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Economic trade-offs in acrylic acid reactor design

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ABSTRACT

The acrylic acid process using air oxidation of propylene presents many interesting design trade-offs, particularly in the design of the reactor. The desired and undesired reactions are highly exothermic and very temperature dependent (large activation energies), so a large flowrate of inert water is also fed to the reactor to act as a thermal sink. Propylene conversion increases with temperature and reactor size, but acrylic acid yield decreases with increasing temperature. The heat of reaction is removed by generaing steam, and the steam pressure is an important design optimization variable since it sets low limits on reactor temperature. Using low-pressure steam gives high acrylic acid yield and lower carbon dioxide generation but requires large reactors. Larger air flowrates increase reactor oxygen concentrations, which reduce reactor volume but increase air compression costs.

This paper explores the effects of the many design trade-offs on capital investment, energy cost and product selectivity.

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1. Introduction

Acrylic acid is a commodity chemical that is widely used in the polymers industry. The commercial petroleum-based process uses propylene with air providing the oxygen to form acrylic acid and byproducts of acetic acid and carbon dioxide. All of the reactions are highly exothermic and have large activation energies, so they are highly sensitive to temperature. There "hot" reactions present challenging design and control problems. In addition to propylene and air, a large amount of steam is fed to the reactor to serve as a thermal sink for the large amount of heat generated by the reactions. There is a significant cost for providing this steam. Air is free but it requires compression to the 4.3 bar reactor pressure, which is set by the downstream operating pressure of an absorber.

The heat of reaction is removed by using a heat exchanger inside the fluidized-bed reactor vessel, which is assumed to act like a CSTR in this paper. A large amount of heat must be removed, and the required heat-transfer area depends on the temperature difference between the reactor and the steam. Valuable high-pressure steam can be generated when reactor temperatures are high, but high reactor temperatures give low selectivity (more carbon dioxide formation). Less valuable low-pressure steam must be used to achieve low reactor temperatures and high selectivity (low carbon dioxide formation).

For a given flowrate of propylene fed to the reactor, there are optimum flowrates of both air and steam since they impact yields, selectivity, required reactor size, heat-exchanger size and optimum reactor temperature.

The process, which was developed many decades ago, is discussed in several books and papers. Most notably, the popular design textbook by Turton et al. (Turton et al., 2003) presents the process as a design project. The process was featured (AIChE, 1986) as the AIChE Student Design Problem in 1986.

Safety is an important issue because of the upper and lower flammability limits of propylene in oxygen. The gaseous mixture in the reactor has high concentrations of inert nitrogen and water. Turton et al. (Turton et al., 2003) suggest that flammability problems can be avoided by keeping the oxygen composition below 5 mol%. Of course this high limit may not be the optimum in some cases since it entails feeding excess air with the inherent higher compression costs.

The reactor described in Turton et al. (Turton et al., 2003) is a fluidized bed reactor that is essentially a CSTR. A later design project from West Virginia (Department of Chemical Engineering, 2016) and a recent paper (Suo et al., 2015) suggest the use of a cooled tubular reactor. In this paper we used the Aspen *RCSTR* model for the reactor. In a later section we discuss the significant differences between these two reactor types and demonstrate that the use of a tubular reactor in this "hot" reaction system is problematic. Reactor runaways, excessive peak temperatures and low acrylic acid yields can easily occur in a cooled tubular reatcor even with a very large number of small tubes to provide large heat-transfer area. The sensitivity of reactor internal temperatures down the length of the reactor to the coolant temperature is extremely high.

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Table 1
Kinetics for gas phase irreversible reactions.

	k	E (kcal/kmol)
ℜ1	4.4167×10^{-5}	15,000
ℜ2	2.4528×10^{-4}	20,000
ℜ3	5.0278×10^{-2}	25,000

Concentration units – Pascals.
Reaction rate – kmols s^{-1} m^{-3} $Pa^{-2.}$

No studies in the open literature have been found that discuss the optimum economic design of the acrylic acid process. That is the purpose of this paper. The study is limited to the reactor portion of the process. This approach should be valid since there are no recycle streams that couple the reaction and separation sections of the process.

2. Base case design

A thorough description of the acrylic acid process is provided by Turton et al. (Turton et al., 2003) and is used as the basis in this paper. Turton does not address the issues of economic optimization and dynamic controllability.

There are three reactions that are assumed to be irreversible and first-order in both propylene and oxygen partial pressures. The first produces the desire acrylic acid product.

$$\Re 1 : C_3H_6 + \frac{3}{2}O_2 \rightarrow C_3H_4O_2 + H_2O$$

The second and third reactions produce the undesired byproducts of acetic acid and carbon dioxide.

$$\Re 2 : C_3H_6 + \frac{5}{2}O_2 \rightarrow C_2H_4O_2 + H_2O + CO_2$$

$$\Re 3 : C_3H_6 + \frac{9}{2}O_2 \rightarrow 3CO_2 + 3H_2O$$

The acetic acid can be sold but is less valuable than acrylic acid. The carbon dioxide represents a significant loss of propylene in addition to adding to emission problems. Therefore the suppression of the production of carbon dioxide is particularly important in this process. Selectivity has a strong impact on the profitability of the process since it affects the amount of the desirable product that is produced. Large increases in capital investment and energy (compressor work) can be economically justified to improve the yield of acrylic acid.

The kinetic provided by Turton use units of kmol/h and kPa. The required units for Aspen reactor simulations must use kmol/s and Pa. The kinetics used in this paper are given in Table 1. Note that the reactions are gas phase and first order. The basis is reactor volume. Aspen UNIQUAC physical properties are used.

Since the activation energies of the undesired reactions are larger than the activation energy of the desired reaction, it is obvious that the optimum reactor temperature should be low. But of course low temperatures produce small reaction rates, so the size of the reactor required to achieve the desired propylene conversion increases as reactor temperature decreases. This is an example of the classical reactor design trade-off between yield (the value of the products produced) and capital investment (the cost of the reactor vessel and catalyst).

Fig. 1 gives the base-case flowsheet used in this paper. The flowrate of vapor propylene is 127 kmol/h. The flowrate of steam is 992.3 kmol/h of saturated low-pressure steam at 160 °C and 6 bar. The flowrate of air is 1362 kmol/h. The original Turton flowsheet used a single-stage compressor, but a two-stage system is used in this paper to keep compressor discharge temperature less than the heuristic maximum of 200 °C. Total compressor work is 2.092 MW. A water-cooled interstage heat exchanger is used to cool the hot gas from the first compressor down to 50 °C before feeding to the second stage compressor

The reactor vessel has a total volume of 118 m^3 and operates at 310 °C and 4.3 bar. A large heat exchanger is installed inside the reactor to remove the large heat of reaction (23.84 MW). High-pressure steam is generated (254 °C) giving a differential temperature driving force of 310–254 = 56 °C. Assuming an overall heat-transfer coefficient in this gas/fluidized solid system of U = 0.28 kW m^{-2} K^{-1}, the required heat-transfer area is 1520 m^2. The volume of this heat exchanger is 38 m^3. The volume of the reaction phase required to achieve the specified propylene conversion is 80 m^3, so the total volume of the vessel is 118 m^3. Using an aspect ratio L/D = 2 gives a vessel diameter of 4.22 m and length of 8.44 m.

The gas leaving the reactor contains acrylic acide (AA), acetic acide (HAc), carbon dioxide (CO_2), water, inert nitrogen, unreacted propylene (C3) and unreacted oxygen. The conversion of propylene in the Turton base case is 95.25%. The selectivity of acrylic acid relative to acetic acid is 13.5. The selectivity of acrylic acid relative to carbon dioxide is 14.7. At the 310 °C reactor temperature used by Turton, there is a significant loss of propylene to produce undesired by-products, particularly carbon dioxide. The air flowrate of 1362 kmol/h produces an oxygen composition in the reactor of 1.36 mol%, which is well below the flammability limit. More air could be fed, which would decrease reactor size but increase compression costs. This is an important design trade-off.

The downstream separation system suggested by Turton consists of an absorber to recover the products from the gas stream, a liquid-liquid extractor and several distillation columns. The off-gas from the absorber is sent to an incinerator, so any unreacted propylene is lost. Therefore the reactor must be designed for high conversion of propylene to avoid loss of valuable raw material.

It is important to note that there is no recycle from the separation section back to the reactor. Therefore the reactor can be optimized independently. In most chemical processes, this is not the case since reactor performance impacts the economics of the separation section.

In the following section we explore the effects of several important design variables on the economics of the process in terms of product value, energy costs and capital investment. The economic objective function is profit, which is defined as the value of the acrylic acid and acetic acid products plus the value of the steam generated in the reactor minus the cost of the propylene and steam feeds minus compressor energy cost minus total annual capital cost.

3. Effects of design variables

The flowrate of propylene is fixed in all cases at 127 kmol/h. The cost of propylene and the value of acrylic acid and acetic acid are taken from ICIS.com student historical chemical price information (ISIS.com, 2016). The conversion of propylene is fixed at 95.25% in all cases so that a direct comparison with the Turton design can be made. In a later section of this paper, the effect of conversion on profitability is quantified. Conversion is maintained constant as other variables are changed by varying reactor volume using an Aspen *Design Spec/Vary* feature. A second Aspen *Design Spec/Vary* is used to achieve a specified value (to be optimized) for the selectivity of acrylic acid relative to acetic acid. As we demonstrate below, setting selectivity fixes reactor temperature uniquely, i.e. there is only one degree of freedom relating selectivity and temperature.

In addition to selectivity, the feed flowrates of air and steam are also design optimization variables. Using larger air feed flowrates increases oxygen composition in the reactor, which results in smaller reactor sizes for a fixed propylene feed flowrate and a fixed propylene conversion. This reduces capital investment in the reactor vessel and catalyst. However, using more air increases compression costs, both energy and capital.

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