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Development of a Sustainability Evaluation and Control Framework for Chemical Processes

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Development of a Sustainability Evaluation and Control Framework for Chemical Processes

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Dissertation submitted to the
Benjamin M. Statler College of Engineering and Mineral Resources
At West Virginia University

In partial fulfillment of the requirements for the degree of

Doctor of Philosophy in
Chemical Engineering

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advanced process control, multi-objective optimization

Abstract

Development of a sustainability evaluation and control framework for chemical processes

Shuyun Li

Industry, government, and society have begun to shift from economic stand-alone focus to the inclusion of sustainability in the decision-making process. This shift can be attributed to the growing environmental and social awareness that makes consumers and stakeholders not only care about product quality and cost, but also products and processes that minimize the environmental impact and conserve natural resources. As a result, some progress has been made in recognizing and understanding the challenges of sustainable development, which helps evaluating the sustainability performance of a specific process/product. In particular, sustainability assessment tools and methodologies have been developed to help the future engineer and scientist with designing and optimizing the chemical processes in terms of sustainability. However, an efficient framework for the integration of advanced process control with sustainability assessment technologies is still missing.

In this dissertation, a novel process systems framework for integrating sustainability assessment, optimization, and advanced control is developed to simultaneously optimize and control chemical process systems at the optimal operating points considering efficiency, environmental, economic and energy aspects. This proposed framework bridges gaps in the literature by addressing the following challenges: 1) assessment of sustainability performance at steady-state and dynamic operations; 2) integration of sustainability indicators into a process control framework. Specifically, the proposed framework contains three main components: an integrated sustainability assessment tool, a multi-objective optimization formulation, and an

advanced control strategy. The integrated sustainability assessment tool is developed using a user-friendly automation interface that enables the communication between process simulation, pollution control units (PCUs), life cycle inventory (LCI) generation, and the U.S. EPA's GREENSCOPE (Gauging Reaction Effectiveness for the ENvironmental Sustainability of Chemistries with a Multi-Objective Process Evaluator) tool. With the sustainability indicators for chemical processes, a multi-objective optimization problem is formulated to identify the Pareto set of most sustainable operating conditions using a genetic algorithm for the decision-making step. To better balance the trade-off between economic and environmental aspects, a sustainable control strategy is implemented to drive the process to the chosen Pareto optimal solution while meeting pre-defined sustainability constraints. For the control implementation, a novel visualization method is developed to visualize the dynamic multidimensional sustainability indicators during transient.

To illustrate the effectiveness of the developed framework, two chemical processes are addressed: i) a continuous fermentation process for bio-ethanol production, for which the implemented sustainable process control scheme can improve the performance in terms of sustainability by 9.65% ~ 16.86% for different operating conditions; and ii) a biomass/coal co-gasification process for syngas production with the end goal of methanol manufacturing, for which the optimal sustainable operating condition is identified using a multi-objective optimization and then control is implemented to drive the system to the chosen setpoint, while maintaining the process within sustainable zones during transient. The performed case studies indicate that the proposed framework can be a powerful tool for assessing and controlling chemical processes for sustainability.

Dedicated to my parents, husband, and son

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Nomenclature

Variables	Definition (Units)
A_1/A_2	Exponential factors in Arrhenius equation
A_M	Area of membrane (m^2)
AI	Analysis indicator
A_T	Heat transfer area (m^2)
C_i	Concentration of component i (kg/m^3)
$C_{p,r}$	Heat capacity of the reactants ($kJ/kg/K$)
$C_{p,w}$	Heat capacity of cooling water ($kJ/kg/K$)
D_{in}	Inlet fermentor dilution rate (h^{-1})
D_j	Cooling water flow rate (h^{-1})
D_{out}	Outlet fermentor dilution rate (h^{-1})
$D_{m,in}$	Inlet membrane dilution rate (h^{-1})
$D_{m,out}$	Outlet membrane dilution rate (h^{-1})
E_{a1}/E_{a2}	Activation energy (kJ/mol)
f_i	Objective function i
F_{ij}	Normalized objective function matrix
K_S	Monod constant (kg/m^3)
K_T	Heat transfer coefficient ($kJ/h/ m^2/K$)
k_1	Empirical constant (h^{-1})
k_2	Empirical constant ($m^3/kg \cdot h$)
k_3	Empirical constant ($m^6/kg^2 \cdot h$)
m_s	Maintenance factor based on substrate ($kg/kg \cdot h$)
m_p	Maintenance factor based on product ($kg/kg \cdot h$)
M	Mixer
MW	Molecular weight ($g/mole$)
α	Membrane permeability (m/h)
P	Correction factor
r_i	Reaction rate of component i (kg/m^3)
R	Gas constant
TI	Temperature indicator
T_j	Temperature of cooling water in the jacket (K)
$T_{w,in}$	Inlet temperature of cooling water (K)
T_r	Temperature of the reactor (K)
$u(t)$	Input variables
V_F	Fermentor volume (m^3)

Variables	Definition (Units)
V_M	Membrane volume (m ³)
V_j	Cooling jacket volume (m ³)
w_i	Weighting factor i
$x(t)$	State variables
Y_{sx}	Yield factor based on substrate (kg/kg)
Y_{px}	Yield factor based on product (kg/kg)
Greek Symbols	
α_i	The number of moles of species in biomass pyrolysis
ρ_r	Reactants density (kg/m ³)
ρ_w	Cooling water density (kg/m ³)
μ	Specific growth rate (h ⁻¹)
μ_{max}	Maximum specific growth rate (h ⁻¹)
ΔH	Heat of fermentation reaction (kJ/kg)
ω_i	Mass fraction of species i in biomass pyrolysis
v_i	Weighted normalized objective matrix
Subscripts	
CO	Carbon monoxide
CO ₂	Carbon dioxide
CH ₄	Methane
H ₂	Hydrogen
H ₂ O	Water
e	Key component inside the fermentor
e ₀	Inlet key component to the fermentor
P	Product (ethanol) inside the fermentor
P ₀	Inlet product to the fermentor
PM	Product (ethanol) inside the membrane
S	Substrate inside the fermentor
S ₀	Inlet substrate to the fermentor
X	Biomass inside the fermentor
X ₀	Inlet biomass to the fermentor

Chapter 1 Introduction

Chemical industries utilize a wide range of feedstocks to manufacture petrochemical, biofuel, food, microelectronics, textile, and pharmaceutical products. At the same time, these industries exert some of the most profound impact on the environment especially due to their ubiquitous nature and the lack of environmental consciousness and efficient sustainable process systems engineering methods. Recently, this situation is changing as society, government, and industry have realized that sustainable practices can be implemented with reduced economic penalty and harm to the environment and human health. Many researchers and private/public initiatives have been working on implementing sustainable development practices. Such practices have components related to sustainable design frameworks and sustainability assessment tools. However, an efficient framework for the integration of advanced process control with sustainability assessment tools is still missing. This dissertation describes the first attempt to directly integrate sustainability assessment tools with advanced control strategies to simultaneously optimize and control chemical processes during operation.

The objective in this research is to provide a systematic framework to optimize and control chemical process systems at the optimal operating points considering efficiency, environmental, economic and energy aspects. The proposed methods in this framework focus on optimization, advanced control and life cycle inventory (LCI) analysis with the application to chemical processes. The specific aims for the proposed approach are:

- *Aim #1: Develop a sustainable control strategy for chemical processes based on a multi-objective optimization method. This sustainable control strategy includes three main steps: process and sustainability evaluation model construction, multi-objective optimization formulation, and implementation of advanced control strategy.*

- *Aim #2: Incorporate LCI analysis into the developed process systems framework. In this specific aim, the developed sustainable control strategy is implemented in reduced models to provide more accurate information on LCI data.*
- *Aim #3: Apply the developed methods to chemical processes. This aim includes two specific tasks: implementation of the developed sustainable control strategy to the selected units of the gasification process and the fermentation process.*

The main results in this dissertation correspond to: (i) development of a comprehensive sustainability tool for LCI generation and evaluation that integrates process simulation, pollution control units, LCI and sustainability indicators in this tool; (ii) integration of the developed tool with multi-objective optimization for better balancing the conflicting sustainability indicators (e.g., economic and environmental aspects); and (iii) development of a sustainable control framework to consider the sustainability performance during transients. Figure 1.1 presents a schematic of the process assessment tool and control framework for sustainability developed in this dissertation.

The contributions of this dissertation have resulted in the following products:

Peer reviewed papers:

- *Li, S., Ruiz-Mercado, G.J., and Lima, F.V., A Novel Process Systems Engineering (PSE) Scheme for Sustainability. (Chapter 7) (In preparation)*
- *Li, S., Ruiz-Mercado, G.J., and Lima, F.V., A Novel Visualization and Control Strategy for Dynamic Sustainability of Chemical Processes. (Chapter 6) (Submitted for publication)*
- *Li, S., Ruiz-Mercado, G.J., and Lima, F.V., Simulation-based Computational Framework for Sustainability Assessment and Pollution Control of Chemical Manufacturing Processes. (Chapter 4) (In preparation)*
- *Li, S., Feliachi, Y., Agbleze, S., Ruiz-Mercado, G.J., Smith, R.L., Meyer, D.E., Gonzalez, M.A. and Lima, F.V., 2018. A Process Systems Framework for Rapid Generation of Life Cycle Inventories for Pollution Control and Sustainability Evaluation. Clean Technologies and Environmental Policy, 20, pp.1543-1561. (Chapter 3)*
- *Li, S., Mirlekar, G., Ruiz-Mercado, G., J., and Lima, F., V., 2016. Development of Chemical Process Design and Control for Sustainability. Processes, 4(3). (Chapter 5)*

- Mirlekar, G., Li, S., and Lima, F., V., 2017. Design and Implementation of a Biologically Inspired Optimal Control Strategy (BIO-CS) for Chemical Process Control. *Industrial & Engineering Chemistry Research*, 56(22).
- Mirlekar, G., Gebreslassie, B.H., Li, S., Diwekar, U.M. and Lima, F.V., 2018. An Integrated Biomimetic Control Strategy with Multi-agent Optimization for Nonlinear Chemical Processes. *IFAC-PapersOnLine*, 51(18):55-60.
- Lima, F., V., Li, S., Mirlekar, G., Sridhar, L., N., and Ruiz-Mercado, G., J., 2016. Modeling and Advanced Control for Sustainable Process Systems. G. Ruiz-Mercado and H. Cabezas (eds.), Elsevier. (Invited Book Chapter)

Figure 1.1 Schematic of process assessment tool and control framework for sustainability developed in this dissertation

Oral presentations:

- Li, S., Ruiz-Mercado, G., J. and Lima, F., V., "A Multi-Layer Process Control Framework for Sustainability: Application to Biomass/Coal Co-Gasification System." In *AICHE Annual Meeting, Orlando, FL, 2019*.
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- Li, S., Agbleze S., Ruiz-Mercado, G., J. and Lima, F., V., "Simulation-Based Computational Framework for Sustainability Assessment and Life Cycle Inventory Generation." In *AICHE Annual Meeting, Pittsburgh, PA, 2018*.
- Li, S., Ruiz-Mercado, G., J. and Lima, F., V., "A Simulation-based Computational Framework for Pollution Control Units (PCU) and Estimation of Life Cycle Inventories (LCI) from Chemical Manufacturing Processes." In *ICOSSE, Cincinnati, OH, 2018*.
- Mirlekar, G., Gebreslassie, B., H., Li, S., Diwekar, U., M., and Lima, F., V., "An Integrated Biomimetic Control Strategy with Multi-agent Optimization for Nonlinear Chemical Processes." In *IFAC ADCHEM, Shenyang, China, 2018*.
- Li, S., Ruiz-Mercado, G., J. and Lima, F., V., "Process Control for Sustainability and LCI Monitoring: Application to Biomass/Coal Co-gasification System." In *AICHE Annual Meeting, Minneapolis, MN, 2017*.
- Li, S., Ruiz-Mercado, G., J. and Lima, F., V., "A Sustainable Framework for Chemical Manufacturing and for the Integration of Advanced Control with Sustainability Assessment". In *AICHE Annual Meeting, San Francisco, CA, 2016*.
- Lima, F., V., Li, S., Mirlekar, G., Sridhar, L., N., and Ruiz-Mercado, G., J., "Modeling and Advanced Control for Sustainable Process Systems". In *AICHE Annual Meeting, Salt Lake City, UT, 2015*.

The outline for the remaining chapters of this dissertation includes a literature review, which is presented first. Then, the developed tool for rapid life cycle inventory (LCI) is introduced, followed by the integrated framework for sustainability assessment. Both tools are demonstrated via a coal/biomass co-gasification process. Next, the process control for sustainability is motivated, using an example associated with a fermentation process. Then, a novel control strategy for

sustainability is proposed, including a novel visualization method for dynamic multivariable sustainability indicators and the addition of a sustainability constraint. This new framework is illustrated considering previous case studies. Finally, this novel control framework is integrated with a multi-objective optimization algorithm for a coal/biomass co-gasification process, followed by the conclusions and recommendations for future work.

Chapter 2 Literature Review

This chapter presents an overview of the reviewed literature to perform this research, including the main topics of sustainable development, life cycle inventory (LCI), sustainability assessment, pollution control units, multi-objective optimization for sustainability, and process dynamics and control for sustainability.

2.1 Sustainable Development

Chemical processes exert some of the most profound impact on the environment especially due to their ubiquitous nature and the importance of chemical products to our modern society (e.g., antibiotics, varieties of foods, energy, fuels, etc.). In recent years, environmental consciousness has been growing and has become critical in the decision-making step of industrial processes. This awareness has led to the formulation of the concept of sustainability and sustainable development in the past century^{1,2}.

In particular, sustainable development has been defined in terms of economic, environmental and social factors, such as the development of economic prosperity and the establishment of a more equitable society without depriving the future generations' standard of living³. The definition of sustainable development provides a guideline for working towards a new and better society. From the perspective of engineers, sustainability is typically considered to have environmental, economic and social dimensions that should be balanced and jointly optimized. The following engineering definition has been proposed for sustainability^{4,5}: *“for a man-made system, sustainable development is a continual improvement in one or more of the three domains of sustainability, i.e., economic, environmental and societal without causing degradation in any of the rest, either now or in the future, when compared, with quantifiable metrics, to a similar system that it is intended to replace.”* In terms

of engineering decision-making, the following definition⁶ is also important: “a sustainable process is one that constrains resource consumption and waste generation to an acceptable level, making a positive contribution to the satisfaction of human needs, and providing enduring economic value to the business enterprise.”

Despite these available definitions, there is still an ongoing debate on the characterization of sustainable development and the assessment of a process design and operation in terms of sustainability. For example, in process systems engineering, what should be the methodologies and approaches employed to obtain a sustainable process operation through design, optimization and control? In the past, there were several contributions and methods developed that focus on the minimization of the environmental impact of chemical industries. Specifically, three basic principles for green engineering, end of pipe technologies, pollution prevention, and water minimization, were introduced⁷. Recently, due to the available sustainability assessment tools and methods, many process systems engineering (PSE) methods have been developed with regards to integrating sustainability into supply chain, process design and multi-objective optimization at different scales. For example, literature on sustainable supply chain management showed the progress of taking into consideration environmental and social impacts by integrating sustainability into the developed framework^{8,9}. Along the same lines, sustainable process design and multi-objective optimization (MOO) methods have been demonstrated on a variety of applications from molecular chemistry¹⁰ to ecosystems¹¹. The detailed literature review on life cycle inventory (LCI), sustainability assessment tools, pollution control units, and PSE methods for sustainability is performed below.

2.2 Life Cycle Inventory

Life Cycle Assessment (LCA) is a standard tool for sustainable decision-making among product and process alternatives¹². Specifically, LCA takes into account mass and energy flows as well as environmental releases in the life cycle of a product, from the extraction of raw materials, production, and use to disposal/recycling¹³. LCA is increasingly applied to identify and quantify the far-reaching impacts of a process/product within its life cycle. For example, an integrated framework of LCA and pollution control/prevention can provide holistic results beyond a single process and thus help to identify those alternatives that enhance sustainability in addition to environmental protection¹⁴. Additionally, the information LCA provides can guide decision-makers (e.g., individual facility, environmental policy makers) to improve decisions in terms of sustainability. Although many contributions have been made in LCA recently, the efficient and accurate modeling of chemical processes for rapid LCI generation is still challenging. LCI, as a fundamental step of LCA, is used to quantify the energy use and raw material inputs as well as environmental releases accurately throughout a product's life cycle.

Currently, there are about 85,500 chemicals reported in the EPA's TSCA Chemical Substance Inventory¹⁵, with 9,626 of those being active in commerce¹⁶. However, in contrast, substances included in the most common LCA databases represent only a portion of these chemicals. In addition, there is a lack of consistency, transparency, and available procedures for finding reliable LCI data. Particularly, obtaining consistent LCI data is one of the most time-consuming steps of an LCA. Poor data availability and inconsistency of data may lead to unrealistic results and conclusions. Some of the existing challenges in LCI generation are due to the lack of systematic process systems (e.g., design and simulation) tools to develop

chemical process models for rapidly obtaining and analyzing LCI results at early development stages.

Typically, there are two methods to generate LCI data for a product, process or activity. The top-down approach relies on facility-level data¹⁷, while the bottom-up approach depends on process design approaches for sets of unit operations¹⁸. Some benefits of the top-down approach are that the data reported by companies can be more realistic. However, some adverse issues regarding the top-down method include large data gaps related to variations in reporting requirements, potential lack of transparency regarding the underlying process technology production rates represented in databases, allocation of facility-level emissions, material and energy inputs to a single chemical process within multi-process facilities, and limited coverage of reported substances¹⁸. In contrast, the bottom-up approach possesses some benefits and limitations as well. Some benefits include estimates of material and energy inputs for a direct LCI connectivity with the life cycle stages beyond the process of interest and process specificity. In addition, there is no need to apply allocation to the collected LCI and the inventory can be tracked down to process equipment unit allocation. However, process modeling assumptions and extensive process systems engineering (PSE) knowledge in process design and simulation are required to develop a full chemical production process and apply a bottom-up approach for LCI modeling.

As described by Subramanian and Golden¹⁹, there are several bottom-up methodologies to deal with LCI estimation data gaps/modeling: molecular structure-based neural network modeling²⁰, input–output schema for calculation of mass and energy flows using heuristics and on-site data²¹, estimating gate-to-gate life cycle using chemical process design techniques²², LCI estimation using the inherent

burden approach²³, obtaining inventory data using stoichiometric equations from technical literature, and proxy LCI data²⁴. Along the same lines, Yao and Masanet²⁵ developed generic unit operation models to estimate the life cycle energy and greenhouse gas (GHG) emissions for chemical processes at early or R&D stages. Another study conducted by U.S. EPA combined the Environmentally-Extended Input-Output (EEIO) analysis with LCA methods based on more recent economic and environmental data of U.S. goods and services²⁶. In addition, other bottom-up approaches employ computer-aided process simulation for estimating LCI data^{27–31}. The bottom-up methods in literature can be roughly grouped in two types: process flow approaches and matrix-based methods³². LCI results from process flow methods are calculated based on process balance models and thus are more accurate when compared to matrix-based methods that employ a set of simultaneous simple equations for each unit. Also, matrix-based LCI³³ can be easily applied for advanced LCI analysis with the limited application to single-output processes.

Although many software and databases have been available for LCA, obtaining reliable Life Cycle Inventory (LCI) data is still challenging. The challenges include: 1) plant data are protected by industrial parties as confidential information; 2) it requires effort and expertise to build LCI model via modeling and calculations; 3) there is a variety of unit operations and process configurations.

Current methods for generating LCI are process simulation, process engineering calculations, molecular structure models and using proxy data. Each approach possesses advantage and disadvantages and LCA practitioners should choose the suitable method based on availability of data and the technique skills. For chemical processes, process simulators (e.g., CHEMCAD³⁴, Aspen³⁵) are widely used to

generate gate-to-gate (from raw material to product) LCI data and calculate sustainability indicators. Such methods take into consideration different operating conditions and process configurations even at the early design stage, although they require process systems engineering (PSE) knowledge. The resulting sustainability results from those methods can provide guidance for the decision maker on selecting the optimal operating conditions and process design.

2.3 Sustainability Assessment

Chemical manufacturing process is recognized as one of the main contributors to natural resources consumption, environmental pollution and ecosystem degradation, although its contribution to societal needs and development is critical. It is urgent and imperative to address this paradox by developing sustainable products and processes for satisfying the needs of present and future generations. Fortunately, growing recognition of the environmental issues has prompted government, industry and individuals to apply sustainability analysis in decision-making steps and daily life. For example, plastics are now being banned in many areas of United States and other countries due to solid waste accumulation in land and oceans. However, there are many other unsustainable chemical products and processes still providing goods and service for the needs of present generations while compromising the ability of future generations to meet their needs. In addition, replacing unsustainable products with sustainable ones in our society is being held back by the difficulty of evaluating sustainability performance of a specific process/product and the lack of appropriate tools for sustainability³⁶. The advancement and maturity of the available tools to a great extent will determine the future engineer and scientist's skill for designing and improving the chemical processes in terms of sustainability.

In this respect, the available sustainability assessment tools and metrics have been developed for quantifying the sustainability performance at different scales^{37–41}. Among these tools, they can be grouped into two main categories: metric-orientated methods and the aforementioned LCA. For metric-orientated methods, their focus is to transfer the abstract concept of sustainability into well-defined indicators in economic, environmental and social aspect within a predefined boundary. On the contrary, LCA is intended to quantify the environmental impact of a selected product or process within its life cycle “from cradle to grave”. Both of such system information analysis methods are useful and complementary for sustainability assessment.

With the deeper understanding of “sustainability” in the engineering perspective, many metrics/indicators have been developed to quantify “three pillars” of sustainability performance (economic, environmental or social aspects)⁴². The resulting Indicators can be classified into three types: 1) one-dimensional indicators which describe the performance in one pillar; 2) two-dimensional indicators which interpret interactive performance in two of the three pillars; 3) three-dimensional indicators which characterize the performance in three pillars. For example, several key sustainability indices developed by American Institute of Chemical Engineers⁴³ and UK Institution of Chemical Engineering⁴⁴ include environmental impact, safety, product stewardship, innovation and societal measures. Such developed indicators are typically aggregated based on subjective weights. A recent tool^{38,45–48} developed by the US Environmental Protection Agency, GREENSCOPE (Gauging Reaction Effectiveness for the ENvironmental Sustainability of Chemistries with a multi-Objective Process Evaluator) was proposed as a systematic methodology for the evaluation of process performance and sustainability. A set of environmental,

material, energy, and economic indicators was employed to describe process aspects in terms of a quantitative sustainability measurement scale. Thus, GREENSCOPE quantitatively characterizes how sustainable the process utilizes energy, material goods and services to generate a valuable product, while maximizing its social and economic benefits, and minimizing or eliminating negative environmental impacts. Besides, GREENSCOPE can provide clear quantified limits for comparing process performances and designs between themselves and determining if some sustainability improvements or better operating conditions have been achieved. In addition, the worst and best case can be adapted according to design needs, decision-makers, and product specifications. The desired GREENSCOPE indicators could also be employed to optimize the process performance if incorporated into multi-objective optimization problems. A recent contribution detailed the implementation and use of this sustainability evaluation and design tool for the manufacturing of biodiesel^{45,47,48}. The capability of this tool is demonstrated to identify the major process aspects or conditions favorable for the attainment of sustainable improvements.

2.4 Pollution Control Units

Over the past several decades, the United States and many other countries have enacted legislation and regulations to limit releases to the environment as well as to alleviate the adverse effects of pollution by human activities. The U.S. Environmental Protection Agency (U.S. EPA) has made important progress to advance environmental protection strategies from end-of pipe treatment to pollution prevention⁴⁹. The Clean Air Act (CAA) of 1970 and the Clean Water Act (CWA) of 1977 are regulatory foundations used to mitigate the environmental and human health concerns associated with air and water quality. In addition, the Toxic

Substances Control Act (TSCA) of 1976 provides EPA the authority to demand reporting, record-keeping and testing requirements, and restrictions relating to chemical substances and/or mixtures manufactured or processed, including imports, in the United States and in the chemical industry. For example, as part of the CAA, EPA is charged with setting the National Ambient Air Quality Standards (NAAQS). These standards limit the ambient concentrations of six criteria air pollutants: ground-level ozone (including volatile organic compounds, VOCs), carbon monoxide (CO), sulfur dioxide (SO₂), particulate matter (PM), nitrogen oxides (NO_x), and lead (Pb). Therefore, as stationary sources of air, solid, and water pollutants, chemical processes are subject to federal, state, and local air quality regulations. Such regulations require chemical plants to undertake several emission-permitting procedures during construction and operation. However, feasibility-level designs typically do not consider the impacts associated with emission control technologies in process sustainability analysis for real-world decision making.

PCUs, as the end-pipe technology for chemical process, have been developed and implemented on waste streams of industrial processes to destroy or remove the pollutant species with extra energy before releasing to environment. For example, different treatments can be selected for typical pollutants (particle matter, VOCs, Acid gas, CO and lead) in the air streams based on the characteristics of the pollutant. The typical air pollution control devices include fabric filters, electrostatic precipitators, incinerator, flare and wet scrubber, etc. For the water treatment plant, it is designed to remove odors, color and turbidity as well as other contaminants, typically including primary treatment (remove solids), secondary treatment (biological processes) and tertiary treatment (deodorize and decolorized the wastewater). One major concern of implementation of such pollution control devices

is that they are expensive and energy demanding, decreasing efficiency and economic performance of industrial processes. Thus, the mindset of implementing pollution control units in industry is to fulfil the environmental legislations and avoid penalties for grossly pollution behaviors. The integration of pollution control, LCI and sustainability assessment can give us new insight and detailed information on how to evaluate comprehensively available solutions for a given waste stream and balance environmental and economic impacts in the decision-making step.

However, the available methods and tools don't take into consideration the process emissions or merely provide roughly estimation on emissions during LCI and sustainability assessment calculations. For example, controlled emission values were calculated as a certain fraction of the involved chemical component in the process^{21,24}, total process emissions are calculated as the sum of estimated fugitive losses, global mass balance fractions, and flue gas emissions from controlled combustion units²², as well as generic emission estimation models are based on direct emissions for energy requirements and plant efficiency²³. In considering some examples of pollution control equipment modeling for inclusion in LCI, Bojarski et al.^{27,23}, described the modeling of process units for the treatment of waste streams (air and liquid) based on black box models and distribution function values. Another example includes equipment modeling and simulation focused on air emissions (flue gas) treatment for carbon capture^{29,50}. In addition, Bhatt et al.⁵¹ evaluated the techno-economic impacts of emission controls to comply with air quality regulations of a bio-refinery and its location and production scale. Therefore, these limitations on controlled emissions data, pollutant-of-interest targeting (i.e., carbon capture), and cost analysis approaches demonstrate the need to develop methods and frameworks for handling controlled emission modeling when simulating LCIs given

the importance of emission streams and regulations in environmental impact evaluations. Moreover, performing a more detailed material and energy balance when implementing pollution control systems will allow designers to consider additional material input flows, accessory equipment, and the energy consumption required for emission controls. In addition, the footprint (construction material (e.g., carbon steel) and land use) associated with these system changes will affect the overall profile of emission controls. At this level of detail through LCI modeling, the importance of considering emission controls for rapid LCI modeling of a chemical manufacturing process was demonstrated in our group⁵².

2.5 Multi-objective Optimization for Sustainability

In recent years, with the progress in understanding sustainability, the incorporation of sustainability into chemical process optimization has become a research highlight in process systems engineering⁵³. In the last two decades, several emerging fields have been proposed in the area of sustainable design and optimization, such as process integration⁵⁴, process intensification⁵⁵, multi-objective optimization^{56–59} and real-time operation along with sustainable corporate-scale management⁶⁰. One common way to incorporate sustainability indicators (environmental and social aspects) into process design and optimization is to treat such indicators as constraints in the problem objective of maximizing profitability or minimizing the cost of the operations. For example, when minimum environmental risks/impacts related to non-routine and routine releases were considered, the optimal trade-off between cost and environmental impacts was obtained by employing the ϵ -constraint method, assuming the environmental impact targets were within ranges imposed by a selected amount defined by ϵ ⁶¹.

In addition, a hierarchical design procedure was proposed to synthesize economically efficient separation processes, taking into consideration environmental factors as constraints⁶². Recently, a modular approach for sustainable chemical process design was developed through the integration of quantitative economics and environmental indicators with qualitative indicators in social aspects⁶³. Compared to the aforementioned methods, multi-objective optimization schemes have a higher potential to obtain the optimal trade-offs between conflicting economic and environmental objectives. For example, a global optimization method for sustainable design was developed, in which a large-scale algae processing network was simultaneously optimized in terms of minimizing the unit cost and global warming potential associated indicators⁵⁹.

Also, life cycle assessment (LCA) principles have been taken into account in the formulation of superstructure multi-objective optimization problems for the design of sustainable chemical process flowsheets. Along the same line, a framework that combines a multi-objective optimization approach, LCA and principal component analysis was introduced and applied to the synthesis of biological processes with economic and environmental concerns. However, LCA methodologies need a large amount of data within a wide boundary, which are usually difficult to obtain, especially in the beginning of a process design. In addition, it is not clear how certain are Life Cycle Inventory (LCI) data obtained from commercial packages for a particular process under study and LCA does not provide boundary values for process related aspects at any stage and scale of a chemical process design. Finally, a review of multi-objective optimization associated with economic and environmental objectives from the process synthesis and supply chain management point of view was presented⁶⁴. Overall, the reported systems literature studies address

optimization methodologies for sustainability focused on three components: decision-making sequence, sustainable design framework and design assessment tools.

2.6 Process Dynamics and Control for Sustainability

Studies concerning the sustainability of real-time process operations are still at the early stages, despite the fact that control techniques and theory have evolved significantly in the last two decades³⁷. For instance, advanced non-linear model predictive control (NMPC) techniques can control non-linear, large-scale chemical processes effectively and safely even at the presence of disturbances and uncertainties. In particular, advanced features of control techniques have been under development in academia, such as economic MPC⁶⁵, stochastic MPC⁶⁶, and safeness-index based MPC⁶⁷. However, to this day, the primary focus of the process control area is to improve the economic or safety related performance of the process, regardless of environmental and social costs. There are only a few reported studies on process operations employing sustainability-oriented control strategies. A recent review⁶⁸ described the challenges of incorporating sustainability goals into process control and stated that sustainability will be a major driver for controller development in the future due to the pressure of taking the sustainable principles into account during process operations. In reference⁶⁹, a method was proposed to integrate deterministic dynamic optimization with optimal control for addressing the sustainability of a batch reactor. Another application of deterministic optimal control strategies was reported to improve energy efficiency in manufacturing processes⁷⁰. In these last two studies, only utilities-related environmental impacts were considered. As described in the literature⁶⁸, the scarcity of studies on sustainable process control can be attributed to the lack of strategies that can effectively

integrate process sustainability aspects into the advanced controller framework, considering the conflicting nature of sustainability indicators (e.g., economic vs. environmental aspects).

Chapter 3 Integrated Tool Development for Rapid Life Cycle Inventory

3.1 Introduction

To bridge the gap between PSE, LCI methods, and pollution control needs identified in the literature, the contribution discussed in this chapter corresponds to the development of a process systems framework that involves the incorporation of PCU modules into process simulation and LCI data generation associated with the PCUs and the entire process. The parameterized PCU modules are developed employing a user-friendly Excel interface with the goal of making the models easier to use by decision-makers with little process data or limited knowledge on specific waste treatment technologies, including non-engineer LCA practitioners. In essence, the proposed PCU reduced models are intended to augment existing capacity of commercial process simulators. Some distinguished features included in the PCU modules are: 1) parameterized input variables with default/suggested values; 2) easy customization for application to different cases; and 3) ability for integration with different commercial process simulation software.

The biomass/coal to acetic acid manufacturing process is employed to illustrate the application of the proposed framework. This case study is selected for analysis as a representative technology that is described in various forms of literature. Currently, there are numerous works published that describe the acetic acid production process^{71–74}, which include its LCI modeling using the top-down¹⁷ and bottom-up approaches¹⁸. Therefore, this study will analyze the LCI modeling implications of implementing technologies to reduce pollutant emissions from chemical manufacturing. A key output of this work is a set of parameterized pollution control modules that can be used by LCA practitioners to include pollution control in

their LCI models by specifying a set of key operational parameters. The current baseline design will consider multiple control devices to reduce emissions.

3.2 Approach

3.2.1 Framework

An overview of the proposed process systems framework is provided in Figure 3.1. In this framework, a chemical process manufacturing simulation is built while considering the different approaches to manufacture the desired product from different feedstocks. Unit operation infrastructure (e.g., steel consumption, land use, etc.) and utility (e.g., heating, cooling, and electricity) requirements change for different feedstocks and product(s) quality. Even though the current framework includes more detailed bottom-up inventory modeling based on process simulation, the PCU modules could just as easily be applied if a practitioner already has information on a waste stream to be treated and can specify the necessary parameters, i.e., skip process simulation and proceed directly to PCU module application. The outputs of the LCI modeling are the desired product, side products, and waste streams. These waste streams are then sent to the developed parameterized (simplified) modules for various PCUs that could append the production LCI with pollution abatement based on user inputs. In this way, the boundaries of the PCU LCI are specific to the control device and not the entire manufacturing process (red box in Figure 3.1). These narrow boundaries enable the control device models to become modular in nature and support plug-and-play application for LCA projects in general. The composition of the waste streams dictates the type of unit operation infrastructure, utility and ultimately the PCU used to remediate such waste streams.

In this contribution, LCI will be generated for the inputs to the process: feedstock, utility and infrastructure as well as outputs: emissions and by/co-product(s). Emissions associated with process energy use (e.g., utility) are outside the boundary of this study as shown in Figure 3.1. Note that PCUs for water discharges and solid waste release inventories are not developed in this chapter, but are also included for a complete representation (these units are described in the next chapter).

Figure 3.1 Process systems framework for pollution control and LCI generation

3.2.2 Pollution Control Units

The design and implementation of PCUs require the evaluation of many aspects such as the waste stream to be treated, physicochemical properties of the pollution streams, selection of control equipment, and evaluation of the exhaust to meet expected outcomes and performance. The quality and quantity of the pollutants directly influence the size of the PCUs. Therefore, any upstream process modification that either can eliminate or minimize the amount of pollutant to be treated will reduce the needs and cost for pollution control. For example, replacing

the feedstock and changing process operating conditions can be considered if an important reduction in pollution generation can be achieved.

For air pollution control, four representative pieces of equipment are developed for obtaining their input/output mass and energy performance and their infrastructure needs (material of construction and land use). However, there are many types of equipment depending on the pollutant characteristics, which can be classified into two main categories: control equipment for removal of pollution particulate and those for the removal of noxious gases⁷⁵. In addition, the EPA⁷⁶ for techno-economic evaluation purposes classifies pollution controls (recapture, destruction, pre-combustion, combustion, post-combustion) according to some of the pollutants that must be in compliance with an air quality standard: CO, volatile organic compounds (VOCs), PM, oxides of nitrogen (NO_x), and some acid gases (primarily SO₂ and HCl).

In this contribution, the focus is placed on demonstrating the needs and benefits of adding the effects of pollution control for rapid LCI modeling of a chemical manufacturing process by designing, modeling, and simulating four PCUs for noxious gas removal. The four air PCUs are designed using Microsoft Visual Basic for Applications (VBA) in Microsoft Excel®. These PCUs simulate the purification of gas-phase waste streams from a chemical process and provide rapid LCI estimates for the corresponding process⁵². The PCUs considered in this study are described below.

Scrubbers

Scrubbers⁷⁷, or gas absorbers, as pollution control devices, are used widely in industry for the purification of waste gas streams containing inorganic contaminants, such as HCl, H₂S, and NH₃ and organics such as CO₂ (see scrubber schematic in Figure 3.2). Some applicable pollutants removed include PM less than or equal to

10 μm in aerodynamic diameter (PM_{10}), PM less than or to equal 2.5 μm in aerodynamic diameter ($\text{PM}_{2.5}$), precursors of secondary PM from hazardous air pollutants (PM_{HAP}), inorganic gases (e.g., SO_2 , ammonia, chlorides), and VOCs. Scrubbers can employ a variety of techniques including packing materials, perforated trays, and sprayers to force close contact between the polluted gas and the gas scrubbing liquid flowing through the scrubber. The liquid solvents used to achieve this removal are water, mineral oils, or non-volatile hydrocarbons. Removal efficiencies typically range from 90.0% to 99.9% and can be attained with higher solvent surface areas, for example, the use of spray nozzles in spray scrubbers. The physical properties of the pollutant and solvent dictate the physical absorption process taking place. The parameters for a wet scrubber (i.e., size, flowrate of solvent) are then determined by the physical properties, removal efficiency, and equilibrium data^{76,78}. Refer to publication⁵² for the full detail of design equations and parameters of this unit.

Figure 3.2 Counter-current packed spray scrubber schematic

Boilers

Contaminated streams that have no chemical recovery value and are combustible (some VOCs) can be treated with boilers. Fire tube and water tube boilers both use waste gas as an auxiliary fuel to produce steam that can be utilized for power or heating needs in a process (see boiler schematic in Figure 3.3). For pollution control purposes, the waste gas is typically combined with natural gas or other fuels, but high combustion temperature and additional pollution controls may be needed to achieve a complete combustion⁷⁹. In a fire tube boiler, the hot gases from the combustion of the waste gas-fuel mixture move through the tubes while the water is heated in the shell of the boiler. Here the hot gases are passed multiple times through the tubes. Design of fire tube boilers are limited by regulations on diameter and operating pressures. In a water tube boiler, water entering the boiler moves through tubes exposed to the heat generated from the waste gas-fuel combustion. The heated water is circulated, while the steam is withdrawn. Refer to publication⁵² for the full detail of design equations and parameters of the boiler when employed as a noxious gas removal unit.

Figure 3.3 A simplified diagram of a gas-fired boiler system

Flare Units

Flare units⁷⁶ are used to completely combust compounds introduced into the unit, typically VOCs (except halogenated compounds), via an open flame (see flare schematic in Figure 3.4). The combustion is considered complete if the products are carbon dioxide and water, while incomplete combustion results in the formation of carbon monoxide or other partially oxidized organic compounds. A flare can achieve VOC destruction greater than 98%. There are three different types of flares in terms of the method for increasing mixing at the flare tip: steam-assisted, air-assisted, and non-assisted. Steam-assisted flares inject steam in the combustion zone to generate turbulence and induce air into the flame. The steam requirements for smokeless burning depends on the composition and flowrate of the mixture⁵². Air-assisted flares increase the mixing required for smokeless operation using compressed air provided by a compressor placed at the bottom of the unit. The amount of compressed air entering the unit is about 1.2 times the steam flowrate since steam is more efficient in preventing smoke formation. This configuration is usually used when steam is not available, or the flare unit is small (when it is not economically feasible for an air-assisted flare with large vent gas flowrate)⁸⁰. A non-assisted flare essentially burns the vent gas without the aid of steam/air. Its use is limited to handle waste gas streams with a low carbon/hydrogen ratio (such as methane) that can burn without producing smoke⁸¹. Refer to publication⁵² for the full detail of design equations and parameters of flare units for VOC destruction.

Figure 3.4 Schematic diagram of a flare system

Thermal Oxidizers

Thermal oxidizers⁷⁶, or incinerators, are one of the best-known methods for industrial waste gas disposal (see thermal oxidizer schematic in Figure 3.5). Thermal oxidizers are used to control the release of VOCs and CO through thermal or catalytic incineration, and are generally used when the waste gases are diluted mixtures of combustible gases and air (air content should be greater than 98%). The advantage of using a thermal oxidizer is that almost any VOCs can be oxidized to CO₂ and water safely and cleanly in the presence of high temperature and enough oxygen. This unit incinerates compounds and typically requires natural gas as an auxiliary fuel to aid in the combustion process. The amount of natural gas required can be decreased by recovering heat from the effluent stream of the combusted products. Heat exchange between the flue gas and inlet stream prior to entering the combustion chamber can

achieve this with typical energy recovery as high as 70%. Refer to publication⁵² for the full detail of design equations and parameters of the thermal oxidizer PCU.

Figure 3.5 Block flow diagram of a thermal oxidizer system

As mentioned above, the objective of the proposed PCU simulators is to introduce a method for estimating the LCI, including mass, energy, material, and footprint of air pollution control technologies to reduce or eliminate the emissions of potentially hazardous air pollutants from industrial waste streams. Table 3.1 provides a summary with brief descriptions, strengths and limitations associated with the different PCUs, which may serve as guidelines for users on how to select the PCUs for particular applications of interest. In general, the scrubber and thermal oxidizer are typically chosen for diluted waste streams, while the boiler and flare systems are more flexible w.r.t. concentrations of the waste streams to be treated.

Table 3.1 Summary on brief descriptions, strengths and limitations of developed PCUs in Chapter 3

PCUs	Brief Descriptions	Strengths	Limitations
Scrubber	<ul style="list-style-type: none"> Absorption is widely used as a pollution control technique for inorganic emissions 	<ul style="list-style-type: none"> Good for inorganic acid gases Raw material and/or product can be recovered 	<ul style="list-style-type: none"> Need suitable solvents that should be easily regenerated or disposed in an environmentally acceptable manner
Boiler	<ul style="list-style-type: none"> Existing boilers can be used to control emission streams containing organic compounds 	<ul style="list-style-type: none"> High destruction efficiency (98%) Small capital cost with no fuel cost High recovery of the combustion heat 	<ul style="list-style-type: none"> Limited in dealing with emission streams with corrosive compounds and variations in terms of flowrate and contents Only applied for low flowrate waste gases (less than 20% of the natural gas volumetric flowrate) with high heating values (higher than 5,589 kJ/m³ (at 1 atm, 20 °C))
Flare	<ul style="list-style-type: none"> Flare is commonly used for disposal of waste gases for chemical plants Flares can be used for controlling almost any VOC emission stream 	<ul style="list-style-type: none"> High destruction efficiency Can handle fluctuations in emitted VOC and inert contents and flow rates 	<ul style="list-style-type: none"> No organics can be recovered Large flowrate of waste streams only No combustion heat can be recovered
Thermal Oxidizer	<ul style="list-style-type: none"> Thermal oxidizer (TO) is used to control a wide variety of continuous emission streams containing dilute VOCs 	<ul style="list-style-type: none"> High destruction efficiency Wide applicability Possible to recover heat energy 	<ul style="list-style-type: none"> No organics can be recovered Capital intensive It is not suitable for streams with highly variable flows

Table 3.2 describes a summary of user input parameters required for each PCU module. In the modules, users just need to adjust operational parameters and perform process design for integration if necessary, as the modules provide guidelines and default values that facilitate the functionality of the framework in generating LCI data for non-engineer users. In particular, the developed PCUs can serve as a plug-and-play role for LCA projects only requiring the information on the waste stream to be treated. Note that many of these data entries have suggested default values, which can be found (in parenthesis) in Table 3.2. For more detailed information on these parameters, please refer to publication⁵². Waste gas flowrate and composition are key parameters for obtaining the LCI results. In addition, the user would need to enter more data if the pollutants of interest are not listed in the internal database. After describing the set of PCUs developed for LCI modeling, and to demonstrate the objectives of this work, the above PCU modules are applied to an acetic acid from biomass/coal simulation case study. The acetic acid case study was chosen due to previous work on applications of the top-down¹⁷ and bottom-up¹⁸ approaches for estimating LCI.

Table 3.2 A summary of user input parameters required for applying each PCU module for LCI modeling

	Pollution Control Unit			
	Scrubber	Boiler	Flare	Thermal Oxidizer
User Input Parameters	Waste gas flowrate			
	Waste gas composition			
	Inlet temperature (30 °C)	Inlet temperature (40 °C)	Inlet temperature (40 °C)	Inlet temperature (40 °C)
	Pressure (~101.325 kPa)	Pressure (≥ 101.325 kPa)	Pressure (> 101.325 kPa)	Pressure (~101.325 kPa)
	Fresh solvent composition (100% solvent)	Excess of air (5%)	Liquid mass fraction (0.05)	Designed control efficiency (99%)
	Designed removal efficiency (99%)		Liquid density (795 kg/m ³)	Designed energy recovery (70%)
	Waste gas viscosity and pollutant diffusivity in air (if not listed in the internal database)	Boiler size in terms of heat content of fuel gas: small size (<29.3 MW) and large size (>29.3 MW). Heat content of waste gas should be smaller than 50% of boiler's heat needs and > 11,630 kJ/kg.	Flare type (steam-assisted)	Operation temperature (871.1 °C)
			Designed combustion efficiency (98%)	Fan efficiency (70%)
			Designed Mach number (0.2)	
	Pollutant diffusivity in air and solvent properties (if not listed in the internal database)	Burner type: the amount of CO, NO _x , VOCs emissions are related to burner type. For smaller size boilers, uncontrolled burners might be able to meet the environmental standards. Controller-Low-NO _x burner is recommended for larger size boilers.	Maximum allowable thermal radiation (1.58 kW/m ²)	
	Packing size and properties: (Raschig rings ceramic, 2'')		Radiation fraction (0.3)	
	Equilibrium data: equilibrium line data and saturation solubility data are required for the primary pollutant; solubility data for other components are needed if it is a multi-component system		Wind velocity (yearly average wind velocity of local area)	
			Recommended horizontal distance to the stack center (50 m). For this recommendation, a typical stack height value can be calculated (30 m).	

3.3 Results & Discussion

3.3.1 Chemical Process Simulation

Due to the increasing projected global energy demand and the need to move away from fossil fuels, biomass has received considerable attention as a feedstock

and energy source. Biomass is a renewable feedstock alternative with the potential for ameliorating the environmental effects of using fossil fuels (e.g., coal). However, the utilization of biomass is facing some challenges, such as limited and intermittent availability/supply, as well as its low energy density. Two scenarios associated with acetic acid manufacturing from coal/biomass are analyzed. In this work, Aspen Hysys³⁵ and CHEMCAD³⁴ are used to model the acetic acid production process from coal/biomass. As described in Figures 3.6 - 3.8, the entire biomass/coal to acetic acid process consists of three subprocesses: (i) the biomass/coal to syngas section which includes gasification, water-gas-shift reaction, and sour gas treatment; (ii) the methanol synthesis; and (iii) the methanol-to-acetic acid subprocess. Note the gasification-to-methanol simulation that includes gasification, water-gas-shift reaction, sour gas treatment, and methanol synthesis step is modelled in Aspen Hysys due to the software capabilities for working with different fluid packages, as well as different sour gas treatment options. Using a previously developed simulation as a reference, the methanol-to-acetic acid process with a production rate of 300,000 t of end product per year is simulated in CHEMCAD.

Methanol Synthesis Process Simulation

Figure 3.6 presents the Aspen Hysys flowsheet setup used for methanol synthesis process from coal/biomass. The flowsheet is built and conditions are obtained based on previously published literature^{82,83}. In this flowsheet, coal and biomass are approximately simplified using pseudo components based on the atomic ratio of hydrogen to carbon. Biomass in this work is assumed to be comprised of wood chips, with the typical composition of 55 wt% carbon, 32 wt% oxygen, and 10 wt% hydrogen, 2 wt% sulfur and 1 wt% of other species⁸⁴. Coal is represented by a pseudo component hydrocarbon⁸⁵ ($C_{18}H_{20}$) based on the weight of C and H in the

coal. With the assumed biomass and coal raw materials as well as oxygen and water, an entrained flow gasifier is used to convert the hydrocarbon feed into raw synthesis gas. In addition, as shown in Figure 3.6, the gasifier island step includes three parts: partial oxidizer (POX) (CSTR100-102), radiant synthesis gas cooler (RSC) (E100) and water quench (MIX-101).

High temperature conditions in the POX can improve the conversion rate to syngas (typical conversion rates for biomass/coal to syngas are 50 wt% / 65 wt%, respectively) and the RSC helps to recover part of the heat via steam generation while cooling the process syngas to around 800°C. Then the quench water drops the water temperature in the syngas to around 200°C. The downstream units from the gasifier are mostly standard gas phase processes, including the sour water gas shift (SWGS) reactor and acid gas removal (AGR) process, followed by the methanol synthesis (MS) step. Before entering the SWGS part, particles and traces of acid gas in raw syngas are removed through a wet scrubber (Scrubber). In the SWGS part, the ratio of hydrogen/carbon in the syngas required for methanol synthesis can be adjusted to 2 even if only biomass is used as feedstock. Then, as shown in Figure 3.7, monoethanolamine (MEA) is used to remove acid gases (H_2S and CO_2) and the sweet syngas from the top of the absorber (T-103) goes to the methanol reactor, while the rich MEA solvent is regenerated by the stripper (T-101). To reach high conversion rate to methanol (~90 %) as well as ensure high methanol purity (99.5 wt%) required by the AA production process, most of the gas stream (in Stream 25) from the top of the separator (V-103) is recycled back to the methanol reactor (GBR-100). The methanol synthesis reaction is exothermic and the optimal reaction temperature for this process is around 200 °C.

stream then enters the isothermal methanol carbonylation reactor (Unit 10) at temperature of 189°C, where the reaction mechanism shown below occurs. In order to achieve a methanol conversion of 98.5% in the simulation, 91.5% of the carbon monoxide is reacted. The outlet reactor stream pressure is reduced using an adiabatic flash valve (Unit 11). The stream is cooled and the resulting vapor-liquid mixture is flashed in Unit 19 to remove non-condensable compounds. The flashed stream (Stream 18), which is rich in acetic acid is then sent to the distillation column (Unit 16) for further purification of the final acetic acid product. The rigorous multi-stage vapor-liquid equilibrium multicomponent column is designed to produce a bottom product stream (Stream 19) with a content of 98 mol% acetic acid. The product stream is depressurized and cooled enough to produce acetic acid (Stream 21) at 45 °C and 101.325 kPa, i.e., ready for storage. In addition, the gas stream from the distillation column (Stream 22) is conditioned in a heat exchanger and sent to the absorption column (Unit 24) where a portion of the valuable condensable compounds are absorbed by using part of the fresh methanol as solvent (Stream 5). The liquid stream from absorber Unit 24 (Stream 24) recovers part of the methyl iodide, methyl acetate, and hydrogen iodide, which are recycled back into the reactor unit. The gas leaving the absorption column (Stream 6) is vented as Gas Releases of uncontrolled air emissions. This stream, along with the Gas Releases from Stream 27, may contain hydrogen iodide, methyl iodide, methanol, methyl acetate and methane, some of which may cause skin and lung irritation, digestive disorders in addition to being an asphyxiant (in the case of methanol)⁸². The pollution control units developed in this work previously described are used next to simulate the remediation process of these waste

streams, as well as to provide more realistic LCI results for use in a sustainability evaluation.

Figure 3.8 CHEMCAD flowsheet for the simulated acetic acid manufacturing process

3.3.2 LCI Results

Incorporation of PCUs into Acetic Acid Process Simulation Results

As mentioned above, many researchers and engineers are trying to reduce or control pollution and emissions from chemical processes, in addition to making their product competitive in terms of cost. The proposed approach of integrating process simulation with PCU modules for LCI generation can be employed across a wide range of applications, for both new product design as well as retrofit/upgrade scenarios. The acetic acid manufacturing process is employed here to illustrate how the developed PCU simulators can enable the rapid estimation of controlled emissions, utility and construction material consumption as well as land footprint

information for LCI generation. The calculations of construction material and footprint are typically based on the plant life time (20 years in this case study), as shown in equations (3.1-3.2).

$$LCI\ Material\ Index = \frac{total\ material\ weight}{product\ yearly\ flowrate \times plant\ life\ time(years)} [kg/kg\ product\ per\ year] \quad (3.1)$$

$$LCI\ Footprint\ Index = \frac{total\ area}{product\ yearly\ flowrate} [m^2/kg\ product\ per\ year] \quad (3.2)$$

Tables 3.3 and 3.4 show the LCI input/output results from the application of three PCUs (scrubber, boiler and flare) to the methanol-to-acetic acid (AA) sub-process. In Table 3.4, the stream compositions are shown without PCUs (under “Simulation”) as well after application of each PCU (with their respective name), in which the LCI outputs include the exit concentration of chemicals from the emission streams (streams 6 and 27 in Figure 3.9) after implementing each PCU as shown in Figure 3.9. The "Emission with PCUs" column depicts the releases after applying the three in-series PCUs (see Figure 3.9) while the LCI inputs show the electricity, utility consumption, facility material and land use associated with the construction and operation of the selected PCUs. Note that the percentage change for inputs (in Table 3.3) is calculated by dividing the PCU subtotal by the simulation inputs (under “Simulation” in Table 3.3) and then multiplying the result by 100%. Also, the percentage change for outputs (in Table 3.4) is calculated by the emissions with PCUs minus the simulation emissions (under “Simulation” in Table 3.4), and then dividing the resulting quantity by the simulation emissions (multiplied by 100%). In addition, as described in Table 3.2, the collection of some waste stream data and the selection of equipment parameters were required for the implementation of the PCU modules for obtaining the corresponding LCI results.

Table 3.3 LCI input results before and after waste streams have been processed by PCUs

LCI Inputs	Units	Simulation	Simulation with emission control units				Percentage change
			Scrubber	Boiler	Flare	PCU Subtotal	
Air	kg/kg AA	0	0	1.63E-1	1.36E-2	1.76E-1	∞
Natural Gas	scm/kg AA	0	0	9.16E-3	1.43E-2	2.34E-2	∞
Purge Gas (Nitrogen)	scm/kg AA	0	0	0	1.24E-3	1.24E-3	∞
Steam	kg/kg AA	7.79E-1	0	-2.84E-1	0	-2.84E-1	-37%
Solvent (Water)	kg/kg AA	0	2.47E+0	0	0	2.47E+0	∞
Electricity	kW/kg AA	5.60E-3	5.90E-5	8.11E-5	0	1.40E-4	3%
Construction Material	kg/(kg AA per year)	2.03E-6	8.43E-8	4.88E-7	1.43E-5	1.49E-5	733%
Footprint	m ² /(kg AA per year)	1.02E-4	4.47E-8	7.73E-7	1.60E-6	2.42E-6	2%

A negative sign (-) represents decrease (in percentage) or generation (for steam in the boiler), while “∞” represents division by zero in calculation of percentages (for cases without corresponding inlet stream).

Table 3.4 LCI output results before and after waste streams have been processed by PCUs

LCI Output	Units	Simulation	Simulation with emission control units			Emissions with PCUs	Percentage change
			Scrubber	Boiler	Flare		
Carbon Monoxide	kg/kg AA	4.39E-2	4.36E-2	7.15E-4	8.73E-4	8.73E-4	-98%
Carbon Dioxide	kg/kg AA	5.45E-4	5.42E-4	9.68E-2	1.36E-1	1.36E-1	24868%
Methane	kg/kg AA	1.97E-4	1.97E-4	2.18E-6	1.09E-9	1.09E-9	-100%
Water	kg/kg AA	1.55E-4	0	6.81E-3	3.21E-2	3.89E-2	25015%
Methanol	kg/kg AA	3.10E-5	0	0	0	0	-100%
Acetic Acid	kg/kg AA	5.89E-4	0	0	0	0	-100%
Methyl Acetate	kg/kg AA	2.14E-3	2.13E-3	0	0	0	-100%
Hydrogen Iodide	kg/kg AA	1.84E-3	0	0	0	0	-100%
Propionic Acid	kg/kg AA	1.57E-7	0	0	0	0	-100%
NOX	kg/kg AA	0	0	2.07E-5	1.96E-5	1.96E-5	∞
PM (< 1 µm)	kg/kg AA	0	0	1.63E-6	1.63E-6	1.63E-6	∞
Nitrogen	kg/kg AA	0	0	1.24E-1	1.34E-1	1.34E-1	∞
Oxygen	kg/kg AA	0	0	1.89E-3	4.50E-4	4.50E-4	∞

A negative sign (-) represents decrease (in percentage) or generation (for steam in the boiler), while “∞” represents division by zero in calculation of percentages (for cases without corresponding inlet stream).

Figure 3.9 Incorporation of PCUs into acetic acid process simulation results for rapid LCI modeling

After performing an engineering evaluation of the complete system, the decision regarding the appropriate pollution control technologies to use needs to be made based on the analysis of the source, component and flowrate of the emission(s). A systematic analysis may be required if a sequence of pollution control technologies should be employed to treat the waste streams. Therefore, it was found for the acetic acid sub-process, waste streams 27 and 6 (see Figure 3.8) should be combined for treatment by the developed PCU modules as shown in Figure 3.9. In addition, as described in Table 3.4, the waste streams from the acetic acid process (denoted as “Simulation”) consists of inorganic acids, VOCs (e.g., methyl acetate, acetic acid, methanol and methane) as well as CO. To effectively treat this stream, the first step is to remove hydrogen iodide (HI) by employing a scrubber, which is the most widely used pollution control device for soluble inorganic contaminants from gas streams. In the developed scrubber module, solvent, packing material, size and operating conditions can be set based on the pollutant of interest and its inlet concentration. For HI, the scrubber is simulated as a packed column containing 2” Raschig Rings, and a shell material of 304 Stainless Steel. From Table 3.4, it can be observed that HI has been effectively removed by the scrubber with an efficiency of 100%. The

scrubber unit was designed based on the required HI removal efficiency (99%). However, 5.3 times the solvent flowrate demanded by the required HI removal efficiency was required to soak the whole packing material of the scrubber tower⁸⁶, resulting in a higher removal efficiency of 100%. Water, methanol, acetic acid, and propionic acid are more soluble in water than HI, thus after scrubber, all of them are zero. In addition, the utility consumption, construction material and footprint results are calculated by the scrubber simulator, as shown in Table 3.3 (see publication⁵² for calculation procedures).

The output from the scrubber mainly consists of CO and methyl acetate and thus can be fed to the boiler to recover the combustion heat value. Since the heat input in this stream is low, a small sized boiler (10 MW) is used with an uncontrolled burner type (see publication⁵² for calculation procedures). It is important to note that waste gas is mixing with natural gas as the fuel for the boiler and the heat input of waste gas should not be larger than that of natural gas. In the design case for boiler simulator, the percentage of waste gas heat input can be adjusted by changing the size of the boiler. In this work, boiler is considered as a pollution control unit that processes all the emissions from the scrubber. However, it might be the case in reality that only part of the waste emissions can be treated by the existing boiler at a specific facility and the rest of the waste stream has to go through other PCUs. For the purpose of demonstrating all the designed PCUs, the outlet stream from the boiler is released to the environment through the flare unit, which causes a large construction material need for the flare unit.

The pollution control devices are thus able to produce a resulting stream after treatment that is more environmentally-friendly. Table 3.4 shows the detailed LCI output results for scrubber, boiler, and flare. Please note that boilers are initially rated

for a specific fuel (e.g., natural gas), and operational performance can degrade, heat transfer equipment can be damaged, and emissions can increase with changes in fuels burned⁸⁷. In addition, there are some restrictions on burning hazardous waste that is not categorized as a fuel in industrial boilers⁷⁹. Those restrictions describe a minimum heating value requirement for the waste, prohibiting their blending to augment the heating value of the waste, and exclusion of burning dioxin-listed wastes. In summary, this table clearly shows the scrubber has the capability to remove those species which have a large solubility in the solvent, such as HI, methanol, and acetic acid, while bringing down the boiler net steam consumption by 36.5%. The large amount of CO₂ released to the environment is due to the boiler and flare converting all combustible species to CO₂. The resulting CO₂ could be sent to carbon capture and storage units for further processing. A comparison between the proposed bottom-up method with commercial LCI databases is available in publication⁵².

Incorporation of PCU models into Methanol Synthesis Simulation Results

The synthesis of methanol, as the main feedstock for acetic acid production, is analyzed through the comparison of gate-to-gate LCI data modeling under two cases: 1) methanol produced from coal; 2) methanol produced from biomass. In addition, the methanol synthesis for both scenarios are studied in order to fulfill the production demand of acetic acid. Both processes have waste streams that are sent to the external PCU modules for treatment. The proposed method provides rapid yet accurate LCI data estimates of controlled emissions that could be used by non-engineer LCA practitioners when the LCI information is not readily available from industry, literature, or commercial software.

Coal-Based Simulation: For this case of coal as the feedstock to generate methanol, a summary of the LCI inputs, with and without the PCUs, including the raw materials and utilities, is presented in Table 3.5. Oxygen, as one of the required resources for the methanol production process, is assumed to be obtained from air separation units that are considered outside of the process LCI boundary. In addition, the boundary does not include pretreatment of raw material (e.g., coal/biomass grinding/drying). The steam reported in Table 3.5 is the steam produced by recovering the heat within the process after the deduction of the steam needed for the process heating duty, as provided by the process simulator. The electricity requirements in this table are estimated based on the assumption that efficiencies for pumps and compressors are 75% and 70%, respectively.

Concerning emissions from the process, as described in Figure 3.6, there are two waste streams that need to be treated prior to release: 1) the waste stream from mixer-106 (waste stream 1), which is composed primary of CO and methanol; and 2) the waste stream from mixer-105 (waste stream 2), comprised mostly of CO₂ and H₂S⁸². Waste stream 2 is assumed to be sent to absorption units to separate CO₂ from H₂S, followed by Carbon Capture and Storage (CCS) and Claus unit technologies to handle the two acid gases, respectively. The developed thermal oxidizer module (see publication⁵² for calculation procedures) unit is employed to treat the VOCs present in waste stream 1 as shown in Figure 3.9, with the generated LCI output results described in Table 3.6. Please note that N₂ and O₂ in the emission stream (in Table 3.6) are calculated based on the excess air required by the thermal oxidizer. By adjusting the operating temperature and residence time of the thermal oxidizer, the destruction efficiency of the VOCs obtained reached as high as 99.5%. Although estimated utility use is reported, the inputs (and emissions) related to fuel

used to generate the steam and electricity are assumed to occur in upstream processes.

Table 3.5 Life cycle inventory inputs for methanol production from coal

LCI Inputs	Units	Simulation	Simulation with	Percent change
			Thermal Oxidizer	
Oxygen	kg/kg MeOH	2.62E+0	2.62E+0	0
Water	kg/kg MeOH	1.11E+0	1.11E+0	0
Coal	kg/kg MeOH	1.61E+0	1.61E+0	0
MEA	kg/kg MeOH	1.33E-5	1.33E-5	0
Steam (Flowrate/Duty)	kg/kg MeOH	4.57E+1	4.57E+1	0
	MJ/kg MeOH	9.78E+1	9.78E+1	0
Cooling Water (Flowrate/Duty)	kg/kg MeOH	7.19E+2	7.19E+2	0
	MJ/kg MeOH	1.32E+2	1.32E+2	0
Electricity	MJ/kg MeOH	3.20E-1	3.51E-1	9.7%
Air	kg/kg MeOH	0	8.21E+0	∞
Natural Gas	scm/kg MeOH	0	8.49E-2	∞
Construction Material	kg/(kg MeOH/yr)	5.76E-4	5.79E-4	0.5%
Footprint	m ² /(kg MeOH/yr)	-	1.85E-7	∞

“∞” represents division by zero in calculation of percentages (for cases without corresponding inlet stream), while “-” means the inventory data is not calculated for the methanol synthesis process footprint

Table 3.6 LCI outputs before and after waste streams have been processed by PCUs per kilogram of methanol produced from coal

LCI Outputs	Units	Simulation	Simulation with Thermal Oxidizer	Percentage change
Methane	kg/kg MeOH	1.41E-3	0	-100%
Carbon Dioxide	kg/kg MeOH	7.03E-3	9.43E-1	13313%
Carbon Monoxide	kg/kg MeOH	5.88E-1	9.18E-3	-98%
Hydrogen	kg/kg MeOH	8.65E-2	0	-100%
Methanol	kg/kg MeOH	2.04E-2	1.02E-4	-99.5%
Nitrogen	kg/kg MeOH	0	6.30E+0	∞
Oxygen	kg/kg MeOH	0	1.91E+0	∞

“∞” represents division by zero in calculation of percentages

Biomass-Based Simulation: The flowsheet for the biomass case study was kept as similar as possible to the coal case study to allow for direct comparison. The operating conditions, such as the oxygen and water flowrates as well as the bypass

fraction to the water-gas shift reactor, were adjusted according to the biomass conversion rate and syngas composition, in order to produce a methanol with similar purity and production rate needed for the subsequent acetic acid synthesis sub-process. For generating LCI results, the considered LCI boundary and assumptions on the efficiencies of pumps and compressors still hold. When compared to the coal case study, the LCI results, reported in Table 3.7, for the oxygen and water inlets are less than those for the coal case study, due mainly to the fact that biomass is richer in oxygen content and consists of 15% water. However, the LCI results for biomass for steam and cooling water usage are greater than those in the coal case study. This can be attributed to the biomass' lower energy density and a larger quantity of biomass being needed to generate the same amount of syngas.

In addition, the syngas quality from the biomass, in terms of H_2/CO , is much lower than that generated from coal. Thus, greater quantities of utilities, such as steam and cooling water, for the biomass are consumed when compared to coal. Electricity estimates for the two cases studies were found to be equivalent. When referring to waste streams, both waste streams exist for the two cases studies: 1) waste stream from mixer-106 (waste stream 1), which is mainly composed of CO and methanol; 2) waste stream from mixer-105 (waste stream 2), including mostly CO_2 and H_2S . The result of treating waste stream 1 employing the thermal oxidizer PCU is shown in Table 3.8, which is similar to the results from the coal case study. However, the acid gases in waste stream 2 that would be sent to downstream units as described above is much lower than that for the coal case study, as shown in Table 3.9. This table depicts the comparison of the results of the uncontrolled emissions from both the coal and biomass-based case studies.

Table 3.7 Raw material and utility life cycle inventory for methanol production from biomass

LCI Inputs	Units	Simulation	Simulation with	Percent change
			Thermal Oxidizer	
Oxygen	kg/kg MeOH	8.01E-1	8.01E-1	0
Water	kg/kg MeOH	1.00E-1	1.00E-1	0
Biomass	kg/kg MeOH	2.74E+0	2.74E+0	0
Steam (Flowrate/Duty)	kg/kg MeOH	4.57E+1	4.57E+1	0
	MJ/kg MeOH	9.78E+1	9.78E+1	0
Cooling Water (Flowrate/Duty)	kg/kg MeOH	7.19E+2	7.19E+2	0
	MJ/kg MeOH	1.32E+2	1.32E+2	0
Electricity	MJ/kg MeOH	3.20E-1	3.54E-1	10.8%
Air	kg/kg MeOH	0	8.21E+0	∞
Natural Gas	scm/kg MeOH	0	5.38E-2	∞
Construction Material	kg/(kg MeOH/yr)	5.76E-4	5.81E-4	0.9%
Footprint	m ² /(kg MeOH/yr)	-	8.55E-7	∞

“ ∞ ” represents division by zero in calculation of percentages (for cases without corresponding inlet stream) while “-” means the inventory data is not calculated for methanol simulation case

Table 3.8 LCI before and after waste streams have been processed by PCUs for biomass case

LCI Outputs	Units	Simulation	Simulation with Thermal Oxidizer	Percentage change
Methane	kg/kg MeOH	1.03E-2	0	-100%
Carbon Dioxide	kg/kg MeOH	1.28E-3	8.76E-1	68337%
Carbon Monoxide	kg/kg MeOH	5.44E-1	8.53E-3	-98.4%
Hydrogen	kg/kg MeOH	7.97E-2	0	-100%
Methanol	kg/kg MeOH	2.04E-2	3.84E-5	-99.8%
Nitrogen	kg/kg MeOH	0	6.30E+0	∞
Oxygen	kg/kg MeOH	0	1.91E+0	∞

“ ∞ ” represents division by zero in calculation of percentages (for cases without corresponding inlet stream)

Table 3.9 Uncontrolled emissions from coal and biomass-based methanol process

LCI Output	Units	Coal Case	Biomass Case
Methane	kg/kg MeOH	6.39E-6	6.51E-5
Carbon Dioxide	kg/kg MeOH	3.09E+0	2.13E+0
Hydrogen Sulfide	kg/kg MeOH	5.86E-2	5.60E-4
Carbon Monoxide	kg/kg MeOH	5.31E-3	9.96E-3
Water	kg/kg MeOH	3.97E-2	2.69E-2
Nitrogen	kg/kg MeOH	7.03E-5	3.26E-5
Hydrogen	kg/kg MeOH	8.37E-4	1.20E-3

Analysis of Coal to AA Production Process

As described in the process simulation section, the entire process can be separated in two parts (methanol synthesis and acetic acid production) and the previous LCI results were obtained and analyzed separately. The LCI input and output results in this section are based on the same functional unit (kg AA) using coal as feedstock, as shown in Tables 3.10 and 3.11. Note the results for the two parts are for the scenario including pollution control unit simulations. Specifically, a thermal oxidizer was used in the coal to methanol part for treating the gas phase waste from the methanol synthesis reactor, while a scrubber, boiler and flare were used for treatment in the methanol to acetic acid process. As shown in Table 3.10, greater quantities of utilities (cooling water, electricity, and steam) were used in the methanol synthesis part when compared to the utility values needed for the methanol to acetic acid process. This can be attributed to the complexity of the methanol synthesis process, which includes gasification, sour water gas shift reaction, acid gas cleaning part and methanol reactor process steps.

For the LCI output results, the first part of the process releases CO, CO₂, H₂S, and small amounts of CH₄, CH₃OH, as well as H₂. While the acetic acid process portion generates CO₂ with small quantities of NO_x, CO and PM. It is important to note the source for each species as this can guide further investigation on how to

handle and treat such emissions. For example, the sources of CO₂ emissions, from the two parts of the process, are different even though both release a high quantity of CO₂. More specifically, CO₂ from the methanol process, which is primarily generated by the water gas shift reaction, can be separated from other species present in the stream and then go to carbon capture and storage (CCS). Additional processing steps are required to collect the CO₂ generated from the acetic acid process, as the majority of CO₂ originates from the combustion in the boiler and flare.

Table 3.10 LCI input for entire process from coal to AA

LCI Input	Units	Coal to Methanol Simulation	Methanol-to-Acetic Acid Simulation	Total
Oxygen	kg/kg AA	1.42E+0	0	1.42E+0
Water	kg/kg AA	5.98E-1	0	5.98E-1
Coal	kg/kg AA	8.70E-1	0	8.70E-1
Carbon Monoxide	kg/kg AA	0	5.09E-1	5.09E-1
Methanol	kg/kg AA	0	5.39E-1	5.39E-1
Methyl Iodide	kg/kg AA	0	2.03E-3	2.03E-3
Steam (Flowrate/Duty)	kg/kg AA	2.47E+1	4.95E-1	2.52E+1
	MJ/kg AA	5.28E+1	1.75E+0	5.46E+1
Cooling Water (Flowrate/Duty)	kg/kg AA	3.88E+2	4.37E-1	3.89E+2
	MJ/kg AA	7.16E+1	3.06E+0	7.46E+1
Electricity	MJ/kg AA	1.90E-1	6.65E-2	2.56E-1
Air	kg/kg AA	4.44E+0	1.76E-1	4.61E+0
Natural Gas	kg/kg AA	4.59E-2	2.34E-2	6.93E-2
Purge Gas (Nitrogen)	kg/kg AA	0	1.24E-3	1.24E-3
Solvent (water)	kg/kg AA	0	2.47E+0	2.47E+0
Construction Material	kg/(kg AA/yr)	3.13E-4	1.49E-5	3.28E-4

Table 3.11 LCI output for entire process from coal to AA

LCI Output	Units	Coal to Methanol Simulation	Methanol-to-Acetic Acid Simulation	Total
Carbon Monoxide	kg/kg AA	7.83E-3	8.73E-4	8.71E-3
Carbon Dioxide	kg/kg AA	2.18E+0	1.36E-1	2.32E+0
Methane	kg/kg AA	3.45E-6	0	3.45E-6
Water	kg/kg AA	2.15E-2	0	2.15E-2
Methanol	kg/kg AA	5.51E-5	0	5.51E-5
Acetic Acid	kg/kg AA	0	0	0
Methyl Acetate	kg/kg AA	0	0	0
Hydrogen Iodide	kg/kg AA	0	0	0
Propionic Acid	kg/kg AA	0	0	0
NO _x	kg/kg AA	0	1.96E-5	1.96E-5
PM (< 1 µm)	kg/kg AA	0	1.63E-6	1.63E-6
Hydrogen Sulfide	kg/kg AA	3.17E-2	0	3.17E-2
Hydrogen	kg/kg AA	4.52E-4	0	4.52E-4

3.4 Conclusions

The objective in this chapter was to develop a generic and integrated framework for rapid LCI generation of PCU modules by adopting systematic methods for process modeling, simulation, and design. Specifically, process simulation that included mass and energy balances was employed for providing LCI data which otherwise may be incomplete without considering the impacts of implementing pollution control systems for process waste streams. The developed PCUs were comprised of modules for treating gas releases that provide LCI information regarding land footprint and utility and material use. The effectiveness of the proposed framework was demonstrated on the acetic acid manufacturing process from a coal/biomass feedstock. The outputs from the acetic acid simulation were used as input streams to the respective PCU modules. Those suitable PCUs were successfully implemented to remove process pollutants and recover the combustion heat. A comparison between LCI results with and without application of the

developed PCU modules demonstrated considerable variations in material compositions, energy demand, and infrastructure that cannot be omitted when generating a suitable LCI. For the current case study, the LCI results, when comparing methanol production from biomass vs. coal, showed the biomass case requires more utility demand (steam and cooling water), while generating less CO₂ and H₂S. In Chapter 7, co-gasification of coal and biomass is investigated as a potentially economically attractive and technically viable alternative to the conversion of biomass to energy and chemicals while improving the sustainability performance of the coal gasification process. Furthermore, an advanced process control strategy^{89,90} is investigated as a potentially sustainable process control approach for biomass/coal co-gasification process. From this investigation, it is anticipated a determination on the optimum combination of coal and biomass to balance the raw material input to reduce emissions without sacrificing desired production rate and profitability that can be achieved. This contribution demonstrates the needs and benefits of adding the effects of pollution control units for rapid LCI modeling of a chemical manufacturing process by designing, modeling, and simulating PCUs for noxious gas removal. These parameterized PCU modules can simplify pollution control modeling when compared to fully simulating the units by providing rapid LCI estimates that could be used by non-engineer LCA practitioners when LCI information is not readily available from industry or literature.

Chapter 4 Integrated Tool Development for Sustainability Assessment

4.1 Introduction

Previous chapter demonstrated the effectiveness and necessity of incorporating PCUs into process simulation for gate-to-gate LCI data generation. Based on previous work, this chapter is focusing on the extension of the capability of the developed PCUs for an integrated sustainability assessment tool. The new features of the proposed tool are: 1) an automation interface between simulators, parameterized PCUs and sustainability assessment tool; 2) PCU models for air, solid and liquid waste treatment; 3) capability to generate GREENSCOPE sustainability indicator results. Specifically, the user-friendly automation interface is built via Microsoft Excel-VBA to enable the communication between process simulators (e.g., CHEMCAD, Aspen) and Excel tools for sustainability assessment, PCUs and LCI generation. The employed Excel tools enable the augmentation of a simulator's capability in terms of waste treatment technologies and sustainability assessment. For the solid and liquid PCUs introduced in this chapter, similar distinguished features are kept as in the other PCUs, such as parametrized input variables with default/suggested values and easy customization for different applications. GREENSCOPE, as one of most comprehensive sustainability assessment tools, can be accessed via the proposed framework to provide additional useful information on where and by how much the implemented PCUs can improve the process performance. The objective of the proposed framework is to provide a generic software interface that facilitates the communication between sustainability assessment tools at different scales (such as GREENSCOPE and LCA) and process simulation packages with the augmented ability of adding suitable PCU techniques.

The developed framework is applied to a case study of an Acetic Acid manufacturing process. The proposed framework is generic and can also be implemented for other applications. The outline of the rest of this chapter is as follows: the overall integrated framework is presented in the next subsection, followed by the details on the newly developed pollution control units and the sustainability assessment tool. Then, the proposed framework is implemented for the addressed case study.

4.2 Approach

Figure 4.1 shows the overview of the proposed framework for integrating process modeling/simulation with pollution control units (PCUs), LCI generation, and sustainability assessment. Specifically, a user-friendly automation interface is built via Microsoft Excel-VBA to enable the communication between process simulators and Excel tools, such as GREENSCOPE, PCUs and LCI generation. In this framework, a chemical process manufacturing simulation is built to monitor utility (e.g., heating, cooling, and electricity) requirements and estimate unit operation infrastructure (e.g., steel consumption, land use, etc.). To augment the capability of commercial simulators in terms of PCU techniques, a library of parameterized PCU models has been developed to deal with air, liquid and solid wastes from a typical chemical plant. The air PCUs were detailed in Chapter 3 and the particle matter (PM), liquid, and solid PCUs are discussed below.

Figure 4.1 Process systems framework for pollution control and sustainability assessment

One characteristic of proposed framework is that the developed user interface can transfer the process data (e.g., stream information) into the PCUs library automatically. Specifically, the user interface can extract all the stream information from the simulator when the simulation converged. Then the user can choose certain waste streams to be treated by the appropriate PCU model to estimate the utility, equipment and end emission to environment associated with this treatment. Figure 4.2 shows an example of the interface in the developed software environment. In this interface, the user can open, run a simulation file, and then match the interested waste streams (stream 13 in the example) with a PCU model (Stripper PCU for water treatment in the example) from the developed PCU library. Upon finishing these steps, the user can click the button of “Upload Waste Stream to PCU” and all the stream info (showing in Figure 4.2(b)) is automatically entered for the selected PCU calculation. The user only needs to check/enter some required PCU parameter values (in the lower part of Figure 4.2(b)) to generate the LCI data. This interface is thus a convenient and easy approach for the generation of the waste stream treatment results by only clicking a few buttons. Moreover, the user can change

operating conditions of the simulation in Excel through the VBA interface and repeat the above procedures to generate waste treatment data for a different case.

CHEMCAD | PCU Model

Load Simulator License

Load Simulation File

View Streams Table

View Units Table

Send Changes

Rerun Simulation

Save Simulation Changes

Release Simulator License

Simulator Version
7140

Simulation File Path
C:\Users\jy\Google Drive\ACS paper draft\Paper Draft\AceticAcid.p

View Streams

Stream Info

12	13	14	15
12.0	13.0	14.0	15.0
32.4	32.1	30.7	30.3
25.0	75.9	189.0	150.0
32.4	32.1	30.7	30.3
-20526.4	-73525.1	-87865.1	-89354.3
1.0	0.5	0.1	0.1
667.5	1404.9	785.5	785.5
18695.5	45616.7	45617.3	45617.3
23.3	55.2	44.2	44.2
14960.2	31489.6	17829.9	17829.9
0.5	9.4	29.0	29.0
0.1	0.1	7.2	7.2
18694.9	18695.3	1612.6	1612.6
0.5	9.4	29.0	29.0
0.1	0.1	7.2	7.2
0.1	454.9	596.4	596.4
0.0	19807.7	14.1	14.1

Waste Stream ID 13 **PCU Name** Liquid PCUs **Stripper**

Upload Waste Stream to PCU

Data Transfer

CHEMCAD | PCU Model

Wastewater

Flowrate of Wastewater* 45616.7305 **kg/h**

Temperature* 75.9466 **°C**

Pressure* 3206.0635 **kPa**

Blower/Pump Efficiency* 70 **%**

Stream Info

Compound	Flowrate
Carbon Monoxide	40.9834
Carbon Dioxide	0.0207
Methane	0.0002
Methanol	43.4220
Acetic Acid	4.1620
Methyl Acetate	9.6956
Hydrogen Iodide	0.5528

Stripper Specification

Removal Efficiency* 90 **%**

Air to Water Ratio* 5

Key Component* Methanol

Packing Material * Raschig rings

PCU Parameters

Ok **Clear** **Cancel** **Help**

PCU Result

Equipment Size, Utility, Emission Results and LCI Report

1. Mass Balance

Compound #	Compound Name	CAS Number	0: VOCs, 1: Product, 2: Inert, 3: Fuel, 4: Global reagent/Solvent, 5: Other	Flowrate, kg/h	LCI flow index, kg/kg raw
1	Air	7806-13-2	5	20500.00	4.487915
2	Water	7732-18-5	5	1.00	0.000000
3	Carbon Monoxide	6300-91-0	5	43.98	0.000000
4	Carbon Dioxide	7440-44-7	5	0.02	0.000000
5	Methane	7509-14-0	5	0.00	0.000000
6	Methanol	6758-18-8	5	43.42	0.000000
7	Acetic Acid	6419-71-7	5	4.16	0.000000
8	Methyl Acetate	79-20-9	5	9.70	0.000000
9	Hydrogen Iodide	7540-70-1	5	0.55	0.000000
10	Propylene Glycol	57-10-3	5	0.00	0.000000

2. Equipment Size

Compound #	Compound Name	CAS Number	0: VOCs, 1: Product, 2: Inert, 3: Fuel, 4: Global reagent/Solvent, 5: Other	Flowrate, kg/h	LCI flow index, kg/kg raw
1	Air	7806-13-2	5	20500.00	4.487915
2	Water	7732-18-5	5	1.00	0.000000
3	Carbon Monoxide	6300-91-0	5	43.98	0.000000
4	Carbon Dioxide	7440-44-7	5	0.02	0.000000
5	Methane	7509-14-0	5	0.00	0.000000
6	Methanol	6758-18-8	5	43.42	0.000000
7	Acetic Acid	6419-71-7	5	4.16	0.000000
8	Methyl Acetate	79-20-9	5	9.70	0.000000
9	Hydrogen Iodide	7540-70-1	5	0.55	0.000000
10	Propylene Glycol	57-10-3	5	0.00	0.000000

3. Energy Supply

Construction Material of Shell	Amount (kg)	LCI Material Index*
Shell (Carbon Steel)	44072.00	0.074901

Figure 4.2 Automation interface between simulators and developed PCUs

Once the data from process simulations and PCU models is obtained, GREENSCOPE indicators can be calculated to describe the performance in efficiency, economic, environmental and energy aspects. Please note that the current interface can only transfer part of the required data (e.g., stream information, unit operation, etc.) to GREENSCOPE and an improved automation interface between the process simulator, PCU and GREENSCOPE is under development in our group.

4.2.1 New Pollution Control Units

Particle Matter PCU: Baghouse

Baghouses^{91–93} (or fabric filters), as particle matter (PM) devices, typically include one or more compartments containing rows of long, cylindrical bags (or tubes) made of woven or felted fabric. Dirty air (dust-laden gas) is directed into the baghouse compartment and can be either on the inside or the outside of the bags depending on the cleaning method. Particles start to accumulate on the surface of the bags until sufficient pressure drop is reached. Generally, the baghouses are operated cyclically, alternating between relatively long period of filtering and short period of cleaning. During cleaning, dust that has accumulated on the bags is removed from the fabric surface and deposited in a hopper for subsequent disposal. The proper design procedures for baghouses and a baghouse model will be illustrated in a forthcoming publication.

Figure 4.3 A simplified baghouse diagram (adapted from EPA report)

Wastewater Treatment PCU: Stripper

Stripping processes are used to remove VOCs or some volatile species (H_2S and NH_3) from waste water. As shown in Figure 4.4, the feed waste water after conditioning typically enters at the top of the tower while the stripping gas (air is used in this simulator) is introduced at the bottom. The proper design procedures for the stripper and the stripper module will be available in a forthcoming publication.

Figure 4.4 A simplified air-stripper schematic diagram

Wastewater Treatment PCU: GAC

Granular activated carbon (GAC) units use a porous adsorptive media with extremely high internal surface area. GACs are manufactured from a variety of raw materials with porous structures, including bituminous coal, lignite coal, peat, wood, coconut shells, among others. Physical and/or chemical manufacturing processes are applied to these raw materials to create and/or enlarge their pores, resulting in a porous structure with a large surface area per unit mass. A schematic diagram of the GAC system is shown in Figure 4.5⁹⁴. In the GAC system, pollutants are adsorbed by the GAC contactors until the carbon is no longer able to adsorb new molecules. At this point, the carbon is considered as “spent” and need to be replaced by new or reactivated carbon. GAC beds also require periodic backwash to prevent head loss or biomass accumulation. The proper design procedures and calculations for the GAC system are based on an EPA report by the Office of Water, which will be available in a forthcoming publication.

Figure 4.5 A simplified GAC schematic diagram (adapted from EPA report)

Solid Waste Treatment PCU: Biomass/MSW Gasifier

Biomass/Municipal Solid Waste (MSW) gasification is a technology that uses a controlled process involving heat, steam, and air/oxygen to convert biomass to H₂ and CO and other products, without combustion. In particular, gasification is the conversion of feedstocks into useful and convenient gaseous fuel or chemicals that can be burned to release energy or used for production of value-added chemicals. This document is to illustrate the proper design procedures for the gasifier system. Gasification of biomass is typically carried out in a relatively high temperature range of 800 to 1000 °C, comparing to 300 to 650 °C for pyrolysis. The design procedure and the example calculation for the gasifier simulator will be available in a forthcoming publication.

4.2.2 Sustainability Assessment Tool: GREENSCOPE

GREENSCOPE, as a sustainability evaluation and design tool by US EPA, facilitates a holistic sustainability performance analysis for chemical processes to help process engineers and decision-makers with comparing multiple processes or locating the area for improving or deciding the optimal trade-offs in terms of sustainability. To quantitatively describe process sustainability performance, GREENSCOPE employs a set of sustainability indicators (SI) in four areas: efficiency (26 SIs), economics (33 SIs), environment (66 SIs) and energy (14 SIs). Specifically, efficiency indicators describe the process performance in terms of mass transfer operations by connecting material input and output with the desired product. Economic indicators are based on the profitability criteria for commercial chemical process considering raw material costs, utility costs, capital and labor costs, etc. Out of ~66 environmental indicators, environmental, health, and safety (EHS) potential

risks are measured according to the involved input materials, operating conditions and potential impact of releases. For the energy indicators, two different thermodynamic methods (energy and exergy) are used to characterize the thermodynamic efficiencies of the process. More detailed information on the indicators' definitions, calculation and application is available in the literature^{45,47,48}. As shown in Figure 4.6, GREENSCOPE is an effective tool to translate process, feedstocks, utilities, equipment, and product information into a sustainability measurement scale.

Figure 4.6 Inputs and outputs of GREENSCOPE framework for sustainability assessment

One important and unique feature of GREENSCOPE is the employed dimensionless sustainability indicator score, which can be calculated by the following equation:

$$\text{Sustainability Indicator Score (\%)} = \frac{(\text{Actual} - \text{Worst})}{(\text{Best} - \text{Worst})} \times 100\% \quad (4.1)$$

Where best case represents 100% sustainable while worst case 0% sustainable for each indicator. Selection of two reference values for normalizing the indicators offers some advantages for applying GREENSCOPE to different scenarios. The dimensionless indicators can be lumped into a two- or three- dimensional sustainability indicator for process optimization or control studies based on a systematic weighting method⁹⁵. Also, indicator scores help the user to identify an area for improvement as they represent the degree of the sustainability performance (higher score means more sustainable). Guidelines on how to select the best and worst case values for the indicators can be found in the literature⁴⁷.

As shown in Figure 4.6, the required input data for GREENSCOPE includes mass & energy flows, equipment, utility information and their associated cost, regulatory classification and toxicological properties, in addition to the best- and worst-case reference values. One effective way of collecting such required process data is by modeling the process via process simulators, which provide with obtaining mass and energy balances information, equipment sizing and cost.

4.3 Results & Discussion

The study below demonstrates a gate-to-gate sustainability performance assessment by implementing the GREENSCOPE and PCU framework on a biomass/coal-to-acetic acid (AA) manufacturing process. The system boundary for the sustainability evaluation is from feedstocks to products / emissions, which corresponds to the “gate-to-gate boundary for GREENSCOPE” in Figure 4.7. The AA process simulation is performed using commercial simulators (Aspen Hysys and CHEMCAD), for which the detailed simulation information was provided in Chapter 3.

Figure 4.7 Integrating process simulation with PCUs for sustainability assessment

4.3.1 Chemical Process Inputs & Emissions

Sustainability assessment needs a clearly defined boundary in which the system will be evaluated. In this work, the entire biomass/coal to chemical manufacturing process constitutes a gate-to-gate boundary for sustainability evaluation (as shown in Figure 4.7). The performed sustainability assessment using GREENSCOPE is then focused on a gate-to-gate analysis (e.g., from the raw materials to end product) where the engineers have the firsthand opportunity to examine the sustainability performance for different process operating conditions or design alternatives.

The required inputs for GREENSCOPE include material and energy flows (encompassing releases, ancillary inputs, and process energy), economic parameters and results (including production costs and revenues), and physicochemical, thermodynamics, and toxicological properties, as depicted in Figure 4.6. GREENSCOPE user guide⁹⁶ provides a complete description of the required data and parameters. The process data for the AA production from biomass/coal is based upon the rigorous steady-state Aspen Hysys simulation

results. The input streams include the feedstock, catalysts, chemicals (solvent), makeup water, etc. The output streams consist of the product, air, wastewater, and solid emissions. The intermediate mass flows between the unit operations within the process are not required as the performed sustainability assessment is for the process level and not the unit operation level.

In addition to mass input-output flows, substance property data that include physicochemical (i.e., density, heat capacity, enthalpy of combustion, etc.), thermodynamic, and toxicological properties (e.g., acute toxicity, chronic toxicity, carcinogenicity, reproductive toxicity, etc.) are also required for the calculation of the environmental-based indicators. Physicochemical and toxicological properties or parameter values can generally be found using various sources depending on conditions or assumptions. The substance potency factor (e.g., PFCO₂, PFH₂S) contributions that are employed to evaluate atmospheric and aquatic effect indicators (e.g., atmospheric acidification potential, ozone-depletion potential, photochemical oxidation potential) are based on GREENSCOPE default values which in turn were collected from the literature. The substance data requirements and potential data sources are also detailed in the GREENSCOPE user guide⁹⁶.

The key inputs for calculating economic-based indicators are derived from the Aspen Economic Analyzer, including equipment sizing and cost as well as operating costs. Specifically, the Aspen Hysys process model solution provides mass and energy balances for each unit operation, from which the capital and operating costs can be estimated based on economic assumptions.

For the AA process, appropriate PCUs have been implemented to treat the waste air, liquid and solid streams before releasing to the environment. For the air waste streams, please refer to the treatment details in Chapter 3. For the liquid waste

streams, the GAC unit is used to remove the heavy metals before releasing to the municipal water treatment plant. Landfill was selected to deposit the ash from gasifier. Refer to Tables A1-A3 for the detailed information on the waste stream treatment results.

4.3.2 GREENSCOPE Results for Different Categories

Environmental

Figure 4.8 shows the environmental indicators with/without PCUs. As expected, the implemented PCUs can effectively improve most of the environmental indicator performances (see results for controlled emissions). In particular, CEI (Chemical Exposure Index), EQ (Environmental Quotient), and GWI (Global Warming Intensity) increased by 35.65%, 41.56%, 34.93%, respectively (when compared controlled to uncontrolled results). Such improvements are mainly due to the removal of the harmful chemicals in air and liquid waste streams.

Figure 4.8 Environmental indicators with/without pollution control units

Efficiency

As shown in Figure 4.9, the radar plots show that some efficiency indicator scores decrease when pollution treatment units are added to the process, especially total material consumption (mmat.,tot.), and Mass Intensity (MI), which dropped by 18.94%, 19.98%, respectively. This can be explained by the fact that extra materials have to be used for designing the flare, scrubber and waste water treatment units.

Figure 4.9 Efficiency indicators with/without pollution control units

Economic

Figure 4.10 shows that the NPV (Net Present Value), EP (Economic Potential), CTM (Capital Cost) and CSRM (Specific Raw Material Cost) indicators dropped by 2.70%, 1.20%, 10.13%, 2.34%, respectively, due to the capital investment and raw material used for designing and implementing the PCUs.

Figure 4.10 Economic indicators with/without pollution control units

Energy

As shown in Figure 4.11, the RSEI (Specific Energy Intensity) and WTE (Waste Treatment Energy) indicators dropped by 3.32%, 1.69%, respectively, while other energy indicators remained the same after implementing the PCUs. The small drop in energy indicator values can be attributed to the fact that part of the waste gas from the methanol synthesis has been used as fuel in the boiler as well as landfill for solid waste and the GAC unit were not energy-intensive steps.

Figure 4.11 Energy indicators with/without pollution control units

4.4 Conclusions

The proposed framework in this chapter can bridge existing gaps between sustainability assessment, LCI generation, pollution control and process modeling (using commercial simulators). Moreover, the developed PCU modules can improve process data collection and have potential for automation with commercial software to reduce the effort for collecting and processing data. The effectiveness of the proposed framework was illustrated through the acetic acid manufacturing process example for which sustainability trade-offs were quantified using GREENSCOPE. Such framework is general and can be applied to any chemical processes.

Chapter 5 Process Control for Sustainability: Motivating Example

5.1 Introduction

As a step forward to address the gap in research on process control for sustainability, a novel framework is proposed in this chapter for process systems that integrates an advanced process control strategy with sustainability assessment tools. The developed framework is employed to identify and assess the optimal process operation in terms of sustainability performance. Specifically, a set of steady-state alternatives for the chemical process is generated through the implementation of an advanced biomimetic control strategy, and the obtained process operating points are evaluated employing selected indicators from the GREENSCOPE assessment tool⁹⁶ in efficiency, environmental, energy and economic aspects. Such a comprehensive assessment of sustainability performance provides information on quantifying the benefits that the implementation of the biomimetic controller brings towards achieving a more sustainable process operation. The developed framework is applied to a fermentation process for bioethanol production. The outline of the rest of this chapter is as follows: the sustainability assessment tools and indicators are presented in the next subsection, followed by the advanced controller development and algorithm. These tools provide a general framework for optimizing and controlling chemical processes in terms of sustainability. Then, the proposed approach is implemented for the case study of a fermentation process.

5.2 Approach

5.2.1 Selected GREENSCOPE Indicators

As stated by the green chemistry and engineering principles^{2,97}, chemical processes and products that reduce or eliminate the use and generation of

hazardous substances should be developed by preventing waste, performing real time analysis and control for pollution and accident prevention, maximizing mass, energy, space and time efficiency, etc⁴⁶. In addition, when a more sustainable performance is achieved, this must be ensured under any type of beyond the gate (front-edge changes) and/or process stage perturbations.

As mentioned above, society, government, and industry have created initiatives regarding the implementation in practice of sustainable development. However, it is often unclear the effects (positive or negative) of these new practices have on the environment. In order to offer a more comprehensive and quantitative description of environmental, social, and economic effects, the U.S. E.P.A. GREENSCOPE tool introduced above aims for supporting decision makers when developing, designing, and evaluating sustainable processes and products. The tool can show which indicators have improved and where additional opportunities for improvement exist. The indicator scores describe product and process performance on a sustainability measurement scale, determining whether chemical products and processes are more or less sustainable. GREENSCOPE is implemented here along with process control for the first time.

5.2.2 Novel Advanced Control Approach

Many biological systems have been a source of inspiration for advanced control methods because of the success of these systems in solving difficult problems encountered in nature. In this subsection, an advanced biomimetic control approach to address the challenges involved in chemical processes is briefly described. This approach is the combination of a biologically-inspired multi-agent-based algorithm with optimal control concepts for the calculation of optimal trajectories of individual agents. The multi-agent-based algorithm is essentially inspired by the ants' rule of

pursuit idea⁹⁸ which is shown schematically in Figure 5.1. As per this ants' rule, the first ant is supposed to find food by walking around at random. This pioneer ant would then trace a wiggly path back to the nest and start "group recruitment." The subsequent ants (or agents) would follow one after the other straighten the trail a little starting from the original path until the agents' paths converge to a line connecting the nest and the food source, despite the individual ant's lack of sense of geometry. Thus, by cooperating in large numbers, ants (or agents) accomplish tasks that would be difficult to achieve individually. This is an excellent example of how biological systems can efficiently solve problems encountered in nature by cooperative behavior.

Figure 5.1 Schematic representation of ant's rule of pursuit

This idea serves as inspiration for the development of a novel optimal control approach for chemical systems to reach the optimal operating point in terms of sustainability. To translate this idea into an optimal control algorithm, first a chemical system with a dynamic model represented by ordinary differential equations and differential-algebraic equations is defined. This dynamic model corresponds to the relationship between the state and control/input variables. The agent's "home" is the initial conditions for each variable while the "food" stands for the desired operating point of the system. The solution of the optimal control problem for each agent gives the trajectories of these variables to connect home to food through an optimal control action. Next, it is assumed that there is an available initially feasible trajectory pair

for the state and control variables, which is obtained through prior knowledge of the system. This trajectory corresponds to agent 0 (a_0) or leader's trajectory for the initialization of the algorithm. In addition, two important parameters that define the leader-follower local interactions need to be specified, the pursuit time, Δ , and the sampling time, δ .

The initial conditions for each state variable of the follower are the follower's trajectory points based on the discretization by the sampling time, δ . The final destination for the follower agent is obtained from the leader's trajectory discretization based on the sampling time, δ , as well as the pursuit time, Δ , outlined in the algorithm in Figure 5.2. The initial conditions and the final destinations are provided to the optimal control solver, in this case *dynopt*, for the computation of the optimal trajectories. Specifically, *dynopt* is a set of MATLAB functions that use the orthogonal collocation on finite elements method for the determination of optimal control trajectories. The inputs of this toolbox are the dynamic process model, the objective function to be minimized, and the set of equality and inequality constraints. The outputs from this toolbox are the optimal control laws and state trajectories. For the first step calculation, the optimal control trajectories of each follower are computed numerically using *dynopt* by aiming at the leader's position at Δ time units as the current target. The obtained control law is then applied for δ time units, before repeating the procedure outlined in Figure 5.2. The developed algorithm employs *dynopt* to solve all the intermediate problems associated with the local interaction of the agents to generate the state and the optimal control trajectories⁹⁹.

Figure 5.2 General structure of the algorithm for the advanced control approach

5.3 Case Study: Fermentation Process Model

Ethanol derived from renewable sources such as corn, sugar cane, and beets is a potential sustainable fuel to control and decrease air pollution from internal combustion engines and reduce the dependence on fossil fuels. Herein, a process model is considered for a homogeneous, perfectly-mixed continuous culture fermentor for ethanol production equipped with an ethanol-selective removal membrane and a cooling jacket for temperature control. A schematic diagram of the fermentation reactor is shown in Figure 5.3. The reactor is modeled as a continuous stirred tank (CSTR) with constant substrate feed flow. The outlet flow from the reactor contains the product, the unreacted substrate, as well as biomass. Biomass plays the role of catalyst for substrate conversion and is the product of fermentation, while substrate is a solution of glucose for feeding the micro-organism (in this case, *Zymomonas mobilis*). Moreover, ethanol is the desired product of the process and

an inhibitor for the enzymatic reactions. To prevent end-product inhibition and improve the productivity and efficiency of the fermentation process, an in-situ ethanol-removal membrane is used so the ethanol is removed as it is being produced.

Figure 5.3 Schematic diagram of the fermentation reactor

The ethanol fermentation process involves living microorganisms and has two main reactions: 1) microbial growth reaction, in which certain amount of substrate is consumed for the growth of biomass under favorable environmental conditions (temperature, pH, etc.) and 2) metabolite reaction, in which substrate (referred to as reactant) is converted into product through the catalytic action of enzymes^{100–103}. For process design and control purposes, several models for fermentation processes are available in the literature based on kinetic expressions of different complexity^{104,105}. For example, cellular components, enzymes, and proteins can be used to express the process kinetics. However, typical models consider only the kinetic expressions of fermentation for constant temperature conditions. The proposed mathematical model here takes into consideration the temperature effect on kinetics parameters, mass and heat transfer, in addition to the kinetic equations modified from the indirect inhibition structural model developed in the literature^{100–103}.

In this structural model, it is assumed the inhibition effect of ethanol is on the formation of a key component (that includes RNA and proteins in biomass), instead of directly on fermentation. To accurately describe the formation rate of the key component at low ethanol concentrations and under substrate-limited conditions, the formation rate expression for the key component is a function of substrate concentration, given by:

$$r_e = f(C_P)f(C_S)C_e \quad (5.1)$$

A Monod-type equation is taken for $f(C_S)$:

$$f(C_S) = \frac{C_S}{K_S + C_S} \quad (5.2)$$

The function $f(C_P)$ is empirically described by a second-order polynomial of the following form:

$$f(C_P) = k_1 - k_2 C_P + k_3 C_P^2 \quad (5.3)$$

The expressions for biomass growth rate and substrate consumption rate can be taken from the classic maintenance model¹⁰⁶, where the biomass growth rate is defined as:

$$r_X = \mu C_X \quad (5.4)$$

in which μ , as the specific growth rate, can be expressed as follows:

$$\mu = \mu_{max} \cdot \frac{C_S}{(K_S + C_S)} \quad (5.5)$$

In addition, the substrate consumption rate can be written as:

$$-r_S = \left(\frac{1}{Y_{sx}}\right) r_X + m_s C_X \quad (5.6)$$

in which the first term accounts for the growth of biomass while the second term for the maintenance of biomass.

The expression for the maximum specific growth rate, μ_{max} , involves the ratio of the key component to biomass, and the temperature effect:

$$\mu_{max} = P \cdot \frac{C_e}{C_X} \cdot f(T) \quad (5.7)$$

in which P is a correction factor and $f(T)$ can be obtained by fitting a set of experimental data from the literature¹⁰⁷ to the following equation:

$$f(T) = A_1 \cdot e^{-\frac{E_{a1}}{RT}} - A_2 \cdot e^{-\frac{E_{a2}}{RT}} \quad (5.8)$$

The dynamic mass balances for the key component, biomass, and substrate are expressed by:

$$\frac{dC_e}{dt} = (k_1 - k_2 C_P + k_3 C_P^2) \frac{C_S C_e}{(K_S + C_S)} + D_{in} C_{e,0} - D_{out} C_e \quad (5.9)$$

$$\frac{dC_X}{dt} = P \cdot f(T) \cdot \frac{C_S C_e}{K_S + C_S} + D_{in} C_{X,0} - D_{out} C_X \quad (5.10)$$

$$\frac{dC_S}{dt} = \left(\frac{-P}{Y_{SX}} \right) \cdot f(T) \cdot \frac{C_S C_e}{(K_S + C_S)} - m_s C_X + D_{in} C_{S,0} - D_{out} C_S \quad (5.11)$$

As the product flows out of the system through the fermentor and the membrane, mass balances are derived for the product in both compartments and are given by:

$$\frac{dC_P}{dt} = \left(\frac{P}{Y_{PX}} \right) \cdot f(T) \cdot \frac{C_S C_e}{(K_S + C_S)} + m_p C_X + D_{in} C_{P,0} - D_{out} C_P - \left(\frac{\alpha}{V_F} \right) (C_P - C_{PM}) \quad (5.12)$$

$$\frac{dC_{PM}}{dt} = \left(\frac{\alpha}{V_M} \right) (C_P - C_{PM}) + D_{m,in} C_{PM,0} - D_{m,out} C_{PM} \quad (5.13)$$

in which

$$\alpha = A_M \cdot P_M \quad (5.14)$$

Using the overall mass balances for the fermentor and membrane, the outlet dilution rate for both compartments are respectively defined as:

$$D_{out} = D_{in} - \frac{\alpha \cdot (C_P - C_{PM})}{V_F \cdot \rho_r} \quad (5.15)$$

$$D_{m,out} = D_{m,in} + \frac{\alpha \cdot (C_P - C_{PM})}{V_M \cdot \rho_r} \quad (5.16)$$

Moreover, the energy balances for the reactor and the cooling jacket are the following:

$$\frac{dT_r}{dt} = D_{in}(T_{in} - T_r) + \frac{r_S \cdot \Delta H}{\rho_r \cdot C_{p,r}} - \frac{K_T A_T \cdot (T_r - T_j)}{V_F \rho_r \cdot C_{p,r}} \quad (5.17)$$

$$\frac{dT_j}{dt} = D_j(T_{w,in} - T_j) + \frac{K_T A_T \cdot (T_r - T_j)}{V_j \rho_w \cdot C_{p,w}} \quad (5.18)$$

Thus, the derived mathematical model for the fermentation process is represented by a set of seven ordinary differential equations for key component, biomass, substrate, product, and temperature and two algebraic equations of outlet

dilution rates. Table 5.1 provides the parameter values of the model and the initial operating conditions used in this *Zymomonas mobilis* fermentation problem (see all variables' definitions and units in the Nomenclature section).

Table 5.1 Parameter values for the fermentation process model

$A_1 = 0.6225$	$K_S = 0.5 \text{ kg/m}^3$
$A_2 = 0.000646$	$K_T = 360 \text{ kJ}/(\text{m}^2 \cdot \text{K} \cdot \text{h})$
$A_T = 0.06 \text{ m}^2$	$m_s = 2.16 \text{ kg}/(\text{kg} \cdot \text{h})$
$A_M = 0.24 \text{ m}^2$	$m_p = 1.1 \text{ kg}/(\text{kg} \cdot \text{h})$
$C_{e,0} = 0 \text{ kg/m}^3$	$P = 4.54$
$C_{x,0} = 0 \text{ kg/m}^3$	$P_M = 0.1283 \text{ m/h}$
$C_{S,0} = 150.3 \text{ kg/m}^3$	$V_F = 0.003 \text{ m}^3$
$C_{P,0} = 0 \text{ kg/m}^3$	$V_M = 0.0003 \text{ m}^3$
$C_{PM,0} = 0 \text{ kg/m}^3$	$V_j = 0.00006 \text{ m}^3$
$C_{p,r} = 4.18 \text{ kJ}/(\text{kg} \cdot \text{K})$	$Y_{sx} = 0.0244498 \text{ kg/kg}$
$C_{p,w} = 4.18 \text{ kJ}/(\text{kg} \cdot \text{K})$	$Y_{px} = 0.0526315 \text{ kg/kg}$
$E_{a1} = 55 \text{ kJ/mol}$	$T_{in} = 30 \text{ }^\circ\text{C}$
$E_{a2} = 220 \text{ kJ/mol}$	$T_{w,in} = 25 \text{ }^\circ\text{C}$
$k_1 = 16.0 \text{ h}^{-1}$	$\Delta H = 220 \text{ kJ/mol}$
$k_2 = 0.497 \text{ m}^3/(\text{kg} \cdot \text{h})$	$\rho_r = 1080 \text{ kg/m}^3$
$k_3 = 0.00383 \text{ m}^6/(\text{kg}^2 \cdot \text{h})$	$\rho_w = 1000 \text{ kg/m}^3$

5.3.1 Open-Loop Simulation

For the *Zymomonas mobilis* fermentation process addressed here, sustained oscillations of biomass, substrate, and product profiles have been widely reported^{108,109}. An effective controller is therefore required to eliminate oscillations and take the process to an optimal operating steady state. However, the design and implementation of a high-performance control algorithm for this fermentation process in terms of productivity and sustainability is a challenging task, mainly due to its highly nonlinear dynamics. To address these challenges, this subsection introduces a new sustainable process control framework that combines the biomimetic control strategy detailed above with the GREENSCOPE sustainability assessment tool. In the performed case studies, the purpose of the implemented biomimetic controller is to keep key state variables at their set points through the optimization of the control

actions. Thus, in this case, the objective function is formulated to minimize the differences between product concentration and temperature (as key state variables) and their set points. The sustainability performance of the process after the controller implementation can then be evaluated through selected GREENSCOPE indicators shown in the Appendix (see Table A4 for indicator details). Specifically, the obtained GREENSCOPE indicator scores provide information on whether the implementation of the biomimetic controller for the fermentation process enables a more sustainable process operation when compared to a base case.

Before the implementation of the sustainable process control framework, it is worth analyzing the dynamics of the fermentation process. In agreement with the literature, the results of open-loop simulations in Figure 5.4 show that oscillations are more prone to occur at high ethanol concentrations due to the end-product inhibition effect. Ethanol has great impact on the cell membrane composition and inhibits enzymatic reactions. Temperature, as another important operating variable, not only affects the activity of biomass, but indicates the energy consumed by the process affecting its economic performance. Thus, an attractive control strategy consists of regulating the concentration of product and the reactor temperature at optimal operating points in terms of process sustainability and productivity. The present study is an extension of previous work¹¹⁰ regarding the fermentation process that had a strategy of controlling product concentration through manipulating D_{in} . In this chapter, the membrane dilution rate, $D_{m,in}$, as well as cooling water flow rate, D_j , are chosen as the manipulated variables for the regulation of ethanol concentration, C_p , and fermentor temperature, T_r , respectively. It is shown below that using $D_{m,in}$ as manipulated variable is an efficient way to stabilize the system and improve the productivity of the reactor.

To analyze the effect of $D_{m,in}$ on the fermentation process, a set of open-loop simulations was completed in which $D_{m,in}$ varied from 0 to 0.45 hr⁻¹ and D_j was set to zero. For these simulations, the system was integrated using *ode15s* solver in MATLAB for the given differential and algebraic equations that were solved simultaneously. Figure 5.4 shows the concentration profiles of the key component, biomass, substrate, product in the fermentor and membrane sides, as well as temperature profiles in the fermentor for the open-loop simulations with different membrane dilution rates. As expected, a higher $D_{m,in}$ can efficiently reduce or even eliminate the oscillatory behavior of the concentrations and can enhance the substrate conversion rate. This can be explained by the reduction of the end-product inhibition when more ethanol is removed through the ethanol-selective membrane at the cost of using more fresh water. It is important to note that this fermentation process has multiple equilibrium states as a consequence of autocatalytic reactions. To obtain an optimal steady-state operating condition in terms of sustainability and examine the effectiveness of the proposed biomimetic controller, an open-loop case is chosen as the benchmark and then higher and lower setpoints are used for closed-loop simulations. Through comparison of the GREENSCOPE indicators for the benchmark and closed-loop simulations, a systematic decision can be made in terms of moving the process operation in the right direction towards a more sustainable steady state.

(a)

(b)

(c)

(d)

(e)

(f)

Figure 5.4 Open-loop simulations: concentration profiles of key component (a), biomass (b), substrate (c) and product in fermentor (d) and membrane side (e) and temperature profile (f) for different $D_{m,in}$ values

5.3.2 Closed-loop Simulations

Four case studies are presented here to evaluate the implementation of the biomimetic control framework for sustainability. The first two cases are designed to demonstrate the effectiveness of the implementation of the proposed controller by its ability to take the system to higher and lower setpoints when compared to the benchmark within the shortest response time possible. These cases use an initial D_{in} value of 0.1h^{-1} . The new achieved steady states are evaluated and compared in terms of sustainability using selected GREENSCOPE indicators. Based on the results of the first two cases, Cases 3 and 4 are then performed to locate the optimal steady-state operation for a higher D_{in} of 0.2h^{-1} , which corresponds to a higher volumetric productivity for the fermentor. For all simulations, the parameter values in Table 5.1 are kept constant.

Case 1: In case 1, the open-loop simulation with $D_{m,in}$ of 0.20 h^{-1} is chosen as benchmark since it represents the highest achievable product concentration with reduced oscillations as it approaches the steady state. In particular, for this case, the dynamic behavior in Figure 5.4 shows oscillations of mid-range amplitudes within 80 hours before the system finally achieves its steady state at around 100 hours. It is important to note there is still some substrate left in the reactor at steady state as depicted in the substrate profile of Figure 5.4. This can be explained by the fact the environmental conditions in this case, such as temperature and ethanol concentration, are not favorable for a high substrate conversion rate. Thus, there should be some room for improvement of process performance by the implementation of an effective control strategy in terms of efficiency and productivity, if the system is optimized to convert all substrate into product. To attain this goal of increasing the process efficiency, a higher setpoint for the controlled variable, C_P , of 65 kg/m^3 , when compared to the steady-state product concentration of the benchmark case, 57.16 kg/m^3 , is used. In addition, an optimal temperature value, 30°C , for T_r is employed in the closed-loop simulation. Both open-loop and closed-loop simulations start at the same initial points and the inlet dilution rate, D_{in} , is kept at 0.1 hr^{-1} . Figure 5.5 and Figure 5.6 depict the closed-loop simulation results for the concentrations of key component, biomass, substrate, product and temperature as well as the input profiles. Note that, with the implementation of the proposed biomimetic control strategy, the original oscillations are eliminated and merely a trace of substrate unreacted, 0.043 kg/m^3 , is left in the reactor. However, in terms of sustainable performance, the radar plot of Figure 5.7 shows the controller implementation only slightly improves three GREENSCOPE indicators in three categories (Efficiency, Economic, and Environmental), Reaction Yield (RY), Water

Intensity (W), and Economic Potential (EP), towards a more sustainable process operation. Another key aspect is the steady-state biomass concentration value of 2.50 kg/m^3 in the closed-loop simulation, which is higher than the open-loop simulation, 2.31 kg/m^3 . This higher value means that more substrate is consumed for biomass growth, rather than for producing ethanol in the new scenario. This fact explains why some of other indicators, such as Resources Energy Efficient (η_E) and Specific Resources Material Costs (C_{SRM}), do not show improvement even though the substrate conversion rate increased by 5.1%.

Figure 5.5 Closed-loop simulation (Case 1): concentration (key component, biomass, substrate, product in fermentor and membrane sides) and input profiles

Figure 5.6 Closed-loop simulation (Case 1): temperature (fermentor and jacket) and input profiles

Figure 5.7 Radar plot with GREENSCOPE indicators for the closed-loop and open-loop simulations (Case 1)

Case 2: As discussed above, ethanol concentration and temperature have great effect on the living biomass and thus controlling the reaction environment at optimal

conditions can enable higher fermentation process efficiency. Based on the fact that a lower product concentration may reduce the effect of product inhibition, a lower value of $C_p = 45 \text{ kg/m}^3$ is defined as the setpoint for the closed-loop scenario and keep the setpoint of T_r at 30°C in Case 2. Figures 5.8 and 5.9 show concentration and temperature profiles as well as the input profiles for the closed-loop simulation. Comparing to the results in Figure 5.5, Figure 5.8 shows that the system reaches the steady state in this case in a shorter time, and with a lower substrate concentration of 0.03 kg/m^3 . In addition, the steady state $D_{m,in}$ increases to 0.61 h^{-1} , which means more ethanol is removed by the membrane to keep a lower ethanol concentration in the reactor. All GREENSCOPE indicators except Water Intensity (W) in Figure 5.10, such as Reaction Yield (RY), Environmental Quotient (EQ), Environmental Potential (EP), Specific Raw Material Costs (C_{SRM}), Specific Energy Intensity (R_{SEI}), and Resources Energy Efficiency (η_E), demonstrate the higher degree of sustainability for the closed-loop scenario. This improvement of sustainability performance can be attributed to the elimination of oscillations and removal of the inhibition effect by the product after the implementation of the biomimetic control strategy.

Figure 5.8 Closed-loop simulation (Case 2): concentration (key component, biomass, substrate, product in fermentor and membrane sides) and input profiles

Figure 5.9 Closed-loop simulation (Case 2): temperature (fermentor and jacket) and input profiles

Figure 5.10 Radar plot with GREENSCOPE indicators for the closed-loop and open-loop simulations (Case 2)

Case 3: It is documented that fermentation processes are characterized by the conflict between yield of the desired product and productivity of the reactor, which are both important performance indicators from a stakeholders' commercial point of view. Operating points that correspond to a good trade-off between yield and productivity may be achieved, if the fermentation process is optimized by manipulating D_{in} . In previous work¹¹⁰, it was showed that a high D_{in} generates high productivity but with a low yield due to the end-product inhibition. One advantage of using $D_{m,in}$ as manipulated variable, however, is to reduce the coupling between yield and productivity. Based on this information, for this case study, a closed-loop simulation with D_{in} of 0.2 h^{-1} is studied, where the setpoints are kept at the same values as in Case 2. Figures 5.11 and 5.12 present the concentrations of key

component, biomass, substrate, product and temperature as well as the inputs profiles for the closed-loop simulation in this case. When compared to the results of Case 2, which are depicted in Figures 5.8 and 5.9, the closed-loop scenario in this case shows that the manipulation of $D_{m,in}$ effectively enables the system to achieve high conversion rate even at high D_{in} . The residual substrate concentration in the fermentor is now 0.075 kg/m^3 , which is slightly higher than that in Case 2 (0.03 kg/m^3). The GREENSCOPE indicators in Figure 5.13 demonstrate that the Specific Energy Intensity indicator (R_{SEI}) becomes more sustainable and environment and economic indicators for Case 2 and Case 3 overlap with each other. Moreover, efficiency indicators for Case 3 are slightly less sustainable than that of Case 2 due to the relatively lower substrate conversion rate.

Figure 5.11 Closed-loop simulation (Case 3): concentration (key component, biomass, substrate, product in fermentor and membrane sides) and input profiles

Figure 5.12 Closed-loop simulation (Case 3): temperature (fermentor and jacket) and input profiles

Figure 5.13 Radar plot with GREENSCOPE indicators for closed-loop simulations with different D_{in} (Case 3)

Case 4: From the performance of the cases above, it is shown that a relatively lower setpoint for C_p will bring benefits to the process in terms of sustainability due

to the reduction of the end-product inhibition. In addition, it is important to note that lower setpoints for C_p should be reachable based on the open-loop dynamic analysis presented above. In this case, to locate the optimal value for C_p in terms of sustainability, the setpoint of C_p is set at 35 kg/m³ in the closed-loop simulation with D_{in} of 0.2 h⁻¹ and then the process performance is compared with that of Case 3. Figures 5.14 and 5.15 show the concentrations of key component, biomass, substrate, product and temperature as well as the input profiles for this closed-loop simulation. The radar plot in Figure 5.16 shows that most selected GREENSCOPE indicators do not change except Water Intensity (W) that reduces its score. This can be explained by the fact that there is little room for improvement in terms of sustainability when compared to Case 3, which has a fermentation process with a high level of efficiency. Therefore, the system has reached its limitation in terms of the optimal C_p setpoint without compromising in process sustainability.

Figure 5.14 Closed-loop simulation (Case 4): concentration (key component, biomass, substrate, product in fermentor and membrane sides) and input profiles

Figure 5.15 Closed-loop simulation (Case 4): temperature (fermentor and jacket) and input profiles

Figure 5.16 Radar plot with GREENSCOPE indicators for the closed-loop and open-loop simulations (Case 4)

5.4 Conclusions

The study in this chapter successfully demonstrated a novel approach for process systems to achieve sustainable operations through the application of an advanced control strategy combined with sustainability assessment tools. The effectiveness of the developed framework was highlighted via a case study of a bioethanol production process. In this case study, closed-loop scenarios were performed with fixed product concentration and optimal temperature setpoints. The steady states of the process were assessed through selected indicators of the GREENSCOPE sustainability assessment tool in 4 categories (efficiency, environmental, economics and energy). The obtained indicator results from GREENSCOPE were used to guide the selection of the fermentation process case with the most sustainable performance. Thus, the proposed framework, if applied to chemical processes, can provide systematic guidelines for decision-makers to determine the process optimal operating points based on the obtained indicator results, which show whether the implementation of the advanced biomimetic controller can improve the system's sustainable performance.

Chapter 6 A Novel Control Strategy for Sustainability of Chemical Processes

6.1 Introduction

As a step forward to contribute in the field of process control for sustainability, in this chapter, the previously developed framework in Chapter 5 that integrated an advanced process control strategy with sustainability assessment tools is enhanced. In the previous chapter, process control was employed to take the system to the optimal process operation in terms of sustainable performance. Then, an offline sustainability assessment was used to comprehensively evaluate the reached steady-state alternatives. An improved steady-state sustainability performance was obtained after the controller implementation without considering the process performance during transient. In the proposed framework of this chapter, the dynamic sustainability assessment during transient is incorporated using a novel visualization method with dynamic radar plots. With the better understanding of the process dynamic behavior in economic, environmental and social aspects, sustainability constraints can be defined and directly embedded into the control strategy so that the control action can be calculated considering the sustainability performance. The effectiveness of the proposed framework is demonstrated via the case study of a fermentation process for bioethanol production. The outline of the rest of this paper is as follows: Subsection 6.2 presents the background on the fermentation process model and the sustainability assessment tools. In Subsection 6.3, the proposed sustainability-oriented framework and the advanced controller for sustainability are described. Subsection 6.4 introduces the visualization method for dynamic sustainability performance with an example. In Subsection 6.5, the proposed framework is applied to the fermentation process to demonstrate the controller's effectiveness.

6.2 Background

6.2.1 Fermentation Process

In this chapter, the continuous fermentation process with *Zymomonas mobilis* for ethanol production from glucose solution is revisited. The schematic of the ethanol fermenter studied is shown in Figure 6.1. This process dynamics have been studied in the previous chapter, including the challenging characteristics of steady-state multiplicity and oscillatory behavior. A set of seven ordinary differential equations (ODEs) for mass and energy balances and two algebraic equations for inlet dilution rate (D_{in}) and membrane dilution rate ($D_{m,in}$) were described in Chapter 5 for this process. Also, Table 5.1 provided the parameter values of the model and the initial operating conditions used in this *Zymomonas mobilis* fermentation process. The same process will be studied in this chapter.

Figure 6.1 Schematic diagram of the fermentation reactor

6.2.2 Sustainability Assessment Tool

Many sustainability tools have been developed for process performance assessment and management. However, most of the available sustainability tools are not comprehensive enough for evaluating the operating performance of chemical processes. A suitable tool should be able to meet the following requirements: 1)

quantify the process impact on social, environmental and economic pillars of sustainability; 2) describe the assessment results in a transparent and standard way; 3) extend traditional sustainability analysis to assess process dynamic performance. GREENSCOPE, as a sustainability evaluation and design tool, can provide a holistic sustainability performance analysis for chemical processes that meets these requirements and helps the process designers and decision-makers with comparing multiple processes or locating areas for analyzing the optimal trade-offs in terms of sustainability. As mentioned above, GREENSCOPE provides dimensionless indicator scores for sustainability performance. The normalized indicators offer some advantages for applying GREENSCOPE to different scenarios. Moreover, the dimensionless indicators can be lumped or aggregated for process optimization or control studies based on a user-selected weighting method. Finally, the dimensionless indicator scores enable visualization of the multi-dimension sustainability performance using radar plots. A novel visualization technique for analyzing process sustainability performance during transient is described in Section 6.4.

6.3 Process Control for Sustainable Process Operations

6.3.1 Integrated Control Strategy for Sustainability

The proposed control framework in this chapter is built as an integrated approach that includes nonlinear process control and online sustainability assessment, as shown in Figure 6.2. The role of the online sustainability assessment part is to monitor the impact of the control action in terms of sustainability and provide information to the controller on the thresholds for selected sustainability indicators. Sustainability concerns/policies can then be successfully translated to process control actions to improve the process sustainable performance.

Figure 6.2 Proposed framework for novel sustainable process control

6.3.2 BIO-CS controller

An in-house control toolbox for BIO-CS⁹⁹ developed in MATLAB (available upon request) is implemented to address the control task. As described above, BIO-CS is an optimal control approach that combines the ants' rule of pursuit idea with multiagent concepts. The resulting agent-based control framework allows each follower agent to update its path toward the set point based on the leader agent's feasible trajectory. As the number of agents progresses, the trajectories converge to an optimal solution. The developed algorithm employs gradient-based optimal control solvers (e.g., dynopt optimization toolbox¹¹¹) in the toolbox for solving the constrained/unconstrained nonlinear optimization problems. The effectiveness of the developed control algorithm has been illustrated via applications associated with fermentation processes¹¹², a hybrid energy system¹¹³, and a coal-fired power plant¹¹⁴. In this chapter, the capability of integrating sustainability into BIO-CS is explored. The sustainability-oriented BIO-CS is formulated as follows:

$$\min_{u^*(t)} J = \int_{\tau_i}^{\tau_s} (||y(\tau) - y_{sp}||_{w1}^2 + ||u(\tau) - u^-(\tau)||_{w2}^2) d\tau \quad (6.1)$$

$$\text{s.t. } \dot{x}(t) = f(u(t), x(t), y(t), p, t) \quad (6.2)$$

$$SI_i \geq SI_{th} \quad (6.3)$$

$$x(t) \in [x(t)^{lb}, x(t)^{ub}] \quad (6.4)$$

$$u(t) \in [u(t)^{lb}, u(t)^{ub}] \quad (6.5)$$

in which $u(t)$, $x(t)$, and $y(t)$ are the input, state and output variables, respectively, and τ stands for time. The optimal input trajectory of the control problem is $u^*(t)$, which is calculated over the sampling time $t \in [\tau_i, \tau_s)$. This calculation is subject to the process model, $f(\cdot)$, sustainability constraints specified by a sustainability index, SI_i , and boundary constraints on $u(t)$ and $x(t)$. Please refer to publication¹¹⁵ for the detailed algorithm of BIO-CS.

6.4 Visualization of Dynamic Sustainability Performance

6.4.1 Visualization Approach

Most of the work in the sustainability area only focuses on steady-state operations, thus ignoring dynamic behavior even though chemical processes exhibit complex dynamics. Understanding the dynamic behavior of sustainable systems and controlling the process to meet the sustainability goals is a critical task in the sustainability field. However, research in this direction is scarce. This fact can be attributed to the complex and integrated nature of the resulting problems when sustainability is incorporated into chemical process operation at different time and space scales. For example, sustainability requires the expansion of the traditional energy, economic and product quality-focus to multiple objectives (e.g.,

environmental, economic and social objectives). Despite of these challenges, it is expected that sustainability will be a major driver for process systems engineering (PSE) to advance the capability of future chemical processes to deal with multiple control targets while balancing conflicting objectives. Before moving to the implementation of the proposed framework, the proposed approach to monitor the process sustainability performance during transient is introduced so that the characteristics of dynamic sustainability performance of the process can be analyzed.

Here process dynamics are referred to the essential relationships among different process variables (e.g., temperature, pressure, concentrations) while dynamic sustainability performance focuses on the understanding of the dynamic nature of the system from the sustainability perspective (e.g., in terms of sustainability indicators). For example, the fermentation process can be operated with fermenter dilution rate (D_{in}), membrane dilution rate ($D_{m,in}$), and cooling water flow rate (D_j) fixed at 0.5 h^{-1} , 0.1 h^{-1} , and 0.1 h^{-1} , respectively. The dynamic sustainability performance of the process can be represented by selected GREENSCOPE indicators, such as Reaction Yield (RY), Water Intensity (WI), Environmental Quotient (EQ), Global Warming Potential (GWP), Specific Raw Material Cost (C_{SRM}) and Specific Energy Intensity (R_{SEI}) (refer to Table A4 in Appendix A for indicator definitions and details). The obtained GREENSCOPE indicator scores translate the process data into sustainability information for process monitoring and analysis in real-time operation. In this chapter, a time-explicit radar plotting technique is developed for displaying the multivariate sustainability information as depicted in Figure 6.3. In this approach, as shown in Figure 6.3(a), each radar plot (or polygon) represents the selected six sustainability indicators with specific score values. According to the definition of a sustainability indicator score,

the center represents 0% sustainable while the outside edge 100% sustainable. Thus, the wider polygon means the better performance in terms of sustainability. Hence, visualization of sustainability performance along the time dimension can be accomplished by stacking multiple polygons on top of one another on the time axis, as shown in Figure 6.3(b). The developed plotting method provides an efficient and intuitive way of presenting high-dimensional time-explicit sustainability performance. However, with the indicator numbers and time horizon increasing, it is hard to identify whether or not the operation is moving towards a more sustainable area especially when some indicators selected are conflicting. To better balance the tradeoff between conflicting indicators as well as help with the decision-making step, a lumped sustainability index (SI) is defined for combining indicators with user-defined weighting factors. An average sustainability index ($\bar{SI}$) can then be derived from the calculated SI values for analyzing or measuring the performance during any specific time interval. The definitions of these indices are shown below in equations (6.6-6.7) .

$$\text{Sustainability Index } (SI(t)) = \frac{\sum w_i \cdot PS_i(t)}{\sum w_i \cdot PS_{max,i}} \quad (6.6)$$

$$\text{Average Sustainability Index } (\bar{SI}) = \frac{\int_{t_0}^{t_f} SI(t)}{(t_f - t_0)} \quad (6.7)$$

where w_i , $PS_{max,i}$, t_0 and t_f are the weighting factors and maximum percent score (PS) for the specific indicator i as well as the initial and final time interval. Note that different weights can be assigned to selected indicators depending on the user preferences or the application. A larger number means higher impact of the indicator on the overall sustainability performance. In this chapter, equal weights for the selected six sustainability indicators has been used throughout this study.

Figure 6.3 Visualization method for monitoring high-dimensional sustainability performance: (a) 2D radar plot; (b) 3D radar plot

6.4.2 Open-loop Simulation Example

The process dynamics have direct relationship with the dynamic sustainability performance of the process. Here open-loop simulation results of the fermentation process are used to illustrate the effectiveness of the proposed dynamic sustainability visualization approach. Figure 6.4 shows the concentration profiles of the key component (C_e), biomass (C_X), substrate (C_S), product in the fermenter (C_P) and membrane sides (C_{PM}) as well as fermenter temperature profile (T_r) with the predefined operating conditions. As reported in Chapter 5, the open-loop fermentation process exhibits oscillatory dynamic behavior. From the sustainability perspective, the six indicators mentioned above have been selected for evaluating the fermentation process in terms of efficiency, environmental, energy and economic aspects and for identifying how the overall performance of the process can be improved in terms of sustainability. As shown in Figure 6.5, most indicators (except WI) follow the trends in the process oscillations shown in Figure 6.4. This can be

explained by the fact that the dilution rates of D_{in} , $D_{m,in}$, and D_j that are associated with WI are kept constant for the open-loop simulation and the other indicators, such as RY, EQ, GWP, C_{SRM} , and R_{SEI} , are strongly related to the process dynamics. Fermentation involves two types of reactions: one is microbial growth reaction and the other is the metabolite reaction for ethanol production. From the process dynamics in Figure 6.4(a), it is clearly shown four distinguished process phases, including 0-1h, 1-5h, 5-18 h and 18-30 h. For the time zone of 0-1h, the substrate is mostly consumed for biomass and key component formation and the yield for ethanol is relatively low. Hence, process performance in terms of sustainability for this region is shown as red in Figure 6.5, which means less sustainable. This color scheme is defined according to the SI value for every time step. It is interesting to note that the most sustainable part of the simulation occurs during the transient stage of 1-5 h, which corresponds to the highest average reaction yield. During 5-18 h, strong oscillations start due to ethanol inhibition and the SI values start to decrease, which is reflected by a gradually changing green color along the time axis in Figure 6.5(a). After 18 h, the system is prone to steady state with light green sustainability status, as shown in Figure 6.5. Through a deeper analysis of the dynamic sustainability performance, note that EQ, C_{SRM} , R_{SEI} and overall sustainability performance improve with the higher RY, while GWP drops with RY increasing. Such monitoring approach thus can help the design and implementation of the controller for keeping the system within a designed sustainable operating range.

Figure 6.4 Process open-loop simulation dynamics: (a) concentration profiles of different components and (b) reactor temperature profile

Figure 6.5 Dynamic sustainability performance of open-loop simulation (red represents less sustainable while green more sustainable according to calculated SI values): (a) 3D sustainability indicator dynamic radar plot; (b) 2D projection of sustainability indicator radar plot

6.5 Results and Discussion

Two case studies are presented here to evaluate the effectiveness of the novel sustainable process control framework. The first case with a fixed D_{in} value of 0.1 h^{-1} is chosen to illustrate the application of the sustainability-oriented control strategy to improve the process sustainability performance. Specifically, the dynamic sustainability performance visualization approach is used to analyze how places with lower sustainability performance can be improved by adding sustainability

constraints to the controller. The second case study shows the framework performance for a more challenging case with a higher D_{in} of 0.5 h⁻¹, which corresponds to a higher volumetric productivity in the fermenter. For all simulations, the parameter values in Table 5.1 are kept constant.

6.5.1 Case 1

The effectiveness of the sustainability-oriented control strategy is first demonstrated using the fermentation process for a setpoint tracking study. In this case study, the optimal setpoints for C_{PM} and T_r are set at 48 kg/m³ and 30 °C, respectively, based on our previous studies. The objective function of the controller is to minimize the difference between the values of the controlled variables, C_{PM} and T_r , with respect to their setpoints by optimizing the input variable ($D_{m,in}$ and D_j) trajectories, as shown in Equation 6.1. Figure 6.6 depicts the closed-loop simulation results obtained for the output and input profiles. Note in this figure that, with the implementation of the proposed BIO-CS, the oscillations observed in the open-loop simulations are eliminated completely and the system reached the desired setpoints in ~3.5 h. Chapter 5 has shown that the steady state obtained here using the controller is more sustainable than the open-loop result. The proposed control strategy in this chapter takes a step forward towards analyzing the sustainability performance along the path from the initial starting point (e.g., during start-up) to the desired steady-state so that sustainability constraints can be defined and added to the controller design. As shown in Figure 6.7(a), three distinguished regions in terms of sustainability performance characteristics can be observed at 0-0.8h, 0.8-2h, and 2-10 h. The time zone of 0-0.8h (reddish zone with $\bar{SI}$ of ~ 0.78) is the start-up, which involves the conversion of substrate to ethanol as well as biomass cell reaction. The relatively low SI for this phase can be explained by the low efficiency

of the fermentation process at the beginning and biomass and key component are not growing enough for completely converting substrate into product. During 0.8-2 h, the overall sustainability performance first improves for a short time and then decreases. This can be attributed to the fact that the reaction yield or efficiency reached the highest level at 1 h and then the water usage starts to increase from 1 to 2 h as shown in Figure 6.6. Note that the WI indicator performance is directly associated with the profiles of the manipulated variables while EQ, GWP, C_{SRM}, and R_{SEI} are more prone to changes with RY. After 2 h, the main variables of the system reach the steady state and thus the sustainability performance kept the same with $\bar{SI}$ of ~ 0.84. By further analyzing the sustainability performance, it is found that 0.8-2 h has relatively low $\bar{SI}$ at 0.77, which can be attributed to the lowest sustainability indicator of WI (lowest value of 58%). In order to make sure the WI score is above a certain threshold during transient, a nonlinear sustainability constraint related to the WI score is added to the BIO-CS controller as follows:

$$\frac{D_{in} \cdot V_f + D_{m,in} \cdot V_m + D_j \cdot V_j}{(WI_{upper} - WI_{lower}) \times \dot{m}_{product}} > 0.7 \quad (6.8)$$

in which the sum of terms in the numerator corresponds to the total water usage in the system, WI_{upper} , WI_{lower} , and $\dot{m}_{product}$ represent the upper and lower boundaries for WI as well as production rate, respectively. The BIO-CS solver implemented can handle such nonlinear constraints effectively. Figures 6.8 and 6.9 show the input and output profiles of the fermentation process and the dynamic sustainability performance, respectively, after the implementation of a WI constraint ($WI > 70\%$). It is shown in Figure 6.9 that the BIO-CS controller with the sustainability constraint can successfully drive the system to the setpoints within a more sustainable range for water use while meeting the constraint. During 0.8-2h, the

sustainability performance with $\bar{SI}$ of 0.84 increases by 9.65%, when compared to the scenario without the constraint ($\bar{SI}$ of 0.77). To clearly show the comparison in terms of the sustainability performance for the cases with/without the added sustainability constraint, Figure 6.10 shows all the sustainability indicators at three representative time points: 1.8 h, 2.1 h, and 10 h. Note that the constrained scenario changes the other sustainability indicators slightly during transient time (during 0-3 h) but the final steady states are the same due to the same setpoints used for both scenarios. By comparing the inputs profiles in Figures 6.6 and 6.8, it is found that BIO-CS optimizes the input profiles of $D_{m,in}$ and D_j to avoid increasing these two variables simultaneously, thus optimizing the WI score. It is worth mentioning that the sustainability constrained problem slightly decreases the controller performance though in terms of smoothness of the input profiles and time to reach steady state.

Figure 6.6 Case 1 - closed-loop simulation without sustainability constraint: output (y_1 and y_2) and input (u_1 and u_2) profiles

Figure 6.7 Case 1 - dynamic sustainability performance without sustainability constraint: (a) 3D sustainability indicator dynamic radar plot; (b) 2D projection of sustainability indicator radar plot

Figure 6.8 Case 1 - closed-loop simulation with sustainability constraint: output (y_1 and y_2) and input (u_1 and u_2) profiles

Figure 6.9 Case 1 - dynamic sustainability performance with sustainability constraint: (a) 3D sustainability indicator dynamic radar plot; (b) 2D projection of sustainability indicator radar plot

Figure 6.10 Case 1 - comparison between control without WI constraint (red line) and control with WI constraint (blue line) at three representative sample points

6.5.2 Case 2

To further investigate the capability of the proposed sustainability-oriented process control framework, a more challenging case with D_{in} of 0.5 h^{-1} , which represents a higher ethanol production rate with the same fermenter size is addressed in Case 2. Operation with higher D_{in} can increase the fermenter productivity which is an important performance indicator from the economic point of view. In this case, the setpoints, the manipulated variable boundaries and the objective function of the controller are kept the same as in Case 1. Figure 6.11 depicts the closed-loop simulation results for the output and input profiles. In this figure, it is shown that the implemented BIO-CS can also successfully eliminate the oscillations and drive this more challenging case to the desired setpoints. Note that the manipulated variables reach their upper boundaries in the first 2 hours which cause higher water consumption, thus worsen the overall sustainability performance. Figure 6.12 shows the dynamic sustainability performance results for Case 2 without the sustainability constraint. Compared with Case 1, the overall sustainability performance of Case 2 for the same obtained steady state is lower than that of Case 1 due to the lower efficiency and more water usage for the high D_{in} operating condition. However, the dynamic sustainability performance shares similar characteristics with Case 1 for the different zones: 1) 0-1 h with low sustainability

performance; 2) 1- 2.5 h for transient time before steady state; 3) 2.5 - 10 h for steady state. From the control results with the sustainability constraint on WI in Case 1, it is anticipated that the sustainability performance before steady state can be improved by adding a sustainability constraint on WI. Moreover, it is known from Figure 6.12 that the WI score for the obtained steady state is of 55.47% and thus a reasonable threshold of 55% is selected for the WI score constraint.

Figures 6.13 and 6.14 show the input and output profiles for the closed-loop simulation as well as the dynamic sustainability performance, respectively, for the scenario with the WI constraint. It is shown in Figure 6.13 that the BIO-CS controller with the sustainability constraint can successfully drive the system to the setpoints within a more sustainable range, while meeting the constraint (WI score > 55%). It is worth mentioning that the controller could not push the system to the setpoints if the WI score constraint was increased to 60%. This is because the controller fails to achieve the setpoints with such high WI threshold (higher than WI score of the obtained steady state). During transient time of 0-2.5 hours, the process sustainability performance in terms of $\bar{SI}$ is 0.66, which increased by 16.86%, when compared to the unconstrained problem with $\bar{SI}$ of 0.56 during the same transient. To clearly show the comparison in terms of sustainability indicators for the two cases with/without the sustainability constraint, Figure 6.15 shows all the sustainability indicators at three representative time points: 0.36 h (the time of lowest WI score for the unconstrained scenario), 2.1 h (the time of highest WI score for the constrained scenario), and 10 h (the time that reached steady state). It is worth mentioning in Figure 6.15 that during transient the other sustainability indicators except WI improve while the sustainability performance of the final steady states are exactly the same for the two scenarios. By comparing the input profiles in Figures 6.11 and 6.13, it is

found that the BIO-CS input profiles for the constrained problem have slightly higher oscillations, which might have been caused by the challenging sustainability constraint as the system is operating close to the boundary of the steady-state WI score.

Figure 6.11 Case 2 - closed-loop simulation without sustainability constraint: output (y_1 and y_2) and input (u_1 and u_2) profiles

Figure 6.12 Case 2 - dynamic sustainability performance without sustainability constraint: (a) 3D sustainability indicator dynamic radar plot; (b) 2D projection of sustainability indicator radar plot

Figure 6.13 Case 2 - Closed-loop simulation with sustainability constraint: output (y_1 and y_2) and input (u_1 and u_2) profiles

Figure 6.14 Case 2 - Dynamic sustainability performance with sustainability constraint: (a) 3D sustainability indicator dynamic radar plot; (b) 2D projection of sustainability indicator radar plot

Figure 6.15 Case 2 - Comparison between control without WI constraint (red line) and control with WI constraint (blue line) at three representative sample points

6.6 Conclusions

This chapter introduced and demonstrated the proposed novel sustainability-oriented control strategy to improve process sustainability during transient. Two case studies of a fermentation process with different dilution rates (D_{in}) were used to illustrate the application of the proposed dynamic sustainability performance visualization approach as well as the benefits of integrating a sustainability constraint into the BIO-CS control strategy. Specifically, integrating process control with dynamic sustainability helps with the understanding of the dynamic characteristics of the system in terms of sustainability. Based on the analysis of the dynamic sustainability performance, regions with lower sustainability percentage can be detected, and a reasonable constraint can be imposed on selected sustainability indicators so that the control actions can be optimized for improving sustainability performance. Such framework successfully improved the sustainability performance of the two addressed cases by 9.65% and 16.86%, respectively.

Chapter 7 Multi-objective Optimization and Sustainable Process Control: Application to Gasification System

7.1 Introduction

In this chapter, the previously developed sustainable process control framework is integrated with a multi-objective optimization method. Specifically, the multi-objective optimization problem is formulated based on economic and environmental objectives. The resulting multi-objective problem can be solved using optimization algorithm (e.g., Genetic Algorithm) to generate a Pareto-optimal set. In Pareto optimal analysis, a compromise among the objectives must be considered. Based on a ranking scheme algorithm for decision making, an optimal solution is selected from the Pareto set and then sent to the controller to define the desired set points. The role of the controller implementation is to drive the process system to the chosen optimal sustainable operating point along predefined sustainability constraints. For the controller design, linear MPC is explored in this chapter with the addition of a sustainability constraint. The state-space model for control purposes is derived from the step responses of a developed dynamic biomass/coal co-gasification model in Aspen Hysys. Control structure selection is determined based on sensitivity analyses and mapping of input and output variables. Here the input variables represent potential manipulated variables for the controller, which are varied in a certain range according to the typical operation, while the output variables correspond to potential controlled variables. In summary, the implemented controller is expected to automatically take the process to the optimal steady state determined by the multi-objective optimization algorithm according to the decision maker.

The effectiveness of the proposed framework is demonstrated via the case study of a biomass/coal co-gasification process. The outline of the rest of this chapter

is as follows: in Subsection 7.2, the proposed framework is presented, including the multi-objective optimization, decision maker algorithm as well as the model predictive control approach. In Section 7.3, the proposed framework is applied to the case study to demonstrate its effectiveness.

7.2 Approach

7.2.1 Framework

As shown in Figure 7.1, the proposed sustainable control strategy contains three main steps: process and sustainability assessment model construction, multi-objective optimization formulation, and implementation of the control strategy. For the model, a rigorous model is developed in Aspen Hysys and then a state-space model is derived for process control purposes. The developed sustainability assessment tools in Chapters 4 and 5 are used to represent the sustainability model. Based on the Aspen Hysys model, a non-dominated sorting genetic algorithm-III (NSGA-III) is used to solve the multi-objective optimization problem to obtain the Pareto frontier, as detailed below. Then MPC is implemented to take the system to the selected setpoints determined by the weighted decision maker method while meeting the sustainability constraints.

Figure 7.1 Schematic of the sustainable control strategy based on multi-objective optimization

7.2.2 Multi-objective Optimization

Genetic Algorithms (GA), unlike the classical methods of combining all objectives into one fitness function, can handle multiple objectives simultaneously. The concept of GA is inspired by the mechanism of natural selection, using chromosomes, crossover and mutation as searching and exploring operators. Specifically, GA generates/updates the current solutions (chromosomes) using crossover and mutation. Typically, the crossover operator stochastically updates the next generations based on the current solutions by combining two parents' solutions while mutation alters the current solutions to explore the new searching space. To efficiently search for Pareto-optimal solutions for multi-objective optimization problem, GA algorithm has been integrated with other selection algorithms. For example, NSGA-II^{116,117} is based on the non-dominated ranking and elite-preservation concepts for passing the diversified solution from one generation to the next. Specifically, the non-dominated solution is a solution that is not possible to be outperformed in all criteria simultaneously, relative to a set of supplied solutions. A set of non-dominated solutions is not necessarily Pareto optimal. To improve the performance of NSGA-II, NSGA-III employs more steps to add more Pareto optimal solution candidates besides general framework and parameters (e.g., population size, crossover probability, etc.) of NSGA-II. As shown in Figure 7.2, NSGA-III starts with generation N random solutions and then crossover and mutation operators are applied to parent population to generate offspring populations, as NSGA-II does. To avoid inter-direction competition, parent and offspring populations are combined. The whole combined population goes through the non-dominated sorting. Starting at the first Pareto frontier, solutions pass to the next parent generation. Typically, the algorithm will reach a frontier that has more individuals than the remaining slots in

the next parent population. In such case, the Pareto frontier points will be normalized using extreme values of the current population. After normalization, all the frontier points are associated with reference direction. Finally, to fill the next parent generation, a niching strategy is applied to select solutions attached to under-represented/un-represented reference directions. Overall, NSGA-III combines non-dominated sorting and niching techniques to locate the well-distributed Pareto frontier solutions in the close vicinity of each supplied reference direction.

Figure 7.2 NSGA-III algorithm flowsheet

7.2.3 Decision Making Algorithm

To automatically select the operating point from the available Pareto frontier solutions, a subjective weighting method is used as the multi-criteria decision-making method. As shown in Figure 7.3, this method involves normalizing the objective values by the minimum value, assigning preference weights for each objective function, multiplying the assigned weights by the normalized value and summing up the resulting scores to obtain the total weighted value for each solution on the Pareto frontier. Based on the obtained weighted scores, the minimum one is automatically selected as the optimal operating point if the problem is a minimization problem.

Figure 7.3 Weighting method for the decision maker

7.2.4 Model Predictive Control (MPC)

As mentioned previously, the chosen Pareto solution is used to define the set points for the controller. For this chapter, the MPC with a sustainability indicator index can be defined by the following optimization problem:

$$\min_{u^*(t)} J = \int_{\tau_i}^{\tau_s} (||y(\tau) - y_{sp}||_{w_1}^2 + ||u(\tau) - u^-(\tau)||_{w_2}^2) d\tau \quad (7.1)$$

$$\text{s. t. } \dot{x}(t) = Ax(t) + Bu(t) \quad (7.2a)$$

$$y(t) = Cx(t) + Du(t) \quad (7.2b)$$

$$SI_i \geq SI_{th} \quad (7.3)$$

$$x(t) \in [x(t)^{lb}, x(t)^{ub}] \quad (7.4)$$

$$u(t) \in [u(t)^{lb}, u(t)^{ub}] \quad (7.5)$$

in which $u(t)$, $x(t)$, and $y(t)$ are the input, state and output variables, respectively, and τ stands for time. The optimal input trajectory of the control problem is $u^*(t)$, which is calculated over the sampling time $t \in [\tau_i, \tau_s)$. The control model corresponds to a state-space model derived from input-output data of a high-fidelity Aspen Hysys model. This control action calculation is subject to the state-space process model, sustainability constraints specified by a sustainability index, SI_i , and boundary constraints on $u(t)$ and $x(t)$.

7.3 Results & Discussions

7.3.1 Gasification Process in Aspen Hysys

Gasification technologies can convert different forms of hydrocarbons into synthesis gas (syngas) in the presence of water and oxygen. The syngas composition and yield depend on the operating conditions of the gasification process as well as the hydrocarbon source. In this work, the entrained flow gasifier is modeled based on the General Electric (GE) gasification technology, including partial oxidizer (POX), radiant synthesis gas cooler (RSC) and water quench sections. As shown in Figure 7.4, the POX part is modeled as three CSTRs with the reaction kinetics as defined in Table 7.1. RSC is modeled as a heat exchanger while the water quench part is considered as a mixer. To overcome the limitation of the current Aspen Hysys

simulation tools in handling solid hydrocarbon materials, a pseudo component, $C_{18}H_{20}$, is used as pseudo coal in the simulation. Also, the biomass is thermally decomposed to release volatile matter (VM), leaving behind a high carbon residue generically known as char during pyrolysis. This process is extremely complex due to the large number of chemical and physical transformations that rapidly and simultaneously occur. The required heat for biomass pyrolysis is provided by the exothermic reactions of partial combustion. Pyrolysis can be simplified as the following equations 7.6 - 7.10:

$$\begin{aligned} Biomass = & \alpha_1 CH_4 + \alpha_2 H_2 + \alpha_3 CO + \alpha_4 CO_2 + \alpha_5 H_2O + \alpha_6 \text{char} (C_{18}H_{20}) \\ & + \alpha_7 H_2S + \alpha_8 N_2 + \alpha_9 \text{ash} \end{aligned} \quad (7.6)$$

$$\omega_{H_2} = 0.157 - 0.868\omega_V + 1.388\omega_V^2 \quad (7.7)$$

$$\omega_{CH_4} = 0.201 - 0.469\omega_V + 0.241\omega_V^2 \quad (7.8)$$

$$\omega_{CO} = 0.428 - 2.653\omega_V + 4.845\omega_V^2 \quad (7.9)$$

$$\omega_{H_2O} = 0.409 - 2.389\omega_V + 4.554\omega_V^2 \quad (7.10)$$

$$\omega_{CO_2} = 0.135 - 0.9\omega_V + 1.906\omega_V^2 \quad (7.11)$$

where α_i is the number of moles of the species after devolatilization¹¹⁸; ω_V is the mass fraction of the volatile matter in the biomass on a dry ash free basis, and ω_i ($i = CO, CO_2, H_2O, CH_4, H_2$) is the mass fraction of species involved in the biomass pyrolysis. The char yield is calculated by the total mass balance, in which the H_2 and H_2S yields are calculated by element balances.

Reaction	Reaction rate expressions (kmol·m ⁻³ ·s ⁻¹)	Ref
$\text{CO} + 0.5\text{O}_2 \rightarrow \text{CO}_2$	$r_1 = 1.0 \times 10^{17.6} \exp(-20130/T) [\text{CO}] [\text{H}_2\text{O}]^{0.5} [\text{O}_2]^{0.5}$	119
$\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$	$r_2 = 5.44 \times 10^{12} \exp(-24358/T) [\text{CH}_4]^{0.3} [\text{O}_2]^{1.3}$	119
$\text{H}_2 + 0.5\text{O}_2 \rightarrow \text{H}_2\text{O}$	$r_3 = 2.85 \times 10^{16} \exp(-20130/T) [\text{H}_2]^{0.25} [\text{O}_2]^{1.5}$	119
$\text{C}_{18}\text{H}_{20} + 9\text{O}_2 \rightarrow 18\text{CO} + 10\text{H}_2$	$r_4 = 1.0 \times 10^6$	85
$\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$	$r_{5f} = 1.612 \times 10^{-6} \exp(-47400/T) P_{\text{CO}} P_{\text{H}_2\text{O}}$ $r_{5r} = 1.224 \times 10^{-3} \exp(-85460/T) P_{\text{CO}_2} P_{\text{H}_2}$	120
$\text{CO} + 3\text{H}_2 \leftrightarrow \text{CH}_4 + \text{H}_2\text{O}$	$r_{6f} = 312 \exp(-30000/T) C_{\text{CO}} (C_{\text{H}_2})^3$ $r_{6r} = 6.09 \times 10^{14} \exp(-257000/T) C_{\text{CH}_4} C_{\text{H}_2\text{O}}$	120

Figure 7.5 shows the communication interface built to connect different software platforms. As shown in this figure, both the steady-state simulation and dynamic simulations are developed in Aspen Hysys while the multi-objective optimization (MOO) and control algorithm are coded in MATLAB. MOO is based on the steady-state model in Aspen Hysys and the connection between MATLAB and Aspen Hysys is accomplished via the component object model (COM) server. The Aspen Hysys dynamic simulation is connected with MATLAB by Aspen OTS and OPC server (OLE (Object Linking and Embedding) for Process Control).

Figure 7.5 Communication interface between different software platforms

7.3.2 MOO Results

NSGA-III is an efficient and powerful algorithm for finding trade-offs between conflicting optimization objectives. The objective of the implemented NSGA-III is to find the optimal feeding ratio for biomass/coal to simultaneously minimize the environmental impact and operating cost objectives, which are defined in equations 7.12 and 7.13, respectively.

$$f_1 = w_1 \cdot SI_{GWP} + w_2 \cdot SI_{m_{s,spec}} + w_3 \cdot SI_{V_{L,spec}} \quad (7.12)$$

$$f_2 = \frac{\text{Operating Cost}}{\text{Syngas Production Rate}} \quad (7.13)$$

$$s.t. \text{ Aspen Hysys Steady – State Model} \quad (7.14)$$

$$x(t) \in [x(t)^{lb}, x(t)^{ub}] \quad (7.15)$$

$$u(t) \in [u(t)^{lb}, u(t)^{ub}] \quad (7.16)$$

in which, f_1 and f_2 are the two objective functions. In f_1 , SI_{GWP} , $SI_{m_{s,spec}}$ and $SI_{V_{L,spec}}$ are the sustainability indices associated with Global warming potential (GWP), Specific solid waste mass ($m_{s,spec}$), and Specific liquid waste volume ($V_{L,spec}$), respectively.

By solving the resulting MOO problem with population size of 120 and generation number of 150, the Pareto frontier result is shown in Figure 7.6. Such Pareto trend shows that better economic performance requires higher waste/emissions (see for example the reference coal case). This can be attributed to the fact that biomass has lower environmental waste index and higher operating cost than coal due to the high cost of pre-treating and lower syngas yield comparing to coal gasification. Additional analysis is performed based on biomass content in the feeding stream. The results in Figure 7.6 show that by adding < 6.65wt% biomass in the gasification feeding, the environmental waste index can decrease dramatically (up to 11.5%) while operating cost does not increase that much. A linear relationship is displayed for the environmental waste and operating cost indices from the biomass content in the feeding between 6.65~23.76%. Also, it is shown that high biomass content (>23.76%) makes the operating cost increase greater than 30%, consistent to the literature on the study of biomass/coal co-gasification^{121,122}.

For this case study, the weighting factors for environmental and operating cost functions are selected as 0.7 and 0.3, respectively. A point can then be chosen by the decision maker using the method described above, as shown in Figure 7.7. For the control implementation, a setpoint tracking study is performed considering this point as reference to the controller.

Figure 7.6 Pareto frontier for biomass/coal co-gasification process

Figure 7.7 Selected operating condition for the MPC controller

7.3.4 MPC Implementation Results

One case study is presented here to evaluate the effectiveness of the sustainable process control framework based on the multi-objective optimization. Based on previous analysis of this gasification process, a 3 by 3 control strategy is selected for the MPC by manipulating coal, oxygen and water flowrates to achieve the setpoints for syngas production rate, gasifier temperature and H_2/CO ratio. The setpoints for the controlled variables are obtained from the decision making algorithm. Figure 7.8 shows the controller input and output trajectories. Note that the controller can take the system successfully to the setpoints. Moreover, the dynamic sustainability performance in Figure 7.8 shows that the control actions can also meet a pre-defined sustainability constraint in this case for $GWP > 0.6$.

Figure 7.8 MPC results: input and output profiles

7.4 Conclusions

This chapter combined the previously introduced sustainability-oriented control strategy with a multi-objective optimization algorithm. Specifically, the multi-objective optimization solution considered the conflicting objective functions to define the setpoints for the sustainable process controller. Such integrated framework is developed to take the system to sustainable operating conditions along a predefined sustainable zone. The effectiveness of the proposed framework is demonstrated via a large-scale biomass/coal co-gasification process.

Chapter 8 Conclusions and Recommendations

In this dissertation, process systems engineering (PSE) methods were developed for evaluating and improving sustainability performance of chemical processes during steady-state and transient operations. In particular, an integrated tool was developed to provide a systematic and comprehensive way of quantifying the sustainability performance of chemical processes. This developed tool was applied to chemical manufacturing processes. In order to further examine and improve process sustainability performance during transient, a multi-variable sustainability visualization method, multi-objective optimization approaches and a sustainable process control strategy were proposed. These developed approaches can fill the knowledge gap regarding the lack of tools for assessing the dynamic sustainability performance of chemical processes.

Below, the major contributions made in this dissertation are summarized as well as some future directions that are worth research attention are provided.

8.1 Major contributions

In Chapter 2, a comprehensive literature review was given considering the current available tools and methods for sustainability of chemical manufacturing processes. Moreover, the limitations and gaps on current sustainability studies for chemical processes were pinpointed.

In Chapter 3, a sustainability assessment tool was developed, focusing on an integrated framework for automatically generate gate-to-gate LCI data based on process modeling, simulation, and design. To augment the current capability of commercial simulators, parameterized PCU tools were developed for providing data for rapid LCI estimation and sustainability assessment. This method showed to be more efficient and accurate than available LCI data base or top-down methods.

Additionally, in Chapter 4, such integrated tool was further expanded to integrate process simulation, PCU, LCI and GREENSCOPE for sustainability indicator calculations and demonstrated with a large-scale biomass/coal-to-AA process. This framework provides a systematic and comprehensive way to evaluate the sustainability performance of chemical processes.

For the dynamic sustainability studies in Chapter 5, the benefit of integrating sustainability assessment tool with process dynamics was presented using a motivating example. The obtained sustainability assessment results can provide systematic guidelines for decision-makers as well as show whether the implementation of an advanced controller can improve the system's sustainability performance. Then, in Chapter 6, a novel sustainability-oriented control strategy was proposed to improve process sustainability during transient. This sustainable process control framework with dynamic sustainability is capable of detecting regions of operation with lower sustainability performance. Using the dynamic sustainability result, a reasonable constraint can be imposed on the sustainability indicators so that control actions can be optimized for improving sustainability performance. Finally, in Chapter 7, the sustainable process control framework was combined with multi-objective optimization. This framework can provide the optimal setpoints in terms of sustainability for the controller considering sustainability aspects during transients.

8.2 Recommendations

Based on the findings presented in this dissertation, the following future directions are recommended:

- The integrated tool for LCI estimation and sustainability assessment is general and can be applicable to any process. Currently, only one case study was

used to demonstrate this framework. It would be interesting if more chemical processes could be tackled. Also, it would be useful if a superstructure optimization algorithm could be equipped with the tool for selecting optimal PCUs for treating certain waste streams.

- Other multi-objective optimization and decision-making algorithms could be tested for the co-gasification processes, such as Particle swarm optimization (PSO) with a more advanced ranking algorithm. It would be interesting to see comparisons among different MOO algorithms.

- In the performed studies, one sustainability constraint was considered where the boundary was set through trial and error. In the future, an online performance analysis system for locating the most important sustainability indicator can be investigated to automatically give the sustainability indicator constraint. Also, it would be meaningful to study a dynamic operability method for guiding the definition of a constraint threshold for improving the controller robustness.

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Appendix A

Table A1. PCU_Flare Unit

Flare Input			Flare Output							
Temperature	°C	30		Gas Phase		Utility			Land	Material
Pressure	kPa	150								
Flare type	-----	Steam-assisted								
Desired CE	%	98								
Local Wind Velocity	m/s	5								
Mach Number	-----	0.2								
Max Allowable Radiation	kW/m²	1.58								
Radiation Fraction	-----	0.3								
Horizontal Distance	m	50								
	Normal	Emergency	Emission Species	kg/hr	wt%	NG,kg	Purge Gas	Steam,kg	m³	kg
Flowrate, kg/s	3.32	3.82				524	45.675	0	471	84313.8
Components, wt%			CO2	5007.49	37.55					
CO2	29.800	26.0269	NO	0.72	0.01					
SO2	0.000	0	CO	32.10	0.24					
NO	0.006	0.005526611	N2	8295.55	62.20					
CH4	0.001	0.0532	CH4	0.00	0.00					
CO	0.220	11.9146	PM	0.06	0.00045					
N2	68.954	59.887								
O2	1.019	0.885								
H2O	0.000	0.0000								
PM	0.001	0.000436311								
Methanol		0.0083								
AA		0.1572								
Methyl Acetate		0.5711								
HI		0.4911								
Methyl Iodide		0.0000								
Propionic Acid		0.0000								

Table A2. PCU_Boiler Unit

Boiler Input		Boiler Output					
Total Flowrate, kg/s	0.474512038				Utility	Material	Land
Temperature, °C	30				kW	kg	m³
Pressure, kPa	100						
Burner Type	Uncontrolled						
Heat Input, MW	5						
Waste Heat, MW	5.07						
MP Steam, kg	10457.16405						
Components	wt%	Emission Species	kg/hr	wt%	2.98	2870.17	227.48
CO	93.82	CO2	3559.07	29.19			
CO2	1.17	SO2	0	0.00			
CH4	0.42	NO	0.76	0.01			
H2O	0.00			0.00			
Methanol	0.00			0.00			
AA	0.00			0.00			
Methyl Acetate	4.59	CH4	0.08	0.00			
HI	0.00			0.00			
Methyl Iodide	0.00			0.00			
Propionic Acid	0.00			0.00			
Natural Gas	336.66	CO	26.3	0.22			
		N2	8235.39	67.54			
		O2	121.7	1.00			
		H2O	250.24	2.05			
		PM	0.06	0.00			

Table A3. PCU_Scrubber Unit

Scrubber Input			Scrubber Output							
Total Flowrate	kg/s	0.503882949		Gas Phase		Utility	Material		Land	Sovent
Temperature	°C	30								
Pressure	kPa	150								
Packing Size	-----	1								
Components	wt%	Equilibrium Data (g/kg water)	Removal Efficiency	kg/hr	wt%	kW	Shell(304), kg	raschig rings,kg	m²	kg/hr
CO	88.8743	0.78	0.59%	1602.65	93.82	2.17	495.74	3499.97	13.16	90995
CO2	1.1056	1.588	0.60%	19.94	1.17					
CH4	0.3988	0.0142	0.02%	7.23	0.42					
H2O	0.3138	10000	100%	0.00	0.00					
Methanol	0.0627	1000	100%	0.00	0.00					
AA	1.1919	1000	100%	0.00	0.00					
Methyl Acetate	4.3295	0.5	0.14%	78.43	4.59					
HI	3.7230	100	100%	0.00	0.00					
				0.00	0.00					
Propionic Acid	0.0003	500	100%	0.00	0.00					

Table A4. Definitions and reference values for selected GREENSCOPE indicators

Category	Indicator	Formula	Unit	Sustainability Value	
				Best Case (100%)	Worst Case (0%)
Efficiency	Reaction Yield (RY)	$RY = \frac{\text{Mass of product}}{\text{Theoretical mass of product}}$	kg/kg	1.0	0
	Water Intensity (WI)	$WI = \frac{\text{Volume of fresh water consumed}}{\text{Sales revenue or value added}}$	m ³ /\$	0	0.1
Environmental	Environmental Quotient (EQ)	$EQ = \frac{\text{Total mass of waste}}{\text{Mass of product}} \times \text{Unfriendliness quotient}$	m ³ /kg	0	2.5
	Global Warming Potential (GWP)	$GWP = \frac{\text{Total mass of CO}_2 \text{ equivalents}}{\text{Mass of product}}$	kg/kg	0	Any waste released has a potency factor at least equal to 1
Economic	Specific Raw Material Cost (C _{SRM})	$SRWC = \frac{\text{Raw material costs}}{\text{Mass of product}}$	\$/kg	0	0.5
Energy	Specific Energy Intensity (R _{SEI})	$R_{SEI} = \frac{\text{Net energy used as primary fuel equivalent}}{\text{Mass of product}}$	kJ/kg	0	100