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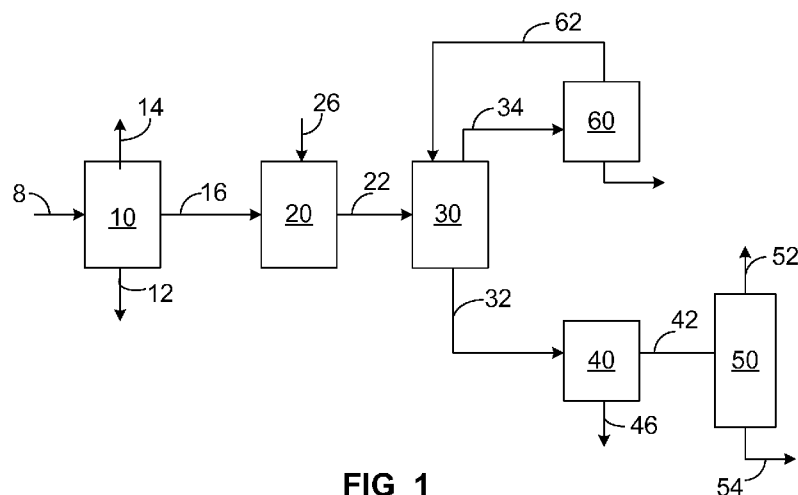


FIG 1

(57) Abstract: A process is presented for producing a purified normal paraffin product stream. The process includes passing a hydrocarbon stream having the desired normal paraffins to an adsorption separation system. A process stream generated from the separation system and having the normal paraffins is passed to an adsorption unit for the selective adsorption of aromatic compounds from the process stream, thereby producing a purified product.

HIGH PURITY HEAVY NORMAL PARAFFINS UTILIZING INTEGRATED SYSTEMS

STATEMENT OF PRIORITY

[0001] This application claims priority to U.S. Application No. 12/976,295 filed on
5 December 22, 2010.

FIELD OF THE INVENTION

[0002] The invention relates to adsorption separation processes. The invention is specifically directed at a process to improve the capacity and purity of normal paraffins.

BACKGROUND OF THE INVENTION

10 **[0003]** The separation of various substances through selective adsorption is an important process for producing pure substances. However, this generally is a batch process, but with the development of simulated moving bed (SMB) technology, the adsorption separation process can be operated on a continuous basis. For simulated moving bed technology, the process uses a multiport rotary valve to redirect flow lines in the process. The simulation of a
15 moving adsorbent bed is described in US 2,985,589 (Broughton et al.). In accomplishing this simulation, it is necessary to connect a feed stream to a series of beds in sequence, first to bed no. 1, then to bed no. 2, and so forth for numerous beds, the number of beds often being between 12 and 24. These beds may be considered to be portions of a single large bed whose movement is simulated. Each time the feed stream destination is changed, it is also necessary
20 to change the destinations (or origins) of at least three other streams, which may be streams entering the beds, such as the feed stream, or leaving the beds. The moving bed simulation may be simply described as dividing the bed into series of fixed beds and moving the points of introducing and withdrawing liquid streams past the series of fixed beds instead of moving the beds past the introduction and withdrawal points. A rotary valve used in the Broughton
25 process may be described as accomplishing the simultaneous interconnection of two separate groups of conduits.

[0004] There are many different process requirements in moving bed simulation processes, resulting in different flow schemes and thus variations in rotary valve arrangement. For example, in addition to the four basic streams described in Broughton

(US 2,985,589), it may be desirable to utilize one or more streams to purge, or flush, a pipeline or pipelines. A flush stream is used to prevent undesirable mixing of components. The flush substance is chosen to be one which is not undesirable for mixing with either main stream, that being purged or that which enters the pipeline after flushing is completed.

5 US 3,201,491 (Stine et al.) may be consulted for information on flushing lines as applied to the process of Broughton (US 2,985,589). It may be desirable to pass fluid through a bed or beds in the reverse direction from normal flow. This is commonly known as backflushing, a subject treated in US (Fickel). Other applications for various arrangements of multiport rotary disc valves may be seen in US 4,313,015 (Broughton); US 4,157,267 (Odawara et al.);
10 US 4,182,633 (Ishikawa et al.); and US 4,409,033 (LeRoy).

[0005] While the multiport rotary disc valve of Carson (US 3,040,777) provided a satisfactory valve design for the simultaneous interconnection of two independent groups of conduits such that each conduit of the first group could be brought into individual communication with every conduit of the second group, it is not suitable when three groups
15 of conduits must be simultaneously interconnected in the same manner. Upon reference to Broughton (US 2,985,589), it can be seen that there are only two groups of conduits which need to be interconnected when the arrangement of the drawing of that patent is utilized. One group consists of the conduits which provide the flows entering and leaving the simulated moving bed adsorbent system, that is, the flows which are switched among the beds, such as
20 the feed stream. A second group consists of the conduits associated with the individual beds, that is, which supply and remove fluid from the beds, one conduit being connected between each two beds. It is to be noted that each conduit of the second group serves that dual function of supply and removal, so that it is unnecessary to provide conduits for supplying fluid separate from those for removing fluid.

25 **[0006]** Adsorption separation uses expensive equipment, and the equipment is not readily replaced to increase the production of a product stream. With increasing demand for the products from adsorption separation processes, increasing the throughput and recovery of the products is desirable without having to replace the equipment.

SUMMARY OF THE INVENTION

30 **[0007]** The present invention improves the purity of a normal paraffin stream by selectively removing aromatic compounds from the extract stream. The process is for the

production of a purified heavy normal paraffin. A hydrocarbon stream is passed to a prefractionation unit to separate out a selected range of hydrocarbons. The prefractionation unit generates a first stream comprising light ends, a second stream comprising heavy ends, and a third stream comprising hydrocarbons in the desired range. The third stream is passed to a hydroprocessing unit where under a hydrogen atmosphere, contaminants within the stream are hydrogenated and removed, creating an effluent stream having reduced contaminants. The effluent stream is processed in an adsorption separation unit, where an extract stream comprising normal paraffins is generated, and a raffinate stream comprising non-normal hydrocarbons is generated. The extract stream is passed to an aromatics adsorption unit to selectively remove aromatic compounds that remain in the extract stream. The aromatics adsorption unit creates a process stream with a reduced heavy aromatic concentration. The process stream is passed to a separation unit to remove residual desorbent and light aromatics. The desorbent and light aromatics are components left in the aromatics adsorption unit during the regeneration of the aromatics adsorbent.

15 **[0008]** Additional objects, embodiments and details of this invention can be obtained from the following figures and detailed description of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] Figure 1 is a process flow of the present invention showing the improvement to achieve a high purity normal paraffin; and

20 **[0010]** Figure 2 is the process for the regeneration of the aromatics adsorber.

DETAILED DESCRIPTION OF THE INVENTION

[0011] A high purity heavy normal paraffin is required for some applications. The high purity, also includes having a low aromatic content. Conventional methods for producing a heavy normal paraffin result in a product that contains an aromatic content greater than 0.5% by weight. The high purity heavy normal paraffins require a purity of greater than 99.5 wt.% with an aromatic content less than 100 ppm by weight. Conventional methods use a high pressure hydrogenation process to saturate the aromatics, but this does not increase the overall purity of the heavy normal paraffin.

[0012] Linear alkylbenzenes (LABs) and secondary alkane sulfonates (SASs) are types of surfactant components used for the production of detergents. The production of LABs

requires a feedstream of linear olefins, which in turn can be produced from linear paraffins. The linear olefins useful for producing SASs for detergent production have linear carbon chains in the 10 to 20 range, and preferably in the 14 to 17 range. The linear olefins for producing LABs for detergent production have linear carbon chains in the 10 to 20 range, and are preferably grouped to within a range of 4 linear carbon chains, with some examples as 10 to 13, 11 to 14, and 14 to 17. One source of linear paraffins in this range is from light gas oil (LGO), which is a product stream cut from crude oil in the 200°C to 320°C range. This also can include hydrocarbons in the kerosene range. The present invention takes a portion of the feedstream, either LGO or other hydrocarbon stream, and further separates the material to provide a purified normal paraffin stream.

[0013] The present invention, as shown in Figure 1, is a process for the purification of a heavy normal paraffin. The process includes passing a hydrocarbon feedstream 8 to a prefractionation unit 10. The prefractionation unit 10 separates the feedstream into three streams. The unit 10 generates a first stream 12 of the heavy hydrocarbons, a second stream 14 of light hydrocarbons, and a third stream 16 of intermediate hydrocarbons. The intermediate hydrocarbons are a desired selected group of hydrocarbons in the range of C14 to C17 hydrocarbons. The third stream 16 includes normal paraffins, aromatics, branched paraffins and other hydrocarbons. The heavy stream 12 comprises hydrocarbons having 18 or more carbon atoms, and the light stream 14 comprises hydrocarbons having 13 or fewer carbon atoms.

[0014] The third stream 16 is passed to a hydroprocessing unit 20, where contaminants, such as sulfur and nitrogen are reacted over a hydroprocessing catalyst under a hydrogen atmosphere 26 and removed. This is done to extend the life of the adsorbent in the adsorption separation unit 30. In addition, the hydroprocessing unit 20 partially hydrogenates some of the unsaturated hydrocarbons, such as olefins and aromatics. Hydrogenating a portion of the olefins increases the paraffin content and can increase the yields of normal paraffins. The hydroprocessing unit 20 generates an effluent stream 22 having a reduced contaminant content. The effluent stream 22 is passed to an adsorption separation unit 30, where normal paraffins are separated from the non-normal paraffins and remaining types of hydrocarbons. The adsorption separation unit 30 generates an extract stream 32 that includes normal paraffins and desorbent, but also includes a small amount of aromatic compounds that the process does not remove to a sufficiently low concentration. The extract stream 32 is

passed to a paraffin extract purification adsorbent system 40 to remove a significant portion of the residual aromatics in the adsorbent stream 32, and to generate a purified extract stream 42 containing normal paraffins and desorbent. The extract stream 32 is not processed through an expensive fractionation column, but is passed directly to the adsorbent system 40.

5 The purified extract stream 42 is passed to an extract fractionation column 50 to separate the stream into a desorbent stream 52 and a normal paraffin product stream 54. The desorbent stream 52 is re-used in both the adsorption separation unit 30 and the adsorbent system 40. The normal paraffin product stream 54 has a heavy aromatic content of less than 0.5 wt%. Preferably, the process will be operated to reduce the heavy aromatic content to less than 100
10 ppm by weight. The heavy aromatics include aromatic hydrocarbons having between 14 and 17 carbon atoms. The adsorption units 40 eliminate the need for an extract fractionation column to separate the extract from the desorbent. In an alternate embodiment, the extract stream 32 can be passed to a fractionation column before passing the extract stream to the adsorbent unit 40. In this embodiment, the desorbent is substantially removed from the
15 extract stream 32, creating an extract stream with reduced desorbent content. The extract stream with reduced desorbent content is passed to the adsorbent unit 40 and residual aromatics are removed.

[0015] The adsorption separation unit 30 also generates a raffinate stream 34 that includes the desorbent, non-normal paraffins and other hydrocarbons. The raffinate stream
20 34 is passed to a raffinate fractionation column 60 to separate the raffinate stream 34 into a desorbent stream 62 and a bottoms stream 64 comprising non-normal paraffins, and other hydrocarbons. The bottoms stream 64 can be passed to other processing units. The desorbent stream 62 is re-used in the adsorption separation unit 30.

[0016] The adsorption separation system used for the continuous processing of
25 hydrocarbons uses a simulated moving bed system, wherein the adsorption separation simulates the counter-current contact of a feedstream with an adsorbent. In a simulated context, the fluid flows down a column of beds, and the solid adsorbent moves up the column of beds.

[0017] The process has four zones: an adsorption zone where the feedstream contacts the
30 adsorbent and selectively adsorbs the desired components thereby creating a raffinate stream; a purification zone where undesired components are flushed from the system to prevent contamination of the desorption zone; a desorption zone, where a liquid desorbent is added to

displace the adsorbed component in the adsorbent beds thereby creating an extract stream; a buffer to prevent the contamination of liquid from desorption zone with the liquid in the adsorption zone. More information on the process is available in numerous patents and references, including US 5,912,395, which is incorporated by reference in its entirety.

5 **[0018]** The adsorption process in the present invention uses molecular sieving where the pores in the adsorbent are sized to allow for normal paraffins, but non-linear molecules are prevented from entering the pores.

10 **[0019]** The process of adsorbing heavy aromatics in the adsorbent unit 40 generates some light aromatics in the purified extract stream 42. The light aromatics include aromatics in the C6 to C8 range, and are light components that are used in the regeneration of the adsorbent in the adsorbent unit 40. The purified extract stream 42 when passed to the separation unit 50, includes in the overhead stream 52 light aromatics which can be re-used in the adsorbent unit 40.

15 **[0020]** The process is a continuous process, and can include two or more adsorbers in the heavy aromatic adsorbent units 40, where at least one adsorber is on-line and processing the extract stream 32, and one adsorber is off-line. When an adsorber is taken off-line, it is regenerated and later returned to on-line status as an on-line unit is taken off-line. The regeneration process, as shown in Figure 2, includes a first step of passing a stream 44 of purge material through the adsorbent unit 40. The purge stream 46 is then passed to a
20 fractionation unit 70. After purging the adsorbent unit 40, a desorbent stream 48 is introduced to the adsorption unit 40. A desorption stream which is separate from the purge stream 46 is generated carrying the heavy aromatic components to the fractionation unit 70. In a preferred embodiment, the invention comprises six adsorbers in the adsorbent unit 40, with four of the adsorbers on-line, while a fifth adsorber is being purged and a sixth adsorber is being regenerated. The process can include more or less adsorbers in the adsorption unit
25 40, depending on the size of the process streams.

30 **[0021]** The purge material can comprise a hydrocarbon stream having a different boiling point than the material in the C14 to C17 range. A light material such as hydrocarbons in the C5 to C10 range is appropriate for displacing larger hydrocarbons left behind in the adsorbent unit 40. In one embodiment, a selection for the purge stream is a mixture of n-pentane and isooctane. The adsorbent is selected to preferentially adsorb aromatic compounds. The desorbent needs to be selected to displace the adsorbed aromatic compound, and to have a

different boiling point from the adsorbed material. A light aromatic compound in the C6 to C8 range is an appropriate choice. In one embodiment, para-xylene is selected for desorbing the heavy aromatics from the aromatics adsorption unit 40.

5 **[0022]** The choice of para-xylene is beneficial to the process, as para-xylene is also used in the adsorption separation unit 30, to purge material in the zone flush of the adsorption separation unit 30. The choice of purge material for the aromatics adsorption unit 40 is the same as the desorbent mixture for use in the adsorption separation unit 30. The process benefits by having the desorbent and purge materials do double duty in that the desorbent and purge materials are used in both adsorption units.

10 **[0023]** The fractionation unit 70 receives the purge stream 46 and the desorption stream which is separate from the purge stream 46 to separate the material recovered from the adsorption unit 40 during regeneration. The separated streams include a first stream 72 comprising the purge material, a second stream 74 comprising the desorbent and a residual amount of the treated feedstream, and a third stream 76 comprising the heavy aromatics in
15 the C14 to C17 range. The heavy aromatics can be returned to the LGO process stream, or other process units. The fractionation unit 70 can comprise a divided wall column or can comprise two separate columns.

20 **[0024]** While the invention has been described with what are presently considered the preferred embodiments, it is to be understood that the invention is not limited to the disclosed embodiments, but it is intended to cover various modifications and equivalent arrangements included within the scope of the appended claims.

CLAIMS:

1. A process for producing a purified heavy normal paraffin, comprising:
 - passing a hydrocarbon feedstream to a prefractionation unit, thereby generating a first stream comprising light ends, a second stream comprising heavy ends, and a third stream
 - 5 comprising the selected hydrocarbons;
 - passing the third stream to a hydroprocessing unit, thereby creating a effluent stream having reduced contaminants;
 - passing the effluent stream to an adsorption separation unit, thereby creating an extract stream comprising normal paraffins, and a raffinate stream comprising non-normal
 - 10 hydrocarbons and desorbent; and
 - passing the extract stream to an aromatics adsorbent unit for selective adsorption of aromatics, thereby creating a process extract stream having heavy aromatic content of less than 0.5 wt%.
- 15 2. The process of claim 1 wherein the heavy aromatic content comprises aromatics in the C14 to C17 range.
3. The process of claim 1 further comprising the process extract stream to a separation unit, thereby creating the purified heavy normal paraffin stream, and a light aromatics stream.
- 20 4. The process of claim 3 wherein the light aromatics stream comprises C6 to C8 aromatics.
5. The process of claim 4 wherein the light aromatics stream comprises para-xylene.
- 25 6. The process of claim 1 further comprising:
 - purging the adsorbent unit, thereby creating a purge stream; and
 - passing a desorbent through the adsorbent unit, thereby creating a desorption stream.
7. The process of claim 6 wherein the adsorbent unit is purged with a purge stream
- 30 comprising light hydrocarbons in the C5 to C10 range.

8. The process of claim 1 wherein the hydroprocessing unit also performs partial hydrogenation of aromatics.
9. The process of claim 1 wherein the heavy aromatic content in the process extract stream is
5 less than 100 ppmw.
10. The process of claim 1 wherein the selected hydrocarbons are C14 to C17 hydrocarbons.

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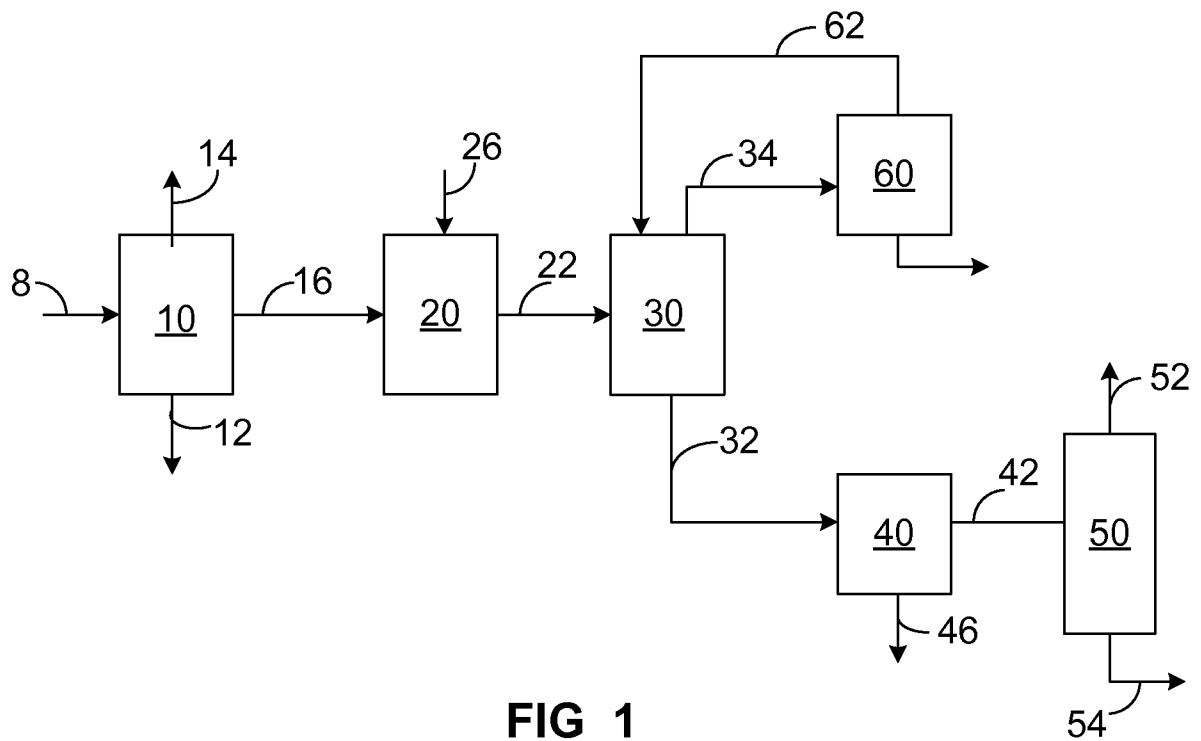


FIG 1

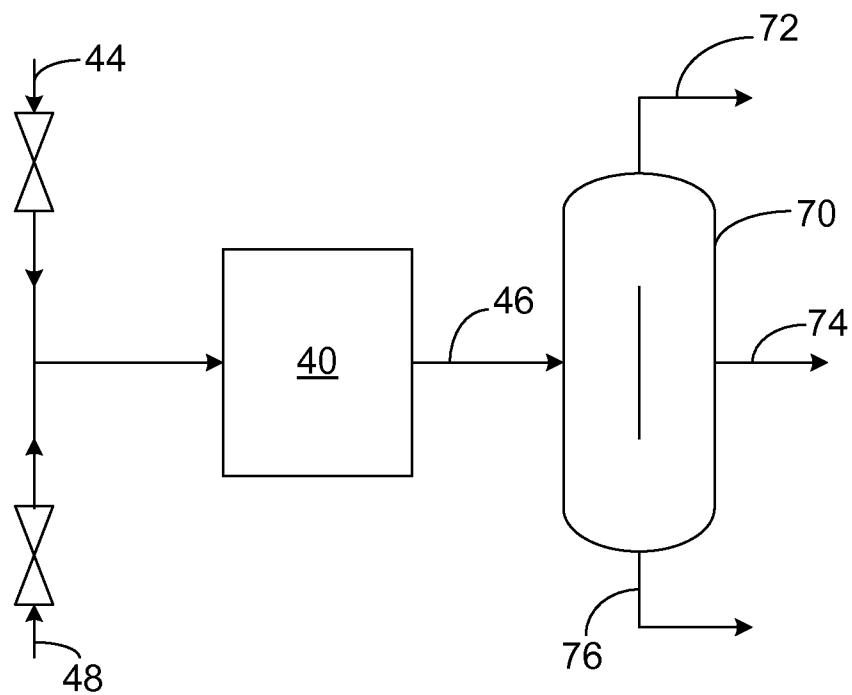


FIG 2