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Plantwide Control of a Green Formic Acid Production Process

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ABSTRACT

This study presents the design and evaluation of a plantwide control (PWC) system for Formic acid (FA) production under unsteady green Hydrogen supply. Starting from a steady-state foundation in Aspen Plus V12, the system was prepared to handle variable inputs and was subsequently transitioned into Aspen Dynamics for real-time responsiveness. The two-level design methodology to build a PWC scheme, which is comprised of equipment-specific and plantwide controllers, effectively managed fluctuations in feed rates ranging up to ±20%, maintaining FA purity and production rate targets. Gradual SRAMP (sinusoidal ramp) adjustments of 1% per hour provided optimal stability. These results confirm the PWC system's effectiveness in maintaining production goals under the variability of throughput.

Keywords: Plantwide Control, Dynamic Simulation

INTRODUCTION

The drive for sustainability is compelling the chemical industry to transition from conventional, non-renewable resources to renewable, green feedstocks. Formic acid (FA), which can be synthesized from green Hydrogen and captured carbon dioxide (CO_2), presents a promising approach for mitigating greenhouse gas emissions while also yielding a versatile chemical with widespread industrial applications. Nevertheless, the shift to renewable sources introduces new challenges—most notably, the variability in feed availability inherent to renewable sources. In response, maintaining stable production and product quality under these fluctuations has underscored the need for advanced control systems, with plantwide control (PWC) emerging as essential for operational reliability.

This work seeks to design an effective PWC system for a highly intensified FA production plant, targeting a stable production rate of FA with a purity of 85% by weight. The complete plant design can be seen in the previous work [1]. The main challenges for the PWC design include the COPure™ absorption system, the divided wall column and the 16 recycle streams within the plant.

To address these challenges, the approach taken first involved reinforcing the steady-state flowsheet's robustness within Aspen Plus V12. This required a comprehensive evaluation of sensitivity across process parameters and equipment to ensure flexibility in adapting to variations in feed flow rates.

With this foundation established, the focus shifted to transitioning the model into Aspen Dynamics for dynamic simulations. This conversion required incorporating additional equipment and pressure control elements to facilitate a pressure-driven simulation that reflects real operational conditions.

Following successful initialization in dynamic mode, a two-level design methodology for PWC system was developed. The first control layer focuses on equipment-specific control strategies but was found insufficient for handling significant variations in feed rates. Consequently, a second plantwide control layer was designed to manage throughput fluctuations and sustain product specifications across varying production capacities.

The final PWC configuration demonstrates that despite the complexities introduced by the DWC and multiple recycle loops, the designed control system maintains FA purity and production rates, even under ±20% throughput disturbances, confirming that PWC can play a critical role in stabilizing renewable-driven processes with inherent variability in feedstock supply.

PROCESS SIMULATION

Process Description

The production process of formic acid (FA) is divided into two main sections [1]: the synthesis of carbon monoxide (CO) and its subsequent conversion to FA. The CO_2 feed is sourced from the CCUS network at 25 °C and 35 bar, while green hydrogen, supplied at 25 °C and 30 bar, is obtained from an electrolyzer (Figure 1).

In the first section, the reverse water-gas shift (RWGS) reaction converts CO_2 and H_2 into CO within a tubular reactor. The process operates at 1.2–1.4 bar, with temperatures ranging from 573–600 °C and a H_2:CO_2 molar ratio of 2.5. Following water removal, the reactor outlet undergoes chemical absorption (COPure™ technology) to isolate CO from unreacted feedstock and impurities. This involves selective chemisorption using a $CuAlCl_4$ complex dissolved in toluene, achieving a CO purity of 99% and a recovery rate of 98%. The CO-$CuAlCl_4$ complex is then dissociated in a stripper for further use.

In the second section, methanol is carbonylated with CO in a continuous stirred-tank reactor (CSTR) at a methanol-to-CO ratio of 5, under conditions of 40 bar and 80 °C. This process yields methyl formate (MF) with high selectivity, achieving moderate per-pass conversions of methanol (14.8%) and CO (74%). Excess methanol is separated and recycled via distillation. The hydrolysis of MF to FA occurs in two stages within packed flow reactors (PFRs). The first reactor operates at 18 bar and 120 °C, with MF reacting with water to produce FA and water, achieving a 10% conversion. The resulting FA acts as a catalyst for further hydrolysis in the second reactor, achieving a 30.5% per-pass conversion with 100% selectivity. The reactor outputs are distilled using a dividing wall column (DWC) to separate FA and water from unreacted methanol and MF, which are recycled. The FA-water mixture is then distilled at 3 bar to overcome the azeotrope, achieving the desired FA purity.

Process Simulation

From the explained process, the aim of the work was

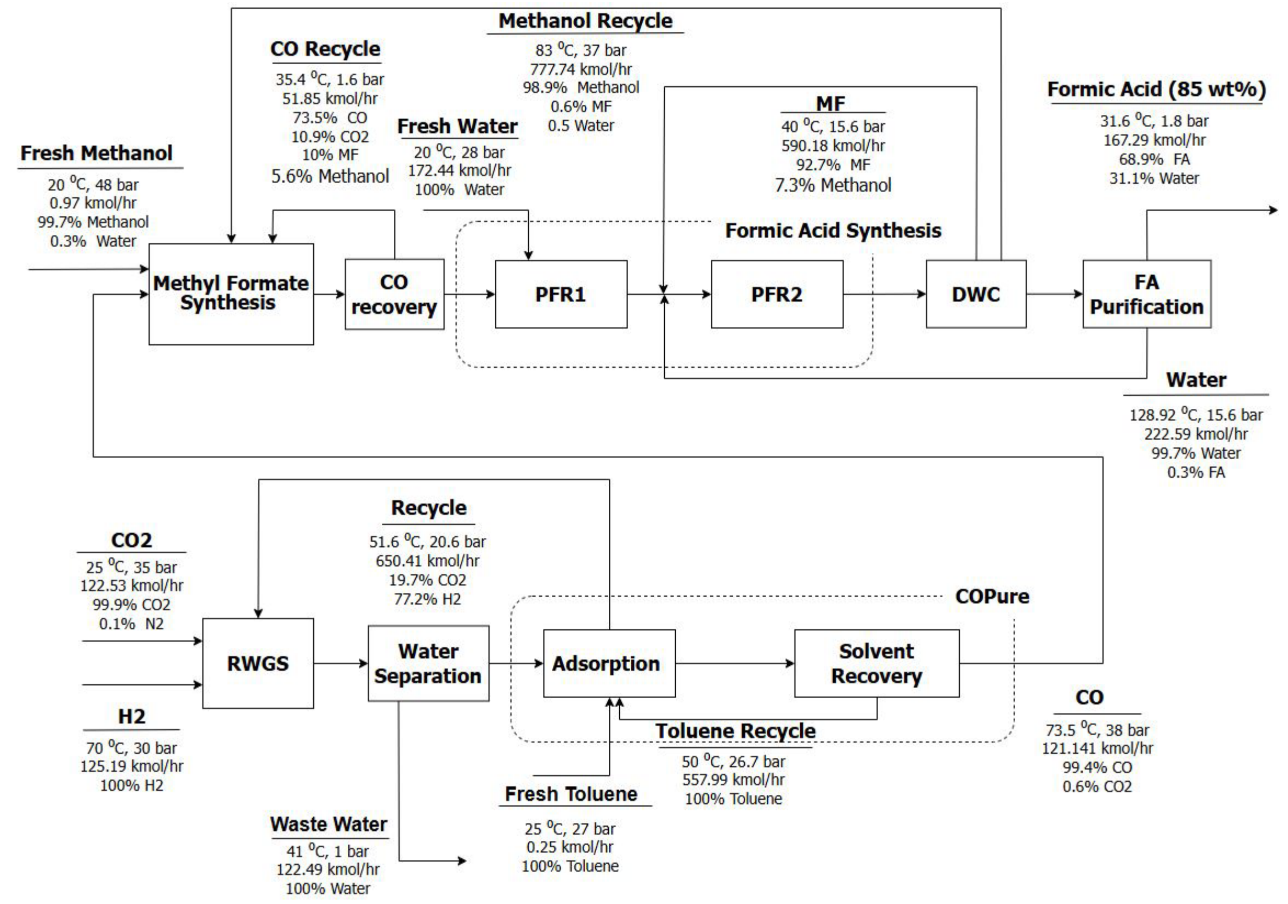

Figure 1. Process Block Flow Diagram

to design a PWC system, starting from the development of a robust steady-state model, simulated in Aspen Plus V12.

Two thermodynamic models were chosen to accurately capture the system's phase behavior across diverse conditions. The RWGS reaction and CO separation processes were simulated with the Peng-Robinson equation of state due to their high-pressure and non-polar components, while the UNIQUAC-HOC model was used for MF and FA production to account for complex liquid-phase interactions.

To enhance the simulation's stability and enable responsiveness to feed fluctuations, critical parameters were identified through sensitivity analysis, allowing the model to accommodate a range of operational conditions. Disturbances in feed composition and flow rates were evaluated, ensuring the process could achieve the desired FA purity and throughput across varied conditions. This steady-state simulation serves as the baseline model, supporting the design of a flexible and resilient dynamic model and the foundation for developing an effective plantwide control system in subsequent stages.

The most challenging aspect of achieving robust and flexible steady-state simulation involved the implementation of calculator blocks and flowsheet design specifications. Calculator blocks, along with DesignSpecs at both the flowsheet and equipment levels, were essential for manipulating key process variables to meet the desired product specifications and ensure mass balance closure across the process.

Achieving convergence across multiple disturbance scenarios in steady-state mode proved to be a valuable predictor of smooth operation during dynamic simulation, ultimately ensuring that the system could transition effectively to Aspen Dynamics for plantwide control analysis.

PWC system Design and Dynamics Simulation

The Integrated Framework of Simulation and Heuristics Method (IFSH) has been widely used for plantwide control (PWC) design [2, 3]. Drawing inspiration from this approach, the methodology begins with defining the objectives of PWC. Plantwide disturbances are then analyzed, and the main throughput variable is identified. Based on these inputs, a two-level control scheme is developed to achieve the desired operational stability and efficiency.

The first control level focuses on stabilizing individual unit operations by implementing primary controllers for critical variables. For example, level control is essential in continuous stirred-tank reactors (CSTRs), where it directly impacts reaction rates. In flash operations and distillation columns, maintaining appropriate liquid levels is equally crucial. The liquid level in flash operations is regulated by adjusting the liquid outlet flow rate, while in distillation columns, the reflux drum and column base levels are controlled via distillate and bottoms flow rates, respectively. Reboiler and condenser temperatures are managed by manipulating their respective heat duties. Similarly, cooler and heater outlet temperatures are controlled by adjusting their thermal inputs. In process-to-process heat exchangers, the temperature on the cold side is regulated by modulating the flow of the hot side through the exchanger. Column and flash pressures are maintained by manipulating the overhead streams and flow controllers manage critical feed streams, including CO_2, H_2, water, toluene, and methanol.

To ensure optimal performance, a closed-loop autotune variation (ATV) test was conducted with a 1 to 10 percent change in the output range. Based on the outcomes of these tests, the Tyreus-Luyben [4] method was implemented to tune the parameters of the controllers in this first level of the control scheme. The Tyreus-Luyben method was applied primarily; however, in some cases, the Ziegler-Nichols [5] method was used.

These controllers ensure steady operation within each plant section, mitigating localized disturbances and maintaining unit-level stability. However, plantwide disturbance analysis revealed that this layer alone could not adequately address larger fluctuations, particularly those related to variable hydrogen supply. While individual units remained stable, the lack of coordination across sections hindered the system's ability to handle interdependencies effectively.

To manage broader disturbances, a second control level was introduced, focusing on overall production stability, quality targets, and material balance across the plant. This layer employs ratio and mass balance controllers to maintain critical system ratios and regulate material flows, particularly within recycle loops.

Several points of the plant required the implementation of these 2nd level controllers to achieve smooth operation. For example, an important aspect of the reactors is to maintain a constant mole ratio for the reactants. One of them is the ratio for H_2 to CO_2 entering the RWGS reactor which is dependent on the fresh H_2 stream flow. At the same time, a make-up stream of Methanol is adjusted based on the required ratio to CO entering the Methyl Formate synthesis reactor. Additionally, Formic Acid is produced in PFR2, for which the required fresh water is checked by a ratio controller at the inlet of the reactor. Continuing on the topic of ratio control, another highly important ratio controller is the one related to the Toluene solvent in the 1st section. The goal is to keep a constant ratio of gas/liquid entering the adsorption column during transitions, while also compensating for the loss of Toluene in other parts of the plant.

Other, more unique controllers have been implemented in the plant, such as the controller for a main path valve and compressor in the 1st section, which affects the main path flowrate and consequently the recycle rate towards the RGWS reactor and therefore the extent of the reaction, with the purpose to keep a specific percentage conversion.

In a similar fashion, the conversion of the reaction in the Methyl Formate Synthesis reactor needs to be controlled and this is done by cascading the level controller of the CSTR, which in turn affects the outlet valve opening, the residence time and the conversion rate. For the same reactor, one of the recycle streams entering it is composed of primarily CO and it is controlled to have a specific flow ratio compared to the “fresh” CO entering the 2nd section. Moreover, this unreacted CO is mainly returned due to a flash separation after the CSTR and it is required that a specific percentage of CO exits as the recycle at the top, which is manipulated by the corresponding valve.

The most complicated controller to implement was the one related to methanol build-up in the 2nd section, which is explained in more detail later. Overall, the 2nd level controllers are essential for sustaining continuous, stable operations and achieving the desired purity of FA and separation efficiency, even under varying input conditions.

With the two-level control design methodology established, the transition to dynamic simulation was initiated. Key adjustments were made to ensure consistent pressure conditions, essential for pressure-driven operation throughout the plant. Control valves were configured to maintain a pressure drop of 2–3 bar, enabling precise flow rate control. Furthermore, controlled pressure differentials were introduced between equipment and across battery limits to drive fluid flow and regulate stream entry and exit effectively. Equipment with holdups, such as reactors, flash drums, reflux drum and sump of distillation columns, were sized to accommodate an inventory corresponding to at least 10 minutes of operation. Additionally, a length-to-diameter ratio of 2:1 was assumed [3]. These adjustments were crucial to ensure a stable and responsive dynamic model.

Figure 2 depicts the two-level control design methodology for the Dividing Wall Column (DWC) system. The DWC system is modeled using two RadFrac columns, one equipped with a reboiler and condenser and the other without, simulating the two chambers separated by a dividing wall within a single column. Four intermediate streams are included to represent the vapor and liquid exchange between the chambers. Additionally, pressure gradient equipment has been introduced between these streams to simulate a pressure gradient for modeling purposes [6].

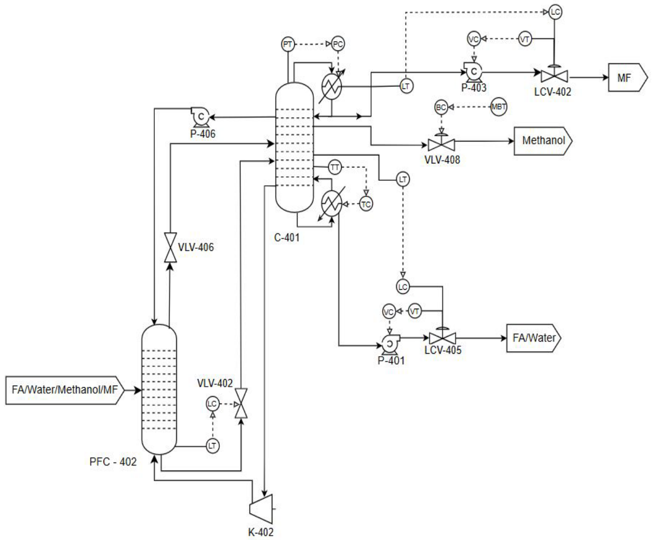

Figure 2. Designed PWC for the DWC

The first level of the control scheme for the DWC incorporates level, temperature, and pressure controllers to ensure stable operation. The levels in the reflux drum and the base of the right column are maintained by adjusting the distillate and bottoms flow rates, respectively. Similarly, the base level of the left column is regulated by controlling the liquid exiting from its bottom. Pressure control for the right column is achieved by manipulating the condenser duty, while the reboiler temperature is controlled by manipulating the reboiler duty. Considering the DWC as part of the overall process, the first level of control alone is insufficient to address plantwide operational challenges. This is where the second level of control becomes critical.

At this level, a mass balance controller is introduced to address methanol accumulation within the system. Methanol is the most difficult component to control, because it is consumed at the Methyl Formate Synthesis reactor and generated at the same time in the 2 PFR reactors (Figure 1). These 3 reactors lie in series along the main path of the process and they are also connected end-to-front through a recycle Methanol stream. Simultaneously, fresh make-up methanol enters the system and some of the methanol is purged from the recycle stream coming out of the CO recovery system. All these points of methanol generation and consumption need to be delicately balanced in order to keep its accumulation in the system at 0. The challenge in achieving that is apparent because of the interconnected nature of the plant. However, at a closer glance it can be seen that for a specific amount of CO entering the 2nd section, the fresh methanol is dynamically changed for a specific reactant ratio in the CSTR. As a consequence, the CSTR and PFR1 rates of change stay “locked in” while the purge stream and its contribution is relatively small in the methanol mass balance. This leaves PFR2 as the only variable to manipulate in order to accomplish 0 accumulation rate. The only way to manipulate the rate of change in PFR2 is by influencing the recycle stream around the reactor composed of unreacted Methyl Formate. This is where the mass balance controller system BC and MBT enter the scene (Figure 2).

To start off, a separate system of logical blocks is used to monitor all the aforementioned points of methanol entry, exit, consumption, and generation across the process and calculates the rate of accumulation of methanol. Its output is used as a process variable in the mass balance controller and set to make it zero. The cascade controller dynamically adjusts the side-draw percentage of the middle stream exiting the DWC column and in continuation it affects the flow of the recycled Methyl Formate stream coming out of the top of the column. By doing so, the mass balance controller effectively minimizes methanol buildup, ensuring a stable material flow and supporting continuous, efficient operation of the process.

During varying throughput scenarios, relying solely on valve adjustments (distillate and bottom flow rates) is insufficient to maintain the levels in the drum and sump. To address this, two additional controllers were implemented to regulate the pump power upstream of the valves. These controllers increase the pump power as needed, providing additional head to the system and ensuring sufficient material flow out of the sump.

RESULT AND DISCUSSION

To evaluate the performance and resilience of the designed plantwide control (PWC) system, dynamic simulations were conducted by introducing controlled disturbances to the CO_2 feed stream as the main throughput manipulator.

These disturbances ranged from a -20% decrease to a +20% increase in throughput flow rate, implemented through a SRAMP function within Aspen Dynamics. The SRAMP function was carefully configured to gradually adjust the CO_2 feed rate over a designated time period, thereby simulating fluctuations in green Hydrogen. By systematically varying the feed rate across this spectrum, the control system's ability to maintain consistent Formic acid (FA) production rates and purity levels under both positive and negative disturbances was thoroughly assessed. Each simulation scenario was monitored to capture key performance indicators such as stabilization time, integral absolute error (IAE), and relative absolute error (RAE) in order to assess the designed control scheme.

This approach provided comprehensive insights into how effectively the PWC system could manage and mitigate the impacts of unsteady feed conditions, ensuring operational stability and product quality despite throughput variations.

The analysis revealed that as the magnitude of feed disturbances increased, the time required for the system to transition from one steady state to another also escalated. It is important to note that steady state is achieved when the Relative Absolute Error (RAE) graph drops below 0.1% and remains within this boundary, indicating that the system has stabilized and deviations are effectively minimized. For instance, in simulations with smaller feed fluctuations, the system quickly adapted, achieving a new steady state within 16.7 hours for a +10% feed disturbance and 42.6 hours for a -10% disturbance. However, with larger changes, the time to stabilize increased, as the control system needed to accommodate more significant adjustments throughout the plant (Figure 3 and Figure 4) with transitions taking 33.7 hours for +20% and 59.5 hours for -20% disturbances. Kink points in Figure 3 are primarily due to the challenges of managing material within the recycle loops during capacity changes.

Figure 5 illustrates the FA purity error relative to the target value of 85 wt%, demonstrating that even under significant throughput variations of ±20%, the FA purity remains within a narrow 0.2% range. This error decreases by an order of magnitude for ±10% changes in throughput, indicating improved purity stability under less severe disturbances. However, the error associated with a throughput drop is slightly higher compared to a throughput increase. This variance is likely due to challenges in managing material within the recycle loops during capacity reduction, which may cause slight imbalances and affect the control system's ability to stabilize purity as efficiently. This behavior is further supported by Figure 4, which show that the stabilization time required for the simulation is longer in scenarios involving a throughput drop compared to those with a throughput increase.

To ensure stability and prevent the simulation solver from crashing, tests were conducted with a conservative feed disturbance rate of 1% per hour. Meaning that, while, Figure 6 to Figure 9 indicate that for moderate changes of ±5% or ±10%, this rate could be increased up to 2.5% per hour; the repercussions of doing so led to higher IAE and FA purity Error values, indicating a trade-off between response speed and error minimization. Importantly, a 2.5% rate is unsuitable for extreme 20% changes, as it caused instability in the solver, indicating a control limitation under more severe fluctuations.

Additionally, the relative absolute error and integral absolute error trend remains almost identical, when throughput is either increased or decreased by the same percentage, reflecting symmetrical control behavior for equivalent rises and drops in feed rates period of +10% change in throughput (moderate flow rate changes). This symmetry highlights the robustness of the control strategy in handling feed variability, ensuring consistent error response regardless of the direction of throughput change.

A comparative analysis between the dynamic and steady-state results for the extreme disturbance scenario, demonstrating that, despite deviations from steady-state targets, the plantwide control objectives were largely achieved. Specifically, the control system maintained the desired production rate and adhered to process constraints, even under the harshest fluctuations. When there is a +20% disturbance in the system, the product flow rate, the overall MF production, and the fresh Methanol flow rate deviate by +0.6%, -2.7%, and -1.1% from steady state, respectively.

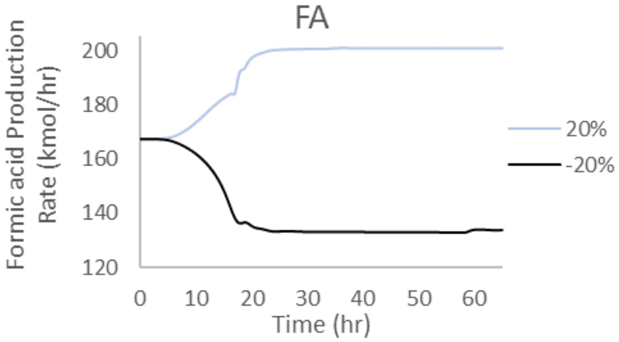

Figure 3. FA production rate for +20% and -20% change in throughput

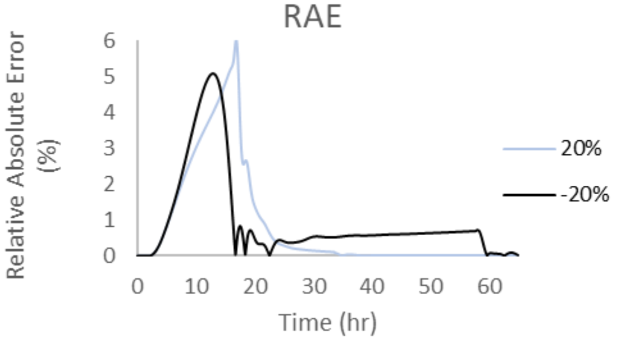

Figure 4. Relative Absolute Error (RAE) for +20% and -20% change in throughput

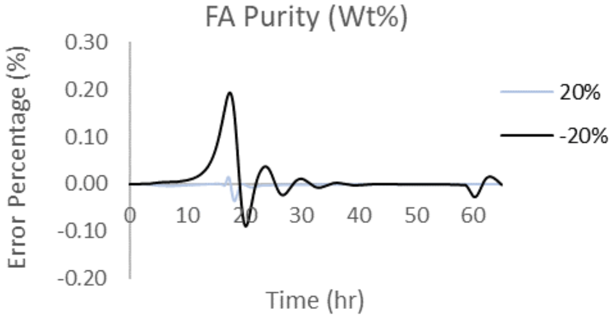

Figure 5. FA purity error relative to 85 wt% for +20% and -20% change in throughput

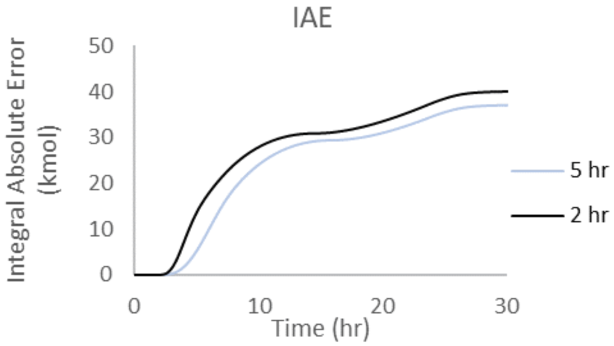

Figure 6. Integral Absolute Error (IAE) for 2 and 5 hr ramp period of -5% change in throughput

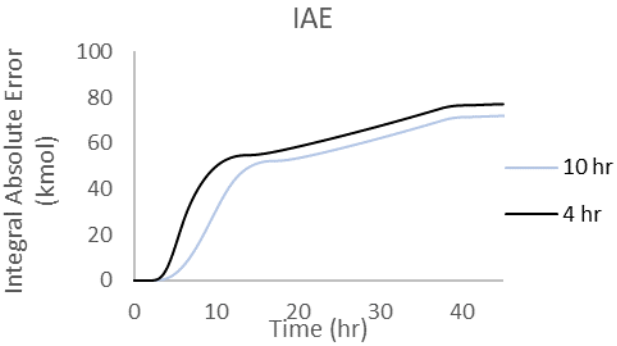

Figure 7. Integral Absolute Error (IAE) for 4 and 10 hr ramp period of -10% change in throughput

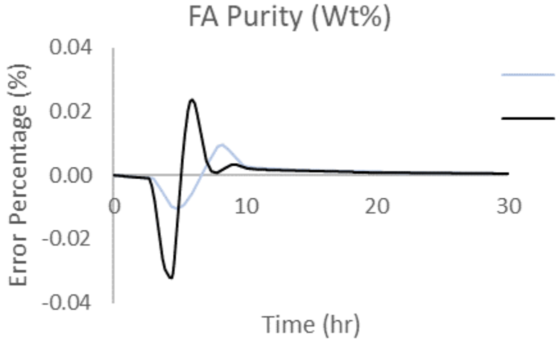

Figure 8. FA purity error relative to 85 wt% 2 and 5 hr ramp period of +5% change in throughput

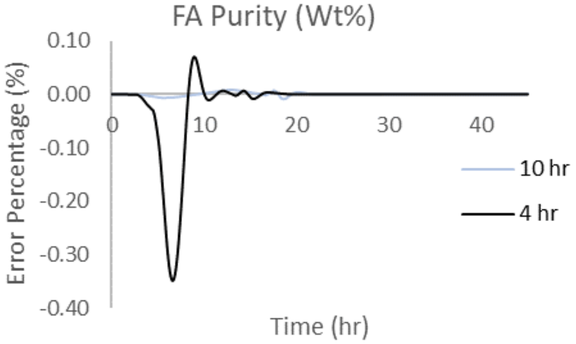

Figure 9. FA purity error relative to 85 wt% 4 and 10 hr ramp

Conversely, with a -20% disturbance, the product flow rate, the overall MF production, and the fresh Methanol flow rate deviate by -0.2%, -2.9%, and +1.9% from steady state, respectively. These results confirm the robustness of the PWC system in adapting to significant disturbances, ensuring stable Formic acid output and maintaining operational requirements within acceptable limits.

CONCLUSION

The designed plantwide control (PWC) system effectively maintained Formic acid (FA) production rates and purity under variable feed conditions caused by unsteady green Hydrogen supplies. The results highlight the impact of the rate of feed changes on the overall control performance, with 1% throughput change per hour identified as a stable rate for maintaining system stability and performance. Despite the complexities of the process, including multiple recycle loops and the divided wall column, the PWC system ensured stable operations. Notably, the FA purity remained within a maximum of 0.2% deviation from the desired 85 wt%, even under the harshest feed flowrate changes of ±20%. The deviation of the FA flow rate in dynamic mode from the steady-state simulation for the +20% and -20% changes in throughput was +0.6% and -0.2%, respectively, further showcasing the robustness of the design. Overall, the evaluation of the PWC design of Formic acid under unsteady Hydrogen supply conditions proved the feasibility of the suggested PWC design on a conceptual level.

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