METHOD FOR CONTINUOUS PERACETIC ACID ANALYSIS

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ABSTRACT OF THE DISCLOSURE

Process for monitoring the peracetic acid content of a gaseous stream, such as the effluent of a vapor phase acetaldehyde oxidation column, by combining the stream with a metal iodide solution and measuring the resulting color intensity of the solution.

The present invention relates to a process for monitoring the peracetic acid content of a fluid stream. More particularly, the invention relates to a process for continuously and rapidly monitoring the peracetic acid content of a gaseous product stream obtained from a vapor phase acetaldehyde oxidation zone.

The production of peracetic acid by reaction of oxygen with acetaldehyde in the vapor phase is known, as described in MacLean et al. United States Patent No. 3,192,256. The product peracetic acid is withdrawn from the reaction zone a gaseous stream in admixture with unreacted oxygen and acetaldehyde, and undesired by-product acetic acid.

The effluent gaseous peracetic acid is very reactive and decomposes rapidly to form acetic acid and oxygen as well as reacting with excess acetaldehyde to form acetic acid. As a result, the peracetic acid is normally used immediately upon withdrawal from the reaction zone. For example, the peracetic acid, which is an excellent oxidizer, may be directly introduced into an epoxidation reaction zone.

Because of the immediate use of the peracetic acid effluent it is highly desirable that a quick and accurate analytical method be made of the effluent stream to assure proper process control in the subsequent unit operations such as the epoxidation zone and the various purification units associated therewith. The peracetic acid oxidation reaction is quite sensitive and any contamination or imbalance of the process conditions will cause a drastic drop in the peracetic acid production rate which will in turn upset the unit operations downstream. Unfortunately, heretofore there was no practical method for rapidly and continuously analyzing or monitoring the peracetic acid content of the effluent gaseous stream before a substantial amount of the peracetic acid decomposed or reacted.

Accordingly, the primary object of the present invention is to provide an improved process for monitoring or analyzing the peracetic acid content of a fluid stream. Another object is to provide a process for rapidly and continuously monitoring the peracetic acid content of a gaseous effluent stream, and particularly the gaseous effluent obtained from an acetaldehyde vapor phase oxidation zone.

In accordance with the present invention, a process is provided for monitoring the peracetic acid content of a fluid stream. A predetermined amount of an aqueous solution of a metal iodide is mixed with a predetermined amount of the fluid stream containing the peracetic acid, whereby the peracetic acid reacts with the metal iodide to liberate iodine according to the following reaction A:

$$\text{CH}_2\text{C}O\text{OH} + 2\text{I}^- \rightarrow \text{CH}_2\text{C}O\text{I} + \text{I}_2 + \text{H}_2\text{O} + \frac{1}{2} \text{O}_2$$

The color intensity of the resulting iodine-containing solution is then measured.

As previously mentioned, the effluent gaseous stream from an acetaldehyde vapor phase oxidation zone comprises peracetic acid, by-product acetic acid, and unreacted or excess oxygen and acetaldehyde. It has been found that when such a gaseous stream is mixed with an aqueous solution of a metal iodide, such as potassium iodide, only the peracetic acid reacts with the iodide, thereby liberating iodine. The reaction is quite rapid, for example, in the range of from about 1 to 30 seconds and usually 1 to 10 seconds. Hence, the peracetic acid undergoes little if any decomposition or by-product reaction from the time it is withdrawn from the oxidation reaction zone, mixed, and reacted with the iodide solution.

The amount of iodine liberated by the reaction is directly proportional to the amount of peracetic acid in the effluent stream. As the iodine is liberated the color intensity of the resulting iodine-containing solution correspondingly increases. As a result, the peracetic acid content of the effluent stream can be determined by measuring the color intensity of the resulting solution. The resulting color intensity is then compared or evaluated with reference to a previously calibrated scale.

Methods for calibrating instruments to measure color intensity are well known. For example, a range of gaseous blends containing known amounts of peracetic acid can be mixed with aqueous iodide solutions. An unknown blend may then be mixed with an iodide solution, always using similar predetermined amounts for the gaseous and aqueous streams, and the resulting color compared with the previously obtained standards to determine the concentration of the peracetic acid.

By using the above process the peracetic acid content of an effluent stream may be continuously and rapidly monitored. Thus, any difficulties in the peracetic acid production can be quickly spotted and corrections made, thereby minimizing problems in the downstream unit operations.

For a better and more complete understanding of the present invention, its objects, and advantages, reference should be had to the following description and to the accompanying drawing which is a schematic flow diagram illustrating a process for monitoring the peracetic acid content of an effluent gaseous stream obtained from an acetaldehyde vapor phase oxidation reaction zone, the peracetic acid being used in an epoxidation zone.

Oxygen and acetaldehyde are introduced via a conduit into any conventional type vapor phase oxidation reaction zone, wherein the acetaldehyde is oxidized at a temperature in the range of from about 80 to 200°C, and preferably from about 140 to 180°C. The oxygen may be supplied to the zone in substantially pure form, or in admixture with an inert diluent, for example, air. It is desirable to have at least 5 mol percent of oxygen, and preferably higher, in the feed mixture. Generally, the optimum reaction time is in the range of from about 5 to 30 seconds, when operating at atmospheric pressure. At higher pressures the reaction rate increases, and optimum time of contact will be less.
Preferably, the oxygen and acetaldehyde reaction is carried out in a reactor, the surfaces of whose walls are substantially inert in the reaction, as fully disclosed in Maslan et al. U.S. Patent No. 3,192,256. Preferably the reactor walls are made of aluminum such as aluminum oxide.

As a result of the above oxidation reaction, peracetic acid is formed, as well as some undesired by-product acetic acid. These products and any unreacted excess oxygen and acetaldehyde are withdrawn from the zone 4 via a conduit 6. Generally the effluent gaseous stream contains up to about 30 percent by volume of peracetic acid, and preferably from about 15 to 28 percent. As previously mentioned, because of the rapid decomposion of the peracetic acid it is desirable to immediately introduce the effluent gaseous stream into an epoxidation zone 8, wherein the peracetic acid is used to epoxidize alkenes introduced via a conduit 9 to obtain an epoxy product recovered via a conduit 10.

A side-stream of the gaseous effluent is diverted from the conduit 12 and introduced into any conventional type liquid-gaseous mixing zone 14, for example, a column wherein the gas is bubbled into the liquid via a porous disc. An aqueous solution of a metal iodide is also introduced via a conduit 16 into the mixing zone 14, wherein the materials are mixed, and a result, the peracetic acid reacts with the metal iodide to liberate iodine according to the aforementioned reaction A.

Any water-soluble metal iodide may be used in the present invention such as alkaline metals and alkaline earth metal iodides, for example, potassium iodide, sodium iodide, and calcium iodide. Preferably, however, potassium iodide is used in order to minimize the amount of water introduced into the system a near-saturated solution, e.g., a solution containing 80 to 100 grams KI per 100 grams water, is conveniently employed. However, any lower concentration may be used if so desired. It is preferred that a slight excess of iodide over the maximum anticipated stoichiometric requirement be introduced into the mixing zone 14 to assure that essentially all of the peracetic acid in the sample stream will be reacted.

Any convenient temperature may be used in the mixing zone 14. Normally, the aqueous solution of the metal iodide is introduced at about room temperature (23° C.) and the peracetic acid effluent is introduced at essentially the temperature at which it is withdrawn from the oxidation reaction zone 4, normally from about 130 to 170° C. Hence, the resulting temperature upon mixing of the materials is normally in the range of from about 50 to 130° C. Atmospheric pressures are usually employed in the zone 14, however, higher or lower pressures may be used if so desired. As previously mentioned, essentially all of the peracetic acid is reacted with the metal iodide within a matter of seconds, normally in the range of from about 1 to 30 seconds, and more preferably from about 1 to 10 seconds.

The resulting iodine-containing solution is withdrawn from the mixing zone 14 via a conduit 18 and introduced into an additional type of color intensity measuring zone 20, for example, a photometric cell, wherein the color intensity of the iodine-containing solution is measured. The effluent iodine solution is withdrawn from the zone 20 via a conduit 22 and normally discarded. Comparing the color intensity with a previously calibrated instrument yields the concentration of the peracetic acid in the effluent gaseous stream.

The feed rate of the effluent gaseous stream via the conduit 12 and of the aqueous solution via the conduit 16 must be the same as the feed rates used to calibrate the color measuring instrument 20.

While it is desirable to introduce a pure aqueous solution of the metal iodide into the mixing zone 14, frequently the aqueous solution contains iodates or other impurities which have a tendency to liberate iodine and thereby interfere with the measurement of the color intensity of the iodine-containing solution. Hence, it is prefered to initially mix the aqueous solution of metal iodide with an acid such as hydrochloric or acetic, and the like to react with the iodates, thereby liberating iodine. The acid-treated aqueous solution of metal iodide is then passed via a conduit 24 into a color intensity measuring zone 26. In this manner, the reference color is always known and the differential intensity, as measured by the zones 20 and 26, may be used to give the correct peracetic acid content. The acid-treated aqueous solution of metal iodide is conveyed to the mixing zone 4 via conduits 28 and 16.

Preferably, the above process is conducted on a continuous basis so that the peracetic acid content may be constantly known. However, intermittent or batch operations may be used if so desired. Typical continuous flow rates are between about 0.04 and 1 gram per minute, e.g., 0.2 grams per minute (130.4 ml per minute), for the gaseous effluent, and correspondingly between about 10 and 250 ml per minute, e.g., 50 ml per minute, for the aqueous iodide solution.

The peracetic acid content of any fluid stream, gaseous or liquid, may be measured or monitored by the above-described technique. The fluid stream to be measured should be essentially free of other peracids or peroxides as they will also react with the metal iodide to liberate iodine and thereby interfere with the intensity measurements.

The present disclosure, preferred embodiment, and mode of operation of the present invention have been described in the foregoing specification. However, it should be understood that the invention which is intended to be protected herein may be practiced otherwise than as described without departing from the scope of the appended claims.

What is claimed is:

1. A process for continuously and rapidly monitoring the peracetic acid content of an effluent gaseous stream obtained from a vapor phase acetaldehyde oxidation zone, said stream comprising peracetic acid, acetic acid, acetaldehyde and oxygen, wherein said peracetic acid gaseous product is to be immediately used, which process comprises:

(a) mixing a predetermined amount of an aqueous solution of potassium iodide with a predetermined amount of said peracetic acid-containing gaseous stream, whereby said peracetic acid reacts with said iodide to liberate iodine, and

(b) measuring the color intensity of the resulting iodine-containing solution.

2. The process of claim 1 wherein the effluent gaseous stream is mixed with the aqueous solution of potassium iodide at a temperature in the range of from about 50 to 130° C. for a period of time in the range of from about 1 to 30 seconds to react essentially all of said peracetic acid with the potassium iodide.

3. The process of claim 2 wherein a near-saturated solution of potassium iodide is used.

4. The process of claim 1 wherein the color intensity of said potassium iodide solution is measured prior to mixing said solution with the gaseous effluent, thereby obtaining a differential color intensity upon measurement of the resulting iodine-containing fluid stream.

5. The process of claim 4 wherein the potassium iodide solution is mixed with an acid to liberate iodine from any iodates prior to mixing said solution with the gaseous effluent.

6. The process of claim 5 wherein the acid is acetic acid.

References Cited


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