Simple and Safe Method for Determining Explosion Limits at Elevated Pressures

Jenq-Renn Chen and Kensin Liu
Dept. of Safety, Health and Environmental Engineering,
National Kaohsiung First University of Science & Technology,
1 University Rd., Yenchau, Kaohsiung, 824, Taiwan

A simple and safe method for determining the explosion limits at elevated pressures and temperatures is developed by using a small explosion test cell with a pressure balancing and containment design. Tests at elevated pressure are achieved by balancing the test-cell pressure and the containment-vessel pressure. If the vapor in the test cell is flammable and ignites, the overpressure will rupture the test cell but remain confined safely by the containment vessel. The method successfully achieved explosion-limit measurement at pressures up to 5.5 MPa with all the equipment components rated at a pressure of only 13.9 MPa. Results are presented for hydrogen and methane at ambient condition and elevated pressures, and shown to be in good agreement with the data in the literature. Preliminary results on the upper explosion limits of cyclohexane at cyclohexane oxidation conditions are also reported. The method will greatly benefit the study of explosion limits at elevated pressures and the safety of hydrocarbon/air oxidation processes.

Introduction

Oxidation of hydrocarbon is one of the most common and important chemical processes. Typical processes like terephthalic acid, caprolactam, and ethylene oxide, all utilize air or oxygen as the oxidant. Nevertheless, oxidation is also one of the most hazardous chemical processes, owing to its potential to undergo uncontrolled oxidation, or the deflagration reaction. The deflagration reaction rapidly raises the pressure and temperature in the reactor and results in severe chemical release, fire, and explosion (Kletz, 1979, 1988). 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 explosion limits near process conditions, usually at elevated pressures and temperatures, differ significantly from those of ambient conditions. Normally, the explosive range increases as increased pressure and temperature. Theoretical predictions of the explosion limit remain difficult and inaccurate (High and Danner, 1987). Thus, experimental determination of the explosion limit is not only preferred but also necessary.

Accurate data on explosion limits also benefit the oxidation process. The rate of oxygen oxidation is usually proportional to the oxygen concentration. The use of oxygen-enriched air for oxidation will normally increase the reaction rate and, therefore, the production capacity. Shahani et al. (1995) have reported that increasing 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. By knowing accurately the explosion limits near the process condition, one can operate the process at an optimum condition without the potential hazards of deflagration.

Normally, a 20-L vessel or a 1-L vessel is recommended for measuring the explosion limits (ASTM, 1999). However, the operation becomes difficult and potentially hazardous as the test pressure increases, owing to increased overpressure from the deflagration. The ASTM standard practice (1999) for flammability tests is thus limited to an initial pressure of 1.39 MPa. For higher pressures, Craven and Foster (1966) 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. (1997) performed explosion tests at 5.5 MPa with a pressure vessel rated at 550 MPa. Thus, a method that can easily and safely perform explosion tests at elevated pressure will greatly benefit the safety assessment of high-pressure oxidation processes.

Correspondence concerning this article should be addressed to J.-R. Chen.

In this work, a simple method for explosion tests at elevated pressures and temperatures is developed by using a small explosion test cell with pressure balancing and containment design. Tests at elevated pressure are achieved by balancing the test-cell pressure and the containment-vessel pressure. If the vapor in the test cell is flammable and ignites, the overpressure will rupture the test cell but remain confined safely by the containment vessel. Details of the method were described. The method successfully achieved explosion tests at pressures up to 5.5 MPa with all the equipment components rated at a pressure of only 13.9 MPa. Test results at ambient condition and elevated pressures are given and shown to be in good agreement with the data in the literature.

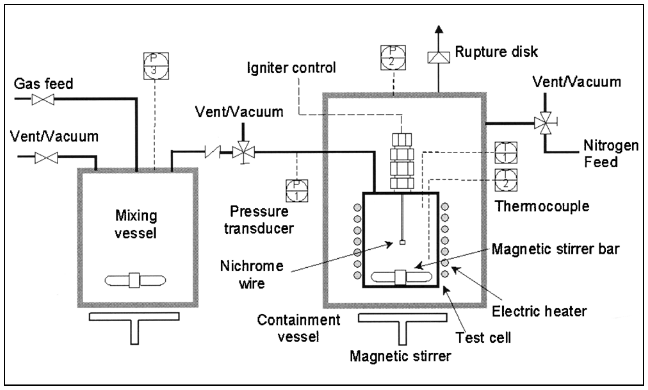

Figure 1. Setup of the explosion test system.

Experimental Setup

The major potential hazard in the explosion tests at elevated pressure lies in the overpressure generated from the explosion. Normally, the overpressure generated can be as high as 10 to 100 times 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. For example, Vanderstraeten et al. (1997) performed explosion tests at pressures up to 5.5 MPa with a vessel pressure rating of 550 MPa. The peak overpressure measured in the the confined vessel can be used to calculate the deflagration index and be used for sizing the deflagration vent (Crowl and Louvar, 2002). 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 vent required. Even if the vent can be installed, the disposal of the very large amount of vented material will pose another safety and environmental issue. Thus, it is the industrial practice as well as the preferred choice that the design and operation of oxidation processes at elevated pressure always be carried out outside the explosion limits rather than to design for coping with the potential explosion hazards. Tests that provide only the explosion limits will be sufficient and preferred if the tests can be safe and simplified.

Ideally, a pressure vessel rated around the test pressure with a sufficiently large deflagration vent would be capable of achieving this goal. However, problems remain with the potential hazards of the venting materials and the potential hazards of inadequate venting, which might lead to a catastrophic vessel rupture. These problems certainly can be 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 vessel to confine any overpressure relief. We thus propose a pressure-balancing and containment method for explosion tests. 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 with overpressure generation and test-cell ruptures, the overpressure will be safely dissipated in the containment vessel. A similar design has been used in a testing device for runaway reactions called the Vent Sizing Package (Leung et al., 1986). Although it would be more straightforward to modify the Vent Sizing Package to perform the explosion tests, a higher rate of data acquisition than that of the 20 Hz in the Vent Sizing Package is still required to capture the fast pressure wave generated from deflagration. In the present work, the containment vessel of the Vent Sizing Package is retained while the test cells, test cell heater, data-acquisition system, igniter controller, pressure, and temperature sensors are all redesigned and replaced.

Figure 1 shows the explosion testing system with pressure-balancing and containment. The system comprises 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 test cell was made of stainless steel sheet with a thickness of 0.2 mm and rated at a pressure of 1.1 MPa. It was cylindrical and had a diameter of 0.05 m and a length of 0.06 m. The volume of the test cell was 0.13 dm^3. The containment vessel had a volume of 4 dm^3 and was rated at a pressure of 13.9 MPa. Thus, the containment vessel allowed the volume expansion and dissipation of the overpressure from the test cell by a factor of 30. Assuming the maximum deflagration overpressure is 10 times the initial pressure, the maximum allowed test pressure P_{allow} would be 10.4 MPa

$$P_{\text{allow}} + \frac{10 P_{\text{allow}}}{30} = 13.9 \text{ MPa}; \quad P_{\text{allow}} = 10.4 \text{ MPa} \qquad (1)$$

This maximum allowed test pressure covers most oxidation processes and is considered sufficient. A higher test pressure can be achieved simply by using a containment vessel with a higher pressure rating.

The ignition source is provided by the fusing of a thin Nichrome wire. Takahashi et al. (1998) have suggested that a metal wire with a high melting point such as tungsten or molybdenum is more suitable for an explosion measurement in vessels of a few to tens dm^3. They found that although a Nichrome wire is usable, it produces scattered data in overpressure measurement. However in the present case, with a small test volume of 0.13 dm^3, the energy from the fusing of tungsten or molybdenum was too large to interfere with the test gas temperature and pressure significantly. Nichrome fusion produces the lowest energy among all other metals, according to Takahashi et al. (1998), and is thus preferred in the present work. A Nichrome wire with a diameter of 0.1 mm was used for the igniter. The length and applied electrical voltage of the wire were adjusted for every test condition to ensure that the fusion of the wire was rapid and did not produce enough energy to interfere with the temperature and pressure of the fuel/oxidant mixtures. For methane explosion tests, a voltage of 110-V AC was applied to a Nichrome wire with a resistance of 1.86 Ω. The Nichrome wire was expected to be fused in the first cycle of AC voltage. The AC current was further restricted by an external fuse with a maximum current of 3 A. The maximum energy produced was estimated to be about 20 J. For hydrogen and cyclohexane explosion tests, a voltage of 3-V DC was applied to a Nichrome wire with a resistance of 0.48 Ω. The DC current was further restricted, however, by an external fuse with a maximum current of 3 A. The maximum energy produced was estimated to be about 9 J.

Pressures and temperatures in the test cell and in the containment vessel were acquired through a 16-bit PCL-816 data-acquisition system from Adventech Co. that is capable of recording data at a rate of 2,000 Hz. The whole system is simpler and safer to operate than conventional high-pressure explosion testing vessels. The drawbacks of the system are difficult to sample the gas composition in the test cell, difficulty in mixing mechanically, potential quench effects from the cell wall, and test-cell replacement if it ruptured or leaked. A mixing vessel with a volume of 0.45 dm^3 was added for the uniform mixing of gases before fed into the test cell. The composition of the mixture in the test cell and the mixing vessel was determined by partial pressures. An independent pressure calibrator with an accuracy of ±1 kPa was used for the partial pressure measurements. A magnetic stirring bar was used to aid the gas mixing. The accuracy of the gas composition from the partial pressures was checked and found to be better than ±0.2 vol % by a calibrated gas analyzer. The gas composition from the partial pressure measurement was then used directly in all tests. The wall effect, as will be shown later, appeared to have negligible effects on the measured explosion limits.

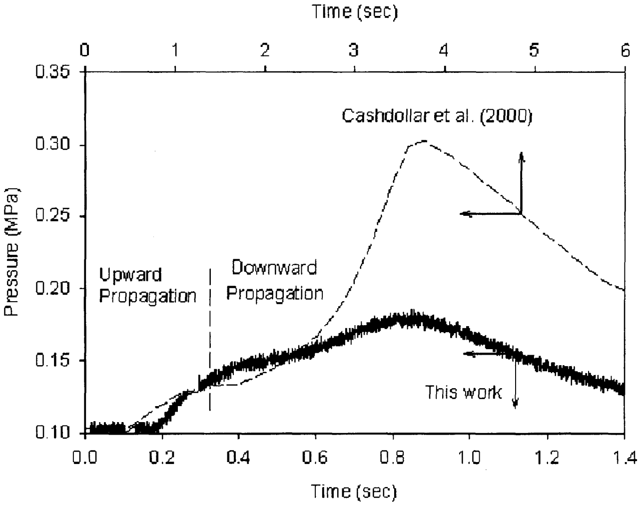

Figure 2. Pressure transients for two-stage flame propagation of ignition of 8.4% hydrogen in air.

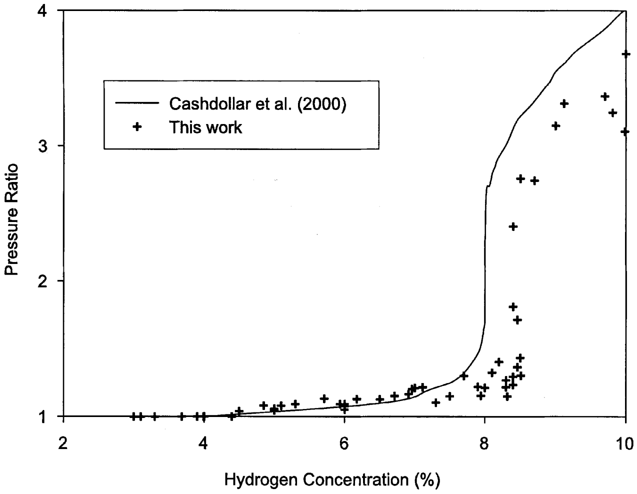

Figure 3. Results of measured maximum pressure rise of hydrogen at concentrations near LEL; the data are expressed in a ratio of maximum pressure to initial pressure.

Results and Discussions

LEL of ambient hydrogen

The lower explosion limit (LEL) of ambient, quiescent hydrogen was used as the first example for testing the validity of the system. The temperature of the tests was 30±1°C and the pressure was atmospheric pressure or 101±1 kPa. Typical literature data give 4% in volume based on U.S. Bureau of Mines tests (Coward and Jones, 1952) from visual observation. The actual flame propagation behavior is more complicated, however, owing to the buoyancy effect. In particular, Cashdollar et al. (2000) observed two-stage pressure rises in a single ignition at a hydrogen concentration of around 8%. The two-stage pressure rises are attributed to two-stage flame propagation in which the first pressure rise is associated with the upward and horizontal flame propagation, while the second pressure rise is associated with the downward flame propagation. Between 4 and 8%, the pressure rise is gradual and the flame does not propagate downward. At a higher concentration than 8%, the flame propagation is isotropic with a very sharp pressure rise.

Our tests successfully recorded the distinct two-stage flame propagation at hydrogen concentration of 8.4%, as shown in Figure 2. Figure 3 shows a comparison of our test results at different hydrogen concentrations with those of Cashdollar et al. (2000) done in a 20-L system. The remarkable rise in pressure ratio after hydrogen concentration greater than 8% is also successfully reproduced by our test. There is, however, a slight deviation in the transition concentration, which occurred at 8.5% in our tests compared with the 8% in the 20-L system. The discrepancy is attributed to the wall quench effect owing to the smaller test volume. The explosion limit is, however, unaffected. Based on a criterion of 3% pressure rise, the LEL of hydrogen in air is 5.0±0.8%, in agreement with the 5.0±0.5% reported in Cashdollar et al. (2000). Based on

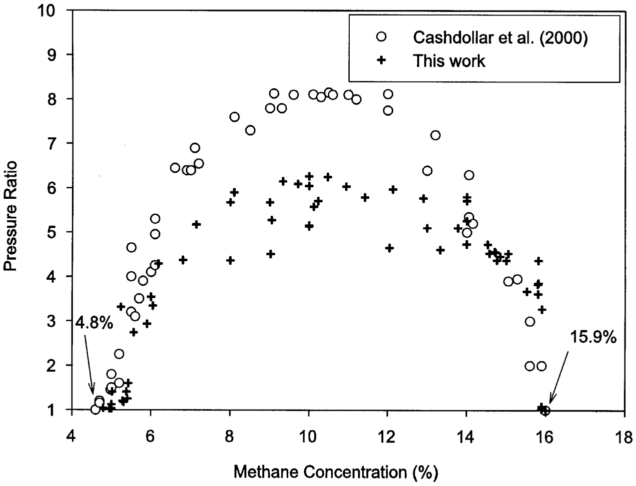

Figure 4. Results of measured maximum pressure rise of methane at ambient condition within the whole explosion limits; the data are expressed in a ratio of maximum pressure to initial pressure.

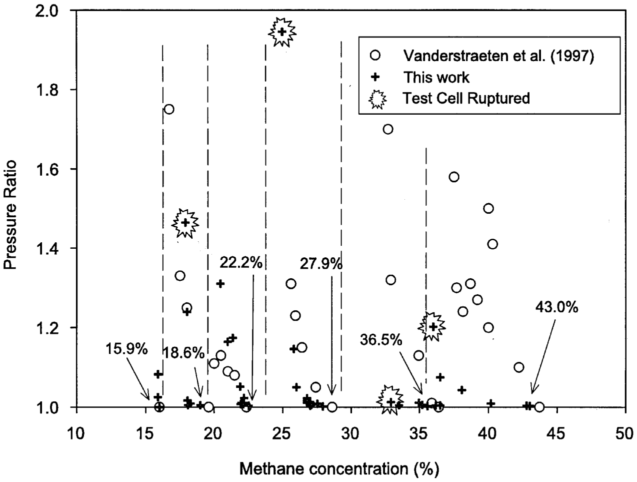

Figure 5. Results of measured maximum pressure rise of methane at elevated pressures near the UEL.

The data are expressed in a ratio of maximum pressure to initial pressure. Data with test cell ruptured is marked with an explosion sign.

the criterion of 7% pressure rise, the LEL of hydrogen in air is 6.0 ± 0.5%, in excellent agreement with the 6.0 ± 0.5% reported in Cashdollar et al. (2000).

LEL, UEL, and maximum pressure rise of ambient methane

The explosion limits of methane have been widely reported. Early work by the U.S. Bureau of Mines based on visual observation gave explosion limits of 5% ~ 15% (Coward and Jones, 1952). Vanderstraeten et al. (1997) reported explosion limits of 4.6 ± 0.3% ~ 15.8 ± 0.4%, and 4.6 ± 0.3% ~ 15.7 ± 0.3%, based on a 8-dm^3 vessel with a tangent criterion and a min-max criterion, respectively. Takahashi et al. (1998) reported explosion limits of 4.7% ~ 16.3% based on a 3-dm^3 vessel. Cashdollar et al. (2000) reported explosion limits of 5.0 ± 0.1% ~ 15.7 ± 0.2% based on a 120-dm^3 vessel with a 7% pressure rise criterion. It is clear that the explosion limits will always be affected by the vessel size, ignition source, and the criterion for an explosion.

A concentration of methane in the explosion range at ambient conditions was used in the present system. Figure 4 shows the results of the measured pressure raise, expressed in terms of the pressure ratio of maximum pressure to initial pressure, as a function of methane concentration. The explosion limit is 4.8 ± 0.1% ~ 15.9 ± 0.1% based on a 3% pressure rise criterion. With a 7% pressure rise criterion, the explosion limits narrowed slightly to 5.0 ± 0.1% ~ 15.9 ± 0.1%. These explosion limits agreed reasonably well with the previously mentioned literature results.

It is also interesting to compare the maximum pressure rise in our tests with other tests using high-pressure rating vessels. Figure 4 also includes results from Cashdollar et al. (2002) on the maximum pressure rise. Our results on maximum pressure rise are systematically lower than those of Cashdollar et al. (2002). The discrepancy is attributed to the elastic behavior of the thin test-cell wall, which allows a certain degree of expansion of the test cell during deflagration. Thus, it is not recommended that the present method be used for measuring the maximum pressure rise even at ambient condition. This drawback is insignificant, as the primary objective of this work is on the explosion-limit measurement. Furthermore, at elevated pressure, the overpressure will rupture the test cell such that the recorded maximum pressure rise is no longer meaningful.

UEL of methane at elevated pressure

It is well known that the upper explosion limits (UEL) increased significantly with increasing pressure (Crowl and Louvar, 2002). Vanderstraeten et al. (1997) have performed a detailed measurement of methane UEL at various pressures up to 5.5 MPa. Their data will be used to validate the present method. The 3% pressure rise criterion requires significant pressure rise at elevated pressure conditions and is no longer used for the explosion-limit criterion. Instead, the min-max criterion suggested by Vanderstraeten et al. (1997) is used, which defines the UEL as the average of the highest flammable concentration and the lowest nonflammable concentration.

The test results at different pressures from 0.1 MPa to 5.5 MPa are shown in Figure 5. Data from Vanderstraeten et al. (1997) are also included for comparison. Tests where the test cell ruptured are also highlighted by enclosing the data point with an explosion mark. Figure 5 clearly shows that the present method reproduces the data of Vanderstraeten et al. (1997) quite well, although the measured maximum pressure rises are again consistently lower than those of Vanderstraeten et al. (1997), owing to the elastic expansion of the test cell's thin wall. Vanderstraeten et al. (1997) proposed a correlation for the UEL of methane at varying pressures and ambient temperature

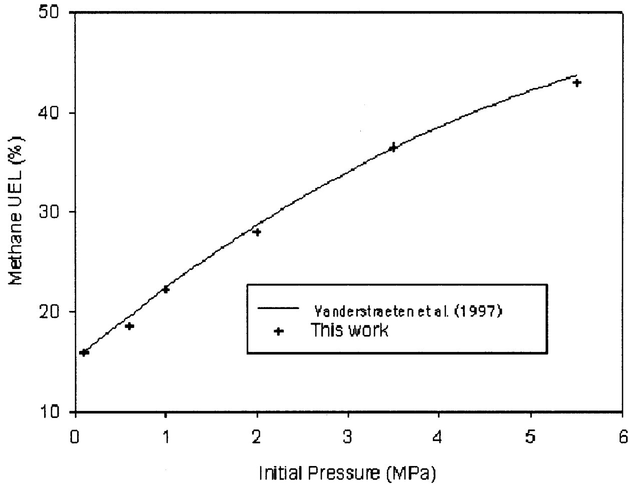

Figure 6. Comparison of methane UEL at different initial pressures with the correlation by Vanderstraeten et al. (1997).

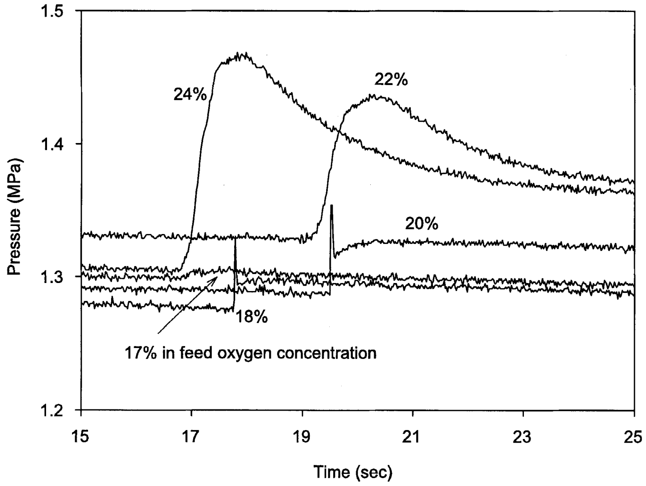

Figure 7. The pressure transients of cyclohexane/air ignition at different feed-oxygen concentrations.

$$UEL(P_1) = UEL(P_0)\left[1+0.0466\left(\frac{P_1}{P_0}-1\right)-0.00269\left(\frac{P_1}{P_0}-1\right)^2\right] \quad (2)$$

where P_0 and P_1 are the ambient pressure and initial test pressure, respectively. Figure 6 shows the comparison of Eq. 2 with the measured UEL. The present method also gives consistently lower UEL, 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. The major cost in the present tests would be the test cells. In most cases where test cells rupture due to overpressure, it is possible to repair and reuse the test cell until it wears out.

UEL of cyclohexane at elevated pressure and temperature

Cyclohexane oxidation is the most important as well as a potentially hazardous reaction in the caprolactam process. The reaction is usually carried out by bubbling air through liquid cyclohexane at temperatures of 413 ~ 443 K and pressures of 1.0 ~ 2.5 MPa. Conversion of cyclohexane is usually limited to 3 ~ 5% to avoid side reactions as well as potential deflagration hazards. The Flixborough tragedy (Lees, 1996), which involved the release of a large quantity of cyclohexane from the oxidation reactors, has been a constant reminder of the potential hazards of this reaction. The incident also in general prevents the industry from utilizing the advantages of using enriched oxygen, except for some special reactor designs (Roby and Kingsley, 1996; Greene et al., 1998). However, there appear to be no data in the literature on the explosion limits near the process condition for cyclohexane oxidation. With the aid of the present simple and safe method of determining explosion limits, we present below some preliminary results on the UEL of cyclohexane near the process conditions as the first step toward a better understanding of the potential hazards of cyclohexane oxidation.

The conditions chosen are 1.30 ± 0.04 MPa and 438.65 ± 0.5 K. The tests are conducted by first heating the cyclohexane liquid in the test cell to its saturated pressure at 438.65 K. Oxygen and nitrogen at known concentrations are fed slowly into the vapor space of the test cell while maintaining the temperature constant. It is assumed that the surface reaction and interfacial mass transport between cyclohexane liquid and oxygen are negligible. Thus, the gas composition can be estimated from the cyclohexane vapor pressure and oxygen partial pressure. The assumption is valid when the vapor is stagnant and the vapor and liquid temperatures are identical. In practice, a certain degree of surface reaction and mass transport are unavoidable. However, feeding oxygen is always done within 10 minutes and the conversion of cyclohexane is always less than 1%. Thus, these effects on the vapor composition are considered to be less than ±0.6% in cyclohexane concentration.

Figure 7 shows the typical pressure transients of cyclohexane/air ignition at different oxygen feed concentrations. Three different behaviors were observed. The first case, occurring at an oxygen feed concentration of 22% 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 an oxygen feed concentration between 18 and 22%, shows only a very short pressure pulse without a noticeable rise in temperature. This is attributed to the cool flame in the vapor mixture. The third case, occurring at an oxygen feed concentration at or below 17%, shows no noticeable pressure or temperature rise, which is attributed to its being inflammable. Figure 8 shows pressure and temperature rises as a function of oxygen feed concentration. With the min-max criterion for UEL, we concluded that the upper explosion limit of cyclohexane in oxygen/nitrogen mixtures at 1.30 ± 0.04 MPa and 438.65 ± 0.5 K occurs at an oxygen feed concentration of 17.5 ± 0.5%.

Feeding normal air to the cyclohexane reactors, which contains 20.9% oxygen, may result in a cool flame upon ignition if the oxygen is not consumed by the cyclohexane. Although this is an indication that deflagration hazards are already presented in all current operating cyclohexane/air reactors, in practice the air is always bubbling through the bottom of

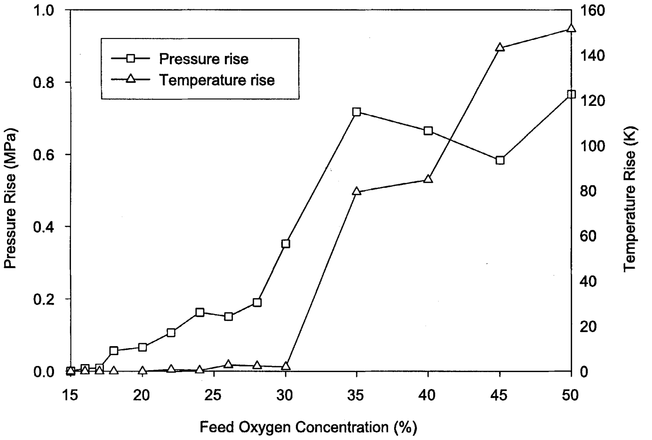

Figure 8. The measured maximum pressure and temperature rises of cyclohexane/air ignition at different feed-oxygen concentrations.

the reactors to ensure that oxygen is consumed or reacted. In addition, all reactors were operated with monitoring of the oxygen concentration in the vapor space. Normally, the warning oxygen concentration is set at 2%, while an oxygen concentration of 5% will result in the immediate shutdown of the whole process. The UEL of 17.5% feed oxygen is equivalent to a vapor-space oxygen concentration of 7.6%. Thus, the current operating practice of using 5% as the shutdown concentration is conservative and 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.

Conclusions

A method for measuring explosion limits was developed by using a small test cell with a pressure-balancing and containment design. The system is simpler and safer to operate than conventional explosion testing vessels. LEL of hydrogen at ambient conditions and UELs of methane at elevated pressures were used for benchmarking the method. The results compared well with the data in the literature using larger vessels. UELs were also reported for cyclohexane at typical oxidation process conditions. The data may lead to improved process safety as well as production efficiency for cyclohexane oxidation. Finally, it should be mentioned that there are a number of factors other than pressure and temperature that could affect the explosion limits. For example Bolk and Westerterp (1999) have reported that flow and obstacles will affect the explosion limits. Nevertheless, the present method provides tests at stagnant conditions that are usually conservative and safe for using in high-pressure oxidation processes.

Acknowledgments

Financial support for this work from the National Science Council, Taiwan, through Grant No. NSC-89-2214-E-327-001 is gratefully acknowledged.

Literature Cited

ASTM, "Standard Practice for Determining Limits of Flammability of Chemicals at Elevated Temperature and Pressure," *Annual Book of ASTM Standards*, American Society for Testing and Materials, West Conshohocken, PA (1999).

Bolk, J. W., and K. R. Westerterp, "Effect of Tube Size and Obstacles on Explosion Limits in Flowing Gases," *AIChE J.*, **45**, 2419 (1999).

Cashdollar, K. L., I. A. Zlochower, G. M. Green, R. A. Thomas, and M. Hertzberg, "Flammability of Methane, Propane, and Hydrogen Gases," *J. Loss Prev. Process Ind.*, **13**, 327 (2000).

Coward, H. F., and G. W. Jones, "Limits of Flammability of Gases and Vapors," Bulletin 503, U.S. Bureau of Mines, Washington, DC (1952).

Craven, A. D., and M. G. Foster, "The Limits of Flammability of Ethylene in Oxygen, Air and Air-Nitrogen Mixtures at Elevated Temperatures and Pressures," *Combust. and Flames*, **10**, 96 (1966).

Crowl, D. A., and J. F. Louvar, *Chemical Process Safety: Fundamentals with Applications*, 2nd ed., Prentice Hall, Upper Saddle River, NJ (2002).

Greene, M. I., C. Sumner, and R. J. Gartside, *Cyclohexane Oxidation*, U.S. Patent No. 5,780,683 (1998).

High, M. S., and R. P. Danner, "Prediction of Upper Flammability Limit by a Group Contribution Method," *Ind. Eng. Chem. Res.*, **26**, 1395 (1987).

Kletz, T. A., "Causes of Hydrocarbon Oxidation Unit Fires," *Loss Prevention Symp.*, **12**, 96 (1979).

Kletz, T. A., "Fires and Explosions of Hydrocarbon Oxidation Plants," *Plant/Oper. Prog.*, **7**, 226 (1988).

Lees, F. P., *Loss Prevention in the Process Industries*, 2nd ed., Butterworth, Boston, MA (1996).

Leung, J. C., H. K. Fauske, and H. G. Fisher, "Thermal Runaway Reactions in a Low Thermal Inertia Apparatus," *Thermochim. Acta*, **104**, 13 (1986).

Roby, A. K., and J. P. Kingsley, "Oxidize Safely with Pure Oxygen," *Chemtech*, **26**(2), 41 (1996).

Shahani, G. H., H. H. Gunardson, and M. S. Chen, "Increase TPA Production," *Hydrol. Processes*, **74**(5), 99 (1995).

Takahashi, A., Y. Urano, K. Tokuhashi, H. Nagai, M. Kaise, and S. Kondo, "Fusing Ignition of Various Metal Wires for Explosion Limits Measurement of Methane/Air Mixture," *J. Loss Prev. Process Ind.*, **11**, 353 (1998).

Vanderstraeten, B., D. Tuerlinckx, J. Berghmans, S. Vliegen, E. Van't Oost, and B. Smit, "Experimental Study of the Pressure and Temperature Dependence of the Upper Flammability Limit of Methane/Air Mixtures," *J. Hazard. Mater.*, **56**, 237 (1997).

Manuscript received Sept. 6, 2002, revision received Feb. 22, 2003.