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A process for removing organic carbonyl-containing contaminants from a hydrocarbon product stream

This invention relates to a process for the removal of carbonyl-containing contaminants from hydrocarbon product streams.

The invention is particularly useful in the purification of butadiene, an important industrial chemical used in the manufacture of synthetic rubber, latex paints, and nylon and in the Diels-Alder condensation for the synthesis of many diverse compounds. In the synthesis of butadiene, small amounts of carbonyl-containing impurities (e.g., acetaldehyde) are produced and it is important that these impurities be removed or they will have an adverse effect on subsequent processes in which the butadiene is a raw material. Although the carbonyl content of the butadiene product stream is low (being typically measured in parts per million), the heretofore used procedures for reducing it to an acceptable level have been undesirably elaborate and expensive.

It is, of course, known to employ an aqueous solution of a reducing agent such as sodium bisulphite to remove carbonyls from a hydrocarbon product stream. U. S. Specification 3,674,887 discloses such a use: however, according to that specification the stream to be purified is absorbed into mineral oil and then twice scrubbed in countercurrent flow, whereafter a two-stage stripping operation is performed to recover the product. Similarly, according to U. S. Specification 3,682,779 the product stream to be purified is first absorbed into oil: and the contacting with the aqueous bisulphite is countercurrent, involving a specially engineered stripping tower.

We have now discovered a continuous process for such carbonyl removal which is simple, reliable and relatively inexpensive; and which effects the removal in a single step, permitting the treated product stream to proceed directly to storage or subsequent processing.

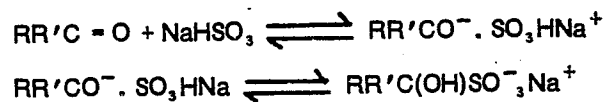
According to the present invention a process for removing organic carbonyl-containing impurities from a hydrocarbon product stream comprises passing that stream, together with an aqueous solution containing an excess (with respect to said impurities) of a reducing agent capable of forming a water-soluble adduct with carbonyl compounds, to an in-line mixer, passing the resulting mixture to a separation zone in which organic and aqueous phases separate, and withdrawing the organic phase from the separation zone.

In-line mixing, being thorough, causes excellent contact between the phases mixed and leads to a high degree of impurity removal at the exposure of only a slight stoichiometric excess of reducing agent.

In a particular embodiment of the invention there is employed a second separation zone, simultaneously or in alternation with the first. The lower portion of either or both zones may

contain column-packing elements designed to enhance contact between the two phases introduced as mixture therein. Advantageously, the position of the interface between the phases in a separation zone is maintained between predetermined limits by withdrawal of a phase from a separation zone in response to a signal generated by movement of the interface.

The invention thus encompasses a process arrangement wherein a continuous stream of such organic hydrocarbon product, bearing the undesired carbonyl-containing compounds, is contacted with an aqueous solution comprising a reducing agent (e.g., sodium bisulfite) suitable for forming on contact a water soluble reaction product with such carbonyl compounds, such reducing agent being in greater, preferably just slightly greater, concentration than the theoretical stoichiometric ratio for reaction of all of the carbonyl in the organic product. For example, an excess of such reducing agent (e.g., sodium bisulfite) will tend to drive the following equilibrium equations to the right:



where R is alkyl, alkylene, aryl, aralkyl, etc., and R' is the same as R or is hydrogen, hydroxy, or ester.

To ensure good contact in the continuous process as embodied herein, the aqueous solution of the reducing agent and the organic product stream are passed through an in-line mixing zone where they are well mixed. The mixture is then introduced into a phase separating zone where a separation of the aqueous and organic phase occurs. The organic is displaced by the denser water solution already in the separator, the organic material traveling in upward direction until it crosses the interface between the two phases. From the point of entry to the interface, the product is once again contacted with water solution as it migrates toward the interface or, optionally, by means of internal tower packing. The "scrubbed" product continues to rise in the separator and, as overhead from the separator, may be passed to an optional second scrubber which acts as a back-up system in case of surge conditions or maintenance of the first system.

The aqueous layer, containing the absorbed carbonyl-bearing compound, is removed at bottom of the phase separator by means of interface level control means. This stream then fed to a flash pot at the cooling to dropped to atmospheric pressure. The organic material remaining in the flash to vapor form and be removed

water then passes to appropriate disposal means.

Understanding of the invention disclosed herein will be facilitated by reference to the single drawing FIGURE, which depicts a flow sheet of a typical process configuration in accord with the invention.

Referring to the Figure, a continuous stream of organic material, in specific embodiment being butadiene in mixture with undesired carbonyl-bearing organic compounds, is supplied directly from production means 1. The organic stream is sent to valve 9 where it is routed either to SYSTEM A via conduit 9a, to SYSTEM B via conduit 9b, or is split, some of it being sent to each system to increase throughput of the overall operation.

The aqueous scrubbing solution is prepared in mixing vat 5 where reducing agent 3 (e.g. sodium bisulfite) is dissolved in water to a convenient concentration. This primary or concentrated scrubbing solution is then pumped out of vat 5 and, if dilution to a lower concentration is necessary, is sent via injection pump 6 to mixing pump 7 where it is diluted to a predetermined concentration of reducing agent by mixing with make-up water 2 and brought to the same pressure as the hydrocarbon product stream from production means 1. The scrubbing solution, which is now at the same pressure as the hydrocarbon product and has a concentration of reducing agent which is 10% to 20% higher than the stoichiometric concentration theoretically required for complete reaction with the carbonyl compounds in the hydrocarbon product, is pumped to valve 8 which directs it to SYSTEM A via conduit 8a or to SYSTEM B via conduit 8b or which splits the stream and sends part of it to each system for simultaneous operation.

Confining the description to SYSTEM A for the moment, the hydrocarbon product (conduit 9a) and the aqueous scrubbing solution (conduit 8a) are introduced into in-line mixing means 10 where they are thoroughly and intimately blended. This mixture is then sent to phase separator 11 for separation of the organic and aqueous phases.

Phase separator 11 is preferably a vertically elongated enclosed container having an overhead outlet means 14 at the top portion for removal of the liquid organic phase and a drain line 17 at the bottom portion for removal of the aqueous phase. Flow of the aqueous phase through drain line 17 is controlled by valve 16, which in turn is operated remotely by interface level control means 15. The phase separator 11 may optionally contain in its lower section a quantity of internal packing material 12 through which the organic/aqueous mixture is percolated while the phases are separating or, alternatively, the separator 11 may be empty and the phases allowed to separate with additional percolation. There are many column packing materials, which are suitable for this

application, a few non-limiting examples being Berl saddles, Intalox saddles and Raschig rings.

The organic/aqueous mixture from in-line mixing means 10 is introduced into the lower portion of phase separator 11. As the organic and aqueous phases in separator 11 begin to separate, the organic phase is displaced by the denser aqueous solution. The "scrubbed" organic phase, being of lesser density than the aqueous solution, travels, up the phase separator 11 until it crosses the interface 13 between the two phases. From the point of entry into phase separator 11 until it reaches 13, the organic product is once again contacted with aqueous solution, such recontact being aided by percolation through packing 12 if such packing is employed. The "scrubbed" product, having now had the major portion of the carbonyl-bearing contaminant removed, continues to travel up the tower and is taken off overhead at outlet means 14.

Interface level control 15 may be any conventional device for detecting the location of interface 13 between the upper organic phase and the lower aqueous phase. Control 15 is adapted to operate valve 16 such that when the aqueous level in phase separator 11 increases to the point where interface 13 reaches some predetermined level 15a, the valve 16 is opened and separated aqueous solution is drained out of the bottom of separator 11 through drain line 17. When the level of the aqueous phase has been reduced such that interface 13 reaches predetermined level 15b, level control 15 causes valve 16 to be closed. In practice it may be preferable that, instead of level control 15 merely causing valve 16 to be either open or closed, the control be of a type which will continuously regulate the degree of openness relative to the position of the interface 13, i.e. the nearer interface 13 is to level 15a the more fully open valve 16 becomes, and the nearer interface 13 is to level 15b the more closed (relatively) valve 16. In some instances, it is desirable that valve 16 be partially open at all times so that there is continuous removal of aqueous phase through drain line 17 at a rate equal to or less than the rate of addition of aqueous phase via conduit 8a. In the latter case, interface level control 15 would serve as a precautionary safety factor should aqueous material enter the phase separator at a rate which is faster or slower than the expected rate. Examples of suitable control devices would include any conventional interface controller useful for normal service applications.

The in-line mixing means 10 is also of conventional type suitable for admitting two or more streams of unlike materials and continuously mixing them to form a single relatively homogeneous stream. An example of such mixing means would be the KOCH ENGINEERING STATIC MIXER.

The aqueous wash solution removed through drain line 17 is taken via conduit 18 to a suit-

able in-plant wash water disposal means where it is brought to atmospheric pressure, and any absorbed organic material is volatilized. The organic vapors are then either collected and recovered or are sent to suitable disposal means, such as a flare where they are burned. The wash water, containing the reaction products of the carbonyl compounds with the reducing agent and any excess reducing agent, is likewise appropriately disposed of.

The cleaned-up product removed overhead from phase separator 11 at outlet 14 is routed to valve 19 from whence it may take one or two directions. If the carbonyl content is sufficiently reduced and the aqueous phase completely or substantially completely separated, the organic stream is sent through conduit 28 to storage facilities where it is held until required for shipment or subsequent synthetic processes, or it may be sent directly to such subsequent processing as deemed necessary. If further scrubbing treatment is desirable, by virtue of requirements to further reduce the carbonyl content of the product or because of incomplete phase separation (for example, as might be caused by surge conditions in SYSTEM A), the overhead stream from outlet 14 is directed into conduit 9b and fed to SYSTEM B.

SYSTEM B is substantially identical to SYSTEM A and serves various purposes. It can be used as a back-up to SYSTEM A in the event of incomplete phase separation therein or the need for further reduction in the carbonyl content of the scrubbed product, or it can serve as a substitute for SYSTEM A to allow for maintenance of that system.

In the event of surge conditions in SYSTEM A, as might result from a sudden and substantial increase in product input or failure of the interface level control 15 and/or drain valve 16 to function properly, thereby causing incomplete phase separation such that the overhead stream being removed at outlet 14 undesirably contains aqueous material as well as organic material, the overhead stream is redirected by means of valve 19 through line 9b and into phase separator 21 where separation and removal of the aqueous phase takes place. The scrubbed organic phase is then taken off at outlet 24 and sent through conduit 28 to the appropriate storage facilities.

Should it become necessary to further reduce the carbonyl content of the "scrubbed" organic product after initial treatment in phase separator 11, for instance because of some especially stringent requirement or because SYSTEM A has for some reason not functioned efficiently enough to meet the usual product specification, the organic stream is redirected through line 9b as above and, together with fresh aqueous scrubbing solution from line 8b, is fed into in-line mixing means 20. The subsequent mixing and phase separation are the same as those described with respect to SYSTEM A. The

scrubbed organic product is taken off overhead at outlet 24 and sent to storage.

At those times when it becomes necessary to shut-down SYSTEM A entirely, as when performing preventive maintenance procedures or replacing malfunctioning equipment, SYSTEM B can be substituted without interruption of the scrubbing operation. To accomplish this the organic product is simply rerouted, by means of valves 9 and 19, through line 9b while the aqueous scrubbing solution is rerouted through line 8b by means of valve 8. SYSTEM A is then completely out of the stream and readily accessible to maintenance personnel while SYSTEM B carries the full output from production means 1.

Non-limiting examples of organic hydrocarbons, the production product of which is likely to contain an impurity of carbonyl compounds and which are amenable to the present process for the removal of such impurity, include any hydrocarbon in the C_4 — C_8 range which is the product of the pyrolysis of other organic compounds. Especially preferred is butadiene.

Compounds suitable for use as reducing agents in the present process include: metal (e.g. sodium) bisulfite; hydrazine; hydroxylamine; and phenylhydrazine; which are water soluble and form water soluble reaction products on contact with carbonyl-bearing organic compounds dissolved in organic medium.

Example

Butadiene, containing 300 ppm carbonyl (as acetaldehyde), is supplied in a continuous stream from conventional production facilities. Such a stream, at a pressure of 150 psia and a temperature of 29°—32°C (85—90°F), enters the system as illustrated in the drawing.

Aqueous scrubbing solution, containing 4—5 wt. % sodium bisulfite, is pumped from vat 5 to pump 7, where it is diluted to 700—900 ppm sodium bisulfite with additional water. This dilute scrubbing solution is then pumped to SYSTEM A at a pressure of 120 psia and ambient temperature.

The two streams are blended in the in-line KOCH STATIC MIXER 10, in proportions resulting in a mixture having a mole ratio of reducing agent to carbonyl compound of 1.1:1 to 1.2:1, and the mixture fed into the lower portion of the phase separator 11 where the organic and aqueous phases are separated (without the use of the optional packing 12) at 125 psia and 27°C (80°F).

The resulting "scrubbed" butadiene product is taken off overhead via outlet 14 from the phase separator and has a carbonyl content (as acetaldehyde) of <2 ppm. It is then sent directly to the normal storage facilities to await appropriate disposition.

The used wash water is drained from the

bottom of the phase separator 11 by means of a drain valve 16, controlled by conventional level control device 15, fed to a flash pot and dropped to atmospheric pressure. Any volatile organic material in the water solution is flashed off and fed to a plant flare system to be burned or is otherwise disposed of. The water is pumped into a cooling tower basin.

Claims

1. A process for removing organic carbonyl-containing contaminants from a hydrocarbon product stream comprising passing that stream, together with an aqueous solution containing a stoichiometric excess with respect to said contaminants of a reducing agent capable of forming a water-soluble adduct with carbonyl compounds, to an in-line mixing zone, passing the resulting mixture to a separation zone in which organic and aqueous phases separate, and withdrawing the organic phase therefrom.

2. A process according to claim 1 wherein a second separation zone is employed simultaneously, or in alternation with the first.

3. A process according to claim 1 or claim 2 wherein said mixture is introduced into a lower portion of a separation zone which portion contains column-packing elements promoting inter-phase contact.

4. A process according to any preceding claim wherein the position of the interface between the phases in a separation zone is maintained between predetermined limits by withdrawal of a phase from the zone in response to a signal generated upon approach of the interface to one of those limits.

5. A process according to any preceding claim wherein said hydrocarbon product is butadiene.

6. A process according to any preceding claim wherein said contaminant is acetaldehyde.

7. A process according to any preceding claim wherein said reducing agent is sodium bisulfite.

Revendications

1. Procédé pour l'élimination des contaminants organiques contenant des composés carbonylés d'un courant d'hydrocarbures, caractérisé en ce qu'il consiste à faire passer ce courant, ensemble avec une solution aqueuse contenant un excès stoechiométrique, par rapport auxdits contaminants, d'un agent réducteur capable de former un produit d'addition soluble dans l'eau avec les composés carbonylés, dans une zone de malaxage en ligne, puis à faire passer le mélange résultant dans une zone de séparation dans laquelle les phases

organique et aqueuse se séparent et à en soutirer la phase organique.

2. Procédé selon la revendication 1, caractérisé en ce qu'une seconde zone de séparation est utilisée simultanément, ou en alternance, avec la première.

3. Procédé selon l'une des revendications 1 ou 2, caractérisé en ce que ledit mélange est introduit dans une partie inférieure d'une zone de séparation, laquelle partie contient des éléments de garnissage de colonne facilitant un contact entre les phases.

4. Procédé selon l'une quelconque des revendications 1 à 3, caractérisé en ce que la position de l'interface entre les phases dans une zone de séparation est maintenue entre des limites prédéterminées par soutirage d'une phase hors de la zone en réponse à un signal engendré lorsque l'interface approche d'une de ces limites.

5. Procédé selon l'une quelconque des revendications 1 à 4, caractérisé en ce que le produit d'hydrocarbure est le butadiène.

6. Procédé selon l'une quelconque des revendications 1 à 5, caractérisé en ce que le contaminant est l'acétaldéhyde.

7. Procédé selon l'une quelconque des revendications 1 à 6, caractérisé en ce que l'agent réducteur est le bisulfite de sodium.

Patentansprüche

1. Verfahren zur Entfernung von organischen carbonylhaltigen Verunreinigungen aus einem Kohlenwasserstoffproduktstrom, dadurch gekennzeichnet, daß der Strom zusammen mit einer wäßrigen Lösung, die einen stöchiometrischen Überschuß (mit Bezug auf die Verunreinigungen) eines Reduzierungsmittels enthält, das zur Bildung eines wasserlöslichen Adduktes mit Carbonylverbindungen in der Lage ist, in eine in Reihe geschaltete Mischzone geleitet, das resultierende Gemisch in eine Trennzone geleitet, worin organische und wäßrige Phasen getrennt werden, und die organische Phase daraus entfernt wird.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß eine zweite Trennzone gleichzeitig oder im Wechsel mit der ersten Zone angewendet wird.

3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß das Gemisch in einen unteren Teil einer Trennzone eingeleitet wird, wobei dieser Teil Kolonnenpackelemente enthält, die die Interphasenberührung fördern.

4. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß die Grenzflächenlage zwischen den Phasen in der Trennzone innerhalb der vorgegebenen Grenzen durch Abziehen einer Phase aus der Zone als Reaktion auf ein Signal aufrechterhalten wird, das beim Annähern der Grenz-

fläche an eine dieser Grenzen erzeugt wird.

5. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß als Kohlenwasserstoffprodukt Butadien verwendet wird.

6. Verfahren nach einem der vorhergehenden

den Ansprüche, dadurch gekennzeichnet, daß die Verunreinigung aus Acetaldehyd besteht.

7. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß als Reduziermittel Natriumbisulfit verwendet wird.

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