues produced from the thermal degradation of the plastic waste comprises char. The char may accumulate at a bottom of a stirred tank reactor. The char may be removed from the reactor, and collected. The collected char may be processed (e.g., chemically, mechanically, and/or physically) to yield useful materials which may be used in different applications, such as activated carbon (adsorbents), additives in epoxy resins, fuel briquettes, soil additives and/or feed for asphalt production.

[0047] In some embodiments, the thermal degradation of the polymeric materials extracts vapor from the molten feedstock to produce a vapor fraction. The vapor fraction may for example be continuously or occasionally removed from a stirred tank reactor, such as through a top of the stirred tank reactor.

[0048] In some embodiments, the third step of the pyrolysis process (block 20) comprises contacting the vapor fraction with a catalyst to form a vapor product comprising carbon-containing materials. The catalytic third step may be performed ex-situ. The contacting of the vapor fraction with the catalyst comprises passing the vapor fraction through the catalyst. In some embodiments, the vapor fraction is arranged to flow out of the stirred tank reactor to enter a catalytic reactor which contains a catalyst.

[0049] In some embodiments, the catalytic reactor comprises one or more fixed bed reactors. In such embodiments, a catalyst is immobilized in the reactor, arranged to contact the vapor fraction as the vapor fraction flows through the catalyst. However, other suitable catalytic reactors may be used. For example, in some embodiments, the catalytic reactor comprises a fluidized bed reactor.

[0050] In some embodiments, the first and/or second steps of the pyrolysis process (blocks 14, 18) further comprises supplying a catalyst to the feedstock. In such embodiments, the catalysis is performed in-situ, i.e., in the reactor within which the first and second steps of the pyrolysis are performed.

[0051] In some embodiments, the method comprises combining ex-situ and in-situ catalysis. In such embodiments, the catalyst is supplied to the feedstock in the first and/or second steps of the pyrolysis process (blocks 14, 18). The vapor fraction, generated from the second step of the pyrolysis (block 18), is additionally contacted with the catalyst to form a vapor product in the third step of the pyrolysis process (block 20).

[0052] In some embodiments, the catalyst comprises a plurality of compounds. The catalyst may comprise a blend of different types of compounds.

[0053] In some embodiments in which the pyrolysis process comprises ex-situ and in-situ catalysis, the catalyst selected for use in the in-situ catalysis is different from the catalyst selected for use in the ex-situ catalysis. In some embodiments, the catalyst selected for use in the ex-situ catalysis comprises 2 to 5 different types of compounds, and in some embodiments, 2 to 4, and in some embodiments, 2 to 3. In some embodiments, one compound is selected for use as the catalyst in the in-situ catalysis.

[0054] The catalyst may comprise a guard bed catalyst and one or more cracking catalysts. The guard bed catalyst may be a substance adapted to remove contaminants, such as HCl, contained in the vapor fraction, and/or to serve as an initial mild catalyst. In some embodiments, the guard bed catalyst comprises an activated carbon.

[0055] In some embodiments, the one or more cracking catalysts comprise a substance adapted to convert hydrocarbon molecules with high molecular weights into hydrocarbon molecules with lower molecular weights. In some embodiments, the one or more cracking catalysts is selected from one or more of a zeolite catalyst (e.g., HZSM-5, HUSY, HMOR, HY, ZSM-5, MCM-22, ZSM-23, ZSM-11, etc.), mesoporous material (e.g., MCM-41, SBA-15, etc.), metal oxide catalyst (e.g., FeO, CaO, ZnO, MgO, Al_2O_3, K_2CO_3, Na_2CO_3, Ni/Al_2O_3, etc.), fluid catalytic cracking (FCC) catalyst, clay catalyst (e.g., montmorillonite), and iron-ore catalyst. In some embodiments, the one or more cracking catalysts comprises two cracking catalysts. In some embodiments, the catalyst comprises, or in some embodiments, consists essentially of three compounds.

[0056] In some embodiments, the catalytic reactor used for performing the ex-situ catalysis comprises a plurality of serially arranged fixed bed reactors, where each one of the compounds is fixed within each of the catalytic reactors. The vapor fraction may pass serially through each of the catalytic reactors to form a vapor product. The vapor product may flow out of the catalyst reactor arranged most downstream from the thermal pyrolysis second step.

[0057] In some embodiments, the catalytic reactor comprising the guard bed catalyst is arranged upstream of the one or more catalytic reactors comprising the one or more cracking catalysts. This arrangement of the catalytic reactors allows the vapor fraction to first contact the guard bed catalyst such as an activated carbon to remove contaminants before contacting the one or more cracking catalysts.

[0058] The one or more cracking catalysts contained in the respective one or more catalytic reactors may be arranged downstream of the catalytic reactor comprising the guard bed catalyst.

[0059] In some embodiments, the one or more catalytic reactors are heated to a third temperature. In embodiments in which a plurality of catalytic reactors are provided, each of the catalytic reactors may be heated to the same temperature, or different temperatures. The third temperature may for example be in the range of from about 300°C to about 550°C, or in some embodiments, between about 350°C to about 450°C.

[0060] Selection of compounds to be used as the one or more cracking catalysts may be based on one or more of the acid site concentration, the type of acidity (e.g., Brønsted or Lewis), and distance among the acidic sites of the compounds. In some embodiments, the selection of compounds for use as the cracking catalysts is based on the relative acid concentration of the acid sites of the one or more compounds. The selection of compounds to be used as the cracking catalysts may be customized for the feedstock.

[0061] The process and system of the invention advantageously allow for converting different materials into desirable products. In some embodiments, the conversion of the different materials is possible by optimizing the type and/or concentration and/or relative placement of the blend of catalysts. The desirable products may be different depending on the intended application of the products. In some embodiments, the desirable products are light hydrocarbons, e.g., hydrocarbons with carbon numbers of 20 or less. In some embodiments, the desirable products are hydrocarbons with carbon numbers in the range of from 5 to 15. In some embodiments, heavy hydrocarbons having carbon numbers of greater than 20 are desired.

[0062] Pyrolysis process 14 may be tuned to optimize one or more of product selectivity and reaction rate by adjusting one or more of:

- the selection and/or amounts and/or relative placement of compounds used as the guard bed catalyst and/or the cracking catalysts;
- operating conditions such as the temperature(s) and/or pressure(s) maintained at each of the first, second and third pyrolysis steps;
- the residence time of the material at each of the first, second and third pyrolysis steps;
- the rate at which the vapor fraction is removed from the second pyrolysis step and supplied to the third pyrolysis step to contact the catalyst; and/or
- the rate at which the vapor fraction flows into each of the plurality of catalytic reactors, etc.

[0063] The vapor product may comprise condensable vapor and/or non-condensable vapor. Condensable vapor comprises hydrocarbon vapors. Examples of non-condensable vapor includes hydrogen gas (H_2), nitrogen gas (N_2), carbon monoxide (CO), carbon dioxide (CO_2), light hydrocarbons, saturated and/or unsaturated, such as methane and ethane, and the like.. In some embodiments, the majority of the light hydrocarbons comprise hydrocarbons with carbon numbers in the range of from about 1 to about 6.

[0064] In some embodiments, the process 10 comprises treating the vapor product downstream of the pyrolysis process 14 to convert the vapor product into one or more useful forms of carbon-containing materials (block 22). In some embodiments, the treating of the vapor product comprises condensing the vapor product (block 24). The condensing may comprise cooling the vapor product to a fourth temperature. The fourth temperature may be lower than the first temperature and/or second temperature and/or third temperature. In some embodiments, the fourth temperature is in the range of from about 50°C to about 80°C, or in some embodiments, in the range of from about 55°C to 70°C. The condensing of the vapor product may result in condensing the condensable vapor into a liquid carbon-containing product, thereby separating the condensable vapor from the non-condensable vapor.

[0065] In some embodiments, the liquid carbon-containing product is further treated to yield a desired product (block 26). For example, in some example embodiments, the liquid carbon-containing product is condensate, and the condensate is further treated to yield a desired condensate product that is compatible with condensate specifications. In some embodiments, the treating of the condensate comprises stabilizing the condensate by removing lighter hydrocarbon components from the liquid carbon-containing product in one or more fractionation towers. In one example, the condensate is arranged to flow through a first fractionation tower within which the light end hydrocarbons (e.g., C16 or less) are removed from the raw product. The removed liquid containing the light ends may be arranged to flow through a second fractionation tower within which liquid petroleum gas (LPG) is separated from the desired condensate product and/or the other potential distillates. The predominant forms of hydrocarbon which make up liquid petroleum gas (LPG) may include propane, butane, and/or isomers of propane and butane. The desired condensate product may comprise C4 to C16 hydrocarbons. In some embodiments, the desired condensate product comprises some C4 hydrocarbons. In some embodiments, a majority of the desired condensate product comprises C5 to C16 hydrocarbons. The desired condensate product and the LPG may be collected and stored separately.

Example Apparatus for Thermal Degradation of Polymeric Materials

[0066] Figures 2 to 4 illustrate an apparatus 100 for thermally degrading polymeric materials according to an example embodiment of the invention. The apparatus 100 may comprise a reactor tank 102 having an open end 103 and an opposing closed end 105. The reactor tank 102 may comprise an inner wall 104 and an outer wall 106 surrounding the inner wall 104. An inner chamber 108 may be defined within the reactor tank 102 having an input end 109 for receiving the molten feedstock containing the polymeric materials. The inner wall 104 and the inner chamber 108 may be separated by a space 110. A cover 112 may be securable to the open end 103 of the reactor tank 102, thereby closing the open end 103 of the reactor tank 102.

[0067] In some embodiments, the dimensions of the input end 109 of the inner chamber 108 are greater than the dimensions of an opposing closed end 111 of the inner chamber 108. The dimensions of the inner chamber 108 may decrease from the input end 109 to the closed end 111. In some example embodiments, the inner chamber 108 comprises a conical shape, having a decreasing diameter from the input end 109 to the closed end 111 of the inner chamber 108.

[0068] Means may be provided to mix the molten feedstock received within the inner chamber 108. In some embodiments, the mixing means comprises a mixer assembly 114. In some embodiments, the mixer assembly 114 comprises a rotatable shaft 116 extending within the inner chamber 108, along a longitudinal axis of the inner chamber 108. The shaft 116 extends from a first end 118 to an opposing second end 120. In some embodiments, a portion of the shaft 116 extends through the cover 112 such that the first end 118 is positioned external to the reactor tank 102. The first end 118 may be connectable to a motor 122 operable to drive a rotation of the shaft 116. In some embodiments, a plurality of mixing members 124 are disposed around the shaft 116. In the illustrated embodiments, the mixer assembly 114 comprises a plurality of mixing rods 126 mounted to the shaft 116. Each of the mixing rods 126 may in some embodiments be arranged to extend orthogonal to the longitudinal axis of the shaft 116. The plurality of mixing rods 126 may be mounted spaced-apart along the longitudinal axis of the shaft 116, arranged parallel to one another. In some embodiments, each one of the plurality of mixing rods 126 comprises a first mixing rod 126A and a second mixing rod 126B. In some embodiments, the first and second mixing rods 126A,B are each secured to a point along the length of the shaft 116, extending away from the shaft 116. The first and second mixing rods 126A,B may be arranged to extend in directions opposite to one another, away from one another. In some embodiments, the first and second mixing rods 126A,B are arranged parallel to one another.

[0069] In some embodiments, the lengths of at least some of the mixing rods 126 may be different so as to accommodate the shape of the inner chamber 108 (e.g., a conically-shaped inner chamber 108). In some embodiments, the length of the mixing rod 126 arranged near the first end 118 of the shaft 116 is greater than the lengths of the mixing rods 126 arranged near the second end 120 of the shaft 116.

[0070] In some embodiments, the mixer assembly 114 comprises a plurality of mixing blades 128, each being coupled to a respective one of the mixing rods 126. The mixing blades 128 may be arranged helically around the shaft 116, along the longitudinal axis of the inner chamber 108.

[0071] In some embodiments, each one of the mixing blades 128 has a first end 128A and an opposing second end 128B. In some example embodiments, one of the first and second ends 128A,B of each one of the mixing blade 126 is oriented at a first point within the inner chamber 108 that is at a minimum distance away from an inner wall 113 defined by the inner chamber 108, and the other one of the first and second ends 128A,B is at a second point within the inner chamber 108 that is at a maximum distance away from the inner wall 113. In some embodiments, the distance between the second point and the shaft 118 is greater than the distance between the first point and the shaft 118.

[0072] In some embodiments, the minimum distance is less than about 10 mm, and in some embodiments, less than about 8 mm, and in some embodiments, less than about 5 mm, measured from the first point to the inner wall 113. A short distance (e.g., of less than about 5 mm) between an end 128A,B of the blade 128 and the inner wall 113 advantageously prevents undesirable coke and/or char built-up within the inner chamber 108.

[0073] In some embodiments, a plurality of connectors 115 may be provided. Each one of the connectors 115 may be arranged to join adjacent mixing blades 128. In some embodiments, a connector 115 joins a first end 128A of one of the mixing blades 128 at one end of the connector 115, and a second end 128B of an adjacent one of the mixing blades 128 at an opposite end of the connector 115.

[0074] Means may be provided to heat the reactor tank 102 to a temperature suitable for thermal degradation of the polymeric materials in the molten feedstock. The heating means may comprise any heat source suitable for supplying heat to the reactor tank 102. In some example embodiments, the heating means comprises a burner operatively connected to the reactor tank 102. The burner may be operable to produce a heat source (e.g., in the form of hot flue gas from a flame) to supply heat to the reactor tank 102. In some example embodiments, the heating means comprises a molten salt bath operatively connected to the reactor tank 102. The molten salt bath may be operable to heat salt into a molten form. A pump (not shown) may be connected to supply the molten salt from the molten salt bath into the reactor tank 102. The molten salt may be arranged to circulate between the inner 104 and outer 106 walls of the reactor tank 102, and/or within the space 110 of the reactor tank 102. In some embodiments, a recycle stream may be arranged from the reactor tank 102 to the molten salt bath to return the cooled molten salt for re-use. In some example embodiments, the heating means comprises an input of hot gas into the reactor tank 102, and/or the inner chamber 108. In such example embodiments, a gas inlet 132 is arranged at the cover 112, aligned to input hot gas such as N_2 and/or flue gas into the reactor tank 102, and/or the inner chamber 108. In some example embodiments, the heating means comprises a steam generator, operatively connected to the reactor tank 102. The steam generator may be operable to generate a superheated steam. A pump (not shown) may be connected to supply the superheated steam into the reactor tank 102. The superheated steam may be arranged to circulate between the inner 104 and outer 106 walls of the reactor tank 102, and/or within the space 110 of the reactor tank 102.

[0075] In some embodiments, a vapor outlet 134 is arranged to allow a flow of vapor fraction generated from the thermal degradation of the polymeric materials in the molten feedstock out of the inner chamber 108. In some embodiments, the vapor outlet 134 may be fluidly connected to the catalytic reactor to allow the flow of vapor fraction downstream into the catalytic reactor. In some embodiments, the vapor outlet 134 is fluidly connected to a condenser. In such embodiments, the flow of vapor fraction is arranged to flow into the condenser directly, bypassing the catalytic reactor within which ex-situ catalysis is performed. .

[0076] In some embodiments, the reactor tank 102 is a batch reactor. In such embodiments, in operation, the molten feedstock is supplied into the inner chamber 108 at the start of the thermal degradation process. The reactor tank 102 may be heated to a desired temperature before or after the addition of the molten feedstock, thereby heating the molten feedstock to the desired temperature. The heating of the molten feedstock to the desired temperature produces a vapor fraction. The vapor outlet 134 of the reactor tank 102 may be fluidly connected to a catalytic reactor, such that the vapor fraction flows into the catalytic reactor, or to a storage tank in some embodiments. The heating of the molten feedstock may produce solid residues, for example, char. The solid residues may be removed from the inner chamber 108 by stopping the thermal degradation process (or at the end thereof), and removing the cover 112 to access the interior of the inner chamber 108.

[0077] In some embodiments, the reactor tank 102 is a continuous reactor. In such embodiments, in operation, the molten feedstock is continuously supplied into the inner chamber 108. In some embodiments, a pipe connects an output of the extruder used in the first step 16 of the pyrolysis process to a feed input of the reactor tank 102. The molten feedstock may be adapted to flow directly from the extruder into the reactor tank 102 at a desired flow rate. The reactor tank 102 may be heated to a desired temperature before supplying the molten feedstock, thereby heating the molten feedstock to the desired temperature. The heating of the molten feedstock to the desired temperature produces a vapor fraction. The vapor outlet 134 of the reactor tank 102 may be fluidly connected to a catalytic reactor, such that the vapor fraction flows into the catalytic reactor, or to a storage tank in some embodiments. The heating of the molten feedstock may produce solid residues, for example, char. The solid residues may be removed from the inner chamber 108 continuously during the thermal degradation process (or at the end thereof).

[0078] Aspects of this invention pertain to a system for converting polymeric materials to carbon-containing products. Figure 5 illustrates an example system 200. The system 200 comprises a pre-treatment zone 202 adapted to pre-treat an initial material (such as plastic wastes) into a feedstock that is suitable to undergo a pyrolysis process. The pre-treatment zone 202 may comprise one or more of a shredder 204, washer 206, dryer 208, sorter 210 and granulator 212.

[0079] An extruder 214 may be arranged downstream of the pre-treatment zone 202. The extruder 214 may be operable to heat the feedstock to a first temperature, melting the feedstock into a molten form.

[0080] The heating of the feedstock may produce vapor. The vapor may be supplied to a separator 216 operable to separate unwanted vapor from a desired vapor product. In some embodiments, the unwanted vapor is supplied to a waste collector 218. In some embodiments, the unwanted vapor is collected in storage 220.

[0081] The molten feedstock may then be supplied to a stirred tank reactor 222 arranged downstream of the extruder 214. The stirred tank reactor 222 may be operable to thermally degrade the polymeric materials in the molten feedstock to form a vapor fraction. The vapor fraction may flow into one or more catalytic reactors 224 operable to convert the vapor fraction into a vapor product comprising carbon-containing materials. In some embodiments, the one or more catalytic reactors 224 comprise three catalytic reactors. In such embodiments, the three catalytic reactors comprise a first catalytic reactor containing a guard bed catalyst, and a second and third catalytic reactors each containing a cracking catalyst. The vapor fraction flows into each of the first, second and third catalytic reactors sequentially. In some embodiments, the vapor fraction flows out of the third catalytic reactor.

[0082] The vapor product may flow into a condenser 226 operable to condense the vapor product to form a liquid carbon-containing product.

[0083] In some embodiments, the thermal degradation of polymeric materials in the molten feedstock produces solid residues. A storage tank 228 may be arranged downstream of the stirred tank reactor for collecting the solid residues.

[0084] In some embodiments, the liquid carbon-containing product flows into one or more fractionation towers 230 operable to form a desired product. One or more storage tanks 232 may be arranged downstream of the fractionation towers 230 for collecting the separated product(s).

EXAMPLE

[0085] An apparatus for thermally degrading polymeric materials of the type illustrated in Figures 2-4 was used to thermally degrade waste plastics comprising a mixture of different types of plastics. The mixed plastics were pyrolyzed (thermally degraded) at a temperature of about 450ºC. In this example, no catalyst was used.

[0086] Table 1 below lists the product yields upon pyrolysis of the mixed plastics using an apparatus of the type illustrated in Figures 2-4.

Table 1. Product Yields Upon Pyrolysis of Mixed Plastics

	Yields
Gas	9-28%
Liquid	70-88%
Solid	2-3%

[0087] Figure 6 is a plot illustrating the carbon number distribution of the carbon-containing products obtained from pyrolyzing mixed plastics using an apparatus of the type illustrated in Figures 2-4.

[0088] Throughout the foregoing description and the drawings, in which corresponding and like parts are identified by the same reference characters, specific details have been set forth in order to provide a more thorough understanding to persons skilled in the art. However, well known elements may not have been shown or described in detail or at all to avoid unnecessarily obscuring the disclosure.

[0089] As will be apparent to those skilled in the art in the light of the foregoing disclosure, many alterations and modifications are possible in the practice of this invention without departing from the scope thereof. Accordingly, the description and drawings are to be regarded in an illustrative, rather than a restrictive, sense.

Claims

1. A process for converting polymeric materials into carbon-containing products, comprising the steps of:

melting a feedstock to produce a molten feedstock by heating the feedstock to a first temperature;

thermally degrading polymeric materials in the molten feedstock to produce a vapor fraction by heating the molten feedstock to a second temperature;

contacting the vapor fraction with a blend of catalysts to form a vapor product; and

condensing the vapor product to produce a liquid carbon-containing product.

2. The process as defined in claim 1, wherein the blend of catalysts comprises 2 to 5 different catalysts.

3. The process as defined in any one of claim 1 or 2, wherein the contacting of the vapor fraction with the blend of catalysts comprises flowing the vapor fraction into a plurality of catalytic reactors, wherein each one of the plurality of catalytic reactors comprises at least one catalyst.

4. The process as defined in any one of claims 1 to 3, wherein the contacting of the vapor fraction with the blend of catalysts comprises supplying at least one catalyst to the feedstock in the melting step and/or to the molten feedstock in the thermal degrading step.

5. The process as defined in any one of claims 1 to 4, wherein the blend of catalysts is selected from one or more of an activated carbon, a zeolite catalyst, mesoporous material, metal oxide catalyst, fluid catalytic cracking (FCC) catalyst, clay catalyst, and iron-core catalyst.

6. The process as defined in any one of claims 3 to 5, wherein the contacting of the vapor fraction with the blend of catalysts comprises:

flowing the vapor fraction into a first catalytic reactor comprising a guard bed catalyst, the vapor fraction contacts the guard bed catalyst to form an intermediate vapor product; and flowing the intermediate vapor product into a second catalytic reactor comprising a first cracking catalyst, wherein the intermediate vapor product contacts the first cracking catalyst to form a vapor product before the condensing step.

7. The process as defined in any one of claims 1 to 6, further comprising the step of pre-treating an initial material to form the feedstock before the melting step.

8. The process as defined in claim 6 or 7, further comprising the step of flowing the vapor product into a third catalytic reactor comprising a second cracking catalyst, the vapor product contacting the second cracking catalyst before the condensing step.

9. The process as defined in any one of claims 6 to 8, wherein the guard bed catalyst comprises an activated carbon.

10. The process as defined in any one of claims 6 to 9, wherein the first cracking catalyst is selected from the group consisting of a zeolite catalyst, mesoporous material, metal oxide catalyst, fluid catalytic cracking (FCC) catalyst, clay catalyst, and iron-core catalyst.

11. The process as defined in any one of claims 6 to 10, wherein the second cracking catalyst is selected from the group consisting of a zeolite catalyst, mesoporous material, metal oxide catalyst, fluid catalytic cracking (FCC) catalyst, clay catalyst, and iron-core catalyst.

12. The process as defined in any one of claims 8 to 11, wherein the compound selected as the first cracking catalyst is the same or different from the compound selected as the second cracking catalyst.

13. The process as defined in any one of claims 8 to 12, wherein the concentration of the first cracking catalyst is the same or different from the concentration of the second cracking catalyst.

14. The process as defined in any one of claims 8 to 13, wherein the acid concentration of the acid sites of the first cracking catalyst is the same or different from the acid concentration of the acid sites of the second cracking catalyst.

15. The process as defined in any one of claims 1 to 14, wherein the second temperature is in the range of from about 300°C to about 800°C.

16. The process as defined in any one of claims 1 to 15, wherein the heating of the molten feedstock to the second temperature comprises circulating molten salt through inner and outer walls of a reactor.

17. The process as defined in any one of claims 1 to 15, wherein the heating of the molten feedstock to the second temperature comprises circulating superheated steam and/or hot flue gas.

18. The process as defined in any one of claims 1 to 17, wherein thermal degrading of polymeric materials in the molten feedstock comprises subjecting the molten feedstock to a pressure in the range of from about 3 to about 20 psig.

19. The process as defined in any one of claims 1 to 18, wherein a residence time in the step of thermal degrading of polymeric materials in the molten feedstock is in the range of from about 30 minutes to about 1 hour.

20. The process as defined in any one of claims 1 to 19, wherein the first temperature is in the range of from about 100°C to about 500°C.

21. The process as defined in any one of claims 1 to 20, wherein the melting of the feedstock comprising conveying the feedstock through an extruder.

22. The process as defined in any one of claims 1 to 20, wherein the melting of the feedstock comprising feeding the feedstock into a heated hopper.

23. The process as defined in any one of claims 1 to 22, wherein the condensing of the vapor product comprises cooling the vapor product to a temperature in the range of from about 55°C to about 70°C.

24. The process as defined in any one of claims 1 to 23, wherein the melting of the feedstock extracts vapor from the feedstock.

25. The process as defined in claim 24, further comprising separating the extracted vapor to remove unwanted vapor from a desired vapor.

26. The process as defined in claim 25, wherein the unwanted vapor comprises hydrogen chloride gas.

27. The process as defined in any one of claims 1 to 26, wherein the thermal degrading of the polymeric materials in the molten feedstock produces solid residues.

28. The process as defined in claim 27, wherein the solid residues comprises char.

29. The process as defined in any one of claims 7 to 28, wherein the initial material comprises mixed plastics.

30. The process as defined in claim 29, wherein the mixed plastics comprises polyvinyl chloride (PVC).

31. The process as defined in any one of claims 1 to 30, wherein the vapor product comprises hydrocarbon condensates.

32. An apparatus for thermally degrading polymeric materials, comprising:

a reactor tank having an inner wall and an outer wall surrounding the inner wall;

an inner chamber disposed within the reactor tank, the inner chamber dimensioned to receive the polymeric materials, wherein the inner chamber has an open end for receiving the polymeric materials and an opposing closed end, the dimensions of the input end is greater than the dimensions of the closed end;

a rotatable shaft disposed within the inner chamber;

a plurality of mixing members disposed around the rotatable shaft, arranged to mix the polymeric materials received in the inner chamber;

a vapor outlet arranged for flowing a vapor product out of the inner chamber; and

means for supplying heat to the reactor tank.

33. The apparatus as defined in claim 32, wherein the inner chamber comprises a conical shape.

34. The apparatus as defined in claim 33, wherein a diameter is greater at the open end of the inner chamber than a diameter at the closed end thereof.

35 The apparatus as defined in any one of claims 32 to 34, wherein the plurality of mixing members comprises a plurality of mixing rods mounted to the rotatable shaft, each one of the plurality of mixing rods being aligned orthogonal to a longitudinal axis of the rotatable shaft.

36. The apparatus as defined in claim 35, wherein the plurality of mixing members are aligned spaced-apart from one another along the longitudinal axis of the rotatable shaft.

37. The apparatus as defined in any one of claims 32 to 36, wherein the plurality of mixing members further comprises a plurality of mixing blades, each being coupled to a respective one of the mixing members.

38. The apparatus as defined in claim 37, wherein each one of the plurality of mixing blades comprises a first end extending to an opposing second end, wherein one of the first and second ends is positioned at a first point within the inner chamber that is at a minimum distance away from an inner wall defined by the inner chamber, and wherein the other one of the first and second ends is positioned at a second point within the inner chamber that is at a maximum distance away from the inner wall.

39. The apparatus as defined in claim 38, further comprising a plurality of connectors, wherein each one of the plurality of connectors arranged to join one of the first and second ends of one mixing blade to one of the first and second ends of an adjacent one of the mixing blades of the plurality of mixing blades.

40. The apparatus as defined in any one of claims 32 to 39, wherein the plurality of mixing members are arranged helically around the rotatable shaft.

41. The apparatus as defined in any one of claims 32 to 40, further comprising a cover securable to an open end of the reactor tank.

42. The apparatus as defined in any one of claims 32 to 41, wherein the means for supplying heat to the reactor tank comprises a molten salt bath operatively connected to the reactor tank configured to supply molten salt through inner and outer walls of the reactor tank.

43. The apparatus as defined in any one of claims 32 to 41, wherein the means for supplying heat to the reactor tank comprises a steam generator operatively connected to the reactor tank configured to supply superheated steam through inner and outer walls of the reactor tank.

44. The apparatus as defined in any one of claims 32 to 41, wherein the means for supplying heat to the reactor tank comprises a burner operatively connected to the reactor tank configured to supply heated flue gas through inner and outer walls of the reactor tank.

45. The apparatus as defined in any one of claims 32 to 44, further comprising a plurality of catalytic reactors flowingly connected downstream of the reactor tank.

46. The apparatus as defined in claim 45, wherein the plurality of catalytic reactors comprises a first catalytic reactor and a second catalytic reactor, the second catalytic reactor flowingly connected downstream of the first catalytic reactor.

47. The apparatus as defined in claim 46, wherein the first catalytic reactor comprises a guard bed catalyst immobilized therein.

48. The apparatus as defined in claim 46 or 47, wherein the second catalytic reactor comprises a first cracking catalyst immobilized therein.

49. The apparatus as defined in claim 47 or 48, wherein the guard bed catalyst comprises an activated carbon.

50. The apparatus as defined in claim 48 or 49, wherein the first cracking catalyst is selected from the group consisting of a zeolite catalyst, mesoporous material, metal oxide catalyst, fluid catalytic cracking (FCC) catalyst, clay catalyst, and iron-core catalyst.

51. The apparatus as defined in any one of claims 46 to 50, wherein the plurality of catalytic reactors further comprises a third catalytic reactor flowingly connected downstream of the second catalytic reactor, wherein the third catalytic reactor comprises a second cracking catalyst immobilized therein.

52. The apparatus as defined in claim 51, wherein the second cracking catalyst is selected from the group consisting of a zeolite catalyst, mesoporous material, metal oxide catalyst, fluid catalytic cracking (FCC) catalyst, clay catalyst, and iron-core catalyst.

53. The apparatus as defined in claim 51 or 52, wherein the compound selected as the first cracking catalyst is the same or different from the compound selected as the second cracking catalyst.

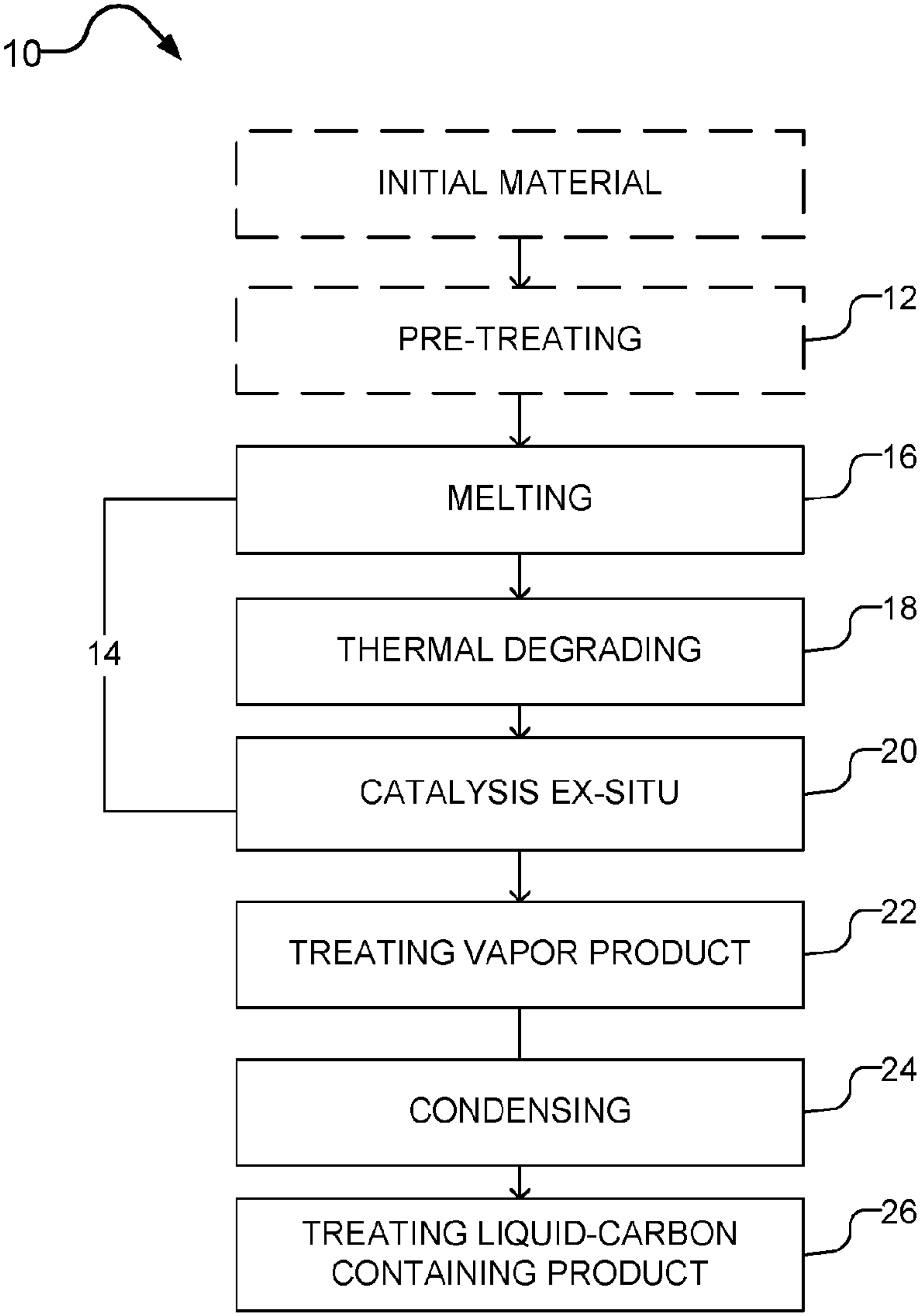
10
INITIAL MATERIAL
PRE-TREATING
12
MELTING
16
THERMAL DEGRADING
18
14
CATALYSIS EX-SITU
20
TREATING VAPOR PRODUCT
22
CONDENSING
24
TREATING LIQUID-CARBON CONTAINING PRODUCT
26

FIG. 1

ABRÉGÉ / ABSTRACT

L'invention divulgue un procédé et un système de conversion de matériaux polymères en produits contenant du carbone. Le procédé comprend la fusion d'une matière première afin de produire une matière première fondue par chauffage de la matière première à une première température, la dégradation thermique de matériaux polymères dans la matière première fondue afin de produire une fraction de vapeur par chauffage de la matière première fondue à une seconde température, la mise en contact de la fraction de vapeur avec un mélange de catalyseurs afin de former un produit de vapeur ; et la condensation du produit de vapeur afin de produire un produit liquide contenant du carbone. L'invention divulgue également un appareil de dégradation thermique de matériaux polymères.

A process and system for converting polymeric materials to carbon-containing products are disclosed. The process comprises melting a feedstock to produce a molten feedstock by heating the feedstock to a first temperature, thermally degrading polymeric materials in the molten feedstock to produce a vapor fraction by heating the molten feedstock to a second temperature, contacting the vapor fraction with a blend of catalysts to form a vapor product; and condensing the vapor product to produce a liquid carbon-containing product. An apparatus for thermally degrading polymeric materials is also disclosed.

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Courtoisie - Lettre confirmant l'entrée en phase nationale en vertu du PCT
Courtesy - Letter Acknowledging PCT National Phase Entry

OYEN WIGGS GREEN & MUTALA LLP
mail@patentable.com

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Les dossiers du Bureau des brevets indiquent que le demandeur s'est conformé aux exigences applicables pour l'entrée en phase nationale en vertu du PCT au Canada au titre du l'art. 154 des *Règles sur les brevets*.

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