Sustainable Acetaldehyde Synthesis from Renewable Ethanol: Analysis of Reaction and Separation Processes

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Abstract

Acetaldehyde can be industrially manufactured by means of ethanol oxidation, ethylene oxidation, and hydration of acetylene. The preferred technology since the 1960s has been the direct oxidation of ethylene via the Wacker process. However, demand for the development of greener processes because of the aggravation of the climate crisis demands process engineers to develop greener processes and reduce reliance on non-renewable feedstocks. Ethanol costs and environmental impact have decreased substantially since the development of the Wacker process in 1957–1959, and alternative catalysts for ethanol oxidation have been evaluated as well. However, the oxidation of ethanol in the gas phase is a cumbersome process because of the dilution of products in inert gas (nitrogen). Therefore, this work evaluates the energy demand of acetaldehyde production via ethanol oxidation. Four synthesis conditions were considered, with air-to-ethanol molar ratios of 3.2, 6.1, 9.0, and 21.6, based on experimental data. Acetaldehyde was recovered using compression, gas absorption, and distillation, using different operating pressures in the gas absorption step. Dilution of reactants and recycling of unconverted ethanol in the synthesis loop has a great impact on the energy demand of the process, and results indicate that a molar ratio of 9.0 of O2 to ethanol is desirable. Despite the high energy demand, this process could be integrated into a sugarcane ethanol biorefinery to integrate the use of renewable feedstock and renewable energy, thus reducing the depletion of fossil resources.

**Keywords**: process simulation, optimization, oxidation, absorption, green chemistry

* 1. Introduction

Acetaldehyde, a key chemical intermediate with versatile applications in the chemical industry, is crucial for synthesizing various compounds, including acetic acid, perfumes, plastics, and pharmaceuticals (Hagemeyer, 2000). The increasing global demand for acetaldehyde has fueled extensive research into optimizing production processes. Traditionally, acetaldehyde is produced through the oxidation of ethylene via the Wacker process, using metal-based catalysts (Jira, 2009). Despite reliability, these methods have drawbacks such as high energy consumption and environmental concerns regarding the use of fossil feedstock (ethylene). Sustainable alternatives are imperative considering the current state of climate change and the use of non-renewable resources.

An alternative for the oxidation of ethylene is the oxidation of ethanol. Ethanol can be produced from renewable sources (*e.g.*, sugarcane, corn), with a considerably low carbon footprint (Cantarella *et al.*, 2023), making it a perfect feedstock to replace ethylene. The catalytic process has been studied in the past (Maciel Filho *et al.*, 1996), considering the use of the Fe and Mo catalysts. However, despite the good conversion performance, recovering the acetaldehyde from the resulting product stream was a cumbersome and energy-intensive task.

Considering examples of studies on biorefinery processes indicating the attractiveness of integrating chemical processes into sugarcane mills (Leal Silva *et al.*, 2022), this work has the goal of revisiting the conversion of ethanol to acetaldehyde. Process design, modeling, and simulation were employed to explore potential operating conditions and their impact on the energy demand of the process.

* 1. Methodology

Ethanol oxidation and acetaldehyde recovery processes were modeled on Aspen Plus 8.6 using the Redlich-Kwong equation of state for the vapor phase and the Non-Random, Two-Liquid activity coefficient model for the liquid phase. Binary interaction parameters for all components were retrieved from the PURE32 database of Aspen Plus. Air was assumed to be composed of N2 and O2 at a molar ratio of 79:21, with both gases considered as supercritical components whose Henry’s constant in water was based on data retrieved from the PURE32 database. The process is shown in Figure 1.



Figure 1. Block flow diagram of the proposed process for oxidation of ethanol to acetaldehyde.

In the process, ethanol (virgin and recycled) was vaporized and mixed with a stream of preheated air containing the desired proportion of O2 to ethanol (3.2, 6.1, 9.0, or 21.6). The oxidation of acetaldehyde, represented in Eq. (1), was indicated on a stoichiometric reactor (*RStoic* model) that operates with a pressure drop of 60 mbar and outlet temperature of 240 °C. The mixture reacted in the presence of a catalyst, and conversion for each process condition was based on experimental data (Maciel Filho *et al.*, 1996). Heat was removed from the reactor as 2 bar saturated steam was produced.

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|  | (1) |

Acetaldehyde was recovered via absorption in water. To reduce the volume of water required to carry out this operation, different operating pressures for the absorption process were tested. The total energy consumption includes the energy demand for the compression of the product stream and the recycling of the water used in the absorption step. Before compression, the reactor outlet stream was cooled to 150 °C, and then it was fed to a series of compressors whose number depends on the final desired pressure: two for 3.1 bar, three for 5.0 bar, four for 8.1 bar, and five for 13 bar. After compression, the product stream was cooled by heat exchange with the air feed stream, available at 25 °C, and then cooled to 5 °C using chilled brine. After cooling, part of the water, acetaldehyde, and ethanol was recovered in a knockout pot, and the gas stream was fed to the bottom of the absorber.

Water was fed at the top of the absorber (*C-01*), with a flow rate required to reduce volatile organic compounds of the leaving gas to a concentration of 20 mgC Nm-3, compatible with European legislation (European Union, 1999). The temperature of the water was a design variable to be analyzed. The gas leaving the top of the absorber was expanded on a turbine with an isentropic efficiency of 83% to drive an electric generator with a mechanical efficiency of 98%. The water containing the acetaldehyde and unreacted ethanol was then heated to its boiling point and fed to a first distillation column (*C-02*) that operates at near atmospheric pressure to recover acetaldehyde at the top. This column included a gas vent in the condenser to remove trace amounts of nitrogen and oxygen that were dissolved in water. Then, in a second column (*C-03*), hydrated ethanol was recovered at the top, yielding water at the bottom to be recycled to the absorber. The water stream was first cooled by heat exchange with the cold stream leaving the bottom of the absorber and, after a purge, it was further cooled to the absorber operating temperature. The purge fraction varies based on the water produced during the oxidation reaction (Eq. 1) and the water required in the absorber; thus, it is calculated using a design specification. Both distillation columns have reflux ratio and number of stages calculated using shortcut methods, and these results were used to model a rigorous column based on the *RadFrac* model of Aspen Plus. In the first distillation column, the reflux ratio was varied to achieve 99.5% recovery of acetaldehyde on the top with 99% purity (the balance is ethanol). In the second column, the reflux ratio was varied so that the mass fraction of water at the bottom was 99.9%.

Process options (different O2 to ethanol molar ratios and different operating pressures for the absorber) were compared based on utility demand: saturated steam at 2 bar for process heaters and reboilers (after the steam credit from the steam produced in the reactor), cooling water and chilled brine for condensers and coolers, and electricity for compression (after the electricity credit from the expansion of the exhaust gas). The chosen plant capacity, 256 kt/y of acetaldehyde, is compatible with the production of anhydrous ethanol in a sugarcane mill processing 4 Mt/y of sugarcane.

* 1. Results and discussion

The first process variable to define is the temperature of the water used in the absorption step. Figure 2 shows the required flow rate of water to achieve the emission standards required for the exhaust gas and the combined reboiler duties of the subsequent distillation columns, C-02 and C-03. This was evaluated only for the case of O2 to ethanol ratio of 21.6, which is the most dilute system with the highest proportion of acetaldehyde to ethanol (the latter having more affinity to water than the former). It was observed that the flow rate of water increased substantially when increasing the temperature of the water. Naturally, as acetaldehyde has a low boiling point, removing it from the gas phase requires a cold solvent to increase its solubility. The increase in water demand is also reflected in the increased reboiler duty of the following distillation columns (C-02 and C-03), with a steep increase observed when working at lower pressures. This happens because, as the pressure decreases, the water demand steeply increases as the temperature rises because the recycled solvent (water) contains 0.1% ethanol. Therefore, it becomes impossible to achieve emission standards for the exhaust gas independently of flow rate.

A graph of a temperature

Description automatically generated with medium confidence

Figure 2. a) water flow rate, b) combined reboiler duties of columns C-02 and C-03, and c) cooler duty for the recycled water stream feeding the absorber for different operating temperatures of the absorption tower (assuming O2 to ethanol ratio of 21.6 – most dilute system).

A counterintuitive result is the demand for cooling the stream of recycled water fed at the top of the absorption tower: cooling the water to lower temperatures reduces the total demand for chilled brine. This happens because the reduced demand for water as the temperature decreases compensates for the increased duty to cool it to a lower temperature. Based on these results, the lowest temperature possible is desired. This conclusion considers that any operating temperature below 20 °C would require chilled brine to adjust the final desired temperature of the feeding streams. Bearing in mind the freezing point of water, the temperature of 5 °C was chosen to ensure operability.

Figure 3 presents the results of the use of process utilities by the different process configurations (different pressures in the absorption step and different O2 to ethanol ratios in the reactor). Generally, the demand for heating and cooling utilities decreases considerably as the pressure of the absorption step is increased: when shifting from 3.1 to 5.0 bar, the steam demand decreases 5–17% depending on the O2 to ethanol ratio. However, this comes at the cost of higher spending with compression power, as observed in Figure 3e. It was observed that the steam demand (Figure 3c) for ratios of 21.6 and 9.0 was almost identical and the lowest for the whole range of evaluated absorption pressure, and it is 9–20% lower than the steam demand of the next best case (ratio of 6.1).



Figure 3. a) cooling water demand, b) chilled brine demand, c) steam demand, d) recovered steam, e) electricity demand, and f) recovered electricity for different pressures of the absorption step and different O2 to ethanol ratios (O2/EtOH in the legend); values are reported per kg of acetaldehyde produced in the process.

Steam demand increased considerably for lower O2 to ethanol ratios because of the need to recycle ethanol. When using a ratio of 21.6, the reaction is almost driven to completion, reaching 96.2%. However, when using a ratio of 3.2, single-pass conversion is 48.2%. A ratio of 9.0 yields a conversion of 79.69% of ethanol. Despite the increased ethanol recycling compared to the ratio of 21.6, the considerably lower excess of air demands less solvent recycling to the absorption tower, which also reduces the demand for steam.

According to Figure 3b, chilled brine demand decreases considerably for the O2 to ethanol ratio of 21.6 as the pressure increases. Because of the large excess of air and the use of low pressure in the absorption tower, the water demand increases substantially (Figure 2a), and the recycling of this water demands chilled brine. For pressures higher than 8 bar, the demand for chilled brine levels off because, despite the decrease in demand to adjust the temperature of the water stream of the recycling loop, there is also an increased demand in column C-02 because the separation between components demands greater reflux (whose cooling is carried out using this utility because of the boiling point of acetaldehyde). However, the chilled brine demand for the O2 to ethanol ratio of 21.6 is only about 10% lower than the demand for the ratio of 9.0 for pressures greater than 8.1 bar. These savings are small compared to the increased electricity demand, which can reach 80% for 13.1 bar when comparing the O2 to ethanol ratio of 21.6 and 9.0.

The proper comparison of process options demands an economic assessment (Leal Silva and Maciel Filho, 2024). Nevertheless, bearing in mind the high cost of compressors and the large electricity demand, the ratio of 21.6 might become prohibitive when considering that the steam demand of both ratios of 9.0 and 21.6 are nearly the same. The process simulation included an estimative of potential power recovery, as shown in Figure 3f. Power recovery was about 30%. Nevertheless, this result needs to be considered with caution because of equipment cost. It is also important to mention that the total demand for steam is compatible with the amount of excess steam that can be produced in sugarcane mills (Leal Silva *et al.*, 2022), which makes the process suitable for integration into sugarcane biorefineries. This strategy can reduce costs and allows the use of biomass as fuel for steam and electricity production, required in the process.

* 1. Conclusions

This work assessed the production of acetaldehyde via ethanol oxidation. Four reaction conditions were simulated, and the separation process, considering absorption on water, was carried out at different pressures in the range of 3–13 bar. According to the results, despite a large excess of air being capable of driving the reaction to almost 100% conversion, recovering the product from such a dilute stream implies a high demand for utilities (mainly electricity for compression). Therefore, a molar ratio of 9.0 of O2 to ethanol is preferable because, despite resulting in a substantial recycling of reactant (ethanol), it results in a similar steam demand and a great reduction in electricity demand. These results considered an overall look at the process, including reaction and separation steps. Therefore, for a more detailed techno-economic analysis, it would be interesting to better optimize individual process steps and analyze additional heat integration potential to decrease the energy demand of the process. It is also important to consider the integration of this process into sugarcane biorefineries so both processes benefit from utility integration.

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