Recent Advances on the Safety of Liquid-Phase Oxidation of Cyclohexane

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Abstract

This paper discussed the recent advances on the safety of liquid-phase oxidation of cyclohexane using air/oxygen, in particular more detailed flammability studies near the process conditions have been performed and a mechanism is proposed for the explosion to occur in liquid-phase oxidation. This paper summarized our past and ongoing work towards to a safer and better process development.

1. Introduction

Liquid phase oxidation of hydrocarbons by air or oxygen is one of the important reactions in the chemical and petrochemical industries. Among these reactions, liquid-phase oxidation of cyclohexane by air is an important route for producing cyclohexanone, cyclohexanol, and precursors such as cyclohexyl hydroperoxide. The oxidation products can be further used to produce caprolactam and adipic acid, which are the basic feedstock for nylon fibers.

Two major routes have been used for cyclohexane oxidation. The classical route oxidizes the cyclohexane directly into cyclohexanol and cyclohexanone, the so-called K/A oil, with the aid of soluble cobalt or chromium salts [1]. The ratio of cyclohexanone to cyclohexanol (K/A ratio) is usually around 0.5~0.6. A recent two-step noncatalytic route by DSM [2] oxidizes the cyclohexane into cyclohexyl hydroperoxide (CHHP) without catalyst and then decomposes the hydroperoxide in a controlled condition to achieve a high K/A value of 1.5. In both routes, conversion of cyclohexane is always limited to 3~5% to avoid side reactions. It is industry's common goal that selectivity to cyclohexanone be maximized, the conversion be maximized, and side products be minimized.

Safety has been a major concern for liquid-phase oxidation of cyclohexane and other hydrocarbons owing to the potential for uncontrolled oxidation; i.e. the deflagration. The deflagration will rapidly raise the pressure and temperature in the reactor and may result in chemical release, fire and explosion [3,4]. To avoid the consequence of deflagration, it is necessary to know the range of operating conditions that can lead to a deflagration, namely the explosion or flammability limits. Early literature such as Berezin et al. [5] did not consider deflagration in the oxygen/cyclohexane mixture to be likely. In 1974, the Flixborough tragedy [6], which involved the release of a large quantity of cyclohexane from the oxidation reactors and resulted in a severe vapor cloud explosion, raised great concerns for the safety of liquid-phase oxidation processes. Although the loss of containment and release in the Flixborough incident is not caused by deflagration, similar events may happen should the deflagration occur. Alexander [7] has provided detailed accounts of hazards in liquid-phase oxidation processes. Practical operating experience also indicates that deflagration in the oxidation reactors is not only possible, it is a scenario that must be carefully evaluated for all liquid-phase oxidation.

Although the cause of the Flixborough incident has been widely addressed and possible inherently safer approaches have been proposed [8], the industry has been very conservative towards process and safety development. Cyclohexane oxidation processes identical or similar to those at Flixborough remain in use. The incident also, in general, prevents industry from utilizing the advantages of using enriched or pure oxygen, except for some special designs of reactors.

The rate of oxidation is usually proportional to the oxygen concentration. The use of pure oxygen or oxygen-enriched air for oxidation will normally increase the reaction rate and, therefore, the production capacity. For example, Shahani et al. [9] have reported that increasing the oxygen concentration by 2% in the feed air will result in a 10% increase in the production capacity of *p*-xylene oxidation to terephthalic acid.

Although switching to oxygen-enriched air or pure oxygen should benefit productivity, the potential deflagration in either the reactor vapor space or the vapor bubbles has been a major constraint that not only prohibits tests at pilot or production scales but also in small lab-scale tests [10]. In fact, there appears to be no literature data on tests using oxygen-enriched air or pure oxygen for cyclohexane oxidation. The safe utilization of oxygen-enriched air also requires accurate data on the flammability limits at the oxidation process conditions, which is usually not available or is difficult to measure.

Recently, Greene et al. [11] performed the first reported cyclohexane oxidation with pure oxygen by using Praxair's Liquid Oxidation Reactor (LOR) [12]. The LOR uses high efficiency stirring and a special enclosure around the stirring area to maximize the oxygen dispersion and utilization while minimizing oxygen escaping into the reactor vapor space. The vapor space is also continuous purged with nitrogen to maintain the oxygen concentration outside the flammable zone. The improvement is significant. The reaction temperature is reduced from 160°C to 149°C and the reaction residence time is reduced from 36 minutes to 8 minutes, while the ratio of cyclohexanone to cyclohexanol is increased from 0.48 to 0.77 and the space-time-yield is increased from 0.45gmol/hr·L to 1.85gmol/hr·L, a four-fold increase in productivity, all for the same cyclohexane conversion of 4%. Therefore, the results indicate that the use of pure oxygen or oxygen-enriched air as the oxidant does increase the productivity, provided that all safety concerns are resolved properly. Interestingly, the LOR technology has not yet been commercialized. Mills and Chaudhari [13] suspected that various technical challenges may occur when the LOR system is scaled-up from the pilot-scale to a commercial process.

One major challenge for the LOR system is to resolve the potential bubble explosion problem [14]. As oxygen enters the cyclohexane liquid, the oxygen bubbles will be saturated with cyclohexane while the oxygen diffuses into the liquid phase and reacts with cyclohexane. It is certain that these oxygen bubbles must enter the flammable range before the oxygen is depleted. Ignition of these potentially explosive bubbles may give rise to overpressure that endangers the reaction system. Also, the bubbles must not be allowed to coalesce into large bubbles, which could result in even more significant overpressure upon ignition. The LOR reactor thus requires very careful control of the oxygen feed, bubble dispersion, and stirring to prevent forming flammable vapor inside the reactor enclosure. The reactor is therefore not intrinsically safe and requires very careful protective measures to ensure safe operations.

In summary, the utilization of pure oxygen has been shown to benefit the productivity, yet it raises more potential hazards than the air-based processes that must be carefully controlled or mitigated. A better understanding of the ignition/explosion mechanism in the liquid phase during oxidation forms the primary objective of our work. The result will benefit the development of an inherently safer process of cyclohexane oxidation using pure oxygen.

2. Flammability Studies in the Vapor Phase

2.1 Flammability Limits at Elevated Pressures and Temperatures

Detailed studies of the flammability for cyclohexane oxidation are crucial to avoid the potential deflagration/explosion hazards. To avoid the consequence of deflagration, it is necessary to know the range of operating conditions that leads to deflagration, namely the explosion or flammability limits.

The flammability limits near process conditions, usually at elevated pressures and temperatures, differ significantly from those at ambient conditions. Normally, the flammable range increases with increased pressure and temperature. Theoretical prediction of the flammable limits remains difficult and inaccurate [15]. It is well known that the upper flammable limits (UFL) increases significantly with increasing pressure [16]. Extrapolation of flammability data into the high pressure range is thus unsafe and direct experimental determination of the flammable limit at true process conditions is not only preferred, but also necessary.

Typically, a 20-liter vessel or a 1-liter vessel is recommended for measuring the flammable limits [17]. However, the operation becomes difficult and potentially hazardous as the test pressure increases owing to increased overpressure from the deflagration. Normally, the overpressure generated can be as high as 10 to 100 times of the initial test pressure. To safely confine the overpressure, it is a common practice that the test vessel and associated fittings be built to withstand pressure that is 10 to 100 times higher than the test pressure. The ASTM standard practice for flammability tests [17] is thus limited to an initial pressure of 1.39 MPa. For higher pressures, special high-pressure vessels are required. For example, Craven and Foster [18] utilized a pressure vessel rated at 55.1 MPa. However, as the pressure rating of the connecting piping was still limited to 13.9 MPa their highest test pressure was only 0.93 MPa. Vanderstraeten et al. [19] performed flammability tests at pressures up to 5.5 MPa with a vessel pressure rating of 550 MPa.

Our first effort [20] was aimed at safe and simple determination of the flammability limits at elevated pressure. The peak overpressure measured in the confined vessel can be used to calculate the deflagration index, which can be used for sizing deflagration vents [16]. However for most oxidation processes carried out at elevated pressures, providing deflagration vents for process vessels is almost impossible or impractical owing to the very large vents required. Even if the vent could be installed, the disposal of the vented material would pose other safety and environmental issues. Thus, it is the industrial practice, as well as a preferred choice, that the design and operation of oxidation processes at elevated pressure should be always carried out outside the flammable limits rather than to design for coping with the potential explosion hazards. Tests that provide only the flammable limits will be sufficient and preferred if the tests can be safer and simplified.

Ideally, a pressure vessel rated around the test pressure with a sufficient large deflagration vent would be capable to achieve the above goal. However, problems remain with the potential hazards of the vented materials and the potential hazards of insufficient venting, which might lead to a catastrophic vessel rupture. These problems can be certainly reduced but not eliminated by reducing the test vessel volume. With reduced test vessel volume, it would be possible to place the test vessel inside a containment to confine any overpressure relief.

We proposed a pressure balancing and containment method for flammability tests [20]. A test cell with an ignition device and low-pressure rating (<1 MPa) is placed in a large containment vessel with high-pressure rating (>10 MPa). Integrity of the test cell at elevated test pressure is maintained by equalizing the containment vessel pressure and the test cell pressure with a padding gas, normally nitrogen. Upon ignition, if the overpressure generation ruptures the test cell, the overpressure will be safely dissipated into the containment vessel. A similar design has been used in the Vent Sizing Package [21] for runaway reactions tests. Although it would have been more straightforward to modify the Vent Sizing Package to perform the flammability tests, the data acquisition rate required to capture the fast waves generated from the deflagration was higher than that of the 20 Hz data sampling in the Vent Sizing Package. In our laboratory, we retained the containment vessel of the Vent Sizing Package while the test cells, test cell heater, data acquisition system, igniter controller, and pressure and temperature sensors are all redesigned and replaced.

Figure 1 shows the schematic diagram of the pressure balancing and containment explosion testing system. The system is comprised of a gas mixing vessel, a containment vessel, and a test cell with an igniter and two K-type thermocouples. Pressures were measured at the feed line to the test cell and at the containment vessel. The ignition source is provided by fusing a thin Nichrome wire (diameter of 0.1 mm). Fusing of Nichrome wires produces the lowest energy among all other metals [22] and is thus preferred in the present work. The length and applied electrical voltage of the wire are adjusted for every test condition to ensure that fusion of the wire is rapid and does not produce too much energy to interfere with the temperature and pressure of the fuel/oxidant mixtures.

The method successfully measured upper flammability limits (UFL) of methane at pressures up to 5.5 MPa [20]. The UFL results compared favorably with those of Vanderstraeten et al. [19] and are shown in Figure 2. The method gives consistently lower UFLs but with a maximum deviation of less than 1% in methane concentration. This is a remarkable result considering the potential hazards and difficulties if the same tests were done by traditional pressure vessels.

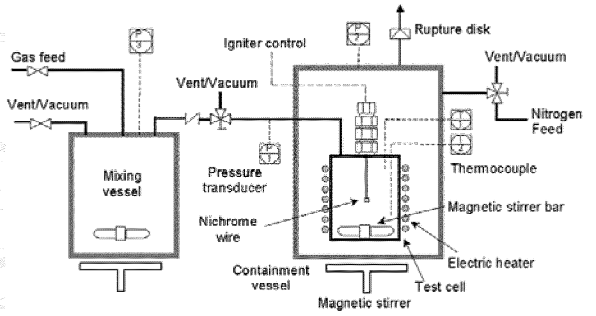

Figure 1. Schematic diagram of the explosion test system [19].

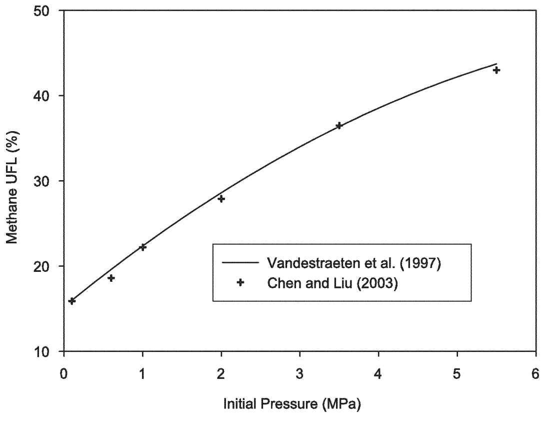

Figure 2. Comparison of measured methane UFL [19] at different initial pressure with the correlation by Vanderstraeten et al. (1997).

2.2 Flammability of Cyclohexane/Oxygen Vapor Mixtures

There appears to be no data in the literature on the flammability limits near the process condition for cyclohexane oxidation. The oxidation is usually operated in a fuel-rich environment and limits the oxygen concentration to below limiting oxygen concentration (LOC) to avoid deflagration. Mills and Chaudhari [13] suggested the MOC is about 8~9 vol% and a normal online oxygen sensor high alarm value set around 4~5 vol%.

With the aid of the above simple and safe method of determining flammability limits, the MOC at a typical cyclohexane oxidation process condition was determined. The conditions chosen were 1.30±0.04 MPa and 165.5±0.5°C. The tests were conducted by first heating the cyclohexane liquid in the test cell to its saturated pressure at 165.5°C. Oxygen and nitrogen at known concentration were fed slowly into the vapor space of the test cell while maintaining the temperature constant. It was assumed that surface reaction and interfacial mass transport between cyclohexane liquid and oxygen is negligible. Thus, the gas composition could be estimated from the cyclohexane vapor pressure and the oxygen partial pressure. The assumption is valid when the vapor is stagnant and the temperature of the vapor and liquid are identical.

Figure 3 shows the typical pressure transients of cyclohexane/air ignition at different feed oxygen concentrations [20]. Three different behaviors were observed. The first case, occurring at feed oxygen concentration of 22 vol% or more, is a clear and significant rise in pressure and temperature, which may be attributed to deflagration in the vapor mixture. The second case, occurring at feed oxygen concentrations between 18 to 22 vol%, shows only a very short pressure pulse without noticeable temperature rise. This is attributed to a cool flame in the vapor mixture. The cool flame is characterized by small explosion pressures and temperatures and is common to hydrocarbon explosions near the UFLs [19]. The third case, occurring at feed oxygen concentration at or below 17 vol%, shows no noticeable pressure or temperature rise, which is attributed to the test composition being outside the flammable region. Figure 4 shows that pressure and temperature rises as a function of feed oxygen concentration. With the min-max criterion for flammability limits, we concluded that the limiting oxygen concentration of flammability for cyclohexane in oxygen/nitrogen mixtures at 1.30±0.04 MPa and 165.5±0.5°C occurred at a feed oxygen concentration of 17.5±0.5 vol%. The min-max criterion defines the flammability limit as the average of the highest flammable concentration and the lowest non-flammable concentration. The 17.5 vol% feed oxygen is equivalent to vapor space oxygen concentration of 7.6%, in close agreement with the suggested value by Mills and Chaudhari [13] in industrial practices.

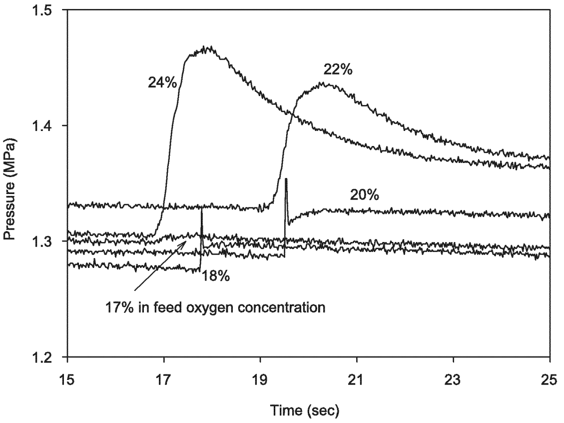

Figure 3. The pressure transients of cyclohexane/air ignition at different feed oxygen concentrations [19].

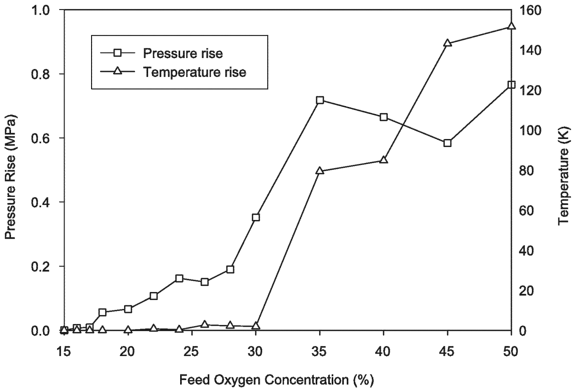

Figure 4. The measured maximum pressure and temperature rises of cyclohexane/air ignition at different feed oxygen concentrations [19].

Feeding normal air to the cyclohexane reactors, which contains 20.9% oxygen, may result in cool flame upon ignition if the oxygen is not consumed by the cyclohexane. Although this is an indication that deflagration hazards are already present in all current operating cyclohexane/air reactors, the air is in practice always bubbled through the bottom of the reactors to ensure that oxygen is consumed or reacted. In addition, all reactors are operated with monitoring of the oxygen concentration in the reactor vapor space. Thus, the current operating practice of using 5% as the oxygen high alarm concentration is safe. In addition, the results indicate that the potential utilization of enriched oxygen is possible, even in traditional stirring reactors, by combining strict oxygen feed control and vapor space oxygen concentration monitoring, if bubble explosion is considered an unlikely scenario.

3. Flammability Studies in the Liquid Phase

3.1 Bubble Explosions

The above discussions indicate that the

flammable bubbles may be formed if the liquid cyclohexane diffuses quickly into the bubble while the oxygen is consumed slowly, yielding fuel and oxygen concentration within the flammable range. Without doubt, the location where flammable bubbles are formed will be in the area close to the air feed lines or air spargers in conventional reactors [7]. In the Praxair LOR system, however, most bubbles are expected to be flammable as there is only cyclohexane and oxygen inside the bubbles. For the bubbles to be non-flammable and fuel rich, the fuel concentrations in the bubbles must pass from the LFL to the UFL, which have very wide range for pure oxygen as the oxidant. The UFLs for hydrocarbons in pure oxygen are known to be much higher than the UFLs in air. For example, the UFL of methane in air at standard conditions is 15 vol% compared to 61 vol% in pure oxygen [16]. Thus, the use of pure oxygen in the oxidation of hydrocarbon without any inert component will significantly widen the flammable range. The flammable bubbles will be a major drawback for the Praxair LOR system if the bubble explosion is a likely scenario and its potential hazards are significant.

Williams et al. [14] argued that bubble explosion is probably not a likely scenario as the energy from an individual bubble is too small and/or the bubbles exploded individually rather than simultaneously. They also performed preliminary tests on the propagation of blast waves in air bubbles in cyclohexane liquid. No extra energy was observed when the blast wave, which was initiated by C-4 explosives, passed through the bubbling liquid. The results are said to be consistent with those of Franke et al. [23] which also found that blast wave will be dissipated by bubbly liquid.

However, the tests done by Williams et al. [14] are limited to ambient conditions with bubbling air rather than pure oxygen. At elevated pressures, the energy stored in every bubble will be much larger than those at ambient pressure. At elevated temperature, the ignition energy will also be reduced, increasing the probability of bubble ignition. The tests done by Franke et al. [23] were also limited to the study of explosion waves propagating in flammable bubbles rather than the ignition of flammable bubbles.

Barfuss et al. [24] performed explosion tests for a single bubble at ambient and elevated pressures. At ambient pressure, they found no significant overpressure during bubbles ignition. At pressures higher than 0.5 MPa, significant overpressure was observed which could reached 2 to 3 times the initial pressure. The pressure wave lasted only about 0.2 ms. It is still not clear how exploding bubbles will affect neighboring bubbles.

The behavior of bubble explosions will be affected by not only the flammable concentration but also by the bubble size, total gas holdup, etc. Smaller bubbles, even if in the flammable range and ignited, may not result in any hazards owing to their small size and small deflagration energy. Our second efforts towards the development take a broad step and are aimed to study ignition behavior in oxygen bubbles near the oxidation process conditions. The primary objective is to assess properly the potential hazards of ignition in flammable bubbles in the oxidation process. Another objective is to seek a safe condition of bubbling that does not lead to bubble explosion and is, therefore, inherently safer.

Figure 5 shows the arrangement of the bubble explosion test rig [25]. The reaction pipe, rated at 15 MPa, has an internal diameter of 0.05 m with length of 1.2 m. Five sets of pressure/temperature sensors and an igniter were installed in the pipe with spacing of 0.2 m. Oxygen was bubbled through a 12.7 mm tube into the bottom of reaction pipe. The gas feed tube is sealed at the end and drilled with 9 holes of 1.6 mm in diameter. Flow of oxygen is controlled by a mass flow controller.

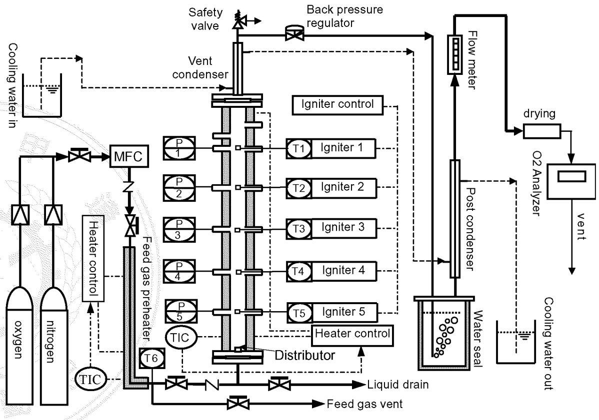

Figure 5 Setup of the bubble explosion test system.

Figures 6 and 7 show two typical pressure transients of bubble explosions in bubbly liquid. Numbering of the tests is indicated by temperature in degree Celsius followed by flow rate of oxygen in standard cm^3/min (sccm), and followed by location of the ignition. In both cases, ignition at the lowest igniter generated oscillatory overpressure very similar to the overpressure observed in the explosion of a single flammable bubble reported by Menon and Lal [26]. The overpressure is found to be dissipated completely in a distance no greater than 60 cm, i.e. the distance from igniter 5 to igniter 2. The explosion energy did not lead to the ignition of neighboring bubbles and triggering of further bubble explosions. The bubbles are indeed flammable, ignitable, and may produce significant overpressure. Yet the overpressure and the explosion energy did not propagate *far* away from the ignition and, therefore, the results are in part consistent with William et al. [14] and Franke [23]. Although the test in Figure 7 shows multiple ignitions and overpressure at P5, it is suspected that the multiple ignitions are a result of ignition of flowing bubbles by the same igniter. We observed a case that has four consecutive ignitions within one second.

Furthermore, all of these ignitions produced roughly the same overpressures and these overpressures dissipated and did not reach igniter 2.

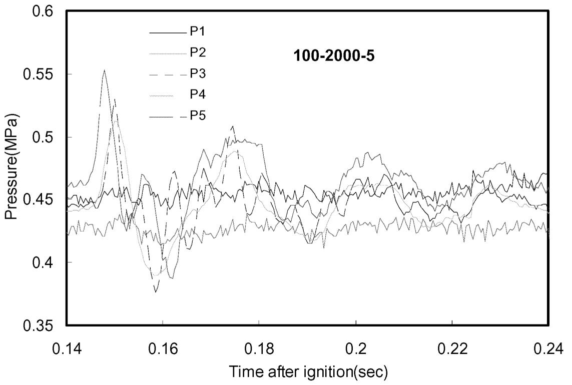

Figure 6 Pressure transients of bubble explosion in bubbly liquid. Test condition: 100℃, oxygen flow rate: 2000 sccm, and ignited at igniter 5.

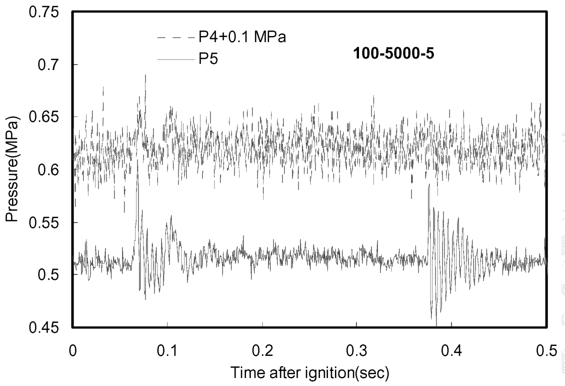

Figure 7 Pressure transients of bubble explosion in bubbly liquid. Test condition: 100℃, oxygen flow rate: 5000 sccm, and ignited at igniter 5. Two consecutive ignitions were observed at 0.08 and 0.38 seconds after ignition.

In general, the generated overpressures are proportional to the oxygen flow rate as shown in Figure 8. This is attributed to the larger bubble size and therefore larger explosion energy at higher oxygen flow rate. Figure 8 shows that bubble ignition is possible even with oxygen flow rate down to 1 standard l/min (slm). Furthermore if the bubble is ignited too close to vapor-liquid interface, the ignition will lead to vapor phase deflagration if the vapor phase is flammable. Figures 9 shows the pressure transients for a bubble ignited at igniter 1 that lead to vapor space deflagration. Note the pressure first increased at P1 and propagated downwards generating significant overpressures of up to 15 MPa. The overpressure was also accompanied by a loud explosion sound. Although such vapor space deflagrations could be prevented in the LOR system, they are still likely to occur in local areas where bubbles coalesce into large bubbles. Thus, there seems to be no safe bubbling condition that could avoid the potential bubble deflagration hazards and enable the inherently safe usage of pure oxygen without other inert component.

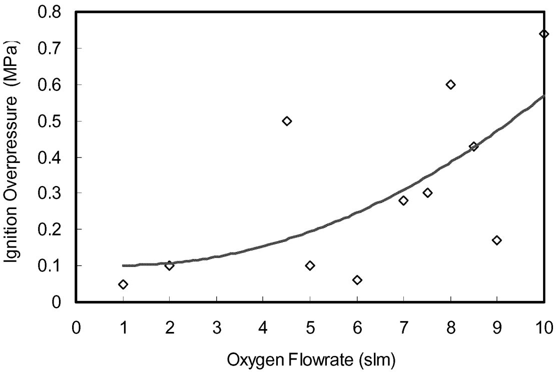

Figure 8 Variation of ignition overpressure from igniter 5 with oxygen flow rate.

3.2 Remote and Delayed Vapor-Space Explosion

We also observed a peculiar behavior of delayed deflagration in certain tests, in particular tests at high temperatures (e.g. 150 °C). Delayed deflagration usually occurs two to three seconds after ignition compared to immediate ignition times of less than one second. The delayed deflagration has a gradual pressure rise prior to a significant deflagration and overpressure in the vapor phase. The deflagration overpressures can exceed 10 MPa which is typical for vapor phase deflagration. In particular, the delayed deflagration is not limited to ignition close to the vapor-liquid interface. Figure 10 shows a typical result for a delayed deflagration. Similar behaviors are also observed in tests at 125 °C. Complete analysis of the bubble explosion is disclosed in Chen and Chen [25].

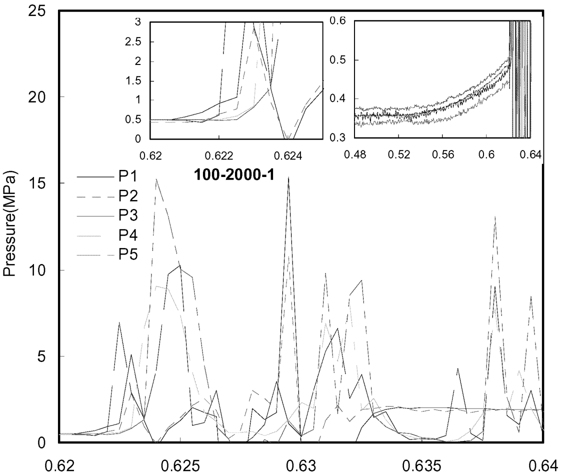

Figure 9. Pressure transients of bubble explosion that leads to vapor space deflagration. Test condition: 100°C, oxygen flow rate: 2000 sccm, and ignited at igniter 1.

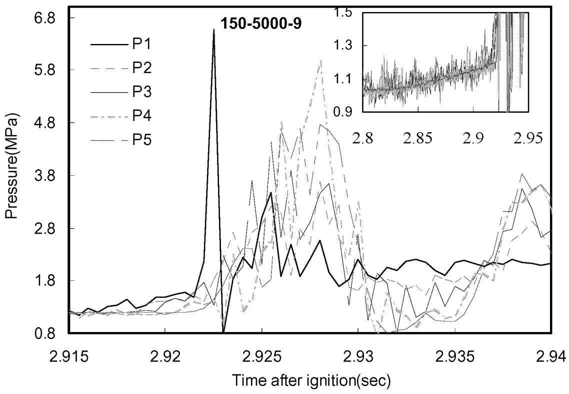

Figure 10. Pressure transients of bubble ignition that leads to delayed deflagration. Test condition: 150 ℃, oxygen flow rate: 5000 sccm, and ignited at igniter 4.

The results at 150°C are actually the first reported experimental findings showing that ignition in the oxidizing liquid can lead to ignition of vapor space at a remote location. In fact, many internal explosions in liquid-phase oxidation system have been attributed to vapor space being flammable without further discussion in the potential ignition source. For example, Kletz [3] has detailed many explosions in oxidation systems but mentioned no specific ignition sources. Some attributed the cause of ignition being initiated by cool flame [27] while others (e.g. Astbury [28]) suggested static electricity is the primary ignition source. One particular theory that fits into the present observation is the free radical ignition as suggested by Alexander [7]. Based on numerous observation of explosion incidents in oxidation systems, Alexander [7] proposed a hypothesis that free radicals from the oxidation reaction in the liquid phase can evaporate into the flammable mixtures near the interface and ignite it. However, Alexander [7] did not provide supporting evidence or mention the details regarding the free radicals.

It is well known that the autoxidation of cyclohexane is a free-radical process that contains chain reactions involving several free radicals (Pohoreki et al., [29]). If the ignition is actuated by the free radicals, these free radicals must not be presented in the normal oxidation reactions or the flammable vapor space will be ignited by these radicals instantaneously upon first reaching flammable regime. Thus, it is likely that some different radical species originated from the decomposition of CHHP by fusing wire is the cause of the ignition. Pohoreki et al. [29] has showed that the cyclohexane oxidation undergo mainly chain reaction involving the cyclohexylperoxy radical while the gas-phase combustion of cyclohexane involves mainly the cyclohexyl radical (Voisin et al, [30]). The thermal decomposition of CHHP is also known to generate cyclohexyloxy and hydroxyl radicals (Gray and William [31]). To complete elucidate the detailed mechanism of the ignition, it is necessary to carry out more detailed analysis of the free radicals which is out of the scope of the present work. The present setup do not allow for the sampling and analysis of the CHHP during ignition tests. However, some iodometric analysis of CHHP for post-ignitedn cyclohexane liquid revealed that CHHP in all 100°C and 125°C tests were no greater than 0.1 wt% while CHHP in the 150°C test with oxygen feed rate of 2000 sccm, the only test without vapor-space explosion, was 0.25 wt%. More studies are required to determine the condition for CHHP to generate the active free radicals.

Our tests with nitrogen bubble flow also showed that oxygen participated significantly in sustaining the free radicals before being carried by the bubble flow to reach the vapor-liquid interface. Thus, a mechanism for the remote and delayed ignition of flammable vapor space to occur is proposed as follows

- Forming significant cyclohexyl hydroperoxide in the cyclohexane liquid.
- Spark or other energy sources are applied to the liquid which lead to decomposition of CHHP and generate active free radicals.
- Active free radicals are sustained with continuous oxygen bubbling.
- Active free radicals are carried by the oxygen bubbles flow to reach the vapor-liquid interface which then act as the ignition source of the flammable vapor space.

The above mechanism improves upon Alexander's theory on free radical ignition and details more clearly how an explosion can occur in a liquid-phase oxidation system. The mechanism is crucial in the designing the cyclohexane oxidation system in particular and all liquid-phase oxidation system in general in that it is not only necessary to avoid forming flammable concentration in the bulk vapor space and in any part of the reactor such as oxygen/air feed lines or spargers, but also to prevent any potential ignition source in the vapor space and in the liquid that capable of decomposing and producing active free radicals.

3.3 Bubbles Flow Behavior

The bubble explosion behavior depends on, other than the flammable vapor concentration, various factors including bubble diameter, gas holdup and flow pattern. The present tests are carried out in homogeneous bubble flow regime with low superficial gas velocity. The selection is chosen to reflect the conditions in cyclohexane oxidation which operates only at low conversion and fine bubble dispersion [32]. The determination of the bubble flow characteristics is however very difficult in that these oxygen bubbles react readily with the cyclohexane liquid resulting in changing bubble characteristics. Pohorecki et al., [32] have studied the bubble flow in nitrogen-cyclohexane system at elevated temperatures and pressures. They provided correlations for mean bubble diameter and vapor holdup. Our current ongoing efforts aim directly at flow visualization of cyclohexane/oxygen bubble under oxidation conditions.

The flow visualization studies require high pressure sight glasses which are more fragile and are thus far more hazardous than closed tests. We have built another bubble explosion test rig with two sight glasses on each side of the pipe. High speed camera is used for capturing the fast response of the bubble flow. Figure 11 is a typical photo of air bubbling through water at 165°C and 1.6 MPa. It is very surprised that the bubbles are not spherical but instead distorted by flow and neighboring bubbles. We will perform in a later stage the visualization of pure oxygen bubbles in cyclohexane at elevated temperatures. The results may help to resolve the true mechanism of delayed explosion in oxidizing liquids.

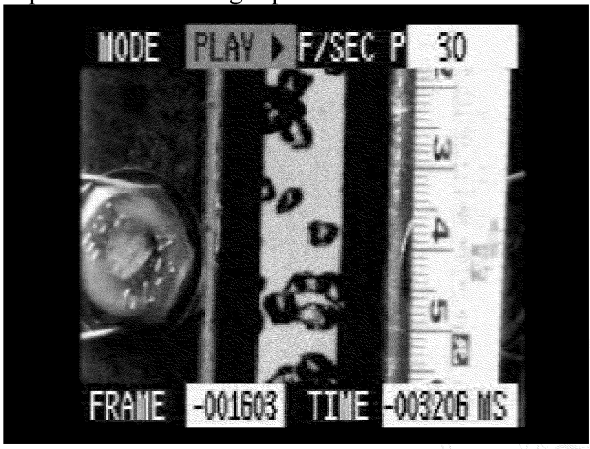

Figure 11 Typical photo of air bubbling through water at 165°C and 1.6 MPa.

In summary, the above results indicated that bubble explosion is not only a likely scenario but also a severe scenario if the ignition is close to a flammable vapor space. Potential delayed ignition, possibly caused by high concentrations of hydroperoxide, may lead to significant overpressure in the vapor space. Thus the all the oxidation processes using pure oxygen, include the LOR process, need to solve the potential bubble explosion problems before undergoing commercial scale-up.

4. A New Inherently Safer Process

4.1 The Method

The former discussions on the flammability of cyclohexane/oxygen vapor or bubbles all indicate that the *direct* utilization of pure oxygen in cyclohexane oxidation is highly dangerous. All existing measures are protective rather than inherently safer. New methods are needed if pure oxygen is to be used. A replacement of nitrogen inerting is required.

We incidentally found that the addition of a small amount of water, which acts as an inert component and does not participate in the oxidation reactions, permits the use of *pure* oxygen as an oxidant for cyclohexane without forming the potentially explosive oxygen/cyclohexane mixtures in either the overhead vapor space or in the oxygen bubbles. The result is an inherently safer process with much increased yield and selectivity to the desired products [33]. The new method is expected to be applicable to other reactants such as all cycloalkanes and leads to better and safer liquid-phase oxidations.

It is well known that cyclohexane and water forms minimum-boiling azeotropic mixtures at elevated temperatures [34, 35]. The vapor pressure of the azeotropic mixture is significantly higher than that of pure cyclohexane. The increased vapor pressure, which comes from water, acts as an inert component in the oxidation reaction, which reduces the UFL of flammability for cyclohexane in oxygen. That is, the water can replace the nitrogen as the inert component and moderate the flammability of cyclohexane/oxygen mixture. The water vapor presents and inerts not only in the overhead vapor space. In oxygen bubbles, water and cyclohexane will diffuse simultaneously into the bubbles achieving the same inerting effect as nitrogen in air. Thus under minimum-boiling azeotropic conditions, pure oxygen or oxygen enriched air can be used as the oxidant, in a controlled manner, for cyclohexane oxidation without any potential hazard of deflagration.

The amount of water added depends on the water partial pressure required to keep the system away from the flammability limits, which in turn also depends on the operating temperature and feed oxygen partial pressure. The operating temperature determines the amount of water partial pressure in the system and also the intrinsic reaction rate. Normally, an operating temperature comparable to, or slightly lower than, the air-based process temperature can be used. Feed oxygen partial pressure is then adjusted for the established azeotropic pressure to ensure that the operation is outside the flammability range. It is always desired that the amount of feed oxygen be checked experimentally at reaction conditions to ensure that the operating condition is safe and far away from the flammable range. Certainly, the more water added the more water partial pressure in the system, which will then allow higher oxygen partial pressure. However, the more water added the lower the productivity due to lower effective reactant volume. A balance between the amount of added water and the feed oxygen partial pressure should always be maintained.

The proposed new method is inherently safer compared with other methods of using pure oxygen. The water vapor presents and inerts not only in the overhead vapor space but also in the oxygen bubbles. Even in case of occurring delayed ignitions in the bubbles, the lack of flammable overhead vapor space in the present case will also prevent the ignition from leading to deflagration. Thus, the concern of potential explosion in the oxygen bubbles is eliminated. The present case remains safe, even in the case of the sudden loss of stirring during the oxidation operation, which may result in decreased oxygen consumption and the potential formation of an flammable environment in other reaction operations without water inerting, it remains safe in the present method. The azeotropic pressure decreases only with temperature, varying insignificantly with stirring. Sufficient time is allowed for actions like nitrogen purge to be taken to ensure the reactors remain safe.

Surprisingly, the added water does not affect the oxidation reaction. Porter and Cosby [36] have proposed that adding 10wt% to 30wt% of water into cyclohexane will inhibit the formation of ester byproducts during oxidation. They, however, did not realize that water could also act as the inert component for cyclohexane such that pure oxygen or oxygen-enriched air could be used. Theoretically, the amount of water added does not affect the reaction. The water however occupied the effective reaction volume, which in turn reduced the space-time-yield. The new method is also not limited by the amount of 10wt%~30wt% water added to the cyclohexane as required by Porter and Cosby [36]. It is only limited by the water partial pressure required to inert the oxygen.

In principle, a vent from the vapor space is not required for the new method. All oxygen feed can be circulated to the liquid and consumption of oxygen is in an optimum state. This results in significant savings in the oxygen used as well as the cost of treating vent gases. Normally, these savings compensate for the cost of using pure oxygen.

The operation of the oxidation can be performed with or without catalysts. There is also no need for special design of the reactors. A single or a series of stirring tanks or bubble columns can be used. The reactors can be operated in continuous or batch mode. Retrofit of the new method to existing reactors is possible and simple. In particular, the reactor can be equipped with a hollow-shaft agitator with gas suction capability, which can benefit the utilization of unreacted oxygen in the reactor vapor space. The operation, however, requires a separate operation of mixing and heating the water with cyclohexane to the azeotropic condition before undergoing oxidation with pure oxygen.

The new method of using oxygen or oxygen-enriched air particularly favors the production of cyclohexanone. The K/A ratio is maximized and the need to separate and convert cyclohexanol into cyclohexanone is greatly reduced. This results in significant economic benefits for the production of cyclohexanone, which is the primary feedstock for caprolactam and adipic acid.

4.2 Results

Figure 12 shows a typical result of oxidation of 93.7wt% cyclohexane/ 6.3wt% water mixture using pure oxygen at 160°C in a bench-scale batch reactor. There is no vent in the reactor. The reactor pressure is controlled by the rate of oxygen feed and the rate of oxygen consumption. Oxygen feed is controlled by limiting the reactor pressure to be 0.1 MPa above the saturation pressure of the liquid. This operating condition has been verified to be outside the flammability range by the above mentioned explosion test method. Figure 13 compares the typical results of explosion tests for the cases of sufficient and insufficient inerting from water vapor for 70.3wt% cyclohexane/29.7wt% water mixture. Both tests are done by heating the cyclohexane/water mixture to the desired temperatures, added pure oxygen to the total pressure of 1.15 PMa, and then ignited. Oxygen partial pressure can be calculated by subtracting the total pressure with the azeotropic pressure. The mixture at 149.1°C provides insufficient partial pressure of water vapor for inerting and significant overpressure generated. The mixture at 165.7°C provides sufficient partial pressure of water vapor and no ignition observed.

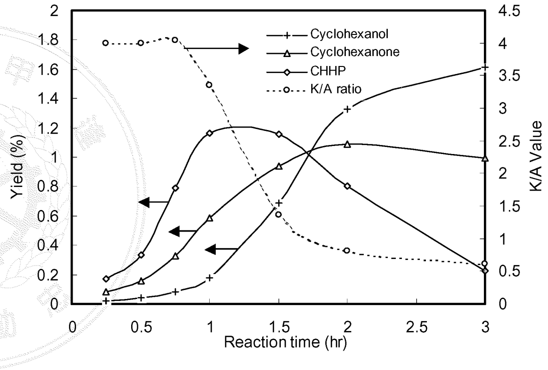

Figure 12. Result of autoxidation of 93.7wt% cyclohexane/ 6.3wt% water mixture using pure oxygen at 160℃.

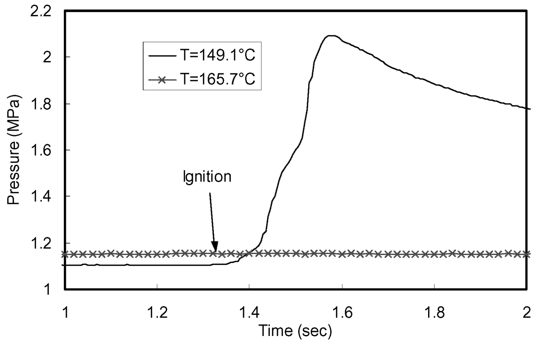

Figure 13. Comparison of explosion tests for sufficient and insufficient inerting from water vapor for 70.3wt% cyclohexane/29.7wt% water mixture. The mixture at 149.1℃ provides insufficient water vapor for inerting and significant overpressure generated.

For comparison, oxidation of pure cyclohexane using air was also carried out and the productivities, expressed in terms of yield per unit reacting volume and unit time, are compared. Table 1 shows the compared productivity of the new method and the air-based oxidation. It is apparent that the new method outperforms the air-based method by as much as a factor of two, depending on the operating temperature. More detailed results are given in Chen et al. [37].

Table 1 Comparison of productivity of the new process and air-based process.

Run^a	Water wt%	Reaction Temp. (°C)	ONE STY^b	OL STY	Total usable STY^c	K/A Ratio
1	6.3	165	70.6	49.0	203.6	1.44
2	6.3	160	44.0	12.9	131.6	3.41
3	6.3	155	24.0	7.8	74.0	3.07
4	29.7	165	21.7	26.1	77.7	0.83
5	29.7	160	23.8	19.6	64.8	1.21
6	29.7	155	12.3	7.5	45.0	1.64
7^d	0	165	35.5	56.1	103.7	0.63

[a] All runs, except run 7, use pure oxygen and feed oxygen partial pressure of 0.1 MPa. All runs use no catalyst.

[b] STY: Space-time-yield with unit of mmol/L hr.

[c] Includes cyclohexanone(ONE), cyclohexanol(OL) and cyclohexyl hydroperoxide(CHHP).

[d] Air run, feed air to total pressure of 1.3 MPa.

4.3 Discussions

While the proposed water moderated oxidation of cyclohexane utilizing pure oxygen offer better productivity and safety compared with the air-based processes, it still cannot prevent the process from occurring the Flixborough type incident if there is a loss of containment. The new method, however, still offer several advantages in case of loss of containment. The liquid volume will be smaller for the same extent of reaction owing to higher productivity. Lower reaction tempearture also implies less liquid flashing during loss of containment. Furthermore, the water will also flash and reduce the cyclohexane concentration, which may reduce the size of flammable vapor cloud.

It is our hope that the improvement in productivity and safety will lead to further improvements in all hydrocarbon oxidation processes. It is also believed that the method may open a new route for hydrocarbon oxidation using pure oxygen which is economically more favored than other oxidants such as hydrogen peroxide, yet is environmentally favored compared with air or nitric acid based oxidation, and is also inherently safer.

5. Conclusions

Systematic studies on the flammability of cyclohexane/oxygen mixtures at elevated pressures and temperatures were made in order to fully understand the hazards in cyclohexane oxidation processes. A new method is proposed which adds water during cyclohexane oxidation as an inert component in both the vapor space and bubbles in the liquid. Pure oxygen is then used as the oxidant, which results in an inherently safer process with better productivity. Although the present work is limited to cyclohexane oxidation, it is believed that the proposed method will open up a new window for developing a safer process of liquid hydrocarbon oxidation using pure oxygen.

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