Model Predictive Control of a Nonlinear Large-Scale Process Network Used in the Production of Vinyl Acetate

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ABSTRACT: In this work, we focus on the development and application of two Lyapunov-based model predictive control (LMPC) schemes to a large-scale nonlinear chemical process network used in the production of vinyl acetate. The nonlinear dynamic model of the process consists of 179 state variables and 13 control (manipulated) inputs and features a cooled plug-flow reactor, an eight-stage gas–liquid absorber, and both gas and liquid recycle streams. The two control schemes considered are an LMPC scheme which is formulated with a convectional quadratic cost function and a Lyapunov-based economic model predictive control (LE MPC) scheme which is formulated with an economic (nonquadratic) cost measure. The economic cost measure for the entire process network accounts for the reaction selectivity and the product separation quality. In the LMPC and LEMPC control schemes, five inputs, directly affecting the economic cost, are regulated with LMPC/LE MPC and the remaining eight inputs are computed by proportional–integral controllers. Simulations are carried out to study the economic performance of the closed-loop system under LMPC and under LEMPC formulated with the proposed economic measure. A thorough comparison of the two control schemes is provided.

INTRODUCTION

Vinyl acetate is mostly used in manufacturing polyvinyl acetate and other vinyl acetate copolymers. Polyvinyl acetate is the fundamental ingredient for polyvinyl alcohol and polyvinyl acetate resins. Three raw materials, ethylene (C₂H₄), oxygen (O₂), acetic acid (HAc), react to form the desired product vinyl acetate (VAc) as well as two byproducts: carbon dioxide (CO₂) and water (H₂O). An inert component, ethane (C₂H₆), enters the process with the ethylene feed stream. The exothermic and irreversible gas phase chemical reactions are

\[
\begin{align*}
\text{C}_2\text{H}_4 + \text{HAc} + \frac{1}{2} \text{O}_2 & \rightarrow \text{VAc} + \text{H}_2\text{O} \\
\text{C}_2\text{H}_4 + 3 \text{O}_2 & \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O}
\end{align*}
\]

where the heat of the \( i \)th reaction \( (h_{\text{rxn},i} = h_{\text{rxn},1} = -42\,100 \text{ kcal/kmol and } h_{\text{rxn},2} = -316\,000 \text{ kcal/kmol, respectively.}

The fundamental challenge of controlling a vinyl acetate process network is operating a highly nonlinear coupled process at an economically optimal steady-state. Luyben and Tyreus\(^1\) presented a detailed process network design for manufacture of vinyl acetate monomer and demonstrated that plantwide control of the process can be accomplished by using a conventional proportional–integral (PI) control scheme. Chen et al.\(^2\) developed a nonlinear dynamic model of a vinyl acetate process in MATLAB based on Luyben and Tyreus’ work, proposed a different control structure using combination of proportional (P) control and PI control loops, and studied the dynamics of the closed-loop system under several set-point changes and disturbances. Oslen et al.\(^3\) proposed modified control structures, specifically focused on improving the liquid inventory system control and the controllability of the azeotropic distillation column using a model predictive controller and a static ratio controller. Subsequently, Luyben\(^4\) modified and optimized a vinyl acetate process flowsheet using the original unit operations presented in the previous work\(^1\) from a steady-state economic point of view using Aspen Dynamics.

Optimizing chemical processes from an economic perspective is an issue of primary importance in industry. The economic optimization of chemical processes is usually realized via a two-layer real-time optimization (RTO) system.\(^6\) In an RTO system, the upper layer utilizes a steady-state process model to compute economically optimal process operation set-points while feedback control systems are used to force the system to track the set-points in the lower layer. MPC is usually adopted in the lower layer due to its ability of taking advantage of a dynamic model of the process to predict its future evolution along a given prediction horizon. MPC solves an online optimization problem to compute optimal control inputs by optimizing a quadratic cost function involving penalties on the deviation of the state and controlled variables from a desired steady-state while taking state and input constraints into account.\(^7,8\) Lyapunov-based MPC (LMPC) provides an explicit characterization of the stability region through utilization of a pre-existing Lyapunov-based controller as an auxiliary controller.\(^9\) Recently, a significant number of efforts have been devoted to integrating MPC and economic optimization of chemical processes in order to manipulate process capacities in response to fast-changing global market demand.\(^10\) Furthermore, the development of MPC with a general economic cost function has been studied in refs 15–19. For example, two economically oriented nonlinear MPC formulations using Lyapunov techniques to guarantee nominal stability...
of the closed-loop system for cyclic processes were studied in ref 18. In refs 15 and 19, MPC schemes using an economic-based cost function with established stability properties via a proper Lyapunov function were proposed, in which an incorporated terminal constraint ensures that the closed-loop system is driven to a steady-state at the end of the prediction horizon. Even though a rigorous stability analysis is discussed in ref 15, it is difficult, in general, to characterize, a priori, the set of initial conditions starting from where feasibility and closed-loop stability (both boundedness and convergence to a potentially economically optimal steady-state) of the proposed MPC are guaranteed. In contrast, a design of economic model predictive control (EMPC) using Lyapunov-based techniques (LEMPC) is able to optimize closed-loop performance with guaranteed stability with respect to general economic considerations for nonlinear systems.17

Economic model predictive control has been applied to several applications.20–22 In ref 22, energy costs in a commercial building were effectively reduced via an economic model predictive control technique with a shrinking prediction horizon; likewise, maximizing revenue from a dispatch-capable integrated gasification combined cycle (IGCC) was studied by using infinite-horizon economic model predictive control in ref 20.

Even though plantwide control designs using conventional control techniques on a vinyl acetate process have been extensively studied, application of model predictive control to a vinyl acetate process network has not been addressed in the literature. Motivated by this, we apply two model predictive control (MPC) schemes to a large-scale vinyl acetate process network: LMPC formulated with a conventional quadratic cost and LEMPC formulated with an economic measure which accounts for the reaction selectivity in the plug-flow reactor and vinyl acetate separation quality in the separator and the absorber. Closed-loop simulations of the vinyl acetate process network with both MPC schemes are carried out to study the closed-loop economic performance as well as compare the two MPC schemes. In the following sections, we introduce the process model which consists of 179 nonlinear ordinary differential equations and 13 manipulated inputs featuring a cooled plug-flow reactor, an eight-stage gas−liquid absorber, and both gas and liquid streams. Next, we formulate the two control schemes for the vinyl acetate process network where the MPC schemes are used to regulate five manipulated inputs and a set of PI controllers are used to regulate the remaining manipulated inputs to maintain closed-loop stability. Lastly, we present closed-loop simulation results and provide a thorough discussion on the comparison between the two control schemes.

**NONLINEAR VINYL ACETATE PROCESS NETWORK**

In this section, we describe the vinyl acetate process network and introduce the nonlinear dynamics of operation units in the process network. The variables used in the model and their definitions are listed in the Nomenclature.

**Process Description.** The vinyl acetate process network flow diagram is shown in Figure 1. The process network is composed of several operation units including a vaporizer (VAP), a plug-flow reactor (RCT), a heat exchanger (HX), a separator (SEP), a compressor (COM), an absorber (ABS), and an acetic acid hold-up tank (TK). In addition to those main operation units, there are a total two heaters (H1 and H2) and three coolers (C3, C4, and C5) prior to the main operation units as shown in Figure 1. Using first principles, a nonlinear process model is obtained for each of these operation units. The carbon dioxide removal unit and the azeotropic distillation in Figure 1 are assumed to be component splitters with fixed CO2 removal efficiency and VAc product recovery ratios, respectively.

An ethylene gas feed stream (S1) enters the process and is mixed with a preheated gas recycle stream (S34). The resulting mixed gas stream (S2) enters the vaporizer along with the acetic acid liquid recycle stream (S3) from the acetic acid hold-up tank. The exit gas stream (S4) from the vaporizer is further heated to a desired reactor inlet temperature. To keep the oxygen composition in the gas recycle loop below the explosive
region while providing sufficient oxygen for the reactions, oxygen is fed prior to the reactor (S5). The catalytic packed bed plug-flow reactor gas effluent (S8) enters the heat exchanger as the hot-side stream. The hot-side effluent from the heat exchanger (S9) is partially condensed through a pressure let-down valve and a cooler. In the separator, the exit liquid stream (S13) consists of mostly heavy components such as VAc, H2O, and HAc; the exit vapor stream (S12) passes through a compressor and a heater before it enters the absorber where the remaining heavy components are further recovered and light components such as O2, CO2, C2H4, and C2H6 are recycled. A large portion of liquid from the base of the absorber is recirculated through a cooler and fed to the second stage of the absorber. The liquid effluents from the separator (S13) and the absorber (S17) are mixed and fed to an azeotropic distillation column in which the overhead stream (S26) contains the final product, vinyl acetate, of the process network. The temperature dependence on the vapor and liquid enthalpy is modeled as follows (i.e., \( \frac{\partial h}{\partial T} \rho = \frac{i}{C} \)): 

\[
\tilde{h}_i = (a_i^T + 0.5b_i^2)MW_i + h_{liq}
\]

(4)

\[
\tilde{h}_i = (a_i^T + 0.5b_i^2)MW_i
\]

(5)

where \( h_i \) denotes the vapor enthalpy of species \( i \) and \( \tilde{h}_i \) denotes the liquid enthalpy of species \( i \). The pressure dependence on heat capacity and enthalpy is assumed to be negligible. The Antoine equation is used to calculate the component saturated pressure \( (p^s_{VAP}) \):

\[
p^s_{VAP,i} = e^{\left(\frac{B_i}{C_i + T(\degree C)} + A_i\right)}
\]

(6)

where the Antoine coefficients, \( \hat{A}_i \), \( \hat{B}_i \), and \( \hat{C}_i \), are listed in Table 3. **Vaporizer.** The vaporizer is assumed to be well mixed, and vapor–liquid equilibrium is also assumed. Only the dynamics of the liquid phase in the vaporizer is taken into account. Vapor pressure and the vapor compositions are found using a bubble-point calculation

\[
\gamma_{VAP,i} = \frac{p^s_{VAP,i}}{p^v_{VAP,i}}
\]

where \( \gamma_{VAP,i} \) represents the activity coefficient of species \( i \) in the liquid phase of the vaporizer. There are eight state variables in the vaporizer such as the liquid hold-up, the molar fractions, and the liquid temperature. The dynamic equations of the vaporizer are as follows:

\[
\frac{d\bar{M}_{VAP}}{dt} = f_{S2} + f_{S3} - f_{S4}
\]

(8)

\[
\frac{d\bar{x}_{VAP}}{dt} = \frac{f_{S2}(\bar{x}_{S2} - \bar{x}_{VAP}) + f_{S3}(\bar{x}_{S3} - \bar{x}_{VAP}) - f_{S4}(\bar{x}_{S4} - \bar{x}_{VAP})}{\bar{M}_{VAP}}
\]

(9)

\[
\frac{dT_{VAP}}{dt} = \frac{[f_{S2}(H_{S2} - H_{VAP}) + f_{S3}(H_{S3} - H_{VAP}) - f_{S4}(H_{S4} - H_{VAP}) + Q_{VAP}]/(\bar{M}_{VAP}C_{VAP})}{\bar{M}_{VAP}}
\]

(10)

where \( \bar{M}_{VAP} \) is the total number of moles in the liquid phase of the vaporizer, \( \bar{x}_{VAP} \) is the mole fraction of species \( i \) in the liquid phase of the vaporizer, and \( T_{VAP} \) is the temperature of the liquid phase of the vaporizer. The maximum allowable liquid volume in the vaporizer is \( V_{max} = 4 \text{ m}^3 \).

**Catalytic Plug-Flow Reactor.** A tubular packed-bed catalytic reactor is used to convert ethylene and acetic acid into the desired product, vinyl acetate. A combustion reaction also consumes ethylene in the reactor. The two reactions are given in eq 1. The reactor length is 10 m, and the diameter is

<table>
<thead>
<tr>
<th>( a_i ) (kcal/kmol)</th>
<th>VAc</th>
<th>H2O</th>
<th>HAc</th>
</tr>
</thead>
<tbody>
<tr>
<td>j</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VAc</td>
<td>0</td>
<td>1384.6</td>
<td>-136.1</td>
</tr>
<tr>
<td>H2O</td>
<td>2266.4</td>
<td>0</td>
<td>670.7</td>
</tr>
<tr>
<td>HAc</td>
<td>726.7</td>
<td>230.6</td>
<td>0</td>
</tr>
</tbody>
</table>

**Table 1.** Wilson Parameters \( (\tilde{a}_i) \) of Each Species Pair Existing in the Liquid Phase of the Vinyl Acetate Process Network Taken from Reference 2
Table 2. Physical Properties of the Species in the Vinyl Acetate Process Network Taken from Reference 3

<table>
<thead>
<tr>
<th>Species</th>
<th>MW (kg/kmol)</th>
<th>SpG</th>
<th>h_C (kcal/kg·°C)</th>
<th>a (kcal/(kg·°C))</th>
<th>b (kcal/(kg·°C²))</th>
<th>ŗ (L/kmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>32.000</td>
<td>0.50</td>
<td>2300</td>
<td>0.30</td>
<td>0</td>
<td>0.218</td>
</tr>
<tr>
<td>CO₂</td>
<td>44.010</td>
<td>1.18</td>
<td>2429</td>
<td>0.60</td>
<td>0</td>
<td>0.230</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>28.052</td>
<td>0.57</td>
<td>1260</td>
<td>0.60</td>
<td>0</td>
<td>0.370</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>30.068</td>
<td>0.57</td>
<td>1260</td>
<td>0.60</td>
<td>0</td>
<td>0.370</td>
</tr>
<tr>
<td>VAc</td>
<td>86.088</td>
<td>0.85</td>
<td>8600</td>
<td>0.44</td>
<td>0.0011</td>
<td>0.290</td>
</tr>
<tr>
<td>H₂O</td>
<td>18.008</td>
<td>1.00</td>
<td>10684</td>
<td>0.99</td>
<td>0.0002</td>
<td>0.560</td>
</tr>
<tr>
<td>HAc</td>
<td>60.052</td>
<td>0.98</td>
<td>5486</td>
<td>0.46</td>
<td>0.0012</td>
<td>0.520</td>
</tr>
</tbody>
</table>

3.71 cm. It is assumed that the reactions only take place in the reactor. Plug flow through the reactor is assumed, and thus, the temperature and concentration gradients are ignored in the radial direction. In addition, diffusion is negligible in the axial direction. Temperature and concentration gradients from the bulk fluid to the external surface of the catalyst are negligible because mass and heat transfer are assumed to be very fast between phases. The mass flow rate per unit cross-sectional area is assumed to be constant. Catalyst deactivation is not considered so the catalyst porosity ε is unity. The catalyst heat capacity constant. Catalyst deactivation is not considered so the catalyst porosity ε respectively. The dynamic model of the reactor is

\[
\frac{\partial \vartheta_R}{\partial t} = \frac{\partial (\vartheta_R \varrho_{cat}(\vartheta_R + \vartheta_C))}{\partial z} + \varrho_{cat}(\vartheta_R \varrho_{f1} + \vartheta_C \varrho_{f2})
\]  

(11)

where \( \vartheta_R \) is the total vapor concentration, \( \vartheta_C \) is the vapor heat capacity, \( z \) is the axial coordinate along the length of the reactor (\( z \in [0, 10] \)), \( \varrho \) is the superficial velocity, and \( \varrho_{f1} \) and \( \varrho_{f2} \) are the stoichiometric coefficients for the reactions 1 and 2, respectively. To approximate the reactor dynamics of eqs 11 and 12, the reactor is modeled in ten sections in the axial direction (\( i = 1, 2, \ldots, 10 \)) and the convective mass transfer and temperature gradients are assumed to have linear dependence in axial direction in each section:

\[
\frac{\partial \vartheta_R}{\partial t} = \frac{1}{(z_i - z_{i-1})} \left( \frac{\partial \vartheta_R}{\partial z} \varrho_{cat}(\vartheta_R \varrho_{f1} + \vartheta_C \varrho_{f2}) \right) + \varrho_{cat}(\vartheta_R \varrho_{f1} + \vartheta_C \varrho_{f2})
\]  

(13)

Table 3. Component Vapor Pressure Antoine Coefficients

<table>
<thead>
<tr>
<th>( i )</th>
<th>( \lambda )</th>
<th>( \beta )</th>
<th>( \c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>9.2</td>
<td>0</td>
<td>273</td>
</tr>
<tr>
<td>CO₂</td>
<td>7.937</td>
<td>0</td>
<td>273</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>9.497</td>
<td>-313</td>
<td>273</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>9.597</td>
<td>-313</td>
<td>273</td>
</tr>
<tr>
<td>VAc</td>
<td>12.654</td>
<td>-2984.45</td>
<td>226.66</td>
</tr>
<tr>
<td>H₂O</td>
<td>14.394</td>
<td>-3984.92</td>
<td>233.426</td>
</tr>
<tr>
<td>HAc</td>
<td>14.523</td>
<td>-4557.83</td>
<td>258.45</td>
</tr>
</tbody>
</table>

Since the Reynold’s number of the packed bed reactor was estimated to be much greater than 1000, the pressure drop throughout the reactor was estimated to be less than 5% of the inlet pressure of the reactor using the Burke–Plummer equation.22,23 Furthermore, the pressure drop does not have a significant effect on the reaction rates as confirmed by extensive open-loop simulations of the reactor model. As a result, the pressure drop throughout the reactor is not taken into account. The expressions of the chemical reaction rates are

\[
r_{1} = 0.10363 \exp \left( \frac{-3674}{T(K)} \right) \times \frac{P_{O_2}P_{C_2H_4}P_{HAc}(1 + 1.7P_{H_2O})}{(1 + 0.583P_{O_2}(1 + 1.7P_{H_2O}))(1 + 6.8P_{HAc})}
\]  

(15)

\[
r_{2} = 1.9365 \times 10^5 \exp \left( \frac{-10116}{T(K)} \right) \times \frac{P_{O_2}(1 + 0.68P_{H_2O})}{(1 + 0.76P_{O_2}(1 + 0.68P_{H_2O}))}
\]  

(16)

where \( r_i \) has units of moles of vinyl acetate produced per minute per gram of catalyst and \( r_{12} \) has units of moles of ethylene consumed per minute per gram of catalyst. Heat released per unit volume by the reactions (\( q_{R}^{\text{RCT}} \)) in the 8th section is removed by water coolant on the shell side of the tubes, and it is calculated by the following equation:

\[
q_{i}^{\text{RCT}} = \varrho_{\text{coolant}}(T_{\text{coolant}} - T_{R}^{\text{RCT}})
\]  

(17)

where \( T_{\text{coolant}} \) is the water coolant temperature on the shell side which is assumed to be uniform and \( T_{R}^{\text{RCT}} = 269.84 \text{kcal/(m}^3\text{min °C)} \) is the overall heat transfer coefficient per unit volume. There are 70 state variables in the reactor model such as fluid temperatures and concentrations of components for each section in the reactor.

Separator. It is assumed that the superheated hot effluent from the heat exchanger becomes saturated vapor through a pressure let-down valve. The saturated vapor is partially condensed through a cooler and then enters the separator. A temperature–pressure (TP) flash calculation, applicable when temperature and pressure are known since the equilibrium constant (\( K \)) mainly depends on temperature and pressure, is implemented to obtain the flow rates and compositions of the vapor (\( f_{S11} \) and \( y_{S11} \)) and liquid (\( f_{S12} \) and \( y_{S12} \)) streams entering the separator. The TP calculation sequence is implemented according to the following steps:

1. Guess the fraction of feed vaporized \( \tilde{a} := 0.84 \) and the fraction of species i in \( S11 \) \( \tilde{y}_{iS11} := \tilde{x}_{iS11}^\text{SEP} \).
2. Calculate \( K_{iS11} = \frac{y_{S11}(x_{S11}T_{S11}P_{S11}^\text{REF} (T_{S11}))}{P_{S11}} \).
3. Calculate \( \tilde{x}_{iS11} = \tilde{y}_{iS11}/(1 + (K_{iS11} - 1)\tilde{a}) \) and \( \tilde{y}_{S11} = K_{iS11}\tilde{x}_{iS11} \).
4. Calculate $\psi = \sum (\tilde{x}_{i1} - \tilde{y}_{i1})$. If $\psi$ is within an acceptable tolerance, STOP. Else, go to step 5.
5. Update the fraction of feed vaporized: $\tilde{a} := \tilde{a} - 0.1\psi$ and go to step 2.

The number of moles and the pressure in the vapor phase are assumed to be constant while the change in the vapor temperature is assumed to exist because it is coupled with the change in the vapor mole fraction. Through extensive simulations, it is found that the change in temperature is insignificant even if mass accumulation and the pressure change of the vapor phase in the vessel are considered. Therefore, one could potentially neglect the change in the vapor temperature in the separator as well. Heat in the liquid phase is removed by a cooling jacket ($T_{coolant}$). There are 16 state variables such as liquid hold-up, molar fractions of components, and temperatures in the liquid phase and the vapor phase as well as the vapor phase pressure. These variables evolve according to the following dynamic equations:

$$\frac{d\tilde{M}^{SEP}}{dt} = \tilde{f}_{S11} - \tilde{f}_{S13}$$ (18)

$$\frac{dx^{SEP}}{dt} = \tilde{f}_{S11} (\tilde{x}_{S11,i} - \tilde{x}_{i}^{SEP}) / (M^{SEP})$$ (19)

$$\frac{dT^{SEP}}{dt} = \tilde{f}_{S11} (H_{S11} - H^{SEP}) - UA^{SEP} (T^{SEP} - T_{coolant}) / (M^{SEP} C^{SEP})$$ (20)

$$\frac{d\tilde{y}^{SEP}}{dt} = \frac{\tilde{f}_{S11} (\tilde{x}_{S11,i} - \tilde{y}_{i}^{SEP})}{(M^{SEP} C^{SEP})}$$ (21)

$$\frac{dT^{SEP}}{dt} = \frac{\tilde{f}_{S11} (H_{S11} - H^{SEP})}{(M^{SEP} C^{SEP})}$$ (22)

The maximum allowable liquid volume in the separator is $v_{max}^{SEP} = 8$ m$^3$.

**Absorber.** The purpose of the absorber is to recover the remaining vinyl acetate from the vapor effluent that leaves the separator. The gas absorber consists of eight theoretical stages ($l = 1, 2, ..., 8$) and a liquid hold-up base. It is assumed that there is no chemical reaction taking place at each stage and the pressure in the absorber is uniform throughout the absorber. A mass transfer rate-based model is implemented to describe the mass transfer and heat transfer between the liquid phase and the vapor phase at each stage; vapor–liquid equilibrium is assumed to exist at the interface in the rate-based model. The liquid hold-up at each stage is assumed to be well mixed.

For convective flow, the mass transfer coefficient is a function of flow rate, pressure and temperature. The mass transfer coefficient in this model, otherwise, is assumed to be constant at each stage. For this reason, the mass transfer rate calculated from the model for a component at each stage might exceed the total mass of the component in the bulk phase. Thus, the maximum mass transfer rate for a component is assumed to be constrained by the amount in the bulk phase. The convective mass coefficient ($k$) is 27.22 kmol/min.

The individual component mass transfer rate ($N_{d,l}^{ABS}$) between two phases at each stage is determined by the following equation:

$$N_{d,l}^{ABS} = \min \{ k(\tilde{y}_{d,l}^{ABS} - \tilde{y}_{d,l}^{INT}), 0.5 N_{d,l}^{ABS} \tilde{y}_{d,l}^{ABS} \}$$

$$n_{d,l}^{ABS} = -N_{d,l}^{ABS}, \text{ if } \tilde{y}_{d,l}^{ABS} < \tilde{y}_{d,l}^{INT}$$

$$n_{d,l}^{ABS} = N_{d,l}^{ABS}, \text{ if } \tilde{y}_{d,l}^{ABS} > \tilde{y}_{d,l}^{INT}$$ (23)

The vapor compositions of species $i$ ($\tilde{y}_{d,l}^{ABS}$) at the interface of the $l$th theoretical stage is obtained using an equilibrium calculation. Two forms of energy transfer occur between the two phases at each stage: conductive heat transfer due to temperature gradients and convective heat transfer due to the transferring components. Conductive heat transfer ($Q_{l}^{ABS}$) and convective heat transfer ($Q_{l}^{ABS}$) from the vapor phase to the liquid phase at $l$th stage are calculated based on the following equations:

$$Q_{l}^{ABS} = UA^{ABS} (\tilde{T}_{l-1} - \tilde{T}_{l}^{ABS})$$ (24)

$$Q_{l}^{ABS} = \sum_{i=1}^{7} n_{d,l}^{ABS} h_{i}^{ABS} (T)$$ (25)

where the overall heat transfer coefficient $UA^{ABS} = 100.8$ kcal/kmol for $l = 1, 2$ and $UA^{ABS} = 50.4$ kcal/kmol for $l = 3, 4, ..., 8$. The absorber is divided into two sections. The bottom section contains two stages and the base. The top section contains six stages. The base has an inlet stream from the first stage and an outlet stream which is split into a circulation stream ($\tilde{f}_{S20}$) and a stream ($\tilde{f}_{S17}$) used to regulate the liquid hold-up of the base. The dynamics of the base are described as follows:

$$\frac{d\tilde{M}_{b}^{ABS}}{dt} = \tilde{f}_{1}^{ABS} - \tilde{f}_{S17} - \tilde{f}_{S20}$$ (26)

$$\frac{dx_{b}^{ABS}}{dt} = \frac{\tilde{f}_{1}^{ABS} (x_{S1,i}^{ABS} - x_{b}^{ABS})}{M_{b}^{ABS}}$$ (27)

$$\frac{dT_{b}^{ABS}}{dt} = \frac{\tilde{f}_{1}^{ABS} (H_{S1}^{ABS} - H_{b}^{ABS})}{M_{b}^{ABS} C_{b}^{ABS}}$$ (28)

where the subscript $b$ denotes the base. A cooled circulation stream is fed to the second stage ($l = 2$) for an initial gas scrubbing. The dynamics of the second stage is described as follows:

$$\frac{d\tilde{M}_{1}^{ABS}}{dt} = (\tilde{f}_{S17} + f_{S20} + n_{net,i}^{ABS} - f_{1}^{ABS})$$ (29)

$$\frac{dx_{1}^{ABS}}{dt} = \frac{\tilde{f}_{1}^{ABS} (x_{S1,i}^{ABS} - x_{1}^{ABS}) + n_{1}^{ABS} (x_{S1,i}^{ABS} - x_{1}^{ABS}) + n_{1}^{ABS} - n_{net,i}^{ABS}}{M_{1}^{ABS}}$$ (30)

$$\frac{dT_{1}^{ABS}}{dt} = \frac{f_{S17} (H_{S1}^{ABS} - H_{1}^{ABS}) + f_{S20} (H_{S20}^{ABS} - H_{1}^{ABS})}{M_{1}^{ABS} C_{1}^{ABS}}$$

$$+ Q_{l}^{ABS} + Q_{l}^{ABS} - n_{net,i}^{ABS} H_{1}^{ABS}) / (M_{1}^{ABS} C_{1}^{ABS})$$ (31)
where $\bar{n}_{\text{net},i}$ is the net amount of material transferring to the liquid phase as shown below:

$$\bar{n}_{\text{net},i} = \sum_{i=1}^{7} n_{\text{ABS},i}$$ \hspace{1cm} (32)

For stages ($i = 1, 3, 4, 5, 6,$ and $7$), there are an inlet liquid stream from the above stage and an outlet liquid stream which leaves the stage. The dynamics of these stages are described by the following equations:

$$\frac{dM_i}{dt} = (f_i^{\text{ABS}} + \bar{n}_{\text{net},i} - f_i) \hspace{1cm} (33a)$$

$$\frac{dx_i}{dt} = \frac{1}{M_i^{\text{ABS}}} \left( f_i^{\text{ABS}} (x_{i+1} - x_i) + n_i - \bar{n}_{\text{net},i} x_i \right) \hspace{1cm} (33b)$$

$$\frac{dT_i^{\text{ABS}}}{dt} = \frac{H_i^{\text{ABS}} (T_i - T_i^{\text{ABS}}) + Q_i^{\text{ABS}} + Q_i - \bar{n}_{\text{net},i} H_i}{M_i^{\text{ABS}} C_i^{\text{ABS}}} \hspace{1cm} (33c)$$

A liquid stream ($f_{S23}$) from the acetic acid hold-up tank which is cooled and enters the last stage ($i = 8$) serves as final gas scrubbing stream. The dynamics of the last stage are described by the following equations:

$$\frac{dM_8^{\text{ABS}}}{dt} = (f_{S23} + \bar{n}_{\text{net},8} - f_8) \hspace{1cm} (34a)$$

$$\frac{dx_8}{dt} = \frac{1}{M_8^{\text{ABS}}} \left( f_{S23} (x_{8,8} - x_8^{\text{ABS}}) + n_8 - \bar{n}_{\text{net},8} x_8 \right) \hspace{1cm} (34b)$$

$$\frac{dT_8^{\text{ABS}}}{dt} = \frac{H_{S23} (T_8^{\text{ABS}} - T_8^{\text{ABS}}) + Q_8^{\text{ABS}} + Q_8 - \bar{n}_{\text{net},8} H_8}{M_8^{\text{ABS}} C_8^{\text{ABS}}} \hspace{1cm} (34c)$$

Since only liquid phase dynamics is considered, the mass flow rate, the compositions, and the temperature of an exit vapor stream from each stage are calculated using steady-state mass, component, and energy balances around the vapor phase at each stage. There are a total of 72 state variables including the liquid hold-up, the compositions, and the liquid temperature at each stage and at the base. The maximum allowable liquid volume in the absorber is $v_{\text{ABS}} = 8.5$ m$^3$.

**Acetic Acid Hold-up Tank.** The acetic acid tank is used to mix the bottom product stream from the azetropore distillation column and the HAc feed stream. The acetic acid hold-up tank allows for a better control of the liquid recycle loop to prevent the snowballing effect. There are four state variables, which are the liquid hold-up, molar fractions of VAc and HAc, and the liquid temperature. The dynamic equations are as follows:

$$\frac{d\bar{n}^{\text{TK}}}{dt} = (f_{S24} + f_{S25} - \bar{T} - f_{S22}) \hspace{1cm} (35)$$

$$\frac{d\bar{x}^{\text{TK}}}{dt} = \frac{1}{M^{\text{TK}}} \left( f_{S24} (\bar{x}_{S24} - \bar{x}^{\text{TK}}) + f_{S25} (\bar{x}_{S25} - \bar{x}^{\text{TK}}) \right) \hspace{1cm} (36)$$

$$\frac{d\bar{T}^{\text{TK}}}{dt} = \frac{1}{M^{\text{TK}} C^{\text{TK}}} \left( H_{S24} - H^{\text{TK}} + f_{S25} (H_{S25} - H^{\text{TK}}) \right) \hspace{1cm} (37)$$

The maximum allowable liquid volume in the tank is $v_{\text{TK}}^{\text{max}} = 2.83$ m$^3$.

**Compressor, Heat Exchanger, Heaters, and Coolers.** The dynamics of the compressor, heat exchanger, heaters, and coolers are assumed to be adequately represented by first-order systems of the following form:

$$\frac{dx}{dt} = \frac{\bar{x} - x}{\tau} \hspace{1cm} (38)$$

where $\bar{x}$ is the steady-state computed by the steady-state energy balance, $x$ is a state variable, and $\tau$ is a time constant.

**Compressor.** Isentropic compression is assumed to calculate the outlet temperature and pressure of the compressor. The actual work input ($W_{\text{C,COM}}$) to the compressor is a manipulated input. The mean specific heat capacity ($C_{\text{COM}}$) is used and assumed to be linearly dependent on the log-mean temperature of the inlet and outlet stream. Two state variables are present in the compressor: the outlet temperature and pressure. It is assumed that a 5 min time constant can be used to describe the dynamics of the compressor.

**Heat Exchanger.** The NTU-Effectiveness method based on the single-tube heat exchanger with counterflow is used to calculate the steady-state heat exchanger exit temperature. The overall heat transfer coefficient $(U_{\text{HX}})$ is correlated according to the nominal overall heat transfer coefficient, and the ratio of the flow rates to the nominal flow rates to the power of 0.8, as follows:

$$U_{\text{HX}} = \frac{U_{\text{ref}}}{2} \left( \frac{f_{S34} M_{W_{S34}}}{m_{\text{cold,ref}}}^{0.8} + \frac{f_{S9} M_{W_{S9}}}{m_{\text{hot,ref}}}^{0.8} \right) \hspace{1cm} (39)$$

where the reference overall heat transfer coefficient is $U_{\text{ref}} = 113.33$ kcal/(min °C), the reference cold flow rate is $m_{\text{cold,ref}} = 498.952$ kg/min, and the reference hot flow rate is $m_{\text{hot,ref}} = 589.67$ kg/min. The exit temperatures for the cold stream and the hot stream are the two state variables in the heat exchanger. A 5 min time constant is introduced to describe the dynamics.

**Coolers and Heaters.** There are three coolers and two heaters in the process. A 2 min time constant is used to describe their dynamics. The exit temperature is a state variable and the heat input is a manipulated input in each of these units.

**Nonlinear Dynamic Model of the Vinyl Acetate Process.** The nonlinear dynamic model of the vinyl acetate process consists of 179 ODEs, 351 algebraic equations, and 23 inequality process constraints. The process constraints include the liquid hold-up volume in vessels, the oxygen composition in the gas loop, the inlet temperature of the reactor, the temperature in the reactor, the hot-side outlet temperature of the heat exchanger, and the pressure drop in the gas loop. In short, the nonlinear dynamic model of the vinyl acetate process network can be described by the following state-space model:

$$\dot{x}(t) = f(x(t), u_i(t), ..., u_{20}(t)) \hspace{1cm} (40a)$$

$$0 = g(x(t), u_i(t), ..., u_{20}(t)) \hspace{1cm} (40b)$$

$$0 \leq h(x(t), u_i(t), ..., u_{20}(t)) \hspace{1cm} (40c)$$

where $x(t) \in R^n$ denotes the vector of state variables of the system and $u_i(t) \in R, i = 1, ..., 20$ denotes the ith control (manipulated) input, respectively. In the nonlinear model of eq 40, the vector function $f$ is the right-hand-side of the nonlinear dynamic equations, the vector function $g$ is the family of...
In this work, we assume that the full system state $(x_t, u_t)$ is fixed along with the available range for each input and steady-state values $u_s$. The steady-state that corresponds to the steady-state input $u_s$ is denoted as $x_s$. We note that in our model seven of the inputs are fixed to specified values.

**MODEL PREDICTIVE CONTROL FORMULATIONS**

In this section, we initially present a novel economic measure which is used in the formulation of the LEMPC and used to assess the economic performance of the closed-loop system under LMPC. Next, we provide a detailed description of the controller synthesis. Subsequently, we introduce the formulations of the Lyapunov-based model predictive control and Lyapunov-based economic model predictive control schemes formulated for the vinyl acetate process network.

**Notation.** The operator $|\cdot|$ is used to denote the Euclidean norm of a vector. The symbol $\Omega_u$ is used to denote the set $\Omega_u := \{x \in \mathbb{R}^n: V(x) \leq r\}$ where $V$ is a scalar function. The symbol $\text{diag}(v)$ denotes a matrix whose diagonal elements are the elements of a vector $v$ and all the other elements are zeros. The superscript $v^T$ denotes the transpose of a vector $v$.

**Economic Measure.** In this work, we aim to maximize the overall vinyl acetate production in the azoetric distillation overhead stream (S26) so an economic measure is chosen to account for the reaction selectivity in the reactor and the separation quality in the separator and the absorber as follows:

$$L(x, u) = A_1 \tilde{x}_{\text{VAc},10} + A_2 \tilde{x}_{\text{CO}_2,10} + A_3 \tilde{x}_{\text{VAc},h} + A_4 \tilde{x}_{\text{VAc},b}$$

(41)

where $L(x,u)$ is the economic measure, $A := [A_1 \ A_2 \ A_3] = [30 \ 1000 \ 1000]$ are the constant weighting coefficients which are chosen such that each term in the economic measure is of the same order of magnitude, $\tilde{x}_{\text{VAc},10}$ and $\tilde{x}_{\text{CO}_2,10}$ are the VAc and CO$_2$ concentrations at the 10th section of the reactor, and $\tilde{x}_{\text{VAc},h}$ and $\tilde{x}_{\text{VAc},b}$ are the vinyl acetate liquid molar fractions in the separator and the absorber base, respectively. The first term of the measure describes reaction selectivity of VAc with respect to CO$_2$ in the reactor. The second term and the third term account for VAc recovery in the separator and the absorber.

**Remark 1.** In this work, the weighting coefficients have been chosen such that each term in the economic cost is significant. In practice, these coefficients would be chosen based on process objectives, operating costs, and material prices.

**Controller Synthesis.** In the process network, the heater (H1) prior to the reactor affects the inlet stream temperature which, in turn, affects the reaction rates and the reaction selectivity. The cooler (C3) prior to the separator determines the quality of flashing streams. The heater (H2) prior to the absorber and the side coolers (C4) and (C5) account for the VAc recovery. Hence, these five inputs have direct influence on the economic measure and on closed-loop economic performance. Therefore, we propose a control architecture which comprises of LMPC or LEMPC regulating the inputs of the heaters and coolers, a set of eight independent PI controllers regulating eight inputs to maintain closed-loop stability, and seven inputs that are fixed. Figure 2 shows the control architecture.

**Table 4. Input Constraints and Steady-State Values**

<table>
<thead>
<tr>
<th>manipulated input ($u$)</th>
<th>loop</th>
<th>input number</th>
<th>range</th>
<th>steady-state ($u_s$)</th>
<th>unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_{\text{MPC}}^{\text{H1}}$</td>
<td>MPC</td>
<td>1</td>
<td>0–50000</td>
<td>5078.69 kcal/min</td>
<td></td>
</tr>
<tr>
<td>$Q_{\text{MPC}}^{\text{H2}}$</td>
<td>MPC</td>
<td>2</td>
<td>10000–50000</td>
<td>1461.14 kcal/min</td>
<td></td>
</tr>
<tr>
<td>$Q_{\text{MPC}}^{\text{C1}}$</td>
<td>MPC</td>
<td>3</td>
<td>0–30000</td>
<td>15491.57 kcal/min</td>
<td></td>
</tr>
<tr>
<td>$Q_{\text{MPC}}^{\text{C2}}$</td>
<td>MPC</td>
<td>4</td>
<td>0–30000</td>
<td>7250.42 kcal/min</td>
<td></td>
</tr>
<tr>
<td>$Q_{\text{MPC}}^{\text{C3}}$</td>
<td>MPC</td>
<td>5</td>
<td>0–5000</td>
<td>1881.2 kcal/min</td>
<td></td>
</tr>
<tr>
<td>$f_{\text{S4}}$</td>
<td>PI</td>
<td>6</td>
<td>8–15</td>
<td>12113.916 kmol/min</td>
<td></td>
</tr>
<tr>
<td>$f_{\text{S5}}$</td>
<td>PI</td>
<td>7</td>
<td>0–2.268</td>
<td>0.47744 kmol/min</td>
<td></td>
</tr>
<tr>
<td>$f_{\text{S6}}$</td>
<td>PI</td>
<td>8</td>
<td>0–8</td>
<td>2.73964 kmol/min</td>
<td></td>
</tr>
<tr>
<td>$f_{\text{S7}}$</td>
<td>PI</td>
<td>9</td>
<td>0–4.536</td>
<td>1.20871 kmol/min</td>
<td></td>
</tr>
<tr>
<td>$f_{\text{S8}}$</td>
<td>PI</td>
<td>10</td>
<td>0–4.536</td>
<td>0.74435 kmol/min</td>
<td></td>
</tr>
<tr>
<td>$Q_{\text{MPC}}^{\text{H1}}$</td>
<td>PI</td>
<td>11</td>
<td>0–143340</td>
<td>16933.247 kcal/min</td>
<td></td>
</tr>
<tr>
<td>$T_{\text{toolax}}$</td>
<td>PI</td>
<td>12</td>
<td>110–150</td>
<td>133.46 deg C</td>
<td></td>
</tr>
<tr>
<td>$W_{\text{VAc}}$</td>
<td>PI</td>
<td>13</td>
<td>0–1000</td>
<td>275.64 kcal/min</td>
<td></td>
</tr>
<tr>
<td>$T_{\text{toolax}}$</td>
<td>fixed</td>
<td>14</td>
<td>0–80</td>
<td>37.72 deg C</td>
<td></td>
</tr>
<tr>
<td>$f_{\text{S1}}$</td>
<td>fixed</td>
<td>15</td>
<td>0–7.56</td>
<td>0.905 kmol/min</td>
<td></td>
</tr>
<tr>
<td>$f_{\text{S18}}$</td>
<td>fixed</td>
<td>16</td>
<td>0–50</td>
<td>15.35 kmol/min</td>
<td></td>
</tr>
<tr>
<td>$f_{\text{S22}}$</td>
<td>fixed</td>
<td>17</td>
<td>0–7.56</td>
<td>0.8125 kmol/min</td>
<td></td>
</tr>
<tr>
<td>$f_{\text{S3}}$</td>
<td>fixed</td>
<td>18</td>
<td>0–4.536</td>
<td>2.1924 kmol/min</td>
<td></td>
</tr>
<tr>
<td>$f_{\text{S27}}$</td>
<td>fixed</td>
<td>19</td>
<td>0–22.68</td>
<td>6.556 kmol/min</td>
<td></td>
</tr>
<tr>
<td>$f_{\text{S30}}$</td>
<td>fixed</td>
<td>20</td>
<td>0–0.02268</td>
<td>0.00318 kmol/min</td>
<td></td>
</tr>
</tbody>
</table>

A summary of which manipulated inputs are controlled by MPC or PI or are fixed along with the available control energy for each manipulated input and steady-state values $u_s$ are given in Table 4. In this work, we assume that the full system state $x$ is measured at every sampling period $(\Delta)$. State measurements are sent to the PI controllers at synchronous time instants $t_q = q\Delta_{sp}, q = 0, 1, \ldots$ and sent to the LEMPC or LMPC at
synchronous time instants \( t_k = k\Delta, \) \( k = 0, 1, \ldots \). Taking into account closed-loop stability consideration, the sampling times for the LMPC/LEMPC and the set of PI controllers are chosen to be \( \Delta p = \Delta \) and \( \Delta = 10\Delta \), respectively, where \( \Delta = 0.001 \text{ min.} \)

The manipulated input vector computed by the PI controllers can be expressed as follows:

\[
\begin{align*}
    u_{p_{i,i}} = K_c(i\eta - \hat{\eta}_i^n) + \frac{K_{nc}}{\tau_i} \int_0^t (\eta - \hat{\eta}_i^n) \, dt' + u_{x_i},
\end{align*}
\]

where \( u_{p_{i}} \) is the input vector of manipulated inputs on the set of PI controllers given by \( u_{p_{i}} = [u_{p_{1,i}} \ldots u_{p_{13,i}}] = [f_4 \, f_{55} \, f_{53} \, f_{55} \, f_{53} \, f_{55} \, f_{53} \, f_{55} \, f_{53} \, f_{55} \, f_{53} \, f_{55} \, f_{53} \, f_{55}] \), \( \eta \) is the vector of the controlled outputs given by \( \eta^T = [Q_{\text{PI}} \, R_{\text{PI}} \, P_{\text{PI}} \, P_{\text{PI}} \, P_{\text{PI}} \, P_{\text{PI}} \, P_{\text{PI}}] \), \( \hat{\eta}_i^n \) is the set-point vector, \( K_c \) is the vector of the integral time constants, \( \tau_i \) is the vector of the integral time constants, \( \tau_i = [\tau_{1f} \, \tau_{7f} \ldots \tau_{13f}] \) and \( t_i \) is the vector of the sampling times.

The parameters for the PI controllers along with the tuning methods used to design these parameters are listed in the Appendix.

**Lyapunov-Based Controller.** In the LMPC and LEMPAC designs proposed in the literature, \( \text{eq} 42 \) the nonlinear system is assumed to be stabilizable by assuming the existence of a Lyapunov-based controller \( \hat{h}(x)^T = [\hat{h}_i(x) \ldots \hat{h}_n(x)] \) that can render the steady-state of the nonlinear system asymptotically stable under continuous implementation while satisfying the input constraints for all the states \( x \) inside a given stability region. The Lyapunov-based controller \( \hat{h}(x) \) used in the vinyl acetate process network is another set of PI controllers, namely

\[
\hat{h}(x)^T = \hat{u}_P^T = [\hat{u}_{p_{1,i}} \ldots \hat{u}_{p_{5,i}}]
\]

where \( \hat{u}_P \) uses the formulation of eq 42, \( \hat{u}_P^T = [Q_{\text{H}1} \, Q_{\text{H}2} \, \ldots \, Q_{\text{C}G} \, \ldots \, Q_{\text{C}G}] \) and the set-point vector \( (\hat{\eta}_i^n)^T = [\hat{\eta}_{1f} \, \hat{\eta}_{7f} \ldots \hat{\eta}_{13f}] \), \( \hat{\eta}_i^n \) is the set-point vector, \( K_c \) is the vector of the proportional gains, \( \tau_i \) is the vector of the integral time constants, \( \tau_i = [\tau_{1f} \, \tau_{7f} \ldots \tau_{13f}] \) and \( t_i \) is the vector of the sampling times. The parameters for the PI controllers along with the tuning methods used to design these parameters are listed in the Appendix.

**Remark 2.** Explicit stabilizing control laws that provide explicitly defined regions of attraction for the closed-loop system have been developed using Lyapunov techniques for various classes of nonlinear systems; the reader may refer to refs 28 and 30–32 for results in this area.

**Remark 3.** We note that the Lyapunov-based controller is typically formulated as a static controller as in refs 9 and 11. Even though PI controllers are dynamic controllers, the set of PI controllers with little integral action can be considered as a Lyapunov-based controller as long as the independent PI control loops can stabilize the process network.

**Lyapunov-Based Model Predictive Control.** LMPC is capable of computing optimal control inputs while accounting for input and state constraints and ensuring the stability of the closed-loop system. The LMPC design follows the formulation of our previous works \( ^{9,11} \) and takes into account the nonlinear system of eq 40 (where, without any loss of generality, \( x_i = 0 \) is the stabilizing steady-state), as follows:

\[
\min_{u_{i}\in [-\infty,\infty]} \int_{t_k}^{t_{k+N}} \left[ \dot{x}^T(t) \hat{Q} \dot{x}(t) + u^T(t) \hat{R} u(t) \right] \, dt
\]

\[
\text{s.t.} \quad \dot{x}(t) = f(x(t), u_1(t), ..., u_{120}(t))
\]

\[
0 = g(x(t), u_1(t), ..., u_{120}(t)), \quad \forall t \in [t_k, t_{k+N}]
\]

\[
0 \leq h(x(t), u_1(t), ..., u_{120}(t)), \quad \forall t \in [t_k, t_{k+N}]
\]

\[
0 \leq u_i(t) \in U_i, \quad i = 1, ..., 13, \forall t \in [t_k, t_{k+N}]
\]

\[
u_{i}(t) = u_{i\text{ fixed}}, \quad i = 6, ..., 13, \forall t \in [t_k, t_{k+N}]
\]

\[
\dot{x}(t_k) = x(t_k)
\]

\[
\frac{dV(x)}{dx} = f(x(t_k), u_1(t_k), ..., u_{120}(t_k)), \quad u_{120}(t_k)
\]

\[
\leq \frac{dV(x)}{dx} = f(x(t_k), \hat{h}_i(x(t_k)), ..., \hat{h}_n(x(t_k)), \hat{u}_{p_{i,6}}(t_k), \hat{u}_{p_{1,6}}(t_k), \hat{u}_{p_{2,6}}(t_k), \hat{u}_{p_{3,6}}(t_k), \hat{u}_{p_{4,6}}(t_k), \hat{u}_{p_{5,6}}(t_k)), \quad u_{120}(t_k)
\]

where \( S(\Delta) \) is the family of piecewise constant functions with sampling time \( \Delta \), \( N \) is the prediction horizon, \( \hat{Q} \) and \( \hat{R} \) are strictly positive definite weight matrices, \( \hat{h} \) is the predicted state trajectory of the nominal system with inputs \( 1, ..., 5 \) computed by the LMPC, \( 6, ..., 13 \) computed by the PI controllers, and fixed inputs \( u_i^\text{fixed} \) for inputs \( 14, ..., 20, \) and initial state \( x(t_k) \). The weighting matrices \( \hat{Q} \) and \( \hat{R} \) are listed in the Appendix.

The optimal solution to this optimization problem is denoted by \( u_i^*(\hat{h}_i(t_k)), \) \( i = 1, ..., 5 \), which is defined for \( \hat{h} \in [\hat{h}_1, \hat{h}_{13}] \). The LMPC is implemented in a receding horizon fashion; namely, the optimization problem of eq 45 is solved along the prediction horizon at each sampling time and \( u_i^*(\hat{h}_i(t_k)), \) \( i = 1, ..., 5 \), are applied to the closed-loop system for \( i \in [\hat{h}_1, \hat{h}_{13}] \). Equation 45a defines a quadratic cost index penalizing state and manipulated input deviation from an operating steady-state
which should be minimized. Equations 45b and 45c are used to predict the future evolution of the nominal model of the system of eq 40. Equation 45d represents the process constraints that must be satisfied along the prediction horizon. Equation 45e accounts for the constraints on the available control energy computed by LMPC. Equations 45f and 45g account for the manipulated inputs regulated by the PI controllers and the manipulated inputs that are fixed, respectively. Equation 45h provides the initial state for the predicted state trajectories which is a measurement of the actual system state. The constraint of eq 45i ensures that the time derivative of the Lyapunov function at the initial sampling time (first move) of LMPC is less than or equal to the time derivative of the Lyapunov function obtained if the Lyapunov-based controller $\dot{h}(x)$ is implemented in the closed-loop system in a sample-and-hold fashion. Through this constraint, the LMPC inherits the stability and robustness properties of the Lyapunov-based controller (the reader may refer to refs 9 and 10 for more discussion and analysis on this issue). The control actions that are applied to the closed-loop system under the LMPC are defined as follows:

$$u_i(t) = u_i^s(t_{t_i}), \quad i = 1, ..., 5, \forall \ t \in [t_i, t_{i+1})$$

Lyapunov-Based Economic Model Predictive Control.

Optimization of a chemical process operation with respect to general economic considerations has received extensive attention. Within process control, one control scheme that addresses both dynamic economic optimization and process control is economic model predictive control. In our previous work,$^{17}$ we introduced an economic model predictive control scheme designed via Lyapunov techniques for nonlinear systems. The formulation of the LEMPC applied to the vinyl acetate process network of eq 40 is:

Figure 3. Trajectory of logarithm of the Lyapunov function $V(x)$ under LMPC.

Figure 4. Trajectories of the manipulated inputs for heaters and coolers under LEMPC.
where $S(\Delta)$ is the family of piecewise constant functions with sampling time $\Delta$, $N$ is the prediction horizon, $L(\tilde{x}(\tilde{r}), u_1(t), ..., u_m(t))$ is the economic measure which defines the objective function, $\tilde{x}$ is the predicted state trajectory of the nominal system with inputs $1, ..., 5$ computed by the LEMPC, $6, ..., 13$ computed by the PI controllers, and fixed inputs $u_{i_{\text{fixed}}}$ for inputs $i = 14, ..., 20$, and initial state $x(t_k)$. The optimal solution to this optimization problem is denoted by $u^*(\tilde{r}|t_k)$ which is defined for $\tilde{r} \in [t_k, t_{k+N})$.

Figure 5. Closed-loop state trajectories under LEMPC of the heaters and coolers.
operates the closed-loop system in a possible time-varying fashion while maintaining the predicted state along the prediction horizon in a predefined set $\Omega_\rho$ to optimize the economic cost function. The second operation mode is realized while the constraint of eq 46j is active. The second operation mode corresponds to operation in which the process is driven by the LEMPC to a steady-state. We note that $\Omega_\rho$, which is a level set of the Lyapunov function $V(x)$, is used to estimate the stability region (e.g., region of attraction) of the closed-loop system under the Lyapunov-based controller $\hat{h}(x)$, $\Omega_\rho$ is a subset of $\Omega_\rho$ that defines the safe set of operation in which the LEMPC, operating in mode 1, may optimize the economic objective freely, and $t'$ is the switching time between mode 1 and mode 2 (e.g., $t'$ can be an integer multiple of the sampling time of the MPC). The switching time $t'$ may be chosen to be arbitrarily large such that the process network is always operated under the LEMPC operating in mode 1 or it may be chosen to manage the trade-off between dynamically optimal process operation and excessive wear on control actuators required to operate a process in a time-varying fashion. If the state leaves the set $\Omega_\rho$, the operation mode of the LEMPC switches to mode 2 operation.

Even though the LEMPC is formulated with an economic cost function to address both process control and dynamic economic optimization of a nonlinear system, no guarantee can be made that the closed-loop economic performance under LEMPC operating mode 1 (possibly leading to time-varying operation) will be better compared to the closed-loop economic performance under LMPC. This issue will be addressed in the subsequent section. In contrast, Heidarinejad et al. recently proposed LEMPC algorithms to ensure improved economic performance under LEMPC where an auxiliary LMPC was used to formulate constraints in the LEMPC optimization problem that guarantee that the closed-loop economic performance with LEMPC be at least as good as LMPC while ensuring the LEMPC uses the same amount of control energy as the LMPC (we refer the reader to ref 27 for detailed results).

Remark 4. The region $\Omega_\rho$ is chosen such that the LEMPC optimization problem of eq 46 remains feasible for any $x(t) \in \Omega_\rho$, $t \geq 0$. Specifically, if $x(t) \in \Omega_\rho \setminus \Omega_\rho$, the LEMPC operates in mode 2 to force the process state to $\Omega_\rho$. Once the process state has converged to the set $\Omega_\rho$, and $t \leq t'$, the LEMPC operates in mode 1. The process state may come out of $\Omega_\rho$ over one sampling period while the LEMPC is operating in mode 1, but $\Omega_\rho$ is chosen to be sufficiently small such that the process state will not come out of $\Omega_\rho$ before the next sampling period. At the next sampling period, the LEMPC operates in mode 2 to force the process state back to $\Omega_\rho$. Therefore, the LEMPC optimization problem always remains feasible for any $x(t) \in \Omega_\rho$, see ref 17 for a detailed proof of this issue.

Remark 5. If the switching time $t' = 0$, the LEMPC always operates in mode 2 and will force the process state to converge to a small neighborhood of the steady-state.

Figure 6. Transient trajectories of the manipulated inputs for heaters and coolers under LEMPC.
APPLICATION OF MPC TO THE VINYL ACETATE PROCESS

In this section, we implement the two model predictive control structures: the LMPC of eq 45 and the LEMPC of eq 46 on the vinyl acetate process network. The simulations are conducted using JAVA programming environment with an Intel Core 2 Quad Q6600 computer. The explicit Euler integration method is used to integrate the nonlinear dynamic process model of eq 40a with a fixed integration step size equal to 0.001 min. The integration step size is chosen to ensure stable numerical integration and sufficient accuracy of the numeric integration. The open source interior point optimizer IPOPT\textsuperscript{33} is used to

Figure 7. Transient closed-loop state trajectories under LEMPC of the heaters and coolers.

Figure 8. State trajectories of the temperature of the cooler prior to the separator (top plot) and state trajectories of the vapor phase vinyl acetate composition in the separator (bottom plot) with LMPC (solid line) and with LEMPC (dashed line).
solve the optimization problems. The prediction horizon of $N = 5$ is chosen for the LMPC and the LEMPC. The first optimized control inputs computed by the optimization problems are applied to the process every sampling time ($\Delta$) following a receding horizon scheme.

In this work, we initially demonstrate that LMPC is capable of driving the closed-loop system to the unstable steady-state that corresponds to the steady-state input listed in Table 4 from an initial state. The steady-state and steady-state input denoted as $x_s$, $u_s$, respectively, have been chosen to satisfy the process (state and input) constraints. The evolution of the Lyapunov function of the closed-loop process network over a 300 min simulation is shown in Figure 3. Since the magnitude of the Lyapunov function is initially large, the Lyapunov function is
plotted on a semilogarithm scale in order to observe the descending trajectory of the Lyapunov function throughout the simulation.

The region $\Omega_{\rho}$ is approximately calculated by extensive closed-loop simulations under LMPC by initializing the process network at different initial states. From these simulations, the region $\Omega_{\rho}$ is defined as the level set $\Omega_{\rho}$ with $\rho = 5600$ which has been taken as the largest level set of the Lyapunov function where the Lyapunov function under LMPC is decreasing over each sampling period for any initial state starting inside $\Omega_{\rho}$. Subsequently, we define the parameter $\rho$ through a series of closed-loop simulations under LEMPC operating in mode 1 only. The region $\Omega_{\rho_{\tilde{\rho}}}$ is the subset of the stability region $\Omega_{\rho}$ used in the formulation of LEMPC of eq 46 (i.e., the set where the process network is allowed to evolve when LEMPC is operating in mode 1). The procedure for determining $\rho$ is as follows: starting from $\rho = 5600$, $\rho$ is decreased until the LEMPC maintains stability of the process network (i.e., boundedness of the state inside of $\Omega_{\rho_{\tilde{\rho}}}$). Through this procedure, the parameter $\rho$ used in the formulation of the LEMPC is $\rho = 3275$.

The LEMPC, operating in mode 1 only, is applied to operate the process network in a possible time-varying (transient) manner as to optimize the economic cost while maintaining the process states inside $\Omega_{\rho_{\tilde{\rho}}}$. The Lyapunov-based constraint of the LEMPC (eq 46i) is formulated with the Lyapunov function based on the steady-state $x_s$ and the parameter $\rho = 3275$. The process network under LEMPC is initialized at the same state as the closed-loop system under LMPC demonstrated in Figure 3. The closed-loop input and state trajectories under LEMPC over the entire 300 min simulation are shown in Figures 4 and 5, respectively. The transient input and state profiles are shown over the first 10 min of the simulation in Figures 6 and 7, respectively. From Figure 4, the LEMPC operates the process network in a time-varying manner (continuously changing control actions being computed for manipulated inputs on LEMPC). However, since the input trajectories change at a high frequency to maintain the process as close as possible to an economically optimal steady-state, the observed behavior of the closed-loop process state is similar to steady-state operation (Figure 5). The high frequency fluctuations (appearing as chattering in the plots) in the computed input profiles by the LEMPC occur because the LEMPC is formulated with an economic cost that does not explicitly depend on the manipulated inputs and the LEMPC (operating in mode 1) does not include a constraint that imposes convergence to a steady-state (this chattering behavior can be eliminated if LEMPC mode 2 is implemented and this has been verified in the present case via simulations).

Compared to LMPC that forces the closed-loop process network to the steady-state $x_s$, LEMPC significantly decreases the duty of the cooler C3 which results in the low recovery of VAc in the separator as shown in Figure 8. Consequently, the majority of VAc from the reactor is recovered in the absorber. Figure 9 shows the temperature and molar fraction of
VAc profiles of the absorber at each stage at the end of simulation under LMPC and LEMPC and points out that the evolution of the closed-loop system under LMPC is different from the evolution of the closed-loop system under LEMPC.

Since the closed-loop process network under LEMPC evolves like steady-state operation, we compare the closed-loop economic performance of the process network under LEMPC with the closed-loop economic performance of the process network under LMPC formulated with the operating steady-state of the LEMPC denoted as $x^*_s$ with corresponding steady-state input $u^*_s$. The steady-state $x^*_s$ is defined from the closed-loop simulation of the process network under LEMPC. Since the control actions computed by the LEMPC and the corresponding state profiles have significant fluctuations as displayed in Figures 4 and 5, $x^*_s$ and $u^*_s$ are computed by averaging out the profiles of the state and inputs over the last 10 min of the simulation to determine the operating steady-state under LMPC. In this manner, the RTO layer (upper-layer economic steady-state optimization) for the closed-loop process network under LMPC is the LEMPC that provides the optimal steady-state by averaging the state profiles. To compare the closed-loop economic performance of the process network under LMPC and LEMPC, we initialize the process network at the same initial state and define the average total economic measure ($J_e$) over two 300 min closed-loop simulations as

$$J_e = \frac{1}{f} \sum_{k=0}^{f} L(t_k)$$

where $t_k = k\Delta$, $k = 0, 1, ..., f$.

Figures 10 and 11 show the closed-loop input and state trajectories of the process network under LMPC over the entire 300 min simulation; meanwhile, Figures 12 and 13 show the closed-loop input and state trajectories over the first 10 min. Figure 14 shows the trajectories of the economic measure under LEMPC and LMPC, in which the average economic performance of the closed-loop system under LEMPC (576.6) is not better than the average economic performance of the closed-loop system under LMPC (576.8). Indeed, the formulation of LEMPC (operating in mode 1 only) utilized in this work does not ensure improved economic performance of LEMPC over LMPC. As observed in Figure 4 and Figure 10, LEMPC, operating in mode 1, allows for unfavorable and impractical trajectories of control inputs compared to the trajectories of control inputs computed by LMPC. In addition, LEMPC requires significantly larger evaluation time than LMPC (on the order of days).

**When is EMPC Needed?** In this work, we applied LMPC and LEMPC to a vinyl acetate process network. The closed-loop economic performance of two simulations under LMPC and LEMPC were similar. This raises an important question when considering the application of EMPC to a chemical process network: When is EMPC needed? With large-scale
process networks such as the vinyl acetate process network, operating process networks in a time-varying fashion as to optimize economic measures while meeting process constraints is difficult because the dynamics of each unit are coupled to the dynamics of the other units through the recycle streams. While the topic of guaranteed closed-loop economic performance has been addressed in ref 27, if we apply the LEMPC introduced in ref 27 to this particular large-scale chemical process network, the LEMPC would compute control actions that would approach the auxiliary LMPC. The computational requirement for solving the LEMPC and LMPC problems in such control framework would not likely be offset by the little improvement in closed-loop economic performance. Therefore, the best operating strategy for large-scale chemical process networks with coupling of process dynamics would likely be operating at the economically optimal steady-state. Since process networks are typically operated continuously for long periods of time, the objective of the controller formulated for steady-state operation is to drive and regulate the process network to a steady-state and the effect of the transient state becomes insignificant on closed-loop economic performance. Hence, the difference in economic closed-loop performance of the process network under LMPC formulated with a conventional quadratic cost and under LEMPC formulated with the economic cost function, but operating in mode 2, will also be insignificant if operation can be maintained at the steady-state (bound on the disturbances is small).

If there exists any time-varying operating strategy that is better than operating at the economically optimal steady-state, then one would have to increase the prediction horizon of the LEMPC in an attempt to improve closed-loop economic performance. The computational cost of increasing the horizon

Figure 13. Transient closed-loop state trajectories under LMPC of the heaters and coolers.

Figure 14. Trajectories of the economic measure under LMPC (solid line) and under LEMPC (dashed line).
may make, however, EMPC impractical to implement. One may consider the closed-loop economic performance of the process network under the other formulations of EMPC in the literature like, for instance, the EMPC studied in refs 15 and 19 where a terminal constraint is used in the formulation instead of the Lyapunov-based constraint of eq 46i in LEMPC. However, the Lyapunov-based constraint allows the LEMPC to operate the system in a time-varying fashion while maintaining the state inside a subset of the estimated closed-loop stability region as opposed to the EMPC with terminal constraint which allows the EMPC to operate the system in a time-varying fashion as long as the system is forced to the operating steady-state at the end of the prediction horizon. Therefore, the terminal constraint is, in some sense, more restrictive in terms of the available time-varying operating trajectories. For this reason, it is also unlikely that using EMPC with a terminal constraint will provide significant economic closed-loop performance improvement in this example compared to MPC formulated with a conventional quadratic cost.

The main advantage of EMPC is when it operates a process in a time-varying (transient) fashion to yield better closed-loop economic performance. Clearly, some processes do not benefit from time-varying operation based on the intrinsic properties of the dynamics. However, these systems may still benefit from application of EMPC if the economic cost function and constraints become time-varying (e.g., the weights $A_1$, $A_2$, and $A_3$ of the economic cost become time-varying). Time-varying economic cost and constraints allows LEMPC to fully manipulate process capacities to meet the continuously changing market demand, feedstock variability and energy cost.

## CONCLUSIONS

In this work, two Lyapunov-based MPC schemes are developed and applied to a large-scale chemical process network used in the production of vinyl acetate. The nonlinear dynamic process network consists of 179 nonlinear differential equations and 13 manipulated inputs and is composed of process units such as a vaporizer, a separator, a plug-flow reactor, a gas–liquid absorber, a process-to-process heat exchanger, and heaters/coolers. Specifically, we propose an economic measure accounting for the reaction selectivity in the reactor and the separation quality of vinyl acetate in the separator and the absorber. Subsequently, a novel control architecture which comprises of a LMPC/LEMPC acting to regulate five manipulated inputs which directly influence in the economic measure and a set of PI controllers acting to regulate the other manipulated inputs to maintain closed-loop stability is applied to the process network. The economic performance of the closed-loop system under LMPC formulated with a conventional quadratic cost function associated with the system steady-state is compared with the economic performance of the closed-loop system under LEMPC which explicitly considers an economic measure as its objective function through extensive simulations.

## APPENDIX: CONTROLLER PARAMETERS

Several closed-loop simulations were completed to tune the proportional–integral controllers. Closed-loop simulations were initially performed under proportional control loops tuned to provide sufficiently small rise times and no oscillation in the controlled outputs. Subsequently, integral action was added to eliminate the residual steady-state errors. For example,

<table>
<thead>
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<th>Table 5: Weights in $P$ Matrix</th>
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the proportional gain and integral time constant for the PI controller that regulates oxygen feed flow rate were chosen to avoid excessive overshoot such that the oxygen concentration in the gas loop is kept outside the explosive region.

The proportional gains ($K_p$), integration time constant ($\tau_i$), and set-points ($\bar{y}_{set}$) for PI controllers are

$$K_p = (10^2)-[1, 0, 1, 1, 75, 0.3, 500]$$

$$\tau_i = [80, 0.1, 350, 200, 50, 40, 4.5, 50]$$

$$\left(\bar{y}_{set}\right)_i = [2.72, 0.01256, 4.425, 1.415, 1.120, 158.5, 128]$$

The proportional gains ($\hat{K}_p$), integration time constant ($\hat{\tau}_i$), and set-points ($\hat{y}_{set}$) for the Lyapunov-based controllers are

$$\hat{K}_p = (10^2)-[2.5, 30, 10, 50, 5]$$

$$\hat{\tau}_i = [80, 220, 7.14, 90, 50, 52.6]$$

$$\left(\hat{y}_{set}\right)_i = [145, 83, 47, 32.5, 40]$$

The weights in positive definite diagonal matrix ($\hat{Q}_e$) and the positive definite diagonal matrix ($\hat{R}_e$) are

$$\hat{Q}_e = (10^{-5})\text{diag}(\bar{x}_s)^{-1}$$

$$\hat{R}_e = \text{diag}[1 \times 10^{-11} \times 1 \times 10^{-4} \times 1 \times 10^{-11} \times 1 \times 10^{-7}]$$

where $\bar{x}_s$ is the steady-state vector. The weights in $\hat{P}$ matrix and the corresponding states are listed in Table 5.

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**Notes**

The authors declare no competing financial interest.

### NOMENCLATURE

#### Roman Symbols

$a_i$ = vapor heat capacity/enthalpy coefficient for species $i$, kcal/(kg °C)

$b_i$ = liquid heat capacity/enthalpy coefficient for species $i$, kcal/(kg °C)

$q_i$ = liquid heat capacity of species $i$, kcal/(kmol °C)

$c_i$ = vapor concentration of species $i$, kmol/m³

$d_i$ = vapor heat capacity of species $i$, kcal/(kmol °C)

$C_i$ = total vapor concentration, kmol/m³

$\hat{C}_i$ = liquid heat capacity, kcal/(kmol °C)

$\hat{C}_i$ = vapor heat capacity, kcal/(kmol °C)

$\hat{c}_i$ = Antoine coefficient of species $i$

$\hat{d}_i$ = Antoine coefficient of species $i$

$\hat{c}_i$ = vapor concentration of species $i$, kmol/m³

$\hat{d}_i$ = vapor heat capacity of species $i$, kcal/(kmol °C)

$H$ = liquid phase enthalpy, kcal/kmol

$k$ = mass transfer coefficient, kmol/min

$K$ = equilibrium constant

$M$ = total moles in vapor phase, kmol

$MW_i$ = molecular weight of species $i$, kg/kmol

$\bar{M}$ = total moles in liquid phase, kmol

$\bar{n}_i$ = mass transfer rate to the liquid phase, kmol/min

$N_i$ = mass transfer rate of species $i$, kmol/min

$p_i$ = partial pressure of species $i$, psia

$P_i^{sat}$ = saturated pressure of species $i$, psia

$q$ = heat rate supplied or removed per unit volume, kcal/(m³ min)

$Q$ = heat rate supplied or removed, kcal/min

$Q_{co}$ = convective heat transfer rate due to transferring materials, kcal/min

$SpG_i$ = specific gravity of species $i$

$T$ = vapor temperature, °C

$T_{coolant}$ = coolant temperature, °C

$T_{l}$ = liquid temperature, °C

$U_{a}$ = overall heat transfer coefficient, kcal/(min °C)

$\bar{U}$ = overall heat transfer coefficient per unit volume, kcal/(m³ min °C)

$\overline{v}$ = liquid volume, m³

$\nu$ = superficial velocity, m/min

$\eta_i$ = molar volume of species $i$, L/kmol

$W_{s}$ = actual work supplied to the compressor, kcal/kmol

$\bar{x}_i$ = mole fraction of species $i$, kmol/kmol

$\bar{y}_i$ = mole fraction of species $i$, kmol/kmol

$z$ = axial coordinate along the length $m$

#### Subscripts

0 = inlet stream of the absorber or the plug-flow reactor

$i$ = component ($i = C_2H_4, O_2, HAc, VAc, CO_2, H_2O, C_2H_6$)

$\alpha$ = vapor -- liquid interface

$j$ = stream number ($j = S1, S2, ..., S34$)

$l$ = section number of the plug-flow reactor ($l = 1, 2, ..., 10$)

$max$ = maximum

$net$ = net amount

$b$ = absorber base

#### Superscripts

$f$ = vessel number ($j = VAP, RCT, HX, SEP, COM, ABS, TK, H1, H2, C3, C4, CS$)

### REFERENCES


