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Capillary reactor for cyclohexane oxidation with oxygen

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ABSTRACT

Cyclohexane oxidation is the first step in the currently used technology for production of Nylon-6 and Nylon-6,6 which employs a two-stage process. In the first stage 80% selectivity to two main products, cyclohexanol and cyclohexanone (KA oil) is obtained at 4–8% cyclohexane conversion in staged bubble columns or stirred tanks. There have been reports that increased oxygen concentration in the gas phase or pure oxygen is beneficial to cyclohexane oxidation and this was confirmed in our previous study (Jevtic et al., 2009). To fully utilize this advantage here, we present a novel, safer capillary reactor for cyclohexane oxidation with pure oxygen. The discrepancy between the experimental and modeling results was attributed to lower than expected mass transfer achieved in the capillary. With a better design for gas–liquid mixing and contacting this type of a reactor could potentially become attractive for gas–liquid reactions of similar nature.

Keywords: Hydrocarbon oxidation; Capillary reactor; Kinetics; Reaction engineering

1. Introduction

Cyclohexane oxidation is practiced on a large scale in the chemical industry worldwide with over 10^6 tons per year of cyclohexanone and cyclohexanol (known as KA oil, Suresh et al., 2000) made. KA oil is the starting material in the production of adipic acid and caprolactum, which are ultimately used in the manufacture of Nylon-6 and Nylon-6,6 (Schuchardt et al., 1993). The desired cyclohexane oxidation products (i.e. cyclohexanol and cyclohexanone) are thus intermediates in a sequence of complicated, multiple, free-radical chain reactions (Berezin et al., 1966; Hendry et al., 1976; Walling, 1969). Both cyclohexanol and cyclohexanone are more readily oxidized than cyclohexane. Over-oxidation leads to a number of byproducts, such as succinic, oxalic, caproic, glutaric, and adipic acids (Wen et al., 1997), and can be minimized only by keeping cyclohexane conversion low. Typically, in industrial processes, cyclohexane in the liquid phase is oxidized with air or a mixture of oxygen and nitrogen where the oxygen concentration is less than 21%. In order to approach plug flow for the liquid reactant, which is needed to maximize the yield of the desired intermediates, the process is conducted either in a series of stirred tank reactors or staged bubble columns. After about 40 min of reaction time at a temperature between 125 and 165 °C and at a pressure of 8–15 bar in the presence of cobalt or manganese salts as a catalyst, cyclohexane conversion of 4% and the selectivity of 80% to cyclohexanone and cyclohexanol are typically achieved (Suresh et al., 2000). Clearly, the process as practiced today demands substantial capital investments, due to large equipment that is required, and imparts substantial operating costs for the separation and recycle of vast amounts of unreacted cyclohexane caused by its low conversion per pass. Improvements are thus possible by increasing the process rate without negatively affecting selectivity, which can then reduce equipment size, or by making direct oxidation to adipic acid more selective. We focus on the concept of increasing the reaction rate in this study.

When reaction rate is dependent on dissolved gas reactant concentration an increase in the gas reactant concentration has a positive effect on the rate for positive reaction orders with respect to that reactant. For example, in the oxidation of p-xylene to terephthalic acid it is reported (Chen, 2004) that increasing the oxygen concentration by 2% in the feed air results in a 10% increase in the production capacity of terephthalic acid. Greene et al. (1998) reported first cyclohexane oxidation with pure oxygen. The reaction was performed

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in the Liquid Oxidation Reactor (LOR) designed and patented by Kingsley et al. (1994). The LOR uses high efficiency stirring, which limits the oxygen escape from the liquid phase into the gas phase, and uses a nitrogen purge in the vapor space above the liquid thereby keeping the oxygen concentration in the gas phase at the safe level. In comparing the cyclohexane oxidation with oxygen to that with air it was established that to reach the desired cyclohexane conversion of 4% the residence time is reduced from 36 min needed with air to 8 min when using oxygen. This was accomplished at slightly reduced operating temperature when using oxygen. An improvement in selectivity and yield was also obtained when using oxygen. In our recent study (Jevtic et al., 2009) in a stirred autoclave operated in a batch and semi-batch (dead end) mode, we have confirmed that in the temperature range of 130–160 °C an increased oxygen concentration (either via increased pressure of air or by increased oxygen mole fraction in nitrogen or by combination of the two) has a beneficial effect on the oxidation rate and leads also to improved yield and selectivity.

This confirmed that the use of pure oxygen or oxygen enriched air and increased pressure could benefit the overall productivity of the cyclohexane oxidation process. The possibility of deflagration has been the major obstacle in assessing the effect of increased oxygen availability not only on pilot scale but in laboratory reactors as well. A great concern regarding the oxidation processes and their safety has been present since the Flixborough accident on June 1st, 1974. It should be noted that this major incident did not happen due to runaway reactions but due to the rupture in the pipe that contained cyclohexane at 150 °C and at 1 MPa. Subsequently, cyclohexane leaked from the pipe, formed the vapor cloud, and, in contact with an ignition source, exploded. In fact, it is said (Berezin et al., 1966) that a mixture of cyclohexane vapor and air is not capable of spontaneous ignition at temperatures up to 250 °C at any pressure (Berezin et al., 1966). Nevertheless, considering the use of pure oxygen or oxygen enriched air in any hydrocarbon oxidation process legitimately raises questions about safety. Thus, the proper choice of the reactor, that would enable the safe operation, is of crucial importance.

Herein, we present an assessment of a capillary reactor as an alternative, novel reactor for safe operation of cyclohexane oxidation with pure oxygen. Its vastly reduced volume to external wall area ratio makes it inherently safer and allows the use of higher pressures. Absence of back mixing due to plug flow should further enhance performance. Our experimental studies in the batch systems (Jevtic et al., 2009) provided the data needed for the capillary reactor sizing and operation. The proposed capillary reactor is not a real micro reactor, since its diameter is of the order of channel size in a monolith. Nevertheless, it should share many of the advantages of the small channels in terms of the improved mass transfer and better temperature control. The objective of this study was to assess whether the capillary reactor can indeed live up to its expectations.

2. Experimental work

2.1. Reactor design

The capillary reactor is chosen due to two important reasons:

(a) Improved safety – keeping the diameter of the reactor small while increasing the length allows for more effective temperature control by wall cooling. The substantially increased wall to volume ratio compared to those achievable with cooling tubes in stirred tanks or bubble columns eliminates hot spot possibilities and reduces runaway chances.

(b) Improved selectivity – favorable flow pattern for reactions in series where desired product is an intermediate, like in the oxidation of cyclohexane, is plug flow which is achievable in a long two-phase flow capillary reactor.

The diameter of the capillary was chosen to prevent the occurrence of local ‘hot spots’ in the reactor. Hot spots can lead to runaway reactions, which are characterized by uncontrolled rise in temperature accompanied by rise in pressure that can results in an explosion. For a walled cooled Plug Flow Reactor (PFR) the largest diameter that insures the absence of the hot spot for cyclohexane oxidation at the reaction conditions was calculated based on established criteria (Barkelew, 1959; Froment and Bischoff, 1990) is 2.5 mm.

Another way to check for the occurrence of the runaway reaction is to calculate Frank-Kamenetskii’s parameter (Frank-Kamenetskii, 1955) δ given by Eq. (1) below and compare it to the critical value for various geometries:

$$\delta = \left(\frac{\Delta T_{ad}}{T_0}\right) \gamma \frac{\tau_c}{\tau_r} \tag{1}$$

Runaway reactions occur when a steady state temperature profile cannot be maintained any more or, in terms of Frank-Kamenetskii’s parameter, when $\delta \geq \delta_{cr}$. δ_{cr} is determined for a number of different geometries and is equal to 0.88 for a plane-parallel, 2.00 for a cylindrical, and 3.32 for a spherical vessel (Frank-Kamenetskii, 1955). In the case of the cyclohexane oxidation in the capillary reactor, δ can be calculated to be 0.04. This value is much smaller than critical values for all vessels mentioned above indicating that runaway reactions are not likely in this capillary reactor when cyclohexane is oxidized at the chosen reaction conditions (temperature 130–165 °C and pressure 1–15 bar).

The length of the capillary reactor was determined based on the residence time necessary to reach about 4–6% cyclohexane conversion over the liquid flow rate range chosen. The liquid and gas flow rate range were chosen based on the extensive review of two-phase flow regimes in capillary tubes (Suo and Griffith, 1964; Triplett et al., 1999; Mishima and Hikibi, 1996) in order to ensure a well characterized flow regime in the tube while satisfying the gas/liquid stoichiometric ratio needed for cyclohexane oxidation. Even though bubbly flow would be preferred due to very large interfacial area between gas and liquid phase, achieving this flow regime would lead to oxygen starved conditions because of the very high liquid to gas flow rates ratios. Thus, the Taylor flow regime was chosen. This flow regime was also confirmed experimentally by flow visualization carried out using transparent, Nylon tubes of the same dimensions as the stainless steel tubes used. Water was used as the liquid and oxygen as gas with liquid and gas velocity of 0.001 m/s to 0.0045 m/s and 0.0036 m/s and 0.012 m/s, respectively. The tests were done at room temperature and pressure ranging from atmospheric to 3 bar. In the Taylor flow regime the reported gas–liquid mass transfer coefficients are high (Kreutzer et al., 2001; van Baten and Krishna, 2004) so that we anticipated the reaction rates to be kinetically controlled. In our previous studies of uncatalyzed cyclohexane oxidation (Jevtic et al., 2009) conducted in