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Sustainable Plantwide Optimizing Control for an Acrylic Acid Process

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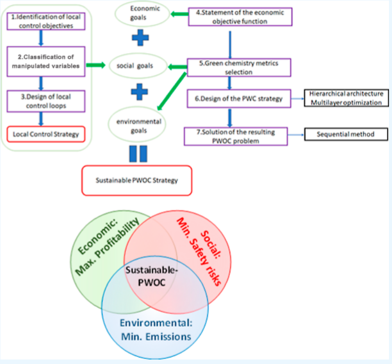
ABSTRACT: This paper presents a sustainable control strategy from a plantwide control (PWC) perspective. The proposed strategy is subjected to testing within an operational environment of an acrylic acid plant. To integrate sustainability tools into the plantwide optimizing control (PWOC) formulation, the present proposal suggests the utilization of green chemistry principles. These principles will be incorporated as constraints within the optimization problem. A comparative analysis is conducted between the proposed sustainable PWOC approach and two alternative structures: a PWOC framework that does not take sustainability issues into account and a conventional PWC structure. The findings indicate that the sustainable PWOC demonstrates superior economic performance from a financial standpoint, reaching the highest cumulative profitability$(1.6274 \times 10^5$ *USD*), exceeding 11.94% in comparison to the PWOC without sustainability concerns, which reach a cumulative profitability of 1.4330×10^5 *USD*, and surpassing 13.01% when compared to the decentralized PWC approach, which reach a cumulative profitability of 1.4158×10^5 *USD*. Additionally, the sustainable PWOC demonstrated a reduced emission impact on the process, with a decrease of 6.17% compared to the unsustainable PWOC and a 9.79% decrease compared to the decentralized approach. This demonstrates that the incorporation of the proposed green chemistry metrics as an explicit component of the formulated PWC problem significantly mitigates the impacts of global warming and human health.



1. INTRODUCTION

Sustainability can be defined as the pursuit of a balanced approach that encompasses economic, social, and environmental objectives while ensuring the preservation of resources for the well-being of future generations.[1,2] Traditionally, the design of control systems has not incorporated the notion of sustainability, leading to favorable control performance at the expense of adverse impacts on the environment and society. Usually, the implementation of process control and optimization techniques has been carried out with the primary goal of enhancing economic objectives and/or achieving precise tracking of set point trajectories. However, within the framework of sustainable process control, it is imperative to incorporate considerations pertaining to environmental and social concerns as well.

Publications pertaining to the sustainable process design encompass the utilization of green chemistry metrics. The production of vinyl chloride monomer (VCM) through the reaction of ethylene and chlorine serves as an illustrative instance wherein green chemistry principles are employed to devise enhanced environmentally friendly process. Azapagic et al.[3] formulated a methodology aimed at effectively incorporating sustainability aspects within the process design framework. Carvalho et al.[4] endeavored to redesign a conventional VCM plant utilizing their SustainPro flowsheet with the aim of enhancing its sustainability, involving a multicriteria GreenPro methodology for the purpose of design. Further applications of the principles of green chemistry in the pursuit of developing more sustainable processes encompass a range of endeavors. These include the advancement of safe and environmentally friendly approaches for synthesizing graphene oxide,[5] the utilization of pyrolysis processes to produce liquid fuel from plastic waste,[6] the exploration of eco-friendly methods for organic synthesis in the medical field,[7] the harnessing of biomass as a renewable feedstock for the acquisition of high-tech bioproducts,[8] the adoption of supercritical fluids and ionic liquids as environmentally benign solvents,[9,10] the green synthesis of nanoparticles utilizing plant extracts,[11] the implementation of innovative technologies in pharmaceutical processing and manufacturing,[12] and the sustainable production of biodiesel using solar energy.[13] Moreover, the application of sustainability principles in process optimization encompasses various domains. Notable instances include studies conducted in the realm of supply chain networks,[14] the development of

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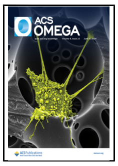

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sustainable alternatives for optimizing batch processes,[15−17] the enhancement of succinic acid production,[18] the manufacturing of solar cells to achieve the highest conversion efficiency,[19] and the improved design of extractive distillation columns through the utilization of multicriteria sustainability analysis.[20] Petrescu et al.[21] measured the best value for global warming potential obtained when biomass was used to generate the steam required by the acrylic acid (AA) process, measuring the global warming potential, human, and environmental potential impacts, from the steady-state point of view.

While advancements have been achieved in integrating sustainability concerns into the process design and, more recently, control system design, it is noteworthy that the aspect of plantwide control (PWC) has not been addressed to the best of the author's knowledge. A comprehensive approach from a plantwide control perspective holds the potential to enhance the operational efficiency of existing and operational plants, not only in economic dimensions but also regarding environmental and social aspects.

On the other hand, the increasing trend of incorporating sustainability factors in the earliest stages of project development aligns with the United Nations Sustainable Development Goals (SDGs).[22] From a plantwide control perspective, the sustainable plantwide optimizing control (PWOC) strategy can contribute to SDG 9 by promoting sustainable development and industrialization through innovation and infrastructure upgrades. This is because sustainable PWOC can optimize production processes by adopting innovative technologies that minimize resource consumption and environmental impact (EI). Additionally, PWOC can help to ensure the sustainable consumption of resources, which is another key aspect of SDG 9.

The implementation of PWOC optimizes production conditions by adopting innovative technologies that minimize resource consumption, as mentioned in SDG 12. This aligns closely with the concept of responsible consumption and production, which advocates for industries and manufacturing facilities to implement measures that reduce their environmental impact and promote sustainable practices in their production processes. These measures include optimizing resource usage, reducing emissions and waste, and adopting cleaner production technologies.

As a result, a plantwide control perspective is adopted to propose a sustainable control strategy, which is then evaluated through in silico testing conducted on an AA production plant. The strategy integrates sustainability considerations into the formulation of PWOC by incorporating principles of green chemistry. These principles are incorporated as constraints within the optimization problem. While the principles of green chemistry have traditionally been employed to enhance safety and minimize process waste, their application has primarily been limited to the process design phase, rather than being utilized to enhance the process control of operational chemical plants. Hence, the incorporation of green chemistry principles into a process with a PWC formulation would establish a robust framework for conducting chemical processes in a profoundly sustainable manner.

Within the framework proposed in this study, safety constraints are articulated in alignment with the conventional principles of green chemistry, serving the purpose of promoting social responsibility. Moreover, innovative green chemistry metrics are introduced to quantitatively assess the environmental implications of process emissions, serving as a means of promoting sustainability from the perspectives of process waste control and optimization.

We propose a novel approach for optimizing control strategies in sustainable manufacturing processes, integrating both environmental considerations and process efficiency. Our method will be compared against conventional control structures such as PID, decentralized control, and deterministic optimization. To model the dynamic behavior of the process, we utilize advanced simulation techniques, incorporating boththe Aspen Dynamics platform for process modeling and the MATLAB optimization toolbox. The integration between the process model and the control algorithms is facilitated through the AM simulation block in Simulink, ensuring a seamless and efficient workflow.

The remainder of this work is structured as follows: A novel green chemistry metric, designed to assess the environmental footprint of emissions, is presented in Section 2. In Section 3, a PWOC is developed and elucidated, followed by its implementation and assessment within an AA plant. In Section 4, the effectiveness of the suggested PWOC method, both with and without the incorporation of sustainable considerations, is compared to the conventional decentralized PWC architecture. Ultimately, in Section 5, comprehensive conclusions are drawn and pertinent recommendations for future research endeavors are delineated.

2. GREEN CHEMISTRY METRIC FOR EVALUATING ENVIRONMENTAL IMPACT FROM A PLANTWIDE PERSPECTIVE

Twelve principles of green chemistry have been proposed to assess the performance of a chemical process.[23] These principles have been implemented worldwide to guide the design of innovative chemical processes and products and aim to reduce the production of waste materials and energy, while advocating for the adoption of eco-friendly and sustainable raw materials. Also, the application of green chemistry principles can improve safety, although these principles are often focus on optimizing material and energy usage the laboratory scale or during process design, phases, rather than implementing changes to enhance the process control of existing chemical plants. This study proposes a set of metrics that can be used to evaluate the sustainability of chemical processes at the PWC level. The goal is to find the best economic conditions for the process while also ensuring that it is safe, environmentally friendly, and sustainable. This can be achieved by measuring the ecological footprint of the production process using indicators, and how well chemical plants adhere to the 11th principle of green chemistry, which is "to use analytical methods to prevent pollution, monitoring chemical processes in real time to identify and control the formation of hazardous substances". Another method to assess the environmental impacts of an entire chemical plant is to assess the quantity of toxic materials that is discharged into the environment. The current mechanism is not sufficient because it does not consider the different levels of harm that different substances can cause, nor the varying degrees to which they can impact the environment. Therefore, the proposal suggests considering the emissions from the process affect the environment across various categories:

i Climate Change
ii Air Pollution
iii Human health (carcinogenic)
iv Depletion of Stratospheric Ozone Layer

(i) Economic objectives:	**(ii) Environmental objectives:**
• Recover, reuse, recycle of material and energy	• Minimization of carbon footprint
• Minimization of raw materials and energy costs	• Minimization of water footprint
• Minimization of capital costs	• Minimization of emissions/waste
• Improvement of process and energy efficiency	• Use of renewable energies
	• Maximization of eco-efficiency
(iii) Social objectives: Assurance of process safety	

Figure 1. Sustainability goals/objectives to be incorporated in PSE.

v Formation of Photochemical Smog

The green metric in this study measures the ecological footprint (EI) of different categories, with regard to the highest allowable exposure limit for pollutants and their various effects on the environment (eq 1)

$$EI = C_i^{*}(PF_{i,j}) \tag{1}$$

The green metric index, the environmental footprint of the plant at each category, is denoted by *EI*, the potency factor of substance *i* for the *j* environmental footprint classification is $PF_{i,j}$, and the level of hazardous substance *i* emitted is represented by C_i, which limits the amount of that substance that can be released into the environment.[24] The PWC problem can be formulated to include constraints on the concentration of emissions, as well as the potency of those emissions. These constraints ensure that the operation of the plant does not exceed safe levels of emissions or cause other environmental damage. This metric ensures that emissions from chemical plants do not exceed safe levels for human exposure or the environment, by tracking the concentration of toxic emissions and comparing it to maximum exposure limits. The metric also considers to evaluate all potential sources of emissions within the plant, so that no harmful substances are overlooked. Emissions from various sources within the plant canhave detrimental effects on the environment , affecting the atmosphere, water sources, and soil . Integrating economic success with a focus on environmental accountability is essential for fostering sustainable practices. One approach to minimizing the environmental impact of a plant is to utilize the Environmental Impact (EI) metric as a constraint during optimization processes.. This ensures that both the states and manipulated variables are bounded within the solution space of the Plant-wide Optimization Control(PWOC) problem,thereby promoting environmentally conscious operational decisions.

To integrate green chemistry principles into a comprehensive control framework tailored for chemical plants, it is important to identify the key principles for the particular scenario and to develop metrics that can be used to measure the risks associated with those principles. In the case study of acrylic acid production, there are two primary safety concerns. The first concern is that the reactor could explode if the oxygen composition is greater than 5% mole. This is because the partial oxidation of propylene can produce a highly flammable gas. Therefore, it is important to carefully monitor the oxygen composition in the reactor and to take steps to prevent it from exceeding 5% mole.[25] The second issue is associated with to the fact that AA polymerization is highly exothermic and can dimerize at temperatures above 110 °C. The lower stages of the azeotropic and rectification columns are required to operate at temperatures below 110 °C because the azeotrope of the mixture boils at this temperature. If the temperature of the bottom stages exceeds 110 °C, the azeotrope will vaporize, and the mixture will not be separated effectively.[26] To address these two concerns, the 12th green chemistry principle, which is accident prevention, is incorporated into the PWC formulation as constraints. These constraints are expressed in eqs 2−4

$$x_{O2,5}(t_0 + \Delta t_{opt}, u_{PW}) < 0.05\left(\frac{\text{kmol}}{\text{kmol}}\right) \tag{2}$$

$$T_{Reb,20}(t_0 + \Delta t_{opt}, u_{PW}) < 110((^{\circ}\text{C}) \tag{3}$$

$$T_{Reb,24}(t_0 + \Delta t_{opt}, u_{PW}) < 110((^{\circ}\text{C}) \tag{4}$$

This study used the environmental footprint metric (1) to assess the environmental impact of acrylic acid production. The EI was evaluated in two categories: global warming and human health. The results showed that toluene emissions had the most detrimental environmental impact in both categories. The environmental footprint metric derived from assessing the concentration of toluene emissions and their potential environmental consequences. The calculation is done according to two equations: eq 5 for climate change and eq 6 for human health

$$EI1 = C_{Tol,14}^{*}(PF_{Tol,GB}) \tag{5}$$

$$EI2 = C_{Tol,14}^{*}(PF_{Tol,HH}) \tag{6}$$

*EI*1 and *EI*2 are the environmental impact on climate change and human health , respectively. $C_{Tol,14}$ is the toluene concentration in stream 14 (the waste stream containing toluene), and $PF_{Tol,GB}$ and $PF_{Tol,HH}$ are the potency factors for toluene in climate change and human health, respectively. These metrics are included as constraints in the PWC formulation, as expressed in eqs 7 and 8

$$EI1(t_0 + \Delta t_{opt}, u_{PW}) < 2101\left(\frac{\text{mg}}{\text{m}^3}\right) \tag{7}$$

$$EI2(t_0 + \Delta t_{opt}, u_{PW}) < 3.247\left(\frac{\text{mg}}{\text{m}^3}\right) \tag{8}$$

Here, t_0, Δt_{opt}, and u_{PW} are the initial time, optimization time horizon, and plantwide variable vector, respectively. The upper limit constraints for toluene concentration are determined by the exposure limit and potency factor for each category.

3. SUSTAINABLE PLANTWIDE OPTIMIZING CONTROL

The point of this section is to propose a framework for addressing the plantwide control problem of existing chemical plants while explicitly regarding sustainability challenges, called

Sustainable Plantwide Optimizing Control(S-PWOC). The proposed methodology was applied to the plantwide control-(PWC) of an acrylic acid process. The main objectives of the methodology were to maximize economic profitability, reduce environmental footprint, and fulfill safety constraints. From a process system and control perspective, the objectives/goals shown in Figure 1 and mentioned in ref 27 are distinguished as being important to propose sustainable practices in process system engineering. In comparison with the PWOC framework that does not consider sustainability issues, the sustainable PWOC approach incorporates green chemistry principles into the formulation of plantwide control strategies with the intent of enhancing the efficacy of the control system. This strategy allows the operation of the plant in a sustainable approach, assuring process safety and reducing EI, while optimizing the economic performance of the process. The PWOC framework without sustainability issues does not take into account social and environmental objectives into the resulting dynamic real-time optimization (DRTO) problem formulation, improving only economic aspects of the process. With the permanent necessity of operating chemical plants in a safer way and addressing the challenges of climate change and environmental degradation caused by human activity requires approaching the control of entire plants (PWOC) from a sustainable perspective.

Noticing the importance of these goals for sustainability in process control, the most significant of them is integrated into the sustainable PWOC framework proposed here. Specifically, a Dynamic Real Time Optimization(DRTO) problem is formulated, which includes economic, controllability, and sustainability aspects. This problem is decomposed in a multilayer PWC structure to assure sustainable objectives with stable controllability of local control variables. Figure 2 depicts the goals/objectives addressed in the sustainable PWOC framework. This approach enables the mitigation of EI and ensures process safety throughout the economic optimization process, making it an efficient means of operating real-world chemical processes. The proposed sustainable control strategy integrates green chemistry principles expressed as restrictions within the PWOC formulation. This integration is established in stage 5 of the proposed sustainable PWOC strategy to evaluate the social and the environmental footprint of the process. This approach allows for the reduction of EI and the assurance of process safety, while optimizing the economic performance of chemical processes. Amidst escalating concerns of climate change and environmental degradation attributable to human, it is no longer sufficient for processes to operate only in an optimal economic and control manner. It is also necessary to reduce their influence on the ecosystem. The predominant impediment to attaining this goal is the concurrent appraisal and optimization of economic, environmental, and social objectives. This is due to the intricate interrelationships between various operating factors and unit processes. In large-scale and intricate systems, like the acrylic acid production process, the multitude of variables involved in the problem makes it challenging to incorporate green chemistry metrics and economic performance. The high nonlinearity of chemical processes and the presence of uncertainties (discrepancies between the plant model and actual operations, as well as fluctuations in raw material and product prices, and disturbances) pose significant challenges to the design and operation of plantwide control systems. A robust and efficient solution approach is imperative to solve the arising dynamic resource trade-off optimization (DRTO) problem.

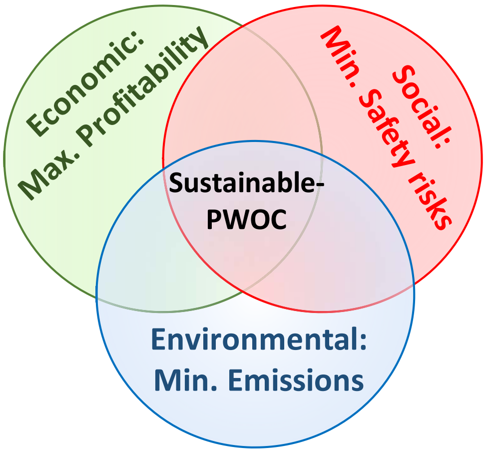

Figure 2. Goals in the sustainable PWOC strategy.

The sustainable PWOC framework is grounded in previous works[28,29] and comprises seven phases, Figure 3. Stages 1−3 are concerned with the determination and development of local control strategies, which are essential for ensuring unit safety assurance (a social responsibility goal). The plantwide control system ensures these conditions using conventional proportional-integral (PI) controllers, incorporating level and pressure regulation strategies. Stage 4 formulates the objective function that is applied to improve the economic performance of the process. Stage 5 assesses the social and environmental footprint of the process and requires the selection of green chemistry metrics to be used as restrictions in the plantwide control (PWC) framework. Stage 6 concerns the architectural design of Plantwide Control(PWC) to fulfill economic, social, and environmental goals while ensuring the controllability of local control variables. Finally, stage 7 establishes the optimization solution methodology utilized for resolving the PWOC issue.

Hereinafter, a concise overview of each stage of the sustainable PWOC strategy is presented, with specific application to the AA process case study. A process schematic to produce acrylic acid is presented in Figure 4, illustrating the local control loops.

3.1. Stage 1: Specification of Essential Local Control Goals.

The primary objectives of these control systems are to ensure the reliable functioning of process units (social responsibility), product integrity, and manufacturing efficiency. Based on process understanding, the subsequent variables are identified as essential local control loops:

- Liquid amounts for flash distillation column, absorber column, azeotropic distillation column, and rectification column.
- Quantities of organic and aqueous phases in a decanter.
- The liquid level in the reflux drum of a rectification column.
- Pressure regulation for reactors, flash vessels, azeotropic columns, and rectification columns.
- Pressure regulation for decanter.

3.2. Stage 2: Categorization of Control Variables.

Control variables can be categorized into local and plantwide. Local manipulated variables are linked to local control loops, whereas plantwide manipulated variables are decision variables for optimization problem. Initially, local manipulated variables (u_{loc}) are chosen based on e process knowledge and their relevance to local control objectives. Plantwide manipulated

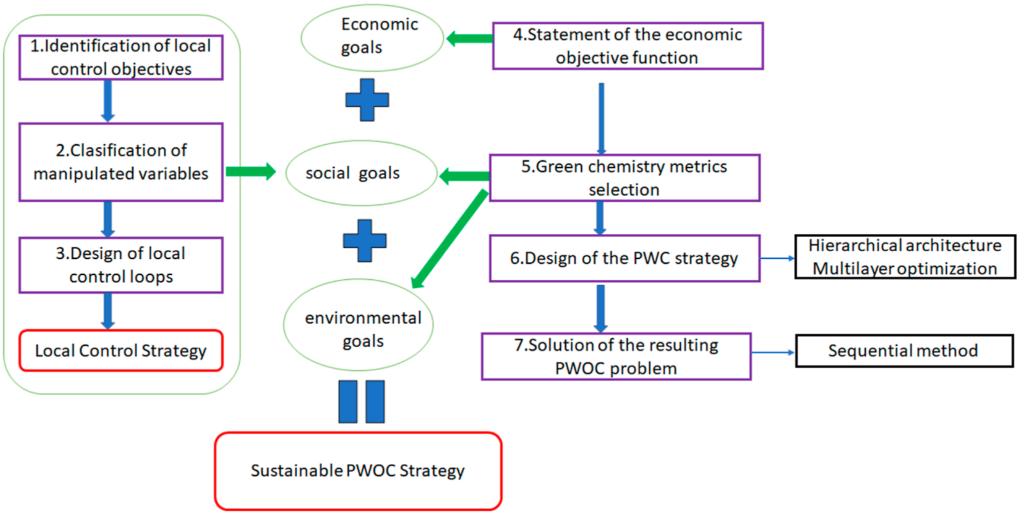

Figure 3. Stages for the sustainable PWOC strategy.

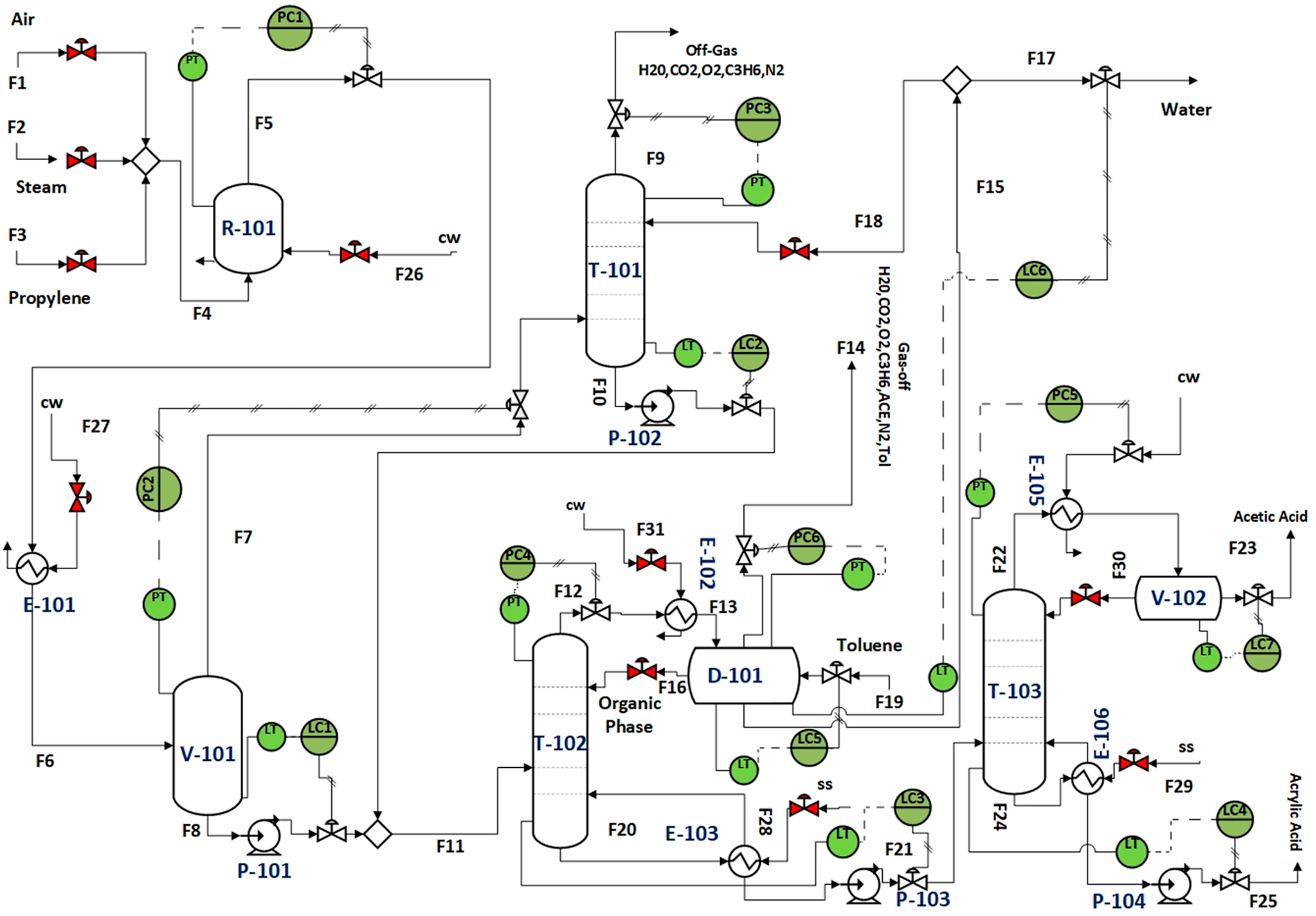

Figure 4. Acrylic acid production plant + local control loops (in green). The final control elements in red correspond to the plantwide manipulated variables.

variables are then selected from the manipulated variables not accounted for local control strategy

The subsequent variables were chosen as control variables to attain local control goals:

- The mass flow rate of liquid at the flash output is used to control the liquid level in the flash tank.
- The mass flow rate of liquid at the absorber outlet is utilized to regulate the liquid level in the absorber column.
- The flowrate of liquid at the outlet of the column for azeotropic distillation is employed to regulate the liquid level in the bottom stage of the column.

- The mass flow rate of liquid at the output of the rectification column is employed to control the liquid level in the bottom stage column.
- The mass flow rate of toluene is used to control the toluene level in the decanter.
- The mass discharge rate of purged water is used to regulate the water level in the decanter.
- The flow rate of the distillate is utilized to regulate the level of the reflux drum in the rectification column.
- The molar flow rate of vapor at the reactor outlet is used to control pressure.
- The molar flow rate of vapor at the flash output can be used to control pressure.
- The molar flow rate of vapor at the absorber output is used to control pressure.
- The molar flow rate of vapor at the top output of the azeotropic column is used to control the pressure in the azeotropic column.
- The mass flow rate of utility fluid is used in the E-105 heat exchanger to control the pressure in the rectification column.
- The molar flow rate of vapor at the decanter outlet is used to control pressure.

The acrylic acid plant has 22 variables that can be manipulated, of which only eleven are used to control the plant locally. The remaining 11 plantwide manipulated variables are employed as decision variables in the dynamic real-time optimization(DRTO) problem that emerges from implementing the sustainable PWOC framework. The following variables were identified as plantwide control variables (indicated in red in Figure 4):

- The flow rates of steam, propylene, and air at the reactor feed stream.
- Flowrate of utility fluid passing through a reactor.
- Utility fluid flow rate in the reboiler of the azeotropic column.
- Utilityfluid flow rate in heat exchanger E-102.
- Utility fluid flow rate in the heat exchanger E-101.
- Flow rate of recycled aqueous phase to the absorber column.
- Flow rate of recycled organic phase to the azeotropic column.
- Reflux flow rate in the rectification column.
- Utility fluid flow rate in the rectification columns reboiler

3.3. Stage 3: Structuring of Local Control Loops. At this stage, the configuration of PI controllers is accomplished to fulfill the local control goals. The tuning of PI controllers can be performed using any of the traditional tuning methods. In this case, the Tyreus−Luyben correlations were employed.

3.4. Stage 4: Formulation of the Economic Objective Function. During this stage, the development of a plantwide profitability function is undertaken, aiming to maximize the overall economic profitability . The formulation of this function hinges upon factors such as product prices of desired products, the cost of raw material costs energy losses, and other pertinent variables. It serves to quantifythe economic efficacy of the plantwide optimization control (PWOC) approach across a prediction horizon. The objective function is crafted as follows

$$\begin{aligned}\varphi = {} & w_1 \int_{t_0}^{t_0+\Delta t_{opt}} F_{AA25}dt + w_2 \int_{t_0}^{t_0+\Delta t_{opt}} F_{ACE23}dt - w_3 \int_{t_0}^{t_0+\Delta t_{opt}} F_1 dt \\ & - w_4 \int_{t_0}^{t_0+\Delta t_{opt}} F_2 dt - w_5 \int_{t_0}^{t_0+\Delta t_{opt}} F_3 dt - w_6 \int_{t_0}^{t_0+\Delta t_{opt}} F_{19}dt \\ & - w_7 \int_{t_0}^{t_0+\Delta t_{opt}} F_{26}dt - w_8 \int_{t_0}^{t_0+\Delta t_{opt}} F_{27}dt - w_9 \int_{t_0}^{t_0+\Delta t_{opt}} F_{28}dt \\ & - w_{10} \int_{t_0}^{t_0+\Delta t_{opt}} F_{29}dt - w_{11} \int_{t_0}^{t_0+\Delta t_{opt}} F_{31}dt \end{aligned} \tag{9}$$

In eq 9, economic factors are represented by w_i, as shown in Table 1 (values shown in Table 1 were obtained from ref 30).

Table 1. Weights Assigned to Economic Factors in Decision Making

factor	description	value (USD/kmol)
w_1	selling price of acrylic acid	173
w_2	selling price of acetic acid	89.94
w_3	cost of air	0.1325
w_4	cost of propylene	55.59
w_5	cost of steam	0.336
w_6	cost of toluene makeup	66.258
w_7	cost of cooling water	2.654×10^{-5}
w_8	cooling water cost	2.654×10^{-5}
w_9	cost of vapor consumption	0.02065
w_{10}	price of vapor consumption	0.02065
w_{11}	cost of cooling water	2.654×10^{-5}

The first term in the equation correlates with the yield of the primary product (acrylic acid), while the second term denotes the generation of the second most important product (acetic acid). The subsequent three factors, each with a distinct weighting, weighted by w_3, w_4, and w_5, collectively contribute to raw material expenses(propylene, steam, and compressed air). The coefficient w_6, which is a weighting term, is used to penalize the amount of toluene makeup in decanter D-101. Ultimately, the factors weighted by w_7, w_8, w_9, w_{10}, and w_{11}, respectively, restrict energy consumption stemming from the utilization of utility fluids in reactor and heat exchangers E-101, E-103, E-106, E-105, E-102. The economic optimization is conducted over a time horizon that begins at time t_0 and extends for a duration of Δt_{opt}.

3.5. Stage 5: Assessment of Green Chemistry Principles. Incorporating of green chemistry metrics into the PWOC approach represents an innovative strategy designed to mitigate operational risks during economic optimization while simultaneously reducing process emissions. Achieving a harmonious balance between economic prosperity, safety assurance, and environmental stewardship in the process is accomplished by imposing limitations on the states and manipulated plantwide variables. The green chemistry metrics outlined in eqs 2−4, 7, and 8 are incorporated as constraints into the PWOC formulation for the acrylic acid process. The first three constraints expressed in eqs 2−4 are related with the 12th green chemistry principle (accident prevention), a social responsibility goal in the sustainable PWOC strategy. The green chemistry constraint (expressed as eq 2) prevents reactor

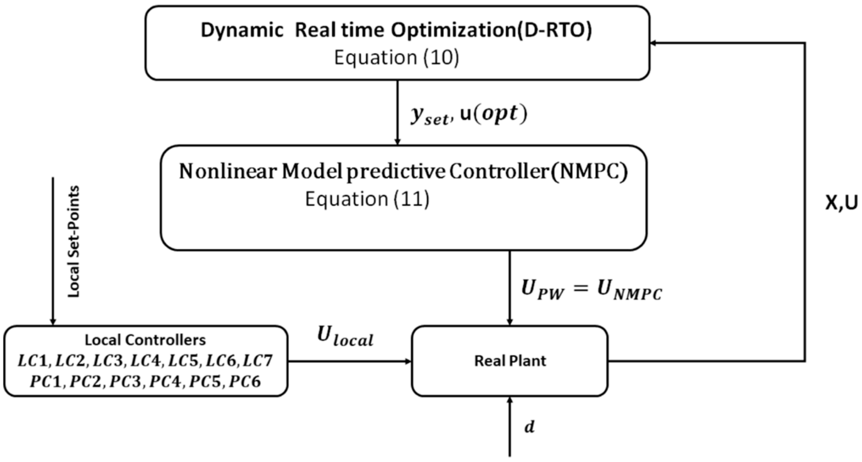

Figure 5. PWOC two-layer structure.

explosion assuring that oxygen composition is lower than 5% during the process. Green chemistry constraints (expressed as eqs 3 and 4) prevent polymerization of AA in the bottom stages of azeotropic and rectification columns. Constraints expressed in eqs 7 and 8 are related with the 11th green chemistry principle (pollution prevention), an environmental responsibility goal in the sustainable PWOC strategy. The green chemistry constraints (expressed as eqs 7 and 8) evaluate the environmental footprint of acrylic acid production in the realms of climate change and human health . The results showed that toluene emissions had the greatest adverse effect on the environment in both categories; therefore, this impact was calculated based on the concentration toluene emissions and its potency factor for both categories.

3.6. Stage 6: Design of the PWC Architecture.

The development of an appropriate PWC framework is essential for the accomplishment of the key goals outlined in the PWOC formulation. Based on the structural configuration, PWC architectures can be categorized into four primary groups:[31] distributed, decentralized, single layer, and multilayer. The two-layer PWC configuration was employed to implement the sustainable PWOC approach, based on the proved stability of this structure to reject disturbances, fulfilling process, and trajectory restrictions by the nature of the (NMPC) .[32,33] Figure 5 illustrates the two-layer optimization-based control structure employed to attain economic, control, environmental, and social goals from the perspective of a sustainable process water optimization and control (PWOC) system.

The comprehensive mathematical representation of the optimization problem outlined in the DRTO layer is provided by eq 10

$$\begin{aligned}
&\min_{u_{PW}=[F_1,F_2,F_3,F_{26},F_{27},F_{18},F_{16},F_{28},F_{30},F_{29},F_{31}]} (-\varphi(\dot{x},\, u,\, t_0,\, \Delta t,\,))\\
&s.\ to.\ f(\dot{x},\, x,\, u,\, d,\, t) = 0\\
&x(t_0) = x_0\\
&u_{\min} \le u_{PW} \le u_{\max}\\
&F_{25}(t_0 + \Delta t_{opt},\, u_{PW}) \ge 70.96[\text{kmol/h}]\\
&x_{AA,25}(t_0 + \Delta t_{opt},\, u_{PW}) \ge 0.995[\text{kmol/kmol}]\\
&x_{O2,5}(t_0 + \Delta t_{opt},\, u_{PW}) < 0.05[\text{kmol/kmol}]\\
&T_{Reb,20}(t_0 + \Delta t_{opt},\, u_{PW}) < 110[^\circ\text{C}]\\
&T_{Reb,24}(t_0 + \Delta t_{opt},\, u_{PW}) < 110[^\circ\text{C}]\\
&EI1(t_0 + \Delta t_{opt},\, u_{PW}) < 2101[\text{mg/m}^3]\\
&EI2(t_0 + \Delta t_{opt},\, u_{PW}) < 3.247[\text{mg/m}^3]
\end{aligned} \tag{10}$$

As can be seen in eq 9, φ is the mathematical expression that defines the economic objective function. The initial constraint depicted by eq 10 embodies the nonlinear dynamic model. The second constraint specifies the initial values of the state variables. The third restrictive condition limits the scope of the search for the optimal solution (i.e., to identify the plantwide control variables). The span's range is established to be from 0 % to 50% beyond the nominal values of the plantwide manipulated variables. The fourth constraint is a projected minimum production goal of AA, with a plant productivity of 51,094 t/year of the AA product. The operation time is defined as 8000 h/year. The fifth restriction guarantees that the quality constraint, the molar fraction of AA, will be equal to or greater than the specified nominal value. The sixth constraint mitigates the potential hazard of reactor detonation. The seventh and eighth constraints mitigate the occurrence of accidents resulting from the polymerization of AA in secondary byproducts. Lastly, the ninth and tenth constraints curtail the plant's impact on climate change and human health by restricting its hazardous emissions, as presented in HSE Books.[24]

The mathematical formulation of the optimal control problem addressed within the NMPC layer is in eq 11

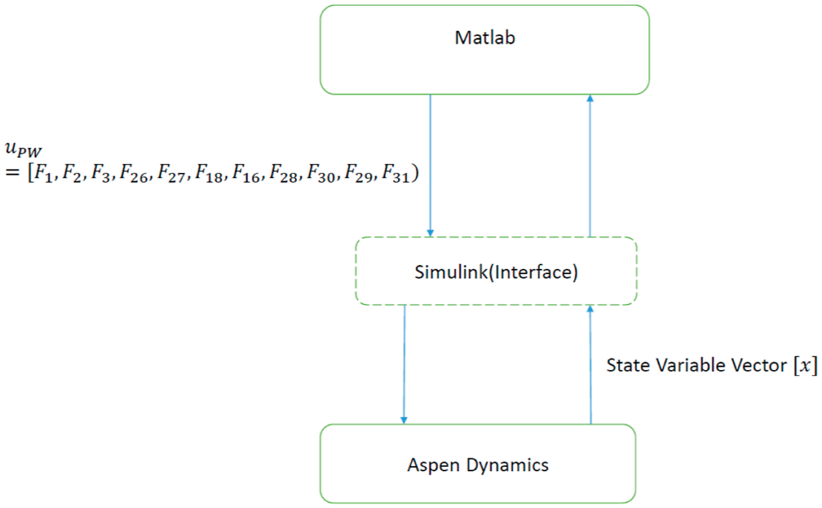

Figure 6. PWOC implementation coupling MATLAB and Aspen Dynamics.

$$\begin{aligned}
&\min_{U_{PW}=[F_1,F_2,F_3,F_{26},F_{27},F_{18},F_{16},F_{28},F_{30},F_{29},F_{31})} (-\Gamma(\dot{x},\ u,\ t_{0mpc},\ \Delta t_{mpc},\ ))\\
&s.\ to.\ f(\dot{x},\ x,\ u,\ d,\ t) = 0\\
&\qquad x(t_{0mpc}) = x_0\\
&\qquad u(t_{0mpc}) = u_{opt}\\
&u_{\min} \leq U_{PW} \leq u_{\max}
\end{aligned} \tag{11}$$

In this hierarchical control system, the DRTO layer provides optimal settings for the manipulated variables, which are then used as set points by the NMPC layer Λ.

$$\Gamma = \int_{t_{0mpc}}^{t_{0mpc}+\Delta t_{mpc}} Q(y - y_{set})^2 + R(u_{PW} - u_{opt})^2 + P(\Delta u_{PW})^2 \tag{12}$$

Three distinct terms converge to form this tracking objective function: the main output variables are penalized for deviating from their set points (y_{set}), the DRTO layer imposes a constraint on the variation of manipulated variables relative to the target trajectories (u_{opt}), the controller also includes a term that constrains large changes in the manipulated variables between successive sample times, thereby preventing oscillatory behavior. The starting time and horizon duration within the NMPC controller are denoted by t_{0mpc} and Δt_{mpc}, respectively. The objective function for trajectory tracking consists of three distinct terms, each weighted by a unique tuning parameter ($P = 0.01$, $Q = 1$, $R = 0.05$). The state variable for tracking the optimal trajectory of the reactor is chosen to be the temperature ($y = [T_R]$). The variable in question has a significant impact on AA production, and this in turn has a major influence on the financial viability of the process.

The constraints presented in eq 11 possess identical significance to those stated in eq 10, except for the third constraint. The third constraint specifically sets the starting state of the decision variables within the NMPC layer to be equivalent to the decision variables provided by the optimization layer. A precise and rigorous dynamic nonlinear model of the process accurately represents the actual plant. This study encompassed the execution of simulation studies, wherein a process that exhibits complete observability was taken into consideration.

3.7. Stage 7: Solution of the Sustainable PWOC Problem. The final step of the sustainable PWOC methodology involves devising a strategy to solve the optimization problem arising from the proposed multilayer architecture as illustrated in Figure 5. The solution to the DRTO problem presented in eq 10 comprises of the optimal values for the control vector u_{PW}, which aim to maximize the objective function φ. The DRTO problem is solved using the sequential approach, specifically employing control vector parametrization. In this method, the manipulated variables are approximated by discretizing them into piecewise constant values

$$u_k(t) = \sum_{i=1}^{z} a_{ik}\psi(t_{i-1},\ t_i),\ \text{for } k = 1,\ \ldots.\ .\ n \tag{13}$$

In this context, z denotes the number of intervals used to discretize the time vector, and each a_{ik} represents the j-th parameter of the polynomial corresponding to with the k-th control variable (u_{ik}) within the i-th time interval. The pulse function ψ is obtained as the variance between successive unit step functions u_k

$$\psi(t_{i-1},\ t_i) = u_k(t_{i-1}) - u_k(t) = \begin{Bmatrix} 0,\ t < t_{i-1}\\ 1,\ t_{i-1} \leq t < t_i\\ 0,\ t > t_i \end{Bmatrix} \tag{14}$$

The variables involved in formulating the consequent nonlinear programming (NLP) problem are represented by the parameter a_{ik} in eq 13 and are derived through the process of numerically integrating the differential algebraic equation (DAE) system forward in time, considering the manipulated variables. The sequential approach is chosen over simultaneous or multiple shooting methods because the sequential formulation is comparatively simpler to develop and implement. This approach solely necessitates the discretization of control inputs while guaranteeing a viable trajectory wherein the DAE system is fulfilled at every stage of the optimization problem.

To address the sequential formulation of the DRTO problem in eq 10, a metaheuristic algorithm, specifically simulated annealing, is employed for its solution. This algorithm obviates the necessity for derivative information, a requisite in gradient-

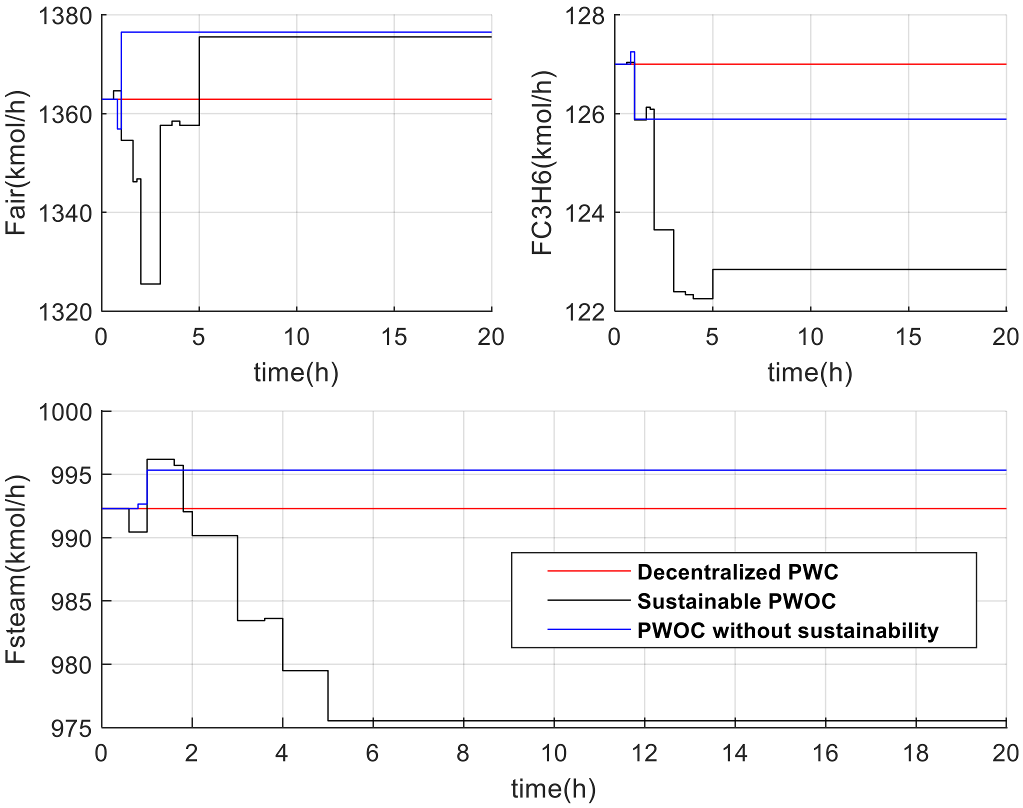

Figure 7. Comparison of the different PWC structures. Air flow rate (top left), propylene flow rate (top right), and steam flow rate (bottom).

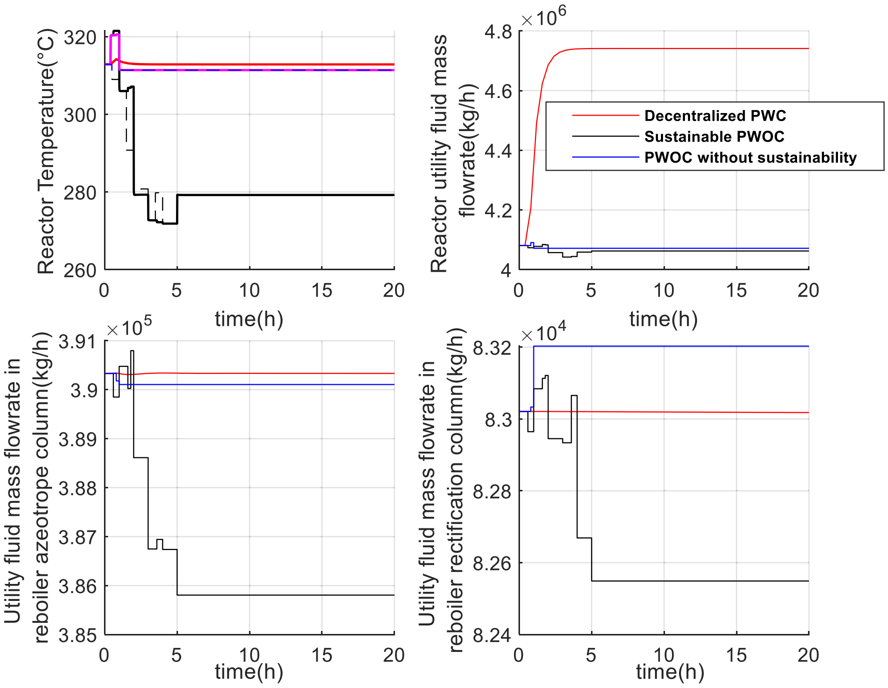

Figure 8. Comparison of the different PWC structures. Reactor temperature (top left), reactor utility fluid flow rate (top right), utility fluid flow rate in the reboiler azeotrope column (bottom left), and utility fluid flow rate in the reboiler rectification column (bottom right).

based methods, resulting in a notable reduction in computational burden.[34] Due to its inherent randomness, it facilitates the exploration of a broader range of manipulated variables, rendering it suitable for addressing large-scale optimization problems with nonlinear dynamics and multiple local optima. An analogous procedure is employed to solve the resulting DyOP problem within the NMPC layer (eq 11). An optimization algorithm was implemented in MATLAB to solve the resulting DRTO problems derived from eqs 10 and 11. The process model employed for evaluating theperformance of the actual plant, optimization, and NMPC layers was developed using Aspen Dynamics. Establishing connectivity

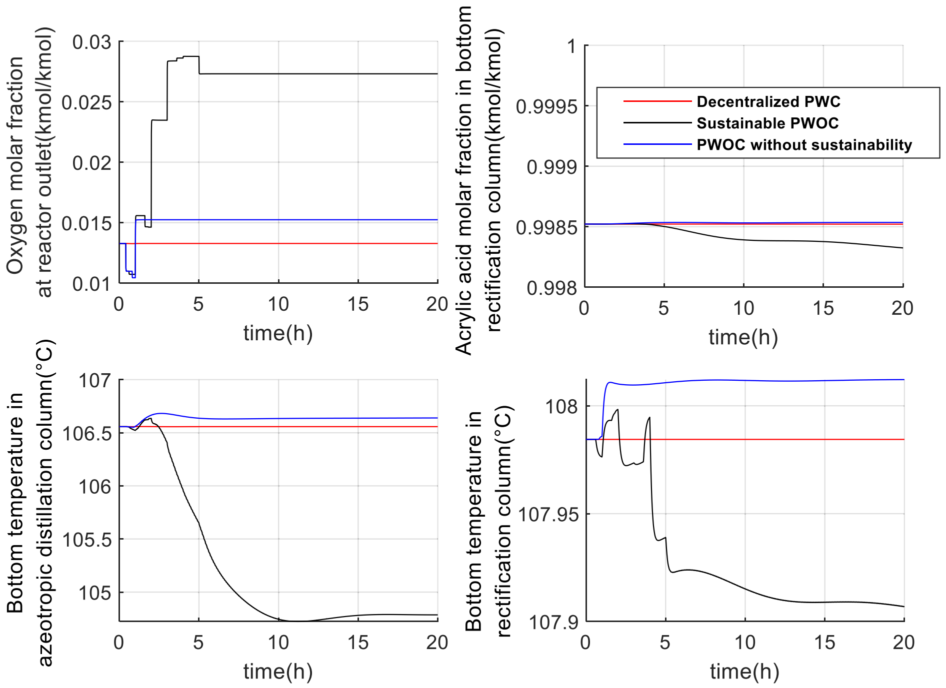

Figure 9. Comparison of the different PWC structures. Oxygen molar fraction at the reactor outlet (top left), AA molar fraction in the bottom rectification column (top right), bottom temperature in the azeotrope column (bottom left), and bottom temperature in the rectification column (bottom right).

between MATLAB and Aspen Dynamics was facilitated by utilizing the AM simulation block within Simulink, as illustrated in Figure 6. Decision variables obtained through MATLAB for the optimization and NMPC layers are transmitted to the Aspen model, where simulations are conducted. Following this, model outputs are sent back to the optimization routine within MATLAB, ensuring the optimization process continues until the specified stopping condition is satisfied. The model utilized in the optimization layer has a prediction horizon of 25 h and is invoked in the event of either a recognized (process) or an unrecognized (uncertainty) disturbance. Additionally, this layer is periodically invoked either every 0.5 h or in the event of a decline in the economic profitability. The NMPC layer employs a prediction horizon of 2 h and is periodically activated every 0.2 h or initiated by a decline in the function utilized to monitor and evaluate system's ability to track desired setpoints or trajectories.

4. RESULTS AND DISCUSSION

In this section,we discuss the results of the proposed sustainable PWOC strategy and compare them with the PWOC framework lacking sustainability and with the typical decentralized PWC control scheme. A sudden increase in air temperature (+10 °C) occurs in the process at time 0.4 h (measured disturbance). Results are compared across three control structures: the traditional decentralized PWC controlscheme, the multilayer PWOC strategy incorporating sustainability, and the multilayer PWOC structure without sustainability considerations. Figure 7 illustrates providing molar profiles for air, propylene, and steam input into the reactor. We note an escalation in the molar flow rate of air accompanied by a decrease in the molar flow rate of propylene until optimal ratios are attained in the sustainable PWOC structure ,thus enhancing acrylic acidproduction. Additionally, reduced steam molar flow rate is attained for the sustainable PWOC , leading to improved economic profit through reduced raw materials costs.

Figure 8depicts profiles for the mass flowrate of the utility fluid utilized for cooling the reactor, as well as the reactor temperature. The decentralized PWC structure necessitates a higher mass flowrate of utility fluid, resulting in increased energy costs and decreased economic profit. Conversely, both other control structures achieve a reduction in reactor utility fluid usage by implementing supplementary tactics , such as reducing the molar flow rates of propylene and steam to cool down the reactor and mitigate the disturbance's effects The dynamic behaviour of the reactor temperature for the analyzed control structures is also illustrated in Figure 8. The decentralized PWC structure, demonstrates good control performance, as its primary goal is to sustain the reactor temperature at a predetermined set point. Bothmultilayer PWOC structures, exhibit a well-tracked temperature trajectory, with notable cooling of the reactor temperature in both cases.This cooling favours the selectivity of the main reaction and , consequently, enhances the profitability.. Significant reductions in utility fluid usage in the reboiler of the azeotropic and rectification columns are observed for the sustainable PWOC structure. This reduction implies energy cost savings and an improvement in economic profitability when green chemistry metrics are incorporated.

Figure 9 presents profiles for the molar oxygen composition in the reactor, acrylic acid molar composition in the bottom's rectification column, and bottom temperatures in the azeotropic and rectification columns. Safe operation of the reactor is ensured for all the analyzed control structures , as the oxygen molar composition remains below 5%, thus mitigating the risk of reactor explosion. Lower temperatures are achieved by the sustainable PWOC structure through a reduction of steam supply in the reboiler. Bottoms temperature constraints in the azeotropic and rectification columns are met for all analyzed structures throughoutthe entire time horizon, preventing acrylic acid polymerization. Product (specifications, specifically the-

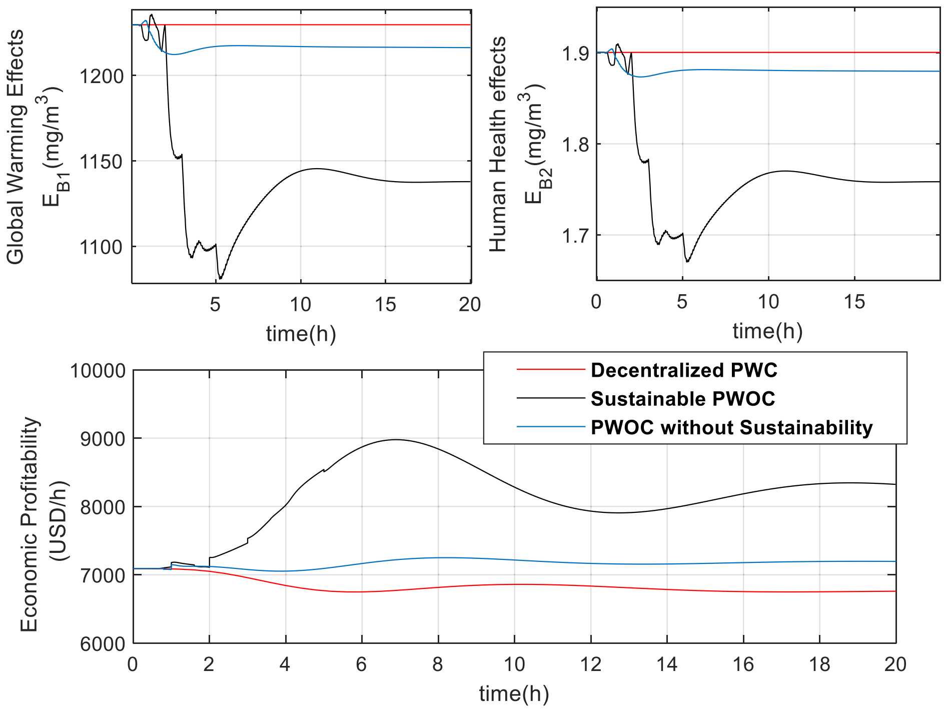

Figure 10. Comparison of the different PWC structures. Economic objective function (bottom), global warming effects (top left), and human health effects (top right).

molar composition of acrylic acid higher than 0.995 mol/mol) , are maintained throughout the complete time horizon for all three analyzed control structures.

Figure 10 displays the economic profitability of the plant alongside profiles of proposed green chemistry metrics for evaluating of the ecological consequences of hazardous emissions. The emission impact of the sustainable PWOC contrasted with that of the non-sustainable PWOC and the decentralized PWC approach using the EI metric outlined in Section 2. This green metric index serves as a tool for assessing the environmental impact of toxic emissions, primarily Toluene vapours, which affect categories such as climate change and human health.

The sustainable PWOC shows better results from an economic perspective in comparison with the conventional decentralized PWC structure. This behavior can be seen in Figure 10 and Table 2. The sustainable PWOC structure reduces energy and raw materials cost as a strategy to propel the process towards maximizing economic efficiency, while the conventional decentralized plantwide control structure does not consider process interactions variables and its primary objective is to maintain the controlled variables at their predetermined targets.

Table 2. Cumulative Profitability Comparison

tested architecture	cumulative profitability (USD)
sustainable PWOC	1.6274×10^5
PWOC without sustainability issues	1.4330×10^5
decentralized PWC	1.4158×10^5

The sustainable PWOC demonstrates a lower emission impact on the process, resulting in significantly reduced effects on climate change and human health when the proposed green chemistry metrics (as presented in eqs 5 and 6) are incorporated into the DRTO layer formulation. Conversely, the traditional decentralized PWC strategy yields higher climate change and human health effects, as its primary objetcive is mantain setting controller variables designated points, without accounting for the environmental implicationsof emissions. Furthermore,the sustainable PWOC structure achieves the optimal economic efficiency among all analyzed control structures .This approach allows for operationunder secure conditions to mitigate accidents and minimize the environmental repercussions Consequently, it emerged as the favored approach for operating the process.

The results showed that toluene emissions had the greatest detrimental effects on the environment encompass climate change and human health effects. Figure 11 shows the toluene makeup in the decanter, which is closely related with toluene emissions in the plant. The incorporation of green chemistry

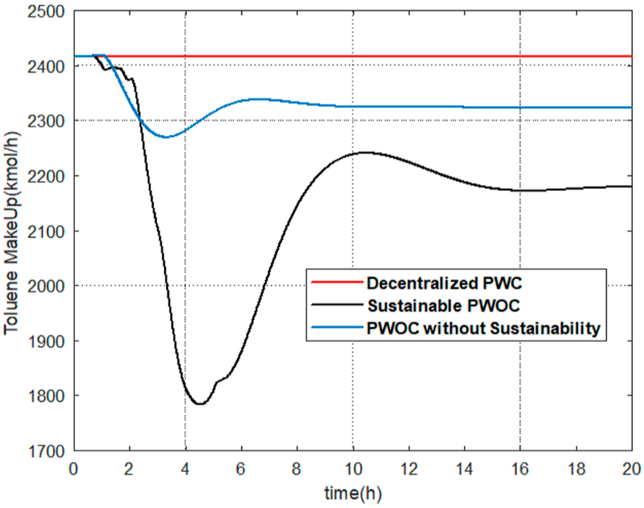

Figure 11. Toluene molar flow rate makeup in the decanter.

metrics as restrictions into the sustainable PWOC strategy reduces toxic toluene emissions, with the consequently reduction in the environmental footprint metric showed in Figure 10, evaluated in climate change and human health categories.

Finally, Table 2 showcases the cumulative profitability of the plant for the three control architectures analyzed. It is evident that the sustainable PWOC structure exhibits the highest economic performance (1.6274 x105 USD), making it the most economically advantageous scheme.. The PWOC structure without sustainability considerations follows closely behind,with a economic performance value of (1.4330 x105 USD), securing the second-best performance in terms of economic viability.The poorest profitabilityis observed by the decentralized PWC structure with a cumulative profitability value of 1.4158×10^5 USD. The sustainable PWOC structure demonstrates superior economic performance from a financial standpoint, in terms of achieving the highest cumulative profitability in comparison with PWOC without sustainability issues and the decentralized PWC structure. The integration of green chemistry metrics demonstrates a trend toward reducing energy and raw material costs . This trend steers the pathway to achievingthe best economic outcomes while simultaneously meeting safety and environmentalcriteria.

Increase in computing time for the sustainable PWOC approach was a disadvantage for this proposed structure compared with the PWOC without sustainability concerns and the decentralized PWC approach. This is due to the high nonlinearity of AA processes, by the intricate interrelationships between various operating variables and unit operations, which makes it difficult to find an optimal solution that satisfies economic, social, and environmental requirements. A challenge for future work is the inclusion of uncertainties (discrepancies in themodel variability inraw material, and product prices) in the sustainable PWOC approach, in order to obtain a more robust solution.

5. CONCLUSIONS

In this research, we introduced, a Sustainable Plantwide Optimization and Control (Sustainable-PWOC) methodology founded on the concept of green chemistry principles, to ensure environmental compliance and safety in process operations. A new metric for assessing the ecological footprintof the process was proposed. The Sustainable PWOC framework involves seven main steps:: identification of essential local control loops, categorization and choosing manipulated variables at both plantwide and local manipulated levels,implementation of PID control loops, formulation of the economic performance index as the primary control system, objective, integration of green chemistry metrics, development of PWC architecture, design of a resolution approach to address the ensuing PWOC challenge.

This PWOC approach was implemented to an acrylic acid production plant, comparing its effectiveness with and without the integrating green chemistry metrics. The sustainable PWOC yielded superior results from both economic and environmental perspectives .Conversely, the conventional decentralized PWC structure exhibited the lowest economic viability and the most significant environmental footprint in terms of plant emissions. These findings underscore the effectiveness of incorporating green chemistry metrics into the PWOC framework, as a sustainable approach This strategy enhances economic profitability ,ensuring the processoperates safely,, and mitigates the consequences of hazardous emissions within the plant.

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Notes

The authors declare no competing financial interest.

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