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(54) **SEPARATION METHODS AND SYSTEMS FOR OXIDATIVE COUPLING OF METHANE**

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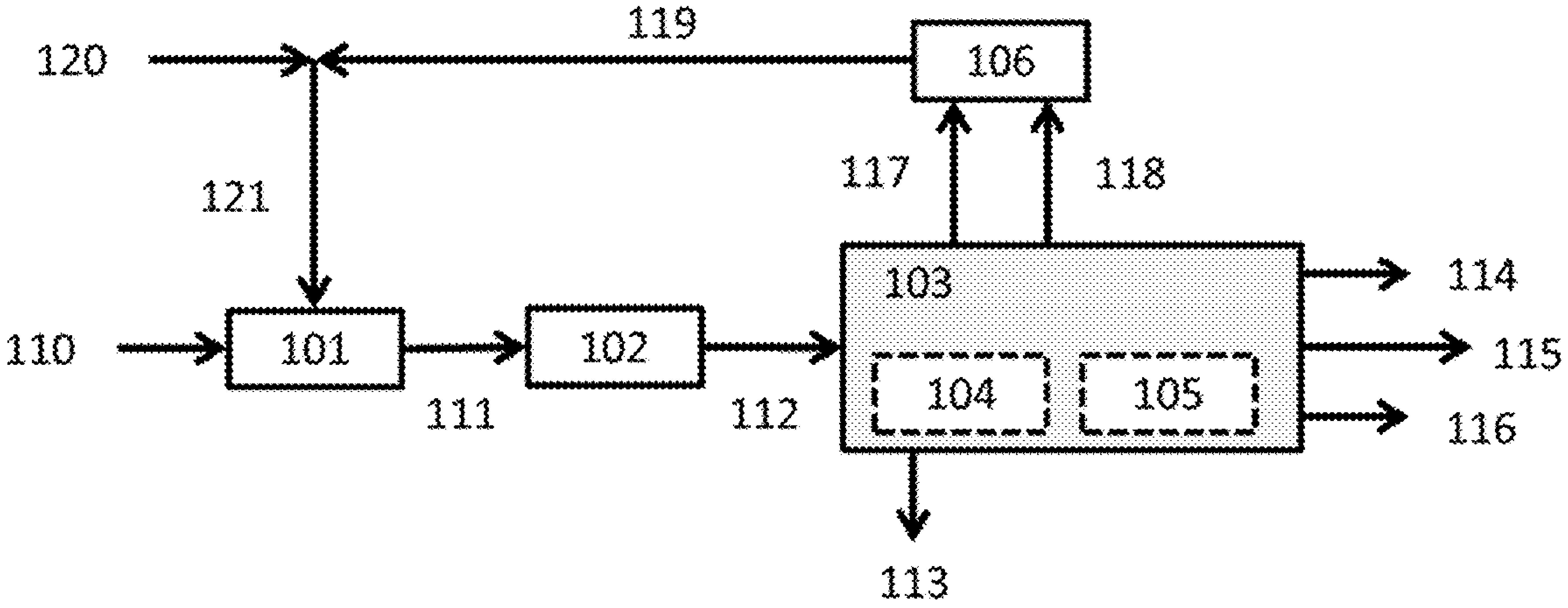
C07C 1/12 (2006.01)

(52) **U.S. Cl.**
CPC . ***C07C 2/84*** (2013.01); ***C07C 1/12*** (2013.01)

(57) **ABSTRACT**

The present disclosure provides a method for generating higher hydrocarbon(s) from a stream comprising compounds with two or more carbon atoms (C_{2+}), comprising introducing methane and an oxidant (e.g., O_2) into an oxidative coupling of methane (OCM) reactor. The OCM reactor reacts the methane with the oxidant to generate a first product stream comprising the C_{2+} compounds. The first product stream can then be directed to a separations unit that recovers at least a portion of the C_{2+} compounds from the first product stream to yield a second product stream comprising the at least the portion of the C_{2+} compounds.



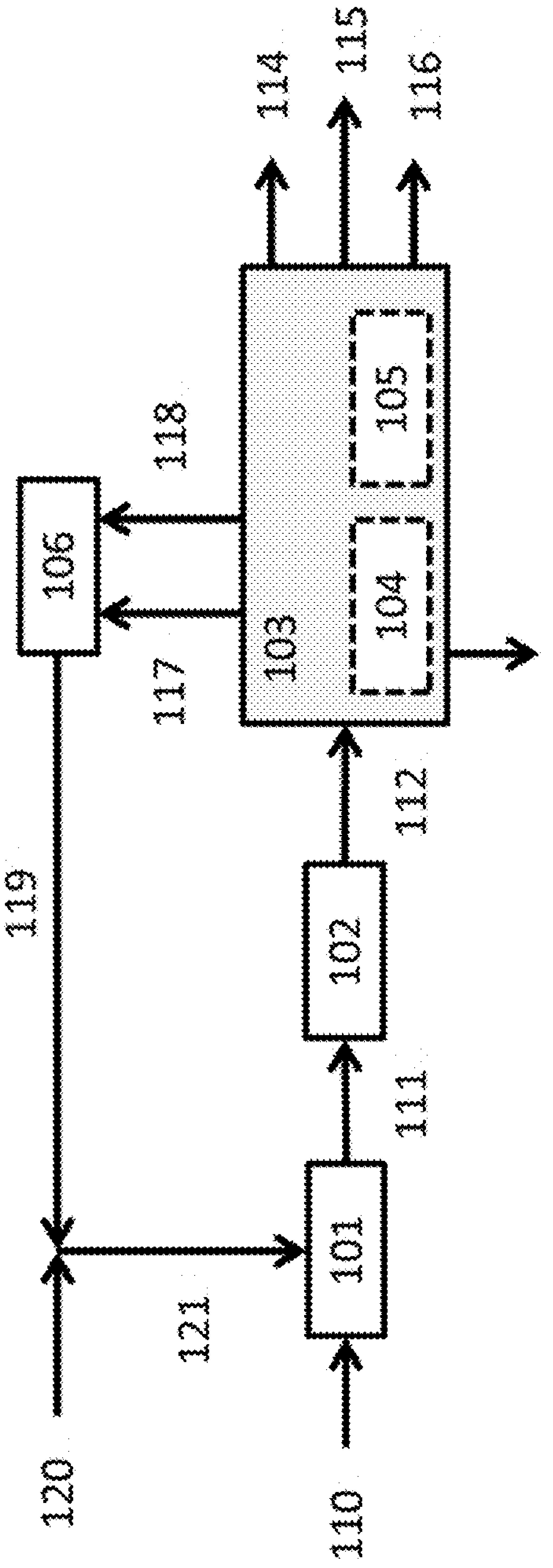

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FIG. 1

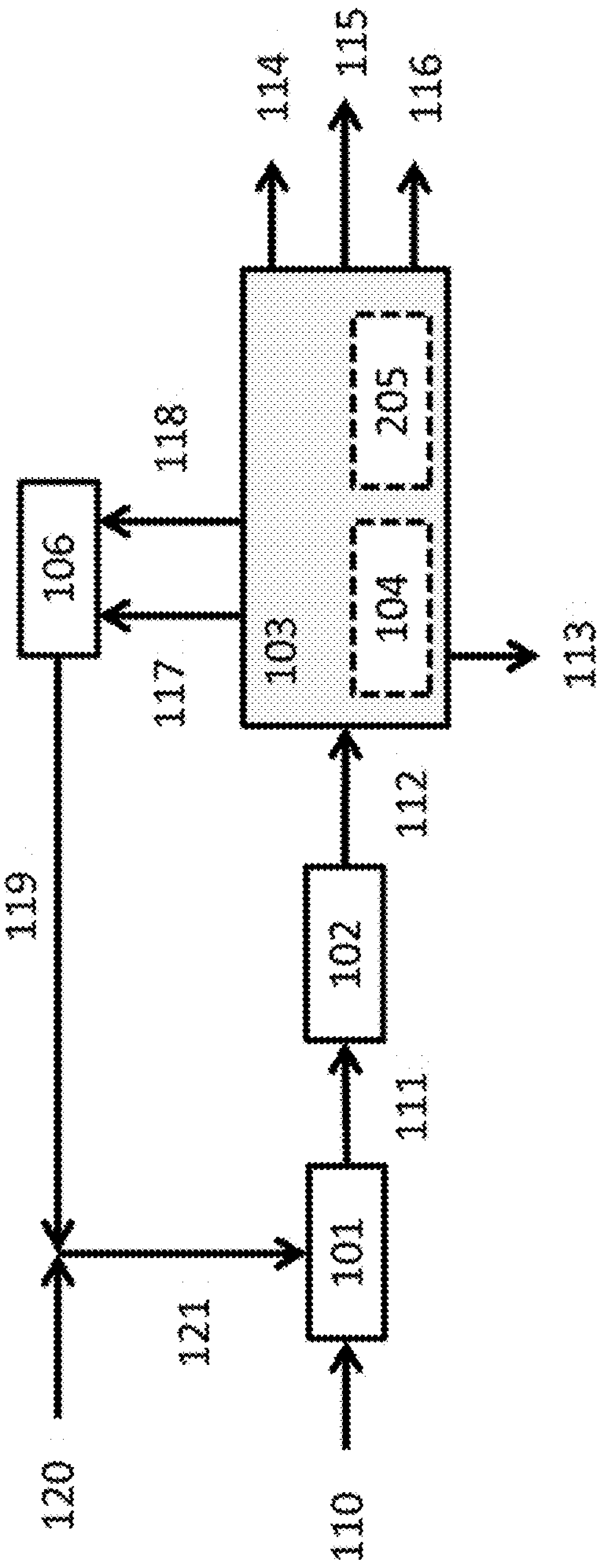
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FIG. 2

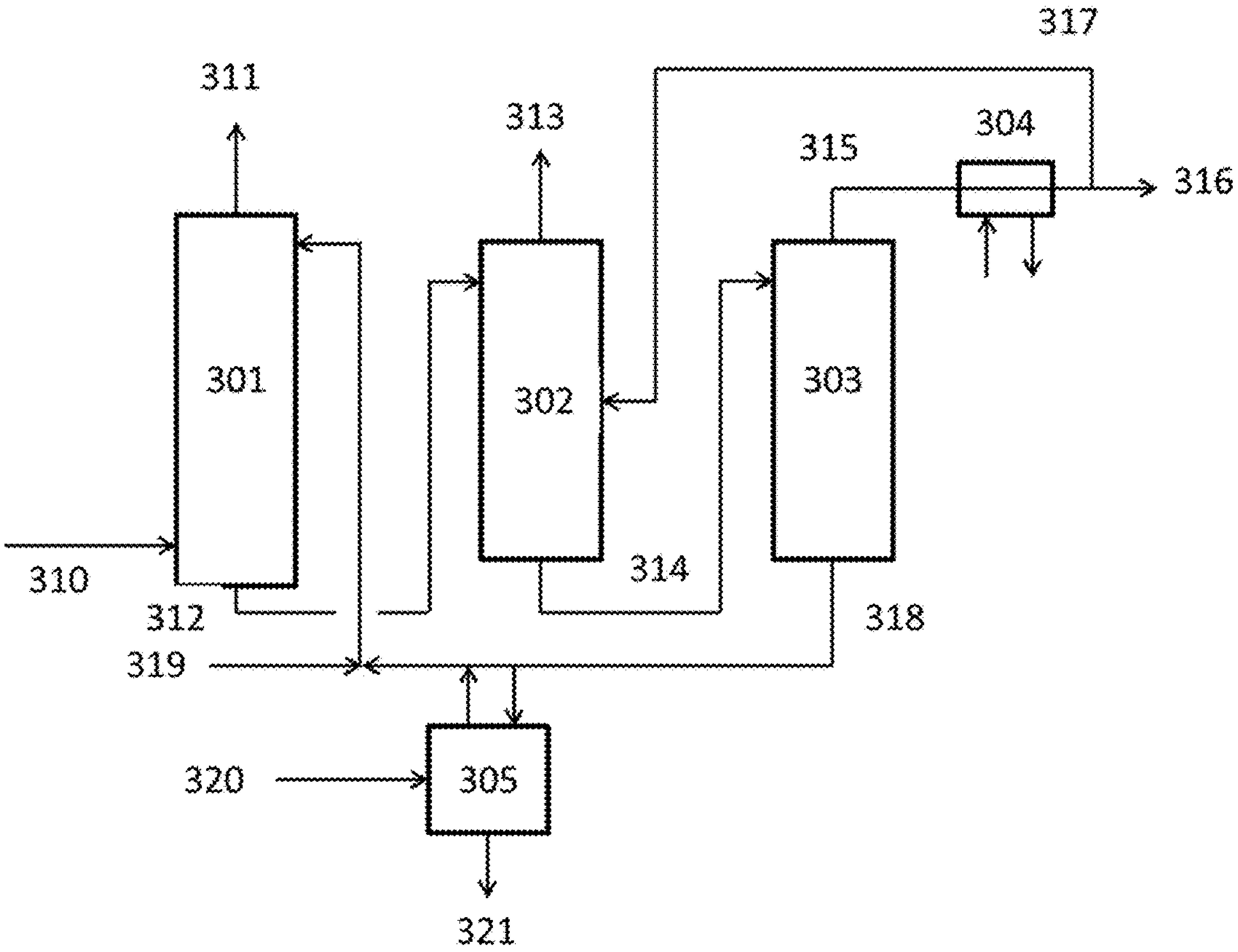
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FIG. 3A

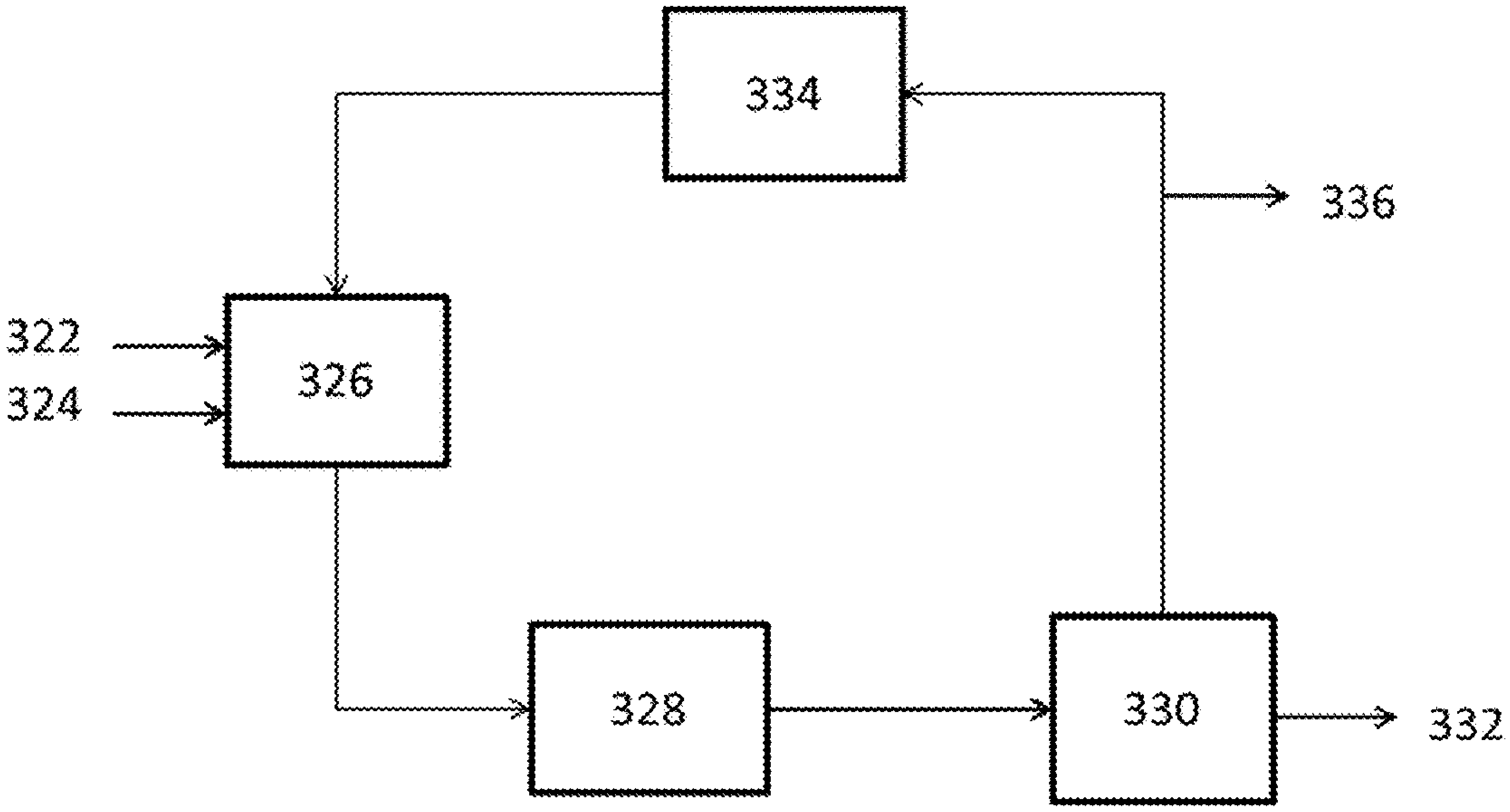

FIG. 3B

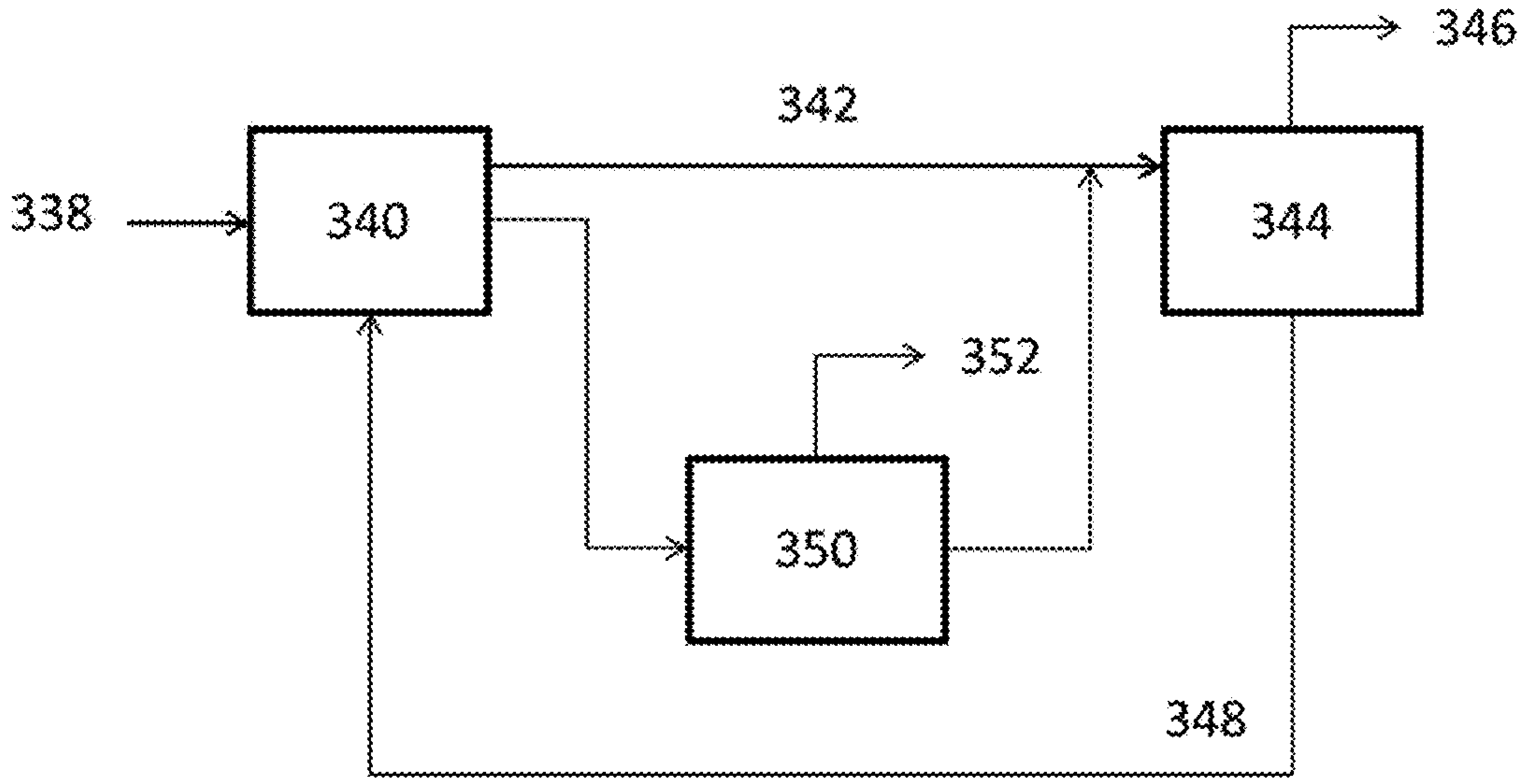

FIG. 3C

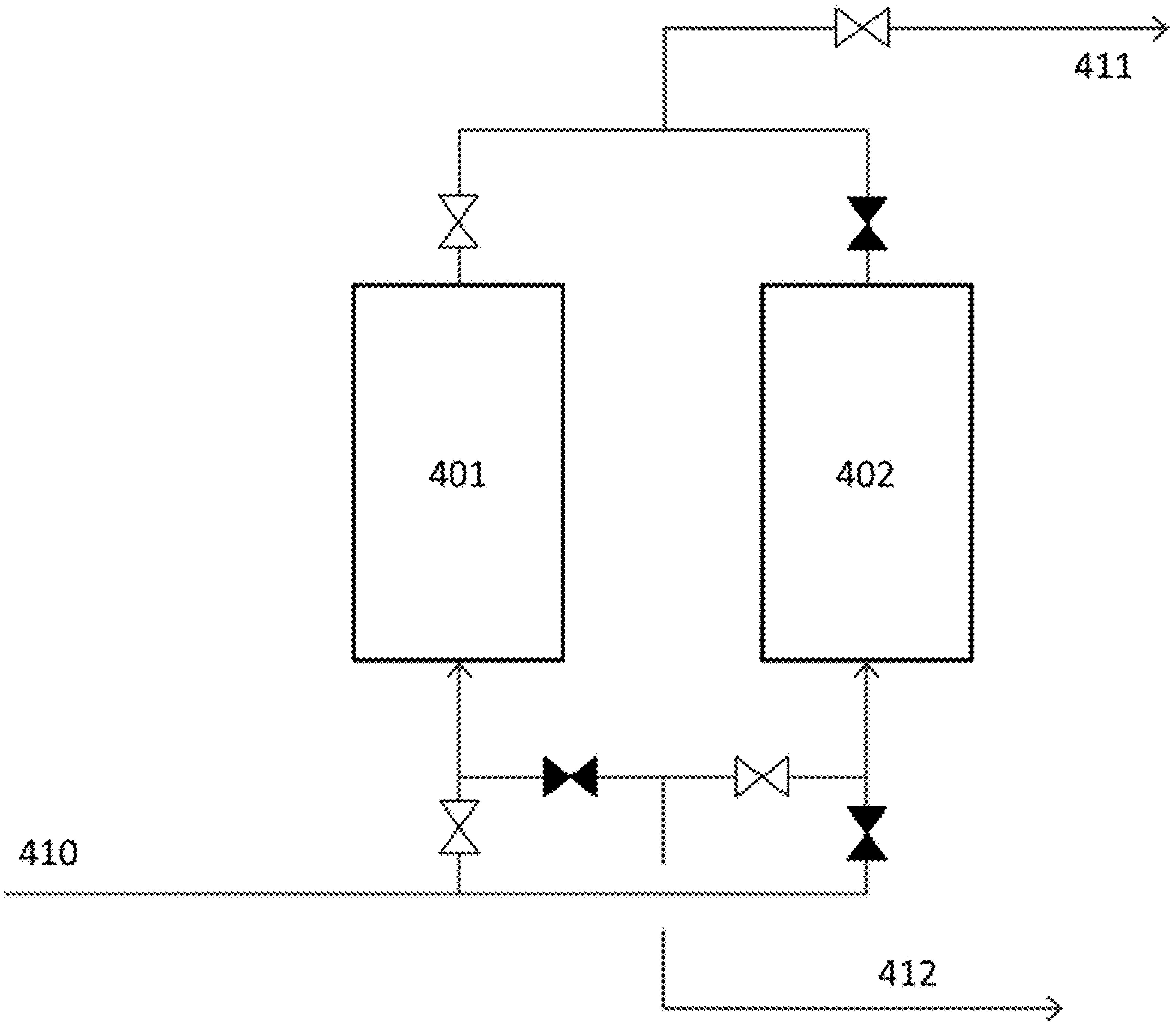

FIG.4

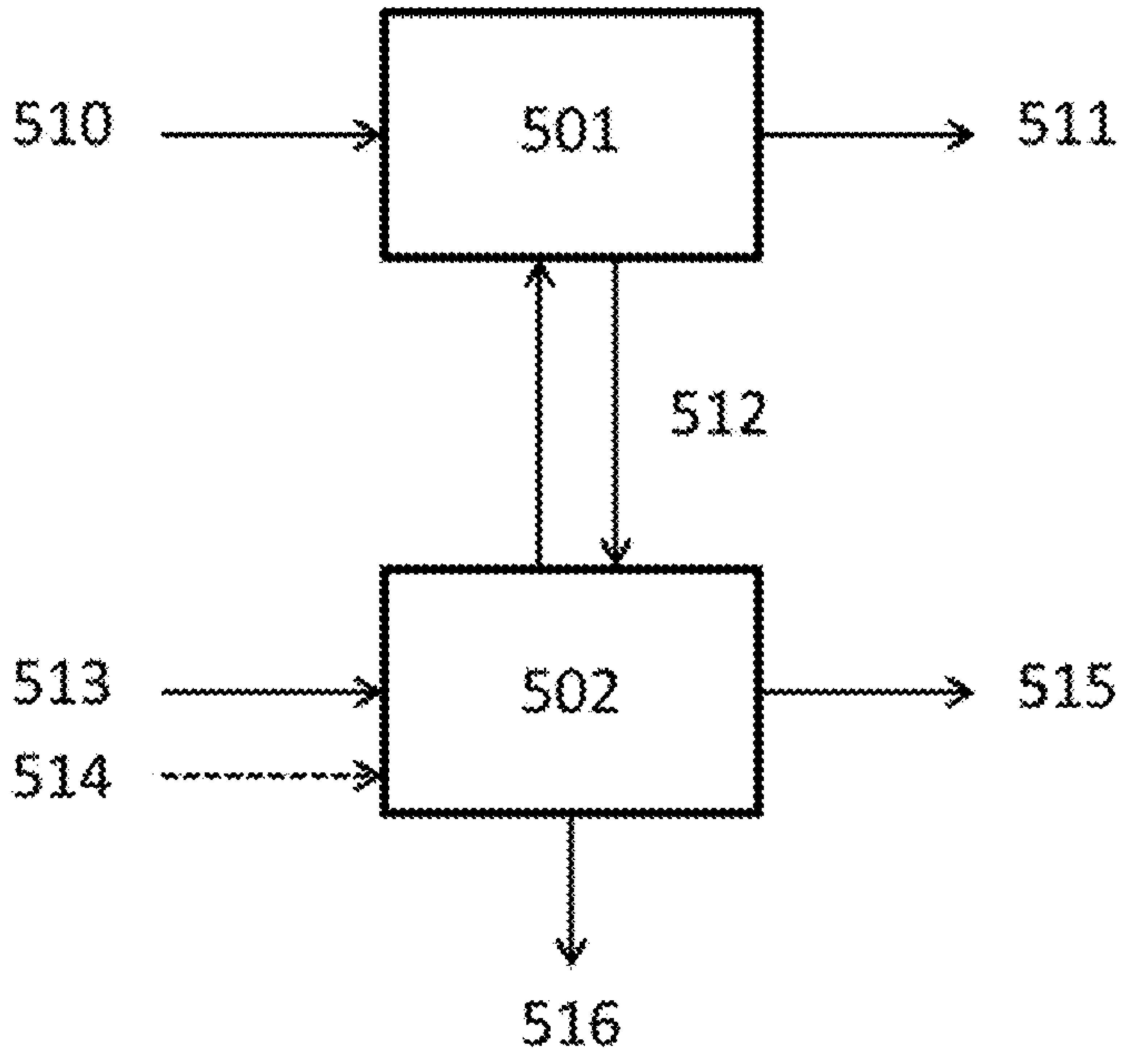

FIG. 5A

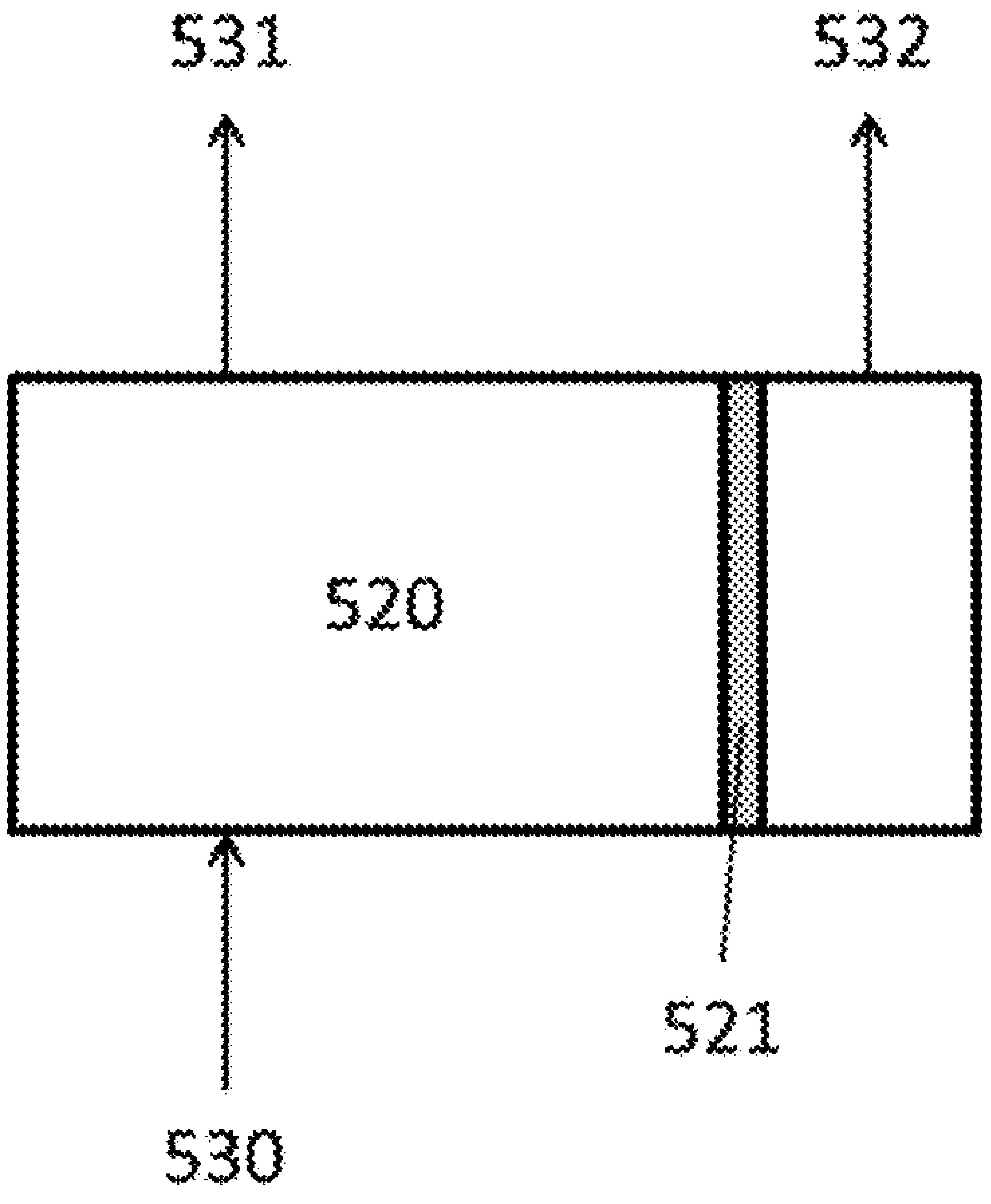

FIG. 5B

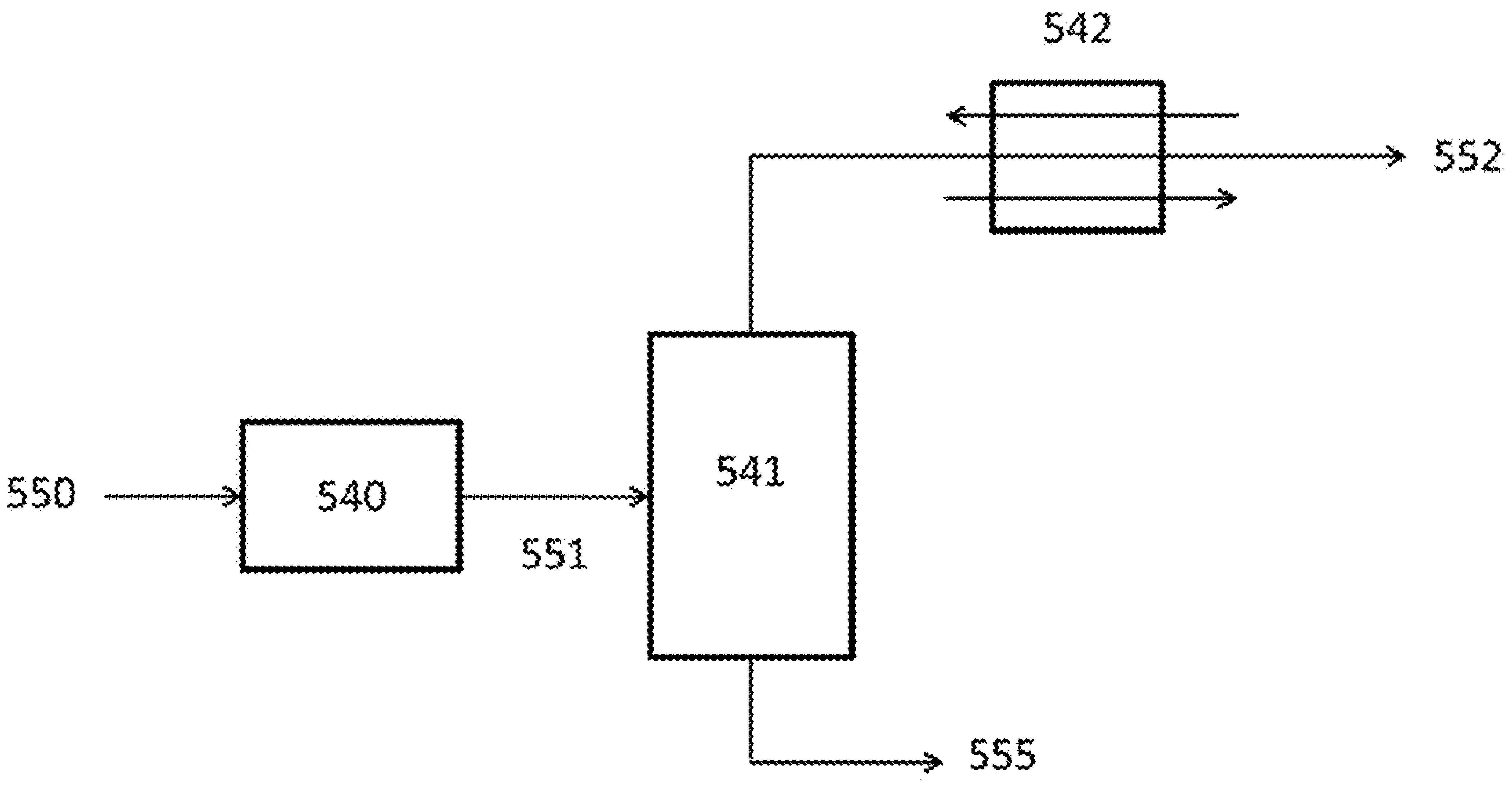

FIG. 5C

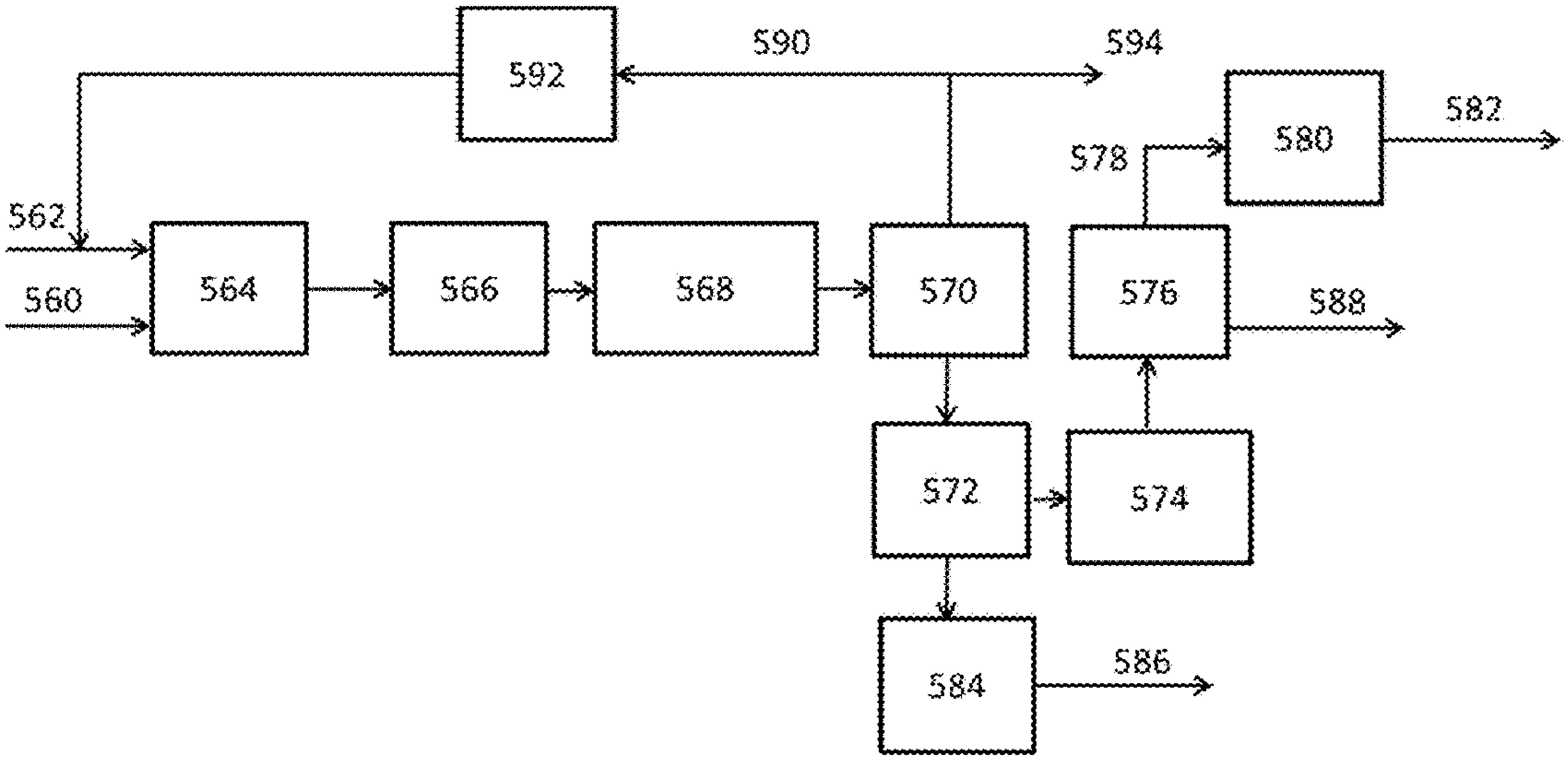
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FIG. 5D

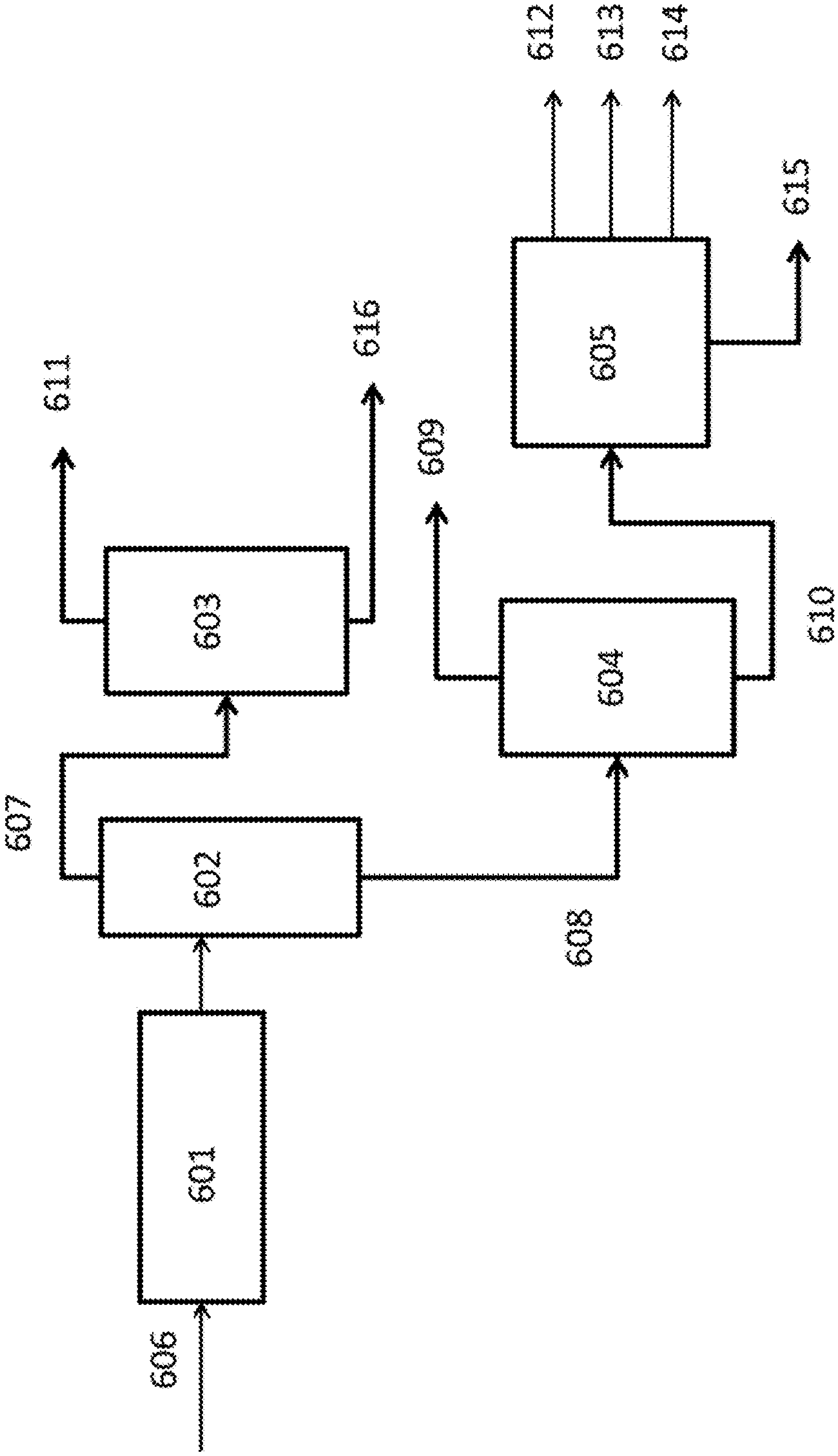

FIG. 6

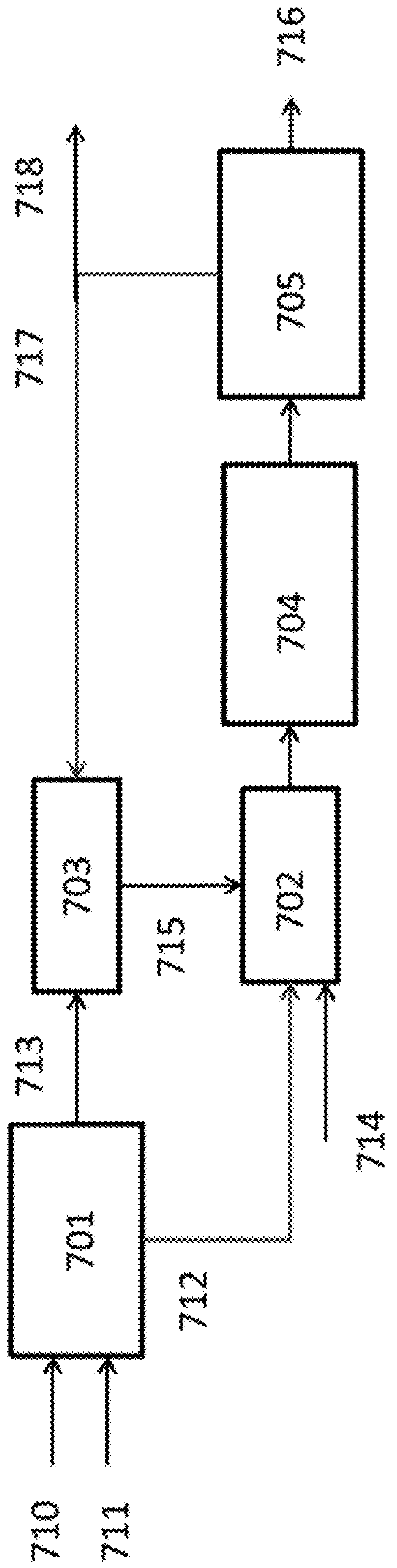

FIG. 7

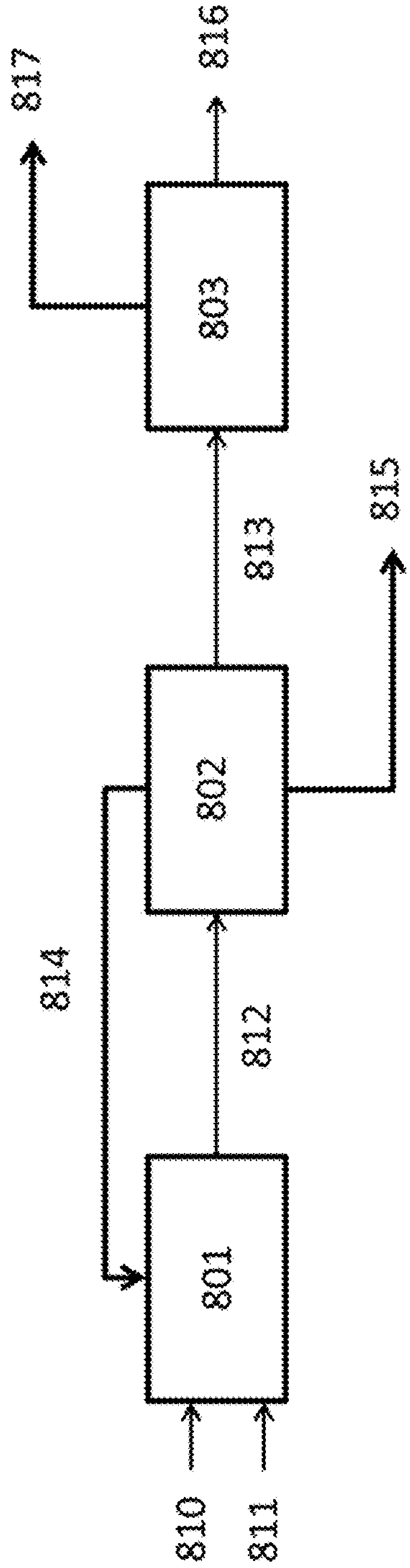

FIG. 8

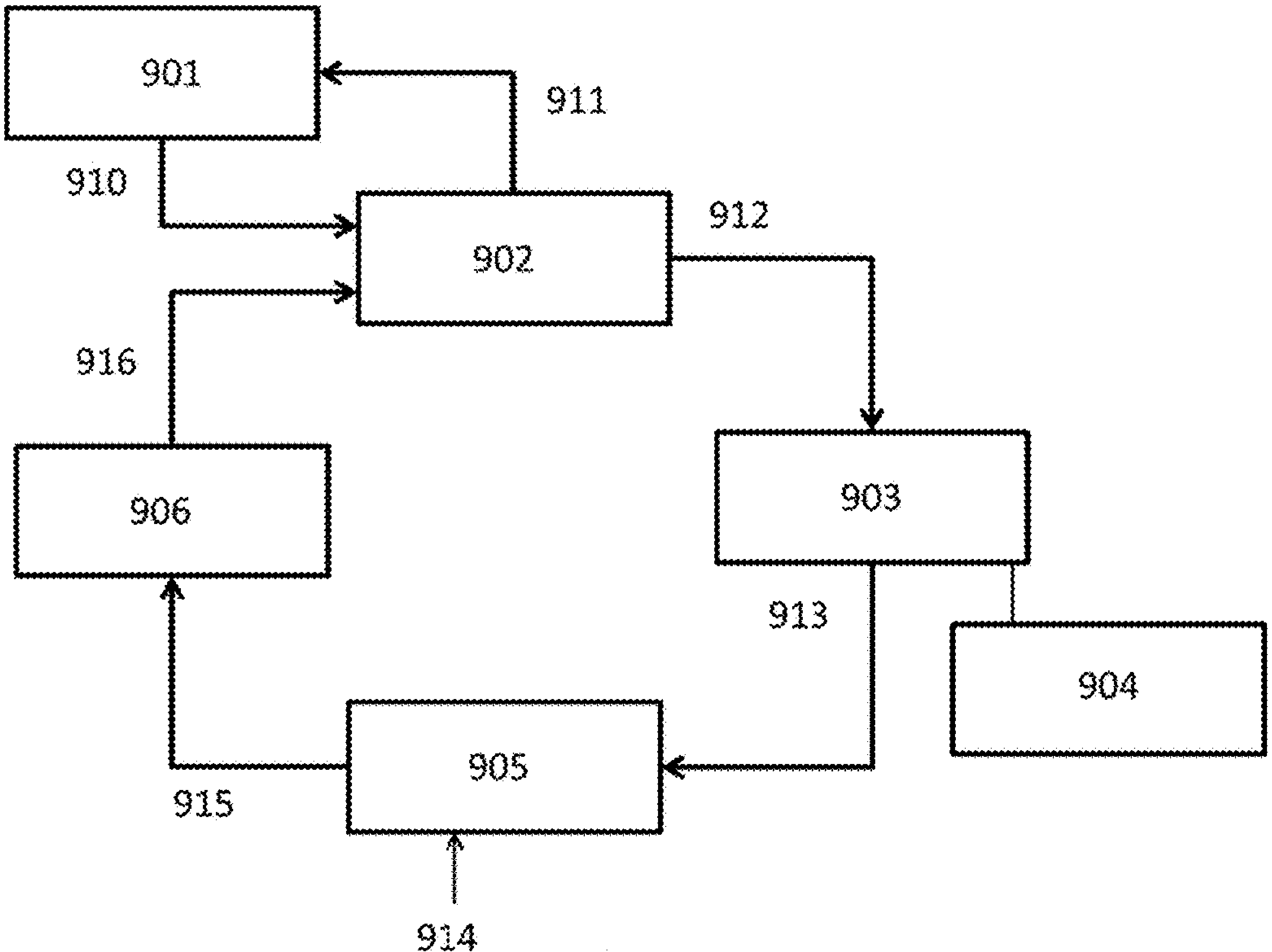

FIG. 9

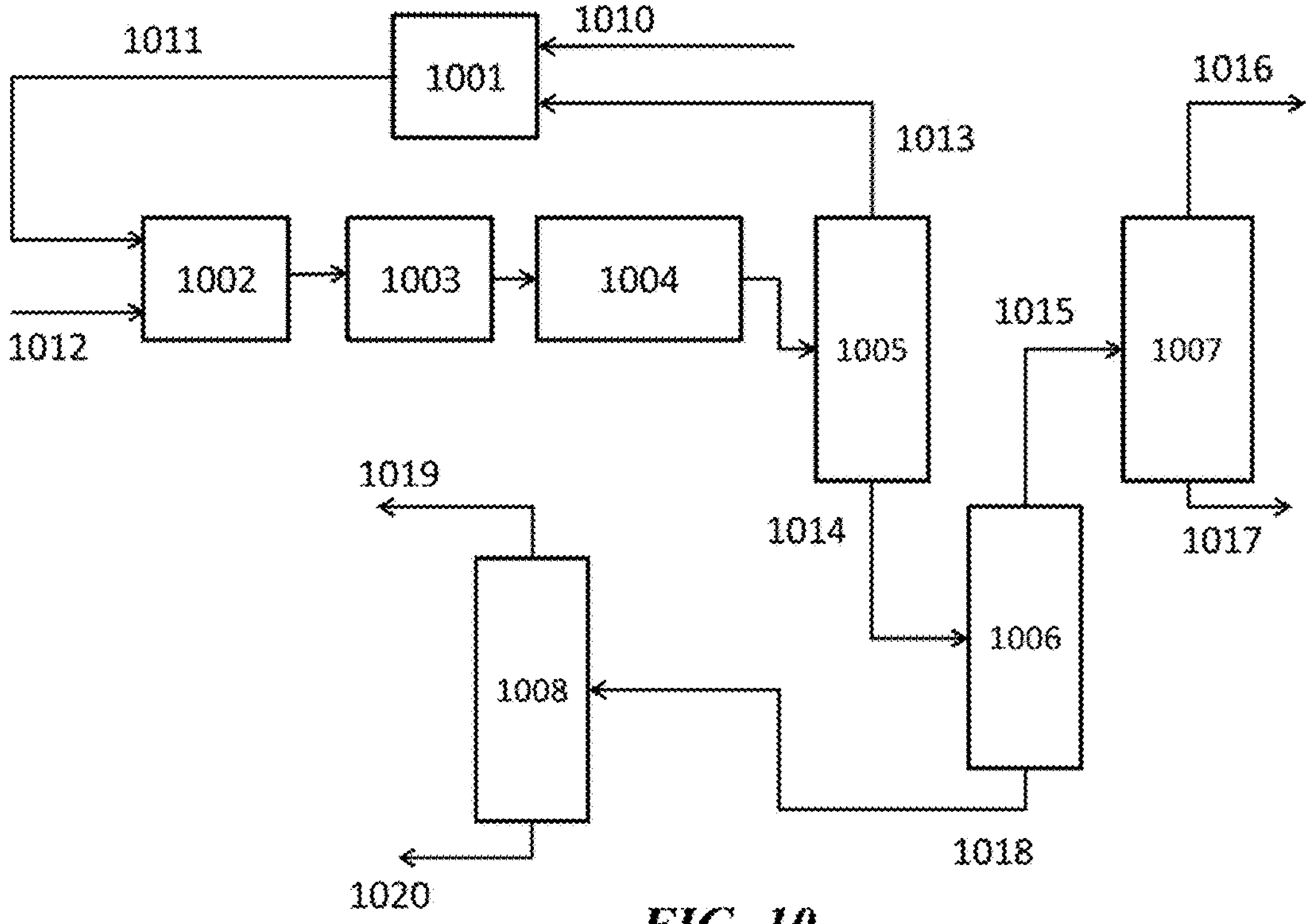
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FIG. 10

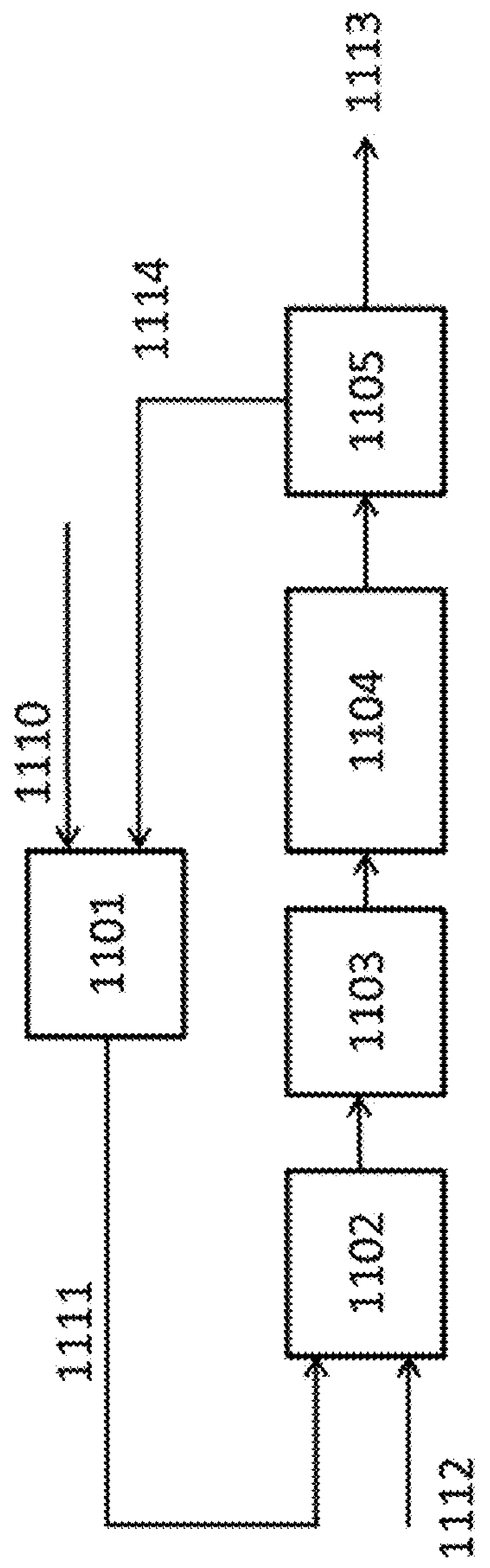

FIG. 11

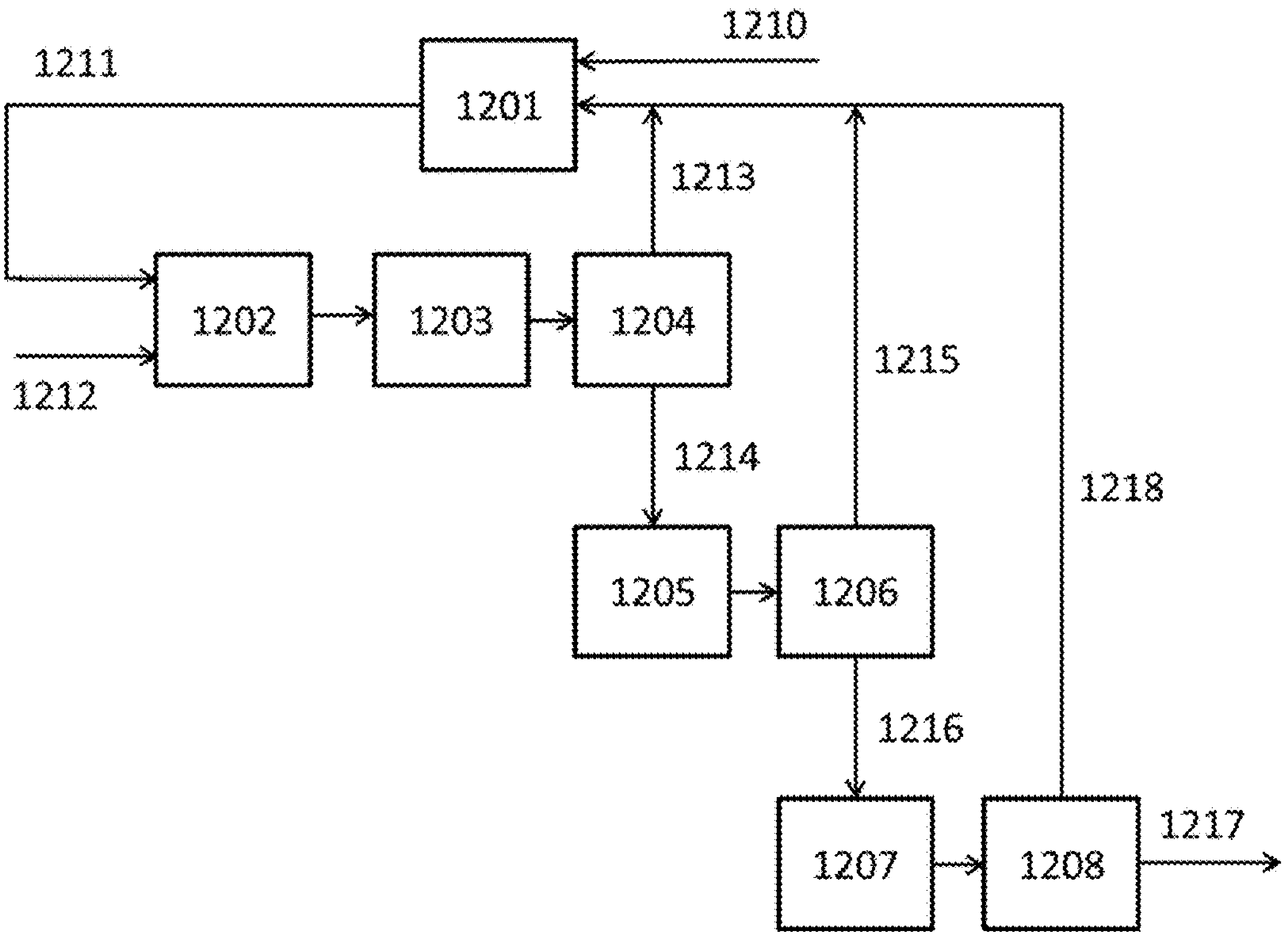
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FIG. 12

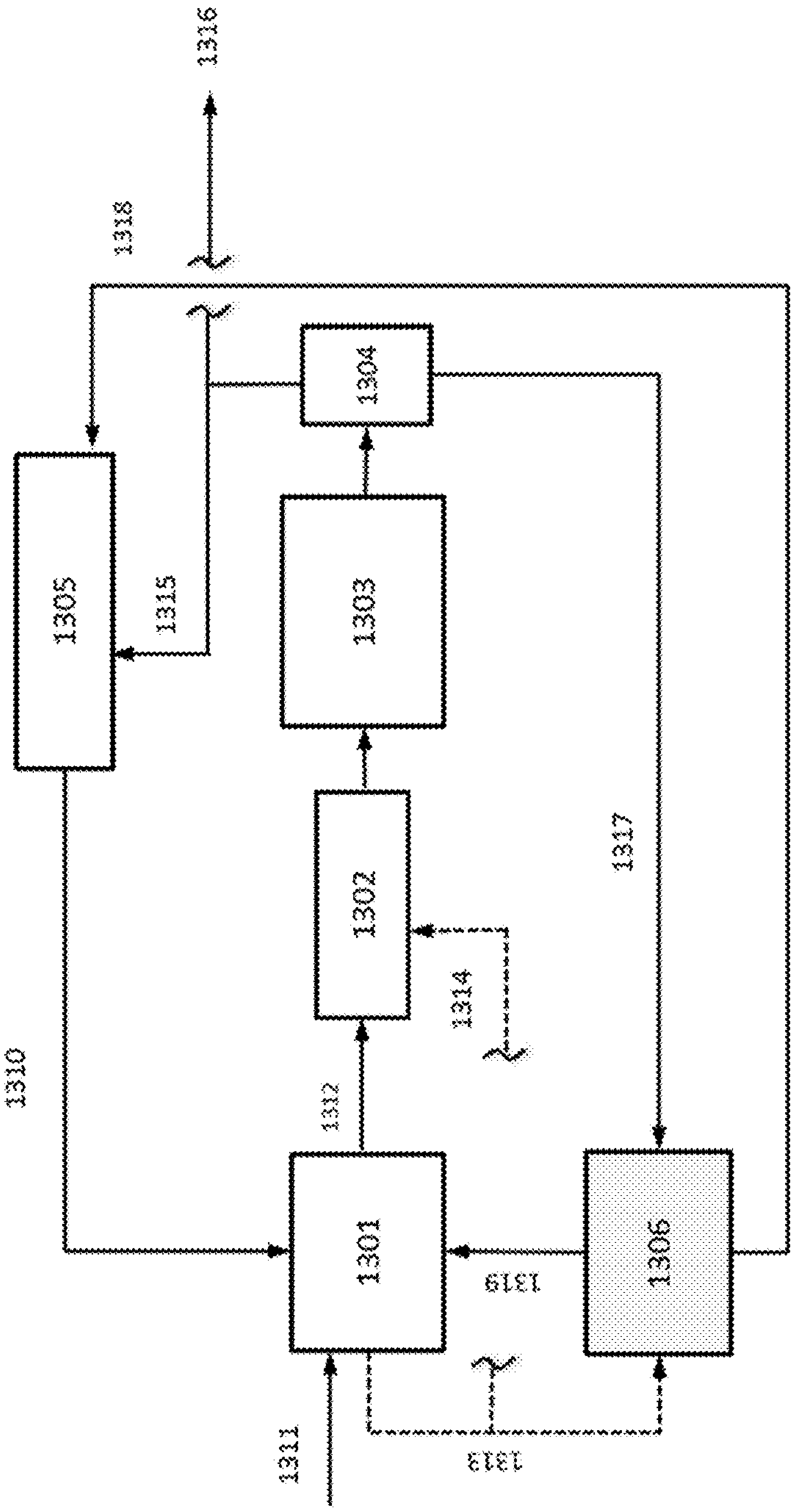
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FIG. 13

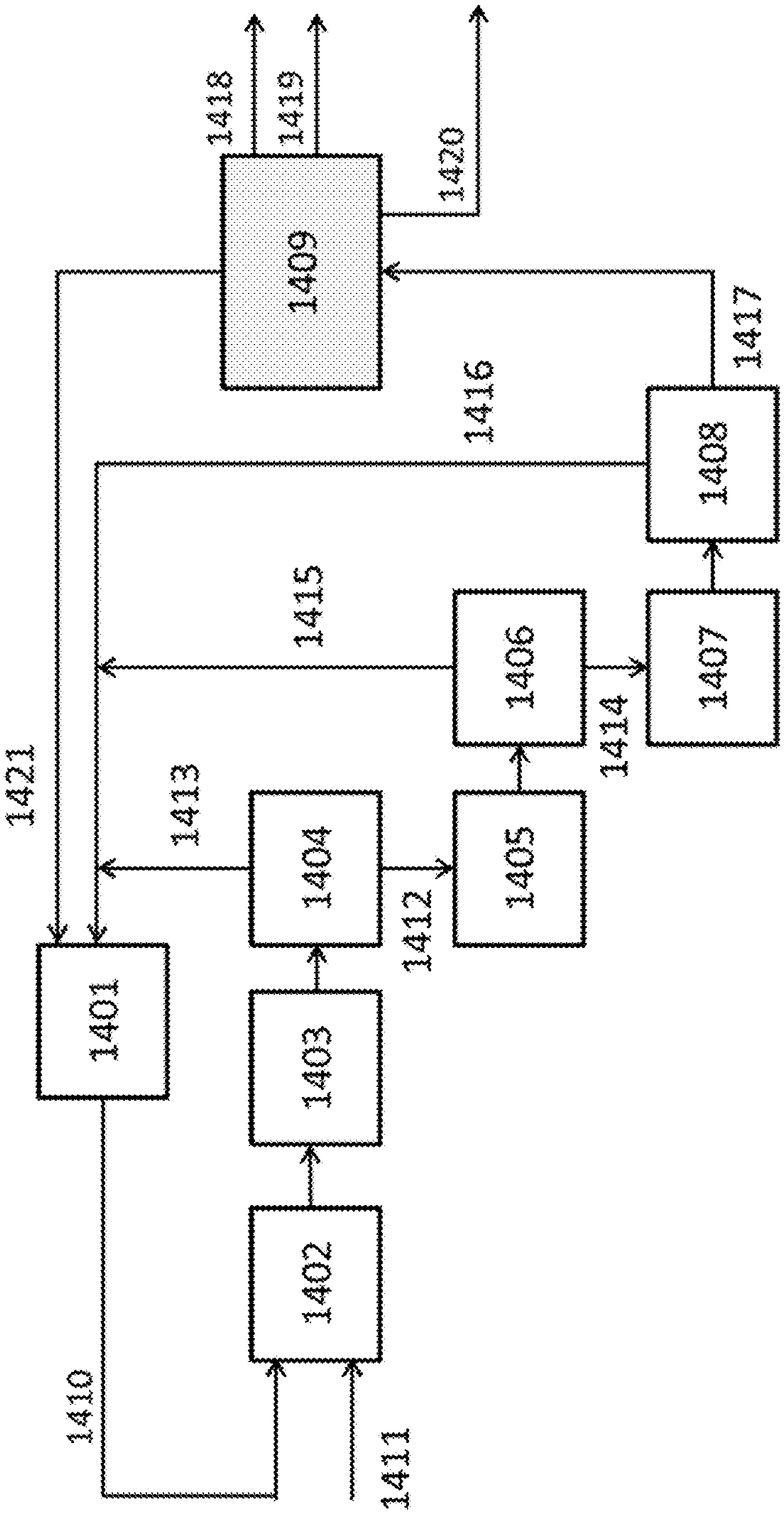
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FIG. 14

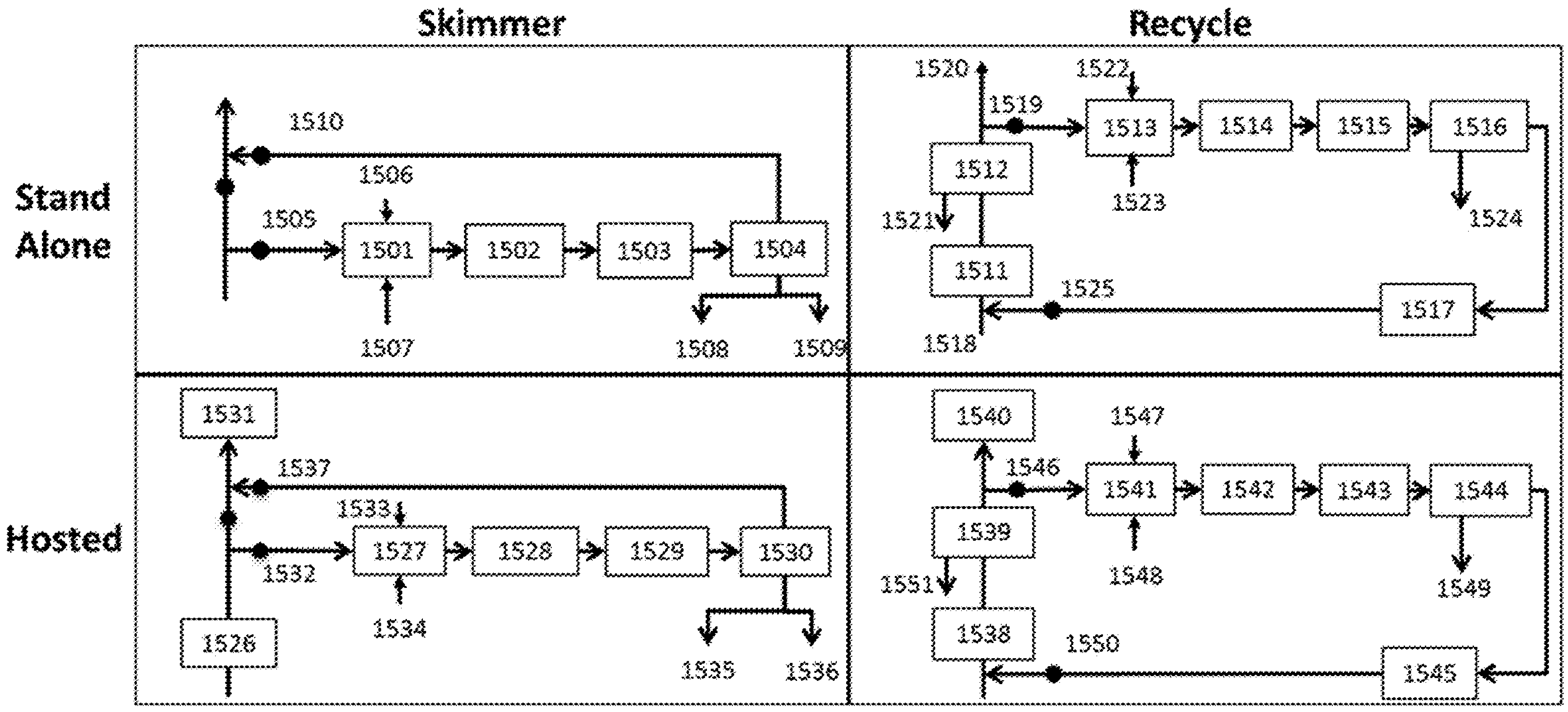
Skimmer
Recycle
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FIG. 15

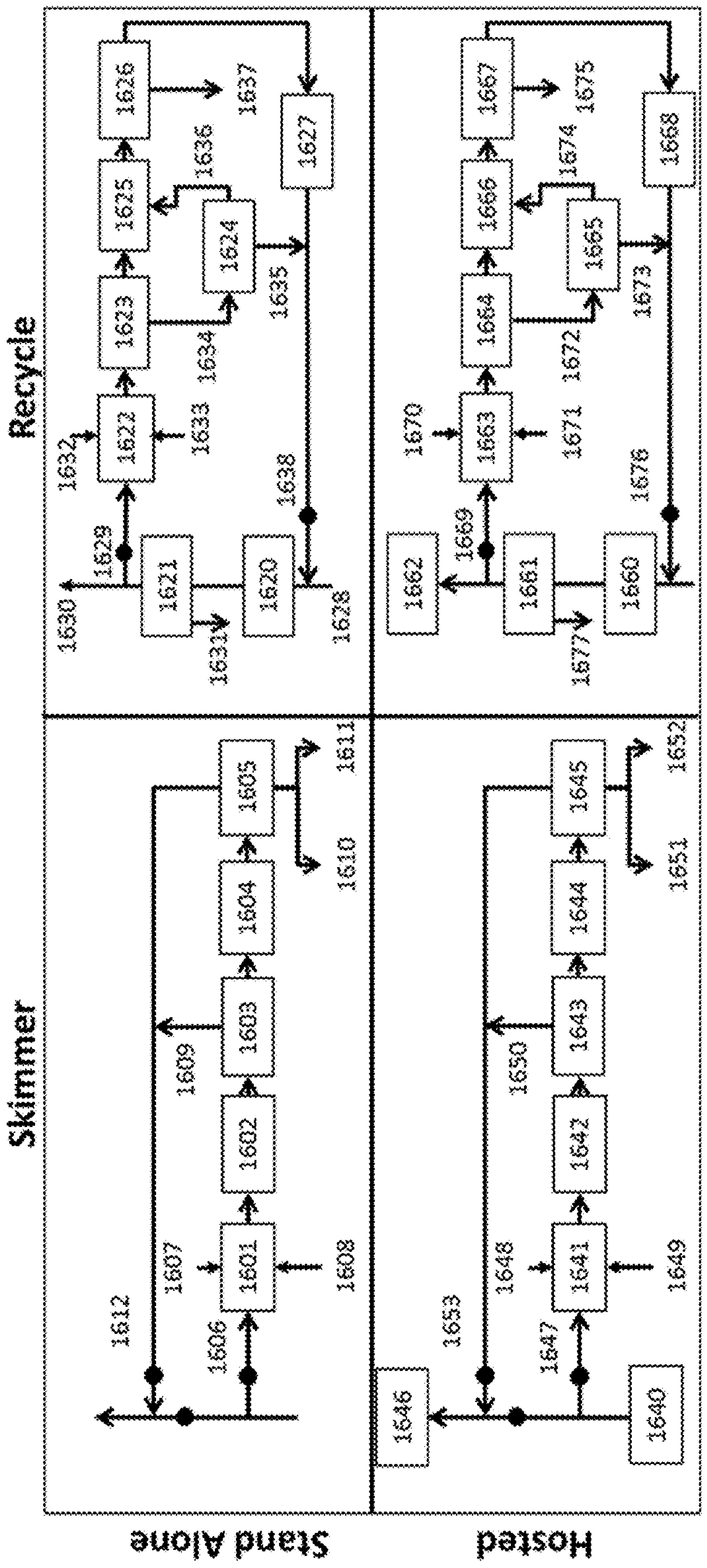
Skimmer
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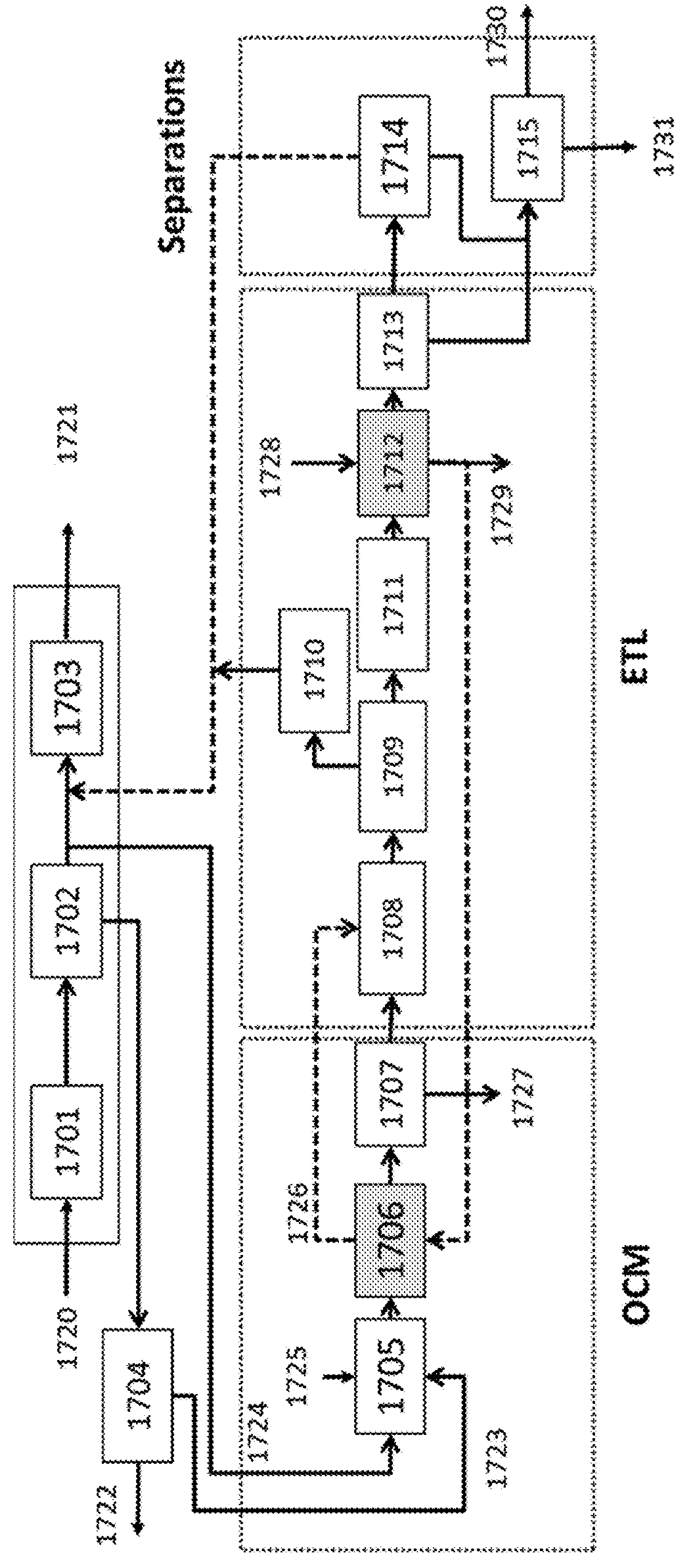
FIG. 16


Separations
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OCM
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FIG. 17

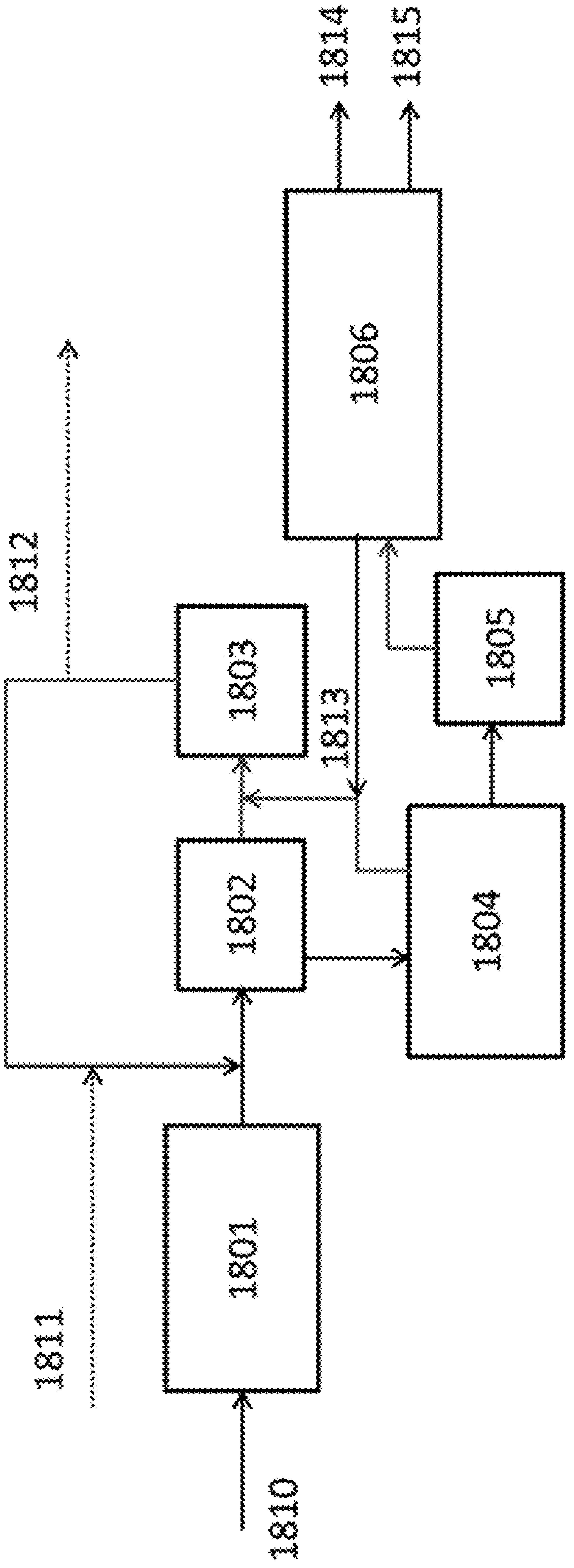

FIG. 18

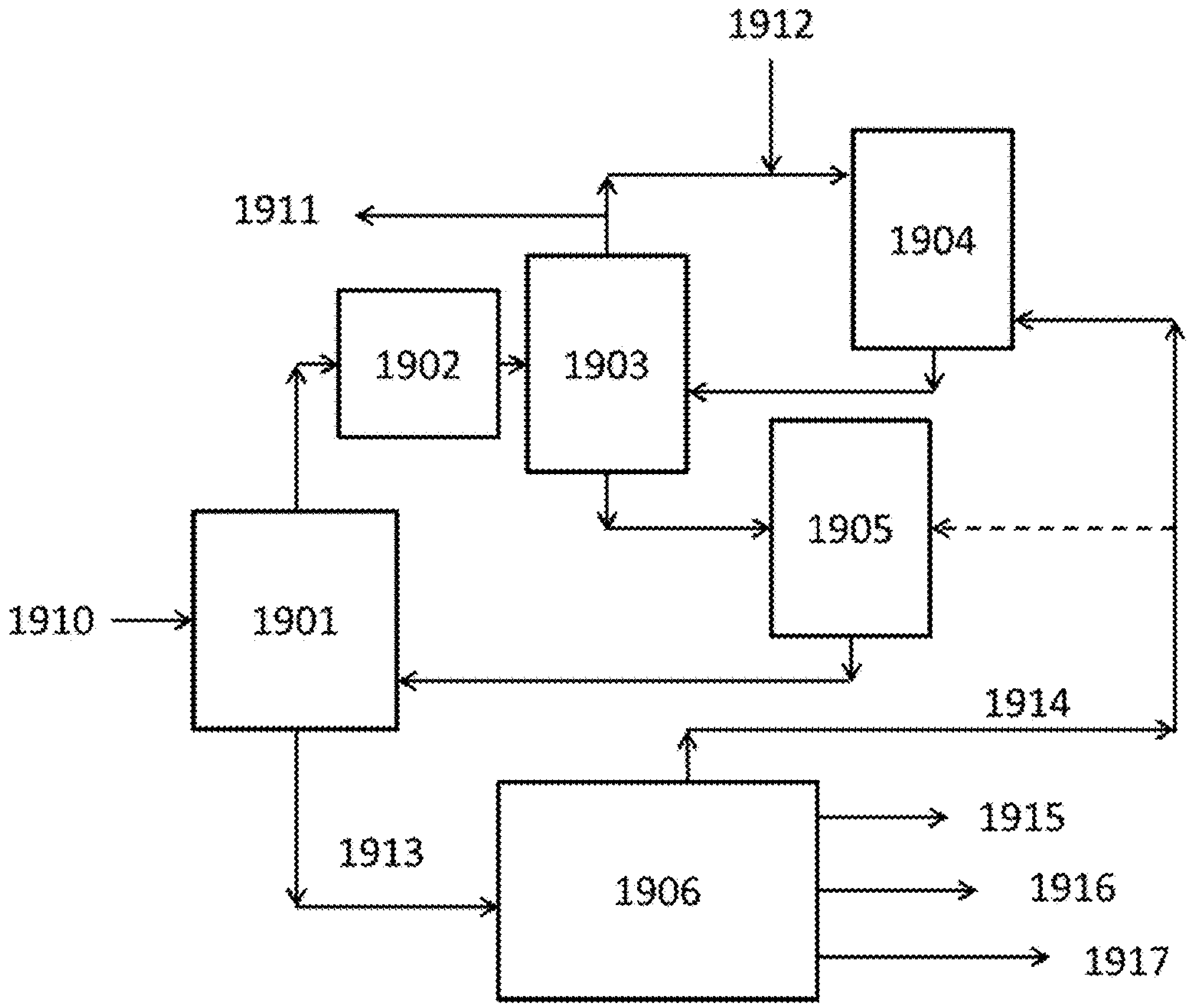
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FIG. 19

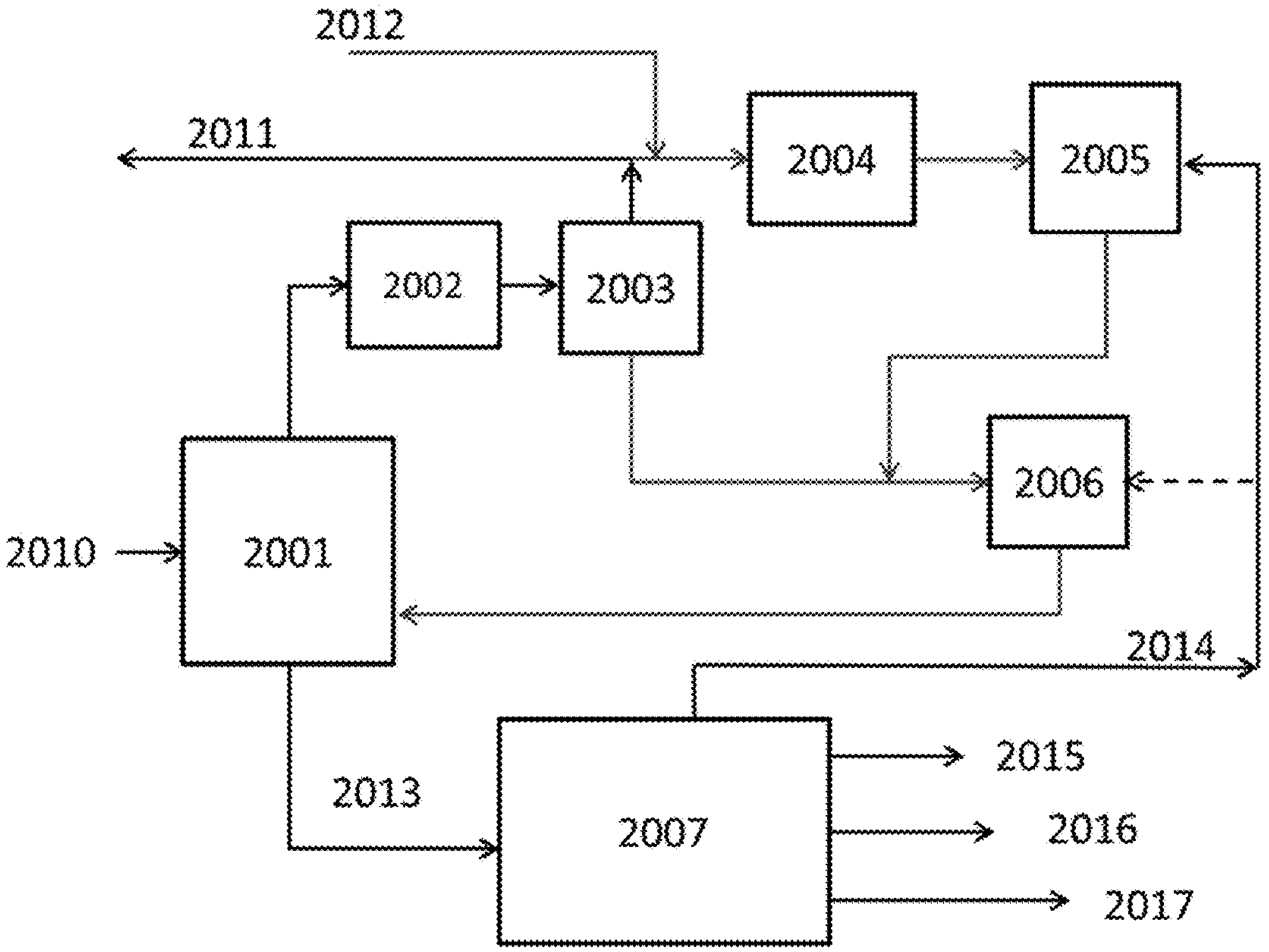
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FIG. 20

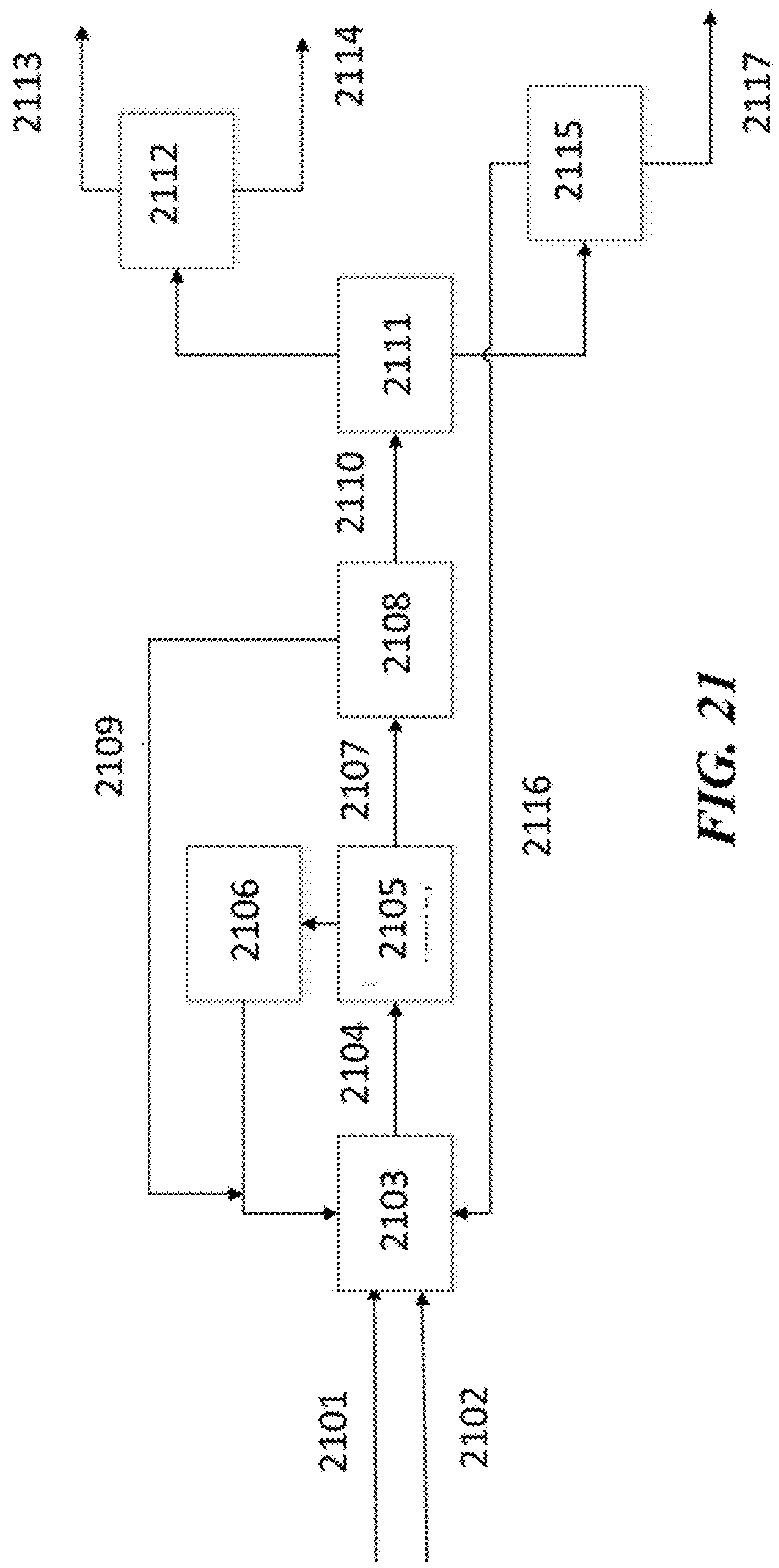
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FIG. 21

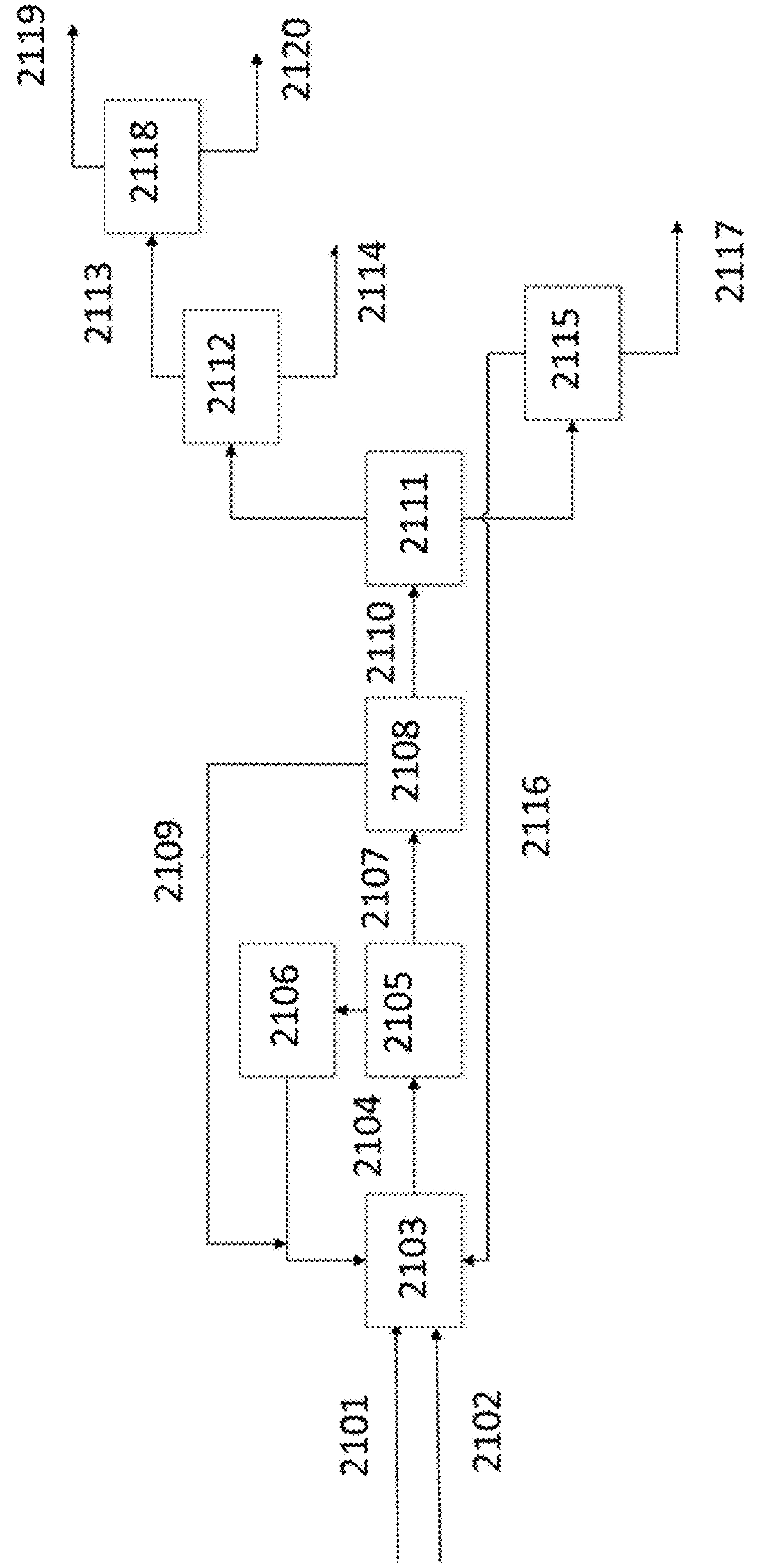
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FIG. 22

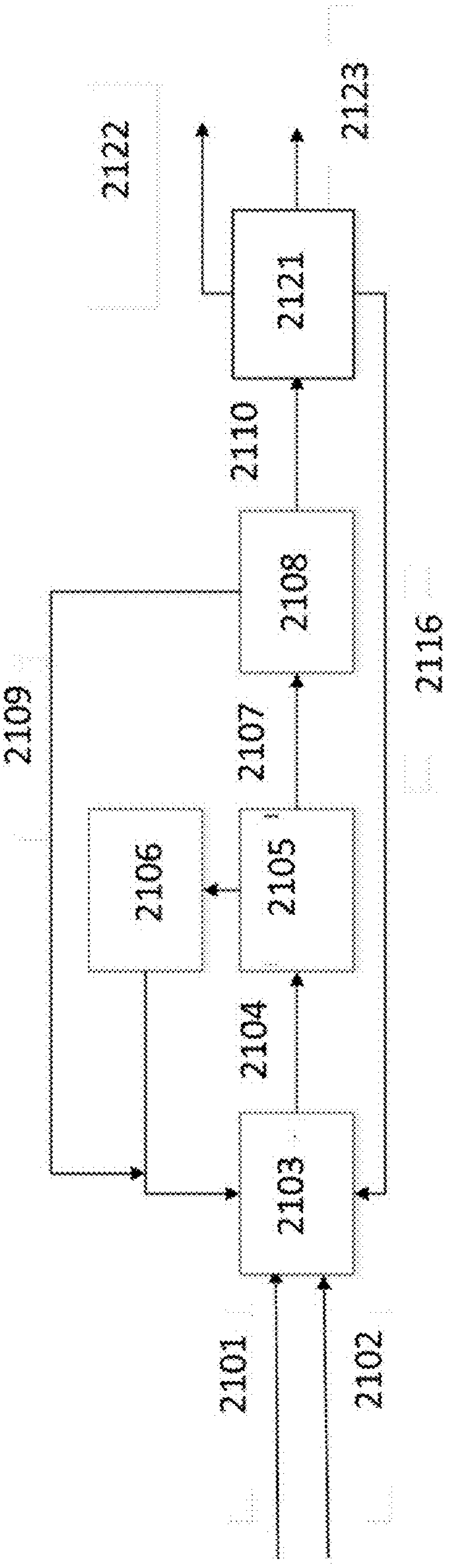
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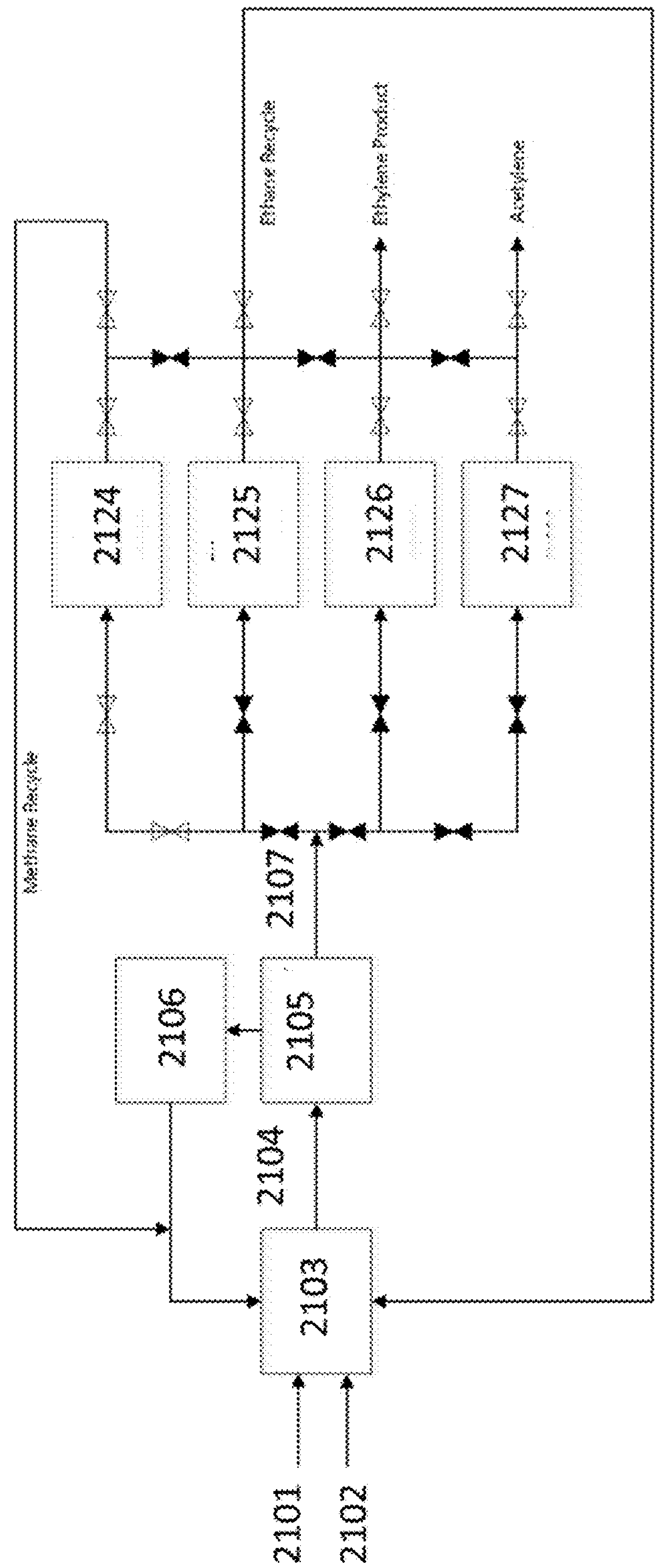
FIG. 23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Methane Recycle
Ethane Recycle
Ethylene Product
Acetylene

FIG. 24

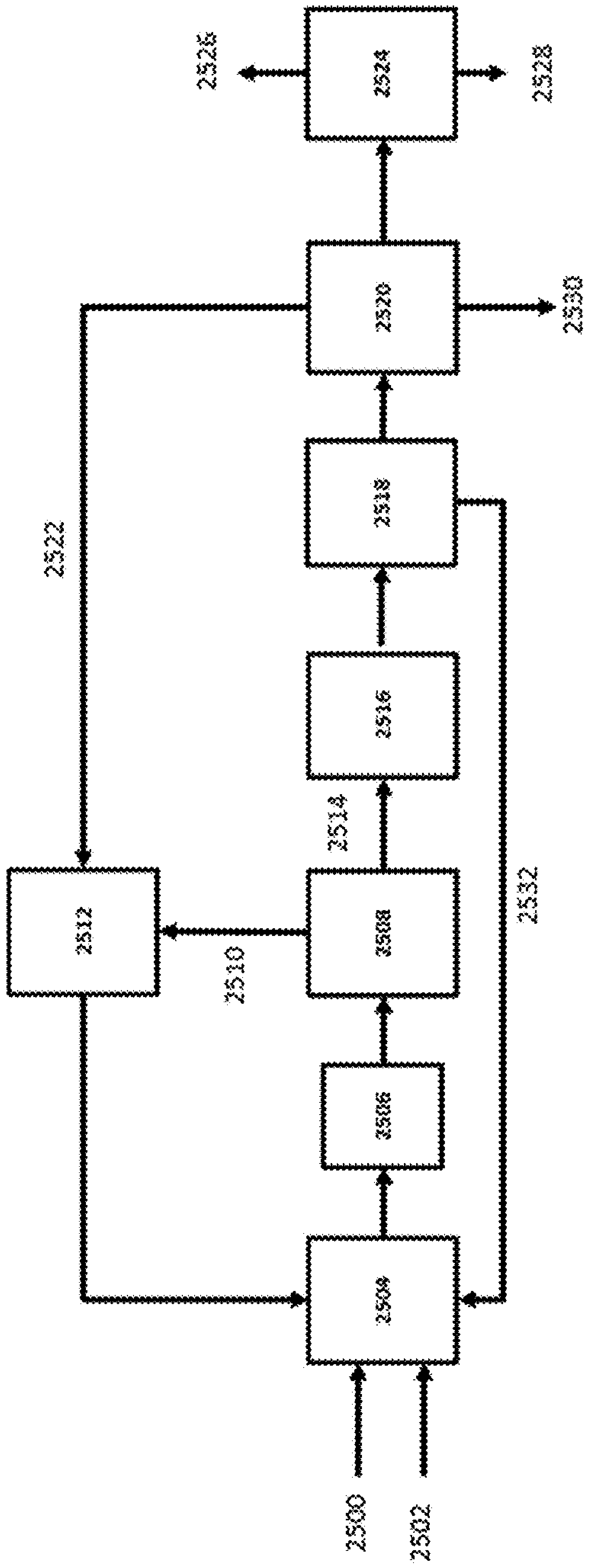
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FIG. 25

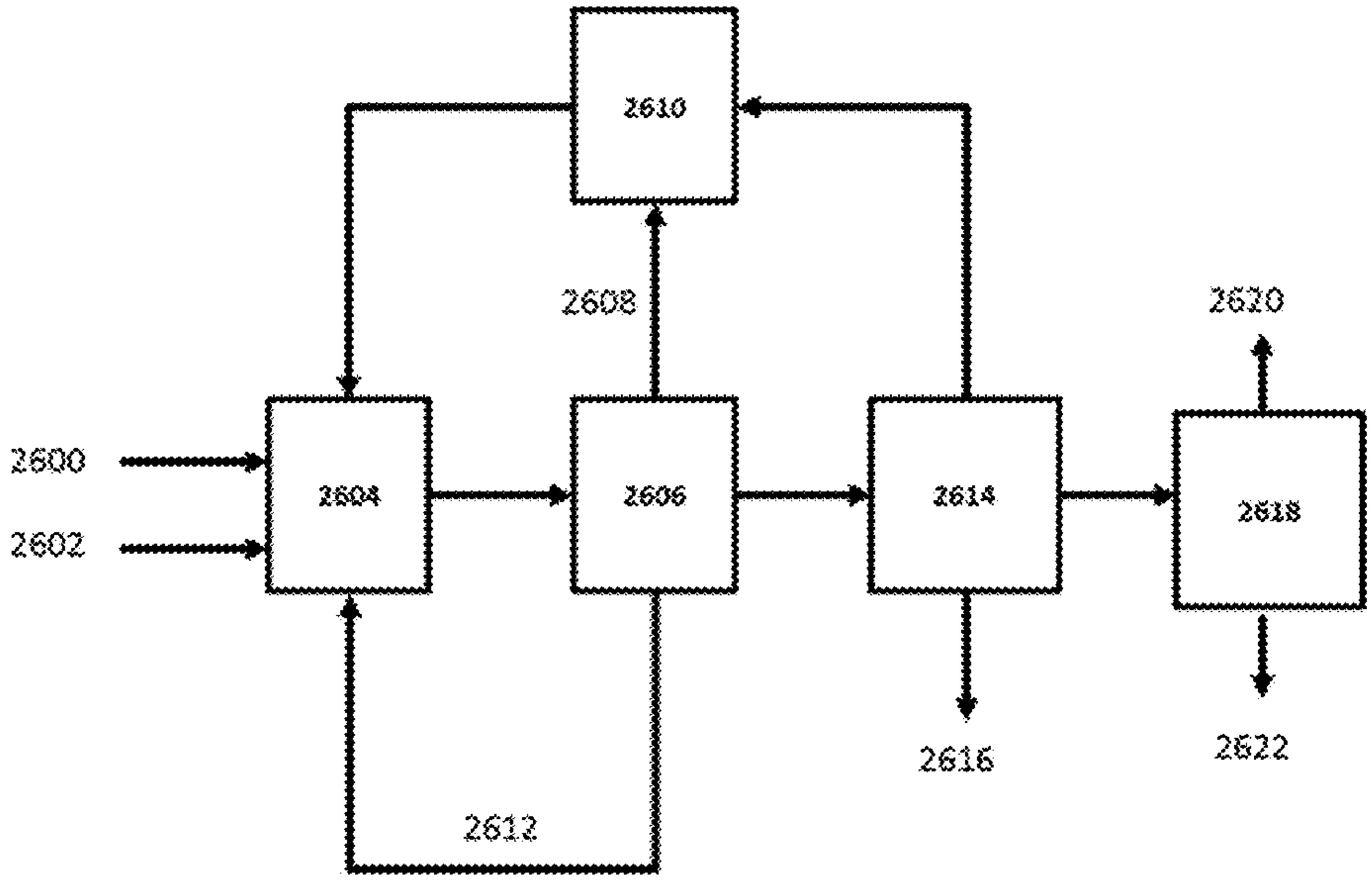

FIG. 26

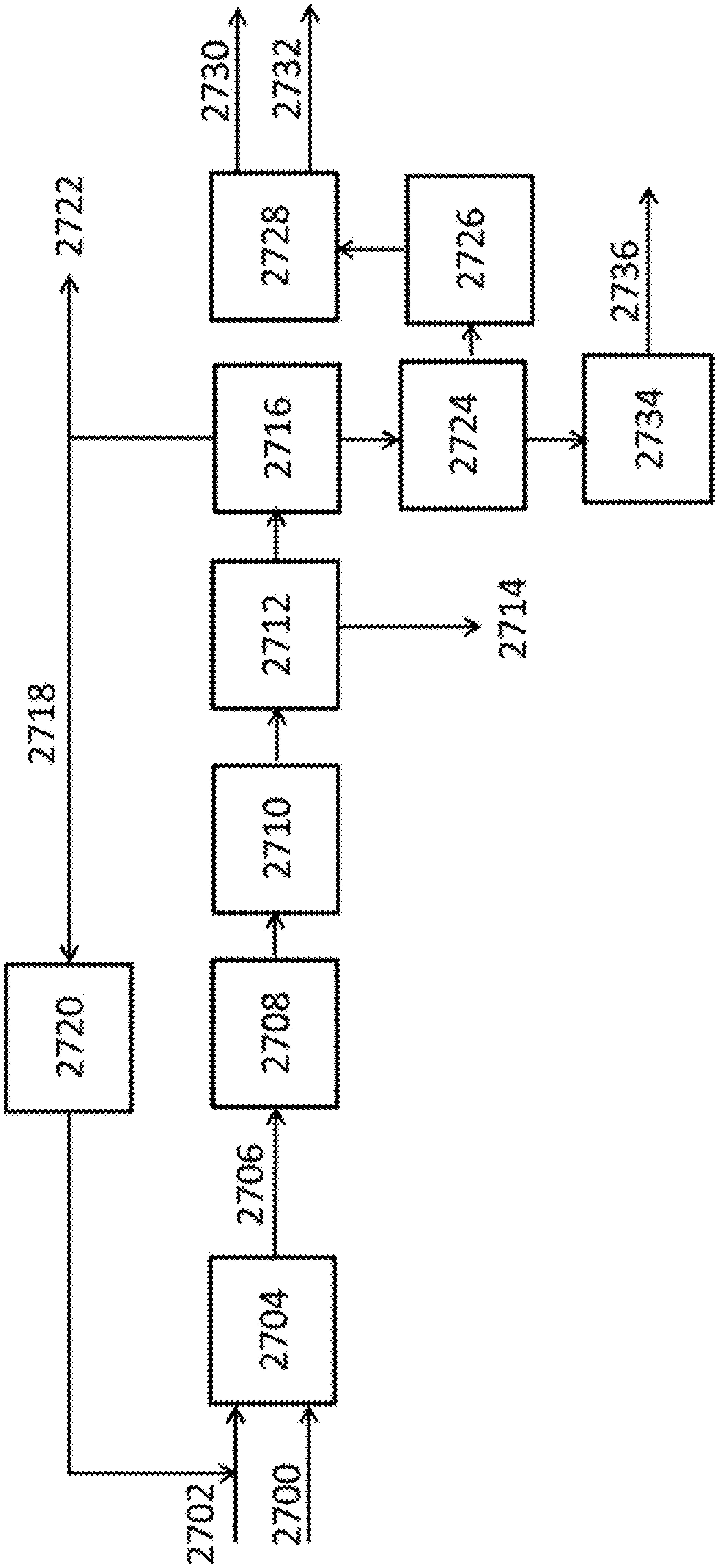
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FIG. 27A

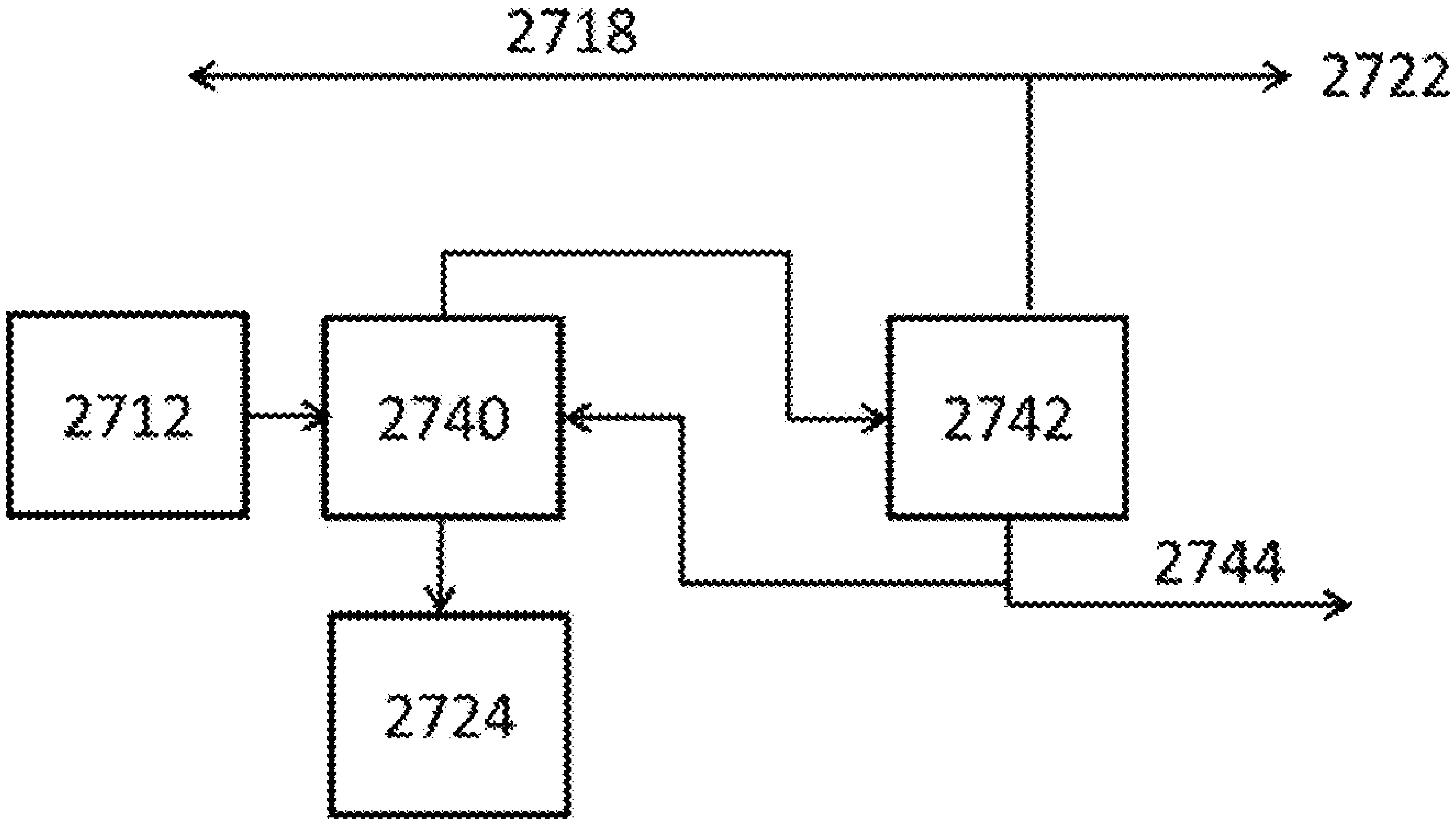

FIG. 27B

SEPARATION METHODS AND SYSTEMS FOR OXIDATIVE COUPLING OF METHANE

CROSS-REFERENCE

[0001] This application claims priority to U.S. Provisional Patent Application Ser. No. 62/242,777, filed Oct. 16, 2015, and U.S. Provisional Patent Application Ser. No. 62/304,877, filed Mar. 7, 2016, each of which is entirely incorporated herein by reference for all purposes.

STATEMENT OF GOVERNMENT SUPPORT

[0002] This invention was made with government support under grant numbers DE-EE0005769 awarded by the United States Department of Energy (DOE). The government has certain rights in the invention.

BACKGROUND

[0003] The modern refining and petrochemical industry may make extensive use of fractionation technology to produce and separate various desirable compounds from crude oil. The conventional fractionation technology may be energy intensive and costly to install and operate. Cryogenic distillation has been used to separate and recover hydrocarbon products in various refining and petrochemical industries.

SUMMARY

[0004] Recognized herein is a need for non-cryogenic separation methods and systems, such as for oxidative coupling of methane (OCM) processes.

[0005] Aspects of the present disclosure provide processes for recovering olefins from a stream containing mix of hydrocarbons by utilizing techniques based the use of adsorbents. In some embodiments, systems and methods enable the separation, pre-separation, purification and/or recovery of hydrocarbons, including, but not limited to, olefins, ethylene, propylene, methane, and ethane, and CO_2, from a multicomponent hydrocarbon stream such as an effluent stream from an oxidative coupling of methane (OCM) reactor or an ethylene-to-liquids (ETL) reactor. The hydrocarbon stream can also be the feed to the OCM or ETL reactor in certain cases. In certain cases, the feed to the ETL reactor is the effluent from OCM reactor. In some cases, a separation process utilizing adsorbents can be used to purify and pre-treat existing hydrocarbon streams (such as refinery off-gases, cracker off-gas, streams from NGL plants, and others), followed by use of the resulting olefin rich stream (e.g., pressure swing adsorption tail gas) as the ETL feed.

[0006] The present disclosure provides various improvements in OCM and ETL processes, such as, without limitation, a separation and pre-separation process to recover desired or predetermined components from an OCM reactor effluent, CO_2 recovery and capture techniques, enhanced heat recovery methods to utilize the OCM reaction heat more efficiently, and techniques and technologies to further reduce the carbon footprint of the OCM process.

[0007] An aspect of the present disclosure provides a method for generating compounds with two or more carbon atoms (C_{2+} compounds), comprising: (a) directing oxygen (O_2) and methane (CH_4) into an oxidative coupling of methane (OCM) reactor that reacts the O_2 and CH_4 in an OCM process to yield a product stream comprising (i) C_{2+} compounds including ethylene (C_2H_4) and (ii) carbon dioxide (CO_2); and (b) directing the product stream from the OCM reactor into a separations unit that employs a CO_2 separation unit to separate the CO_2 from the product stream and enrich the C_{2+} compounds in the product stream, which CO_2 separation unit employs (i) sorbent or solvent separation of CO_2, (ii) membrane separation of CO_2, (iii) cryogenic or low temperature separation of CO_2 having an operating temperature greater than a boiling point of methane and less than a boiling point of CO_2, (iv) metal-organic framework-based separation, or (v) antisublimation separation of CO_2.

[0008] In some embodiments of aspects provided herein, the product stream is directed into the separations unit through one or more additional units. In some embodiments of aspects provided herein, the sorbent or solvent separation of CO_2 employs an amine based absorption unit. In some embodiments of aspects provided herein, the sorbent or solvent separation of CO_2 employs a Benfield process. In some embodiments of aspects provided herein, the sorbent or solvent separation of CO_2 employs diethanolamine. In some embodiments of aspects provided herein, the sorbent or solvent separation of CO_2 employs glycol dimethylether. In some embodiments of aspects provided herein, the sorbent or solvent separation of CO_2 employs propylene carbonate. In some embodiments of aspects provided herein, the sorbent or solvent separation of CO_2 employs Sulfinol. In some embodiments of aspects provided herein, the sorbent or solvent separation of CO_2 employs a zeolite. In some embodiments of aspects provided herein, the sorbent or solvent separation of CO_2 employs active carbon. In some embodiments of aspects provided herein, the CO_2 separation unit comprises a membrane CO_2 separation unit. In some embodiments of aspects provided herein, the membrane separation of CO_2 employs a polymeric membrane. In some embodiments of aspects provided herein, the membrane separation of CO_2 employs a metallic membrane. In some embodiments of aspects provided herein, the membrane separation of CO_2 employs a ceramic membrane. In some embodiments of aspects provided herein, the membrane separation of CO_2 employs a hybrid membrane comprising a membrane supporting a solvent or sorbent. In some embodiments of aspects provided herein, the membrane separation of CO_2 employs a poly ionic liquid membrane. In some embodiments of aspects provided herein, the membrane separation of CO_2 employs a supported ionic liquid membrane. In some embodiments of aspects provided herein, the membrane separation of CO_2 employs a polyetherimide membrane. In some embodiments of aspects provided herein, the membrane separation of CO_2 employs an amorphous fluoropolymer based membrane. In some embodiments of aspects provided herein, the method further comprises directing the CO_2 from the product stream to a methanation reactor that reacts the CO_2 to yield a methanation product stream comprising methane. In some embodiments of aspects provided herein, the method further comprises directing the methane in the methanation product stream to the OCM reactor. In some embodiments of aspects provided herein, the method further comprises separating the product stream into (i) an ethylene product stream comprising ethylene and (ii) a C_{3+} product stream comprising compounds with three or more carbon atoms (C_{3+} compounds). In some embodiments of aspects provided herein, the method further comprises directing ethane from the product stream to the OCM reactor. In some embodiments of aspects provided herein, the method further comprises, prior to directing the product stream into the separations unit, compressing the product stream. In some embodiments of aspects provided herein, the CO_2 separation unit employs the sorbent or solvent separation of CO_2. In some embodiments of aspects provided herein, the CO_2 separation unit employs the membrane separation of CO_2. In some embodiments of aspects provided herein, the CO_2 separation unit employs the cryogenic or low temperature separation of CO_2 having an operating temperature greater than a boiling point of methane and less than a boiling point of CO_2. In some embodiments of aspects provided herein, the CO_2 separation unit employs the metal-organic framework-based separation. In some embodiments of aspects provided herein, the CO_2 separation unit employs the anti-sublimation separation of CO_2.

[0009] Another aspect of the present disclosure provides a method for generating compounds with two or more carbon atoms (C_{2+} compounds), comprising: (a) directing oxygen (O_2) and methane (CH_4) into an oxidative coupling of methane (OCM) reactor that reacts the O_2 and CH_4 in an OCM process to yield a product stream comprising (i) C_{2+} compounds including ethylene (C_2H_4) and (ii) carbon dioxide (CO_2); (b) directing the product stream from the OCM reactor into a first CO_2 separation unit that separates at least some of the CO_2 from the product stream to produce an enriched stream comprising (i) the C_{2+} compounds and (ii) at least some of the CO_2; (c) directing the enriched stream to a cryogenic separations unit that separates the C_2H_4 from the C_{2+} compounds to produce an ethylene stream comprising (i) the C_2H_4 and (ii) the CO_2; and (d) directing the ethylene stream to a second CO_2 separation unit that separates the CO_2 from the ethylene stream to produce an ethylene product stream.

[0010] In some embodiments of aspects provided herein, the enriched stream contains at most about 2.0 mol % CO_2. In some embodiments of aspects provided herein, the enriched stream contains at most about 1.0 mol % CO_2. In some embodiments of aspects provided herein, the enriched stream contains at most about 0.5 mol % CO_2. In some embodiments of aspects provided herein, the first CO_2 separation unit comprises a membrane, a pressure swing absorption (PSA) unit, an amine unit, or any combination thereof. In some embodiments of aspects provided herein, the second CO_2 separation unit comprises a membrane, a pressure swing absorption (PSA) unit, an amine unit, or any combination thereof. In some embodiments of aspects provided herein, the cryogenic separations unit comprises a de-methanizer.

[0011] Another aspect of the present disclosure provides a method for generating compounds with two or more Carbon atoms (C2+ compounds), comprising: (a) directing oxygen (O_2) and methane (CH_4) into an oxidative coupling of methane (OCM) reactor that reacts the O_2 and CH_4 in an OCM process to yield a product stream comprising (i) C_{2+} compounds including ethylene (C_2H_4) and (ii) carbon monoxide (CO) and/or carbon dioxide (CO_2); and (b) directing the product stream from the OCM reactor into a separations unit that selectively separates olefins from the paraffins.

[0012] In some embodiments of aspects provided herein, the separations unit selectively separates ethylene from paraffins. In some embodiments of aspects provided herein, the separations unit comprises an absorber stripper unit employing pi-complexation. In some embodiments of aspects provided herein, the separations unit comprises a membrane unit including a membrane contactor employing pi-complexation. In some embodiments of aspects provided herein, the separations unit comprises a pressure swing adsorption (PSA) unit comprising a sorbent having dispersed metal ions that are capable of complexing with the olefins. In some embodiments of aspects provided herein, the PSA unit comprises a sorbent selected from a zeolite, a molecular sieve sorbent, a carbon molecular sieve, an activated carbon, a carbon nanotube, and a polymeric resin. In some embodiments of aspects provided herein, the method further comprises using an oxidizing agent to regenerate stabilize the pi-complex. In some embodiments of aspects provided herein, the oxidizing agent comprises HNO_3 or $KMnO_4$. In some embodiments of aspects provided herein, the separations unit comprises (i) a pressure swing adsorption (PSA) unit, (ii) a temperature swing adsorption (TSA) unit, or (iii) a membrane unit employing a metal-organic framework (MOF), and the olefins separated in (b) comprise ethylene.

[0013] Another aspect of the present disclosure provides a method for generating compounds with two or more carbon atoms (C_{2+} compounds), comprising: (a) directing oxygen (O_2) and methane (CH_4) into an oxidative coupling of methane (OCM) reactor that reacts the O_2 and CH_4 in an OCM process to yield a product stream comprising (i) C_{2+} compounds including ethylene (C_2H_4) and (ii) C_1 compounds including un-reacted CH_4; and (b) directing the product stream into a separations unit that separates the C_{2+} compounds from the C_1 compounds, which separations unit does not contain a de-methanizer.

[0014] In some embodiments of aspects provided herein, the separations unit contains a distillation column and an oil absorber. In some embodiments of aspects provided herein, the distillation column does not condense methane.

[0015] Another aspect of the present disclosure provides a method for generating compounds with two or more carbon atoms (C_{2+} compounds), comprising: (a) directing oxygen (O_2) and methane (CH_4) into an oxidative coupling of methane (OCM) reactor that reacts the O_2 and CH_4 in an OCM process to yield a product stream comprising (i) C_{2+} compounds including ethylene (C_2H_4) and (ii) C_1 compounds including un-reacted CH_4; (b) directing the product stream into a pre-separations unit that produces (i) a bottoms stream comprising the C_{2+} compounds and (ii) an overhead stream comprising the C_1 compounds and at least some of the C_{2+} compounds; and (c) directing the overhead stream into an oil absorber that removes the at least some of the C_{2+} compounds to produce a C_1 stream.

[0016] In some embodiments of aspects provided herein, the OCM process is integrated with a methanol to olefins (MTO) unit, a steam cracker, or a metathesis process. In some embodiments of aspects provided herein, the pre-separation unit does not include a de-methanizer. In some embodiments of aspects provided herein, the pre-separation unit does not condense methane. In some embodiments of aspects provided herein, the overhead stream comprises at least about 10% C_{2+} compounds. In some embodiments of aspects provided herein, the overhead stream comprises at least about 5% C_{2+} compounds. In some embodiments of aspects provided herein, the overhead stream comprises at least about 1% C_{2+} compounds. In some embodiments of aspects provided herein, the overhead stream comprises at least about 0.1% C_{2+} compounds.

[0017] Another aspect of the present disclosure provides a method for generating compounds with two or more carbon atoms (C_{2+} compounds), comprising: (a) directing oxygen (O_2) and methane (CH_4) into an oxidative coupling of methane (OCM) reactor that reacts the O_2 and CH_4 in an OCM process to yield a product stream comprising (i) C_{2+} compounds including ethylene (C_2H_4) and (ii) C_1 compounds including un-reacted CH_4; and (b) directing the product stream into a separations unit containing a metal organic framework (MOF) that produces (i) a bottoms stream comprising the C_{2+} compounds and (ii) an overhead stream comprising the C_1 compounds.

[0018] In some embodiments of aspects provided herein, the method further comprises (c) directing the overhead stream to a methanation unit for converting carbon dioxide (CO_2) and/or carbon monoxide (CO) into methane (CH_4); and (d) directing the CH_4 into the OCM reactor. In some embodiments of aspects provided herein, the method further comprises (e) directing the bottoms stream to a second separations unit containing a metal organic framework (MOF) that separates olefins from paraffins. In some embodiments of aspects provided herein, the separations unit comprises a pressure swing absorber (PSA) that contains the MOF. In some embodiments of aspects provided herein, the separations unit comprises a temperature swing absorber (TSA) that contains the MOF. In some embodiments of aspects provided herein, the C_1 compounds include hydrogen (H_2).

[0019] Another aspect of the present disclosure provides a method for generating compounds with two or more carbon atoms (C_{2+} compounds), comprising: (a) directing oxygen (O_2) and methane (CH_4) into an oxidative coupling of methane (OCM) reactor having a catalytic section and a cracking section to produce an OCM product stream, which catalytic section reacts the O_2 and CH_4 to yield ethylene (C_2H_4), ethane (C_2H_6) and heat, which cracking section uses the heat to convert C_2H_6 into C_2H_4, and which product stream comprises (i) C_{2+} compounds including ethylene (C_2H_4) and ethane (C_2H_6) and (ii) C_1 compounds including un-reacted CH_4; (b) directing the product stream into a separations unit containing a metal organic framework (MOF) that produces (i) a first stream comprising the C_2H_4, (ii) a second stream comprising the C_2H_6 and (iii) a third stream comprising the C_1 compounds; (c) directing the second stream into the cracking section; and (d) directing the third stream into the catalytic section.

[0020] In some embodiments of aspects provided herein, the third stream is directed to a methanation unit prior to directing to the catalytic section, which methanation unit converts carbon dioxide (CO_2) and/or carbon monoxide (CO) into methane (CH_4). In some embodiments of aspects provided herein, the separations unit comprises a pressure swing absorber (PSA) that contains the MOF. In some embodiments of aspects provided herein, the separations unit comprises a temperature swing absorber (TSA) that contains the MOF. In some embodiments of aspects provided herein, the C_1 compounds include hydrogen (H_2).

[0021] Another aspect of the present disclosure provides a system for generating compounds with two or more carbon atoms (C_{2+} compounds), comprising: (a) an oxidative coupling of methane (OCM) reactor configured to receive oxygen (O_2) and methane (CH_4) and react the O_2 and CH_4 in an OCM process to yield a product stream comprising (i) C_{2+} compounds including ethylene (C_2H_4) and (ii) carbon dioxide (CO_2); and (b) a separations unit fluidically coupled to the OCM reactor and configured to receive the product stream from the OCM reactor, wherein the separations unit comprises a CO_2 separation unit to separate the CO_2 from the product stream, and to enrich the C_{2+} compounds in the product stream, which CO_2 separation unit employs (i) sorbent or solvent separation of CO_2, (ii) membrane separation of CO_2, (iii) cryogenic or low temperature separation of CO_2 having an operating temperature greater than a boiling point of methane and less than a boiling point of CO_2, (iv) metal-organic framework-based separation, or (v) antisublimation separation of CO_2.

[0022] In some embodiments of aspects provided herein, the separations unit comprises one or more additional units, and the product stream is directed into the separations unit through the one or more additional units. In some embodiments of aspects provided herein, the sorbent or solvent separation of CO_2 employs an amine based absorption unit. In some embodiments of aspects provided herein, the sorbent or solvent separation of CO_2 employs a Benfield process. In some embodiments of aspects provided herein, the sorbent or solvent separation of CO_2 employs diethanolamine. In some embodiments of aspects provided herein, the sorbent or solvent separation of CO_2 employs glycol dimethylether. In some embodiments of aspects provided herein, the sorbent or solvent separation of CO_2 employs propylene carbonate. In some embodiments of aspects provided herein, the sorbent or solvent separation of CO_2 employs Sulfinol. In some embodiments of aspects provided herein, the sorbent or solvent separation of CO_2 employs a zeolite. In some embodiments of aspects provided herein, the sorbent or solvent separation of CO_2 employs active carbon. In some embodiments of aspects provided herein, the CO_2 separation unit comprises a membrane CO_2 separation unit. In some embodiments of aspects provided herein, the membrane separation of CO_2 employs a polymeric membrane. In some embodiments of aspects provided herein, the membrane separation of CO_2 employs a metallic membrane. In some embodiments of aspects provided herein, the membrane separation of CO_2 employs a ceramic membrane. In some embodiments of aspects provided herein, the membrane separation of CO_2 employs a hybrid membrane comprising a membrane supporting a solvent or sorbent. In some embodiments of aspects provided herein, the membrane separation of CO_2 employs a poly ionic liquid membrane. In some embodiments of aspects provided herein, the membrane separation of CO_2 employs a supported ionic liquid membrane. In some embodiments of aspects provided herein, the membrane separation of CO_2 employs a polyetherimide membrane. In some embodiments of aspects provided herein, the membrane separation of CO_2 employs an amorphous fluoropolymer based membrane. In some embodiments of aspects provided herein, the system further comprises a methanation reactor that is configured to receive the CO_2 from the product stream and react the CO_2 to yield a methanation product stream comprising methane. In some embodiments of aspects provided herein, the methane in the methanation product stream is directed to the OCM reactor. In some embodiments of aspects provided herein, the product stream is further separated into (i) an ethylene product stream comprising ethylene and (ii) a C_{3+} product stream comprising compounds with three or more carbon atoms (C_{3+} compounds). In some embodiments of aspects provided herein, ethane is directed from the product stream to the OCM reactor. In some embodiments of aspects provided herein, the product stream is compressed, prior to being directed into the separations unit. In some embodiments of aspects provided herein, the CO_2 separation unit employs the sorbent or solvent separation of CO_2. In some embodiments of aspects provided herein, the CO_2 separation unit employs the membrane separation of CO_2. In some embodiments of aspects provided herein, the CO_2 separation unit employs the cryogenic or low temperature separation of CO_2 having an operating temperature greater than a boiling point of methane and less than a boiling point of CO_2. In some embodiments of aspects provided herein, the CO_2 separation unit employs the metal-organic framework-based separation. In some embodiments of aspects provided herein, the CO_2 separation unit employs the antisublimation separation of CO_2.

[0023] Another aspect of the present disclosure provides a system for generating compounds with two or more carbon atoms (C_{2+} compounds), comprising: an oxidative coupling of methane (OCM) reactor configured to receive oxygen (O_2) and methane (CH_4) and react the O_2 and CH_4 in an OCM process to yield a product stream comprising (i) C_{2+} compounds including ethylene (C_2H_4) and (ii) carbon dioxide (CO_2); a first CO_2 separation unit fluidically coupled to the OCM reactor and configured to receive the product steam from the OCM reactor, wherein the first CO_2 separation unit separates at least some of the CO_2 from the product stream to produce an enriched stream comprising (i) the C_{2+} compounds and (ii) at least some of the CO_2; a cryogenic separations unit fluidically coupled to the first CO_2 separation unit and configured to receive the enriched stream from the first CO_2 separation unit, wherein the cryogenic separations unit separates the C_2H_4 from the C_{2+} compounds to produce an ethylene stream comprising (i) the C_2H_4 and (ii) the CO_2; and a second CO_2 separation unit fluidically coupled to the cryogenic separations unit and configured to receive the ethylene stream from the cryogenic separations unit, wherein the second CO_2 separation unit separates the CO_2 from the ethylene stream to produce an ethylene product stream.

[0024] In some embodiments of aspects provided herein, the enriched stream contains at most about 2.0 mol % CO_2. In some embodiments of aspects provided herein, the enriched stream contains at most about 1.0 mol % CO_2. In some embodiments of aspects provided herein, the enriched stream contains at most about 0.5 mol % CO_2. In some embodiments of aspects provided herein, the first CO_2 separation unit comprises a membrane, a pressure swing absorption (PSA) unit, an amine unit, or any combination thereof. In some embodiments of aspects provided herein, the second CO_2 separation unit comprises a membrane, a pressure swing absorption (PSA) unit, an amine unit, or any combination thereof. In some embodiments of aspects provided herein, the cryogenic separations unit comprises a de-methanizer.

[0025] Another aspect of the present disclosure provides a system for generating compounds with two or more Carbon atoms (C2+ compounds), comprising: an oxidative coupling of methane (OCM) reactor configured to receive oxygen (O_2) and methane (CH_4) and react the O_2 and CH_4 in an OCM process to yield a product stream comprising (i) C_{2+} compounds including ethylene (C_2H_4) and (ii) carbon monoxide (CO) and/or carbon dioxide (CO_2); and a separations unit fluidically coupled to the OCM reactor and configured to receive the product stream from the OCM reactor, wherein the separations unit selectively separates olefins from the paraffins.

[0026] In some embodiments of aspects provided herein, the separations unit selectively separates ethylene from paraffins. In some embodiments of aspects provided herein, the separations unit comprises an absorber unit employing pi-complexation. In some embodiments of aspects provided herein, the separations unit comprises a membrane unit including a membrane contactor employing pi-complexation. In some embodiments of aspects provided herein, the separations unit comprises a pressure swing adsorption (PSA) unit comprising a sorbent having dispersed metal ions that are capable of complexing with the olefins. In some embodiments of aspects provided herein, the PSA unit comprises a sorbent selected from a zeolite, a molecular sieve sorbent, a carbon molecular sieve, an activated carbon, a carbon nanotube, and a polymeric resin. In some embodiments of aspects provided herein, the system further comprises an oxidizing agent used to regenerate and/or stabilize the pi-complex. In some embodiments of aspects provided herein, the oxidizing agent comprises HNO_3 or $KMnO_4$. In some embodiments of aspects provided herein, the separations unit comprises (i) a pressure swing adsorption (PSA) unit, (ii) a temperature swing adsorption (TSA) unit, or (iii) a membrane system employing a metal-organic framework (MOF), and the olefins separated comprise ethylene.

[0027] Another aspect of the present disclosure provides a system for generating compounds with two or more carbon atoms (C_{2+} compounds), comprising: an oxidative coupling of methane (OCM) reactor configured to receive oxygen (O_2) and methane (CH_4) and react the O_2 and CH_4 in an OCM process to yield a product stream comprising (i) C_{2+} compounds including ethylene (C_2H_4) and (ii) C_1 compounds including un-reacted CH_4; and a separations unit fluidically coupled to the OCM reactor and configured to receive the product stream from the OCM reactor, wherein the separations unit separates the C_{2+} compounds from the C_1 compounds, and wherein the separations unit does not contain a de-methanizer.

[0028] In some embodiments of aspects provided herein, the separations unit contains a distillation column and an oil absorber. In some embodiments of aspects provided herein, the distillation column does not condense methane.

[0029] Another aspect of the present disclosure provides a system for generating compounds with two or more carbon atoms (C_{2+} compounds), comprising: an oxidative coupling of methane (OCM) reactor configured to receive oxygen (O_2) and methane (CH_4) and react the O_2 and CH_4 in an OCM process to yield a product stream comprising (i) C_{2+} compounds including ethylene (C_2H_4) and (ii) C_1 compounds including un-reacted CH_4; a pre-separations unit fluidically coupled to the OCM reactor and configured to receive the product stream from the OCM reactor, wherein the pre-separations unit produces (i) a bottoms stream comprising the C_{2+} compounds and (ii) an overhead stream comprising the C_1 compounds and at least some of the C_{2+} compounds; and an oil absorber fluidically coupled to the pre-separations unit and configured to receive the overhead stream from the pre-separations unit, wherein the oil absorber removes the at least some of the C_{2+} compounds to produce a C_1 stream.

[0030] In some embodiments of aspects provided herein, the OCM process is integrated with a methanol to olefins

(MTO) unit, a steam cracker, or a metathesis process. In some embodiments of aspects provided herein, the pre-separation unit does not include a de-methanizer. In some embodiments of aspects provided herein, the pre-separation unit does not condense methane. In some embodiments of aspects provided herein, the overhead stream comprises at least about 10% C_{2+} compounds. In some embodiments of aspects provided herein, the overhead stream comprises at least about 5% C_{2+} compounds. In some embodiments of aspects provided herein, the overhead stream comprises at least about 1% C_{2+} compounds. In some embodiments of aspects provided herein, the overhead stream comprises at least about 0.1% C_{2+} compounds.

[0031] Another aspect of the present disclosure provides a system for generating compounds with two or more carbon atoms (C_{2+} compounds), comprising: an oxidative coupling of methane (OCM) reactor configured to receive oxygen (O_2) and methane (CH_4) and react the O_2 and CH_4 in an OCM process to yield a product stream comprising (i) C_{2+} compounds including ethylene (C_2H_4) and (ii) C_1 compounds including un-reacted CH_4; and a separations unit fluidically coupled to the OCM reactor and configured to receive the product stream from the OCM reactor, wherein the separations unit contains a metal organic framework (MOF) that produces (i) a bottoms stream comprising the C_{2+} compounds and (ii) an overhead stream comprising the C_1 compounds.

[0032] In some embodiments of aspects provided herein, the system further comprises a methanation unit fluidically coupled to the separations unit and configured receive the overhead stream from the separations unit, wherein the methanation unit converts carbon dioxide (CO_2) and/or carbon monoxide (CO) into methane (CH_4), and wherein the CH_4 is directed into the OCM reactor. In some embodiments of aspects provided herein, the system further comprises a second separations unit fluidically coupled to the separations unit and configured receive the bottoms stream from the separations unit, wherein the second separations unit contains a metal organic framework (MOF) that separates olefins from paraffins. In some embodiments of aspects provided herein, the separations unit comprises a pressure swing absorber (PSA) that contains the MOF. In some embodiments of aspects provided herein, the separations unit comprises a temperature swing absorber (TSA) that contains the MOF. In some embodiments of aspects provided herein, the C_1 compounds include hydrogen (H_2).

[0033] Another aspect of the present disclosure provides a system for generating compounds with two or more carbon atoms (C_{2+} compounds), comprising: an oxidative coupling of methane (OCM) reactor configured to receive oxygen (O_2) and methane (CH_4) and react the O_2 and CH_4 to produce an OCM product stream, the OCM reactor having a catalytic section and a cracking section, which catalytic section reacts the O_2 and CH_4 to yield ethylene (C_2H_4), ethane (C_2H_6) and heat, which cracking section uses the heat to convert C_2H_6 into C_2H_4, and which product stream comprises (i) C_{2+} compounds including ethylene (C_2H_4) and ethane (C_2H_6) and (ii) C_1 compounds including un-reacted CH_4; and a separations unit fluidically coupled to the OCM reactor and configured to receive the product stream from the OCM reactor, wherein the separations unit contains a metal organic framework (MOF) that produces (i) a first stream comprising the C_2H_4, (ii) a second stream comprising the C_2H_6 and (iii) a third stream comprising the C_1 compounds, and wherein the second stream and the third stream are directed into the cracking section and the catalytic section respectively.

[0034] In some embodiments of aspects provided herein, the third stream is directed to a methanation unit prior to directing to the catalytic section, which methanation unit converts carbon dioxide (CO_2) and/or carbon monoxide (CO) into methane (CH_4). In some embodiments of aspects provided herein, the separations unit comprises a pressure swing absorber (PSA) that contains the MOF. In some embodiments of aspects provided herein, the separations unit comprises a temperature swing absorber (TSA) that contains the MOF. In some embodiments of aspects provided herein, the C_1 compounds include hydrogen (H_2).

[0035] Another aspect of the present disclosure provides a non-transitory computer-readable medium comprising machine-executable code that, upon execution by one or more computer processors, implements any of the methods above or elsewhere herein.

[0036] Another aspect of the present disclosure provides a system comprising one or more computer processors and a non-transitory computer-readable medium coupled thereto. The non-transitory computer-readable medium comprises machine-executable code that, upon execution by the one or more computer processors, implements any of the methods above or elsewhere herein.

[0037] Additional aspects and advantages of the present disclosure will become readily apparent to those skilled in this art from the following detailed description, wherein only illustrative embodiments of the present disclosure are shown and described. As will be realized, the present disclosure is capable of other and different embodiments, and its several details are capable of modifications in various obvious respects, all without departing from the disclosure. Accordingly, the drawings and description are to be regarded as illustrative in nature, and not as restrictive.

INCORPORATION BY REFERENCE

[0038] All publications, patents, and patent applications mentioned in this specification are herein incorporated by reference to the same extent as if each individual publication, patent, or patent application was specifically and individually indicated to be incorporated by reference.

BRIEF DESCRIPTION OF THE FIGURES

[0039] The novel features of the invention are set forth with particularity in the appended claims. A better understanding of the features and advantages of the present invention will be obtained by reference to the following detailed description that sets forth illustrative embodiments, in which the principles of the invention are utilized, and the accompanying drawings or figures (also “FIG.” and “FIGs.” herein), of which:

[0040] FIG. **1** shows an example oxidative coupling of methane (OCM) system with advanced separation;

[0041] FIG. **2** shows an example OCM system with auto refrigeration (e.g., methane refrigeration);

[0042] FIG. **3**A shows an exemplary OCM system with a silver complexation ethylene recovery subsystem;

[0043] FIG. **3**B shows an example of an OCM process with an integrated membrane contactor subsystem;

[0044] FIG. **3**C shows an example of a membrane contactor;

[0045] FIG. **4** shows an exemplary pressure swing adsorption (PSA) system;

[0046] FIG. **5**A shows a schematic of CO_2 separation methods;

[0047] FIG. **5**B shows a schematic of CO_2 separation methods;

[0048] FIG. **5**C shows a schematic of CO_2 separation methods;

[0049] FIG. **5**D shows a schematic of CO_2 separation methods;

[0050] FIG. **6** shows an example CO_2 distillation system;

[0051] FIG. **7** shows an example water electrolysis sub system;

[0052] FIG. **8** shows an example OCM system with CO_2 as a quench medium;

[0053] FIG. **9** shows an example organic Rankine cycle (ORC) subsystem;

[0054] FIG. **10** shows an exemplary typical OCM system;

[0055] FIG. **11** shows an exemplary OCM system with a single stage PSA unit;

[0056] FIG. **12** shows an exemplary OCM system with a multi stage PSA unit;

[0057] FIG. **13** shows an exemplary retrofit of OCM to a cracker, with a single stage PSA unit;

[0058] FIG. **14** shows an exemplary retrofit of OCM to a cracker, with a multi stage PSA unit;

[0059] FIG. **15** shows exemplary configurations of ethylene to liquids (ETL) systems without PSA;

[0060] FIG. **16** shows exemplary configurations of ETL systems with PSA;

[0061] FIG. **17** shows an exemplary PSA unit integrated with an OCM-ETL system for a midstream application;

[0062] FIG. **18** shows an exemplary PSA unit integrated with an OCM-ETL system in a natural gas liquids (NGL) application;

[0063] FIG. **19** shows an exemplary PSA unit integrated with an OCM-ETL system for a refining application;

[0064] FIG. **20** shows an exemplary alternate scheme for a PSA unit integrated with an OCM-ETL system for a refining application;

[0065] FIG. **21** shows an exemplary OCM process scheme employing metal-organic framework (MOF) separations;

[0066] FIG. **22** shows an exemplary OCM process scheme employing MOF separations;

[0067] FIG. **23** shows an exemplary OCM process scheme employing MOF separations;

[0068] FIG. **24** shows an exemplary OCM process scheme employing MOF separations;

[0069] FIG. **25** shows an exemplary OCM process scheme employing MOF separations;

[0070] FIG. **26** shows an exemplary OCM process scheme employing MOF separations;

[0071] FIG. **27**A shows an example of OCM separations using an oil absorption tower; and

[0072] FIG. **27**B shows an example of a pre-cut and absorption system.

DETAILED DESCRIPTION

[0073] While various embodiments of the invention have been shown and described herein, it will be obvious to those skilled in the art that such embodiments are provided by way of example only. Numerous variations, changes, and substitutions may occur to those skilled in the art without departing from the invention. It should be understood that various alternatives to the embodiments of the invention described herein may be employed.

[0074] The term "higher hydrocarbon," as used herein, generally refers to a higher molecular weight and/or higher chain hydrocarbon. A higher hydrocarbon can have a higher molecular weight and/or carbon content that is higher or larger relative to starting material in a given process (e.g., OCM or ETL). A higher hydrocarbon can be a higher molecular weight and/or chain hydrocarbon product that is generated in an OCM or ETL process. For example, ethylene is a higher hydrocarbon product relative to methane in an OCM process. As another example, a C_{3+} hydrocarbon is a higher hydrocarbon relative to ethylene in an ETL process. As another example, a C_{5+} hydrocarbon is a higher hydrocarbon relative to ethylene in an ETL process. In some cases, a higher hydrocarbon is a higher molecular weight hydrocarbon.

[0075] The term "OCM process," as used herein, generally refers to a process that employs or substantially employs an oxidative coupling of methane (OCM) reaction. An OCM reaction can include the oxidation of methane to a higher hydrocarbon and water, and involves an exothermic reaction. In an OCM reaction, methane can be partially oxidized and coupled to form one or more C_{2+} compounds, such as ethylene. In an example, an OCM reaction is $2CH_4+O_2 \rightarrow C_2H_4+2H_2O$. An OCM reaction can yield C_{2+} compounds. An OCM reaction can be facilitated by a catalyst, such as a heterogeneous catalyst. Additional by-products of OCM reactions can include CO, CO_2, H_2, as well as hydrocarbons, such as, for example, ethane, propane, propene, butane, butene, and the like.

[0076] The term "non-OCM process," as used herein, generally refers to a process that does not employ or substantially employ an oxidative coupling of methane reaction. Examples of processes that may be non-OCM processes include non-OCM hydrocarbon processes, such as, for example, non-OCM processes employed in hydrocarbon processing in oil refineries, a natural gas liquids separations processes, steam cracking of ethane, steam cracking or naphtha, Fischer-Tropsch processes, and the like.

[0077] The terms "C_{2+}" and "C_{2+} compound," as used herein, generally refer to a compound comprising two or more carbon atoms. For example, C_{2+} compounds include, without limitation, alkanes, alkenes, alkynes and aromatics containing two or more carbon atoms. C_{2+} compounds can include aldehydes, ketones, esters and carboxylic acids. Examples of C_{2+} compounds include ethane, ethene, acetylene, propane, propene, butane, and butene.

[0078] The term "non-C_{2+} impurities," as used herein, generally refers to material that does not include C_{2+} compounds. Examples of non-C_{2+} impurities, which may be found in certain OCM reaction product streams, include nitrogen (N_2), oxygen (O_2), water (H_2O), argon (Ar), hydrogen (H_2) carbon monoxide (CO), carbon dioxide (CO_2) and methane (CH_4).

[0079] The term "small scale," as used herein, generally refers to a system that generates less than or equal to about 250 kilotons per annum (KTA) of a given product, such as an olefin (e.g., ethylene).

[0080] The term "world scale," as used herein, generally refers to a system that generates greater than about 250 KTA of a given product, such as an olefin (e.g., ethylene). In some examples, a world scale olefin system generates at least about 1000, 1100, 1200, 1300, 1400, 1500, or 1600 KTA of an olefin.

[0081] The term "item of value," as used herein, generally refers to money, credit, a good or commodity (e.g., hydrocarbon). An item of value can be traded for another item of value.

[0082] The term "carbon efficiency," as used herein, generally refers to the ratio of the number of moles of carbon present in all process input streams (in some cases including all hydrocarbon feedstocks, such as, e.g., natural gas and ethane and fuel streams) to the number of moles of carbon present in all commercially (or industrially) usable or marketable products of the process. Such products can include hydrocarbons that can be employed for various downstream uses, such as petrochemical or for use as commodity chemicals. Such products can exclude CO and CO_2. The products of the process can be marketable products, such as C_{2+} hydrocarbon products containing at least about 99% C_{2+} hydrocarbons and all sales gas or pipeline gas products containing at least about 90% methane. Process input streams can include input streams providing power for the operation of the process. In some cases, power for the operation of the process can be provided by heat liberated by an OCM reaction. In some cases, the systems or methods of the present disclosure have a carbon efficiency of at least about 50%, at least about 55%, at least about 60%, at least about 65%, at least about 70%, at least about 75%, at least about 80%, at least about 85%, or at least about 90%. In some cases, the systems or methods of the present disclosure have a carbon efficiency of between about 50% and about 85%, between about 55% and about 80%, between about 60% and about 80%, between about 65% and about 85%, between about 65% and about 80%, or between about 70% and about 80%.

[0083] The term "C_{2+} selectivity," as used herein, generally refers to the percentage of the moles of methane that are converted into C_{2+} compounds.

[0084] The term "specific oxygen consumption," as used herein, generally refers to the mass (or weight) of oxygen consumed by a process divided by the mass of C_{2+} compounds produced by the process.

[0085] The term "specific CO_2 emission," as used herein, generally refers to the mass of CO_2 emitted from the process divided by the mass of C_{2+} compounds produced by the process.

[0086] The term "unit," as used herein, generally refers to a unit operation. A unit operation may be one or more basic steps in a process. A unit may have one or more sub-units (or sub-systems). Unit operations may involve a physical change or chemical transformation, such as separation, crystallization, evaporation, filtration, polymerization, isomerization, and other reactions. A unit may include one or more individual components. For example, a separations unit may include one or more separations columns or an amine unit may include one or more amine columns.

Separations

[0087] Various non-cryogenic separation techniques have been increasingly employed for gas separations, purifications and recovery of hydrocarbons. Membrane based processes and adsorbents have been intensively studied for large scale applications for olefins recovery. Since the development of synthetic adsorbents and pressure swing adsorption (PSA) cycles, adsorption has been playing an increasingly important role in gas separation and purification.

[0088] PSA technology can be used in a large variety of applications: hydrogen purification, air separation, CO_2 removal, noble gases purification, methane upgrading, n-iso paraffin separation and so forth. While new applications for gas separations by adsorption are continually being developed, the most important applications have been air separation (for production of O_2 and N_2) and hydrogen separation (from fuel gas). Approximately 20% of O_2 and N_2 are currently produced by PSA. The increasing industrial applications for adsorption have stimulated a growing interest in research and new applications.

[0089] Processes of the present disclosure can employ a variety of different separations techniques, alone or in combination. For example, OCM processes can employ amine and caustic systems for CO_2 removal, molecular sieve guard beds for water removal, and cryogenic distillation or other separation techniques for recovery and purification of hydrocarbon components. Cryogenic separation can refer to separations using temperature levels below 120 K or about −153° C. Other techniques include Selexol™ and Rectisol™ processes for CO_2 removal.

[0090] OCM product effluent can comprise a mixture of hydrocarbons including but not limited to methane, ethane, ethylene, propane, propylene, butanes, butenes, and higher hydrocarbons. OCM product effluent can also comprise varying amounts of other components such as H_2, N_2, CO, CO_2 and H_2O. The product of an OCM reaction can include ethylene. The ethylene product can be polymer grade, refinery grade or chemical grade. Depending on the purity level required, different separation and/or purification techniques can be employed with the OCM process. To recover high purity ethylene, separation methods such as those discussed herein can be used to remove a wide range of components.

[0091] Advantages of the advanced OCM processes described herein can include reducing the cost, reducing the number of unit operations ("units") used, and hence improving the overall process for producing high purity polymer grade ethylene. Overall conversion and carbon efficiency can also be improved. The separation methods disclosed herein can also improve the overall conversion and carbon efficiency.

[0092] The different separation and purification techniques discussed herein can be used to separate the OCM product effluent (e.g., process gas) into a plurality of streams, including but not limited to a first stream comprising methane, hydrogen, carbon monoxide and other lighter inerts and a second stream comprising ethane, ethylene, propylene, and higher hydrocarbons. Separation systems or subsystems employed can include those discussed herein, such as a cryogenic demethanizer, a membrane separation system, or a PSA based system.

[0093] The separation techniques discussed herein can be employed to remove CO_2, such as from an OCM product effluent stream. One or more separations techniques can be used to remove CO_2 including but not limited to absorption, adsorption, CO_2 distillation, and membrane separation. The separation technique can be non-cryogenic.

[0094] FIG. **1** shows a block flow diagram for an exemplary OCM process. Oxygen **110** and methane **121** can be fed into an OCM reactor **101** for conversion into higher hydrocarbon compounds including ethylene. The OCM product stream **111** can be directed to a compressor **102**, and the compressed product stream **112** can be fed into a separations system **103**. The separations system can include pretreatment units **104**, such as impurity and CO_2 removal units, as well as separations units **105**, such as cryogenic, non-cryogenic, complexation, membrane, and other separations units. The separations system can be a combination of more than one separation techniques, such as those discussed in this application. The separation system can replace CO_2 removal, moisture removal, and cryogenic separation systems of existing OCM process systems. The compressor system may not be required for some types of separation processes. From the separations system, CO_2 can be vented **113**, ethane **114** can be recovered, for example for recycling to the OCM reactor, ethylene product **115** can be recovered, and C_{3+} products **116** can be recovered. Additionally, CO_2 **117** and methane **118** can be directed from the separations system into a methanation unit **106**. The methanation unit can produce methane from the CO_2, for recycling **119** back to the OCM reactor. Additional methane **120** can be added to the OCM reactor supply stream **121**.

Auto Refrigeration

[0095] OCM process systems can use refrigeration subsystems to condense overhead vapors, for example from a demethanizer, a deethanizer, and/or a C_2 splitter. The temperatures employed can be in the range from about 12° C. to about −100° C. These low temperatures can be achieved through the use of multiple refrigeration systems, such as ethylene refrigeration and propylene refrigeration systems, to provide different levels of refrigeration. These can be similar to those employed in existing steam crackers.

[0096] Alternatively, an open loop methane refrigeration system can be employed to provide refrigeration for a demethanizer. OCM product effluent can comprise methane as the major component, for example at a concentration of at least about 50 mol %, 60 mol %, 70 mol %, 80 mol %, 90 mol %, or more. The demethanizer can have the lowest temperature requirements in the entire separations unit. Use of methane refrigeration (e.g., auto-refrigeration) can provide benefits such as elimination of the need for an additional refrigeration system (e.g., new) for any added capacity. For grassroots or greenfield OCM applications, this can considerably reduce refrigeration compressor sizes needed. In some cases, an entire refrigeration system can be eliminated. FIG. **2** shows a block flow diagram for an exemplary open loop methane refrigeration system, such as can be used in gas processing plants and steam crackers to produce chilling for condensing overhead vapors from a demethanizer. Most elements of FIG. **2** correspond to the description in FIG. **1**; the separations unit **205** can include an open loop methane refrigeration system to provide cooling for the separations. The system can be combined with a single or multiple stage (e.g., two-stage) expansion system (e.g., Joule Thompson) to chill the incoming feed. In certain cases, multiple separate lighter products are recovered, such as a light H_2-rich stream, a low pressure methane rich stream, and a high pressure methane rich stream.

Mixed Refrigeration

[0097] Another alternative to ethylene and propylene refrigeration subsystems is the use of a mixed refrigeration system. The mixed refrigerant can be, for example, a mix of methane, ethylene and propylene. The mixed refrigerant can be a mix of ethane and propane. A wide range of possible mixed refrigerants can be employed, and can be selected based on, for example, the availability of certain components and the degree of refrigeration required. A mixed refrigerant system can provide advantages for use with an OCM reactor system, including the use of only one refrigeration sub system. Rather than two refrigeration systems each comprising multiple stages of refrigerant compressor, associated vessels, exchangers, and other components, the process can use a single refrigeration system. This can substantially reduce capital cost. This can also reduce equipment count, which can be a benefit especially for OCM retrofits at places where plot space may be a concern.

Pi Complexation

[0098] Pi complexation techniques can be used to separate alkenes from alkanes. Some metal ions complex selectively with unsaturated organic compounds. Some of these complexes are reversible while others are irreversible. For example, aqueous silver salt in solution forms reversible complexes with olefins, and forms irreversible complexes with acetylenes. This property can be employed in an OCM process to recover ethylene and propylene from OCM reactor effluent.

[0099] As shown in FIG. **3**A, separation of ethylene and/or propylene by metal complexation can be divided into three major sections: absorption, purification or venting of impurities, and desorption. An exemplary process is provided for separation of ethylene and/or propylene from a purified multi-component gas stream from the OCM reactor. FIG. **3**A shows a process for purifying a stream containing ethylene using an aqueous silver nitrate solution. Metal complexation (e.g., silver or cuprous ion complexation) can be used to separate ethylene and/or propylene from a purified multi-component gas stream produced via OCM comprising C_2 compounds, C_3 compounds, and lighter components such as hydrogen and nitrogen. First, the multi-component gas stream **310** can be introduced into an absorber **301** with aqueous silver salt solution, such that the ethylene and/or propylene undergo absorption or complexing with the silver metal ions, and such that trace acetylenes react with the silver metal ions. Vent gas **311** can be removed from the absorber. Then, the silver salt solution stream **312** can be vented **313** in a vent column **302** at reduced pressure to remove any dissolved low molecular weight components. Then, the resulting silver salt solution stream can be treated in a stripper **303** to separate the absorbed or complexed ethylene and/or propylene from the silver salt solution, and further treated in a treatment unit **304** to release the trace acetylenes. Purified ethylene **316** can be recovered, and some product can be recycled **317**. The aqueous silver salt stream **318** can then be recycled to the first step, in some cases after regeneration in a regeneration unit **305** with $AgMnO_4$ **320**. MnO_2 **321** can be removed from the regeneration unit. H_2O_2 **319** can be added to the solvent stream being returned to the absorber.

[0100] Useful adsorbents include but are not limited to metal compounds, such as silver or copper, supported on high surface area carriers with a plurality of pores. These adsorbents can be used in pressure swing adsorption or temperature swing adsorption processes. When operating pressure and/or temperature is changed, the silver or copper compound can release the alkene-rich component from the adsorbent. These adsorbents can be very effective for selective adsorption of alkenes such as ethylene, propylene, and mixtures of these from gaseous mixtures.

[0101] When a gaseous component solubilizes in a liquid and complexes with its ions, the loading of the gas can be affected by its partial pressure and the temperature and the concentration of the complexing ions in the solution. Therefore, by changing the physical conditions separately or collectively, the active gaseous component can either be formed into or out of the solution. Adjusting or swinging one or more physical parameters can be used to carry out an ethylene or propylene separation using an aqueous silver nitrate solution. Purification or venting of impurities can result in a product stream that is free or substantially free of impurities including but not limited to CO_2, sulfur compounds, acetylenes, and hydrogen. Acetylene and hydrogen can cause operational problems and so the process gas can be treated to bring the concentration of such impurities to within an acceptable limit.

[0102] Metal complexation can be used in combination with other processes, such as membrane-based processes, or a PSA system with metal ions dispersed on the sorbent. For good adsorption, the cations can be spread (e.g., with high dispersion) on solid substrates with a high surface area. There are at least three types of metal complexation sorbents that can be used in the methods and systems described herein (i.e., monolayer or near monolayer salts supported on porous substrates, ion-exchange zeolites, and ion-exchange resins). For bulk separation, the monolayer salts on porous substrates and ion-exchange resins can be more suitable in some cases. Ion-exchange zeolites are usually more suitable for olefin recovery or purification. Substrates for supporting salts may include Y-Alumina (porous), silica gel, activated carbon, TiO_2, and a number of zeolites. The metal ion can be Ag^+ or Cu^+ ion.

[0103] Membrane contactors using a silver nitrate solution or a copper salt solution can be used to separate the olefins from the OCM effluent stream. The contactor can include the salt solution in a membrane module or unit. Many such modules or units can be put together in a contactor system where the salt solution is circulated. Such membrane contactors can result in substantial olefin recovery from a feed containing a mixture of olefins and paraffins (e.g., propane and/or propylene). The process described herein can be used to separate ethylene from the OCM effluent containing methane and ethane, resulting in elimination of whole, or part of the cryogenic recovery system in a typical OCM system.

[0104] As described herein, OCM process can be integrated with a Permylene membrane system to recover or separate the bulk of ethylene. In some cases, Permylene membranes can be used to separate olefins from paraffins. The Permylene process can use a flat sheet composite structure based on chitosan material and silver cations as facilitating agents. Chitosan can be produced by the deacetylation of chitin, which is the structural element in the exoskeleton of crustaceans. Chitosan can act as the active layer of the Permylene membrane. In contact with an aqueous solution containing silver ions, a hydrogel can be formed and the silver ions can form metal complexes with the olefins. The olefin molecules can be transported across the membrane under the influence of the olefin partial pressure differential between the feed and permeate sides of the membrane and can be released on the low pressure permeate side. Gases without a carbon-carbon double bond are rejected.

[0105] In some instances, an oxidizing agent can be used to either stabilize or improve the formation of the desired metal complex with olefin, and/or to regenerate or destabilize the undesired complexes formed. For example, in a copper based system, adding nitric acid can improve the stability of formation of the metal-olefin complex.

[0106] FIG. **3**B shows an example of a membrane contactor module (or unit) with an OCM system. The membrane contactor module separates the incoming feed into an olefin rich product stream and a lighter reject stream. The lighter stream can contain predominantly methane, CO, CO_2 and some ethane, and is recycled to the OCM loop (e.g., to methanation and back to OCM reactor). The pretreatment comprises acetylene and diene removal, since those are more active in forming metal-complexes than olefins. The lean (olefin depleted) solution can be recycled back to the membrane contactor, as shown in FIG. **3**C. The metal complex can be subjected to a low pressure and/or a high temperature in order to break the olefin-metal complex and recover the olefin and metal solution.

[0107] FIG. **3**B shows an example of an OCM process with an integrated membrane contactor module. The OCM feedstock **322** (e.g., comprising methane) and oxygen feed **324** (e.g., air) can be mixed and reacted in an OCM module **326**. The OCM product can be pre-treated **328** and sent to a membrane contactor module **330**. The membrane contactor module can provide an olefin-rich stream **332** and send some of the remaining material back to a methanation module **334**. Some of the material can be purged **336**. The methanation module **334** can produce methane and recycled to the OCM module **326**.

[0108] FIG. **3**C shows an example of a membrane contactor module. The feed **338** (e.g., from a pre-treatment unit **328**) can go into a membrane unit **340**. The olefin rich stream **342** can be sent to a first flash vessel **344**, which produces an olefin product **346**. The lean solution **348** (e.g., depleted in olefin) can be recycled to the membrane unit **340**. In some cases, the membrane contactor module contains a second stage, in this example a second flash vessel **350** can produce a C_1 recycle stream **352**.

Membranes

[0109] Membranes can be used to perform a variety of separations, such as separations of olefins and paraffins, or separations of CO_2. A membrane can be essentially a barrier that separates two phases and restricts transport of various chemicals in a selective manner. Polymer membranes can be used to separate mixtures such as propylene/propane mixtures and ethylene/butene mixtures. Separations in polymeric membranes are dependent on the solubility and diffusion of the species through the membrane. While zeolite-based separations are predominantly depended on molecular size differences, the differing permeation of olefins through a polymeric membrane can be largely attributed to differences in solubility, which can depend on the critical temperature and the kinetic diameter. Membrane separations can be employed even when there are small molecular size differences.

[0110] The OCM process can utilize a membrane based separation process to further enhance the efficiency and energy consumption of the process. Cryogenic distillation can be used for the separation of alkenes, but is highly energy intensive. Membrane based separations can be used for a variety of purposes in the context of an OCM process, such as to separate and purify ethylene product from OCM reactor effluent, to separate a stream rich in CO_2, to separate a stream containing lighter hydrocarbons and inerts, or to separate C_2 compounds from C_1 and lighter compounds.

[0111] Membranes can include but are not limited to isotropic membranes, anisotropic membranes, and electrically charged membranes. A membrane can be a ceramic membrane, a metal membrane, or a liquid membrane. An isotropic membrane can be a microporous membrane or a non-porous dense membrane. Membranes can be used for separations including but not limited to CO_2 separation, paraffin-olefin separation, or selective recovery of pure ethylene from the OCM reactor effluent. Polymer derived carbon molecular sieve membranes can be used to separate paraffins from olefins. These membranes can be used, for example, to separate ethylene from a mix of methane and ethane.

[0112] Membrane separations can be used in combination with other types of separation and purification subsystems to remove other impurities such as acid gases, hydrogen, and nitrogen.

[0113] Transport through a membrane can take place when a driving force is applied to the components in the feed. A driving force can be a pressure differential or a concentration (activity) gradient across the membrane. Membrane based separation techniques can be used in an OCM process by applying either of the above mentioned driving forces. A membrane based separation can also be a component of a hybrid separation set-up, such as a membrane and an absorption system (e.g., a membrane contactor) or a membrane in a pressure swing adsorption (PSA) or a temperature swing adsorption (TSA) system.

[0114] An OCM reactor can employ membranes as a part of the reactor system to effectively separate the ethylene product within the reactor system itself. A section of the reactor can include membranes that aid in recovering the ethylene product, with a methane rich stream being recycled to a methanation system and eventually to the OCM reactor. Such a system can also use advanced heat recovery or quench methods so as to facilitate the use of membranes.

Pressure Swing Adsorption (PSA) and Adsorption Technology

[0115] Cryogenic separation (e.g., distillation) can be used for the recovery of ethylene, propylene, and other components from olefin plants, refinery gas streams, and other sources. These separations can be difficult to accomplish because of the close relative volatilities, and can have significant temperature and pressure requirements for operation. The ethane/ethylene distillation can be performed at about −25° C. and 320 pounds per square inch gauge (psig) in a column containing over 100 trays. Distillation of propane and propylene can be performed at about −30° C. and 30 psig. These can be some of the most energy intensive distillations in the chemical and petrochemical industry. In general, the use of distillation towers to separate recover and purify components is an energy intensive process.

[0116] The present disclosure provides the use of adsorbents that can achieve separation and purification of olefin rich streams. In particular, the present disclosure applies the use of PSA-based adsorbent systems to separate, purify, and recover olefins like ethylene and propylene from streams containing one or more impurities such as methane, hydrogen, carbon monoxide, carbon dioxide, ethane, or others. The streams, or parts of the streams, can be generated via an OCM process, an ETL process, or combinations thereof. The streams can be final product streams where PSA is used to recover and purify the final product. The streams can be intermediate streams which are purified prior to use as a feed in a subsequent process, such as an ETL process, an ethylene cracker (steam cracker), a refining unit, a fuel gas system, a natural gas recovery plant or any other product fractionation or product treatment unit.

Pressure Swing Adsorption (PSA)

[0117] A pressure swing adsorption (PSA) process cycle is one in which desorption takes place at a different (e.g., lower) pressure than the adsorption pressure. Reduction of pressure can be used to shift the adsorption equilibrium and affect regeneration of the adsorbent. Low pressure may not be as effective as temperature elevation in totally reversing adsorption, unless very high feed to purge pressure ratios are applied. Therefore, most PSA cycles are characterized by high residual loadings and thus low operating loadings. These low capacities at high concentration require that cycle times be short for reasonably sized beds (e.g., seconds to minutes). These short cycle times are attainable because particles of adsorbent respond quickly to changes in pressure. Major uses for PSA processes include purification as well as applications where contaminants are present at high concentrations.

[0118] As shown in FIG. **4**, the PSA system can comprise two fixed bed adsorbers **401** and **402** undergoing a cyclic operation of four steps—adsorption, blowdown, purge, and pressurization. The PSA system can receive a feed **410** and produce a product stream **411**, with a PSA off gas stream **412**. For improving the performance of the basic Skarstrom™ cycle (FIG. **4**), additional operation steps can be employed such as pressure equalization, product pressurization, and co-current depressurization. Besides these steps, the number of beds can be modified to achieve the optimal operation and multi-bed processes can be used in commercial applications like hydrogen recovery. Similarly, a TSA system can be used where a swing in temperature causes the sorption and desorption.

[0119] PSA cycles are used primarily for purification of wet gases and of hydrogen. High pressure hydrogen employed in processes such as hydrogenation, hydrocracking, and ammonia and methanol production can be produced by PSA beds compounded of activated carbon, zeolites and carbon molecular sieves. Other exemplary applications include: air separation, methane enrichment, iso/normal separations, and recovery of CO and CO_2.

Adsorbents

[0120] Adsorbents can be natural or synthetic materials, such as those having amorphous or microcrystalline structure. Exemplary adsorbents useful for large scale operation include but are not limited to activated carbon, molecular sieves, silica gels, and activated alumina. Other useful adsorbents include pi complexation sorbents, silver and copper complexation adsorbents, zeolites, synthetic zeolites, mesoporous materials, activated carbons, high surface area coordination polymers, molecular sieves, carbon molecular sieves (CMS), silica gels, MCM, activated alumina, carbon nanotubes, pillared clays, and polymeric resins.

[0121] For systems where the incoming stream is a multi-component mixture of gases and the number of compounds to be separated cannot be removed by a single adsorbent, different layers of adsorbents can be used. For example, hydrogen purification from a methane stream in a reforming operation, where H_2 is contaminated with H_2O, CO_2, CO, and unconverted CH_4, can employ activated carbon to remove H_2O and CO_2 in combination with additional layers of different adsorbents used to increase the loading of CO.

[0122] Zeolites, molecular sieves, and carbon molecular sieves (CMS) can be used for most industrial separations employing PSA. Inorganic materials, like special kinds of titanosilicates, can be used for kinetic separations.

[0123] For systems specifically configured to separate ethane/ethylene and propane/propylene, exemplary types of adsorbents include zeolites/molecular sieves and pi complexation sorbents. Zeolites/molecular sieves can be used for kinetic separation, such as separation based on higher diffusivity of olefins over that of paraffins. The use of 4A zeolite is one such example. For example, a three-bed system can be used to recover olefins from a stream containing 80-85% olefins and 10-15% paraffins, using a 4A type zeolite at elevated temperatures (e.g., the Petrofin process). Pi complexation sorbents, such as $AgNO_3/SiO_2$, can give excellent results as compared to 4A zeolite. PSA units as discussed herein can employ a range of different sorbents, including but not limited to a zeolite/molecular sieve sorbent, a pi complexation based sorbent, a carbon molecular sieve sorbent or any other form of activated carbon, carbon nanotubes, polymeric resin based sorbents, or other sorbents.

[0124] Adsorbents can be selected based on a number of different criteria. Adsorbent selection criteria can include capacity for the target components (e.g., affinity for the desired components to be separated from the multi-component feed stream), selectivity between components competing for same adsorption sites, regenerability of the adsorbent, (e.g., the ability of the adsorbent to release the adsorbed target components at a reasonable pressure rate of gas diffusion into the adsorbent—this can also affect the size of the bead that is chosen and consequently the pressure drop across the bed; an insufficient diffusion rate can require smaller diameter beads that can result in higher pressure drop and hence increased operating costs), and chemical compatibility (e.g., selecting an adsorbent resistant to chemical attack that may poison or destroy the adsorbent, such as liquid hydrocarbons causing physical breakdown of the adsorbent resulting in loss of efficiency and back pressure).

[0125] Separations, such as of ethylene and propylene, can be conducted using an amorphous fluoropolymer based membrane. Facilitated transport using silver ions can selectively transport ethylene and/or propylene. The membrane can be a part of a membrane contactor system. The feed to the system can be of a low to moderate olefin concentration. The feed to the system can contain other hydrocarbons, including, but not limited to, methane, ethane, propane, butane, butenes, C_5 components and higher hydrocarbons. The feed can also contain CO_2, CO, H_2, and inert components, such as nitrogen.

CO_2 Separation

[0126] There are many technologies available for CO_2 capture, such as from flue gases, natural gas, or from any process gas rich in CO_2. Various processes for post-combustion or pre-combustion capture can be used reduce CO_2 emissions. FIG. **5**A, FIG. **5**B, FIG. **5**C, and FIG. **5**D show exemplary schematics of different separation methods available to separate CO_2 from a process gas or a flue gas.

[0127] OCM processes can utilize an amine based absorption system for CO_2 removal, which can be followed by use of a caustic scrubber to obtain high degree of separation. The amine system is prone to corrosion, solvent degradation, and above all, has high energy requirements. Separations with sorbents and/or solvents can involve placing the CO_2 containing gas in intimate contact with a liquid absorbent or a solid sorbent that is capable of capturing the CO_2. As shown in FIG. **5**A, a stream with CO_2 **510** can be directed into a capture vessel **501**, where it contacts sorbent which captures CO_2 from the stream. The stream, with reduced or removed CO_2, can then exit **511** the vessel. Sorbent **512** loaded with captured CO_2 can be transferred to a sorbent regeneration vessel **502** where it releases the CO_2 after being heated (e.g., with the use of energy **513**), after a pressure decrease, or after any other change in the conditions around the sorbent, thereby regenerating the sorbent. Spent sorbent **515** and CO_2 **516** can be removed from the vessel, and make up sorbent **514** can be added. After the regeneration step the sorbent can be sent back to capture more CO_2 in a cyclic process. The sorbent can be a solid. Solid sorbent can remain in a single vessel rather than being cycled between vessels; sorption and regeneration can be achieved by cyclic changes (e.g., in pressure or temperature) in the vessel where the sorbent is contained. A make-up flow of fresh sorbent can be used to compensate for natural loss of activity and/or sorbent losses.

[0128] Amine scrubbing technology can be used to remove acid gases from process gases. Primary amines (e.g., MEA, DGA), secondary amines (e.g., DEA, DIPA), tertiary (e.g., MDEA, TEA), sterically hindered amines, chilled ammonia, potassium carbonate, and other compounds can be used to remove CO_2 from process gases. Traditional amine based systems can be characterized by high energy requirements and solvent degradation. Improved solvents, which can require less energy for regeneration of the solution, include the Benfield process and two stage diethanolamine. Combination with an OCM process can reduce the energy consumption of amine scrubbing processes. Improved solvents can reduce the energy requirements by as much as 40% compared to the traditional MEA solvents. This has the potential of reducing the energy, and hence steam, consumption of the OCM process, thereby increasing the amount of steam available for export from the OCM, or making alternative waste heat recovery methods feasible.

[0129] Physical absorption solvents used can include but are not limited to glycol dimethylethers (e.g., Selexol) and propylene carbonate (e.g., IPTS/EC). Regeneration of the solution can be performed by vacuum flashing and air stripping; this approach can consume significantly less energy than in chemical absorption. In using physical solvents CO_2 can be released mainly by depressurization, thereby avoiding the high heat of consumption of amine scrubbing processes.

[0130] Mixed or hybrid solvents can include but are not limited to Sulfinol (sulfolane, water, and amine), such as Sulfinol-M and Sulfinol-X.

[0131] Solid adsorbents, such as zeolites and activated carbon, can be used to separate CO_2 from gas mixtures. In pressure swing adsorption (PSA), a gas mixture can flow through a packed bed of adsorbent at elevated pressure until the concentration of the desired gas approaches equilibrium. The bed can be regenerated by reducing the pressure. In temperature swing adsorption (TSA), the adsorbent can be regenerated by raising its temperature. In general usage, adsorption is not yet considered attractive for large scale separation of CO_2 because the capacity and CO_2 selectivity of available adsorbents are low. However, when the OCM process is a recycle process, an adsorbent based separation method can be used to separate bulk CO_2 followed by consuming the remaining CO_2 in a methanation reactor system, or by using a caustic scrubber to treat the remaining CO_2.

[0132] Many different types of membrane materials (e.g., polymeric, metallic, ceramic) can be used for CO_2 capture to preferentially separate CO_2 from a range of process streams. FIG. **5**B shows an exemplary schematic of separation of CO_2 from a gas stream **530** in a separation vessel **520** using a membrane **521**. CO_2 can be removed from the stream via the membrane, and CO_2 and other gases can exit the vessel in separate streams **531** and **532**. The main limitation of currently existing membranes is the occurrence of severe plasticization of the membrane in the presence of high pressure CO_2. Due to excessive swelling of the polymer membrane upon exposure to CO_2, the performance (e.g., selectivity) can decrease significantly, thus reducing the purity of the CO_2 and consequently reducing the possibilities for reuse of the gas. Energy requirements can be significantly lower for membrane based technologies; for example, membrane technology can use 70-75 kWh per ton of recovered CO_2 compared to significantly higher values for pressure swing adsorption (e.g., 160-180 kWh), cryogenic distillation (e.g., 600-800 kWh), or amine absorption (e.g., 330-340 kWh), making membrane technology an attractive option for integration with OCM for CO_2 separation.

[0133] Membrane and amine technologies can be combined to form a hybrid process to capture CO_2. Micro-porous hollow fiber membranes can be used for CO_2 separation using amine-based chemical absorption processes. Micro-porous membranes can be used in a gas-liquid unit where the amine solution is contacted with CO_2 containing gas. Using the membrane can lead to a reduction in the physical size and weight of the gas-liquid contacting unit. The separation is based on reversible chemical reaction, and mass transfer occurs by diffusion of the gas through the gas/liquid interface as in traditional contacting columns. Such a hybrid membrane contactor can provide a high contact area between gas and liquid, reduce or essentially eliminate foaming and flooding problems, and give better operational flexibility while reducing solvent degradation problems.

[0134] A membrane contactor can combine the advantages of membrane technology and solvent absorption for CO_2 separation. A membrane contactor is a combination of advanced membrane techniques with an effective absorption process. A membrane contactor is a hybrid mass exchanger where a porous membrane separates two phases. The selective sorbent performs the separation while the membrane facilitates the mass exchange process by expanding the phase contact surface area. The modified surface properties can improve the selectivity of the process by selectively inhibiting the transport of one of the mixture constituents. Compared to a conventional column device, membranes can allow for up to five times increase in yield per unit volume. Since the sorptive liquid flows within capillaries and both phases are not directly contacting each other, membrane absorbers can operate in any spatial configuration (horizontal or vertical) and at any flux rations between both phases. Also, there is no flooding or uneven packing moisturization. Since the system operates with unchanging yields, independent of the diameter and height; scaling up is fairly simple. Membranes used can be micromembranes or ultrafiltration membranes made a variety of different polymer and ceramic materials. Polypropylene fiber membranes can be used to separate CO_2 from CH_4, for example by using amines like MEA as absorption liquid. Hollow fiber membranes, such as porous polypropylene, perfluoroalkoxy (PFS), and asymmetric poly(phenylene oxide) hollow fiber membranes with a dense ultrathin skin at the outside of the membrane can also be used. Besides amines as absorption liquid, other absorption liquids may be used, such as aqueous sarcosine salt solutions, for example in a gas-liquid membrane contactor system. A membrane contactor can be used to separate the CO_2 from the OCM effluent in which CH_4 is the major component. Membrane contactors can also be used for separation of olefins and paraffins, and the separation of CO_2 from light gases.

[0135] An activator, such as piperazine, diethanolamine, and arsenic trioxide, can be used to further enhance the effectiveness of CO_2 capture. DGA and tertiary amines may provide more improvement than primary or secondary amines.

[0136] Gas selective poly ionic liquid membranes, which are polymerized room temperature ionic liquids (RTIL), can be used to be highly selectively separate CO_2. RTILs can be synthesized as a monomer and subsequently polymerized to obtain gas selective membranes. The ionic nature of the polymers can result in tight arrangements between the oppositely charged ionic domains in the poly RTIL, which can eventually prevent the membrane from excessive swelling and deterioration of its performance at increased pressure and/or temperature. This intrinsic property of poly RTIL can be used to increase the resistance against plasticization and to restrict strong swelling of the polymer membrane to maintain its permeation properties in the presence of a strong plasticizing agent such as CO_2 at higher pressures. For example, an imidazolium-based poly RTIL can be used as base material and the length of the alkyl chain can serves to strengthen or weaken the ionic interactions within the poly RTIL. High pressure mixed CO_2/CH_4 gas separation measurements at different temperatures.

[0137] Gas components like CO_2, from N_2 or CH_4 can be separated with supported ionic liquid membranes. Ionic liquids are molten salts with a very low melting point (many are liquids at room temperature). Many ionic liquids show a high solubility for carbon dioxide and hence can be highly suitable for use with an OCM process. For example, ionic liquids can include but are not limited to imidazolium, pyrollidinium, pyridinium, cuanidinium, phosphonium, morpholinium, piperidinium, sulfonium, ammonium, hexafluorophosphate, tetraflouroborate, alkylsulphate, triflate, dicyanamide, bis(trifluoromethylsulfonyl)imide, and combinations thereof. Specific advantages of ionic liquids include very low to negligible vapor pressure, good dissolution characteristics for many substances, and lack of flammability or toxicity. Ionic liquids can have good thermal, mechanical and chemical stability as well as favorable densities and viscosities. The required specifications can be adjusted easily by the large number of possible combinations of anions and cations when formulating an ionic liquid. Ionic liquids can be used as chemical solvents, catalysts, electrolytes in fuel cells as well as for gas-separation and storage by absorption. Ionic liquid membrane systems can comprise an adequate porous support material, e.g. a polymer film, coated by ionic liquids. The system can separate CO_2 and sulfur compounds from different gas mixtures. Competitive selectivity and permeability are obtained for the separations.

[0138] Novel membrane materials, such as polyetherimides, can be used as membrane material with improved plasticization resistance for CO_2 removal, for example with an OCM process. Other membrane materials that can be used include, but are not limited to, polymeric membranes based on or comprising polyamides, polysemicarbazides, polycarbonates, polyarylates, polyaniline, poly(phenylen oxide), polysulfones, polypyrrolones, or combinations thereof. In some cases, the polymeric membrane is solvent resistant and can reduce the plasticization effects of hydrocarbons in the feed stream, e.g., polyketone, polyether ketone, polyarylene ether ketone, polyimide, polyetherimide, and/or polyphenylene sulphide, which have intrinsic solvent inertness and can therefore withstand organic rich operation conditions.

[0139] An adequate porous support material, e.g. a polymer film, coated by ionic liquids can be used in continuous separation of CO_2 and sulfur compounds from different gas mixtures, including a methane rich stream. This separation can improve the efficiency of OCM processes. The OCM reactor effluent can enter the supported ionic liquid separation subsystem, and CO_2 and other contaminants can be removed from the process gas. Other contaminants can include but are not limited to traces of sulfur compounds, inerts, CO, SO_2, H_2S, and tetrahydrothiophene (THT).

[0140] CO_2 can be separated from other gases by cooling and condensation, for example as shown in FIG. **5**C. A stream containing CO_2 **550** can be compressed in a compressor **540**, and the compressed stream **551** can be directed to a distillation column **541**. Some components can be recovered from the overhead stream **552**, with heat recovered in a heat exchanger **542**. Other components can be recovered from the bottoms **555**. Cryogenic separation is widely used commercially for streams that already have a high concentration of CO_2 (typically greater than 90%). Cryogenic separation of CO_2 has the advantage that it enables direct production of high purity liquid CO_2 that can be used as a feedstock to convert the carbon to higher value hydrocarbons, or otherwise be captured. The amount of energy required can be high, and water may need to be removed before the feed gas is cooled.

[0141] Low temperature distillation can give better results when there is a high concentration of CO_2 in the feed gas. For the OCM process gas, the CO_2 concentration can be increased by, for example, having a recycle stream, or by using a modified OCM reactor where excess CO_2 is used as a quench medium for the reaction heat. Low temperature separation can refer to separations using temperature levels above −90° C.

[0142] As shown in FIG. **5**D, another method of the present disclosure for removing CO_2 from the OCM system involves a two-step CO_2 removal. The first step can be a bulk CO_2 removal, followed by the recovery section (e.g., cryogenic fractionation system), and then a second polishing step to remove the CO_2 from the purified ethylene product to meet the polymer grade ethylene specifications.

[0143] As shown in FIG. **5**D, oxygen **560** can be fed with methane **562** into an OCM reactor **564**. The effluent can be compressed **566**. The first (bulk) CO_2 removal **568** can be carried out before the cryogenic section. The first CO_2 removal lowers the CO_2 content to a level tolerable in the cryogenic de-methanizer **570**. The demethanizer is operated at conditions that ensure that no CO_2 freezes and all of the residual CO_2 that is not removed in the bulk separation **568** is separated with the heavy C_{2+} stream at the bottom and sent to the de-ethanizer **572**. An acetylene hydrogenation system **574** and a C_2 splitter **576** can follow the de-ethanizer **572** to produce high purity ethylene **578**. The high purity ethylene can contain the residual CO_2 that is not removed by the first CO_2 removal unit **568**. This residual CO_2 can be removed by a second CO_2 removal step **580** to produce polymer grade ethylene **582**. In some cases, a depropanizer **584** can be used to produce a C_{3+} product **586**, ethane **588** can be recycled to (the cracking section of) the OCM reactor **564**, and C_1 compounds **590** can be methanated **592** and returned to the OCM reactor **564** or purged **594**. In some cases CO_2 from the first **568** or second **580** CO_2 removal units can be send to the methanation reactor **592** (not shown).

[0144] The first (bulk) CO_2 separations system can be a membrane or a PSA system, an amine removal system, or any other solvent based CO_2 removal system as described herein. The final CO_2 removal step can be a caustic tower, a membrane based system, a PSA based system, or any other CO_2 removal system as described herein. The ethylene product CO_2 removal system **580** can be followed by further drying and/or purification steps.

[0145] One advantage of the two step process described herein can be energy saving that arise from decreasing the gas volumes being processed for the final CO_2 removal step. If CO_2 removal is done entirely upstream of the demethanizer, the energy consumption is much greater than described in FIG. **5**D because the entire methane rich recycle stream dilutes the CO_2. When final CO_2 removal is performed at the back-end, the ethylene product has a far lower flow rate and hence the final CO_2 removal step is more energy efficient.

[0146] The concentration of CO_2 going into the de-methanizer (following the first CO_2 removal unit) can be any suitable amount (i.e., such that CO_2 doesn't freeze in the de-methanizer). In some embodiments, the concentration of CO_2 going into the de-methanizer is about 0.1 mol %, about 0.2 mol %, about 0.3 mol %, about 0.4 mol %, about 0.5 mol %, about 0.6 mol %, about 0.7 mol %, about 0.8 mol %, about 0.9 mol %, about 1.0 mol %, about 1.2 mol %, about 1.4 mol %, about 1.6 mol %, about 1.8 mol %, about 2.0 mol %, about 2.2 mol %, about 2.4 mol %, about 2.6 mol %, about 2.8 mol %, about 3.0 mol %, about 3.5 mol %, about 4.0 mol %, or about 5.0 mol %. In some cases, the concentration of CO_2 going into the de-methanizer is at least about 0.1 mol %, at least about 0.2 mol %, at least about 0.3 mol %, at least about 0.4 mol %, at least about 0.5 mol %, at least about 0.6 mol %, at least about 0.7 mol %, at least about 0.8 mol %, at least about 0.9 mol %, at least about 1.0 mol %, at least about 1.2 mol %, at least about 1.4 mol %, at least about 1.6 mol %, at least about 1.8 mol %, at least about 2.0 mol %, at least about 2.2 mol %, at least about 2.4 mol %, at least about 2.6 mol %, at least about 2.8 mol %, at least about 3.0 mol %, at least about 3.5 mol %, at least about 4.0 mol %, or at least about 5.0 mol %. In some cases, the concentration of CO_2 going into the de-methanizer is at most about 0.1 mol %, at most about 0.2 mol %, at most about 0.3 mol %, at most about 0.4 mol %, at most about 0.5 mol %, at most about 0.6 mol %, at most about 0.7 mol %, at most about 0.8 mol %, at most about 0.9 mol %, at most about 1.0 mol %, at most about 1.2 mol %, at most about 1.4 mol %, at most about 1.6 mol %, at most about 1.8 mol %, at most about 2.0 mol %, at most about 2.2 mol %, at most about 2.4 mol %, at most about 2.6 mol %, at most about 2.8 mol %, at most about 3.0 mol %, at most about 3.5 mol %, at most about 4.0 mol %, or at most about 5.0 mol %. In some cases, the concentration of CO_2 going into the de-methanizer is between any of the two values described above, for example, between about 0.5 mol % and about 2.0 mol %.

[0147] FIG. **6** shows a schematic of CO_2 separation using distillation. OCM reactor effluent **606** can be fed to a treatment unit **601**, such as a molecular sieve dryer, a sulfur removal bed, or an acetylene removal bed. The treated gas is fed to the first distillation column **602** that separates the bulk of the methane from the CO_2 and other heavier hydrocarbons. Depending on the CO_2 concentration in the stream **606**, the bottom stream **608** may contain at least about 50%, 60%, 70%, 80%, 90%, or more (or any value in between) of the incoming CO_2. The overhead from 607 contains majority of the methane and other light gases and is fed to the column **603**. Column **603** further recovers methane rich gas **611**, which can be the feed to a methanation system. The bottoms product **616** may be recycled or sent as a purge to the fuel gas system. The CO_2 rich gas **608** is distilled in the CO_2 column **604** to recover pure CO_2 **609** in the overhead. The bottoms product **610** can contain some methane along with ethane, ethylene, and other heavier hydrocarbons, and can be sent to recover the ethylene product in a separator **605**. The CO_2 product can be sent to methanation unit, and a part of the CO_2 can be recycled to achieve the desired concentration of CO_2 in the feed stream **606**. Such a CO_2 distillation sub system can offer many benefits, including but not limited to reducing the loop size of the OCM process considerably, as the function of the existing cryogenic demethanizer can be reduced by a large extent. Additionally, amine and caustic systems can be replaced by cryogenic or low temperature distillation systems.

[0148] Alkaline salt-based processes can be used for carbon dioxide removal. These processes can utilize the alkali salts of various weak acids, such as sodium carbonate and potassium carbonate. These processes can provide advantages such as low cost and minimal solvent degradation. Processes that can be used for H_2S and CO_2 absorption include those using aqueous solutions of sodium or potassium compounds. For example, potassium carbonate can absorb CO_2 at high temperatures, an advantage over amine-based solvents.

[0149] Hot potassium carbonate (K_2CO_3) solutions can be used for the removal of CO_2 from high-pressure gas streams, among other applications. Potassium carbonate has a low rate of reaction. To improve CO_2 absorption, mass transfer promoters such as piperazine, diethanolamine, and arsenic trioxide can be used. Less toxic promoters such as borate can also be used, for example with flue gas streams (see, e.g., Ghosh et al., "Absorption of carbon dioxide into aqueous potassium carbonate promoted by boric acid", Energy Procedia, pages 1075-1081, February 2009, which is hereby incorporated by reference in its entirety). To limit corrosion, inhibitors can be added. These systems can be known as activated hot potassium carbonate systems. Licensed hot activated potassium carbonate systems include the Benfield and the Catacarb process. The processes can be used for bulk CO_2 removal from high-pressure streams, but can also produce high-purity CO_2.

[0150] Flue gas impurities such as SOx and NOx can reduce the operational efficiency of the potassium carbonate as a solvent. SO_2 and NO_2 may not able to be released from the solvent under industrial conditions. Selective precipitation of the impurity salts formed by SOx and NOx can be used to remove such compounds (see, e.g., Smith et al., "Recent developments in solvent absorption technologies at the CO2CRC in Australia" Energy Procedia, pages 1549-1555, February 2009, which is hereby incorporated by reference in its entirety).

[0151] A variety of materials can be used as CO_2 sorbents through chemical reactions and physical absorptions, including but not limited to soda-lime, active carbon, zeolites, molecular sieves, alkali metal oxides, silver oxide, lithium oxide, lithium silicate, carbonates, silica gel, alumina, amine solid sorbents, metal organic frameworks and others.

[0152] Physical impregnation of CO_2-reactive polymers, such as tetraethylene pentamine or polyethyleneimine, inside a porous support, such as alumina, pumice, clay or activated carbon, can be used for CO_2 removal. Amine based sorbents can be easily regenerated. Alternatively, a mixture of an amine compound with a polyol compound can be impregnated in a porous support. The polyol compound can be used to increase the CO_2 desorption rate of the amine. The supported amine-polyol sorbent can comprise at least about 1 wt %, 5 wt %, 10 wt %, 15 wt %, 20 wt %, 25 wt %, 30 wt %, 35 wt %, or more amine and/or polyol. In some cases, the supported amine-polyol sorbent can comprise from about 1 wt % to about 25 wt % amine and from about 1 wt % to about 25 wt % polyol, with the balance being the support. Solid sorbent can adsorb and desorb CO_2 a relatively high rates at ambient temperatures. Enhanced CO_2 cyclic removal capacities in either dry or humid air flows can further be achieved by using a solid sorbent at an increased amine concentration of amines from about 35 wt % to about 75 wt %.

[0153] Solid sorbents that can selectively remove multiple gases can be used to remove CO_2, H_2O, nitrogen oxides, and hydrocarbons. This can be achieved by using composite adsorbents, for example by using a mixed adsorbent of alumina and zeolite to remove CO_2 and H_2O simultaneously.

[0154] CO_2 can be separated from flue gas using an ion pump method instead of relying on large temperature and pressure changes to remove CO_2 from a solvent. Ion pump methods can dramatically increase the overlying vapor pressure of CO_2. As a result, the CO_2 can be removed from the downstream side of the ion pump as a pure gas. The ion pumping can be obtained from techniques including but not limited to reverse osmosis, electro dialysis, thermal desalination methods, or an ion pump system having an oscillation flow in synchronization with an induced electric field.

[0155] By making use of energy such as renewable or nuclear energy, carbon dioxide and water can be recycled into sustainable hydrocarbon fuels in a non-biological process. Various pathways can enable such a conversion, for example by H_2O and CO_2 dissociation followed by fuel synthesis. The methods of dissociation can include heat, electricity, and solar driven methods such as thermolysis, thermochemical loops, electrolysis, and photoelectrolysis. High temperature electrolysis can make efficient use of electricity and heat, provide high reaction rates, and integrate well with fuel synthesis.

[0156] Synthetic analogues of enzymes as a polymer thin film supported on micro-porous substrates can be used to separate CO_2 from gas mixtures. For example, a polymer thin film containing carbonic anhydrase mimicking sites can supported on a porous substrate and can separate CO_2 from a stream containing O_2 and N_2. The system can be, for example, about 30% lower in cost compared to amine-based systems.

CO_2 Anti-Sublimation

[0157] Carbon capture (e.g., CO_2 capture) can be used to reduce greenhouse gas (GHG) emissions. For example, carbon can be captured from stationary fired sources (e.g., flue gas emissions from fired equipment in power plants and industry). CO_2 capture technologies may be cost prohibitive. The cost of disposing CO_2 can be divided into: separation (for example, the cost range for CO_2 separation from flue gas using amine absorption is \$30-\$50 per ton of CO_2); compression (for example, CO_2 is compressed typically to 2000 psi for pipeline delivery and compression costs can range from \$8-\$10 per ton of CO_2); pipelines (for example, CO_2 pipelining costs can range from \$0.7 to \$4 per ton CO_2 per 100 km); and injection (for example, compressed CO_2 injection to geological reservoirs on land can cost from \$2-\$8 per ton CO_2.

[0158] The separation of process CO_2 from the OCM process can be simpler and less expensive than a CO_2 capture from a flue gas system. Flue gas CO_2 capture may have inherent challenges, which are absent from the OCM system CO_2: low pressure (for example, the typical flue gas pressures are at or about atmospheric pressure, and therefore involve high volumes that can need to be compressed and treated, resulting in bigger and hence more expensive equipment); high temperature (for example, flue gases can exit a furnace or heater at a high temperature); oxygen content (for example, oxygen can cause corrosion problems); NOx and fly ash content (for example, this can cause degradation in certain systems); and CO_2 concentration (for example, in flue gases CO_2 concentration can range from 10%-15%; in OCM CO_2 concentrations can be 95% and higher post amine system or 4-6% at OCM outlet).

[0159] To integrate well with OCM, a CO_2 separation process can be: less energy and capital intensive than current designs (e.g., amine system); scalable downwards and upwards; capable of reliable and continuous operation; able to take advantage of high CO_2 concentrations and convert to high purity CO_2, which can be used as a feedstock for other operations.

[0160] CO_2 anti-sublimation can be used to remove CO_2 (e.g., from flue gas). CO_2 anti-sublimation can use an SO_2 removal unit followed by a water cooling step. The water can be eventually removed, for example first as liquid then below the triple point as ice. Dry flue gas can be further cooled until CO_2 precipitates. The process can employ anti-sublimating CO_2 on a low temperature surface, thus transforming the carbon dioxide from its gaseous phase to a solid phase frosted on a cold surface. Anti-sublimation can allow CO_2 capture at a pressure slightly higher than atmospheric. CO_2 anti-sublimation can be used with a flue gas system (flue gas composition, e.g., in mol %: CO_2 15%, H_2O 13%, N_2 70% and O_2 3%) at various temperatures (e.g., about 51° C.).

[0161] The triple point of CO_2 is −56.4° C. and 5.11 atm. For 100% pure CO_2 at a pressure P' (where P' is less than 5.11 atm) the frosting temperature can be given by $T'=(P'-15.6)*(22.1/4.11)$. Accordingly, for a pressure of 4.5 atm, $T=-59.6°$ C.

[0162] The sublimation temperature of a substance within a gas mixture can depend on its partial pressure (its corresponding concentration within the mixture). Table 1 shows frosting temperatures at different exemplary CO_2 concentrations.

TABLE 1

Frosting temperature versus concentration.

Concentration (% v/v)	100	10	1	0.1
Frosting temperature (° C.)	−78.5	−103.1	−121.9	−136.7

[0163] For use in an OCM process, a CO_2 anti-sublimation unit may encounter higher pressure of OCM effluent (e.g., feed to CO_2 capture system), lower CO_2 concentration, and higher hydrocarbon content (e.g., methane, ethane, ethylene). Lower CO_2 concentration can be addressed by a recycle.

Process Configurations

Electrolysis to Generate Oxygen and Hydrogen for OCM Process

[0164] Electrolysis can be used to produce industrial hydrogen. OCM processes can have a lot of synergistic benefit from deploying a water electrolysis subsystem with the OCM process. The water electrolysis unit can replace an air separation unit (ASU) to supply the oxygen required for the OCM process. The products from the electrolytic unit can be consumed within the OCM process: oxygen can be consumed within the OCM reactor and hydrogen can be used in a methanation reactor. Availability of more hydrogen in the methanation unit has the potential to increase the carbon efficiency to about 100%, by converting the CO_2 produced in the OCM reaction to methane, which can be recycled back to the OCM reactor. The OCM unit can be a net exporter of high purity excess hydrogen, after consuming the entirety of the CO_2 produced in the OCM Process.

[0165] The water electrolysis subsystem can be an electrolytic cell employing alkaline water electrolysis, a proton exchange membrane electrolysis system, or a steam electrolysis system. The electricity source to the electrolytic sub system can be renewable, such as photo voltaic/solar power, which can make the entire system 100% carbon efficient with a zero carbon footprint. A storage system for oxygen, or a backup power supply, may be used to ensure the continuous supply of oxygen and hydrogen.

[0166] With steam electrolysis, a substantial part of the energy needed for the electrolysis process can be added as heat, which can be much cheaper than electric energy, and which the OCM reactor can produce in abundance. Therefore, integration of steam electrolysis can take advantage of the extra heat from the OCM reactor to provide energy for the steam electrolysis. This can be of particular benefit to OCM deployments where no additional steam or power is required.

[0167] FIG. **7** depicts an exemplary electrolysis subsystem combined with an OCM system. The electrolysis subsystem **701** can take water **710** and electric power **711** as inputs and generate pure oxygen **712** and hydrogen **713** as products. The oxygen can be fed into an OCM reactor **702** with a methane feed **714**, for conversion to higher hydrocarbon products including ethylene. The OCM product stream can be compressed in a compressor **704** and separated in a separations unit **705**. Higher hydrocarbon products **716** can be recovered from the separations unit, and other compounds such as methane and CO_2 can be recycled **717** and/or purged **718**. The recycle stream can be directed to a methanation unit **703**, which can generate methane **715** using the hydrogen from the electrolysis subsystem. The extra hydrogen that is now available to the methanation unit can enable the conversion of most or all of the CO_2 produced in the OCM process to methane, which can drive the process to a higher efficiency. The process can also be almost 100% emission free. The CO_2 produced in the process that may be discarded as waste may be converted to methane and hence to ethylene in the OCM reactor.

Different Quench Media for the OCM Reaction

[0168] The OCM reaction is highly exothermic. Various quenching media can be used to extract the OCM reaction heat. For example, CO_2 can be injected to extract the heat, which results in the OCM effluent containing excess CO_2, such effluent can be suitable for the advanced CO_2 recovery methods described herein. FIG. **8** shows an exemplary system where CO_2 **814** is removed from an OCM product stream **812** (generated in an OCM unit **801** from an oxygen stream **810** and a methane stream **811**) in a CO_2 separation unit **802** and recycled from back to the OCM reactor **801**. A waste gas or purge stream **815** can also be removed from the CO_2 separation unit. The OCM product stream **813** can then be separated in a separations unit **803** into a product stream **816** comprising ethylene and a purge and/or recycle stream **817**. Separation methods can include low temperature separation, membrane separation, or other separation methods discussed herein. The OCM loop can be decreased to just a CO_2 recycle stream. The system can also comprise a methanation unit (not shown).

[0169] Such an approach can provide advantages including a smaller recycle loop and more efficient CO_2 removal methods, resulting in lower capital expenditure (CAPEX). This can also result in the feasibility of small distributed scale OCM units, since after the removal of excess CO_2, the relatively richer ethylene stream needs fewer treatment and recovery steps.

Heat Recovery

[0170] Waste heat from the OCM process can be used to generate superheated high pressure steam that can be used in the process, exported to other users on site, or can be used to generate power. Excess process heat can also be used to preheat the feed streams. Other uses for excess heat can be less capital intensive, and offer a greater operational flexibility and low maintenance. Thermoelectric energy conversion can be used to convert waste heat to power. Example uses for waste heat include single fluid rankine cycles (e.g., steam cycle, hydrocarbons, and ammonia), binary/mixed fluid cycles (e.g., ammonia/water or mixed hydrocarbon cycle).

Organic Rankine Cycle

[0171] The organic Rankine cycle (ORC) can be used to generate power from heat. In ORC, an organic component is used instead of water. The organic compound can be a refrigerant, a hydrocarbon (e.g., butane, pentane, hexane), silicon oil, or a perfluorocarbon. The boiling point of the organic fluid can be lower than that of water, which can allow recovering heat at a lower temperature than in the traditional steam Rankine cycle.

[0172] Owing to the exothermicity of the OCM reaction, the ORC system can be deployed as a waste heat recovery method for use with OCM. Waste heat at relatively low temperature can be recovered by an intermediate heat transfer loop and used to evaporate the working fluid of the ORC.

[0173] FIG. **9** shows an exemplary OCM system with an ORC subsystem. The working fluid can be chosen which can be condensed with cooling water or air at normal atmospheric pressure. FIG. **9** shows the heat source as the OCM reaction heat from an OCM unit **901**. Heat can be recovered from the OCM product stream **910** in an evaporator **902**, and the product stream **911** can then be directed for downstream processing from the OCM unit. The heat recovered in the evaporator can be used to evaporate a working fluid stream **912**, which can then be directed to a turbine **903** to generate power in a generator **904**. From the turbine, the working fluid **913** can be directed to a condenser **905** and cooled using a cooling medium **914**. The cooled working fluid **915** can then be pumped by a pump **906** in a stream **916** back to the evaporator.

Thermoelectric Power Generation

[0174] The OCM process can make use of a heat exchanger with thermoelectric (TE) generators for heat recovery. A Thermoelectric Power Generator (TPG) can have four basic components: Heat source, P and N type semiconductor stack (or a TE module), heat sink (cold side), and an electrical load (output voltage). The TE module can include two or more of P-type and N-type semiconductor pellets connected in series or parallel depending on the served load.

[0175] The TE devices can be solid state engines that do not require any working fluid. Thermoelectric materials can provide efficiencies of up to 15% or greater. Thermoelectric generators coupled with heat exchangers can produce electricity even at temperatures as low as 350 K with low maintenance. TE modules can be used with OCM including large bulk TE modules and thin film or micro TE modules.

[0176] For high temperatures, micro TE modules can be used. Micro TE modules can also have low equipment weights. TE devices can be very reliable, scalable, and modular. Some TE modules can give best results at small scales. The OCM process can generate medium level waste heat that is highly suitable for a TE device to generate power.

OCM and ETL Systems with Advanced Separations Sub-Systems

[0177] PSA technology can be applied to processes including those involving a hydrocarbon stream containing a mix of the following hydrogen, carbon dioxide, carbon monoxide, methane, ethane, ethylene, propane, propylene, butanes, butenes and/or other higher hydrocarbons needing to be purified or separated into desirable products (e.g., ethylene, methane, hydrogen, or propylene).

[0178] Hydrocarbon streams can be produced via traditional refining and petrochemical processes. Hydrocarbon streams can be produced from OCM or ETL reactor systems.

[0179] The present disclosure provides the use of PSA in processes and systems for oxidative coupling of methane (OCM) and ethylene-to-liquids (ETL) operations, and the application of adsorbent based processes used in conjunction with OCM and ETL processes to generate significant process improvements and enhance the economic value of the processes. OCM systems are described in, for example, U.S. Patent Publication No. US 2015/0210610, which is entirely incorporated herein by reference. ETL systems are described in, for example, U.S. Patent Publication No. 2015/0232395, which is entirely incorporated herein by reference.

[0180] An OCM system, such as that shown in FIG. **10**, can include an OCM or OCM-post-bed-cracking (PBC) reactor **1002**, a process gas compression system **1003**, a process gas treatment system **1004**, a cryogenic separations system, and a methanation system **1001**. The feed to the OCM system can be an oxygen feed **1012** and a methane source feed **1011** (such as a natural gas feed stream or other methane source). In some cases, additional ethane feed can be supplied to the PBC section of the OCM reactor, where paraffins such as ethane in the OCM product stream and/or additional ethane can be cracked to olefins such as ethylene. The separations sub-system can comprise a series of fractionation towers, like a demethanizer **1005**, deethanizer **1006**, C_2 splitter **1007**, depropanizer **1008**, debutanizer, and others. Overhead **1013** from the demethanizer can be directed into the methanation system along with hydrogen or natural gas **1010** to produce additional methane. The bottoms stream **1014** from the demethanizer can be directed to the deethanizer. The overhead stream **1015** from the deethanizer can be directed to the C_2 splitter, and there split into ethylene **1016** and ethane **1017** streams. The bottoms stream **1018** from the deethanizer can be directed to the depropanizer, and there split into a C_3 product stream **1019** and a C_{4+} product stream **1020**. The cryogenic separations system can comprise additional ethylene and propylene refrigeration sub-systems to provide for the chilling requirements of the system.

OCM Process Standalone with Advanced Separations Systems

[0181] In certain cases, the separations section of the OCM system can be eliminated, or partially eliminated, by utilizing an advanced separations method as discussed in this application. The advanced separation method can be a PSA unit or a membrane based method, or a cryogenic system. FIG. **11** shows an exemplary schematic of OCM with a PSA unit. The PSA unit can separate methane, CO_2, CO, and/or H_2 from ethane, ethylene, propane, propylene, and/or higher hydrocarbons. Methane **1111** and oxygen **1112** can be directed into an OCM reactor **1102** and reacted to produce higher hydrocarbon products including ethylene. The OCM product can be compressed in a process gas compression system **1103**, treated in a process gas treatment system **1104**, and separated in the PSA **1105** into a product stream **1113** and a recycle stream **1114**. The recycle stream can be directed to a methanation unit **1101**, which can also receive a natural gas stream **1110** and produce methane for the OCM reactor. The extent of separation and degree of recovery can depend on the type of adsorbent(s), pressure differential, and number of PSA stages employed. The feed to the PSA unit can have one or more of the following components: H_2, N_2, O_2, CO, CO_2, CH_4, ethane, ethylene, acetylene, propane, propylene, butanes, butenes, butadiene, water, and higher paraffinic and olefinic components. The PSA product gas can comprise components including but not limited to: H_2, N_2, CO, CO_2, CH_4, O_2, ethane, ethylene and acetylene. PSA product gas can comprise components from about 0% to about 99.99% recovery. The PSA tail gas can comprise less than or equal to about 99.99%, 90%, 80%, 70%, 60%, 50% or less ethylene. The PSA tail gas can comprise at least or equal to about 50%, 60%, 70%, 80%, 90%, 99.99% or more ethylene. The PSA tail gas can comprise about less than or equal to about 99%, 90%, 80%, 70%, 60%, 50%, 40%, 30%, 20%, 10%, 1% or less ethane. The PSA tail gas can comprise at least about 0.1%, 1%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, 99% or more ethane. The PSA tail gas can comprise about less than or equal to about 60%, 50%, 40%, 30%, 20%, 10%, 1% or less methane, hydrogen, acetylene, N_2, O_2, H_2O and/or CO_2. The PSA tail gas can comprise at least about 0.1%, 1%, 10%, 20%, 30%, 40%, 50%, 60% methane, hydrogen, acetylene, N_2, O_2, H_2O and/or CO_2. Based on the process configuration, including the type of adsorbents employed, pressure differential and the operation, various different recoveries are possible.

[0182] As discussed above, the PSA unit can comprise one or more adsorbent materials that can be suitable to achieve the component recoveries. The sorbent can be a zeolite/molecular sieve based material, a carbon based sorbent, or a π-complexation sorbent. In some cases the sorbent material can be a polymeric resin, carbon nanotubes, and carbon fibers. The PSA unit can be configured to have layers of different sorbents so as to result in high recoveries from the multi-component feed streams to the desired products.

[0183] In certain cases the PSA can be a multi stage unit (see, e.g., FIG. **12**). In such a unit, an OCM reactor **1202** can receive a methane stream **1211** and an oxygen stream **1212**, and react the methane and oxygen to produce higher hydrocarbon products including ethylene in an OCM product stream. The OCM product stream can be compressed in a first compressor **1203** and directed to a first PSA separation **1204**. The tail gas **1214** from the first PSA can be compressed in a second compressor **1205** and fed to a second PSA separation **1206**, the tail gas **1216** from which can be compressed in a third compressor **1207** and separated in a third PSA separation **1208**. The tail gas from the third PSA can be the final purified stream **1217** containing ethylene up to 99.9% purity. PSA product streams **1213**, **1215**, and **1218** can be directed to recycle, such as via a methanation unit **1201** along with a natural gas stream **1210**. Each PSA stage can be a dual-bed PSA or a multi-bed PSA system.

[0184] In certain cases, the process requirements can dictate that only a limited amount of recovery is required in the PSA unit and subsequent recovery and purification is performed in a fractionation column or the gas is a feed for a downstream process unit. The downstream process unit can be an ETL system, an ethylene steam cracker system, a gas processing plant, NGL extraction plant, a refinery off-gas separations system, or other process unit.

Retrofits for OCM

[0185] OCM can be employed to convert a feedstock comprising methane to ethylene and other olefins. Historically, ethylene has been produced via steam cracking of gaseous or liquid hydrocarbon feedstocks like ethane, propane, LPG, or naphtha. As in most of the refining and petrochemical operations, a steam cracking operation can involve a cryogenic fractionation or a separations section that consists of a series of fractionation columns to successively recover various components at high product purity.

[0186] The present disclosure includes the application of PSA processes to an OCM retrofit of an existing ethylene cracker (e.g., steam cracker).

[0187] An example application for OCM combined with a PSA unit involves an existing petrochemical plant such as a steam cracker is considering low cost ways to add ethylene capacity. A typical revamp to add capacity may include addition of, or debottlenecking of, the existing fractionation towers for the entire flow addition for the revamp. However, as shown in FIG. **13**, the use of a PSA unit as disclosed herein can provide a low cost alternative to traditional revamps. An OCM unit with a PSA unit retrofitted to an existing steam cracker can be an effective way of adding ethylene capacity at a low marginal cost. The advantages of adding a PSA unit include that no additional cryogenic separation is required for the added capacity. For ethylene revamps, one of the key areas during debottlenecking may be the refrigeration systems and/or the fractionation columns, but utilizing the PSA to separate or pre-separate the additional product stream can result in a simpler and easier debottlenecking. As in shown in FIG. **13**, for example, the tail gas from the PSA can be sent to the cracker system where the ethylene is recovered.

[0188] FIG. **13** shows an example of an OCM process integrated with an existing ethylene cracker using a PSA system for separations. The OCM reactor **1301** takes in methane **1310** and oxygen **1311** and produces an OCM effluent **1312** having CO_2, CH_4 and C_2H_4, in some cases amongst other components, such as H_2 and CO. The OCM reaction can be exothermic and can produce steam **1313**. The OCM effluent can be compressed in a compressor **1302** and optionally treated in an acid gas removal system **1303**, and fed into a pressure swing adsorption (PSA) unit **1304**. In some cases the acid gas removal system may have an additional knock out drum to condense and separate any condensates and water. It also can include a drier to remove water. The PSA unit can produce a product stream that can include H_2, CH_4, ethane, CO_2 and CO. The overhead stream **1315** can be fed into a methanation subsystem **1305** (e.g., methanation reactor) to provide methane for the OCM reactor, and some of the overhead stream can be purged **1316** to a fuel gas system, for example. Additional methane can be provided by way of a natural gas stream or other methane stream. The PSA tail gas **1317** can comprise most of the ethylene, the content of which may range from about 50% to about 99.9% depending on the process configuration and operation of the PSA system. The PSA tail gas can also comprise H_2, CO, CO_2, CH_4, ethane, propane, propylene, butanes, butenes, and other components. The process of FIG. **13** can further include an existing ethylene cracker **1306**. The PSA tail gas can be fractionated using existing separations capacity in the ethylene cracker. The heavy components can be processed in the fractionation towers of the ethylene cracker, optionally first being compressed in the existing process gas compressor of the ethylene cracker. In some cases, the heavy components stream can be routed to the CO_2 removal unit of the existing ethylene cracker subsystem to meet the CO_2 specification. The OCM reactor can receive a C_2 recycle stream **1319** from the cracker complex.

[0189] The combination of a new OCM unit and an existing ethylene cracker can provide synergistic benefits. It can provide for a low cost alternative to add ethylene capacity to the existing cracker. In some cases, prior to retrofit of an ethylene cracker with OCM, the entire overhead from the existing demethanizer is used as fuel gas, and can now be available as one of the feeds to the methanation unit. In some cases, the demethanizer overhead off-gas comprises up to 95% methane, which can be converted to ethylene in the OCM reactor, hence increasing the total ethylene capacity. In some cases, the hydrogen content in the existing demethanizer overhead is substantial, and may be enough to meet the hydrogen requirement of the methanation unit.

[0190] In some cases, retrofitting an ethylene cracker with OCM reduces (or allows for reduction of) the severity of cracking in the existing cracker, enabling value addition by increasing the production of pyrolysis gasoline components in the cracker effluent, as the OCM reactor produces the ethylene that may be needed to achieve the total system capacity. The cracker can then be operated on high propylene mode to produce more propylene and at the same time meeting the ethylene production rate by the new OCM unit. This retrofit can result in greater flexibility for the ethylene producer with respect to the existing cracker operation.

[0191] In some instances, the overall carbon efficiency can be increased as the methane and hydrogen from the existing demethanizer off-gases can be utilized to convert the carbon dioxide and carbon monoxide to methane, which is fed to the OCM reactor.

[0192] In some instances, ethane and/or propane recycle streams from the existing cracker can be routed to the OCM unit (e.g., instead of the cracking furnaces). These recycle streams are typically routed to the cracking furnaces where they are cracked to extinction. This can provide an advantage over routing the recycle streams to OCM over the cracking furnace, such as higher selectivity to ethylene in the OCM process.

[0193] In certain cases, more than one stages or PSA columns may be employed to achieve higher recovery and higher product purity. As in shown FIG. **14**, for example, up to 99.9% recovery is possible using the multi stage PSA units. An OCM reactor **1402** can receive a methane stream **1410** and an oxygen stream **1411**, and react the methane and oxygen to produce higher hydrocarbon products including ethylene in an OCM product stream. The OCM product stream can be compressed in a first compressor **1403** and directed to a first PSA separation **1404**. The tail gas **1412** from the first PSA can be compressed in a second compressor **1405** and fed to a second PSA separation **1406**, the tail gas **1414** from which can be compressed in a third compressor **1407** and separated in a third PSA separation **1408**. The tail gas from the third PSA can be the final purified stream **1417** can be directed to a cracker unit, such as an existing cracker unit, where it can be processed and separated into an ethylene product stream **1418**, a propylene product stream **1419**, and an additional product stream **1420**. PSA product streams **1413**, **1415**, and **1416** can be directed to recycle, such as via a methanation unit **1401**, along with a demethanizer off gas stream **1421** from the cracker unit. Each PSA stage can be a dual-bed PSA or a multi-bed PSA system.

[0194] The application of a PSA unit to OCM systems, standalone or retrofits to existing facilities exhibits immense potential in terms of cost savings and ease of integration and retrofit to existing facilities.

ETL Systems

[0195] FIG. **15** shows various exemplary configurations for an OCM-ETL process. In the upper left, FIG. **15** shows a standalone skimmer configuration, where a methane stream **1505** can be directed into an OCM reactor **1501** with an oxygen feed **1506** and optionally an ethane feed **1507**. The OCM reactor product stream can be directed into a compressor **1502** and then into an ETL reactor **1503**. The ETL product stream can be directed into a gas separations unit **1504**, where it can be separated into a C_{2+} product stream **1508**, a C_{5+} product stream **1509**, and an overhead stream **1510** comprising methane which can be returned to a pipeline, sold to a consumer, or otherwise used. In the upper right, FIG. **15** shows a standalone recycle configuration, where a methane feed stream **1518** (e.g., from a natural gas pipeline) is directed into a treatment unit **1511** and then into a separations system (e.g., cryogenic) **1512**. A methane feed stream **1519** can be directed to an OCM reactor **1513**, while another methane stream **1520** can be purged or used for power generation. A C_{2+} stream **1521** can also be recovered from the separations system. An oxygen feed stream **1522** and optionally an ethane stream **1523** can also be directed into the OCM reactor, and the reactor can produce an OCM product stream. The OCM product stream can be directed into a compressor **1514** and then into an ETL reactor **1515**. The ETL product stream can be processed in a knockout drum **1516** or other separator to remove a C_{5+} product stream **1524**. The remaining ETL product stream can be directed to a compressor **1517** and recycled to the treatment unit. In the lower left, FIG. **15** shows a hosted skimmer configuration, where a methane stream **1532** can be directed from a separations system **1526** (e.g., cryogenic) into an OCM reactor **1527** with an oxygen feed **1533** and optionally an ethane feed **1534**. The OCM reactor product stream can be directed into a compressor **1528** and then into an ETL reactor **1529**. The ETL product stream can be directed into a gas separations unit **1530**, where it can be separated into a C_{2+} product stream **1535**, a C_{5+} product stream **1536**, and an overhead stream **1537** comprising methane which can be returned to a recompressor **1531**. In the lower right, FIG. **15** shows a hosted recycle configuration, where a methane stream is directed into a treatment unit **1538** and then into a separations system (e.g., cryogenic) **1539**. A methane feed stream **1546** can be directed to an OCM reactor **1541**, while another methane stream can be directed to a recompressor **1540**. A C_{2+} stream **1551** can also be recovered from the separations system. An oxygen feed stream **1547** and optionally an ethane stream **1548** can also be directed into the OCM reactor, and the reactor can produce an OCM product stream. The OCM product stream can be directed into a compressor **1542** and then into an ETL reactor **1543**. The ETL product stream can be processed in a knockout drum **1544** or other separator to remove a C_{5+} product stream **1549**. The remaining ETL product stream can be directed to a compressor **1545** and recycled **1550** to the treatment unit.

[0196] FIG. **16** shows similar configurations as FIG. **15**, with an added pressure swing adsorption (PSA) unit to pre-separate the OCM effluent to remove most of the methane, hydrogen, CO and CO_2 from the olefinic stream, which is then fed to the ETL reactor. This can result in a feed to the ETL reactor that is concentrated in olefins. Though the process remains similar, the entire ETL and separations train becomes considerably smaller; that is, larger capacities can be achieved in the same set-up or same footprint. In some cases this can improve the ETL reaction operation. In the upper left, FIG. **16** shows a standalone skimmer configuration, where a methane stream **1606** can be directed into an OCM reactor **1601** with an oxygen feed **1607** and optionally an ethane feed **1608**. The OCM reactor product stream can be directed into a compressor **1602** and then into a PSA unit **1603**. A light stream **1609** comprising methane, hydrogen, CO and CO_2 can be directed from the PSA back to a pipeline, sold to a consumer, or otherwise used. An olefinic stream can be directed from the PSA to an ETL reactor **1604**. The ETL product stream can be directed into a gas separations unit **1605**, where it can be separated into a C_{2+} product stream **1610**, a C_{5+} product stream **1611**, and an overhead stream **1612** comprising methane which can be returned to a pipeline, sold to a consumer, or otherwise used. In the upper right, FIG. **16** shows a standalone recycle configuration, where a methane feed stream **1628** (e.g., from a natural gas pipeline) is directed into a treatment unit **1620** and then into a separations system (e.g., cryogenic) **1621**. A methane feed stream **1629** can be directed to an OCM reactor **1622**, while another methane stream **1630** can be purged or used for power generation. A C_{2+} stream **1631** can also be recovered from the separations system. An oxygen feed stream **1632** and optionally an ethane stream **1633** can also be directed into the OCM reactor, and the reactor can produce an OCM product stream. The OCM product stream can be directed into a compressor **1623**, and at least a portion **1634** of the OCM product stream can be directed from the compressor into a PSA unit **1624**. A light stream **1635** comprising methane, hydrogen, CO and CO_2 can be directed from the PSA back to the treatment unit. An olefinic stream **1636** can be directed from the PSA to an ETL reactor **1625**. The ETL product stream can be processed in a knockout drum **1626** or other separator to remove a C_{5+} product stream **1637**. The remaining ETL product stream can be directed to a compressor **1627** and recycled to the treatment unit. In the lower left, FIG. **16** shows a hosted skimmer configuration, where a methane stream **1647** can be directed from a separations system **1640** (e.g., cryogenic) into an OCM reactor **1641** with an oxygen feed **1648** and optionally an ethane feed **1649**. The OCM reactor product stream can be directed into a compressor **1642** and then into and then into a PSA unit **1643**. A light stream **1650** comprising methane, hydrogen, CO and CO_2 can be directed from the PSA to a recompressor **1646**. An olefinic stream can be directed from the PSA to an ETL reactor **1644**. The ETL product stream can be directed into a gas separations unit **1645**, where it can be separated into a C_{2+} product stream **1651**, a C_{5+} product stream **1652**, and an overhead stream **1653** comprising methane which can be returned to the recompressor. In the lower right, FIG. **16** shows a hosted recycle configuration, where a methane stream is directed into a treatment unit **1660** and then into a separations system (e.g., cryogenic) **1661**. A methane feed stream **1669** can be directed to an OCM reactor **1663**, while another methane stream can be directed to a recompressor **1662**. A C_{2+} stream **1677** can also be recovered from the separations system. An oxygen feed stream **1670** and optionally an ethane stream **1671** can also be directed into the OCM reactor, and the reactor can produce an OCM product stream. The OCM product stream can be directed into a compressor **1664** and at least a portion **1672** of the OCM product stream can be directed from the compressor into a PSA unit **1665**. A light stream **1673** comprising methane, hydrogen, CO and CO_2 can be directed from the PSA back to the treatment unit. An olefinic stream **1674** can be directed from the PSA to an ETL reactor **1666**. The ETL product stream can be processed in a knockout drum **1667** or other separator to remove a C_{5+} product stream **1675**. The remaining ETL product stream can be directed to a compressor **1668** and recycled **1676** to the treatment unit.

[0197] The ETL reactor can be a tubular, packed bed, moving bed, fluidized bed, or other reactor type. An ETL reactor can be an isothermal or adiabatic reactor. The ETL system can benefit from a feed concentrated in olefins. The ETL reactor system can use a recycle stream to control and moderate the temperature increase in the reactor bed due to the highly exothermic nature of the ETL reactions. ETL systems are described in, for example, U.S. Patent Publication No. 2015/0232395, which is entirely incorporated herein by reference.

[0198] In some cases, one or more of the fractionation towers can be deemed redundant if using the PSA, as an example, a demethanizer may not be required and the sales gas or purge gas to fuel can be sent from the PSA itself.

Retrofit Applications for Midstream and Refining

[0199] Systems, such as those of FIG. **17**, can be integrated with an existing gas processing plant where one or more of the existing subsystems can be utilized. The utilization may arise from the fact that the existing subsystems are no longer used, or have an additional capacity available to allow for the integration.

[0200] FIG. **17** shows an exemplary application of an OCM-ETL system using a PSA system for pre-separations to an existing gas processing plant, where one or more existing sub systems may be utilized. As shown in FIG. **17**, the existing separations sub-system can be integrated with the OCM-ETL system to add value by converting natural gas to higher value liquid hydrocarbons. The PSA unit can be used to pre-separate the lighter components like methane, hydrogen, carbon monoxide, carbon dioxide, ethane, and other components, and the olefin rich stream can be sent to the ETL reactor that converts the olefins to higher molecular weight liquid hydrocarbons. One advantage of using a PSA system is the reduction in net additional feed to the existing separation system, which can be de-bottlenecked easily. If the separation system is no longer in use, addition of a PSA can bring about larger total capacities that can be achieved by adding larger OCM-ETL systems. A natural gas stream **1720** can be directed to a treatment unit **1701** and then into a separations system (e.g., cryogenic) **1702**. At least portion of a methane stream **1724** from the separations unit can be directed to an OCM reactor **1705**, while a portion of the methane stream can be directed to a compressor **1703** and used as sales gas **1721** or other purposes. A higher hydrocarbon stream can be directed from the separations system to a C_2 removal unit **1704**, which can produce a natural gas liquids stream **1722** and a C_2 stream **1723**. The C_2 stream can be fed into the OCM reactor with the methane stream and an oxygen stream **1725**, and reacted to form higher hydrocarbon products including ethylene. The OCM product stream can be directed into a heat recovery system **1706**, which can generate a high pressure superheated (HPSH) steam stream **1726**. The OCM product stream can then be directed to a knockout drum to recover a condensate stream **1727**. The OCM product stream can then be directed to a compressor **1708**, which can operate using the HPSH steam stream. From the compressor, the OCM product stream can be directed to a PSA unit **1709**. From the PSA unit, light stream comprising methane, hydrogen, CO and CO_2 can be directed to a methanation unit **1710**, and an olefinic stream can be directed to an ETL reactor **1711** and reacted to form higher hydrocarbon products. The ETL product stream can be directed to a heat recovery unit **1712**, where boiler feed water (BFW) **1728** can be heated, at least a portion of which can be fed **1729** to the heat recovery unit **1706**. The ETL product stream can then be directed to another knockout drum **1713**. The overhead stream from the knockout drum can be directed to a low temperature separations unit **1714**, while the bottoms stream from the knockout drum can be directed to a C_4 removal unit **1715**, which can produce a C_4 stream **1730** and a C_{5+} stream **1731**. Overhead from the low temperature separations unit, as well as product from the methanation reactor, can be directed back to the compressor **1703**.

[0201] OCM-ETL systems of the present disclosure can be integrated into and combined into conventional NGL extraction and NGL fractionation sections of a midstream gas plant. Where NGLs in the gas stream are declining (or gas is dry), the deployment of OCM-ETL can utilize an existing facility to produce additional liquid streams. The implementation of OCM-ETL can allow for the generation of on specification "pipeline gas." The products from the facility can be suitable for use (or on specification or "spec") as pipeline gas, gasoline product, hydrocarbon (HC) streams with high aromatic content, and mixed C_4 products. The PSA systems discussed above can be employed to separate, pre-separate or purify the hydrocarbon feed streams in the integrated NGL OCM-ETL system. FIG. **18** shows an exemplary NGL extraction facility integrated with an OCM-ETL system. As shown in FIG. **18**, for example, the feed to the PSA **1802** can be the net incoming gas from the treatment system **1801**, which can treat a methane stream (e.g., natural gas) **1810**. The PSA system can separate the feed to the OCM reactor **1803**, which is mostly methane and lighter components with some ethane to utilize a PBC section of the OCM reactor, and the feed to the ETL reactor **1805**, which can first be processed in a natural gas liquids extraction system **1804**. The feed to the ETL system can be the PSA tail gas and OCM effluent comprising ethylene, propylene, ethane, propane, hydrogen, methane, and other components. In some cases, the OCM effluent can be directly fed to the ETL reactor. In some cases the OCM effluent is hydrogenated and fed to the ETL system. In some cases, as shown for example in FIG. **18**, the OCM effluent is fed back to the PSA unit for separation; additional natural gas **1811** can be added, and a stream can be recovered **1812** (e.g., for use as pipeline gas). In some examples, the system may have a methanation unit that takes in the effluent from ETL reactor or OCM reactor and converts the CO, CO_2 and H_2 to methane, thereby further increasing the carbon efficiency of the process. The existing NGL extraction and product fractionation **1806** sub-systems can then be used to fractionate the final products, including into a mixed C_4 stream **1814** and a C_{5+} product stream **1815**.

Refining

[0202] Refinery gas typically contains valuable components like hydrogen, methane, ethane, ethylene, propane, propylene, and butane. Most commonly, refinery off-gases (ROG) are exported to the fuel gas system, thereby losing the value of the components contained therein. The OCM-ETL process can be used to improve the value of products as the OCM converts the methane to ethylene and the ETL converts olefins (e.g., those existing in the ROG and those generated by OCM) to higher value liquids as C_4 components, gasoline blends, or aromatic components.

[0203] FIG. **19** shows an exemplary PSA unit integrated to a refinery process scheme. A refinery gas plant **1901** can receive gas **1910** from cracking or other units. The PSA unit **1903** (after, for example, treatment of the gas in a treatment unit **1902**) can separate components in refinery gas plant off gas to methane and a C_{2+} cut which contains most or all of the olefinic materials. The methane can be used as refinery fuel **1911** and/or directed to an OCM unit **1904** with post-bed cracking. The OCM feed can be supplemented with additional natural gas **1912**. The olefinic materials can be directed to an ETL reactor **1905**. The OCM effluent can also be routed to the PSA where the olefins produced in the OCM are also sent to the ETL reactor. In some cases, the OCM effluent can be routed to the ETL reactor. In some cases, the OCM effluent may be hydrogenated before being sent to the PSA unit or ETL reactor. Some techniques may dictate the use of a cryogenic demethanizer in place of the PSA, but the application of PSA to pre-separate the refinery off-gas into a product stream and a tail gas stream containing the heavier hydrocarbons which is the feed to ETL reactor can result in significant cost savings. The product stream can contain methane, ethane, CO, CO_2, and other components, with of each component from 1 to 99%. A C_{3+} stream **1913** from the refinery gas plant can be directed to a product fractionation system **1906**, which can provide a C_2/C_3 stream **1914** (which can be directed to the OCM reactor), an iC_4 stream **1915**, a gasoline blend stream **1916**, and/or a kerosene/jet stream **1917**.

[0204] As shown in FIG. **20**, in some cases the system can have a methanation unit to further improve the carbon efficiency of the process. A refinery gas plant **2001** can receive gas **2010** from cracking or other units. The PSA unit **2003** (after, for example, treatment of the gas in a treatment unit **2002**) can separate components in refinery gas plant off gas to methane and a C_{2+} cut which contains most or all of the olefinic materials. The methane can be used as refinery fuel **2011** and/or directed to a methanation unit **2004**, and then to an OCM reactor **2005** with post-bed cracking. The methanation feed can be supplemented with additional natural gas **2012**. The olefinic materials can be directed to an ETL reactor **2006**. The OCM effluent can be routed to the ETL reactor. In some cases, the OCM effluent can also be routed to the PSA where the olefins produced in the OCM are also sent to the ETL reactor. In some cases, the OCM effluent may be hydrogenated before being sent to the PSA unit or ETL reactor. Some techniques may dictate the use of a cryogenic demethanizer in place of the PSA, but the application of PSA to pre-separate the refinery off-gas into a product stream and a tail gas stream containing the heavier hydrocarbons which is the feed to ETL reactor can result in significant cost savings. The product stream can contain methane, ethane, CO, CO_2, and other components, with of each component from 1 to 99%. A C_{3+} stream **2013** from the refinery gas plant can be directed to a product fractionation system **2007**, which can provide a C_2/C_3 stream **2014** (which can be directed to the OCM reactor), an iC_4 stream **2015**, a gasoline blend stream **2016**, and/or a kerosene/jet stream **2017**.

Metal-Organic Frameworks (MOFs) for Hydrocarbon Separation

[0205] The separation section of OCM unit can employ cryogenic distillation systems. In some cases, the distillation section can be partially or completely replaced by efficient advanced separation technologies that operate at higher/room temperatures, such as membranes or PSA. This can result in energy savings.

[0206] Among the materials used for membranes and adsorption beds, metal-organic frameworks (MOFs) can be highly beneficial. MOFs can comprise metal ions and organic linkers. MOFs can be highly porous sponge-like materials. The choice of metal ion and linker can define the structure and hence the properties of MOFs. MOFs can exhibit advantages of both organic and inorganic moieties. They can be more advantageous than zeolites due to higher surface areas and higher flexibility in pore sizes (e.g., based on their synthesis). They can be better than typical membranes for separation since they can be more robust, more mechanically and thermally stable, and can avoid issues such as carrier poisoning or reduction of complexing agents.

[0207] The process effluent from OCM can comprise light gases, such as methane, hydrogen, carbon dioxide, ethylene, ethane, acetylene, propane, propene and C_{4+} compounds. MOFs can be used to separate C_{2+} compound streams from the bulk CH_4 and H_2 in effluent. MOFs can also be used to recover ethylene from a mixed stream of C_2 compounds, C_3 compounds and C_{4+} compounds, remove CO_2, and recover hydrogen for further processing.

[0208] Different combinations of MOFs can be synthesized to provide different separation properties. MOFs can be useful in hydrocarbon separation due to their capability of separating component gases by mechanisms such as molecular sieving, characteristic gate opening pressures for different penetrant molecules or other changes in the structure of the MOFs due to adsorbent/adsorbate interactions. Without being limited by theory, adsorption selectivity can arise from interactions using π-complexation between the double bond in ethylene molecules and partial positive charges of coordinatively unsaturated metal ions (e.g., Cu(II)). MOFs such as HKUST-1 can be used to separate ethylene from ethane. Other MOFs capable of separating ethylene over ethane include Ag^+ based MOFs, Co_2(2,5-dihydroxyterephthalate, or “dhtp”), and Mg_2(dhtp). MOFs such as ZIF-7, ZIF-8, and ZIF-4 can be used for selective adsorption of paraffins (e.g., ethane) over ethylene due to the gate-opening effect or the breathing behavior of the MOF. ZIF-8 can adsorb alkanes (e.g., methane) over alkenes (e.g., ethylene). The selectivity of this separation can be controlled by adjusting the hydration level of the MOF. MOFs such as ZIF-67, SBMOF-1, SBMOF-2, Cu-TDPAT, USTA-33a, ZJU-61, USTA-33, USTA-10a can be used for selective separation of methane from other hydrocarbons such as C_2 compounds. The MOF M_2(dobdc) can be used to effectively separate acetylene, ethylene, ethane, and methane collectively or individually from their mixtures. The M_2(dobdc) can be in the meta form M_2(m-dobdc) or the para form M_2(p-dobdc). The metal can be any suitable metal such as iron (Fe), nickel (Ni) or cobalt (Co). Further information on these MOFs can be found in PCT Publication No. WO 2015/066693A1, which is incorporated herein by reference in its entirety. IRMOFs, such as MOF-5, can be used for separation of hydrogen from hydrogen/methane and hydrogen/C_2 mixtures. RPM3-Zn can be used to separate C_1-C_4 paraffins. MOFs such as UTSA-100, SIF SIX, ZJU-5 can be utilized for acetylene removal from the olefins stream where back-end acetylene removal is used rather than acetylene hydrogenation. MOFs such as M-(dobdc) can be modified with amines to selectively remove CO_2. Several MOFs such as ZIF-68-70, 78, 79, 81 82, MOF-11, MOF-508b, PCN-60, 61, MIL-100, MIL-101, ZIF-8, SNU-9, MIL-102(Cr), MIL-53(Cr) have been studied for removal of CO_2 from methane and nitrogen and can be utilized for, e.g., a front end CO_2 removal system. MOFs such as M_2(dobpdc) can be used to remove CO_2 from other gases and can be used for CO_2 removal front or back of the OCM process described herein. MOFs such as Fe-BTTri can be used for CO removal from various components such as CO_2, N_2, CH_4 and can be used for back end CO removal in the OCM unit.

[0209] MOFs can be used in the adsorbent beds of PSA/TSA system or as a part of membrane based applications. As part of membrane systems, they can be incorporated in thin film membranes or mixed matrix membranes (MMMs). With MMMs, MOFs have shown improved gas separation qualities, with increased permeability and selectivity using MMMs. Mixed matrix membranes can combine the advantages of easy and cheap fabrication of polymer membranes with the improved gas separation properties of different MOFs.

[0210] For an OCM process, MOFs can be utilized for separation of various light hydrocarbons. In FIG. **21**, for example, oxygen **2101** and methane **2102** feed the OCM reactor **2103**. The process effluent **2104** comprising mainly hydrogen, CO, CO_2, CH_4, C_2H_4, C_2H_6 and C_{3+} hydrocarbons is first sent to a pretreatment unit **2105**. Any potential contaminants to the downstream recovery systems (e.g., contaminants to membranes, adsorbent beds containing zeolites, polymers or MOF membranes or adsorbents) can be removed in this unit. This unit can include a CO_2 removal system, acetylene removal bed for diene sensitive beds, sulfur removal bed, or molecular sieve dryer. Hydrogen can also be recovered from this stream, for example by utilizing an MOF bed selective to hydrogen over other light hydrocarbons such as methane. Hydrogen removal can be important for separation systems using adsorbents/membranes that are sensitive to hydrogen in the operations that follow. The hydrogen, CO_2 and CO streams can be sent to the methanation unit **2106** for further conversion to methane. The outlet **2107** from the pretreatment unit can then be sent to a C_1/C_{2+} bulk separation unit **2108** capable of separating methane from C_2 and higher hydrocarbons. This separation unit can be a PSA, membranes made of zeolites such as CaX, NaX zeolite, microporous titanosilicates such as ETS-4, ETS-10, or selective MOF adsorbents/membrane systems that can perform the same function (for example, MOFs such as SBMOF-1, SBMOF-2, Zn-SIFSIX-Pyrazine, PCN-250, Cu-TDPAT, ZIF-67, ZJU-61, USTA-33, and USTA-10 can be used). These materials can be used for separating the light components including N_2 and H_2 along with methane and hence may not require any pre-treatment beds prior to a C1/C2+ bulk separation unit. A methane gas stream **2109** separated can be recycled back to the OCM reactor. Alternatively, the outlet from the C_1/C_2 separation containing methane can be recycled back to the methanation unit **2106**, for example if the stream contains portions of CO, CO_2 or H_2. The C_{2+} stream **2110** can then be sent into an olefin/paraffin separation unit **2111**, for example made of MOFs, zeolites, or polymeric membranes in a PSA or membrane unit. MOFs that can be useful for this operation include HKUST-1, CO_2 (dhtp), Mg_2 (dhtp), M (dobdc) (M can be Mg, Mn, Fe, Co, Ni, Zn), ZIF-7, ZIF-8, ZIF-4, and other Ag ion based MOFs such as Ag-MIL-101, Silver-Organic Frameworks Constructed with 1,1'-Biphenyl-2,2',6,6'-tetracarboxylic Acid or Silver m-phosphonobenzoate Ag_6(m-$O_3PC_6H_4CO_2$)$_2$, Ag(I) coordination polymer with 2,5-dimethylpyrazine ligand. Polymeric adsorbents capable of silver complexation such as Ag+ exchanged Amberlyst resin can also be used for such applications. The olefins stream can then be sent into a separator **2112** such as a flash unit operation or distillation column or any other separation system (e.g., PSA/TSA/membranes) that can separate pure ethylene **2113** from the C_{3+} olefins **2114**. A combination of the separation techniques can also be used to recover polymer grade ethylene. The paraffin stream can also be sent into a separator **2115** such as flash operation, distillation section, PSA, TSA unit, or membrane system to separate ethane from C_{3+} paraffins. Ethane can be recycled **2116** back to the OCM reactor. Alternatively, the entire paraffin stream **2117** can also be recycled back into the OCM reactor to take advantage of the post bed cracking section of the reactor to convert into further ethylene. Separation of paraffins can also be performed using MOF adsorbent beds of RPM3-Zn.

[0211] In FIG. **22**, a similar process scheme as FIG. **21** is proposed, except for the acetylene removal unit **2118** location, separating acetylene **2119** from ethylene **2120**. Here the acetylene removal unit is downstream of the ethylene/propylene+ separation unit. This scheme can be utilized when acetylene is not a contaminant/poison to the olefin/paraffin separation beds or any of the separation systems prior to olefin separation unit (MOF/PSA/membrane systems). This scheme can be utilized if olefin/paraffin separation system is based on non-Ag^+ adsorbent beds/membranes such as Fe-MOF-74. In such a system, acetylene removal can be performed on the final product stream using MOF adsorbent beds/membranes selective to acetylene removal, for example, USTA-67a.

[0212] In FIG. **23**, the OCM effluent, after pre-treatment and hydrogen recovery (where necessary), is sent to adsorbent beds in a PSA system or to a membrane system containing MOFs such as M_2(dobdc) (meta or para form, M can be Mg, Mn, Fe, Co, Ni) **2108**, **2121** that are by themselves capable of separating all the lighter hydrocarbons into individual components (CH_4, C_2H_4, C_2H_6, C_2H_2). In such a system, the effluent from pre-treatment section can be first sent into an initial methane removal unit (PSA with multiple beds for simultaneous adsorption/desorption to run the process continuously). The desorbed mixture of C_{2+} streams can then be separated into ethylene **2122**, ethane **2116** and acetylene **2123** based at least in part on their different elution rates from the adsorbent bed (permeation times if membranes were to be used). Multiple beds operating simultaneously for this unit can help with continuous separation of the C_2 streams. Such a scheme can use a C_{3+} removal system (PSA/membrane based on MOFs) for removing the C_{3+} components prior to the methane removal unit.

[0213] FIG. **24** represents a similar system utilizing MOFs such as M_2(dobdc) (meta or para form, M can be Mg, Mn, Fe, Co, Ni) capable of separating individual light hydrocarbons, but each running in a different mode. A system utilizing 4 different adsorption systems (e.g., PSA) **2124**, **2125**, **2126**, and **2127**, with each bed operating in different mode is represented. Each bed is either in CH_4 removal mode **2124**, C_2H_2 removal mode **2127**, C_2H_4 recovery mode **2126** or C_2H_6 removal mode **2125**. Using different valve-sequencing for the process gas (feed and outlet) between beds, the feed gas can be directed appropriately and effectively separated continuously into individual components thus recovering ethylene without lag times that may be generated in the adsorbent beds.

[0214] FIG. **25** shows another example of an OCM system. In this case, oxygen **2500** and methane **2502** can be fed into an OCM reactor **2504** to produce an OCM effluent. The OCM effluent can be sent through a pre-treatment unit **2506** (e.g., for water, sulfur removal) followed by a (bulk) separation unit **2508** such as PSA or membranes that utilize adsorbent materials capable of separation C_1 compounds from C_{2+} compounds. These materials can be adsorbents that aid in separation using molecular size differences (e.g., CaX Zeolite, ETS-4). This PSA/membrane can separate the quenched OCM reactor effluent into two streams. The methane rich stream with hydrogen **2510** can be recycled back to OCM via methanation **2512**. The C_{2+} compounds **2514** can be fed into an optional acetylene hydrogenation unit **2516** that selectively hydrogenates acetylene to ethylene and ethane. This stream can then be fed to the an olefin/paraffin separation module **2518** containing, for example adsorbents or membranes with pi-complexation materials such as silver ion MOFs, resins such as Ag+ exchanged Amberlyst 15 resin or M_2(dobdc) (meta or para form, M can be Mg, Mn, Fe, Co, Ni) MOFs, or any material which can selectively separate olefin from paraffins. A post-CO_2 removal unit **2520** can follow. A post CO_2 removal unit can reduce the cost since the operation can be performed on a stream with much lower flow rate. The CO_2 removal unit may use liquid absorption or CO_2 removal adsorbents in a PSA or TSA or a membrane system. The CO_2 stream **2522** can then be recycled into the methanation reactor for further conversion into methane. The CO_2-free stream can then be sent into an acetylene removal unit (if acetylene is not hydrogenated prior to olefin/paraffin separation) utilizing materials and adsorbents capable of removing acetylene from ethylene such as UTSA-100, SIFSIX, or ZJU-5 (not shown). Once free from acetylenes, the product stream can go through a final separation unit **2524** to separate ethylene **2526** and propylene **2528**. In some cases, some CO_2 can be vented **2530** and/or the C_{2+} paraffin stream **2532** can be recycled to (the cracking section of) the OCM reactor **2504**.

[0215] FIG. **26** shows another example of an OCM system. In this case, oxygen **2600** and methane **2602** can be fed into an OCM reactor **2604** to produce an OCM effluent. The OCM effluent can, after pre-treatment where necessary (not shown), can be sent to an olefin recovery module **2606**. The olefin recovery module can contain adsorbent beds in a PSA or TSA system and/or can be a membrane system containing MOFs such as M_2(dobdc) (meta or para version, M can be Mg, Mn, Fe, Co, Ni for example) that are by themselves capable of separating the lighter hydrocarbons into individual components or groups thereof (e.g., CH_4, C_2H_4, C_2H_6, C_2H_2). In such a system, the effluent from pre-treatment section can be sent into an initial bulk lights removal unit (e.g., PSA with multiple beds for simultaneous adsorption/desorption to run the process continuously and remove methane and lighter components). The desorbed mixture of C_{2+} streams (with lower amounts of C_1 and lighter components) can then be separated into ethylene, ethane and acetylene based at least in part on their different elution rates from the adsorbent bed (permeation times if membranes were to be used). Such a configuration can use a C_{3+} removal system (e.g., PSA/membrane based on MOFs) for removing the C_{3+} components prior to the methane removal unit. The separations module can send a stream of C_1 molecules and hydrogen **2608** to a methanation unit **2610** and/or can send C_{2+} paraffins **2612** to (the cracking section of) the OCM reactor **2604**. A back-end CO_2 and acetylene removal unit **2614** can then be utilized to purify olefins stream from CO_2 and acetylenes. The CO_2 removal unit can include typical CO_2 removal liquid absorption columns or PSA/TSA/membranes systems that incorporate CO_2 removal adsorbents. Acetylene removal may be performed by adding additional acetylene selective MOF beds such as UTSA-100, SIF SIX, ZJU-5. A back-end purification system can greatly reduce the operating and capital cost of removal units. The CO_2 removal unit can send CO_2 to methanation **2610** and/or to vent **2616**. An olefin separation module **2618** can produce an ethylene stream **2620** and a propylene stream **2622**.

[0216] In summary, different MOFs can be utilized for their specific selectivities and adsorption capabilities, for example in MMMs or adsorbent beds as PSA systems for hydrocarbon separation of the OCM effluent. MOFs can be very advantageous for their on-purpose synthesis and high surface areas (highest surface area/gram compared to any other material). MOFs in combination with other separation systems (such as polymeric membranes, zeolites, and cryogenic distillation) can be used in novel process schemes to produce OCM product (e.g., ethylene).

Separations Systems Using an Oil Absorption Tower

[0217] Another aspect of the present disclosure provides a method and system for separating the OCM reactor product mixture using an oil absorption system along with distillation. The oil absorption system may include (a) an oil absorption and stripper system and/or (b) an oil absorption system preceded by a pre-separation column to do a bulk separation between C_1 and C_2 compounds. This system can eliminate the need of a demethanizer, thereby reducing the overall energy consumption and capex by eliminating the need for C_2 or C_1 refrigeration.

[0218] As shown in FIG. **27**A, oxygen **2700** and methane **2702** can be fed to an OCM reactor **2704** and reacted to produce an OCM effluent **2706**. The OCM effluent can be compressed **2708**, and the compressed stream can be sent to a treatment unit **2710**. The treatment unit can include a CO_2 removal system, drying and/or removal of oxygenates. The treatment unit can be followed by a heavies removal system **2712**. The heavies removal system can remove C_{4+} compounds **2714**. The overhead from the heavies removal system can be fed to a pre-separation and absorption system **2716**. The overhead **2718** from the pre-separation and oil absorption system can consist mainly of the C_1 and lighter components. The majority of the methane rich overhead product can be recycled to the OCM reactor via a methanation reactor system **2720**. A small fraction can be purged **2722** to remove any inerts building up in the system, alternately, the C_1 fraction can be sent to the fuel gas. The C_{2+} components (e.g., propane, propylene, ethane, ethylene, methane, and lights such as H_2) can be sent to a de-ethanizer **2724** followed by acetylene hydrogenation **2726** and a C_2 splitter **2728** to produce high purity polymer grade ethylene **2730**. Ethane **2732** can be recycled to OCM (not shown). A C_3 splitter **2734** can be used to produce a propylene product **2736**.

[0219] FIG. **27**B shows an example of the pre-separation and absorption system **2716** comprising a pre-separation column **2740** and an oil absorption unit **2742**. The pre-separation column can be a distillation column which performs a bulk separation between C_1 and lighter components and C_2 and heavier components. In this instance, bulk separation implies that the distillation doesn't necessarily achieve high purity streams (non-sharp distillation). The overhead from the pre-separation column, which consists of C_1 and lighter components can be sent to an oil absorber where the circulating lean oil absorbs C_2 and heavier components to complete separation of C_1 from C_{2+} components. The heavy oil can be regenerated in the first pre-separation column. Alternatively, the oil can be regenerated in a separate system **2744**. One advantage of using a pre-separation column and an oil absorption system is the reduction in the energy consumption that is incurred in a conventional cryogenic demethanizer.

[0220] In some cases, the feed to the separation system can be the product from either an OCM reactor as discussed above, an OCM process integrated with a Methanol to Olefins (MTO) unit, an OCM process integrated with a steam cracker, or an OCM process integrated with a dimerization and metathesis unit for example.

[0221] Methods and systems of the present disclosure can be combined with or modified by other methods and systems, such as those described in U.S. patent application Ser. No. 14/591,850, filed Jan. 7, 2015, now published as U.S. Patent Pub. No 2015/0232395; U.S. patent application Ser. No. 13/936,783, filed Jul. 8, 2013, now published as U.S. Patent Pub. No. 2014/0012053; U.S. patent application Ser. No. 13/936,870, filed Jul. 8, 2013, now published as U.S. Patent Pub. No. 2014/0018589; U.S. patent application Ser. No. 13/900,898, filed May 23, 2013, now published as U.S. Patent Pub. No 2014/0107385; U.S. patent application Ser. No. 14/553,795, filed Nov. 25, 2014, now published as U.S. Patent Pub. No. 2015/0152025; U.S. patent application Ser. No. 14/592,668, filed Jan. 8, 2015, now published as U.S. Patent Pub. No. 2015/0210610; and U.S. patent application Ser. No. 14/789,953, filed Jul. 1, 2015, now U.S. Pat. No. 9,334,204, each of which is entirely incorporated herein by reference.

[0222] While preferred embodiments of the present invention have been shown and described herein, it will be obvious to those skilled in the art that such embodiments are provided by way of example only. It is not intended that the invention be limited by the specific examples provided within the specification. While the invention has been described with reference to the aforementioned specification, the descriptions and illustrations of the embodiments herein are not meant to be construed in a limiting sense. Numerous variations, changes, and substitutions will now occur to those skilled in the art without departing from the invention. Furthermore, it shall be understood that all aspects of the invention are not limited to the specific depictions, configurations or relative proportions set forth herein which depend upon a variety of conditions and variables. It should be understood that various alternatives to the embodiments of the invention described herein may be employed in practicing the invention. It is therefore contemplated that the invention shall also cover any such alternatives, modifications, variations or equivalents. It is intended that the following claims define the scope of the invention and that methods and structures within the scope of these claims and their equivalents be covered thereby.

1. A method for generating compounds with two or more carbon atoms (C_{2+} compounds), comprising:

(a) directing oxygen (O_2) and methane (CH_4) into an oxidative coupling of methane (OCM) reactor that reacts said O_2 and CH_4 in an OCM process to yield a product stream comprising (i) C_{2+} compounds including ethylene (C_2H_4) and (ii) carbon dioxide (CO_2); and

(b) directing said product stream from said OCM reactor into a separations unit that employs a CO_2 separation unit to separate said CO_2 from said product stream and enrich said C_{2+} compounds in said product stream, which CO_2 separation unit employs (i) sorbent or solvent separation of CO_2, (ii) membrane separation of CO_2, (iii) cryogenic or low temperature separation of CO_2 having an operating temperature greater than a boiling point of methane and less than a boiling point of CO_2, (iv) metal-organic framework-based separation, or (v) antisublimation separation of CO_2.

2. (canceled)

3. The method of claim **1**, wherein said sorbent or solvent separation of CO_2 employs an amine based absorption unit.

4.-**19**. (canceled)

20. The method of claim **1**, further comprising directing said CO_2 from said product stream to a methanation reactor that reacts said CO_2 to yield a methanation product stream comprising methane.

21. (canceled)

22. The method of claim **1**, further comprising separating said product stream into (i) an ethylene product stream comprising ethylene and (ii) a C_{3+} product stream comprising compounds with three or more carbon atoms (C_{3+} compounds).

23.-**56**. (canceled)

57. A method for generating compounds with two or more carbon atoms (C_{2+} compounds), comprising:

(a) directing oxygen (O_2) and methane (CH_4) into an oxidative coupling of methane (OCM) reactor that reacts said O_2 and CH_4 in an OCM process to yield a product stream comprising (i) C_{2+} compounds including ethylene (C_2H_4) and (ii) C_1 compounds including un-reacted CH_4; and

(b) directing said product stream into a separations unit containing a metal organic framework (MOF) that produces (i) a bottoms stream comprising said C_{2+} compounds and (ii) an overhead stream comprising said C_1 compounds.

58. The method of claim **57**, further comprising:
- (c) directing said overhead stream to a methanation unit for converting carbon dioxide (CO_2) and/or carbon monoxide (CO) into methane (CH_4); and
- (d) directing said CH_4 into said OCM reactor.

59. The method of claim **57**, further comprising:
- (e) directing said bottoms stream to a second separations unit containing a metal organic framework (MOF) that separates olefins from paraffins.

60. The method of claim **57**, wherein the separations unit comprises a pressure swing absorber (PSA) that contains the MOF.

61. The method of claim **57**, wherein the separations unit comprises a temperature swing absorber (TSA) that contains the MOF.

62. The method of claim **57**, wherein the C_1 compounds include hydrogen (H_2).

63. A method for generating compounds with two or more carbon atoms (C_{2+} compounds), comprising:
- (a) directing oxygen (O_2) and methane (CH_4) into an oxidative coupling of methane (OCM) reactor having a catalytic section and a cracking section to produce an OCM product stream, which catalytic section reacts said O_2 and CH_4 to yield ethylene (C_2H_4), ethane (C_2H_6) and heat, which cracking section uses said heat to convert C_2H_6 into C_2H_4, and which product stream comprises (i) C_{2+} compounds including ethylene (C_2H_4) and ethane (C_2H_6) and (ii) C_1 compounds including un-reacted CH_4;
- (b) directing said product stream into a separations unit containing a metal organic framework (MOF) that produces (i) a first stream comprising said C_2H_4, (ii) a second stream comprising said C_2H_6 and (iii) a third stream comprising said C_1 compounds;
- (c) directing said second stream into said cracking section; and
- (d) directing said third stream into said catalytic section.

64. The method of claim **63**, wherein said third stream is directed to a methanation unit prior to directing to said catalytic section, which methanation unit converts carbon dioxide (CO_2) and/or carbon monoxide (CO) into methane (CH_4).

65. The method of claim **63**, wherein the separations unit comprises a pressure swing absorber (PSA) that contains the MOF.

66. The method of claim **63**, wherein the separations unit comprises a temperature swing absorber (TSA) that contains the MOF.

67. The method of claim **63**, wherein the C_1 compounds include hydrogen (H_2).

68.-**129**. (canceled)

130. A system for generating compounds with two or more carbon atoms (C_{2+} compounds), comprising:
- an oxidative coupling of methane (OCM) reactor configured to receive oxygen (O_2) and methane (CH_4) and react said O_2 and CH_4 to produce an OCM product stream, said OCM reactor having a catalytic section and a cracking section, which catalytic section reacts said O_2 and CH_4 to yield ethylene (C_2H_4), ethane (C_2H_6) and heat, which cracking section uses said heat to convert C_2H_6 into C_2H_4, and which product stream comprises (i) C_{2+} compounds including ethylene (C_2H_4) and ethane (C_2H_6) and (ii) C_1 compounds including un-reacted CH_4; and
- a separations unit fluidically coupled to said OCM reactor and configured to receive said product stream from said OCM reactor, wherein said separations unit contains a metal organic framework (MOF) that produces (i) a first stream comprising said C_2H_4, (ii) a second stream comprising said C_2H_6 and (iii) a third stream comprising said C_1 compounds, and wherein said second stream and said third stream are directed into said cracking section and said catalytic section respectively.

131. The system of claim **130**, wherein said third stream is directed to a methanation unit prior to directing to said catalytic section, which methanation unit converts carbon dioxide (CO_2) and/or carbon monoxide (CO) into methane (CH_4).

132. The system of claim **130**, wherein the separations unit comprises a pressure swing absorber (PSA) that contains the MOF.

133. The system of claim **130**, wherein the separations unit comprises a temperature swing absorber (TSA) that contains the MOF.

134. The system of claim **130**, wherein the C_1 compounds include hydrogen (H_2).

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