A Novel Process of Autoxidation of Cyclohexane Using Pure Oxygen

Jenq-Renn Chen,*,† Hsiao-Hui Yang,† and Chung-Ho Wu‡

Department of Safety, Health and Environmental Engineering, National Kaohsiung First University of Science & Technology, 1 University Road, Yenchau, Kaohsiung 824, Taiwan, and China Petrochemical Development Co., Hsiao-Kang Plant, Kaohsiung, Taiwan

Abstract:
Autoxidation of liquid cyclohexane utilizing pure oxygen to produce cyclohexanone, cyclohexanol, and their precursors is achieved in a medium of cyclohexane/water mixture. The addition of water, which acts as an inert component, permits the use of pure oxygen without forming the potentially explosive oxygen/cyclohexane mixtures in the overhead vapor space as well as in the oxygen bubbles. The result is an inherently safer process for cyclohexane oxidation with increased yield and selectivity to the desired products. The use of pure oxygen improves not only the productivity and safety but also reduces the emission and benefits the environment.

Introduction

Liquid-phase oxidation of hydrocarbon by air or oxygen is one of the important reactions in the chemical and petrochemical industries. Among them, 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 or adipic acid which are the feedstock for Nylon fibers.[1]

Current industrial processes of cyclohexane oxidation utilize stirring tanks or bubble columns with air as the oxidant at temperatures between 130 and 170 °C with or without catalysts. Pure oxygen or oxygen-enriched air is rarely used due to safety concerns even though it is known that reaction rate and selectivity could be increased with increasing oxygen concentration in the air.[2] The main concerns lies in the fact that potential explosive mixtures could be formed in the reactor vapor space and the vapor bubbles if oxygen concentration in the feed is too high. The explosive mixtures, upon ignition, could lead to significant increases in temperature and pressure inside the reactor and possibly rupture the reactors.[3] It is always desired to operate the air/oxygen oxidation reaction outside the flammability range of the hydrocarbon. An inert component such as nitrogen is commonly employed to bring the oxygen concentration to less than the minimum oxygen concentration for inflammability. In gas-phase oxidation, nitrogen, carbon dioxide, or water vapor has been widely used as the inert component. In liquid-phase oxidation, nitrogen is always the primary choice for the inert component, which comes naturally from the air. The use of air in liquid-phase oxidation, however, requires continuous venting of nitrogen so that fresh air can enter. Employment of other inert components such as carbon dioxide does not benefit the operation or reaction selectivity except for some special case such as terephthalic acid process.[4] To replace air by pure oxygen therefore requires a replacement for nitrogen inerting or measures to mitigate the potential deflagration.

The advantages of using of pure oxygen instead of air are, however, very clear.[5] The rate of oxidation is increased with pure oxygen owing to higher oxygen partial pressure. The operating temperature and pressure of the reaction can be reduced accordingly. Capital cost of the oxygen compressors and their operating energy cost are also lower. There is also a minimum need for using pure oxygen to purge overhead inert gases in comparison with that of air-based processes which must continuously purge the oxygen-depleted nitrogen. The cost of treating vent gas is thus greatly reduced, which usually can compensate the cost of pure oxygen.

A special reactor design called liquid oxidation reactor (LOR) has been proposed,[6] which is said to allow the use of pure oxygen or oxygen-enriched air in the oxidation of cyclohexane. The result, when comparing with traditional air oxidation processes, showed that the reaction temperature is reduced from 160 to 149 °C, reaction residence time reduced from 36 to 8 min, while the ratio of cyclohexanone to cyclohexanol (K/A ratio) increased from 0.48 to 0.77, the productivity increased from 0.45 to 1.85 gmol/h·L, 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 did increase the productivity, provided that all safety concerns are resolved properly. The LOR has a special enclosure around the stirrer where most of the oxygen is fed, reacted, and consumed. The remaining unreacted oxygen escaping from the enclosure will pass to the vapor space and be diluted by nitrogen before being treated and vented into the atmosphere. Although the productivity is increased by a factor of about four, there are remaining concerns on the potential explosions inside the

* Author to whom correspondence should be addressed. Email: jrc@ccms.nkfust.edu.tw. Fax: +886-7-6011061.
† National Kaohsiung First University of Science and Technology.
‡ China Petrochemical Development Co.

(1) Wittocff, H. A.; Reuben, B. G. *Industrial Organic Chemicals*; Wiley: 1996.
(2) Shahani, G. H.; Gunardson, H. H.; Easterbrook, N. C. *Chem. Eng. Prog.* **1996**, *91*, 66.
(3) (a) Kletz, T. A. *Loss Prev. Symp.* **1979**, *12*, 96. (b) Kletz, T. A. *Plant/Oper. Progr.* **1988**, *7*, 226.
(4) Yoo, J. S.; Jhung, S. H.; Lee, K. H.; Park, Y. S. *Appl. Catal., A* **2002**, *223*, 239.
(5) Roby, A. K.; Kingsley, J. P. *CHEMTECH* **1996**, *26*, 41.
(6) (a) Greene, M. I.; Sumner, C.; Gartside, R. J. Cyclohexane Oxidation. U.S. Patent 5,780,683, July 15, 1998. (b) Greene, M. I.; Sumner, C.; Gartside, R. J. Cyclohexane Oxidation. U.S. Patent 6,008,415, December 29, 1999.

vapor bubbles in the reactor. The cyclohexane will diffuse into the oxygen or oxygen-enriched bubbles while oxygen will diffuse out into the liquid during bubbling. There will be a certain regime where the vapor mixtures in the bubbles enter the flammable range. Ignition of these potentially explosive bubbles may still give rise to overpressure that endangers the reaction system.[7] The reactor also requires very careful controls of the feed oxygen and stirrer to prevent forming explosive vapor inside the reactor enclosure. The reactor is thus not intrinsically safe but requires careful protective control measures to ensure safe operations. A recent review also concerns the practical difficulties in the scale-up of the LOR process.[8]

In this contribution, we present a novel method that solves the potential flammability problems in the vapor phase and oxygen bubbles yet the advantages of utilizing pure oxygen are retained.

Methodology

It is well know that cyclohexane undergoes free radical oxidation reaction with oxygen even in the absence of catalyst at elevated temperature.[9] The reaction is a multistage, free-radical chain reaction comprising chain inhibition, chain propagation, and chain termination steps. A typical noncatalytic reaction mechanism consists of first forming an intermediate cyclohexyl hydroperoxide and then subsequently decomposing into cyclohexanol and/or cyclohexanone. Further oxidation leads to ring opening and acid derivatives. The conversion of cyclohexane is thus usually limited to less than 10%. The limited conversion is a result of maintaining selectivity and avoiding excess oxygen in the vapor space of the reactors.

It is also known that cyclohexane and water form a minimum-boiling azeotrope.[10] The vapor pressure of the azeotrope is significantly higher than that of pure cyclohexane. We found that the increased vapor pressure, which comes from water, can act as an inert component in the oxidation reaction. Thus, under positive azeotropic conditions, pure oxygen or oxygen-enriched air can be used, in a controlled manner, as the oxidant for cyclohexane oxidation without any potential hazard of deflagration. The flammability of the vapor mixture in the reactor overhead space and in the oxygen bubbles can be controlled by adjusting the partial pressure of the feed oxygen. The safe operating conditions can be estimated or preferably determined by an explosion-testing apparatus that is capable of performing explosion testing at reaction conditions[11] to ensure that the operating conditions are safe and far away from explosive range. The method is inherently safer compared with other methods of using pure oxygen. Not only the vapor space but also the oxygen bubbles are inerted by water vapor. Thus, the concern of potential explosion in the oxygen bubbles is

eliminated. Even in the case of sudden stopping of the stirring during the oxidation operation, which may result in decreasing oxygen consumption and forming a potential explosive environment in other oxidation operations, it remains safe in the present case. The azeotropic pressure decreases only with temperature but varies insignificantly with stirring. Sufficient time is allowed for actions such as nitrogen purge to be taken to ensure the reactor remains safe.

Although the added water acts as an inert component to prevent deflagration of cyclohexane and oxygen, it must not affect the reaction. It is known that water has a retarding effect on the oxidation reaction and limits the conversion of cyclohexane oxidation to a maximum of 25−30%.[12] Nevertheless, the added water does not affect the oxidation reaction in a practical sense. In practice, the conversion of cyclohexane oxidation is always limited to below 5% and therefore the retarding effect will be minimized. It is also reported in an earlier work[13] that adding 10−30 wt % of water into cyclohexane during oxidation will inhibit the formation of ester byproducts. This work, however, did not realize that water can also act as the inert component for cyclohexane such that pure oxygen or oxygen-enriched air can be used. Theoretically the amount of water added does not affect the reaction. The water, however, occupies the effective reaction volume, which in turn reduces the space−time yield. In fact, the present method is not limited by the amount of 10−30 wt % water added to the cyclohexane. It is only limited by the water partial pressure required to inert the oxygen. The amount of water added is dependent on the operating temperature and can be determined from experimental testing on the flammability of the mixtures. Usually the less water added, the better is the yield. The increased yield can be as high as twice that of employing air at the same conditions.

In principle, there need be no vent from the vapor space at all. All oxygen fed can be recirculated to the liquid and consumption of oxygen is in an optimum state. This results in significant saving in the oxygen used as well as the cost of treating vent gases. Normally, these savings compensate 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, but a series of stirring tank reactors are usually preferred. The reactors can be operated in a continuous or batch mode but preferably in continuous mode. Retrofit of the present 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 present method of using oxygen or oxygen-enriched air particularly favors the production of cyclohexanone. The cyclohexanone/cyclohexanol ratio (K/A ratio) is maximized, and the need to separate and convert cyclohexanol into cyclohexanone is greatly reduced. This results in significant

(7) Williams, W. R.; Mahoney, W. J.; Baker, Q.; Thistlethwaite, K. *1998 AIChE Annual Meeting*, Miami, FL, 1998.
(8) Mills, P. L.; Chaudhari, R. V. *Catal. Today* **1999**, *48*, 17.
(9) Pohorecki, R.; Baldyga, J.; Moniuk, W.; Podgórska, W.; Zdrójkowski, A.; Wierzchowski, P. T. *Chem. Eng. Sci.* **2001**, *56*, 1285.
(10) (a) Snee, T. J. *Process Saf. Environ. Prot.* **2001**, *79B*, 81. (b) Kister, H. Z. *Distillation Design*; McGraw-Hill: New York, 1992.
(11) Chen, J. R.; Liu, K. *AIChE J.* **2003**, *49*, 2427.

(12) Suresh, K.; Sridhar, T.; Potter, O. E. *AIChE J.* **1988**, *34*, 69.
(13) Porter, P.; Cosby, J. N. Process for Oxidation of Cycloaliphatic Compounds. U.S. Patent 2,565,087, August 21, 1951.
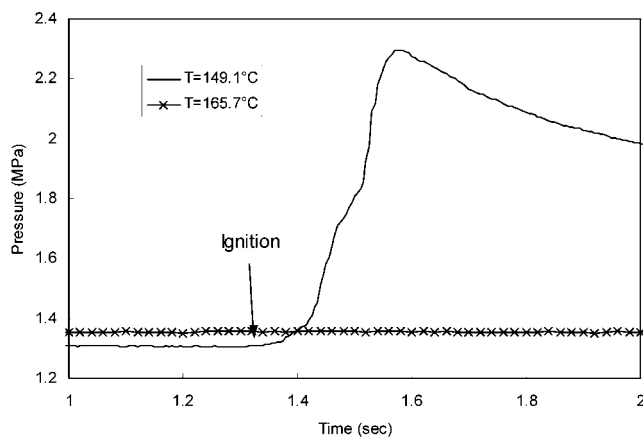
Figure 1. Comparison of explosion tests for sufficient and insufficient inerting from water vapor for 70.3 wt % cyclohexane/29.7 wt % water mixture. The mixture at 149.1 °C provides insufficient water vapor for inerting and significant overpressure generation.

Figure 2. Results of cyclohexane oxidation with 6.3 wt %water and oxygen partial pressure of 0.1 MPa at 160 °C. Byproducts are ring-opening products including adipic acid, glutaric acid, succinic acid, and their esters.

economic benefits for the production of cyclohexanone, which is the primary feedstock for caprolactam and adipic acid.

Assessment of Safe Operating Conditions

To perform the reaction, it is necessary to operate the reaction in a safe, inflammable operating range to avoid potential hazards of deflagration. The safe operating conditions are determined by the reaction temperature, water content, and amount of feed oxygen. These parameters in turn affect the reactivity and productivity of the reaction.

Our starting condition fixes the water content to 29.7 wt %, which is equivalent to 25 vol % of water in cyclohexane/water mixture. The vapor pressure of the cyclohexane/water mixture at 165 °C is measured to be 1.31 MPa. Adding 0.1 MPa oxygen to the mixture gives a maximum oxygen concentration of 7.04 mol % in the overhead vapor space and vapor bubbles, which is smaller than the reported minimum oxygen concentration of 7.6 mol %[14] of cyclohexane/nitrogen mixture and is thus considered inflammable. Figure 1 compares the typical results of explosion tests for the cases of sufficient and insufficient inerting from water vapor for 70.3 wt % cyclohexane/29.7 wt % water mixture. Both tests are done by heating the cyclohexane/water mixture to the desired temperatures, adding pure oxygen to the total pressure of 1.36 PMa, and then igniting. Oxygen partial pressure can be calculated by subtracting the azeotropic pressure from the total pressure. The mixture at 149.1 °C provides insufficient partial pressure of water vapor for inerting, and generates significant overpressure. The mixture at 165.7 °C provides sufficient partial pressure of water vapor, and no ignition is observed. Complete flammability data will be a proprietary property.[15]

It should be noted that the tests with thermal equilibrium conditions give rise to maximum cyclohexane concentration in the vapor space and thus represent the worst possible case
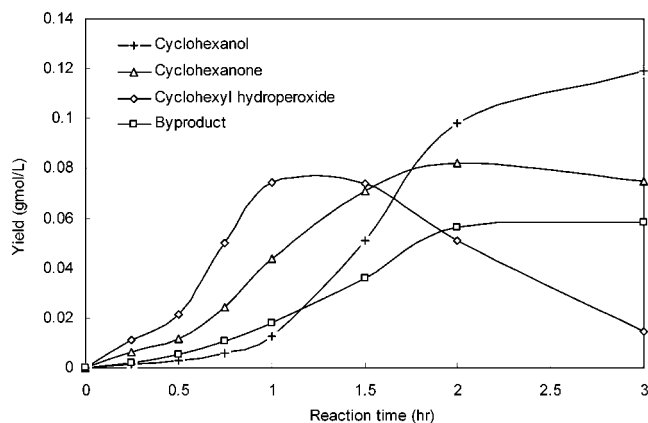
for the cyclohexane/water/oxygen mixture to be ignited in either the vapor phase or in the vapor bubbles. Thus, the safe conditions imply safe conditions in both the vapor phase and the vapor bubbles. The inert effect is always effective and depends only on liquid temperature, which governs the water partial pressure in the vapor phase. Therefore, the present method is inherently safer compared with existing air-based or oxygen-based methods of cyclohexane oxidation. In any case, it is still necessary to monitor the oxygen partial pressure in the vapor space to ensure no excess oxygen is fed.

Results

Figure 2 shows a typical result of cyclohexane/water oxidation using pure oxygen. The reaction mixture contains 6.3 wt % water and is maintained at 160 °C. Feed oxygen is controlled by maintaining the feed oxygen pressure to be 0.1 MPa higher than the liquid vapor pressure. It is clear from Figure 1 that before 2 h of reaction, the production of cyclohexanone exceeds that of cyclohexanol, giving cyclohexanone/cyclohexanol (K/A) ratios greater than one. The maximum K/A ratio even exceeds 3 at reaction time of 1 h. The favor of production of cyclohexanone is a result of using pure oxygen, which inhibits the formation of cyclohexanol in the early stages of the reaction. However, cyclohexanone and cyclohexanol are easier to be oxidized than cyclohexane, and further oxidation diminishes its yield.[16] It should be noted that the metal wall has a catalytic effect on the decomposition of CHHP. The wall catalytic effect in the small-scale laboratory reactors can be very significant and affect the kinetic behavior of oxidation.[17] Thus, the present results are intended to be a demonstration of the benefits of utilizing pure oxygen over conventional air oxidation rather than a detailed analysis of the oxidation chemistry.

Figures 3−5 compare the yields of cyclohexanone, cyclohexanol, and cyclohexyl hydroperoxide from runs with different reaction temperatures and different water contents. For comparison, a run using air and pure cyclohexane is also

(14) Chen, J. R.; Liu, K. *AIChE J.* **2003**, *49*, 2427.
(15) Wu, C. H.; Chen, J. R.; Yang, H. H. Liquid-Phase Oxidation of Cycloalkane Compounds. ROC Taiwan Patent Applications Number 92103368, February 2003.
(16) Suresh, A. K.; Sharma, M. M.; Sridhar, T. *Ind. Eng. Chem. Res.* **2000**, *39*, 3958.
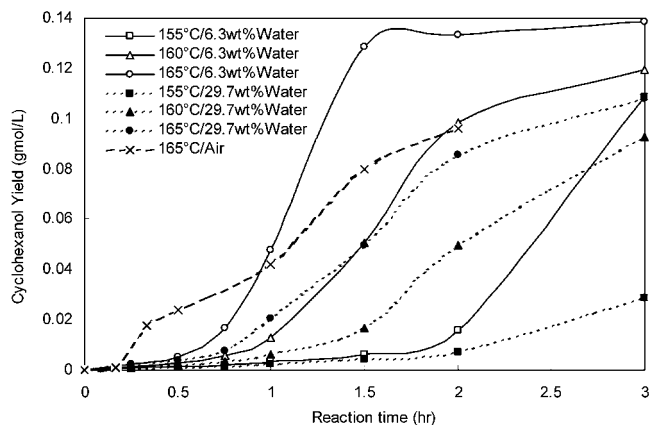(17) Wen, Y.; O. E. Potter; Sridhar, T. *Chem. Eng. Sci.* **1997**, *52*, 4593.

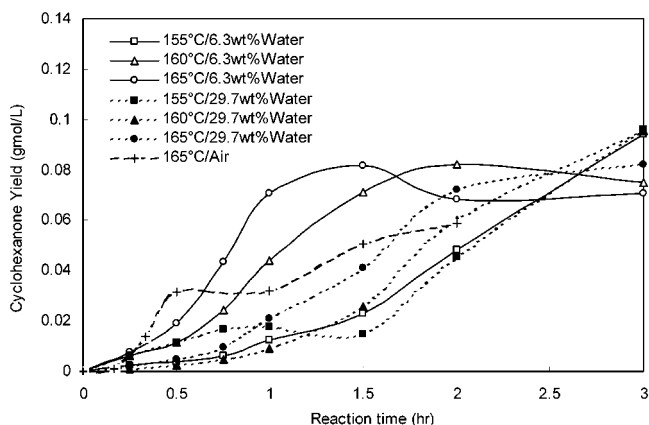**Figure 3.** Comparison of cyclohexanol yield for different reaction temperatures and water contents.

Figure 4. Comparison of cyclohexanone yield for different reaction temperatures and water contents.
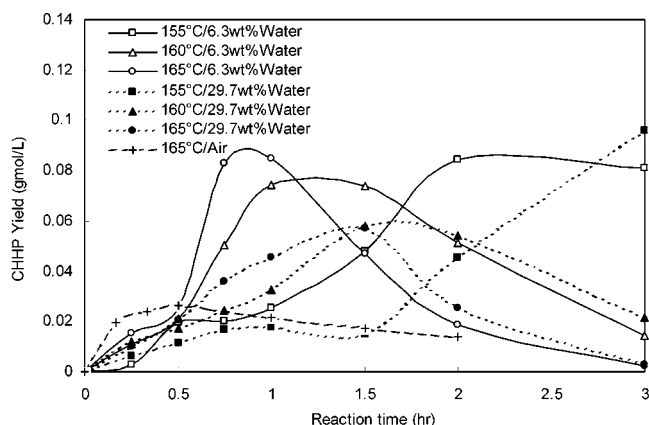

Figure 5. Comparison of cyclohexyl hydroperoxide (CHHP) yield for different reaction temperatures and water contents.

included. These results show clearly that the yield increases with increasing reaction temperature and decreasing water content. The runs with the proposed method have slightly longer induction periods compared with that of the air run, but their yields eventually outperformed. The productivities, expressed in molar yield per unit volume and time, for these results are summarized in Table 1. As the results were obtained in batch operation, which always includes an induction period, only the maximum productivity is shown in the table. It is clear from Table 1 that under the same

Table 1. Comparison of maximum productivity for cyclohexane at different temperatures and water contents[a]

run	water content (wt %)	reaction temp (°C)	cyclohexanone productivity (mmol/L·h)	cyclohexanol productivity (mmol/L·h)	total usable productivity[b] (mmol/L·h)	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[c]	0	165	35.5	56.1	103.7	0.63

[a] All runs, except run 7, use pure oxygen and oxygen partial pressure of 0.1 MPa. The pure oxygen runs utilize a hollow-shaft agitator without any vent, while the air run utilizes a vent condenser and continuous venting of oxygen-depleted air. [b] Includes cyclohexanone, cyclohexanol, and cyclohexyl hydroperoxide. Productivities of unit time were quoted based on batch time. Productivities quoted exclude products soluble in water phase, which is considered negligible except at very early stage of reaction. All reactions were carried out with a 3-L stainless steel reactor charged with 1.5 L of reactant, equipped with a hollow-shaft, air-induced stirrer, and stirred at a speed of 900 rpm. [c] Air run. Feed air to a total pressure of 1.3 MPa.

reaction temperature, the productivity of using pure oxygen exceeds that of using air by a factor of about two. In particular, the production of cyclohexanone is also increased by a factor of 2, while production of cyclohexanol is decreased slightly. This result favors the caprolactam process where the desired product is cyclohexanone rather than cyclohexanol. The improvement of the proposed method is, however, less than that of the LOR technique in which the productivity is quadrupled compared with that of conventional air oxidation. The reduced improvement is attributed to the retarding effect of water on the reaction rate. In addition, both cyclohexanone and cyclohexanol dissolve slightly in water, and the productivity in the organic phase reduces further. With higher water content, the productivity decreases even further, owing to reduced reaction volume and possibly higher water-retarding effect.

Conclusions

In conclusion, we have developed a novel method for the autoxidation of cyclohexane with pure oxygen. The method gives better productivity compared with that of conventional air oxidation. In particular, the method is inherently safer and more suitable to scale-up compared with the existing LOR technique utilizing pure oxygen. Although the present work focuses on autoxidation of cyclohexane, it can also be applied to catalytic oxidation and to other hydrocarbons that form azeotropic mixtures with water or any other inert liquid. 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.

Acknowledgment