Techno-economic Analysis and Life Cycle Assessment of Renewable Acetaldehyde from Sugarcane Ethanol

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Acetaldehyde has been historically synthesized from ethanol via oxidation. However, since the 1960s, the cost of feedstock and conversion process has gradually driven manufacturers to prefer the liquid-phase oxidation of ethylene. However, the aggravation of the effects of the climate crisis demands a shift from fossil feedstocks to renewable feedstocks to reduce society's CO_2 footprint. Moreover, sugarcane ethanol production is a more mature process nowadays, delivering a low-cost renewable chemical. Bearing all this in mind, this work analyzes the viability of the production of acetaldehyde via oxidation of sugarcane ethanol. The key idea is to integrate the process into a sugarcane biorefinery to take advantage of the surplus energy of optimized distilleries to provide renewable energy for acetaldehyde production. The oxidation process of ethanol to acetaldehyde in the gas phase was simulated using literature data. Process data for the remaining sections of the sugarcane biorefinery were based on literature data as well. Based on equipment sizing and processing capacity, a cash flow analysis was performed to determine the best operating conditions for acetaldehyde production via ethanol oxidation. Results have shown that the conversion of ethanol to acetaldehyde using this process is competitive and can increase the earnings of the biorefinery. A life cycle assessment was performed as well to compare the carbon intensity of acetaldehyde produced from ethanol to the carbon intensity of acetaldehyde produced via direct oxidation of ethylene, showing a reduction of 85%. Results demonstrate that the oxidation of ethanol represents a renewable alternative with economic potential when integrated into a sugarcane biorefinery.

1. Introduction

Acetaldehyde (ethanal) is an important chemical intermediate with applications in chemicals, perfumes, pharmaceuticals, and plastics. It can be used in the production of acetic acid, acetone, ethyl acetate, acetic anhydride, pyridines, and alkylamines (Hagemeyer, 2014). Since the 1960s, acetaldehyde has been mostly produced via liquid-phase oxidation of ethylene in the presence of a metal catalyst (Jira, 2009), in the Wacker process, while there are still some commercial plants working with partial oxidation of ethanol and hydration of acetylene. Despite the reliability of mature technology, the Wacker process has drawbacks such as high consumption of energy and the use of a non-renewable raw material — ethylene, produced via steam cracking of petroleum fractions or natural gas liquids (Moulijn et al., 2013). In the face of the current climate crisis, alternative processes to replace non-renewable chemicals with green chemicals must be developed (Ncube et al., 2023).

Ethanol oxidation was the preferred route to produce acetaldehyde before the development of the Wacker process, which took over as the preferred process option by 1968 in the United States (Hagemeyer, 2014). During this time, the Wacker process became more economically attractive because of feedstock costs. However, since then, ethanol production from corn and sugarcane has grown significantly, and costs reduced (Cantarella et al., 2023), which might make this raw material attractive again. Moreover, bearing in mind the effects of the climate crisis, it is important to move away from non-renewable sources by developing and improving chemical processes that are based on green chemicals and renewable feedstocks, such as ethanol. In this context, the catalytic conversion of ethanol to acetaldehyde has been studied using Fe and Mo catalysts (Maciel Filho et al., 1996), and the recovery process has been studied as well in terms of process design and

energy demand (Leal Silva and Maciel Filho, 2024). Nevertheless, it is still needed to identify the economic competitiveness of the process and determine potential bottlenecks.

One of the potential tools to ensure the economic success of green chemicals is their integration into large biorefineries (Lopes et al., 2021). As the process for production of renewable acetaldehyde demands ethanol and energy (heat and electricity), integrating this process into a sugarcane biorefinery with surplus electricity production could enable cost-competitive production of renewable acetaldehyde (Solarte-Toro and Cardona Alzate, 2021). Therefore, this study presents a techno-economic analysis of the production of acetaldehyde from sugarcane. Twelve scenarios of different process conditions for the conversion of ethanol were integrated into a conventional, optimized sugarcane biorefinery via process simulation. These scenarios were compared to a standard sugarcane biorefinery producing ethanol and electricity in terms of economic indicators to assess the feasibility of acetaldehyde production from sugarcane. Results of mass and energy balance were also used to estimate the carbon footprint of renewable acetaldehyde, which was compared to the standard value for the fossil-based chemical.

2. Methodology

Figure 1 shows the proposed biorefinery layout to produce acetaldehyde. The biorefinery processes were simulated in Aspen Plus 8.6 (Aspen Tech, Inc., Bedford, USA). Ethanol production from sugarcane juice and burning of sugarcane bagasse to produce steam and electricity were simulated based on process conditions reported in the literature for the optimized process currently implemented in modern sugarcane processing facilities in Brazil (Dias et al., 2016), assuming a processing capacity of 4 million t of sugarcane per year, operating 200 d/y (during sugarcane harvest). The base scenario, called ET-0, represents the case in which the biorefinery produces only ethanol and electricity — all sugarcane bagasse is consumed by the biomass boiler.
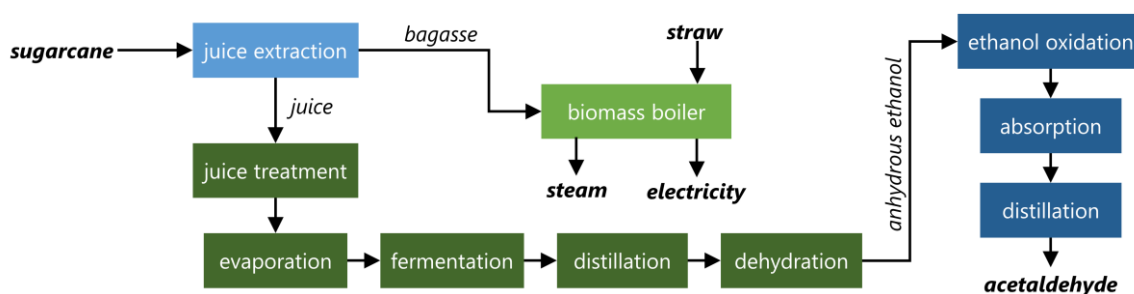

Figure 1: Proposed biorefinery layout to produce acetaldehyde from sugarcane ethanol.

The ethanol oxidation step to produce acetaldehyde was based on the process design provided in the literature as well (Leal Silva and Maciel Filho, 2024). In this process, ethanol was vaporized and mixed with air with molar ratios of O_2 to ethanol of 3.2, 6.1, and 9.0. The mixture was then passed through a fixed bed reactor, simulated by an *RStoic* model, with conversion based on experimental results (Maciel Filho et al., 1996). Recovery of acetaldehyde was a cumbersome task because it was mixed with nitrogen (from air). In this case, to avoid the use of organic solvents, the gas stream was compressed and passed through a gas absorber to recover the acetaldehyde and unconverted ethanol. In this absorber, the gas stream was contacted with a cold water stream (5 °C) whose flow rate was calculated so that the concentration of volatile organic compounds in the gas was reduced to 20 mg C/Nm^3, compatible with European legislation (European Union, 1999).

For each of the three above-indicated reaction conditions, four absorber pressures were evaluated because the working pressure affects the water flow rate demanded to recover the acetaldehyde. This resulted in a total of twelve scenarios of different process conditions. Scenarios were named A3-1, A3-2, A3-3, and A3-4 for the molar ratio of 3.2 and each possible working pressure for the absorber (3.1 bar, 5.0 bar, 8.0 bar, and 13 bar corresponds to -1, -2, -3, and -4, respectively), and similar naming was used for the other molar ratios (A6-x for the molar ratio of 6.1 and A9-x for the molar ratio of 9.0). The aqueous solution containing acetaldehyde was then distilled to recover the acetaldehyde as the product of the process. From the remaining aqueous solution, ethanol was recovered and recycled to the oxidation reactor and water was recovered and recycled to the gas absorber. Electricity for the compressors and heating and cooling utilities for the other unit operations were drawn from the biorefinery utilities section, represented by the biomass boiler in Figure 1.

The capital cost of equipment for the conversion of ethanol to acetaldehyde was estimated based on the results of mass and energy balances provided by the process simulator and the module costing technique (Turton et al., 2018). The reactor was dimensioned as a scaled-up multi-tubular reactor based on previous results (Maciel

Filho et al., 1996). Distillation columns were initially designed based on short-cut methods, and the provided results were then used in the rigorous *RadFrac* model of Aspen Plus, which can be used to estimate column dimensions. The absorber was modeled using the *RadFrac* model as well, assuming a random packing of Pall rings of 25 mm. Heat exchangers were dimensioned based on heat exchange area, which was calculated using the heat duty, the mean temperature difference, and the overall heat transfer coefficient calculated using Aspen Exchanger Design and Rating 8.4.

Based on these results, the bare module cost (C_{BM}) for equipment at base conditions was calculated using Eq. (1). In this equation, B_1 and B_2 are constants that are particular to each process equipment, available in tables in the literature (Turton et al., 2018). F_P is the pressure factor, which increases the demand for construction material as the operating pressure increases, and it is calculated using Eq. (2) and constants C_1, C_2, and C_3, particular to each equipment type, with values available in the literature (Turton et al., 2018). F_M is a constant that is related to the material of construction. In this case, as acetaldehyde is not corrosive, a combination of carbon steel and stainless steel was chosen depending on the service and temperature for which each unit operation was intended. The value of this constant depends on the equipment type, and these values are available in the literature as well (Turton et al., 2018). C_p^0 is the base purchase cost of equipment at standard conditions, calculated using Eq. (3). C_p^0 is a function of constants K_1, K_2, and K_3, particular to equipment type with values available in the literature (Turton et al., 2018), and A, which is the capacity or sizing parameter for each equipment (*e.g.* heat transfer area for heat exchangers). The sum of these costs yields the capital expenditure (CapEx) of the acetaldehyde plant.

$$C_{BM} = (B_1 + B_2 F_P F_M) C_p^0 \tag{1}$$

$$log_{10}(F_P) = C_1 + C_2 \, log_{10}(P) + C_3 (log_{10}(P))^2 \tag{2}$$

$$\log_{10}(C_p^0) = K_1 + K_2 \log_{10}(A) + K_3 (\log_{10}(A))^2 \tag{3}$$

The CapEx of the sugarcane ethanol plant and the utility section (cogeneration of heat and power based on biomass and cooling water section) of the biorefinery were estimated based on results from the literature (Dias et al., 2016; Leal Silva et al., 2022). Operational expenditure (OpEx) included cost with sugarcane ($21.0/t), straw ($28.9/t), additional inputs for ethanol production ($0.066/$L_{ethanol}$), wastewater treatment ($0.222/$m^3_{wastewater}$), labor cost (average monthly wage of $1280), maintenance (3% of CapEx), and taxes (34% of net income according to Brazilian law) (Brazilian Ministry of Economy, 2023; Dias et al., 2016; Leal Silva et al., 2018; Souza et al., 2022; Ulrich and Vasudevan, 2006). Revenue was obtained by selling ethanol (in scenario ET-0, $810/t), acetaldehyde (in all other scenarios, $1010/t), and electricity (in all scenarios, $48.1/MWh). Linear depreciation was assumed, and a project lifetime of 30 years was chosen, with a catalyst service time of 10 years. Economic parameters suitable for the sugarcane sector in Brazil were based on previous literature (Dias et al., 2016). The results of CapEx and OpEx were then combined in a cash flow analysis to calculate the internal rate of return of each biorefinery scenario.

Life cycle assessment (LCA) was performed for the scenario producing acetaldehyde with the best internal rate of return. The study considered a cradle-to-gate attributional LCA with the system boundary defined in Figure 2. The goal was to determine the carbon footprint of 1 kg of acetaldehyde as the functional unit. Emissions were allocated based on the revenues of the biorefinery because electricity is a product as well and it is incompatible with the functional unit of mass. Feedstock was assumed to be sugarcane produced in the state of São Paulo, Brazil, according to data available in the Ecoinvent database 3.8 (Ecoinvent Association, 2021, Zurich, Switzerland). Additional process inputs were included as well (Dias et al., 2016; Souza et al., 2022). The assessment was conducted using the ReCiPe 2016 midpoint hierarchist method implemented on openLCA 1.11.0 (GreenDelta GmbH, 2022, Berlin, Germany).
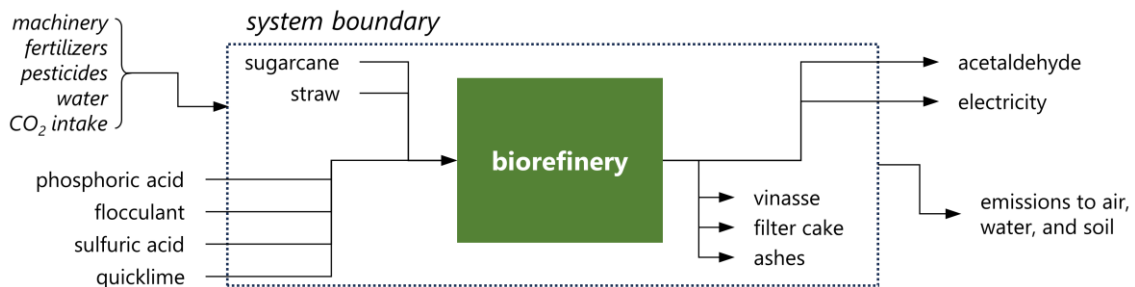

Figure 2: System boundary considered in the life cycle assessment of the biorefinery.

3. Results and Discussion

Figure 3a shows the composition of the CapEx of each biorefinery scenario. Cogeneration of heat and power is the biggest contributor to the total CapEx of the biorefinery because no other use was given to the sugarcane bagasse except for burning to produce steam and electricity. As such, it represents 48% to 49% of the total CapEx of each scenario producing acetaldehyde. Electricity is a biorefinery product of low value-added. In this case, condensing turbines are employed to maximize electricity production, which is then sold to the grid, and these turbines are costlier than backpressure turbines that could be used otherwise if no excess steam was produced. The acetaldehyde process has a large electricity demand because of the compressors employed in the recovery process: the electricity demand of the total process (sugarcane extraction, ethanol production, and acetaldehyde production) increases sharply depending on recovery conditions, from +57% to +154% compared to the base scenario (0-ET). The integration into the biorefinery means that electricity is produced onsite at a reduced cost, which is fundamental to ensuring the economic feasibility of the process.
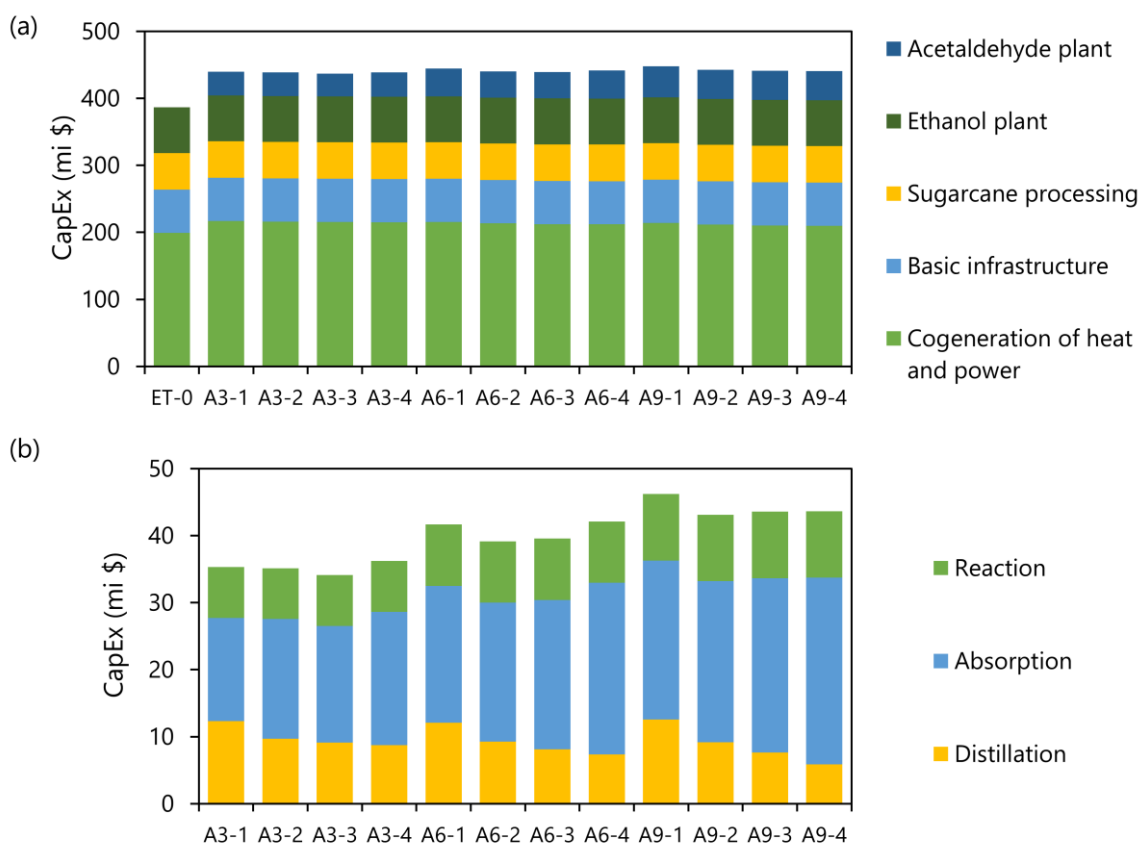

Figure 3: a) CapEx composition of each biorefinery scenario, including the base case ET-0, and b) CapEx composition of the acetaldehyde plant.

The acetaldehyde plant is fairly inexpensive compared to the total CapEx of the biorefinery, ranging from 8% to 10%. The major contributor to the CapEx of the acetaldehyde plant is the absorption step, mainly because of the compressors required to deliver the gas stream at the pressure required by the absorber. Figure 3b shows the composition of the CapEx of the acetaldehyde plant, and it is possible to observe that the share of the absorption step increases as the amount of excess air being used increases (higher O_2 to ethanol molar ratio, scenarios A3-x *vs.* A6-x *vs.* A9-x) or as the operating pressure of the absorber increases for each given O_2 to ethanol molar ratio (variations -1, -2, -3, or -4 for each A3-x, A6-x, or A9-x). Additionally, as the excess gas increases, conversion increases, and less ethanol is recycled. Therefore, the capital cost associated with ethanol distillation decreases as the ratio of O_2 to ethanol increases. Also, as the pressure increases, the amount of water required in the gas absorber decreases, which decreases the capital cost associated with water recycling inside the acetaldehyde plant. Therefore, in the graph of Figure 3b, the capital cost of the distillation section of the acetaldehyde plant gradually decreases from left to right.

Figure 4a shows the calculated internal rate of return of all scenarios producing acetaldehyde. The results indicate that the best scenario is the one with an O_2 to ethanol molar ratio of 6.1 whose acetaldehyde is recovered on a gas absorber working at 5.0 bar (scenario A6-2). In this scenario, single pass conversion is only 62.78%. However, the additional recycling of ethanol is more economically attractive than working with a larger excess of O_2 or a greater pressure in the gas absorber, both factors that increase expenses related to gas compression. Scenarios using an O_2 to ethanol molar ratio of 9.0 present comparable results as the ones using an O_2 to ethanol molar ratio of 6.1, with the pressure of 5.0 bar being the best one. In the case of an O_2 to ethanol molar ratio of 3.2, the optimal pressure is not clear, but the trend of the results indicates that if low pressures are required to work in this process, a lower excess of air might be desired. Nevertheless, the internal rate of return for a higher excess of O_2 is preferable.
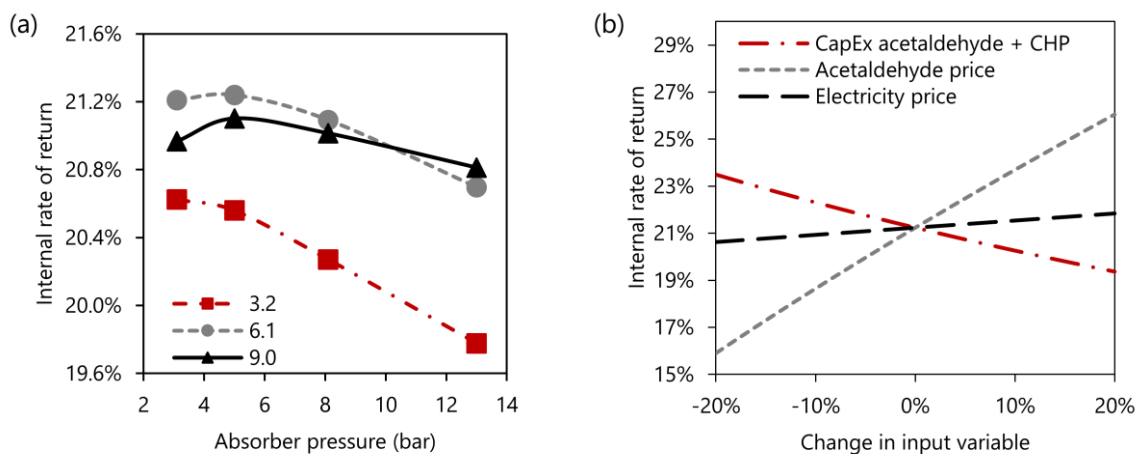

Figure 4: a) internal rate of return of the biorefinery for each O_2 to ethanol molar ratio (3.2, 6.1, and 9.0) for the four gas absorber pressures and b) sensitivity analysis of the CapEx and prices of acetaldehyde and electricity for scenario A6-2 (O_2 to ethanol molar ratio of 6.1 and gas absorber pressure of 5 bar).

Figure 4b shows the sensitivity analysis for the CapEx and prices of electricity and acetaldehyde. Changes of ±20% in electricity price have a minimal impact on the internal rate of return because, in general, electricity has low participation in the revenues, ranging from 10.1% (in scenario A9-4) to 11.5% (in scenario A3-1). In contrast, changes of ±20% in acetaldehyde price can make the internal rate of return range from 15.9% to 26.1%. Therefore, the process can be deemed economically viable because, despite fluctuations in acetaldehyde price of ±20%, the internal rate of return of the biorefinery is, in general, greater than a minimum acceptable rate of return of 12%, which is generally required for sugarcane biorefineries in Brazil (Dias et al., 2016). Sensitivity analysis was performed on the CapEx related to the cogeneration of heat and power, cooling utilities, and the acetaldehyde plant, which are the primary sources of uncertainty in capital cost estimation since the capital cost of the other sections was based on data validated with industrial data (Dias et al., 2016). According to these results, errors of ±20% in the CapEx of these sections, which represent 57% to 58% of the total CapEx, can yield an internal rate of return in the range of 19.4% to 23.5%. For comparison, the internal rate of return of scenario ET-0, producing only ethanol and electricity, was 20.0%, thus indicating that this additional option for the sugarcane industry is competitive with ethanol.

The calculated carbon footprint of acetaldehyde produced via the Wacker process, according to the Ecoinvent database, is 1.5437 kgCO$_2$e/kg, whereas the carbon footprint of the acetaldehyde produced from sugarcane ethanol via the process of scenario A6-2 is 0.2247 kgCO$_2$e/kg. This 85% reduction is attributed to the avoided use of fossil fuels in the processing of raw materials into acetaldehyde, which was accomplished by using sugarcane bagasse to produce steam and electricity in the integrated biorefinery. As this is a cradle-to-gate LCA, this analysis does not consider the final use of acetaldehyde. In the case of renewable acetaldehyde, if this molecule were to be used in the synthesis of fuels, the greenhouse gases produced during its combustion would be considered biogenic carbon, thus not contributing to the total emissions of the fuel.

4. Conclusion

This work analyzed the production of acetaldehyde from sugarcane via oxidation of ethanol. A total of twelve scenarios were analyzed, consisting of a combination of different reaction and recovery conditions. Capital

expenditures of each biorefinery scenario were calculated, indicating that the use of higher pressure in the gas absorber had a significant impact on the capital cost of this section of the plant. Considering the integrated biorefinery, the scenario with the best internal rate of return was the one using an O_2 to ethanol molar ratio of 6.1 combined with a gas absorber working at 5.0 bar. This was the combined result of reduced energy spending with power to compress gas and reduced energy spending in the distillation of acetaldehyde, unconverted ethanol, and water to be recycled to the gas absorber. These conditions led to an internal rate of return of 21.2%, greater than the base scenario in which the biorefinery produces ethanol and electricity (20.0%). Life cycle assessment was used to determine the carbon footprint of acetaldehyde produced from sugarcane, which based on the best process conditions was 0.2247 $kgCO_2e/kg$. This value is 85% lower than the emissions related to the production of acetaldehyde via the Wacker process. Overall, these results indicate that the production of acetaldehyde from sugarcane is a techno-economically feasible process, with the potential to replace fossil-derived acetaldehyde produced via the Wacker process.

Acknowledgments

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