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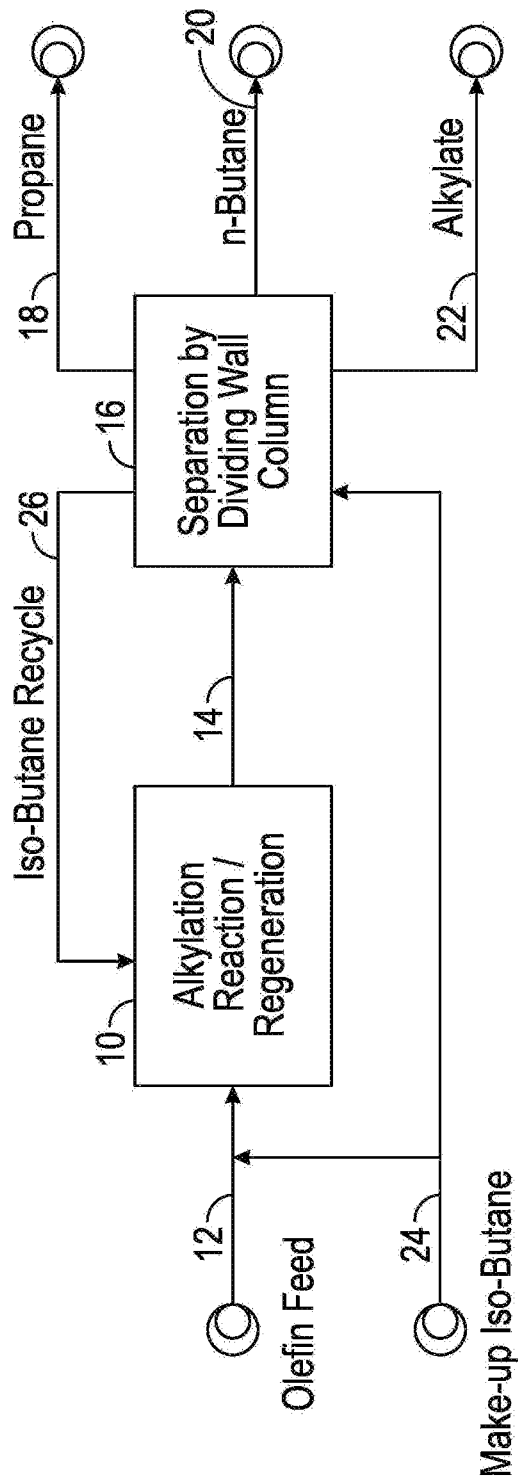


FIG. 1

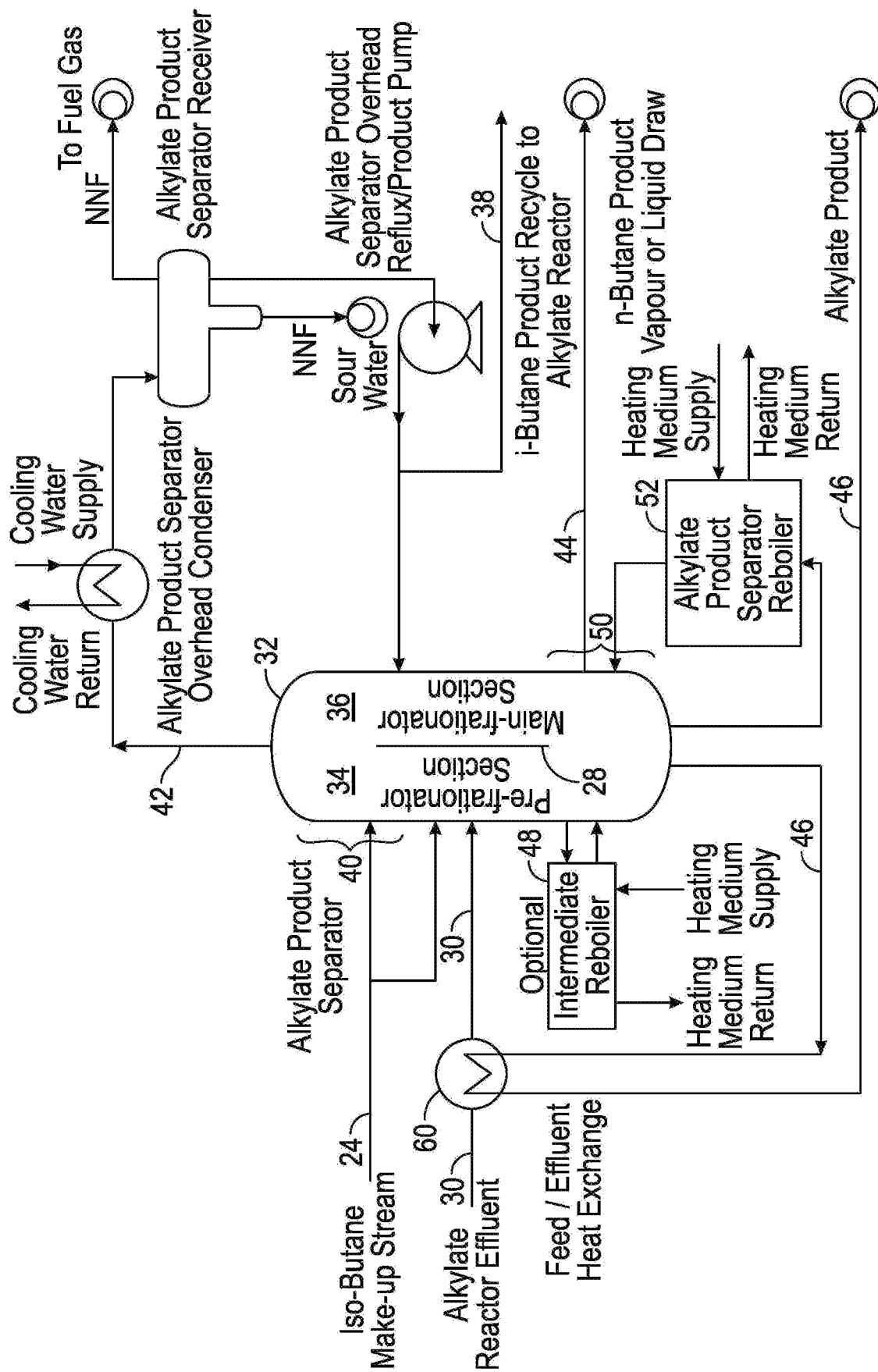


FIG. 2



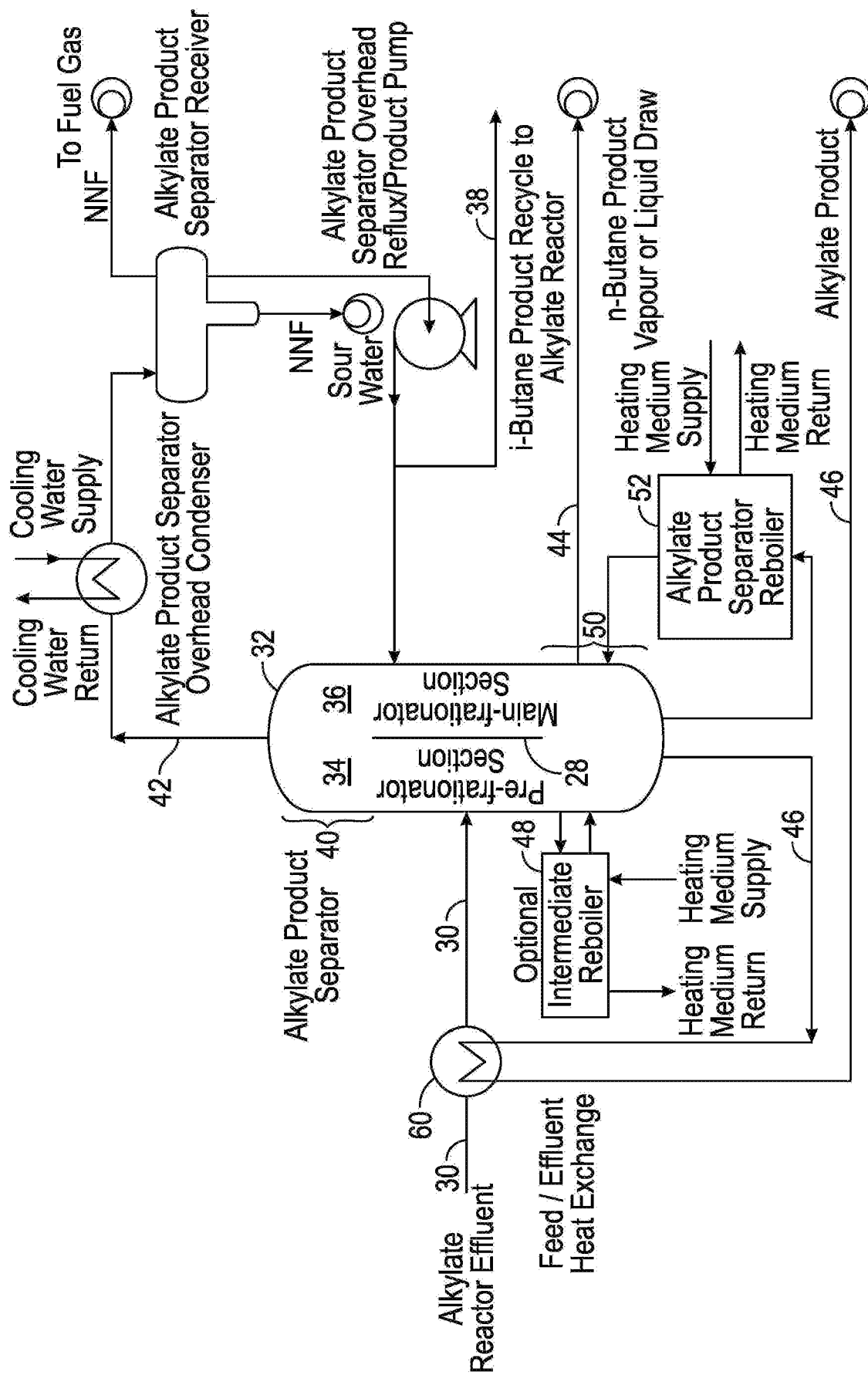


FIG. 4

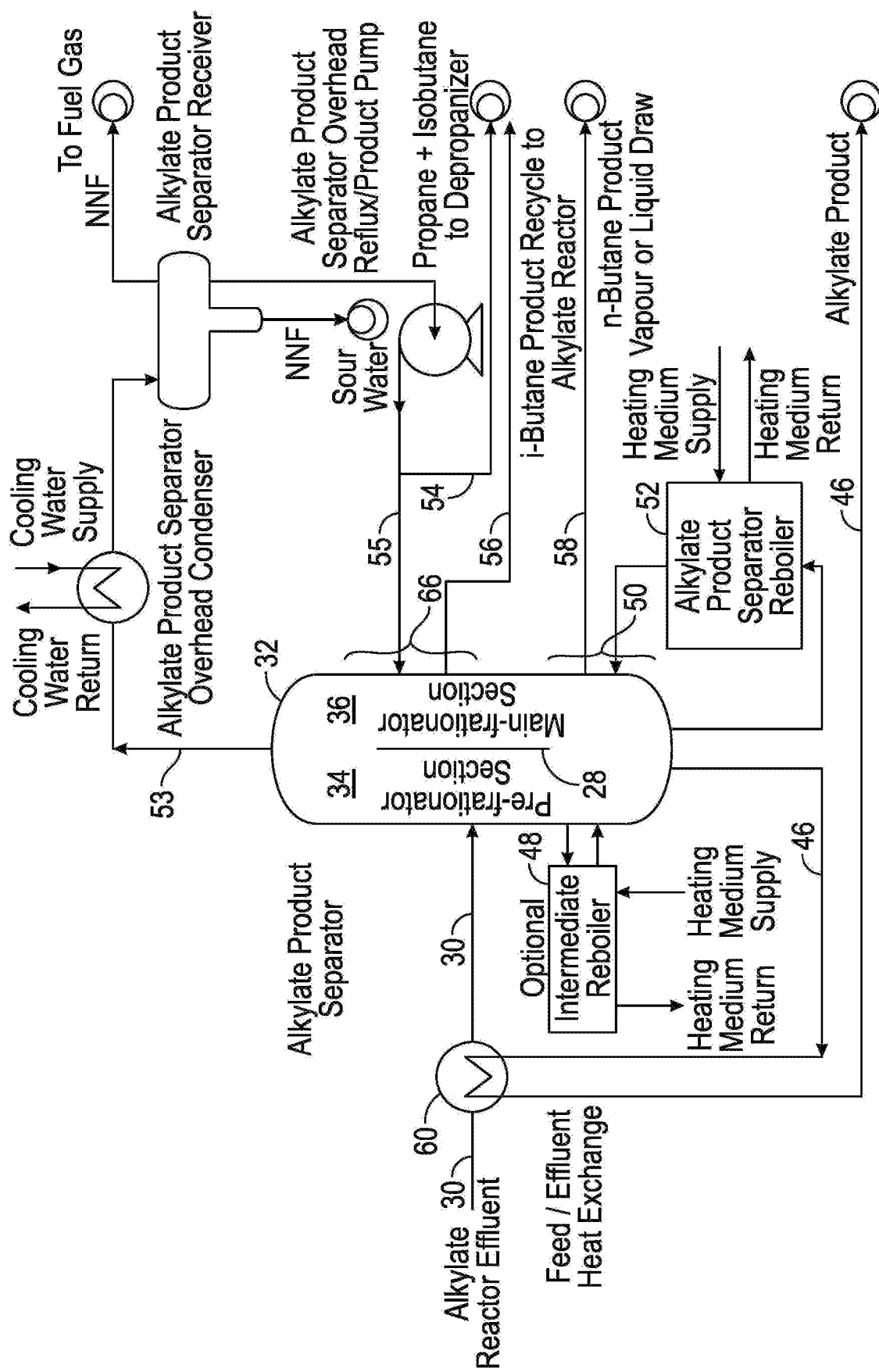


FIG. 5

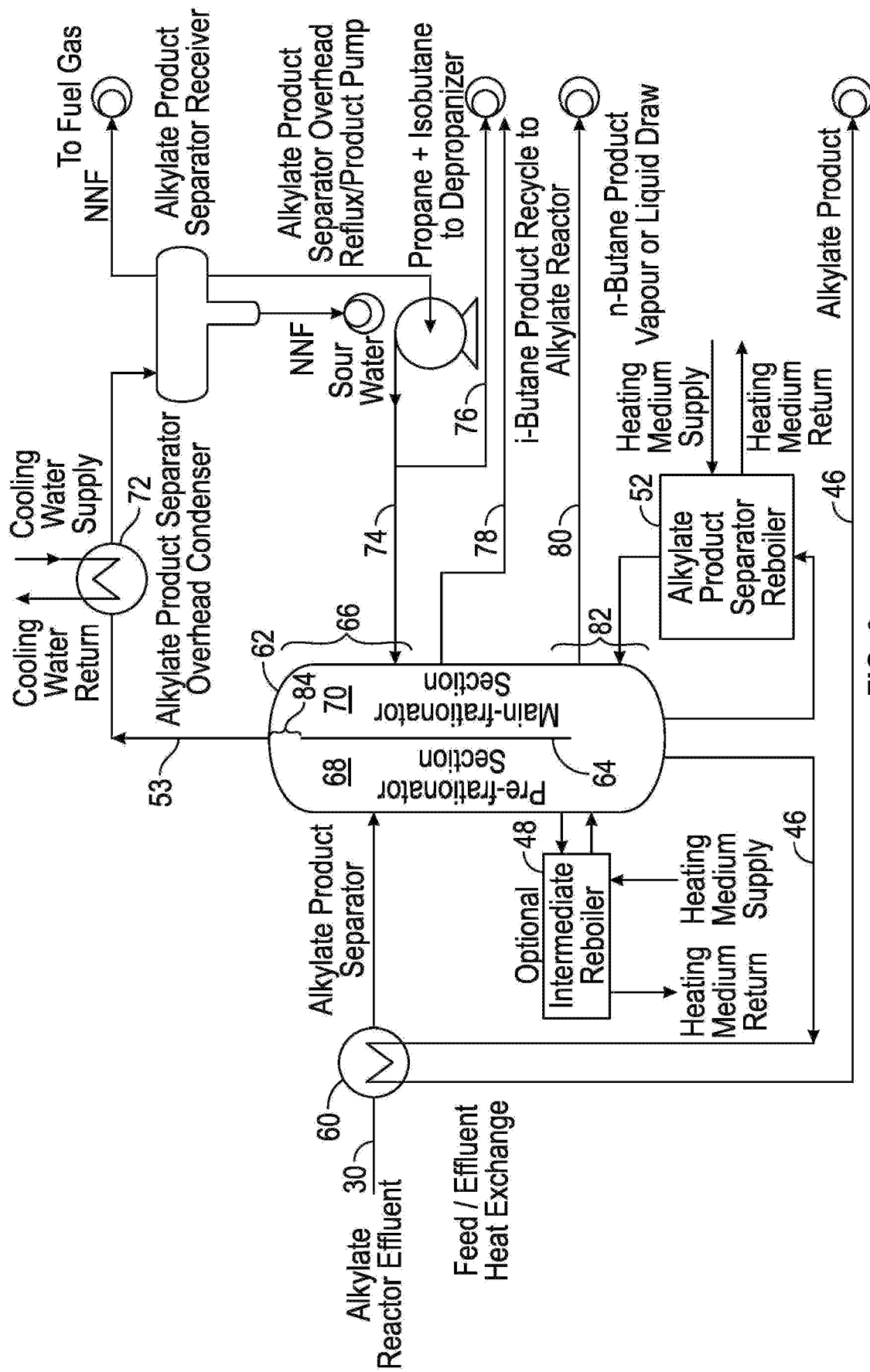


FIG. 6

## DIVIDING WALL COLUMN IN ALKYLATION PROCESS FOR REACTOR RECYCLE AND PRODUCT SEPARATION

### TECHNICAL FIELD

**[0001]** The present invention relates to alkylation processes for converting isoparaffins and low molecular weight alkenes into an alkylate product, and more particularly relates to such alkylation processes that include a dividing wall column.

### BACKGROUND

**[0002]** Alkylation is a chemical process used in petroleum refining to convert isoparaffins (*e.g.* iso-butane) and low molecular weight alkenes (*e.g.* propylene, butylene, and/or amylenes) into alkylate, a high octane gasoline component. These isoparaffins and alkenes are fed into a reactor, where under the presence of a solid acid catalyst or a liquid acid catalyst (*e.g.* sulfuric acid or hydrofluoric acid) they combine to form alkylate. The reactor effluent is sent to a distillation train to provide product separation and to recover excess iso-butane component which is recycled back to the reactor. Amylenes are defined herein as one of a group of metameric hydrocarbons, C<sub>5</sub>H<sub>10</sub>, of the ethylene series.

**[0003]** Conventional column schemes in the distillation train include, when no propane is in the system, a conventional three-product column. In the case where propane is in the system, there is conventionally used either a four-product column potentially followed by a two-product depropanizer, or a two-product column (for separating propane from the mixture) followed by a conventional three-product column (separating iso-butane, n-butane, and an alkylate product).

**[0004]** It is always desirable to improve alkylation processes and systems by improving efficiency, reducing utility and energy requirements, reducing CO<sub>2</sub> and/or NO<sub>x</sub> emissions, enhancing plant safety, reducing iso-butane loss, reducing capital requirements, reducing equipment footprint requirements, and/or improving the value of the products.



## SUMMARY

**[0005]** There is provided, in one non-limiting embodiment an alkylation system that includes an alkylation reaction / regeneration section that receives feed comprising olefin and make-up iso-butane, which alkylation reaction / regeneration section delivers alkylate reactor effluent to a dividing wall column (DWC) that also receives make-up iso-butane, where the DWC separates the alkylate reactor effluent into product streams including, but not necessarily limited to an iso-butane product stream, a n-butane product stream, and an alkylate product stream.

## BRIEF DESCRIPTION OF THE DRAWINGS

**[0006]** FIG. 1 is a non-limiting, schematic illustration of an alkylation plant block flow diagram illustrating separation by a dividing wall column (DWC) as described herein;

**[0007]** FIG. 2 is a non-limiting, schematic illustration of a flow diagram of an alkylate product separator DWC illustrating iso-butane as an overhead product and make-up stream to the DWC;

**[0008]** FIG. 3 is a non-limiting, schematic illustration of a flow diagram of an alkylate product separator DWC illustrating iso-butane as an overhead product and make-up stream to the DWC together with an intermediate reboiler with a bottoms product;

**[0009]** FIG. 4 is a non-limiting, schematic illustration of a flow diagram of an alkylate product separator DWC illustrating iso-butane as an overhead product;

**[0010]** FIG. 5 is a non-limiting, schematic illustration of a flow diagram of an alkylate product separator DWC illustrating iso-butane as a side draw product; and

**[0011]** FIG. 6 is a non-limiting, schematic illustration of a flow diagram of an alkylate product separator DWC illustrating iso-butane as a side draw prod-

uct together with a DWC where the dividing wall is at or near the top of the column.

#### DETAILED DESCRIPTION

**[0012]** FIG. 1 shows a block flow diagram of a general alkylation process. The alkylation reaction/regeneration block configuration depends on the type of acid catalyst (solid or liquid) used in the process. The make-up iso-butane stream can be mixed with the olefin feed or fed to the fractionator depending on the composition of the make-up iso-butane stream. It has been discovered that a dividing wall column can be used as a fractionator to produce an iso-butane rich stream as a reactor recycle and simultaneously to separate various other products depending on the alkylate reactor effluent composition. Dividing wall column configurations which can be used as a fractionator block in an alkylation process are presented and discussed herein.

**[0013]** More specifically as shown in FIG. 1 is an alkylation reaction / regeneration section **10**, sometimes simply called a reactor herein, that receives olefin feed **12** and produces alkylate reactor effluent **14** to dividing wall column **16** which separates the feed **14** into a propane-containing stream **18**, a n-butane product stream **20**, and an alkylate product stream **22**. Also shown is make-up iso-butane **24** supplied to alkylation reactor **10** and DWC **16**, as well as iso-butane recycle stream **26** from DWC **16** to reactor **10**. As mentioned, the olefin feed may be propylene, butylene, and/or amylenes (C5). In one non-limiting embodiment, operators will preferentially feed the alkylation unit with butylene because this yields the highest quality alkylate (*i.e.* octane and vapor pressure). Also, butylene has a lower-valued alternative use than propylene. Propylene can also be used when there is an insufficient volume of butylene available and/or it is not possible to sell the propylene as a separate product. Amylenes can also be used sometimes as a supplemental feed, but this is less common.

**[0014]** While FIG. 1 schematically illustrates the general process and system herein, there are a number of more specific, non-limiting embodiments

as will be discussed. In general there is a first embodiment where there is no propane present in the system as generally illustrated in FIGS. 2-4. There will also be discussed a second embodiment where there is propane present in the system as generally illustrated in FIGS. 5 and 6.

**[0015]** FIGS. 2 to 4 show a variety of dividing wall column configurations which can be used as an alkylation unit fractionation process, when an alkylation unit **10** does not have propane in the system and a make-up iso-butane stream **24** mainly contains C4 molecules. FIG. 2 shows a dividing wall column configuration when the alkylate reactor effluent **30** is fed to the pre-fractionator section **34** of the dividing wall column **32**. DWC **32** has a main-fractionation section **36**. A dividing wall **28** is present between the pre-fractionator section **34** and the main-fractionation section **36**. Depending on the make-up iso-butane stream **24** composition and required iso-butane product stream **38** specification, the make-up iso-butane stream **24** can be routed to the pre-fractionator section **34** of the dividing wall and/or to the top section **40** of the dividing wall column **32**. In this FIG. 2 configuration, the overhead vapor product **42** of DWC **32** will be an iso-butane rich stream which can be condensed and recycled to the alkylation reactor **10** as stream **38**. The side draw product **44** will be a n-butane rich product stream, which depending on the heat integration in the plant, can be taken as a liquid or a vapor draw. Alkylate product stream **46** will be taken as a dividing wall column bottoms product. Alkylate product **46** can be routed to the battery limit after preheating the column feed **30** in heat exchanger **60**. Optional intermediate reboiler(s) **48** at the lower energy level(s) can be used as an option in the bottom section **50** of the dividing wall column **32** to minimize the use of higher grade energy in the column main reboiler **52**.

**[0016]** FIG. 3 shows a dividing wall column configuration similar to FIG. 2 except the alkylate product routing is different. FIG. 3 shows that the alkylate product **46** can be used as an intermediate reboiler **48** heating medium before it preheats the column feed **30**.

**[0017]** FIG. 4 shows a dividing wall column configuration similar to FIG. 2 except for the make-up iso-butane stream routing. FIG. 4 assumes that the

make-up iso-butane is a concentrated iso-butane stream, mixed with the olefin feed upstream of the reactor **10**, and that it does not require fractionating in the fractionation section of the alkylation process. Stated another way, in one non-limiting embodiment there is an absence of a fractionation section of the alkylation reaction / regeneration section, configured to fractionating the mixture.

**[0018]** In another non-limiting embodiment, FIG. 5 shows a dividing wall column configuration when an alkylation unit **10** has propane in the system. The alkylate reactor effluent **30** is fed to the pre-fractionation section **34** of the dividing wall column **32**. An overhead vapor stream **53** is removed from the dividing wall column **32**. After condensing at least, a portion is sent to OSBL (outside battery limits) as propane rich stream **54** with possible or optional further separation in a two-product depropanizer (not shown). The balance is sent to the top section **66** of DWC **32** as alkylate product separator reflux stream **55**. An iso-butane rich stream **56** can be taken from the main-fractionator section **36** of the DWC **32** as a first side draw product and recycled to the alkylate reactor **10**. The first side draw product **56** can be taken as a vapor or a liquid draw as per the heat integration requirement of the system. A normal-butane rich stream **58** as a second side draw product can be taken from the main-fractionation section **36** side of the dividing wall column **32** or the bottom section **50** of the dividing wall column **32**. The second side draw product **58** can be taken as a vapor or a liquid draw as per the heat integration requirement of the system. The alkylate product **46** is taken from the bottom section of the dividing wall column **32** and routed to the battery limit after heat exchange in the feed/effluent heat exchanger **60** to preheat the column feed **30**. As shown in FIG. 3, the alkylate product **46** can also be used as an intermediate reboiler **48** heating medium to optimize the main reboiler energy requirement.

**[0019]** FIG. 6 presents a schematic illustration of another non-limiting, unique dividing wall column **62** configuration with the dividing wall panel **64** starting from the top section **66** of the column **62**. The dividing wall panel **64** may start at or near the top of column **62**. As defined herein, "at the top" means that there is no space between the top of the dividing wall panel **64** and the

inside top of the column **62**. As further defined herein, "near the top" of column **62** means a minimum of 12-inch (304.8 mm) distance **84** between the DWC **62** top tangent line and the top of the dividing wall panel **64**.

**[0020]** The alkylate reactor effluent **30** is fed to the top tray (not shown) of the pre-fractionation section **68** of the dividing wall column **62**. Vapors from the pre-fractionation section **68** and the main-fractionation section **70** are condensed in the overhead system **72** (alkylate product separator overhead condenser) and a reflux stream **74** from the overhead condenser **72** is fed to the top tray (not shown) of the main fractionation section **70** of the DWC **62**. A propane rich stream **76** can be taken as a side draw from the main fractionation section **70** of the DWC **62**. In one non-limiting embodiment, this propane and isobutane stream **76** is sent to a depropanizer (not shown). An iso-butane rich stream **78** can be withdrawn from the main-fractionation section **70** of the DWC **62** and sent back to the alkylate reactor **10** as a recycle stream. The second side draw product **78** can be taken as a vapor or liquid draw as per the heat integration requirement of the system. A normal-butane rich stream **80** as a third side draw product can also be taken from the main fractionator side **70** of the DWC **62** or the bottom section **82** of the dividing wall column **62**. The third side draw product **80** can be taken as a vapor or liquid draw as per the heat integration requirement of the system. The alkylate product **46** is taken from the bottom section **82** of the DWC **62** and routed to the battery limit after heat exchange in the feed/effluent heat exchanger **60** to preheat the column feed **30**. As shown in FIG. 3, the alkylate product can also be used as an intermediate reboiler **48** heating medium to optimize the main reboiler energy requirement.

**[0021]** It will be appreciated that the system and process described herein is not limited to any particular temperature ranges, pressure ranges, flow rates, stream compositions, and the like. It is expected that the system and process, now that it is described, can be modified by one of ordinary skill in the art to be applicable to a variety of reactor effluent compositions and other conditions and parameters as necessary.

**[0022]** It will be appreciated that the DWC can be a tray column, a packed column, or a combination of both.

**[0023]** It will also be appreciated that the systems and processes described herein will have a number of technical and commercial advantages.

Technical advantages include, but are not necessarily limited to:

- Improvement of fractionation efficiency;
- Reduced utility requirements;
- Reduced overall energy requirements;
- Reduced CO<sub>2</sub>/NO<sub>x</sub> emissions;
- Enhanced plant safety due to less hydrocarbon inventory; and
- Reduced iso-butane loss from the system.

**[0024]** Commercial advantages include, but are not necessarily limited to:

- 20-30% less capital requirement as compared to the conventional column solutions;
- Improvement in fractionation economics;
- Less plot space (equipment footprint) requirement;
- Advantages for plant upgrading/debottlenecking;
- Overall improvement in the value of products; and
- Alternative use of existing assets to improve the overall economics of the plant.

**[0025]** In the foregoing specification, the invention has been described with reference to specific embodiments thereof. However, the specification is to be regarded in an illustrative rather than a restrictive sense. For example, equipment, columns, DWCs, processes, reactants, olefins, isoparaffins, products, alkylates, and operating conditions falling within the claimed or disclosed parameters, but not specifically identified or tried in a particular example, are expected to be within the scope of this invention.

**[0026]** The present invention may be practiced in the absence of an element not disclosed. In addition, the present invention may suitably comprise, consist or consist essentially of the elements disclosed. For instance, there may

be provided an alkylation system, where the alkylation system consists essentially of or consists of an alkylation reaction / regeneration section that receives feed comprising olefin and make-up iso-butane, which alkylation reaction / regeneration section delivers alkylate reactor effluent to a dividing wall column (DWC) that also receives make-up iso-butane, where the DWC separates the alkylate reactor effluent into product streams comprising, consisting essentially of, or consisting of an iso-butane product stream, a n-butane product stream, and an alkylate product stream.

**[0027]** The words "comprising" and "comprises" as used throughout the claims, are to be interpreted to mean "including but not limited to" and "includes but not limited to", respectively.

**[0028]** As used herein, the word "substantially" shall mean "being largely but not wholly that which is specified."

**[0029]** As used herein, the singular forms "a," "an," and "the" are intended to include the plural forms as well, unless the context clearly indicates otherwise.

**[0030]** As used herein, the term "about" in reference to a given parameter is inclusive of the stated value and has the meaning dictated by the context (e.g., it includes the degree of error associated with measurement of the given parameter).

**[0031]** As used herein, the term "and/or" includes any and all combinations of one or more of the associated listed items.

CLAIMS:

1. An alkylation process comprising:  
feeding an olefin stream and a make-up iso-butane to an alkylation reaction /  
5 regeneration section to produce an alkylate reactor effluent;  
feeding the alkylate reactor effluent and an additional make-up iso-butane to a  
dividing wall column (DWC) to separate the alkylate reactor effluent into a plurality of DWC  
effluent streams comprising:  
an iso-butane recycle stream,  
10 a n-butane product stream, and  
an alkylate product stream; and  
recycling at least a portion of the iso-butane recycle stream to the alkylation  
reaction / regeneration section.

15 2. The alkylation process of claim 1, the plurality of DWC effluent streams further  
comprising a propane stream.

3. The alkylation process of claim 1, wherein feeding the alkylate reactor effluent and  
an additional make-up iso-butane to a dividing wall column (DWC) further comprises  
20 feeding the alkylate reactor effluent and the additional make-up iso-butane to a pre-  
fractionator section of the DWC.

4. The alkylation process of claim 1, further comprising:  
drawing the iso-butane recycle stream as an overhead product of the DWC;  
25 drawing the n-butane product stream from as a side draw of the DWC; and  
drawing the alkylate product stream as a bottoms product of the DWC.

5. The alkylation process of claim 4, further comprising:  
preheating the alkylate reactor effluent by heat exchange with the alkylate product  
30 stream prior to feeding the alkylate reactor effluent to the DWC; and  
routing the alkylate product stream to a battery limit.

6. The alkylation process of claim 4, further comprising flowing the alkylate product  
stream through an intermediate reboiler.

16 11 23



7. The alkylation process of claim 6, further comprising:  
preheating the alkylate reactor effluent by heat exchange with the alkylate product stream after the alkylate product stream has flowed through the intermediate reboiler and prior to feeding the alkylate reactor effluent to the DWC; and  
5 routing the alkylate product stream to a battery limit.

8. The alkylation process of claim 4, wherein at least a portion of the make-up iso-butane fed to the alkylation reaction / regeneration section comprises at least a portion of the iso-butane recycle stream and it is combined to the olefin stream upstream of the  
10 alkylation reaction / regeneration section to form a mixture.

9. The alkylation process of claim 8, further comprising directly delivering the mixture to the alkylation reaction / regeneration section without fractionating the mixture.

15 10. An alkylation process comprising:  
feeding an alkylate reactor effluent containing propane to a pre-fractionator section of a dividing wall column (DWC);  
routing a DWC overhead product containing propane to a depropanizer column;  
drawing an iso-butane recycle stream from a first side draw of a main-fractionator  
20 section of the DWC;  
recycling the iso-butane recycle stream to an alkylation reaction / regeneration section;  
drawing an n-butane product stream from a second side draw of the main-fractionator section of the DWC or of a bottoms section of the DWC, wherein the second  
25 side draw is selected from the group consisting of vapor, liquid, or a combination thereof;  
and  
drawing an alkylate product stream as a bottoms product of the DWC.

30 11. The alkylation process of claim 10, further comprising:  
preheating the alkylate reactor effluent by heat exchange with the alkylate product stream prior to feeding the alkylate reactor effluent to the DWC; and  
routing the alkylate product stream to a battery limit.

35 12. The alkylation process of claim 10, further comprising flowing the alkylate product stream through an intermediate reboiler.

13. The alkylation process of claim 10, further comprising feeding to a top tray of the main fractionator section of the DWC a reflux stream from an overhead condenser configured to condense vapors from the pre-fractionator section of the DWC and the main fractionator section of the DWC,

5 wherein the alkylate reactor effluent is fed to a top tray of the pre-fractionator section of the DWC.

14. The alkylation process of claim 13, wherein the DWC overhead product containing propane is drawn as a side draw from the main fractionator section of the DWC.