Systems Integrations for the Holistic Design of Second Generation Biorefineries

Aikaterini D. Mountraki

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Systems Integrations for the Holistic Design of Second Generation Biorefineries

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Aikaterini D. Mountraki M.Sc. Eng.

Under the direction of

Professor Antonis C. Kokossis, CEng, FIChemE, FRSA, FIET

Department of Process Analysis and Plant Design
School of Chemical Engineering
National Technical University of Athens,
Athens, Greece

Industrial Advisor

Dr. Bouchra Benjelloun-Mlayah, R&D Manager

Compagnie Industrielle de la Matière Végétale
109, Rue Jean Bart - Diapason A, Labège
Toulouse, France

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Defended on 27 March 2019 in front of the jury

1. **Professor Antoniss C. Kokossis** (supervisor)
School of Chemical Engineering, NTUA, Greece

2. **Professor Nikolaos Papayannakos**
School of Chemical Engineering, NTUA, Greece

3. **Emeritus Professor Nikolaos C. Markatos**
School of Chemical Engineering, NTUA, Greece – Visiting: Texas A&M University, Qatar

4. **Professor Eleni Grigoropoulou**
School of Chemical Engineering, NTUA, Greece

5. **Professor Maria Loizidou**
School of Chemical Engineering, NTUA, Greece

6. **Associate Professor Anastasia Detsi**
School of Chemical Engineering, NTUA, Greece

7. **Associate Professor Dimitrios Karonis**
School of Chemical Engineering, NTUA, Greece

Invited Jury Member

Dr. Bouchra Benjelloun-Mlayah (co-supervisor)
Directrice R&D, Compagnie Industrielle de la Matière Végétale (CIMV), France

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My PhD journey wasn't always pretty, but it certainly has been a great adventure. It took me some time to realize that C.P. Cavafy was right *:

> "*Laistrygonians, Cyclops,*
> *wild Poseidon—you won't encounter them*
> *unless you bring them along inside your soul,*
> *unless your soul sets them up in front of you*. "

Even though there were some casualties over the years, I wouldn't have missed it for anything in the world, because "the journey changes you; it should change you." **

* Ithaca, Constantine P. Cavafy (1863-1933)

**Anthony Bourdain (1956-2018)

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Ν᾽ αγαπάς την ευθύνη. Να λες: "*Εγώ, εγώ μονάχος μου έχω χρέος να σώσω τη γης. Αν δε σωθεί, εγώ φταίω.*"

Love responsibility. Say: "*It is my duty, and mine alone, to save the earth. If it is not saved, then I alone am to blame.*"

Νίκος Καζαντάκης (1883-1957), Ασκητική (1923)

Nikos Kazantzakis (1883-1957), Ascesis: The Saviors of God (1923)

Abstract

The development of integrated biorefineries is a multidimensional problem, which combines the traditional process design problem with the synthesis problem of product portfolios and multiple processing paths at various technological readiness levels (TRLs). The complexity and the size of the combined problem do not allow the development of a single optimization model. However, this thesis presents an approach to systems decomposition for the design problem of second generation biorefineries. The framework combines various design scales and tools for modeling, integration, and synthesis. The main objective is to simultaneously reduce the cost and the environmental impact, while optimizing the use of the utilities. Challenges include (i) the management of the data acquired by various sources (literature or experimental) and at various accuracy levels due to different TRLs (pilot, laboratory, or theoretical stage), (ii) the systematic screening of processing paths while considering the technological attributes, (iii) the impact of alternative designs on the utility consumption (mass and energy), (iv) the endogenous symbiotic options when revamping existing installations, and (v) the integrated waste management.

The approach makes use of surrogate-based optimization primarily to harmonize data coming from different sources, but also to assist in the systematic development of lower-grain models. Surrogates are employed to address deviations between the fine models and the experimental data by handling certain process and property parameters as degrees of freedom. Their use is illustrated by the synthesis of the value chain, where superstructures are developed as bipartite graphs of sinks and sources, organizing the processes as modular units that can be modified, replaced, and/or re-engineered. The synthesis problem is demonstrated in a network of twenty-one different processes, each accounted of separate surrogates. Next, the study continues with an optimization model that sets utility targets, simultaneously for mass and energy consumption, and to screen alternative technological options. The framework is applicable to both grassroots and retrofit designs. Lastly, the approach is extended for the integrated waste management and treatment. For this purpose, decision trees are proposed to classify the waste streams with criteria related to their physical state (liquids, solids and gases) and their qualitative characteristics. The optimization problem is formulated as a mixed-integer nonlinear programming problem. The objective function considers economic and environmental criteria, while the integration framework and the treatment technologies are considered as degrees of freedom.

Results show that surrogates led to significant improvements, and, when assisted by the simulation models, their selections were verified on industrial scale. In the process synthesis problem, results coming from nominal screening were rejected due to the qualitative characteristics of the streams and the technological constraints. The simultaneous integration of utilities and process design options demonstrated significant cost savings by reducing the energy consumption and proposing more efficient recycling/recuse configurations. The results of the retrofit problem showed a marginal preference for bioethanol production (partly due to the maturity of technology) but with coproduction of specialties and the integration of new technologies. The integrated waste management yielded significant savings in using decentralized treatment and nonconventional solutions. Results demonstrate the immense importance of the integrated design, confirming that the industrial biorefinery cannot compete with the equivalent conventional units without sufficient integration.

The research of this thesis has assisted in the industrial development of laboratory and pilot technologies, which were originally developed in France.

Περίληψη

Η ανάπτυξη σύγχρονων βιοδιυλιστηρίων αποτελεί σύνθετο σχεδιαστικό πρόβλημα καθώς, εκτός από τη συμβατική ανάπτυξη και την ολοκλήρωση των επιλεγμένων διεργασιών, απαιτείται η ταυτόχρονη ανάπτυξη χαρτοφυλακίων προϊόντων με επιλογές ανάμεσα σε διεργασίες με διαφορετικά επίπεδα ωριμότητας. Η πολυπλοκότητα και το μέγεθος του συνδυαστικού προβλήματος καθιστούν ανέφικτη την ανάπτυξη ενός ενιαίου μοντέλου βελτιστοποίησης. Εν τούτοις, η παρούσα διατριβή παρουσιάζει ένα συστημικό μεθοδολογικό πλαίσιο αποικοδόμησης που είναι κατάλληλο για το γενικευμένο πρόβλημα των βιοδιυλιστηρίων δεύτερης γενιάς. Η μεθοδολογία συνδυάζει εναλλακτικές σχεδιαστικές κλίμακες και εργαλεία προτυποποίησης που αφορούν στην αναπαράσταση και στη σύνθεση των επιμέρους βιο-διεργασιών. Η συστημική προσέγγιση στοχεύει στην ταυτόχρονη μείωση κόστους, στον περιορισμό των περιβαλλοντικών επιπτώσεων και στην καλύτερη διαχείριση βοηθητικών παροχών. Συστημικές προκλήσεις περιλαμβάνουν (i) τη διαχείριση δεδομένων που προέρχονται από διαφορετικές πηγές (βιβλιογραφία ή πειράματα), σε κάθε περίπτωση με διαφορετική ακρίβεια λόγω διαφορετικής πειραματικής προέλευσης και τεχνολογικής ωριμότητας (πιλοτική εγκατάσταση, εργαστήριο, θεωρητικό στάδιο), (ii) τη συστηματική σύγκριση εναλλακτικών επιλογών επεξεργασίας, λαμβάνοντας υπόψη τεχνολογικά χαρακτηριστικά, (iii) την επίδραση των σχεδιαστικών επιλογών στην κατανάλωση βοηθητικών παροχών (ενέργειας και μάζας), (iv) τις ενδογενείς συμβιωτικές επιλογές κατά την αναβάθμιση υφιστάμενων μονάδων με νέες τεχνολογίες και (v) την ολοκληρωμένη διαχείριση αποβλήτων.

Η μελέτη των διεργασιών βασίζεται στη χρήση υπολογιστικών προτύπων υποκατάστασης (surrogate models) που εναρμονίζουν δεδομένα από διαφορετικές πηγές και συμβάλλουν στην διαμόρφωση υπολογιστικών εργαλείων γενικότερης χρήσης. Τα πρότυπα υποκατάστασης (surrogates) εξομαλύνουν αποκλίσεις σε υπολογισμούς, γενικεύουν τη χρήση πειραματικών δεδομένων και λειτουργούν με βαθμούς ελευθερίας που περιλαμβάνουν σχεδιαστικές και θερμοδυναμικές παραμέτρους (διεργασίες, ρεύματα). Η χρήση τους παρουσιάζεται στη σύνθεση διεργασιών με υπερδομές και στην ανάπτυξη δικτύων ολοκλήρωσης ανάμεσα σε ρεύματα-πηγές (sources) και ρεύματα-αποδέκτες (sinks). Τα προβλήματα σύνθεσης μελετήθηκαν για 21 εναλλακτικές διεργασίες, ο σχεδιασμός των οποίων μελετήθηκε τόσο μεμονωμένα όσο και στο πλαίσιο της ολοκλήρωσής τους με τις υπόλοιπες διεργασίες. Η μελέτη οδήγησε σε μαθηματικό πρότυπο για την ταυτόχρονη βελτιστοποίηση βοηθητικών παροχών στη βιομηχανική μονάδα (ενέργειας και μάζας) καθώς και στην περαιτέρω ολοκλήρωσή της με σχεδιαστικές επιλογές. Η προσέγγιση εφαρμόζεται τόσο στη διαμόρφωση νέων μονάδων (grassroots design) όσο και σε προβλήματα επανασχεδιασμού (retrofitting). Το μεθοδολογικό πλαίσιο περιλαμβάνει, τέλος, την ολοκληρωμένη διαχείριση και επεξεργασία των αποβλήτων. Για το σκοπό αυτό προτάθηκαν δέντρα αποφάσεων που συσχετίζουν ρεύματα αποβλήτων με κριτήρια που σχετίζονται με τη φυσική τους κατάσταση (υγρά, στερεά και αέρια) και με τα ποιοτικά χαρακτηριστικά των συστατικών τους. Η ανάλυση οδήγησε σε μαθηματικό πρόβλημα βελτιστοποίησης που επιλύθηκε με τεχνικές μεικτού ακέραιου μη-γραμμικού προγραμματισμού. Η βελτιστοποίηση βασίζεται σε οικονομικούς και περιβαλλοντικούς όρους, ενώ οι βαθμοί ελευθερίας περιλαμβάνουν το πλαίσιο ολοκλήρωσης και τις τεχνολογίες επεξεργασίας.

Τα πρότυπα υποκατάστασης κατέδειξαν σημαντικές βελτιώσεις και, υποβοηθούμενα από προσομοιώσεις, οδήγησαν σε επιλογές που πιστοποιήθηκαν σε βιομηχανική κλίμακα. Στη σύνθεση, λύσεις προερχόμενες από την ονομαστική διαλογή απορρίφθηκαν λόγω ποιοτικών χαρακτηριστικών των ρευμάτων και των τεχνολογικών περιορισμών. Η ταυτόχρονη

ολοκλήρωση πολλαπλών βοηθητικών παροχών και των σχεδιαστικών επιλογών οδήγησε σε σημαντική μείωση κόστους, περιορίζοντας την κατανάλωση ενέργειας και προτείνοντας αποδοτικότερα πλαίσια ανακύκλωσης και αναγέννησης παροχών. Η προτεινόμενη λύση του προβλήματος επανασχεδιασμού διατηρεί οριακή προτίμηση στην παραγωγή βιοαιθανόλης (εν μέρει και λόγω της ωριμότητας της τεχνολογίας) αλλά με συμπαραγωγή εξειδικευμένων προϊόντων και την ενσωμάτωση νέων τεχνολογιών. Η ολοκληρωμένη διαχείριση αποβλήτων αποφέρει σημαντική μείωση κόστους και προτρέπει σε αποκεντρωμένες μονάδες επεξεργασίας. Τα αποτελέσματα καταδεικνύουν την τεράστια σημασία του ολοκληρωμένου σχεδιασμού, αποδεικνύοντας πως χωρίς ικανή ολοκλήρωση η βιομηχανική μονάδα αδυνατεί να ανταγωνιστεί με τις συμβατικές μονάδες παραγωγής προϊόντων αντίστοιχων με εκείνων του βιοδιυλιστηρίου.

Η έρευνα της παρούσας διατριβής οδήγησε στην προώθηση σε βιομηχανική κλίμακα τεχνολογιών εργαστηρίων και πιλοτικών εγκαταστάσεων που αρχικά αναπτύχθηκαν στη Γαλλία.

Résumé

La conception des bioraffineries est un problème multidimensionnel. En plus de la conception traditionnelle de procédé, il faut intégrer les particularités de production d'un éventail de produits conséquent utilisant des technologies de maturité différente. Devant l'ampleur et la complexité des défis à relever, il ne peut y avoir de méthode d'optimisation unique. Cette thèse vient présenter une approche systématique du développement industriel de bioraffineries multi-produits. Le cadre proposé est généralisable aux différentes échelles de conception et combine des outils de modélisation, d'intégration et de synthèse de procédés. Cette approche a pour objectif la réduction simultanée du coût et de l'impact environnementale en optimisant la gestion des utilités. Les défis confrontés sont (i) la gestion des données d'origine variée (littérature ou expérimentale) de précision inégale en raison des différents niveaux de maturité technologique (phase pilote, de laboratoire ou théorique), (ii) la recherche et l'analyse systématique des voies de traitement, tout en tenant compte des caractéristiques technologiques, (iii) l'impact des conceptions alternatives sur la consommation des utilités (masse et énergie), (iv) les options endogènes de symbiose industrielle lors du renouvellement (réorganisation, refonte)de la réingénierie des installations existantes, et (v) la gestion intégrée des déchets.

Dans l'approche systématique proposée, la modélisation des procédés utilise des modèles de substitution pour harmoniser les données d'origine différente, mais aussi pour assister le développement systématique des simulations dont certaines informations d'ingénierie sont manquantes. Les modèles de substitution sont utilisés pour réduire les écarts entre les modèles détaillés et les données expérimentales en traitant certains paramètres opérationnels et thermodynamiques comme degrés de liberté. Pour la synthèse de la chaîne de valeur, l'approche utilise des superstructures sous forme de graphes bipartites mêlant sources et cibles et en organisant les procédés en unités modulaires capables d'être facilement modifiées ou remplacées. Cette synthèse est démontrée et validée pour un ensemble de 21 procédés différents, chacun représenté par son modèle de substitution. Ensuite, un modèle mathématique permet d'optimiser simultanément la consommation des utilités (énergétiques et massiques) mais également de trouver des alternatives technologiques à la configuration initialement prévue grâce aux modèles préétablis. Ce modèle est capable d'identifier et d'exploiter les synergies de diverses étapes d'un procédé, que ce soit sur la conception de nouvelles installations ou sur la rénovation d'installations existantes. Enfin, l'approche systématique proposée est adaptée pour la gestion intégrée des déchets. Des logigrammes sont développés pour la classification des effluents de déchets selon leurs phases (liquide, solide ou gaz), mais également sur les solutions de traitement adaptées. La méthode de synthèse emploie des superstructures. Elle est formulée comme un modèle d'optimisation non linéaire en nombres entiers mixtes. Ce modèle propose alors une hiérarchisation des solutions de traitement des déchets en fonction du procédé de la bioraffinerie et des performances optimales de celle-ci.

Les résultats de la modélisation montrent que les modèles approximatifs de substitution sont fiables et ils peuvent également identifier les lacunes des modèles détaillés. Les résultats de la synthèse du procédé montrent que les solutions initialement envisagées ont été rejetées en raison des caractéristiques qualitatives des flux ainsi que des contraintes technologiques. L'intégration multi-utilités en fonction des options de conception du procédé révèle d'importantes économies potentielles en réduisant la consommation des secteurs les plus énergivores. La solution au problème de réingénierie suggère que la production de bioéthanol soit maintenue sur l'installation existante et que les investissements dans les nouvelles technologies doivent se

focaliser sur la production de produits spécialisés à plus haute valeur ajoutée. La gestion intégrée des déchets peut réduire le coût de traitement des effluents grâce aux unités de traitement décentralisées et des solutions non conventionnelles. En conclusion, la conception intégrée est cruciale, car, à l'échelle industrielle, des bioraffineries ne peuvent pas concurrencer les unités conventionnelles équivalentes sans une intégration suffisante.

La recherche de cette thèse a contribué au développement industriel des technologies de laboratoire et des technologies pilotes initialement développées en France.

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Chapter I

Introduction

This chapter sets the ground for the reader to understand the specific points of concern. First, it presents the context of the study by providing a brief history of the biorefinery concept to date and by placing the study within the broad research area. Secondly, it discusses the motivation and identifies the key points of concern. Then it presents the aim and scope as well as the significance of this work. Finally, it sketches out the structure of the thesis for the reader to see how the aim of the research is achieved.

1.1 The Biorefinery Concept

The urge to reduce the dependency on fossil fuels gave birth to the biorefinery concept. The first identified attempt to define the term "biorefinery" describes a specific three-step process where (i) the biomass feedstock is pretreated through fermentation, (ii) the fermentation broth is purified, and finally (iii) other products are produced (Levy et al., 1981). A more general conceptualization of biorefining was proposed more than a decade later by the U.S. Department of Energy: "Biorefinery is an overall concept of a processing plant where biomass feedstocks are converted and extracted into a spectrum of valuable products" (U.S. Department of Energy, 1997). The need to ensure the production of *multiple products*, the establishment of *industrial synergies*, and the development of *sustainable processes* is reflected on I.E.A.'s definition: "Biorefining is the sustainable synergetic processing of biomass into a spectrum of marketable food and feed ingredients, products (chemicals, materials) and energy (fuels, power, heat)" (I.E.A., 2014).

Biorefineries emerged as the green equivalent of the conventional oil refineries, which transform vegetative matter instead of oil into fuels and chemicals. Therefore, biomass treatment technologies evolved to treat more complex raw materials and to produce more valuable products. Depending on their feedstock, biorefineries are classified into different generations. First generation biorefineries (1G) use edible raw materials (e.g. corn, sugarcane, oil seeds, vegetable oils, etc.) or energy crops (e.g. miscanthus, sorghum, switchgrass, carinata, etc.) and produce mainly bioethanol or biodiesel. The competition of cultivated raw materials with arable land and water resources led to second generation biorefineries (2G), which use nonedible biomass, or agricultural and forest residue, or non-competitive, short term energy crops and can produce a large variety of chemicals, fuels, or food and feed ingredients. Third generation biorefineries (3G) use non-conventional raw materials, like algae (macro- and micro-), municipal waste, manure, or textiles and can produce a long list of chemical, fuels, proteins, or pigments and hope to contribute building a zero-waste economy. Finally, fourth generation Biorefineries (4G) use carbon dioxide (CO_2) and non-edible crops as feedstock, scoping for negative CO_2 emissions (Moncada & Aristizábal, 2016).

The design of sustainable biorefineries is an open field of research with three main research domains (Brundtland & Khalid, 1988), (Figure 1.1). Firstly, the social domain reflects the social approval of the potential impact of the project on the standards of living. Secondly, the environmental domain reflects the potential impact of the project on the natural resources and the bio-diversity. Finally, the economic domain reflects the potential impact on the economic growth. Given that policy-makers have the responsibility to guard the use of fair and ethic practices, it is assumed that the social approval is likely to increase if a process is economically and environmentally efficient. The present thesis is located within endeavors to develop a systematic framework to optimize the design of biorefineries, focusing mainly on factors affecting the economic domain and its intersection with the environmental domain.

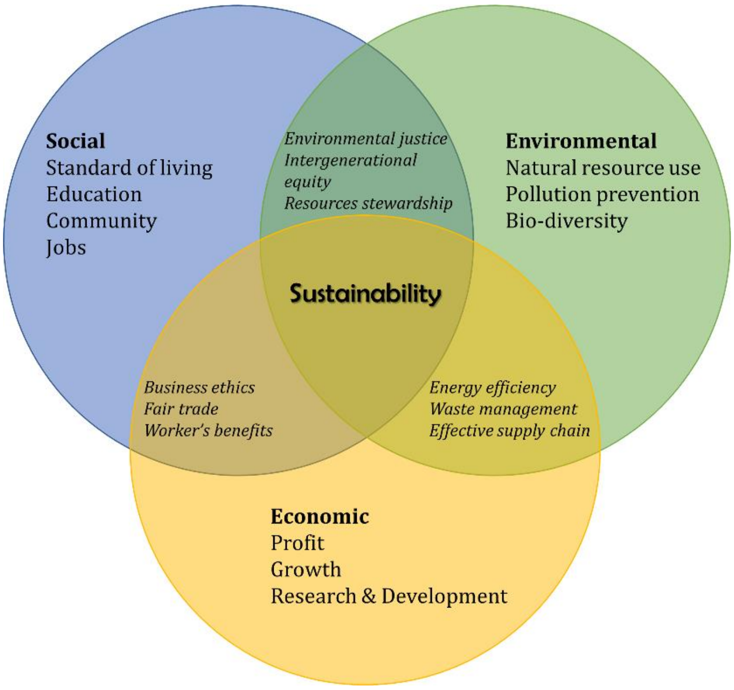

Figure 1.1. Research Domain of Sustainability.

1.2 Research Motivation

The production of first-generation biofuels is characterized by mature commercial markets and well understood technologies, but they are limited in their ability to achieve their sustainability targets (Sims et al., 2008). The "food vs. fuel" dilemma has increased the interest in developing biofuels from non-food biomass. Aiming for a more efficient use of biomass, second generation biorefineries started treating the non-edible part of the plant (lignocellulosic material), which is considered "agricultural waste". However, the industrialization of lignocellulosic biorefineries is following a slower pace or facing failures. Abengoa, for example, took a significant governmental loan for a full-scale 2G bioethanol plant in the U.S. (U.S. Energy Department, 2011) but filed for bankruptcy on March 2016 (Fitzgerald, 2016). The Spanish multinational corporation seemed to have difficulties in finding investment funds and "the whole reason Abengoa Solar had to get the guarantee from the government is that no private lender thought the risk was worth it" (Minder, 2016). The problem is that either bioprocesses are faulty evaluated as profitable or that the investors are not convinced of their commercial success.

Biorefineries are often blamed as energy-demanding and expensive plants. Energy efficiency in conventional chemical industries is restricted to 5-15%, especially in large commercial units (U.S. Department of Energy, 2015). Are such savings to expect in real-life biorefineries? Systematic methods have been developed to optimize the individual processes, but the optimal selection of raw materials, processes, and products remains a challenge. Despite the fact that systematic solutions evaluate various products as profitable, ethanol remains the first (if not the only) investors' choice. Moreover, for biorefineries to keep their "green identity", the sustainable operation became an imperative requirement for their industrial development.

To date, there has not been sufficient research that examines the technological details of the value chain paths. If technological paths have different requirements in energy and water, it is equally important to analyze how the integration of processes affect the consumption of those resources. Moreover, some technological paths may be restricted on the type of biomass they can accept and/or produce products of different quality. It is necessary to understand how the technological constraints affect the profit potential of the integrated process. Systematic methods treat hitherto value chain options as de facto unconstraint association options. It is essential to understand how the options for direct investment, industrial partnership, or technological competition affect the map value chain options. In summary, if we could systematically combine the technological details with the chemical paths and test different integration options, it would be quite intriguing to know the degree to which these factors affect the efficiency of the process.

1.3 Aim and Scope

The thesis introduces procedures to tackle systematically the design decision problems that come up during the industrial development of second generation biorefineries. The approach uses models of different detail levels to explore the trade-offs between operating and capital cost throughout the value chain tree. Options for different feedstocks, pretreatment technologies, product portfolios, production paths, and waste treatment technologies are evaluated. Implications of utility consumption are also addressed. Industrial synergies, retrofit, and grassroots design are considered for steady state operation. The procedures combine tools for process flowsheeting, surrogate-based optimization, pinch analysis, graphs, superstructures, process synthesis, and mathematical optimization. The aim of this work is not to propose a single optimization method for finding the optimum process design. Rather the thesis aims at developing and combining tools of different design scales that can help engineers and investors to set targets and screen design options during the different phases of industrial process development.

1.4 Thesis Overview

The present thesis consists of eight further chapters:

Chapter II overviews the existing research on the systematic design of sustainable biorefineries from an economic and environmental perspective. More specifically, it focuses on the attempts of process systems engineering to assist in the development of sustainable biorefineries. Contributions to the domains of process synthesis, process integration, and process flowsheeting applicable on biorefinery systems are also summarized. The goal is to reveal the limitations of the existing knowledge that this thesis seeks to overcome.

Chapter III presents a new systems approach for the modular integrated design of multiproduct biorefineries. More specifically, the framework starts by decomposing the problem to different design scales. Next, it discusses how to organize the building elements of each scale so as to automatically develop the superstructure of alternative space. Lastly, it presents how to combine systems engineering tools over the design scales to achieve the integrated modular design.

Chapter IV deals with the challenge of raw data, coming from different sources and at difference confidence levels. Data used in current research were provided by various sources (literature or experimental) and at uncertain levels of confidence due to different technology readiness levels of the processes under study (pilot, laboratory, or theoretical stage). Surrogate-based optimization is used to produce reliable and harmonized data. The dual role of surrogates is revealed: a) assist in the systematic development of fine models, searching systematically for shortcomings in the process and property systems, but also b) serve as reliable coarse models.

Chapter V deals with the challenge to assess, at an early stage, the competitive advantage of a process in comparison with antagonistic technologies. The modular process synthesis model is introduced, which employs the modular graph presented in Chapter III for the automated alternative space development. The case studies demonstrate the impact of the source-sink principle on the network configuration. Streams are produced and required at different qualities, deepening the processing technology.

Chapter VI tackles the challenge about utility consumption and its impact on the design. A new targeting model is introduced for the simultaneous utility network optimization. The use of multiple utilities is optimized simultaneously, while process modifications are screened as integer options. However, due to the size and the complexity of the problem, compromises are made to keep the formulation simple and linear. The method postulates steady state operation and known operating efficiency.

Chapter VII extends the targeting model presented in Chapter VI to revamp biorefinery installations, while considering options for industrial synergies. The method systematizes the combined grassroots-retrofit problem and integrates synthesis tools to screen the portfolio of products and look for synergies.

Chapter VIII extends the systems approach to integrated waste management systems to address both, the generation of the waste streams, depending the selected biorefinery units, and the waste treatment technologies. The integrated system includes options for alternative treatment technologies and decentralized and centralized management strategies.

Chapter IX extracts the conclusions and the significance of this thesis and sketches future research directions.

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Chapter II

Background

This chapter provides a literature review of the systems approaches applied to the design of sustainable biorefineries from an economic and environmental perspective. More specifically, it focuses on the attempts of process systems engineering to assist in the development of sustainable biorefineries. Contributions to the domains of process synthesis, process integration, and process flowsheeting applicable on biorefinery systems are also summarized. It is intended to reveal the limitations of the existing knowledge that this thesis seeks to overcome.

2.1 Integrated Biorefineries

The biorefinery design is a complex and multifaceted problem. To break down the size of the problem, related research seems to follow the classification scheme proposed by I.E.A (2014), according to which a biorefinery system consists of the following elements: (i) feedstocks, (ii) processes, (iii) platforms, and (iv) products (Figure 2.1).

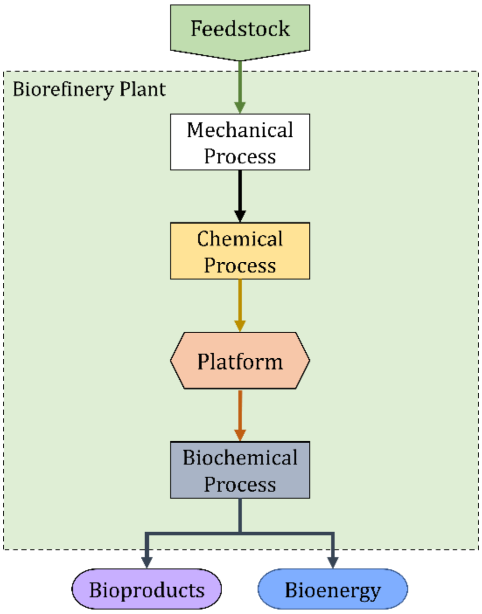

Figure 2.1. Classification scheme of a biorefinery (I.E.A., 2014).

The element of feedstock is used to describe all possible types of biomass used as candidate raw materials. The element of processes incorporates all the mechanical, (thermo-)chemical, and biochemical processing paths. Platforms include the intermediate products, which may serve as final products of a biorefinery process or as linkages between different biorefinery concepts. The products include biofuels (e.g. biodiesel and bioethanol), bio-energy (heat and power), bio-based chemicals (e.g. methanol, succinic acid), and materials accessible to end-users. Figure 2.2 shows the plethora of possible design configurations, even when limiting the intermediate platforms to the top 30 building blocks (Werpy et al., 2004).

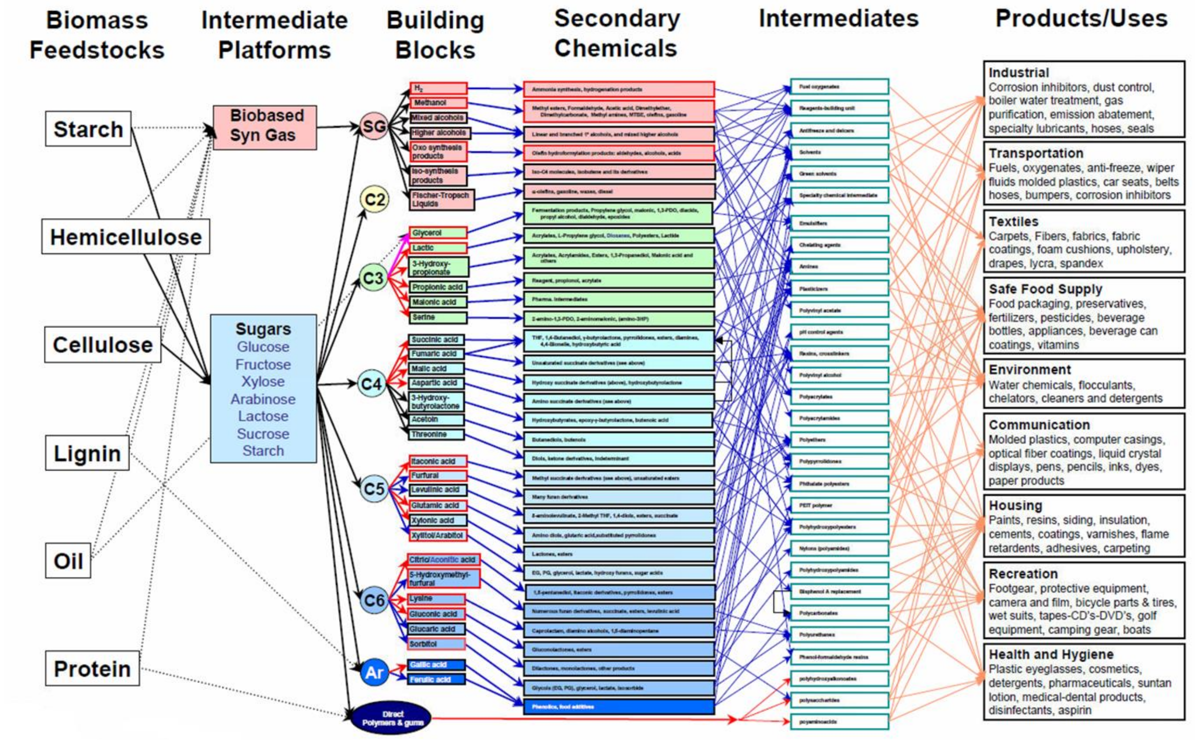

Figure 2.2 Biobased product flow-chart for biomass feedstocs (Werpy et al., 2004)

A portfolio on combinations of feedstocks, processing paths, technologies, and final products will contain virtually unlimited number of cases. In addition, the technological paths have different technology readiness levels (TRLs). The TRL scale (Figure 2.3) was first introduced by NASA in the 1970s as a tool for assessing the maturity of technologies during complex system development (Mankins, 2009; Olechowski et al., 2015). The value chain tree of a biorefinery includes processes from TRL1 (e.g. HMF from cellulose) to TRL9 (e.g. bioethanol from glucose). Moreover, the borderlines between the different technological concepts are vague, since there could be plenty of synergetic interactions to maximize the environmental and economic value of the products (Voogand, 2018). The size and the complexity of the problem calls for a systematic approach able to look into the theoretical and technological aspects of the systems for a better use of resources, considering also options for endogenous and exogenous synergies.

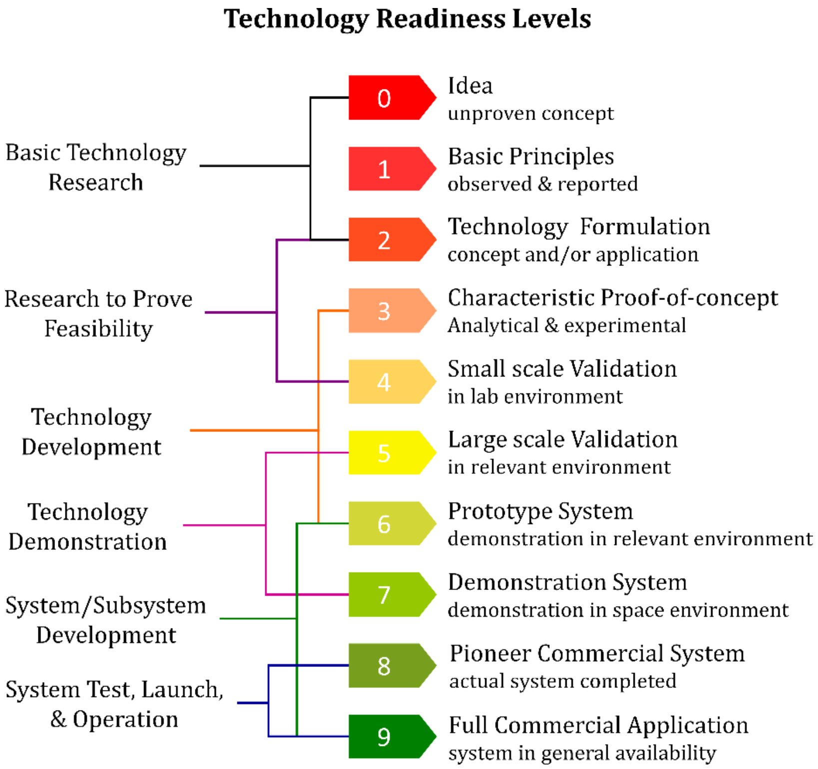

Figure 2.3 Technology Readiness Levels adapted for process development

2.2 Systems Engineering and Design Challenges

Systems engineering employs process integration and its three components, synthesis, analysis, and optimization, to systematically address the challenges of systems design. Process Integration is a holistic approach useful to integrate environmental issues with other process objectives, such as profitability, yield enhancement, debottlenecking, and resources reduction. Process synthesis combines and integrates process units and streams to meet the design objectives. Process analysis involves the decomposition of the whole into its constituent elements to study the behavior of the process performance. Optimization involves the selection of the "best" solution amongst a set of candidate selections (El-Halwagi, 1998). Systems engineering is employed to assist in the development and design of sustainable biorefineries by extending the systems integration concept to biorefinery applications.

A recent review on the methodologies related to the design and evaluation of biorefineries (Moncada & Aristizábal, 2016) identified three main methodological trends as (i) conceptual, (ii) early-stage, and (iii) optimization methods, which follow a design strategy based on hierarchy, sequencing, or integration. The conceptual design is based on stand-alone experimental processes, follows a holistic approach, and includes three types of analysis: (a) technical, (b) economic, and (c) environmental. The early stage methodologies scope to compare biorefinery process concepts to an equivalent petrochemical counterpart, without considering the design details (mainly looking the reaction yields). The optimization approach targets to maximize the yield or the economic potential with regards to conversions and techno-economic data.

Kokossis and Yang (2010) proposed a three-layer approach (Figure 2.4), emphasizing the need for coordinated efforts to enable the information flow between the systems technologies. Process synthesis and process integration are used to coordinate a concept-based level analysis (strategic decisions), ahead of design. Then, the process flowsheeting layer is used to conduct evaluations of techno-economic trade-offs and sustainability objectives. Daoutidis et al. (2013) underlined the involvement of external factors (governmental policies, environmental considerations and market conditions) in the decision making for biorefinery designs. Moncada and Aristizábal, (2016) proposed a conceptual approach that combines (i) hierarchy strategy for the selection of feedstocks, platforms, and products, (ii) sequencing strategy to establish a logical order to relate processes and products, and (iii) integration strategy to set targets for the use of resources. The latter approach is extended to select the minimum processing capacity (Serna-Loaiza et al., 2018).

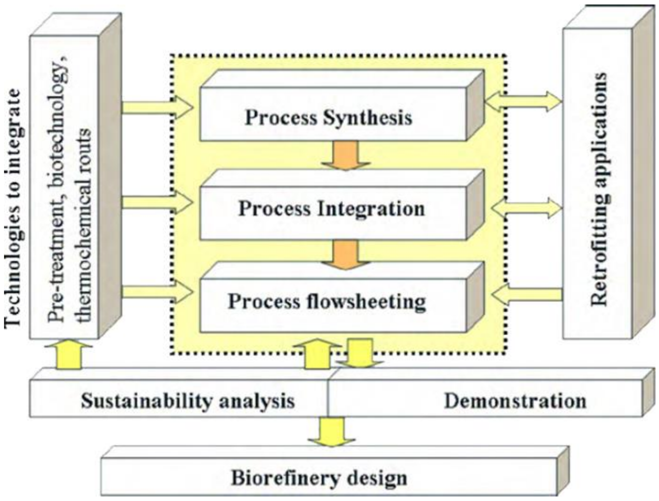

Figure 2.4 Roles of systems tools in the design of biorefineries (Kokossis & Yang, 2010)

To summarize, process systems engineering is employed for the selection of raw materials, products, processing paths (platforms and processes), and processing capacities. It is also applied for the optimization of the processing yields, the use of resources, and the costing, while considering external (policies, environmental considerations, and market conditions.) and internal (yields, budget, etc.) restrictions. The frameworks may involve conceptual, early-stage, or optimization-based approaches, which follow hierarchical, sequencing, and/or integration design strategies. However, existing methodologies do not count holistically for synergies nor for technological restrictions when coupling different processing paths.

2.3 Process Synthesis

Process synthesis provides a systematic way to screen options in the form of a network that attain the economic, environmental, and/or social objectives. Major approaches to synthesize optimal process flowsheets that meet the desired objectives include heuristics, decomposition, and optimization-based methods (Martín & Grossmann, 2012; Yuan et al., 2013; Chen & Grossmann, 2017). Heuristics are limited to a neighborhood of options by adding or modifying sequentially the process units of a base case. Decomposition techniques break down a large and complex problem into several smaller, hierarchical sub-problems that are easier to deal with. The hierarchical decomposition basic approach decomposes the whole synthesis problem into five hierarchical levels (Douglas, 1988): 1) selection of the operation mode (continuous vs. batch), 2) decision of the input-output structure (raw materials – products), 3) decision of the recycling structure, 4) arrangement of the separation system, and 5) configuration of the heat exchanger network. Decomposition techniques come with good initial flowsheets but are limited in their ability to consider interactions between different decision layers.

Optimization based methods explicitly consider the trade-offs and interactions among subsystems and rigorously search through a proposed design space for the optimal configuration.

They involve three major steps: 1) postulation of the space of alternatives represented by a superstructure, 2) formulation of the mathematical programming model, and 3) solution of the formulated problem. Limitations arise in the ability to define an appropriate search space, to select a suitable degree of approximation, and to solve the resulting optimization problems (Chen & Grossmann, 2017). A recent trend has become to combine some of these concepts to a hybrid framework (Kravanja & Grossmann, 1997; Tay et al., 2011; Tula et al., 2015; Teo et al., 2017) scoping to absorb merits of each combined approach and to mitigate the computational burden. Synthesis models are formulated at three major levels of detail (Martín & Grossmann, 2012): (i) high level aggregated models, expressed in terms of major features like mass and energy flows (e.g. Papalexandri & Pistikopoulos, 1998), (ii) coarse models, involving relatively simple (non)linear models (e.g. Kocis & Grossmann 1987), and (iii) rigorous models that rely on detailed and complex models (e.g. Grossmann et al., 2005).

Applications in biorefineries deal with the production of a single or multiple products, focusing on the total value chain problem or on particular processing options (Martín & Grossmann, 2012; Yuan et al., 2013). Models may stochastically create the search space (Kelloway & Daoutidis, 2013) or use superstructures to compare competitive processing (Vyhmeister et al., 2018) and reaction pathways (Andiappan et al., 2015), to search the best biomass valorization options (Goh & Ng, 2015), or the best pathways for products (Kiskini et al., 2016). Existing methods may be integrated with the total site analysis (Stefanakis et al., 2014; Pyrgakis & Kokossis, 2016), adopt environmental criteria (Tsakalova et al., 2015; Celebi et al., 2017), involve enterprise units (Lai et al., 2018), or consider uncertainties in the budget (Gong et al., 2016). However, flexibility in the design and uncertainty in the value chain remain a challenge. Moreover, the quality of the intermediate and final streams is diplomatically omitted, ignoring any technological differences. The comparison of the technological paths usually employs techno-economic evaluations using scenario-based techniques.

2.4 Process Integration

Process integration dates back to the 1970s and was conceived as a response to the oil crisis. It provides a systematic way to conserve resources and reduce cost by providing a mapping strategy based on thermodynamically derived upper bounds (Klemeš, 2013). Naturally, the first attempts were focused on the energy efficiency and savings. The energy consumption problem is systematically addressed by pinch analysis (Linnhoff & Hindmarsh, 1983). For the systematic design of heat exchanger networks (HENs), most methods consider that the temperatures and the flowrates of the mass network are fixed. The same methods also include options for grassroots or retrofit design, continuous or batch operation, with or without area targeting (Morar & Agachi, 2010; Klemeš & Kravanja, 2013). But, more recently, the transshipment model (Papoulias & Grossmann, 1983) is extended to use variable inlet and outlet temperatures (Navarro-Amorós et al., 2013), and this new model is further improved with variable flowrates (Kong et al., 2017; Quirante et al. 2017) and multiple thermal utilities with area targeting (Quirante et al., 2018).

The first systematic attempt to address the water consumption problem resulted in a superstructure formulation of allocation options (Takama et al. 1980). Following the concept of energy pinch, water-pinch introduced the limiting water profile in graphical representations based upon concentration and mass loads (Wang & Smith, 1994). For the fixed load problems, systematic methods include options for water losses or gains, for continuous or batch processes, for grassroots or retrofit design, for single or multiple contaminants, for single or multiple, pure or impure, supplied water sources, and for regeneration or discharge (Yoo et al., 2007; Foo, 2009;

Khor et al., 2014). The problem of water network synthesis can be divided into three subclasses: A) direct reuse/recycle network, B) regeneration network, and C) total water network (Bagajewicz 2000; Jeżowski, 2010; Khor et al., 2014). Existing models use evolutionary algorithms, stochastic optimization, and superstructures formulated as mixed integer nonlinear programming (MINLP) or as mixed integer linear programming (MILP) after linearization (Bagajewicz 2000; Yoo et al., 2007; Jeżowski, 2010).

In a more general formulation, mass exchange networks (MENs) (El-Halwagi & Manousiouthakis, 1989) are searching for ways to transfer certain materials from a set of rich streams to a set of lean streams, targeting for the maximum extent of mass exchange amongst the process streams and the minimum usage of external lean streams. Mass exchange methods include the equivalent of the transshipment model (El-Halwagi & Manousiouthakis, 1990; Alva-Argaez et al., 1999), the material recovery pinch diagram (El-Halwagi et al., 2003), the source composite curve (Bandyopadhyay, 2006), the property-based automated targeting technique (Ng et al., 2010), the material surplus composite curve (Saw et al., 2011), and the material flow cost accounting (Wan et al., 2015). The sequential approach of prioritized cost is proposed for multiple mass utilities, where each material is prioritized based on its cost, following a single (Shenoy & Bandyopadhyay, 2007) or a multiple objective approach (Priya & Bandyopadhyay, 2017). In this case, regeneration is not taken into account, since it is a mass exchange unit. Nevertheless, the mass and the energy network are naturally linked together.

The combined problem of water and energy consumption was first addressed by a conceptual design method (Savulescu and Smith, 1998). Then, a two-stage procedure was introduced, combining direct and indirect heat transfer (Savulescu et al., 2002). Graphical tools based on pinch method include the water energy balance diagram (Leewongtanawit & Kim, 2009), the heat surplus diagram (Manan et al., 2009), the superimposed mass and energy curves (Alwi et al., 2011), and the 4H-F diagram (Liao et al., 2016). Generally, conceptual design methods come with good graphical visualization and simple operability, but they cannot easily deal with multiple contaminants and trade-offs among the capital and the operational cost. Mathematical programming-based methods follow a simultaneous or sequential optimization approach (Yoo et al., 2007; Jeżowski, 2010; Ahmetović et al., 2015). Although sequential methods are easier to solve, they cannot fully consider the trade-offs between the cost for the supplied water, the energy cost, and the investment cost. Simultaneous methods are based on complex superstructures, while a decomposition strategy is proposed to decompose the MINLP problem into two sub-problems: MILP and NLP, which were sequentially solved with an iterative procedure (Ahmetović et al., 2015; Zhao et al., 2019). The basic elements identified are the water-using processes, the regeneration units, and the treatment units. The water-using processes include units with mass-transfer (quality controlled, fixed load) or without mass transfer (quantity controlled or fixed-flow-rate).

Applications on bioprocesses are mainly scenario-based, studying the production of bioethanol from either starchy or lignocellulosic biomass, or the production of biodiesel by transesterification by heterogeneous or homogeneous catalysis (alkali, acid or enzymes in both cases) (Grossman et al., 2014), or the production of pulp by Kraft (Savulescu et al., 2005; Kermani et al., 2017). However, existing methods consider only the simultaneous use of water and energy (or one main component and energy), handling any other substance as contaminant. Nonetheless, when multiple contaminants need to be considered, current techniques are challenged by the complexity introduced. None of the known frameworks can hitherto address the simultaneous problem for the regeneration of multiple materials. Furthermore, various technological options can exist for the regeneration of a substance, resulting in multiple network designs. Practical reasons (control, operation) may also impose an intermediate storage stage. Moreover, every design decision in the mass utility network produces a new thermal profile for the energy utility network. The combinatorial nature of the utility network calls for the development of a systematic approach that is able to deal with the high dimensionality of the design problem.

2.5 Process Flowsheeting

Flowsheeting aggregates simple chemical and physical processes based on the mathematical descriptions of fundamental chemical and physical laws. The systematic development of a simulation model starts by collecting information about the existing components, the process units and their interconnections, the design specifications of the operating pressures, temperatures, the flowrates, and the compositions. Then the physical problem is defined by selecting the property methods and support data for the components and by calculating the heat and mass balances per process unit (Westerberg et al., 1979; Dimian et al., 2014). The major challenge is the representation of the design knowledge, which demands a deep understanding of the process, the physicochemical phenomena, and the equation system (Babi, 2015; Esche et al., 2017), especially when dealing with processes at (very) low technology readiness level (TRL). The agreement between the process simulation and the real process is the touchstone of a good simulation model, and the difficulty lies in choosing the suitable model for a process unit and in making the appropriate assumptions to avoid unnecessary complexity (Upreti, 2017).

A great number of simulation models is developed for the case of biorefining processes, focusing mainly on bioethanol production (Gnansounou & Dauriat, 2010; Humbird et al., 2011; Zhang et al., 2018) and expanding on alternative valorization processes for process development (Terelak et al., 2005; El-Zanati et al., 2006; Martín & Grossmann, 2016), for comparison analysis (Baral & Shah, A., 2017; Mountraki et al., 2017; Moncada et al., 2018), for process control (Prunescu et al., 2015; Gomes et al., 2018), or for process revamp (Mosqueira-Salazar et al, 2013; Dias et al., 2014). However, process modelling for biorefining processes is still facing challenges due to the lack of property data, the complexity of the materials, and the constant influx of new processes and technologies. The fact that models are produced for different purposes and by different developers has as a result a vast heterogeneity in the formats and the confidence level of the models. Nevertheless, a simulation model is a detailed and expensive model, in both construction and computational time.

Simple in-out meta-models are used almost since the beginning of computational simulation (Barton 1992; Chen et al., 2006). Surrogates are used for prediction by fitting the fine model directly (e.g., by polynomial models) or by getting trained to fit the data (e.g., by artificial neural networks) (Koziel & Leifsson, 2016; Garud et al., 2018). Surrogate-based optimization is used to support process design, including research on sampling, model fitting, model validation, and design space exploration (Barton & Meckesheimer, 2006; Wang & Shan, 2007; Li et al., 2010; Bhosekar & Ierapetritou, 2018). Palmer and Realff (2002) proposed a methodology for the optimization of process simulations with the use of surrogates and predictive surfaces plots. Caballero and Grossmann (2008) presented a methodology for the rigorous optimization of nonlinear programming problems in which the objective function and/or some constraints were noisy implicit black box functions. They substituted the black box modules by meta-models based on kriging interpolation and used a refining stage and a successive bound contraction in the domain of independent variables until reaching the acceptable accuracy level. Boukouvala and Ierapetritou (2013) combined surrogate-based optimization tools, black-box feasibility, and noise handling tools for the optimization of expensive noisy flowsheet models. Cozad et al., 2014 introduced a model-building methodology that identifies highly accurate surrogates. They started by building a low-complexity surrogate, which was gradually improved through the use of derivative-free optimization solvers to adaptively sample new simulation or experimental points. Kieslich et al. (2018) presented an algorithm that integrates some common techniques of black-box optimization with a Smolyak-grid-based search algorithm, aiming to locate the global optimum of box-constrained problems using input–output data. However, hitherto no method questions the validity of the fine model. The quality of the simulation model and consequently the quality of the meta-model depends on the successful physical and chemical representation of the real system.

Closing the background review, I would like to make a reference to Professor Floudas' perspective on the opportunities for systems engineering to assist in sustainability (Floudas et al., 2016). First, multi-scale modeling is highlighted as pivotal in tackling large and complex problems as well as in proposing innovative solutions. Another issue is the assessment and discovery of new materials toward a selective process with flexible product yields. Technical feasibility is important to be assessed on a supply network scale. Additionally, the value chains need to be strategically designed and optimized over a long-term horizon. Finally, it is important to address systematically uncertainties in prices, feedstock availability, demands, cost parameters, and process parameters.

2.6 Thesis Contribution

Despite the availability in systems methods, process optimization in biorefineries appears to be scenario-based. Holistic methods ignore synergies, different technology readiness levels, and linking constraints due to technological (in)compatibilities. Integration studies are mainly focused on the consumption of energy and/or water, neglecting the impact of other resources. Moreover, the simulation of biorefinery processes remains a challenge due to the complexity of the materials and the low technological maturity. Nevertheless, the industrialization of biorefineries requires a two-direction research: i) introvert research to develop new and improve existing technologies and ii) extrovert research to assess technological integrations and industrial collaborations. This thesis suggests a new methodological framework for the introvert and extrovert development of biorefinery processes, taking into account the need for different detail levels per design scale.

The scientific contribution in summary:

- A new systematic approach is proposed for the modular integrated design of multiproduct biorefineries. The framework renders generalization in various design scales and combines tools for modeling, targeting, and synthesis. The challenges to tackle are (i) the management of the raw data, (ii) the systematic screening of possessing paths while considering the technological attributes, (iii) the impact of process modifications on the utility consumption, (iv) the industrial synergies when revamping existing installations, and (v) the integrated management of the waste streams.
- Surrogate-based optimization is employed to harmonize data coming from different sources, but also to assist in the systematic development of lower-grain models. A new framework is proposed for the systematic selection of the property and the process systems, when developing a flowsheeting model. Given a library of components,

    thermodynamic models, and unit operation models, the objective is to develop surrogates that minimize the deviations with the given data (literature or experimental).

    - A new modular synthesis method is introduced that allows the automatic creation of the space of alternative based on the "source-sink compatibility" principle. Superstructures are formulated as a bipartite graphs of sink and source locations, organizing the processes as modular units that can be modified, replaced, and/or re-engineered. Given the available materials, the source and sink locations, and the process units, the method is to search for the processing paths that valorize best the available raw materials, while considering the technological constraints.
    - A new method is devised to set targets simultaneously for the consumption of mass and energy utilities and to screen options for process modifications. This work extends existing methods to multiple-utilities networks, accounting for multiple regeneration units, in parallel and for several materials, and introduces the concept of interconnected superstructures through hypergraphs. Network design does not pivot on a central component (water, H2, etc.), but the role of any a priori peer components is defined by their impact on the objective function.
- The aforementioned targeting method is extended to revamp existing installations and to screen possible synergies (endogenous or exogenous). The approach combines grassroots and retrofit optimization techniques with synthesis tools for the technological upgrade of the existing processes. The modular representation makes it possible to search for potential interactions between the different process units.
- A new methodology is proposed to holistically address the management problem of both the waste streams as well as the waste treatment technologies. The proposed methodology highlights a systematic and generic approach. Decision maps are developed to allocate waste streams to treatment options. Next, the proposed mapping is structured as a synthesis problem that is formulated and optimized in the form of a mixed-integer nonlinear programming problem (MINLP). The optimization selects technologies, and the optimal solution determines the management strategy (centralized vs. decentralized).

A real-life biorefinery technology developed by Compagnie Industrielle de la Matière Végétale (CIMV) is used as a case study. Results assisted in the construction of its industrial scale unit.

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Chapter III

Proposed Methodology

This chapter introduces a systems approach for the industrial development of multiproduct biorefineries. First, the different modeling scales are described. Next, it is discussed how to organize the building elements of each scale so as to automatically develop the superstructure of the alternative space. Lastly, it is presented how to combine the different systems tools over the integration of different scales to result in the integrated biorefinery design.

3.1 Motivation and Challenges

The design of integrated biorefineries encompasses the complex tasks to pursue improvements in both stand-alone and integrated configurations. It is essential for the future plants to be sustainable, to have multiple products, and to scope for synergies (I.E.A., 2014). Nevertheless, biorefienery processes are at different technology readiness level (TRL) and, thus, is important to assess the technical feasibility of the integrated scheme. Multiscale modelling assisted by systems tools for process design, integration, and synthesis can tackle such large and complex problems and also propose innovative solutions (Floudas et al., 2016). However, models of different design scales require different data management. Existing methods for the selection of raw materials, processing paths, and processing scale involve mainly conceptual, early-stage, or optimization-based approaches and do not count holistically for synergies nor for technological feasibility.

This chapter proposes a multiscale framework for the design of integrated biorefineries. The approach combines process modelling, synthesis, and integration tools at different design scales to deal with the different TRLs. Scoping for flexible and reconfigurable manufacturing systems, the problem is composed by modular units. Technological constraints and efficiency targets are set for each module individually, as well as conjointly with other modular units. An iterative procedure evaluates the resulted design.

3.2 Problem Statement

The problem can be stated as one where given is a set of

- components (biomass, chemicals, fuels, energy, etc.)
- chemistries that require and provide those components.
- technologies at different TRLs that require and provide streams of components at a given quality but are also linked with the chemistries.

The problem is to optimally design a multiproduct biorefinery plant and determine

- which value chain paths (feedstock, intermediate, products, and technologies) to combine and build the biorefinery (direct investment)
- which value chain paths to collaborate with (industrial synergies)
- the optimal design of the selected technologies

The approach applies techniques of structured programming to break the problem down into solvable sub problems. Two-way refinement is followed: a) top down refinement moves from a general description to detailed statements and b) bottom up refinement leads to a more compact design. Modular units are used for the formation of the value chain, and the synthesis of these modules in a so-called "module hierarchy", allowing the design of reconfigurable manufacturing systems. The objective functions account for economic (e.g. capital investment, operational costs, profit) and environmental targets (e.g. energy use, greenhouse gas emissions).

3.3 Integration of Scales

A multiproduct biorefinery is a complex system that is composed of many subsystems that may interact with each other. The complex problem can be decomposed to sub-problems that extend from the molecular to the global market scale (Figure 3.1). A top-down analysis decomposes the problem to its smaller components, while a bottom-up analysis combines components to reach a more aggregated scale. *Molecular scale* studies require information about molecular forces and structures and may assist in product design (e.g. Behler, 2011; Kalakul et al., 2018), estimation of properties (e.g. Jhamb et al., 2018), the intensification of a physicochemical phenomenon (e.g. Struebing et al, 2013), or in integrated product-process design (e.g. Papadopoulos et al., 2016). The study of *chemistry and physics* (and biology) involves computer aided techniques (e.g. Linke & Kokossis, 2003; Panayiotou et al., 2016; Mountraki & Straathof, 2017) to search for innovative pieces of equipment. Computational fluid dynamic (CFD) analysis is used for *equipment design* (e.g. Stehlik et al., 2005), and the design is validated by experimental data to support scale up studies. A *process section* design problem combines various pieces of equipment to create a processing step. The scope of a process section analysis may be the achievement of a specific quality of the outflow stream. A *process* is the combination of multiple process sections, usually for upstream (USP), conversion (CP), and downstream (DSP) processing.

Raw materials, products, utilities, costing, and environmental targets need to be analyzed before moving to *industrial plant scale* problems, where the marge of error in design calculations needs to be minimized. Studies at *industrial site* scale set targets for the utility requirements, the emissions, and the waste management by accounting which industrial plants co-exist in a specific location (e.g. Dhole & Linnhoff, 1993; Ajayi et al., 2017). Different industrial sites, as parts or as whole, may interact with each other by exchanging products and/or services and form networks of *industrial synergies* (e.g. Lignos et al., 2016). Finally, *market analysis* is a quantitative and qualitative assessment, which allows to determine how suitable a particular market is for a specific industry. Market trends are analyzed locally or globally, scoping to identify the potential strengths, weaknesses, opportunities, and threats (SWOT) (e.g. Peters et al., 1994; Subhadra & Edwards, 2011). Detailed or coarse models can be used at each scale. For example, equipment studies can use a detailed CFD model or a conceptual code of superstructures. Depending the design scale and the type of the model (detailed vs. conceptual), different information is required.

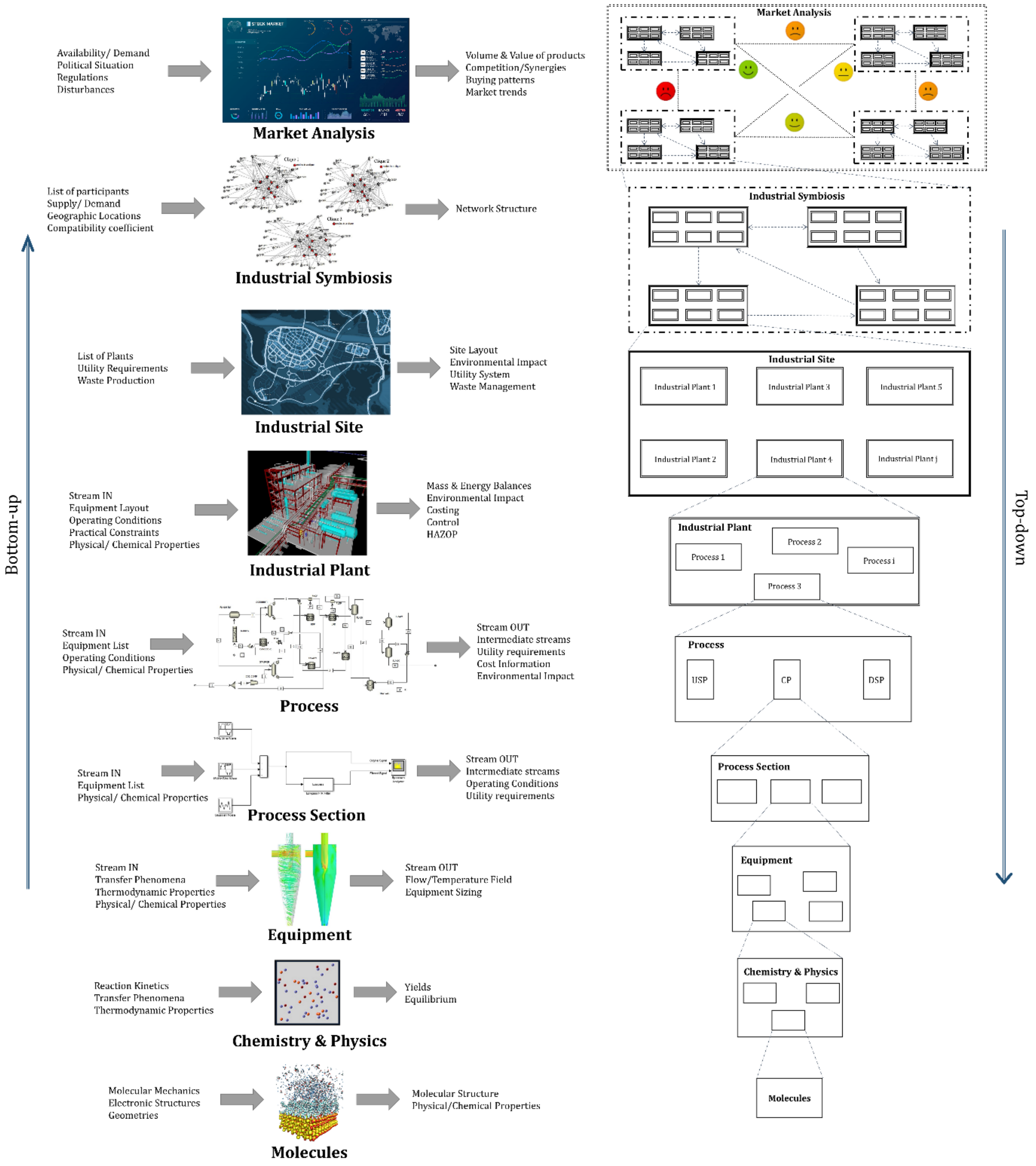

Figure 3.1 Modeling Scales

Top-down and bottom-up design methodologies can be very complementary and may involve alternating between their design elements. However, integrating models of different scales is challenged by the disparity of information required per modeling scale. Each decomposition step must be accompanied by a data refinement step.

3.4 Building Units

The building blocks include materials (N), processing units (M), source (I) (splitters), and sink (J) (mixers) locations (Figure 3.2). Each process unit requires and provides materials at a specific quality. Rather than denoting the connections between the components and the technologies, the approach uses design rules to indicate which connections are possible. Therefore, different units can be combined together according to the compatibility between the sources and the sinks. For each decomposition level, the design problem can be represented by a graph, using the information of the lower level to describe the building elements. The graph for the level of plant design, for example, uses processes as building elements. When moving to the process design level, each process is composed of process sections, which, in their turn, have process units as their building elements.

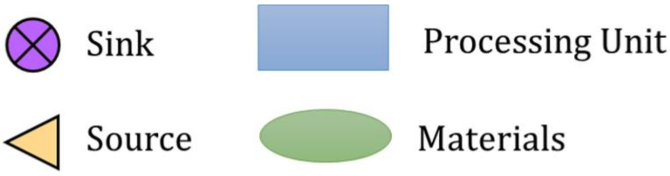

Figure 3.2. Building Units

The modular unit (Figure 3.3) contains a process unit and the related sinks and sources. Each sink has information about the materials required by the process unit and each source holds information about the materials provided by the process unit. The retraction, addition, and/or replacement of a modular unit does not affect the formulation of the synthesis problem, but only the availability of the processes and components. There is no need to pre-build a superstructure, since it is automatically formulated based on "source-sink compatibility" principle. The ex-ante superstructure is a bipartite graph of sinks and sources. Every edge can be seen as a flow path and the graph can be handled as a transportation network (Diestel, 2017).

Figure 3.3. The Modular Unit

Let us assume a design problem for the downstream processing section (DSP) of an ethanol production process (Figure 3.4a). Information is available about the quality constraints of both required (sink) and provided (source) streams. The compatible units are those which either accept or produce at least one of the existing materials at the desired quality, or connect with one of the unit which does. A first search in our data base came up with seven possible units (Figure 3.4b). Figure 3.4c shows the resulted graph that meets the source-sink compatibility principle. M7 does not participate in the calculations since it does not satisfy the source-sink compatibility constraint. This is how the modular graph composition allows the automated postulation of the space of alternatives, avoids unnecessary complexity, and offers better controllability over the size of the problem.

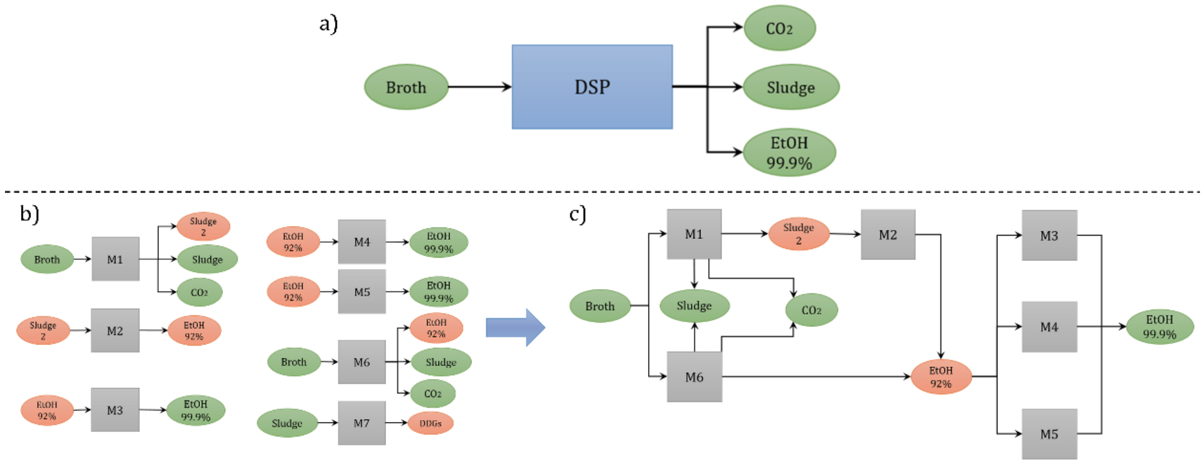

Figure 3.4 Illustrative Example

3.5 Modules Representation and Properties

Depending the type of the link, modules have different relational structures. Four types of relationships are introduced, based on their source-sink type of connection:

i. *Investable* modules have an exclusive relationship of the type "supplier-receiver".
ii. *Synergistic* modules have a non-exclusive relationship of the type "supplier-receiver".
iii. *Competitive* modules compete for the same sources (upstream competition) and/or sinks (downstream competition).
iv. *Neutral* modules have nothing in common.

Figure 3.5 shows an example of the relationship structures. Four separate investable structures are identified. M1 is neutral to all other modules. M2 and M4 have exclusive relationship, but they compete with M3 for raw material supply. M3 and M5 have a synergistic relationship but are not investable, because they don't have exclusive "supplier-receiver" relationship. As it can be seen from this illustration, the synthesis graph is not necessarily rooted nor connected.

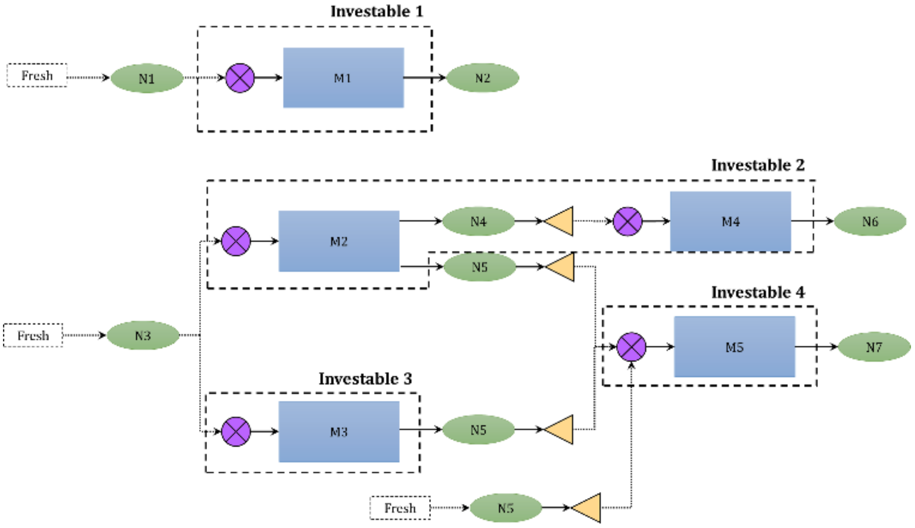

Figure 3.5. Relationship Structures

3.6 Module Integration

The proposed approach introduces the two-way process design and expands the existing layer iterative approach (Kokossis & Yang, 2010) by embedding multiscale design tools (Figure 3.6). The bottom-up direction focuses on the development and improvement of new technologies as individual units, while the top-down direction deals with their interactivity. The framework can be applied for both grassroots and retrofit applications. First, data coming from different TRLs are pretreated to ensure that the modeling stage provides other layers with uniformed and reliable information. Then, targets are set about the operation (e.g. energy, water, LCA, etc.) of each individual unit. Synthesis stage screens amongst different standalone modules, but also searches for potential benefit in associations. Descending again to the integration step a new, total site analysis sets targets for the operation of the new configurations. Finally, the modeling stage validates results and translates them into a design proposal.

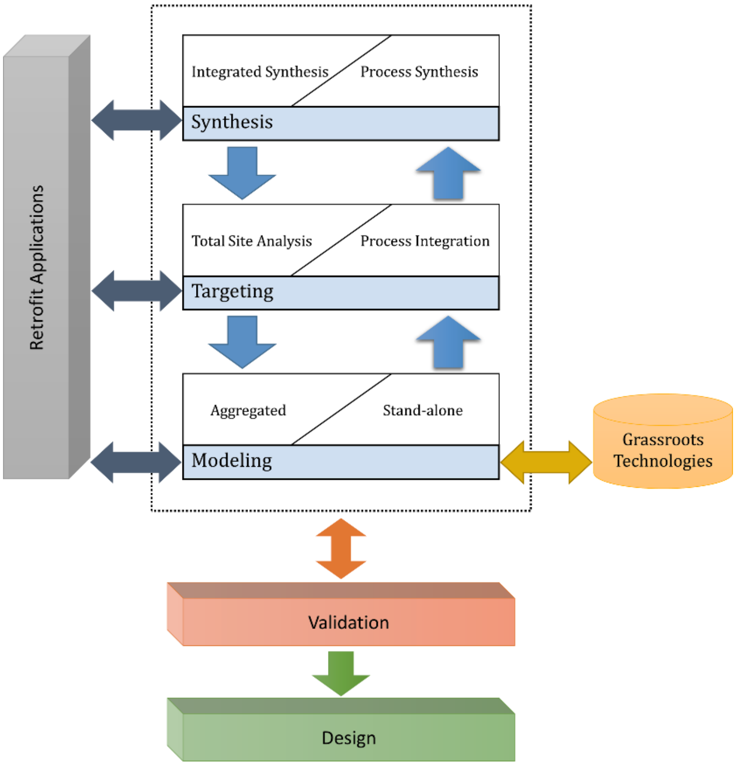

Figure 3.6 Analysis Layers

Figure 3.7 summarizes the methods developed for the needs of this thesis, which are presented in detail in the chapters that follow. Despite the known difficulties in modeling, integrating, and synthesizing biorefinery processes, new challenges also came up. Starting with the modeling stage, various types of models are combined at different design levels. This means that models for technologies at different TRLs are used and that data are provided at different confidence levels. Surrogates emerge as the key to data harmonization. Chapter IV combines process flowsheeting and surrogate-based optimization to a systematic methodology for developing models of better confidence level. After setting targets for the individual modules, Chapter V demonstrates the impact of the technological constraints and the source-sink principle on the configuration of the value chain. Conditional synthesis can reveal environmental loopholes in terms of water and energy consumption.

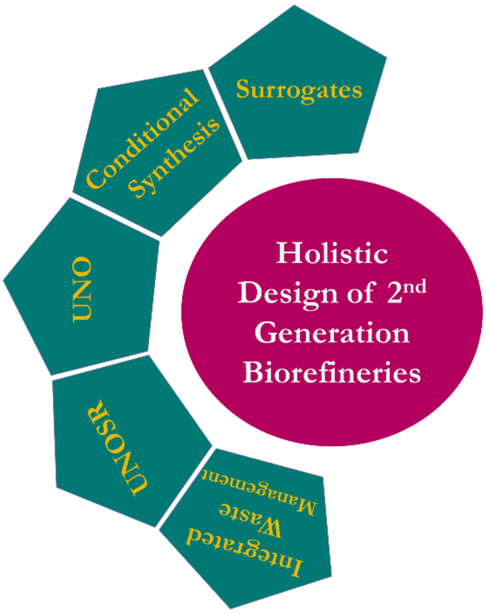

Figure 3.7 Framework and Tools

Moving on to the integration stage, depending the technology, utilities may have different impact on the cost function and/or the environmental footprint. Sequential techniques are mainly focused on water and energy consumption and give different results from the simultaneous methods. Chapter VI presents a method for the utility network optimization (UNO), which simultaneously sets targets for the mass and energy utility consumption, including process modifications in the form of integer options. Chapter VII extends the method presented in Chapter VI to revamp existing installations. Process integration and synthesis tools are combined to evaluate the synergistic potential between old and new units (UNOSR). Finally, Chapter VIII extends current framework to integrated waste management systems. The integrated problem is systematically leading to the holistic evaluation of options and the development of designs that are economic and efficient.

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Chapter IV

Development and Integration of Surrogates

Surrogate modelling is the key to harmonize data coming from different sources. This chapter presents a methodology to harmonize data coming from different sources, but also to assist in the systematic development of lower-grain models. The proposed approach makes use of components, thermodynamic, and unit operation models available in existing libraries.

4.1 Motivation and Challenges

The development of a reliable simulation model is the first step in a series of evaluation and optimization studies. However, a simulation model is a detailed and expensive model, in both construction and computational time. Simpler meta-models are often used, but rough approximations produce models of low reliability, which cannot support upper level integration and optimization studies. Surrogates exploit black-box nature problems and have attractive computational simplicity. The concept is that a cheap (coarse) model provides an effective optimization surrogate for a more detailed (fine) model. An optimization routine is applied directly to the coarse model (surrogate), which is a function (or a model) that replaces the original fine model. However, hitherto no method questions the validity of the fine model. Biomass is a complex material that introduces significant uncertainty in the process design and the quality of the mass and energy balances. Despite the fact that property and process model libraries are developed to ensure consistency over the flowsheet, the selection of the appropriate models hinges on the design engineer (Seider et al., 2009). The quality of the simulation model and, consequently, the quality of the meta-model depends on the successful physical and chemical representation of the real system. The simulation of biorefinery processes is a challenging task because of (i) the complex materials, (ii) the nonconventional processes, and (iii) the uncertainty in the thermodynamic description of the system.

This chapter presents a methodology for the systematic development of flowsheet models with the aid of surrogate-based optimization. Given a library of components, property, and process models, the objective is to develop surrogates that minimize the deviation with the given data (literature or experimental). The approach makes use of components, thermodynamic, and unit operation models available in existing libraries. The systematic procedure starts by collecting information about the existing components and the thermodynamic models for the property system and then continues by setting up the unit operations and their interconnections for the process system. Surrogates are produced as artificial hybrid models processing mixtures of components that “emulate” complex substrates modeled by mixtures of conventional components, whose selection and composition remains a degree of freedom and should match the experimental data. The framework is applied for the modelling of a real-life lignocellulosic organosolv technology developed by Compagnie Industrielle de la Matière Végétale (CIMV). Surrogates are developed for each process section. The models are validated with data provided by the experimental groups. Flexibility analysis is conducted to search the reliable limits within which the models can be used.

4.2 Problem Statement

From a systems perspective, a flowsheet is an ordered combination of process units that transforms incoming materials, energy, and information streams to new output streams that are led to other process units. A process unit stands for a piece of equipment or a process step that integrates the property and the process system. The property system consists of components and thermodynamic models. The process system comprises unit operation models, connectivity rules, and operating parameters. Streams entering a process unit are transformed to exit streams by the combined effect of the property and process systems (Figure 4.1).

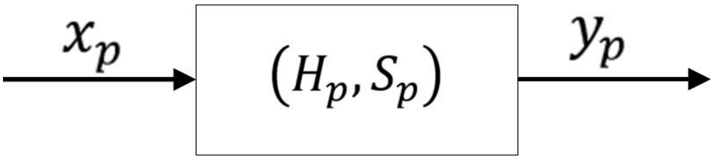


Figure 4.1. Process unit p

Let us postulate a surrogate for the approximation of a process unit (Eq.4.1).

$$y_p = f(x_p, H_p, S_p) \qquad Eq. 4.1$$

Given are:

- a plant comprised by p∈P process units
- a library with m∈M unit operation models
- a library with c∈C components
- a library with g∈G thermodynamic models
- a set of real data, $(\tilde{x}_p, \tilde{y}_p) \in D_p$

The objective is to compose surrogates for each process unit about

- the property system (H_p): the components and the thermodynamic models as a function of the existing components
- the process system (S_p): the process unit models, along with connectivity rules, and operating parameters as a function of the process unit models

So as to minimize the error between the surrogates and the experimental data.

4.3 Methods

The setup of the process system results from a reducible structure, while the property system optimizes the selection and the composition of the components. The overall regression process is an optimization problem of the form (Eq.4.2):

$$\min_{(H_p, S_p)} \varepsilon_p = \sum_p \left\| \tilde{y}_p - f(x_p, H_p, S_p) \right\| \qquad Eq. 4.2$$

s.t.

$$x_p^L \leq x_p \leq x_p^U$$

The selection in c_p relates to components available to use (discrete options). Given that conventional flowsheeting technologies involve thermodynamic models that stand as procedural closed-form models, the selection in g_{c_p} relates to thermodynamic models available to use (discrete options). The selection of m_p relates to unit operation models available to use (discrete options). Each process unit has u_{m_p} parameters to optimize. The selection of u_{m_p} has a continuous nature as it relates to model parameters and flowrates that regress available experimental data.

The modeling problem (Eq.4.3) is a series of subsequently decomposed in two individual optimization problems (Eq.4.4 & Eq.4.5):

$$\min \qquad \varepsilon_{H_p,S_p} = \varepsilon_{1\,H_p,\bar{S}_p} + \varepsilon_{2\,\bar{H}_p,S_p} \qquad Eq.4.3$$

where

$$\varepsilon_{1\,H_p,\bar{S}_p} = \sum_{p} \left\| \tilde{y}_p - \sum_{c_p} f_1\left(x_{c_p,\bar{m}_p}, H_{c_p}, \bar{S}_p\right) \right\| \qquad Eq.4.4$$

and

$$\varepsilon_{2\,\bar{H}_p,S_p} = \sum_{p} \left\| \tilde{y}_p - \sum_{m_p} f_2\left(x_{\bar{c}_p,m_p}, \bar{H}_p, S_{m_p}\right) \right\| \qquad Eq.4.5$$

4.3.1 The Property-Process Modelling Cycle (PPMC)

An iterative procedure is used to validate both, the surrogate and the fine model (Figure 4.2). Starting with the fine model, surrogates are used to validate the setup of the property and the process. The validation step verifies whether the results generated by the surrogates are consistent with the experimental data, before moving on to the training of the surrogate for the total process.

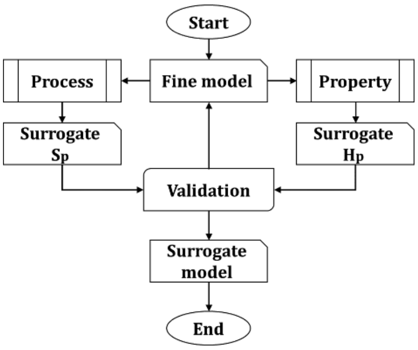


Figure 4.2. Property-Process Modelling Cycle

The plant consists of P process units, and a surrogate is developed for each p. To coordinate the individual optimization problems, an iterative approach makes use of hierarchical lists for the candidate components, decision maps for the thermodynamic, and hierarchical lists for the configuration of the unit operation models deployed. The final flowsheet has individualized process S_p and property models H_p for each process unit. The model for the total plant reconciles all property and process systems by selecting the supersets of components and models used in all process units. The error between the surrogate and the experimental data helps to identify shortcomings and drives the amendments of the fine model. The solution approach follows a two-step iterative procedure for each process unit (Figure 4.3):

- (i) An iterative sequential approach to select c_p and consequently to select g_{c_p}
- (ii) An iterative sequential approach to select a configuration of m_p
- (iii) A direct optimization approach to select u_{m_p}

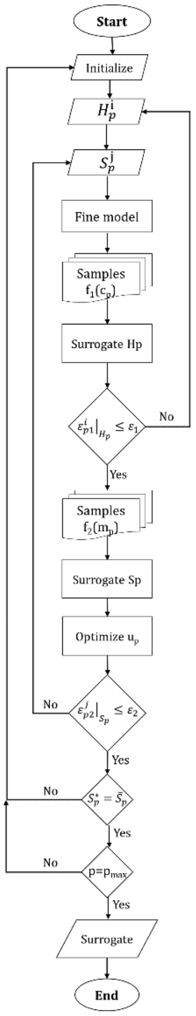


Figure 4.3 PPMC Steps

4.3.2 Property Model Selection

The successful description of the property system involves four tasks:

(i) Selection of the components available in the databank
(ii) Description of the non-databank components and missing parameters
(iii) Selection of the appropriate thermodynamic model
(iv) Validation

Components are the materials that exist throughout the process as reactant, product, catalyst, solvent, or inert. They can be a pure element or any organic or inorganic substance, including solids, polymers, and electrolytes. Moreover, there are components which are *available* in commercial databases (Nielsen et al., 2001; Dimian et al., 2014), which do not exist in the database and need to be introduced manually as *hypotheticals*, and those which in reality are complex materials or blends and are simulated as a mixture of *pseudo-components*. However, in small compositions, it is not obvious which components are important for the calculations. The approach searches which available, hypothetical, and pseudo- components are meaningful for the simulation. All components possibly present in the process unit are listed in descending order, and each iteration increases gradually the number of selected components. Their known or expected composition need to be normalized to unity (Eq.4.6).

$$\sum_{c^i} \bar{x}^i_{p,c} = 1 \qquad\qquad Eq. 4.6$$

Where $\bar{x}$ the input about the composition of the inlet stream (s) per iteration i. Ordered subsets $c^i \subseteq C$ increase gradually their cardinality as the iterations increase.

Table 4.1 lists some of the thermodynamic models available in simulators. When choosing a property method there are four factors that should be considered: (i) the nature of the existing components, (ii) the composition of the mixture, (iii) the pressure and the temperature range, and (iv) the availability of parameters. The approach employs existing decision trees (Carlson, 1996; Edwards, 2000) for the selection of the appropriate thermodynamic model (Figure 4.4).

Table 4.1. Thermodynamic Models

Equation of State Models	**Activity Coefficient Models**	**Special Models**
Benedict-Webb-Rubin (BWR) Lee Starling	Electrolyte NRTL	API sour-water
Hayden-O'Connell	Flory-Huggins	Braun K-10 (BK10)
Hydrogen-fluoride (HF)	Pitzer	Chao-Seader
Ideal gas law	Bromley-Pitzer	Kent-Eisenberg
Lee_Kesler (LK)	NRTL	Steam Tables
Lee-Kesler-Plocker (LKP)	UNIQUAC	REFPROP
Peng-Robinson (PR)	UNIFAC	GERG
Perturbed Hard Chain	Wilson	Maxwell-Bonnell
Redlich-Kwong (RK)	Scatchard-Hildebrand	Grayson-Streed
Soave-Redlich-Kwong (SRK)	Van Laar	
Predictive SRK	Redlich-Kister	
SRK or PR with Wong Sandler mixing rule		
SRK or PR with modified Huron-Vidal 2 mixing rule		
Sanchez-Lacombe for polymers		

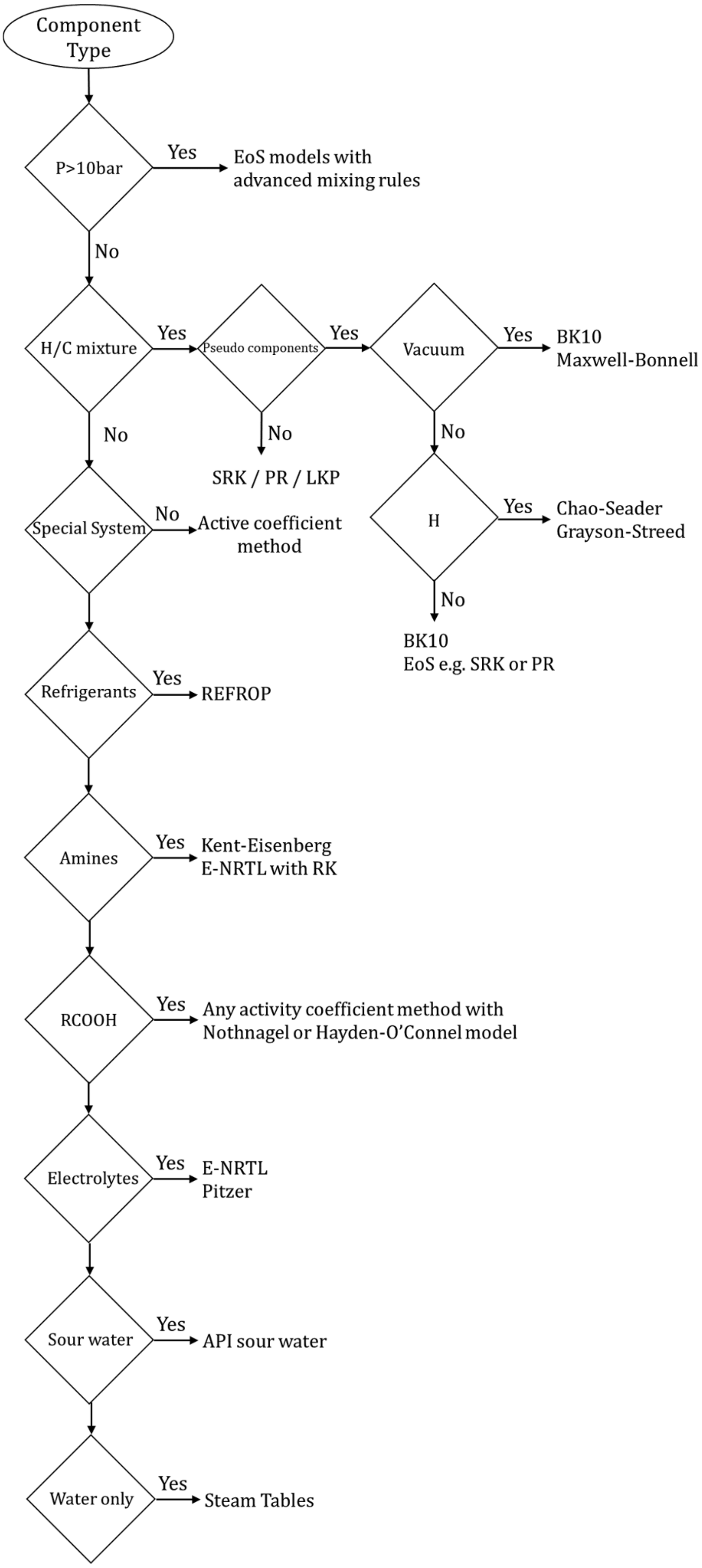


Figure 4.4. Simplified Property-Component Type Allocation Map

For each selected subset of components there are k options of thermodynamic models (Eq.4.7).

$$g_p^i = \sum_k \sum_c \tilde{g}_{p,c,k}^i \, z_{p,c,k}^i \qquad Eq. 4.7$$

Where z^i a binary variable to select the thermodynamic model as a function of the existing components (Eq.4.8 & Eq.4.9).

$$\bar{x}_{p,c}^i - \sum_k z_{p,c,k}^i \leq 0 \qquad Eq. 4.8$$

$$\sum_k z_{p,c,k}^i = 1 \qquad Eq. 4.9$$

Given that the process units are connected, the outgoing stream of unit p is the incoming stream of unit p+1 (Eq.4.10).

$$y_p = x_{p+1} = \tilde{y}_p \qquad Eq. 4.10$$

Therefore, the iterations stop when

$$\tilde{y}_p - y_p^i \leq \varepsilon_1 \qquad Eq. 4.11$$

If the convergence criterion is not satisfied, but there is a significant improvement between two iterations (Eq.4.12), the number of components is increased (i=i+1).

$$\left| \frac{d\varepsilon_{p1}}{di} \right| \leq \varepsilon_3 \qquad Eq. 4.12$$

Otherwise, the error on the controlled variable(s) indicates need for amendments in the property parameters. The thermodynamic models use property parameters to predict physical properties for pure components, binary systems, single-phase or ternary mixtures. In some cases, the parameters of the property methods do not fit well with the experimental data or are unknown. In such cases the parameters can be estimated either by theoretical models, like the group contribution method or by data regression, based on experimental data. At the end of the iterative procedure for the overall plant, each process unit may have different number of components, but the superset for the global model contains all the existing components (Eq.4.13):

$$C = \max_p C_p^* \qquad Eq. 4.13$$

Eq.4.4 describes the design of the property system sub-problem (repetition Eq.4.4).

$$\varepsilon_{1\,H_p,\bar{S}_p} = \sum_p \left\| \tilde{y}_p - \sum_{c_p} f_1\left(x_{c_p,\bar{m}_p}, H_{c_p}, \bar{S}_p\right) \right\| \qquad Eq. 4.4$$

Figure 4.5 summarizes the iterative procedure for the setup of the property system.

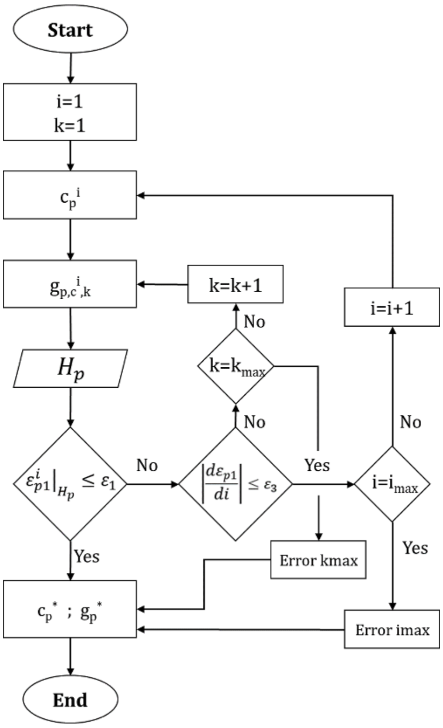
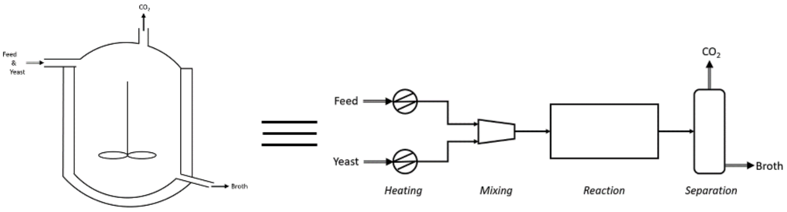


Figure 4.5. Property System Loop

4.3.3 Process Model Selection

The process system is described by the selected unit operation models (m_p) and operating conditions (u_{mp}). The unit operation models are used to represent actual pieces of equipment, which may perform any single operation of mixing, reaction, separation, temperature and pressure change or any combination of those. The models may be rigorous or shortcut. They are characterized as *conventional* if they exist in commercial model libraries or as *nonconventional* if they represent a specialized piece of equipment. Nonconventional unit operation models can be introduced as user-models or can be synthesized by combining conventional models. A fermenter, for example, can either be introduced as an aggregated nonconventional model or as a combination of conventional models for heating, mixing, reaction, and separation (Figure 4.6).



Nonconventional model

Combination of conventional models

Figure 4.6: Fermenter modeling options

However, each simulation option has different input requirements. For example, a rigorous model for a hydro-cyclone separation can only be used if the particle distribution of the components is known and if the appropriate thermodynamic model to describe the mixture behavior is available. Thus, different configurations α (unit operation model & connectivity) are listed in descending order for each process unit, depending the complexity and the accuracy preferences (Eq.4.14).

$$\alpha_p^j = \sum m_p^j \qquad Eq. 4.14$$

Each m_p has u_{mp} operating parameters to optimize. The selection of u_{mp} has a continuous nature as it relates to model parameters and flowrates that regress available experimental data. The modeling approach requires an initial guess of the operating conditions, based on experimental or literature data. Then the surrogate model is used to optimize the initial guess. The iterations stop when

$$\tilde{y}_p - y_p^j \leq \varepsilon_2 \qquad Eq. 4.15$$

Eq.4.5 describes the property system optimization sub-problem (repetition Eq.4.5).

$$\varepsilon_{2\,\bar{H}_p, S_p} = \sum_p \left\| \tilde{y}_p - \sum_{m_p} f_2\left(x_{\bar{c}_p, m_p}, \bar{H}_p, S_{m_p}\right) \right\| \qquad Eq. 4.5$$

If the controlled variables fail to converge within the permitted limits, it is an indication that the selected unit operation model is not the appropriate, so it moves to the next configuration on the list (j=j+1). Figure 4.7 summarizes the iterative procedure for the setup of the process system.

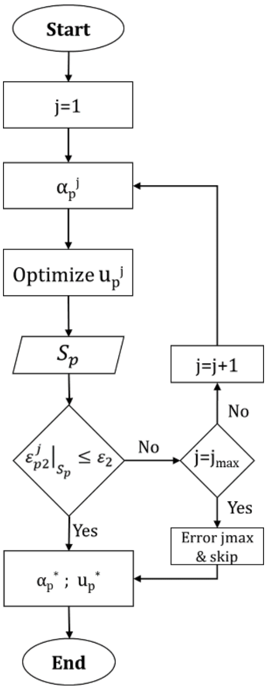


Figure 4.7. Process System Loop

4.3.4 Validation Stage

The simulation model can be used for operation, control, and/or prediction. Thus, it will have different initial conditions, by changing for example the capacity of the model or by using different raw materials. The surrogates are used to verify the safe extrapolation of the initial operating conditions. The approach adopts a flexibility analysis to verify whether the same model can be used for different case studies. New scenarios basically mean new x_p; thus, the source of uncertainty is exogenous. The question is what is the range $x^L<x_p<x^U$ within which the selected c_p and m_p result in an acceptable ε_p by adapting the u_{mp}. To find the feasible region for which the same simulation model can be used, the feasibility index (Halemane & Grossman, 1983) is adapted. Let us assume that H_p and S_p correspond to the design variables, x_p correspond to the

uncertainty parameters, and u_p correspond to the control variables. The flexibility test is run for the minimum and maximum nominates of the input vectors x_p. The feasibility function ψ is

$$\psi(H_p, S_p, x_p) = \min_{u_{m_p}} \delta \qquad Eq. 4.16$$

s.t.

$$\varepsilon_p \leq \delta$$

4.4 Results

The proposed methodology is applied on the CIMV biorefinery. Aspen Plus is selected as the modelling environment since is widely used in the industry and offers links (through CAPE-OPEN) with most of the commercial tools on simulation (SuperPro, gProms etc). The annual operating factor is set at 8,000 hr/yr. The scope is to develop models that will serve as a reliable base for current and future process integration and optimization studies. It is intended to gather information about the mass balances, the energy requirements, and the cost of the main equipment. The design of the control operation, the pump, and the heat exchange networks is beyond the scope of this study. Therefore, the models postulate steady state operation and focus on the design of the main process.

4.4.1 Background Process

The lignocellulosic biorefinery of CIMV organosolv offers a proven technology for the fractionation of a wide range of non-food related lignocellulosic resources coming from agricultural residues (straw, bagasse, etc.) (Lam et al., 2001a; 2001b; Snelders et al., 2014), fibrous plants (miscanthus, hemp, flax, stem, etc.) (Mire 2004; Mire et al., 2005), and forest residues (softwood, hardwood, etc.) (BIOCORE 2014; Wild et al. 2015). Experimental data is available by a pilot factory (100kg/hr dry matter) in operation since 2006. The global process consists of eight process sections (Figure 4.8): 1) biomass handling 2) extraction 3) delignification 4) de-acidification and 5) washing of the cellulosic pulp 6) evaporation of the extraction liquor 7) treatment of the lignin, and 8) concentration of the sugar syrup. Lignin and soluble sugars are dissolved in the organic acids in the extraction stage, while the cellulosic pulp undergoes a flocculation treatment until the washing stage. Soluble sugars are obtained in a form of syrup and lignin in a form of powder. If necessary, the celluloses and hemicelluloses produced can be further hydrolyzed to glucose and xylose respectively, while silica production is a supplementary option, which depends on the feedstock type and the interest for this additional investment cost.

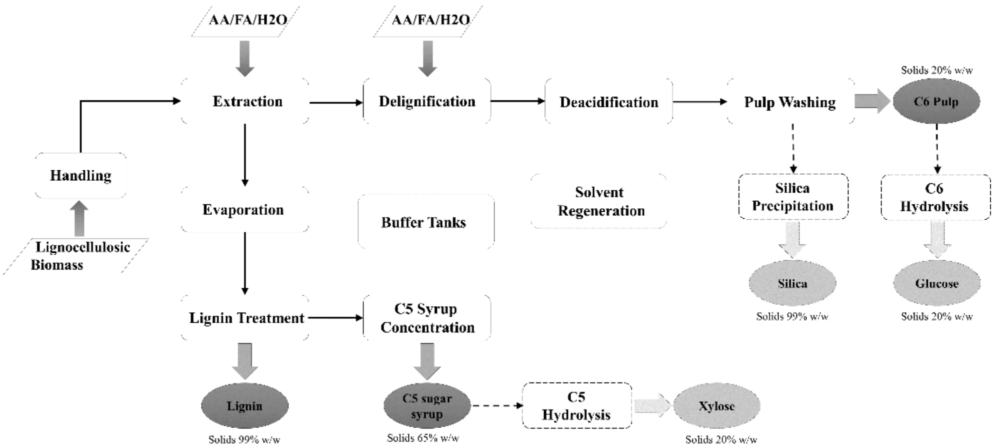


Figure 4.8. BFD of CIMV process (permission CIMV)

For confidentiality reasons, process design is not discussed in detail. Neither the internal balances nor the operating conditions of the equipment units are presented. Moreover, to avoid confusion, only the final versions of the data are presented. Some results from obsolete versions are displayed to justify the need for amendments and to demonstrate the evolution of the quality of the models.

4.4.2 Methodological Steps and Model Development

At first, the property and the process systems are initialized for all the process units. In this case, a process section equals a process unit.

Property System (H_p)

The degrees of freedom in the property system are the existing components and the selected thermodynamic models. Lignocellulosic biomass (wheat straw) is a complex material that cannot be simulated as a conventional component (Vassilev et al., 2010). Nevertheless, some properties of the key biomass components are available in the form of a databank (Wooley & Putsche, 1996); therefore, it is possible to consider biomass as a mixture of pseudo-components. Thus, it is postulated that biomass consists of five major fractions: celluloses (C6), hemicelluloses (C5), lignin, minerals, and other. Each major fraction is composed by candidate subcomponents, which are listed in descending order (Table 4.2) based on characterizations found in online databanks (Phyllis, 2012; S2Biom, 2015), and experimental data. The following conventional components are also present throughout the total process: water (H_2O), acetic acid (AA), formic acid (FA), hydrogen peroxide (H_2O_2), sodium hydroxide (NaOH).

Table 4.2. Candidate Components – run 01

i	**Conventional**				
	H2O	AA	FA	H2O2	NaOH
	Biomass (mixture of pseudo-components)				
	C5	**C6**	**Lignin**	**Minerals**	**Other**
1	Xylan	Glucan	Insoluble	SiO2	Rest soluble
2	Arabinan	Galactan	Soluble	Acetyl	Rest insoluble
3	Lyxan	Mannan	Oxidized	KCl	Fat
4	Riban	Rhamnan		Si	Oils
5		Fructan		K	Waxes
6				Ca	pigments

The number of active components is a degree of freedom, depending the composition of the streams and is gradually increased, until the termination criteria are met. The following output variables $(\tilde{y}_p)$ are used as controlled variables to validate the resulted property system:

- Temperature
- Pressure
- Vapor fraction
- Heat duty
- Mass flow
- Composition wt.%

Based on the type of the existing components (organic acids) and the operating conditions (pressures near to atmospheric and temperatures<200°C), the options about the thermodynamic models are narrowed down to those presented in Table 4.3.

Table 4.3. Candidate Thermodynamic Models

j	Biomass	Carboxylic acids
1	NRTL	NRTL
2	NRTL-RK	NRTL-HOC
3	UNIQUAC	UNIF-HOC
4	PENG-ROB	UNIQ-HOC
5	SRK	NRTL-NTH
6		UNIQ-NTH
7		VANL-NTH

Process System (S_p)

The degrees of freedom in the process system are the configurations of the unit operation models (α = models + connectivity) and their operating parameters. The options in unit operation models are limited by the information available about the property system. For example, it is not possible to use a crystallizer model without any solubility data. Thus, the simple model "Heater" is selected to simulate the temperature change of the streams since there is no information available about the exchanger area, nor the thermal stream coupling. In fact, it is intended to estimate the heat duty due to streams temperature change and extract data for the heat integration analysis. Model "Heater" can also be used to change the pressure of a stream, but it cannot provide any insight about the electricity requirements, the net positive suction head (NPSH), nor the efficiency as the model "Pump". Model "Valve" can be used to estimate the pressure drop ratio factor, the pressure recovery factor, and the valve flow coefficient. Since, current simulations do not scope to design the pump system, the models are listed by decreasing complexity. Simplicity is also favored for the reaction simulation. "RStoic" is set as the first option, followed by the model "RYield", postulating that kinetics are unknown or unimportant. Neither "RGibbs" require the reaction stoichiometry, but it uses Gibbs free energy minimization with phase splitting to calculate the equilibrium. Lastly, "REquil" performs both reaction stoichiometry and chemical equilibrium calculations.

Table 4.4 presents the options in unit operation models as selected by existing libraries (Aspen Plus, 2017). Shortcut models, tuned with experimental data, are set at the top of the list in the case of solid separation applications. A split fraction is set for each component in "Sep", while "Sep2" offers over additional specifications such as the component purity or recovery. Input liquid-to-solid ratio and mixing efficiency are required for "SWash" (single stage) and "CCD" (multi-stage).In the case of the evaporation and distillation operations, the rigorous model "RadFrac" is promoted in the listing, because calculations for the energy balances and the design of the columns are important for the integration studies. "Flash2" is another rigorous model for single stage vapor-liquid or vapor-liquid-liquid phase equilibrium calculations. "Dryer" simulates continuous drying while considering the particle size distribution change within the drier. Model "Distl" simulates multistage multicomponent columns with a single feed stream and two product streams, as the "DSTWU" shortcut model. Complex models are omitted, given the unit operations of the real process. It is a deliberate choice to leave out user-defined models and explore the performance of different configurations using conventional models.

Table 4.4. Candidate Unit Operation Models

k	T-change	P-change	Reaction	Solid Filtration	Single-stage separations	Columns
1	Heater	Heater	RStoic	Sep	RadFrac	RadFrac
2		Valve	RYield	Sep2	Flash2	Distl
3		Pump	RGibbs	CCD	Dryer	DSTWU
4			REquil	SWash		Sep
5						Sep2

The following output variables $(\tilde{y}_p)$ are used as controlled variables to validate the selected configuration for the process model:

- Operating temperature
- Operating pressure
- Pressure drop
- Yield
- Efficiency
- Mass flow
- Composition wt.%

➢ Fine Model Tuning

As a starting point, a capacity of 150ktn/yr dry wheat straw is selected, while it is intended to systematically scan different feedstock types and capacities. The error threshold is set at 10% for the internal flows and at 5% for the product streams and effluents. Outflows are critical for the validation of the models, because the accuracy error is transferrable to any associated analysis. To ensure consistency when extracting data, the following assumptions are adopted:

- Temperature of supplied external streams: 15°C
- Temperature of supplied acids: 20°C
- Temperature of effluents: 35°C
- Streams at vapor phase (e.g. top stream from an evaporator) are condensed by setting $\Delta T=-1$ and vapor fraction=0
- Only isothermal mixing is allowed

Separate models are developed for each process section (Figure 4.8) and integrated into a complete flowsheet, featuring all recycle streams, energy loads, and buffers (for water and solvents). It is postulated that straw biomass delivered to the handling section is ready-to use. If any handling is required, it is only mechanical, so no model is developed. Each process section is simulated in a hierarchy block for better debugging control. To tackle any inflexibility issues due to solid handling processes, operating parameters are adjusted to tune the controlled variables at given check points. For example, instead of tuning SEP models each time with experimental data, the stream fraction is adapted to so that the resulted streams meet the quality criteria.

□ Extraction Section (p=1)

Extraction is the first reaction stage, which combines impregnation with the aquatic mixture of organic acids (AA/FA/H_2O at 55/30/15 wt.%) and biomass fractionation at 105°C and atmospheric pressure. The final selections for the property system are presented in Table 4.5.

Table 4.5. Property System for Extraction – run 01

H_p (p=1)					
i	**Conventional**				
	H2O	AA	FA		
	Biomass				
i	**C5**	**C6**	**Lignin**	**Minerals**	**Other**
1	Xylan	Glucan	Insoluble	SiO2	Rest soluble
2	Arabinan	Galactan		Acetyl	Rest insoluble
3				KCl	
j	**g_c**				
1	NRTL				

The extraction stage is a patented process (Benjelloun-Mlayah et al., 2011). The nonconventional unit operation is modelled as a combination of conventional models: HEAT for temperature change, RStoic for the reaction stage, and Sep for the filtration of solids. Figure 4.9 shows the connectivity amongst the unit operation models.

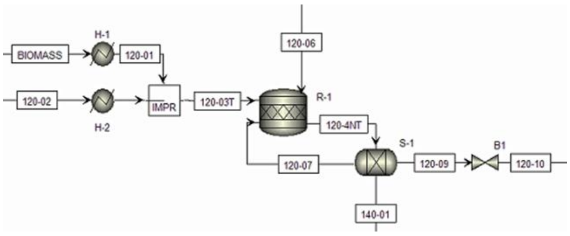


Figure 4.9. Extraction Section – run 01

Table 4.6 shows the accuracy error in stream flows, when the extraction section is modeled as a stand-alone process or as a part of the total process. As part of the total process, input streams 120-02 and 120-06 become recycling streams and need validation. Values that fail to meet the accuracy constraint are noted in grey.

Table 4.6. Flows error in Extraction – run 01

#stream	Total Mass %	Total MS %	Total Acids %	H2O %
Stand-alone				
120-07	-3.41	-1.81	-6.36	7.95
120-10	1.41	-2.05	0.43	8.99
140-01	1.26	-0.75	0.80	5.15
Total process				
120-07	-10.39	6.38	-11.64	-21.33
120-09	-0.59	-3.78	2.08	-9.26
130-01	1.39	7.14	2.46	-8.78
120-02	-0.75	10.09	4.28	-21.93
120-06	1.17	663.11	-0.82	3.65

The experimental value of kappa (Li & Gellerstedt, 1998) is used as the controlled variable for R-1 and is controlled by reaction efficiency. After extraction, kappa needs to be maximum 25, which means that lignin should be maximum at 4.5%wt.% dry mass (DM). The operating parameter in this case (reaction efficiency) is fixed with experimental data and cannot be adjusted otherwise. The solid content of stream 130-01 should range from 10 to 15% wt.% and is controlled by the split fraction parameter in S-1. The stand-alone model meets the design specification constraints, but fails to satisfy the lignin content as part of the total process (Table 4.7). This is mainly due to the error imported by the recycling streams 120-02 and 120-06.

Table 4.7 Controlled variables for p=1 – run 01

	Controlled variable	Stand-alone	Total process
120-10	Lignin % ≤4.5 DM	4.46	5.64
130-01	10 ≤Total MS % ≤15	14.49	18.25

- Delignification Section (p=2)

During the second reaction stage, the extracted mixture is delignified at 85°C using the organic solvent mixture (AA/FA/H_2O at 55/30/15 wt.%) enriched by hydrogen peroxide (H_2O_2). The existing components for biomass are the same as the extraction section, except for lignin component where i=3 is selected (Table 4.8).

Table 4.8. Property System for Delignification – run 01

H_p (p=2)					
i	**Conventional**				
	H2O	AA	FA	H2O2	
	Biomass				
i	**C5**	**C6**	**Lignin**	**Minerals**	**Other**
1	Xylan	Glucan	Insoluble	SiO2	Rest soluble
2	Arabinan	Galactan	Soluble	Acetyl	Rest insoluble
3			Oxidized	KCl	
j	**g_c**				
1	NRTL				

The delignification stage is also a patented process (Benjelloun-Mlayah et al., 2012). The hydrogen peroxide oxidizes the organic acids to peroxo-acids (RCOOH + H_2O_2 → RCOOOH + H_2O). Peroxo-acids act as a solvent for the lignin and improve the delignification efficiency and its selectivity (Kham et al, 2005). The reactor is modeled by a RSTOICH model and solid handling stage is simulated by a SEP model tuned with experimental data. Figure 4.10 shows the resulted flowsheet.

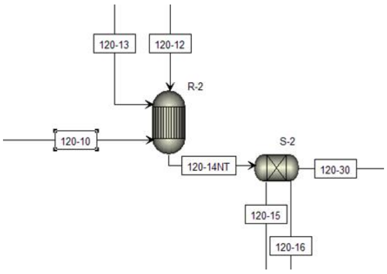


Figure 4.10. Delignification Section – run 01

Table 4.9 shows the accuracy error in stream flows as a stand-alone process and as a part of the total process. In the total process, input stream 120-12 becomes recycling streams and need validation, while stream 120-10 equals stream 120-09 and is validated for p=1. Values that fail to meet the accuracy constraint are noted in grey.

Table 4.9. Flows error in Delignification –run 01

#stream	**Total Mass %**	**Total MS %**	**Total Acids %**	**H2O %**
Stand-alone				
120-15	9.41	8.14	9.91	7.60
120-16	0.47	-6.07	3.05	9.83
120-30	4.50	1.86	5.63	8.00
Total process				
120-15	188.03	270.22	204.96	105.69
120-16	62.21	-70.22	73.81	50.57
120-30	7.19	5.86	8.26	6.99
120-12	1.11	662.75	0.88	3.52

Lignin content is set as the controlled variable for the S-2. After delignification step, kappa should be lower or equal to 12 (maximum lignin content: 2.2%wt.% DM). The reaction parameters are fixed based on the experimental data, while split fraction in S-2 is used as a secondary control variable. The stand-alone model meets the design specification constraints, but, as part of the total process, the error imported by streams 120-10 and 120-12 cannot be rectified (Table 4.10).

Table 4.10 Controlled variables for p=2 – run 01

	Controlled variable	Stand-alone	Total process
120-30	Lignin % ≤2.2 DM	2.08	6.30

- Deacidification Section

Deacidification step removes acids from the cellulosic pulp before washing. Table 4.11 presents the resulted property system. The number of biomass components does not seem to have any impact on the calculations.

Table 4.11. Property System for Deacidification – run 01

H_p (p=3)					
i	**Conventional**				
	H2O	AA	FA		
	Biomass				
i	**C5**	**C6**	**Lignin**	**Minerals**	**Other**
1	Xylan	Glucan	Insoluble	SiO2	Rest soluble
j	**g_c**				
1	NRTL-HOC				

The process is simulated as a conventional evaporation using a RADFRAC model with three stages: 1) kettle reboiler (bottom stage) 2) exchange phase 3) feed. Figure 4.11 presents the resulted flowsheet. Heater E-1 simulates the condensation of the evaporated solvent mixture (ΔT=-1, vapor fraction = 0). The operating pressure controls the operating temperature, which must not exceed the 105°C to avoid C5 degradation.

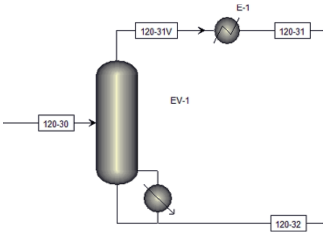


Figure 4.11. Deacidification Section

Table 4.12 shows the accuracy error in stream flows, as a stand-alone process and as a part of the total process. Neither the standalone, nor the total process model meet the accuracy constraint. Deviations in total MS are inserted due to imported error from stream 120-30.

Table 4.12. Flows error in Deacidification –run 01

#stream	Total Mass %	Total MS %	Total Acids %	H2O %
Stand-alone				
120-31	0.28		-0.06	1.53
120-32	-0.39		1.47	-40.75
Total process				
120-31	-4.53		-5.90	0.72
120-32	24.18	5.86	288.12	165.59

Total MS in the dried pulp is set as the controlled variable and (92%wt.% ±3%) and is controlled by the reboiler duty in EV-1 (Table 4.13).

Table 4.13 Controlled variables for p=3 – run 01

	Controlled variable	Stand-alone	Total process
120-31	89 ≤Total MS % ≤95	91.98	92.03

- Pulp Washing Section

Deacidified pulp is treated with an aquatic mixture of sodium hydroxide (NaOH). Bleached pulp undergoes a two-stage washing with process water, until its water content is raised at 90% wt. Table 4.14 presents the resulted property system.

Table 4.14. Property System for Pulp – run 01

H_p (p=4)					
i	**Conventional**				
	H2O	AA	FA	NaOH	
	Biomass				
i	**C5**	**C6**	**Lignin**	**Minerals**	**Other**
1	Xylan	Glucan	Insoluble	SiO2	Rest soluble
			Soluble	Acetyl	Rest insoluble
			Oxidized		
j	**g_c**				
1	NRTL				

The process is patented (Delmas & Avignon, 2004). Washing and filtration stages are simulated mainly by SEP models tuned with experimental data. Figure 4.12 presents the resulted flowsheet.

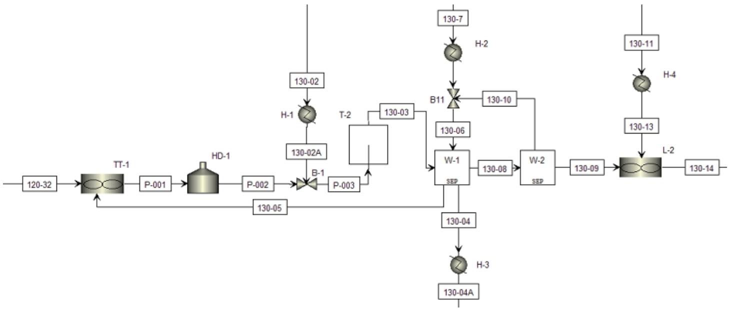


Figure 4.12. Pulp Washing Section – run 01

Table 4.15 shows the accuracy error in the stream flows for the pulp section as a stand-alone process and as a part of the total process.

Table 4.15. Flows error in Pulp –run 01

#stream	Total Mass %	Total MS %	Total Acids %	H2O %
Stand-alone				
130-05	5.61	0.82	2.57	1.28
130-10	8.88		0.23	0.98
130-04	-0.50	-0.46	3.53	1.02
130-14	6.24	-3.81	1.50	4.97
Total process				
130-05	-7.78	0.94	4.33	2.17
130-10	10.01		0.42	-0.18
130-04	-1.57	0.83	3.96	1.68
130-14	12.45	-10.30	0.41	10.01

The split fraction in W-2 controls the maximum kappa at 7 (lignin max: 1.3%wt.%), after the first washing stage and the water content in product C6 pulp at 90% wt ±5% (Table 4.16).

Table 4.16 Controlled variables for p=4 – run 01

	Controlled variable	Stand-alone	Total process
130-09	Lignin % ≤1.3 DM	1.24	4.22
130-14	85 ≤H2O % ≤95	89.42	90.28

- Evaporation Section

The evaporation section involves a number of stages that concentrate the extraction liquor from 10% to 65% wt.% dry, so that the product achieves high (the highest possible) concentration in lignin and hemicelluloses. Table 4.17 shows the resulted property system. The number of biomass components does not seem to have any impact on the calculations.

Table 4.17. Property System for Evaporation – run 01

H_p (p=5)					
i	**Conventional**				
	H_2O	AA	FA		
	Biomass				
i	**C5**	**C6**	**Lignin**	**Minerals**	**Other**
1	Xylan	Glucan	Insoluble	SiO_2	Rest soluble
j	**g_c**				
1	NRTL-HOC				

The evaporators are modeled as conventional RadFrac models and Heaters are used for the phase and temperature change. The first two stages deploy evaporators connected in series, while the third stage deploys two additional evaporators connected in parallel (Figure 4.13). This arrangement was dictated by the need to cope with reduced evaporation efficiency as the liquor is particularly viscous. We note that the pilot unit tested this arrangement with falling film evaporators.

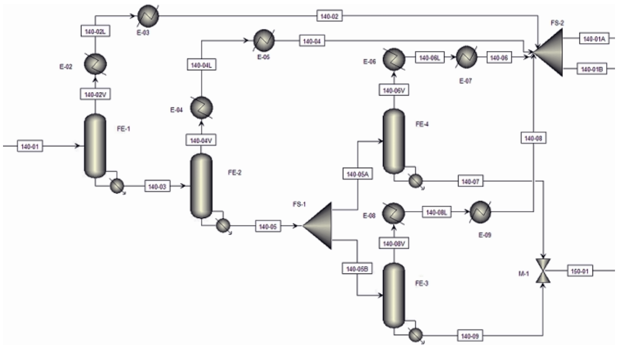


Figure 4.13. Evaporation Section – run 01

Table 4.18 shows the error in the stream flows as a stand-alone process and as a part of the total process. Neither the standalone, nor the total process model meet the accuracy constraint. Deviations in the Total MS are inserted due to deviations in stream 140-01 for p=1.

Table 4.18. Flows error in Evaporation –run 01

#stream	**Total Mass %**	**Total MS %**	**Total Acids %**	**H2O %**
Stand-alone				
140-01A			-0.80	3.94
140-01B	2.38		1.56	6.42
150-01	-0.87		12.72	-70.00
Total process				
140-01A	-4.00		-1.46	8.94
140-01B	-5.00		-1.93	8.42
150-01	0.55	7.14	33.00	-88.80

The reboiler duty of the evaporators controls the total MS of the C5 syrup, which at the end should be between 60 to 65%wt.% (Table 4.19).

Table 4.19 Control variables for p=5 – run 01

	Controlled variable	Stand-alone	Total process
150-01	60 ≤Total MS % ≤65	62.24	64.84

- Lignin Treatment Section

The concentrated extraction liquor goes under a treatment to separate lignin. Table 4.20 presents the property system for the lignin treatment section.

Table 4.20. Property System for Lignin – run 01

H_p (p=6)					
i	**Conventional**				
	H2O	AA	FA		
	Biomass				
i	**C5**	**C6**	**Lignin**	**Minerals**	**Other**
1	Xylan	Glucan	Insoluble	SiO2	Rest soluble
			Soluble		Rest insoluble
j	**g_c**				
1	NRTL				

Lignin treatment is a patented process (Delmas & Benjelloun-Mlayah, 2013). The nonconventional process is modeled as a combination of conventional models. Lignin precipitation (LP-1) is modeled as a Heat model and the multiple washing–filtration treatment is modeled as a SEP and a CCD model (efficiency-based), tuned with experimental data (Figure 4.14). Stream 150-08 is the product stream for lignin.

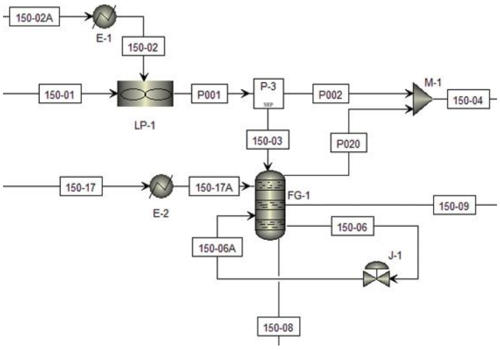


Figure 4.14. Lignin Treatment Section – run 01

Table 4.21 shows the error in total flow and compositions, as a stand-alone process and as a part of the total process.

Table 4.21. Flows error in Lignin –run 01

#stream	Total Mass %	Total MS %	Total Acids %	H2O %
		Stand-alone		
150-04	-0.02	7.32	-59.38	1.53
150-09	-0.13	89.84	96.92	-2.55
150-08		-1.82	16.25	2.60
		Total process		
150-04	-3.75	118.29	-83.19	-4.62
150-09	-55.43	2.05	-14.35	-64.07
150-08	11.78	12.83	-71.34	5.81

The dry matter of the streams after each washing stage are used as control variables. The total MS after the first washing stage should be between 63-65%, after the second 55-57%, and after the third 51-53% wt.%. The CCD model does not offer control over the intermediate stream compositions, so the efficiencies of the intermediate washing stages are used instead (Table 4.22).

Table 4.22. Efficiency error in Lignin (total process) – run 01

#stage	Efficiency error %
1	16.25
2	96.04
3	-59.38

- C5 Syrup Concentration Section

After the precipitation of lignin, the C5 sugars need to be separated from the organic solvent. The maximum allowed temperature is 105°C to avoid C5 degradation. Table 4.23 shows the resulted property system.

Table 4.23. Property System for C5 Syrup – run 01

H_p (p=7)					
i	**Conventional**				
	H2O	AA	FA		
	Biomass				
i	**C5**	**C6**	**Lignin**	**Minerals**	**Other**
1	Xylan	Glucan	Insoluble	SiO2	Rest soluble
j	**g_c**				
1	NRTL-HOC				

The liquor is first concentrated by evaporation and then purified by stripping until reaching 65% wt.% concentration in C5 sugars. The evaporation step is modeled as a Radfrac model with three stages and a kettle, while stripping is modeled as a Sep model, tuned with experimental data. Heat models are used to simulate the condensation of the vapor streams. Figure 4.15 presents the resulted flowsheet. Stream 160-08 is the product stream for the C5 sugar syrup.

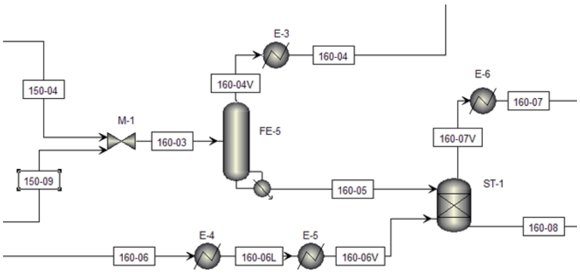


Figure 4.15. C5 Syrup Concentration Section – version 01

Table 4.24 shows the error in stream flows for the stand-alone and the total process model.

Table 4.24. Flows error in C5 Syrup –run 01

#stream	Total Mass %	Total MS %	Total Acids %	H2O %
Stand-alone				
160-04	4.48		8.86	3.72
160-07	-6.63		-30.99	-3.66
160-08	-0.65		-5.92	-1.00
Total process				
160-04	-33.33		-18.26	-35.95
160-07	12.84		50.99	8.19
160-08	51.64	89.25	-4.02	-4.86

Total MS after the evaporation step is controlled by the reboiler duty of FE-5 at 55-57% wt.% and after the stripping step is controlled by the split fraction in ST-1 at 60-65%wt.%.

Table 4.25 Controlled variables for p=7 – run 01

	Controlled variable	Stand-alone	Total process
160-05	55 ≤Total MS % ≤57	55.99	56.04
160-08	60 ≤Total MS % ≤65	60.00	64.98

The shortcut model SEP is used because Radfrac model for stripping came up with large deviations in the stripping efficiency, even for the stand-alone model (Table 4.26). Since stripping process requires no heating or cooling, the option to tune mass balances with a shortcut model is relatively safe.

Table 4.26. Efficiency error in C5 Syrup section (stand-alone) – run 01

Efficiency error %	SEP	RADFRAC	
		NRTL	NRTL-HOC
H2O	0.78	14.27	12.17
Acids	0.11	-4.87	-2.76

- Solvent Regeneration

All effluent streams from the evaporation, the pulping, the C5 sugars concentration, and the deacidification sections feed a distillation column to recover acids from water. Table 4.27 shows the resulted property system.

Table 4.27. Property System for Distillation – run 01

H_p (p=8)					
i	**Conventional**				
	H2O	AA	FA		
	Biomass				
i	**C5**	**C6**	**Lignin**	**Minerals**	**Other**
1	Xylan	Glucan	Insoluble	SiO2	Rest soluble
j	**g_c**				
1	NRTL-HOC				

The distillation column is modeled as a Radfrac model. Figure 4.16 presents the resulted flowsheet. Stream 170-04 is the regenerated water and stream 170-05 has the regenerated acids.

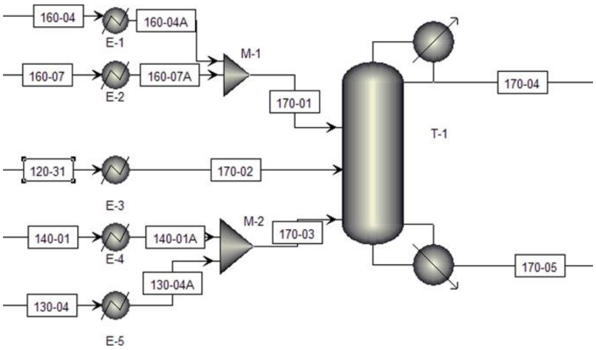


Figure 4.16. Solvent Regeneration Section – single effect

Table 4.28 shows the error in mass flows as a stand-alone and as a part of the total process.

Table 4.28. Flows error in Distillation –run 01

#stream	Total Mass %	Total MS %	Total Acids %	H2O %
Stand-alone				
170-04	-6.58		-0.04	-6.48
170-05	7.86		6.65	0.06
Total process				
170-04	10.42		10.56	10.42
170-05	6.07		6.09	5.93

Reflux ratio and reboiler duty are used as control variables to achieve the desirable mass purity: 99.2 % wt.% for distillate water and 92% wt.% for bottoms acids (Table 4.29).

Table 4.29 Controlled variables for for p=8 – run 01

	Controlled variables	Stand-alone	Total process
170-04	H2O %=99.2	99.2	99.2
170-05	Total Acids % =92.0	92.0	92.0

- Storage Tanks

Two intermediate storage tanks are used for the central management of the solvent. The central tank accepts pure solvent steams (without solids), such as recycles acids from the solvent regeneration and the evaporation sections. The intermediate tank is used to shortly store streams coming from the extraction and delignification sections, which contain impurities. Both tanks accept make up streams for the acids, so as to control the composition of the solvent (55/30/15). Table 4.30 presents the resulted property system.

Table 4.30. Property System for Tanks – run 01

H_p (p=9)					
i	**Conventional**				
	H2O	AA	FA		
	Biomass				
i	**C5**	**C6**	**Lignin**	**Minerals**	**Other**
1	Xylan	Glucan	Insoluble	SiO2	Rest soluble
2	Arabinan	Galactan	Soluble	Acetyl	Rest insoluble
3			Oxidized	KCl	
j	**g_c**				
1	NRTL				

Storage tanks are modeled as two identical vessels based on FLASH2 model, operating at 80°C and atmospheric pressure. The vent streams are used to validate that the operating conditions do not produce acid vapors. Figure 4.17 shows the resulted flowsheet.

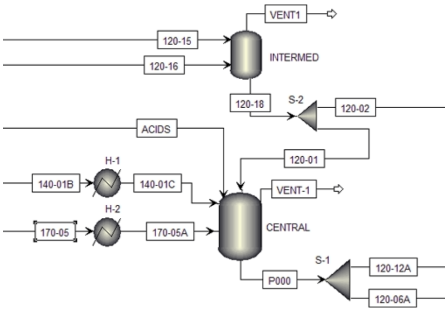


Figure 4.17. Storage Tanks Section – version 01

Table 4.31 shows the stream flows for, as a stand-alone and as a part of the total process model.

Table 4.31. Flows error in Tanks –run 01

#stream	Total Mass %	Total MS %	Total Acids %	H2O %
Stand-alone				
120-02				
120-06				
120-12				
Total process				
120-02	-0.75	10.09	4.28	-21.93
120-06	1.17	663.11	-0.82	3.65
120-12	1.11	662.75	0.88	3.52

Preliminary Extrapolation Analysis

Before starting testing new scenarios, a sensitivity analysis is performed to understand the role of different design variables. Figure 4.18 shows how the feed composition changes when increasing the number of the secondary components. 5% is set as the threshold for selecting an additional secondary component. The combination of components that respects the error threshold includes: i=1 for the lignin fraction; i=2 for C5, C6, and other; i=3 for the minerals.

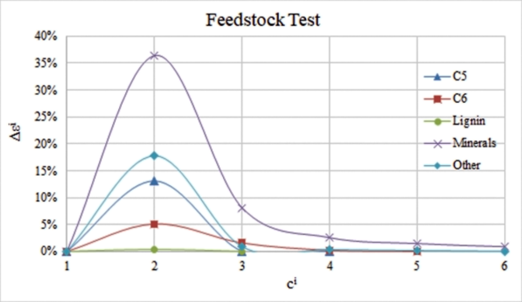


Figure 4.18. Feed composition test

A distillation column with 40 theoretical stages is used to study how the total theoretical stages and the feed stage affect the purity of the distillate and the reboiler duty. The feed stage shows a global optimum at the 12th stage (Figure 4.19a), which is also the global maximum of the reboiler duty (Figure 4.19b). On the other hand, Figure 4.19c shows that the purity of the distillate increases with the augmentation of the theoretical stages and so does the duty of the reboiler (Figure 4.19d). The optimal feed stage is not always in the middle of the column. This implies the generation of numerous scenarios.

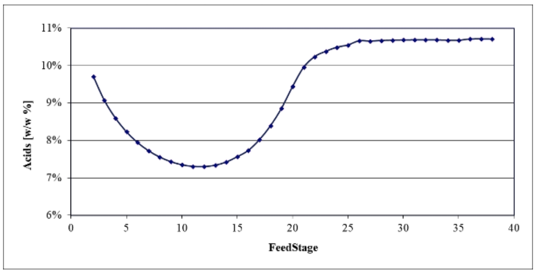


Figure 4.19a. Feedstage vs acids purity on top

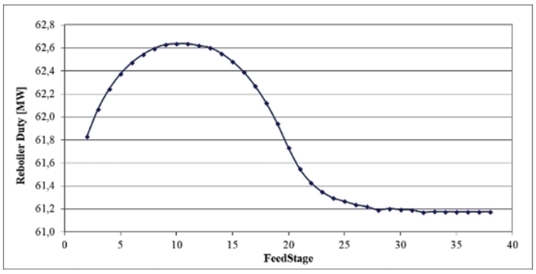


Figure 4.19b. Feedstage vs reboiler duty

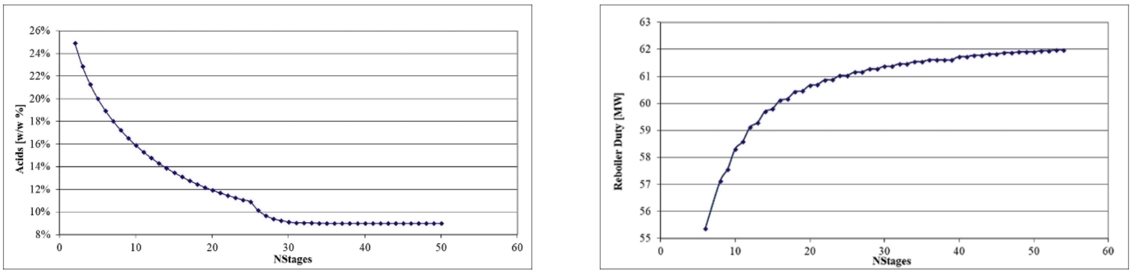


Figure 4.19c. NStages vs acids purity on top
Figure 4.19d. NStages vs reboiler duty

Figure 4.19. Sensitivity Analysis

Comments on version 01

Briefly, when process sections are simulated as stand-alone models, the resulted error is within limits, for most of the cases, but when they become part of the total process the deviation increases. This is mainly due to the recycling streams, which accumulate previous discrepancies. Whereas standalone models can choose the number of the components, the total process model uses the highest cardinality (Table A1, in the Appendix A). Nevertheless, the interest of using such a detailed feed composition is in doubt, since it demands a large amount of experimental data to validate all the streams in the process flowsheet. Moreover, the reactor models are based on reaction stoichiometry and, thus, are sources of error due to the fact that biomass degradation reactions cannot be described by simple stoichiometry approximations. In addition, when rigorous models are used for equilibrium calculations including the organic acids, the standalone calculations resulted in significant errors, indicating the incapacity of the selected thermodynamic models to appropriately describe the property system. Finally, the preliminary extrapolation analysis showed that each variable behaves differently, but this behavior is not completely independent from other variables. Even when analyzing only a part of the process, we have to deal with large amount of data.

- Fine Model Amendments

The first run gave valuable insight into which are the shortcomings of the fine models. First results showed that simulation amendments need to target the thermodynamic models. The amended property system has regressed thermodynamic models with experimental data. The amended process system has incorporated process modifications proposed by the experimental groups to achieve new technological improvements. The scope of those modifications is to develop a more flexible and reliable fine model that will allow the safe extrapolation of the resulted surrogates to different operating scenarios.

Property System (H_p)

Starting with the selection of components, the first version describes biomass as a mix of pseudo-components. This representation creates dependency on detailed laboratory analysis for the validation step, and models are inflexible about the feed type, given the uncertainty of biomass composition. Previous results showed that the cardinality of existing components increases gradually, meaning that an existing component in the (p-1)-unit (preceding) may be the parent of the new component in the p-unit (active). This gives an insight about how the structure of the biomass changes as it moves along the processing steps. It seems that the polyvalent treatment aptness of CIMV process is due to the mild and gradual reformation of the biomass structure during the different processing steps. Figure 4.20 shows the transformation course of biomass:

(i) The extraction step removes the polymers of lignin and hemicellulose, which are not strongly attached on the plant fibers
(ii) The delignification step cuts integrated lignin off the fibers of cellulose
(iii) The washing section ends up with relatively pure cellulose fibers

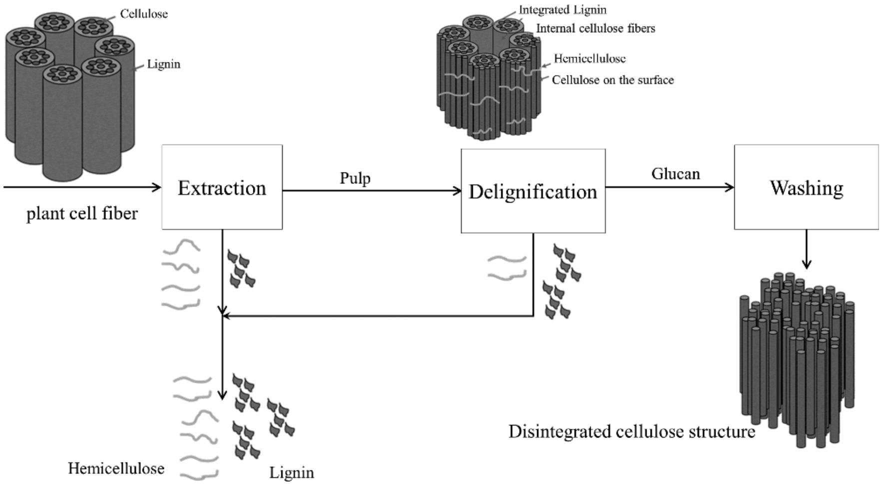


Figure 4.20. Biomass structure transformation throughout the CIMV process

Table 4.32 shows the new candidate components. Biomass, pulp, and glucan are complex components, given the fact that they contain other components integrated in their structure; thus, they are modeled as nonconventional components. C5 syrup, C6 pulp, and lignin are mixtures of the solubilized sugars, the minerals and other substances. The new version increases gradually the complexity of the property system while respecting the process complexity and the availability of experimental data.

Table 4.32. Candidate Components

<table>
<tr><th colspan="5">Conventional</th></tr>
<tr><td>H2O</td><td>AA</td><td>FA</td><td>H2O2</td><td>NaOH</td></tr>
<tr><th colspan="5">Nonconventional</th></tr>
<tr><td>Biomass</td><td>Pulp</td><td colspan="3">Glucan</td></tr>
<tr><th colspan="5">Mixture of pseudo-components</th></tr>
<tr><th>C5 syrup</th><th>C6 pulp</th><th colspan="3">Biolignin</th></tr>
<tr><td>C5</td><td>C6</td><td colspan="3">Lignin</td></tr>
<tr><td>C6</td><td>C5</td><td colspan="3">C5</td></tr>
<tr><td>Lignin</td><td>Lignin</td><td colspan="3">C6</td></tr>
<tr><td>SiO2</td><td>SiO2</td><td colspan="3">SiO2</td></tr>
<tr><td>Mineral</td><td>Mineral</td><td colspan="3">Mineral</td></tr>
<tr><td>Other</td><td>Other</td><td colspan="3">Other</td></tr>
</table>

The property parameters of the nonconventional components need to be described. Table 4.33 shows the data used for the poplar biomass description. The values need to meet the following consistency requirements (Aspen Plus, 2017):

- PROXANAL values for fixed carbon, volatile, and ash sum to 100.
- SULFANAL values sum to the ULTANAL value for sulfur.
- ULTANAL value for ash equals the PROXANAL value for ash.
- ULTANAL values sum to 100.

Table 4.33. Biomass description as a nonconventional component (wheat straw)

Wheat straw Biomass					
PROXANAL	**%**	**SULFANAL**	**%**	**ULTANAL**	**%**
Moisture	15.00				
Ash	7.00	Pyritic	0.09	Ash	7.00
Volatile	75.80	Sulfate	0.08	C	46.10
Fixed Carbon	17.20	Organic	0.03	H	5.90
				N	1.00
				Cl	0.40
				S	0.20
				O	39.40
sum	100.00	sum	0.20	sum	100.00

Data for pulp and glucan as nonconventional components are shown in Table A2 and Table A3, respectively, in the Appendix. Moving on to the thermodynamic models, Rönsch and Wagner (2012) concluded, from statistical measurements, that the correlation developed by Mott and Spooner achieves the best agreement with the heating values of wood and straw. Therefore, model HCOALGEN is used as the property method for the combustion correlation (option 4), and model DCOALIGT is used for the density correlation of the nonconventional components.

First run failed to converge the stream flows, especially for the organic solvent mixtures, indicating defects in the thermodynamic models and the equilibrium calculations. Available thermodynamic models cannot predict correctly the azeotrope between FA-H2O at 107.2°C and 77%wt.%. Therefore, the basic model NRTL-HOC is regressed with experimental data. Figure 4.21 compares the regressed model with some of the thermodynamic models existing in the Aspen database for P=1atm. Figure 4.21a shows that after 30% wt.% in water, NRTL-HOC overestimates the vapor composition in the solvent mixture, while the other models underestimate it. Figure 4.21b shows that only model NRTL predicts well the vapor phase of AF, but when it comes to the AA vapor composition (Figure 4.21c) it underestimates it until around 30% H_2O wt.%. Figure 4.21d shows that model NRTL-HOC overestimates the temperature of the AA vapor phase, model UNIF-HOC underestimates it, while NRTL underestimates it until the region of 0.75-0.82, after which it overestimates the temperature of vapor AA-H_2O mixture.

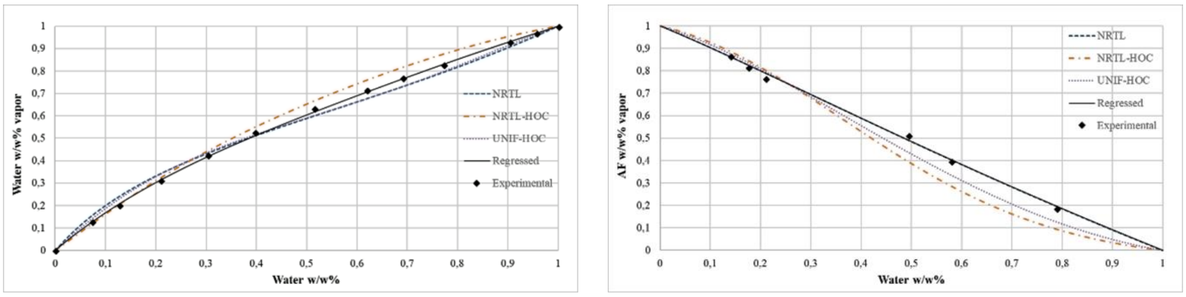


Figure 4.21a. H_2O vs. H_2O vapor %wt.%

Figure 4.21b. H_2O vs. AF vapor %wt.%

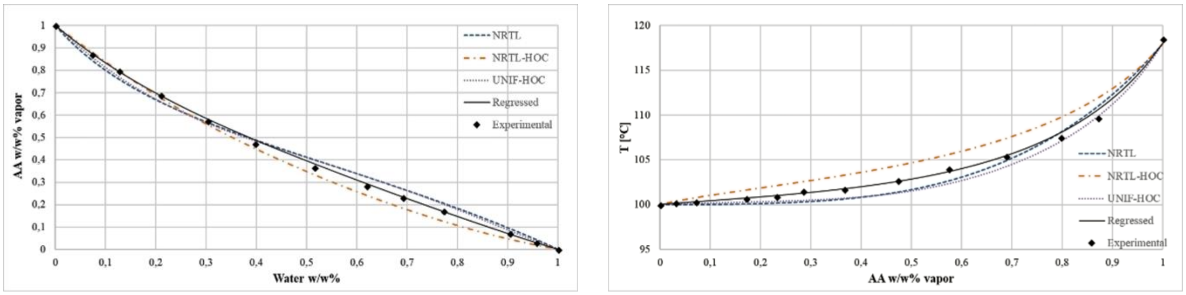


Figure 4.21c. H_2O vs. AA vapor %wt.%

Figure 4.21d. AA vapor %wt.% vs. T

Figure 4.21. VLE comparison of thermodynamic models

Process System (S_p)

The capacity of the new model is set arbitrarily at 300kt/yr dry biomass, to create a new capacity point. Moreover, it is decided that the configuration of the columns (deacidification, evaporation, distillation, etc.) should be dictated by the energy integration analysis. Therefore, all columns are simulated as a single effect unit, unless a specific arrangement is imposed for technical reasons.

In this case, the description of the property system and the selection of the active components is a simpler task (Tables A4 to A12 in the Appendix A). When not mentioned otherwise, the control and controlled variables of the process system are the same as the first run. The new models per process section are presented below.

- Extraction Section

The simulation of biomass as nonconventional components does not allow the use of stoichiometric reactions for the description of biomass fractionation; thus, RYIELD model tuned with experimental yields is used instead (Figure 4.22). Moreover, the SEP model is replaced by two SSPLIT models (sub-stream splitting) for better controllability. Lignin content is set as the controlled variable for P-1.

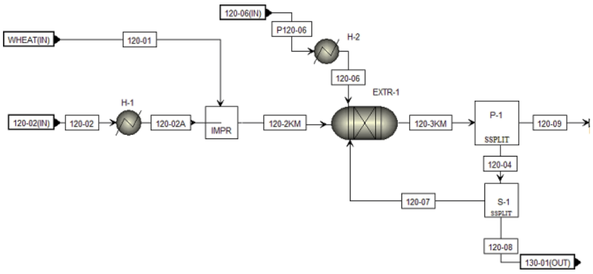


Figure 4.22. Extraction Section

- Delignification Section

Delignification reactor is modelled as RYIELD model, based on the experimental yields (Figure 4.23). Delignification step fractionates pulp into glucan, C6, C5, lignin, and minerals, while H_2O_2 gives H_2O and O_2, tuned with the experimental data.

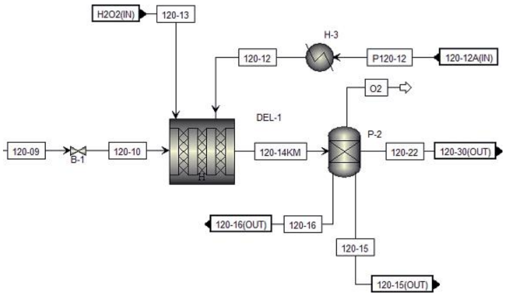


Figure 4.23. Delignification Section

- Deacidification Section

The modeling of the deacidification section has not changed (Figure 4.11).

- Pulp Washing Section

RYIELD model is used to simulate the bleaching of the deacidified pulp (Figure 4.24).

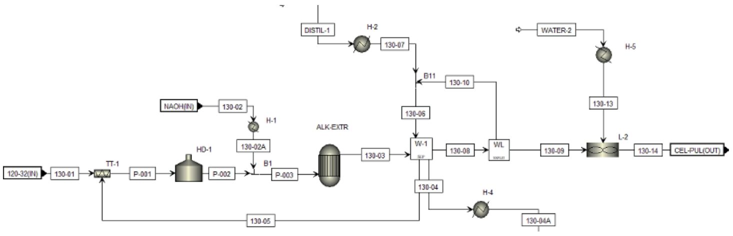


Figure 4.24. Pulp Washing Section

☐ Evaporation Section

A flash unit is added before the evaporation of the extraction liquor, to control the pressure drop (Figure 4.25).

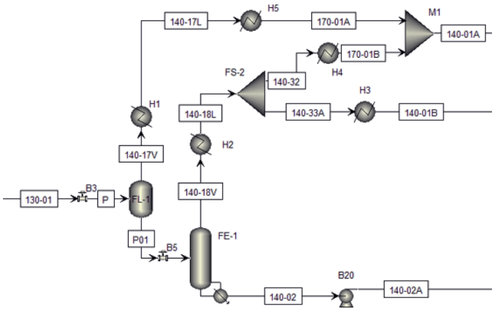


Figure 4.25. Evaporation Section – single effect

☐ Lignin Treatment Section

To gain in controllability between the washing stages, the multistage CCD washer is replaced by three individual washing stages (SEP models) (Figure 4.26) to tune the controlled variables.

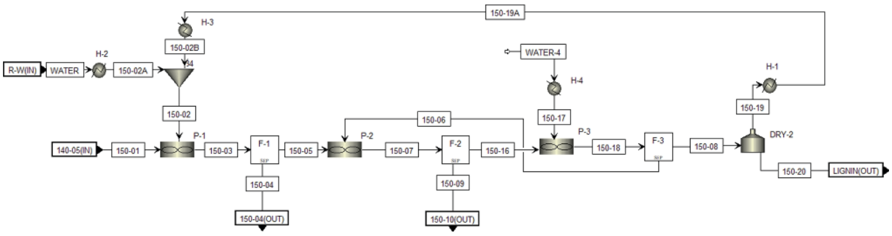


Figure 4.26. Lignin Treatment Section

☐ C5 Syrup Concentration Section

Thanks to the regressed property models, the rigorous model RADFRAC can be used for the simulation of C5 stripping (Figure 4.27).

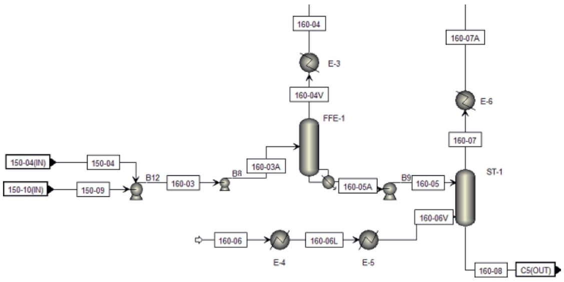


Figure 4.27. C5 Syrup Concentration Section – single effect

- Solvent Regeneration

The modeling of the process units has not changed (Figure 4.16), but the distillation column no longer accepts streams with solids. Moreover, it is decided that the operating temperature should not exceed 170°C due to corrosion issues.

- Storage Tanks

The modeling of the storage units has not changed (Figure 4.17).

Model Validation

The question is what is the impact of the amendments on the calculations of the simulation model? The aggregated representation of the biomass components and the refinement of the unit operation models improved the mass balances calculations, while the regressed thermodynamic model improved both mass and energy balances. Table 4.34 shows how the mass balances of the distillation column change with the different thermodynamic models. For all cases, the distillation feed and the design specifications were the same. Even though the error of the NRTL and NRTL-HOC model is within the 5% limit, this deviation provokes larger errors in the mass balances of the organic solvent (AA and FA).

Table 4.34. Mass balances comparison of thermodynamic models

		Regressed	**NRTL**	**NRTL-HOC**	**UNIF-HOC**
	IN	**Bottom**			
Total [tn/hr]	100.00	15.57			
H2O	85.00%	8.00%	8.00%	8.00%	8.00%
AA	10.00%	60.20%	64.20%	63.40%	0.30%
FA	5.00%	31.80%	27.80%	28.60%	91.70%

The most important impact of the improved thermodynamic models is on the energy balances (Figure 4.28). The mass balance estimations of the NRTL-HOC model, for example, are the closest to those of the regressed model, but the reboiler duty is overestimated by 43%. Model UNIF-HOC, on the other hand, overestimates the reboiler duty only by 7% but has large deviations in the mass balance calculations.

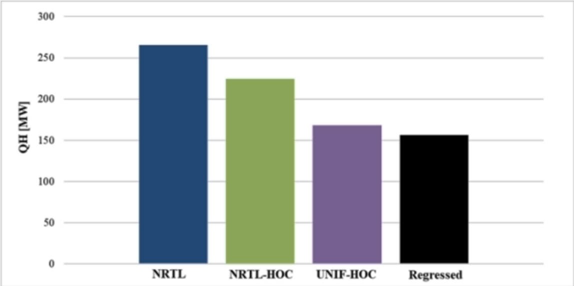


Figure 4.28. Thermodynamic models & reboiler duty estimation

Table 4.35 compares the composition of the products as calculated by the experimental groups to those calculated by the Aspen model. The error in the composition of the product streams is less than 0.5%.

Table 4.35. Comparison of product composition (wheat straw)

DM	C6			C5			Biolignin		
wt.%%	CIMV	Aspen	Error	CIMV	Aspen	Error	CIMV	Aspen	Error
C6	85.60%	85.26%	-0.34%	2.50%	2.97%	0.47%	0.03%	0.04%	0.01%
C5	12.90%	12.93%	0.03%	47.50%	47.38%	-0.12%	5.30%	5.29%	-0.01%
Lignin	1.25%	1.26%	0.01%	0.00%	0.00%		93.73%	93.75%	0.02%
Minerals	0.25%	0.23%	-0.02%	20.00%	19.87%	-0.13%	0.94%	0.93%	-0.01%
Other	0.00%	0.00%		30.00%	29.78%	-0.22%	0.00%	0.00%	

Model extrapolation

To test the flexibility of the model in relation to its treatment capacity, multiple runs are conducted for a range of feedstock inflow from 8 to 1,000 ktn/yr (dry biomass). Only the operational parameters are modified so as to satisfy the control variables. Figure 4.29 shows how the accuracy error is affected as the capacity of the model changes. Results show that the model is resilient to capacity fluctuations. The accuracy error in the composition of the products remains below ±3% for all the runs. The largest deviation appears in the total flows, where the model underestimates the total C6 pulp flow by -2.5%.

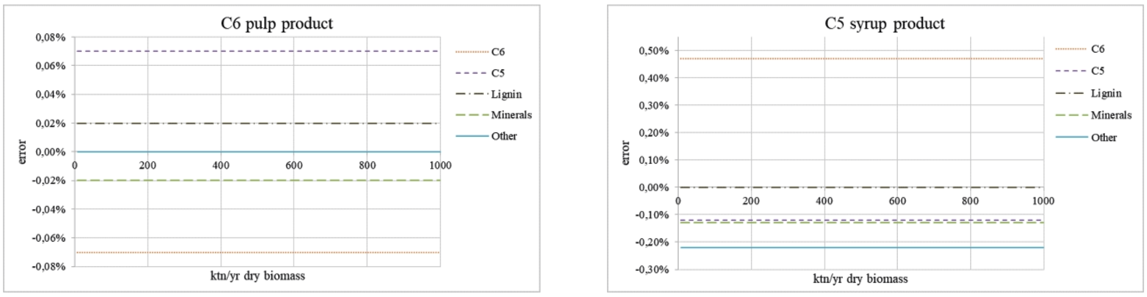


Figure 4.29a. C6 pulp vs. model capacity

Figure 4.29b. C5 syrup vs. model capacity

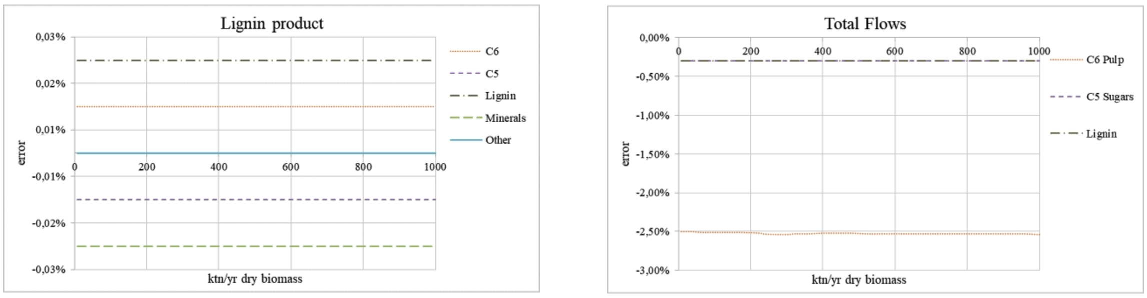


Figure 4.29c. Lignin vs. model capacity

Figure 4.29d. Total product flows vs. model capacity

Figure 4.29. Accuracy error in the product streams for different model capacities

The uncertainty in the composition of the biomass also bears significant impact on the quality and the quantity of the final products. The model is resilient to composition variations of the biomass type used for its development. However, when changing the feedstock type, some small technical modifications may be required (e.g. residence time, reaction yields, solvent composition, etc.). We have run the model for the different feedstocks by adjusting only the technical modifications and keeping the capacity at 800ktn/yr dry biomass. All the rest (components, process and property models) remain the same. Results show that the model is also resilient to different feedstock types. As in the case of the capacity range, the largest deviations appear for the estimation of the total flow of the C6 pulp product stream (Figure 4.30).

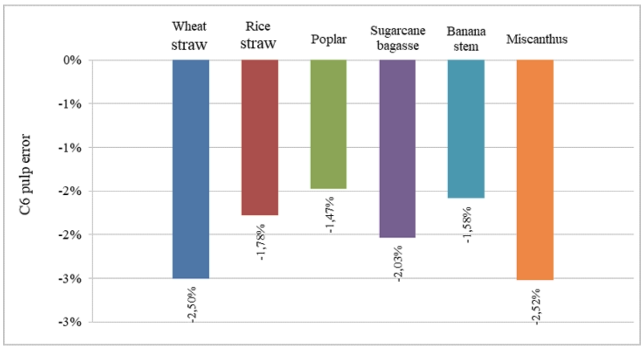


Figure 4.30. Accuracy error in the C6 pulp product stream for different feedstock types

4.4.3 Model Results

Flexibility analysis shows that the overall mass balances are resilient to capacity changes. This actually means that the models are linear and depend on the composition of the feed. Therefore, for n different feedstock types on dry mass basis, the total flow of q products depends on the total biomass inflow (Eq.4.17), and the flow of c components per q product depends on the inflow of the components (Eq.4.18). The parameters of the surrogates for the different feedstock types along with the expected stream composition are presented in the Appendix (Tables A13 to A24).

$$F_{n,q}^{OUT} = \alpha_{1\ n,q} \cdot F_n^{IN} \qquad Eq.4.17$$

$$F_{n,q,c}^{OUT} = \alpha_{2\ n,q,c} \cdot F_{n,c}^{IN} \qquad Eq.4.18$$

Surrogates about the consumption of supplied utilities (mass and energy), the production of effluent streams, and the cost estimation depend on the integration strategy. For example, for a capacity of 170kt/year dry biomass the equipment cost is estimated at 140.28 MM$ ($2016) (±20%) when choosing a double effect distillation column in the regeneration section and at 137.26 MM$ (2016) (±20%) when choosing a single effect.

4.5 Discussion

The proposed framework is applied for the modelling of a real-life biorefinery plant. The first iteration collected information about the development of the fine model. Then, the simulation model was used to generate sample data for the development of the surrogates. The validation analysis revealed weaknesses in the description of the biomass components, the property, and the unit operation models. The approach gave an insight about how biomass is transformed along the processing steps and assisted in the selection of more appropriate unit operation models. As a result, instead of simulating biomass as a mixture of pseudo-components, it is decided to use nonconventional components so as to follow a more aggregated formation. Discrepancies in the energy balances suggested to amend the existing thermodynamic models by data regression. Eventually, the amended fine model gains in accuracy, flexibility, and simplicity. Targeted improvements helped to avoid unnecessary complexity in the simulation of the components and the unit operation models. The resulted simulation model can be used for a wide range of treatment capacities and biomass types. The development of a reliable fine model follows the development of a reliable surrogate. The surrogates developed by this procedure can be used for conducting upper level analysis, without losing in liability.

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Chapter V

Synthesis of Flexible and Conditional Value Chains

Process synthesis is to evaluate which processing path is the best-suited for a portfolio of products depending the raw materials. This chapters introduces a new conditional synthesis model, which employs surrogates, developed in accordance to the methodology presented in Chapter IV, and the modular graph presented in Chapter III. The case studies demonstrate the impact of the source-sink principle on the configuration of the product portfolio.

5.1 Motivation and Challenges

Biorefinery synthesis methods scope to choose the processing paths that valorize best the available raw materials and produce a profitable portfolio of products that satisfy the imposed constraints. Mathematical programming (Quaglia et al., 2015) and ontology engineering (Kokossis et al., 2016) are employed to assist the tasks of design space definition representation, as superstructure development remains a challenge. However, the application of these methods is limited by the complexity associated with the mathematical formulation of the sub problems. Previous work in biorefinery synthesis starts with a given value chain tree, screening processing paths in search of the optimum configuration of raw materials, conversion processes, and product portfolios. A common approach is to start with a core technology (e.g., pretreatment), then add pre- and post-processing units for feedstock preparation and product separation and upgrading. Although existing approaches can lead to operational configurations, they may hinder the innovation of new configurations. The screening procedure is based on hierarchical structures "raw materials-to-intermediates-to-products", ignoring technological incompatibilities due to product/feed quality constraints. Each technology has different quality standards about the acceptable feed streams but also about the produced streams. Nevertheless, a superstructure of biorefinery processes can be seen as a complex network (Kivelä et al., 2014).

This chapter presents a new method for the conditional synthesis of biorefineries. The design space is automatically created and superstructures are formulated as complex networks. Each process is seen as a module interface that expresses which elements are provided and required. The elements defined in the interface are detectable by other modules. Each module unit comprises a set of transformation rules, descriptions of the incoming and out coming flows, and a control condition. A module can also import formal parameters that allow to leave parts of a system unspecified for later actualization. This modular approach allows the design of reconfigurable manufacturing systems but also allows the detection of potential relationships amongst the building units. Module units can be handled as skids of the overall configuration but also as indicators to identify similarities in the process network. Three case studies are used to demonstrate the impact of the connectivity rules in the final network design. The first case performs process synthesis by screening only the main component that is produced/required. The second case controls the quality of the stream accepted per module. Finally, units that improve the quality of the streams are activated.

5.2 Problem Statement

The problem can be stated as one where given is a set of

- utilities that relate to materials (e.g. biomass, water) or energy (e.g. steam, cooling water)
- sink and source locations that relate to mass exchange
- process units that relate to source and/or sink locations. The units may also relate to suppliers, processes, consumers, or waste treatment facilities.

Mass sources and sinks physically relate to process units that feature products and raw materials at a known quality. Given are the availability of the raw materials, the conversions, and the energy requirements of each process unit. However, the number and the relationships of the active process units as well as the flows of the network remain a variable and a degree of freedom. The systems approach is to determine the configuration of the process network that maximizes the potential profit for the given raw material availability and satisfies the quality constraints of the process inflows.

5.3 Methods

The method uses the building blocks (Figure 3.2) and the modular unit (Figure 3.3) as presented in Chapter III. Each process provides materials, which may be sold as products, used as gate streams to feed another processing unit, or be discharged to waste treatment (Figure 5.1). Each process requires materials, which may be provided by supply or other process units. The different modules can be combined together according to their product-feed compatibility, searching not only for the existence of a main component (e.g. C5 sugars) but also for the quality of the stream in general. Each process has quality standards for the feed and product streams. Therefore the source locations (splitters) have the information about the quality of the streams they distribute, and the sink locations (mixers) have the information about the quality range they can accept. The optimization problem is to define which modular units exist and whether a material stream is sold as product or used as a feed stream for another process.

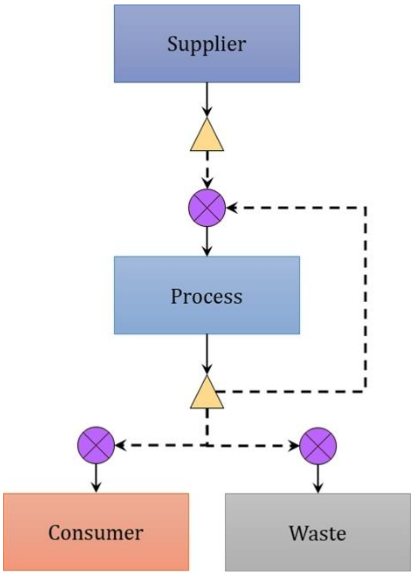

Figure 5.1. Modules Connectivity

5.4 Mathematical Formulation

The conditional synthesis model is formulated as a mixed-integer linear programming problem (MILP). Binaries are assigned to select the active modules and determine the type of their relationship. The model includes basic mass and energy balances, expressions that account for the economic flows, and a set of logical constraints. However, when both flows and compositions are variables, the model is nonlinear. To keep the model linear, a reasonable set of assumptions could be that

- processes operate at a continuous, steady-state, and fixed performance mode
- piecewise linearized models can be used for the estimation of the equipment cost
- sinks have known bounds for the capacity, based on the linearized cost models, and for the quality of the inflow, based on the fixed performance
- sources have fixed compositions, based on the fixed performance

The following sets are denoted:

N= {n| raw materials and utilities}
I= {i| sources that are related to suppliers $i \in I^S$ or processes $i \in I^P$} = $\{I^S \cup I^P\}$
J= {j| sinks that are related to consumers $j \in J^B$, processes $j \in J^P$, or waste treatment $j \in J^W$} = $\{J^B \cup I^P \cup I^W\}$
M= {m| process units that are related to I and J}

The continuous variables of the problem are:

For the mass balances [ktn/yr]

F_{ij}	Flow between sources and sinks
$F_{mj}^{IN}, F_{mi}^{OUT}$	Flow in or from process unit m
$\bar{F}_{mjn}^{IN}, \bar{F}_{min}^{OUT}$	Material flow from and to process unit m

For the energy balances [MW/yr]

Q_{mn}^{H}, Q_{mn}^{C}	Hot or cold energy requirements per process unit m

For the costing [M$/yr]

$Cost_m$	Annualized equipment purchase cost of process unit m
$Cost^{Total}, Cost^{CI}, Cost^{OP}, Cost^{M}, Cost^{W}, Cost^{E}$	Cost for the sum total, capital investment, operating, materials, waste treatment, and energy
$Revenue$	Total revenue
$Profit$	Potential profit

The binary variables of the problem are:

Z_m	The existence of process unit m

The parameters of the problem include economic, operational, and bounds information:

Economic [M$/ktn or M$/MW]

pp_n	Purchase price of the utility n
sp_j	Selling price of stream going to consumer $j \in J^B$
tp_n	Treatment price of the utility n

Operational

ξ_{mji}	Conversion factor of sink j to source i for unit m, [ktn/ktn]
q_{nm}^{H}, q_{nm}^{C}	Hot and cold requirements per unit m [MW yr/ktn]
c_{in}	Concentration on the source locations [ktn n/ktn]

Bounds

c_{jn}^{UB}, c_{jn}^{LB}	Upper and lower concentration boundaries on the sink locations [ktn n/ktn]
F_{mj}^{UB}	Upper capacity boundary for flow per sink per processing units [ktn/yr]
RA_n	Raw material availability [ktn/yr]
LU	Big number

5.4.1 Mass Balances

The flow entering a process unit is the summation of the sources feeding the related sinks (Eq.5.1).

$$F_{mj}^{IN} - \sum_{i} F_{ij} = 0 \qquad Eq.5.1$$

The component flow entering a process unit equals the summation of the component flows coming from the sources (Eq.5.2).

$$\bar{F}_{mjn}^{IN} - \sum_{i} F_{ij} \cdot c_{in} = 0 \qquad Eq.5.2$$

The outflow of a process unit depends on its throughput (Eq.5.3).

$$F_{mi}^{OUT} - \sum_{j} F_{mj}^{IN} \cdot \xi_{mji} = 0 \qquad Eq.5.3$$

The outflows of a process unit equals the summation of its distributed flows (Eq.5.4).

$$F_{mi}^{OUT} - \sum_{j} F_{ij} = 0 \qquad Eq.5.4$$

The material flow leaving a process unit equals the summation of the distributed material flows (Eq.5.5).

$$\bar{F}_{min}^{OUT} - \sum_{j} F_{ij} \cdot c_{in} = 0 \qquad Eq.5.5$$

Raw material flows are limited by the availability of the materials (Eq.5.6).

$$RA_n - \sum_{m} \sum_{i \in I^S} F_{mi}^{OUT} \cdot c_{in} \geq 0 \qquad Eq.5.6$$

Sinks have permitted composition boundaries (Eq.5.7 & Eq.5.8).

$$F_{mj}^{IN} \cdot c_{jn}^{UB} - \sum_{i} F_{ij} \cdot c_{in} \geq 0 \qquad Eq.5.7$$

$$F_{mj}^{IN} \cdot c_{jn}^{LB} - \sum_{i} F_{ij} \cdot c_{in} \leq 0 \qquad Eq.5.8$$

5.4.2 Energy Balances

The energy requirements are estimated as a function of the throughput (Eq.5.9 & Eq.5.10).

$$Q_{mn}^{H} - q_{nm}^{H} \sum_{j} F_{mj}^{IN} = 0 \qquad Eq.5.9$$

$$Q_{mn}^{C} - q_{nm}^{C} \sum_{j} F_{mj}^{IN} = 0 \qquad Eq.5.10$$

5.4.3 Investment Cost

A process unit exists if it has inflow (Eq.5.11).

$$\sum_{j} F_{mj}^{IN} - LU \cdot Z_m \leq 0 \qquad Eq.5.11$$

The equipment purchase cost is annualized with respect to the chosen depreciation factor and the life of investment and is a function of the throughput of the process unit (Eq.5.12).

$$Cost_m = a_m \sum_{j} F_{mj}^{IN} + \beta_m \cdot Z_m \qquad Eq.5.12$$

Where α is the slope and β is the fixed parameter for each process unit m.

5.4.4 Objective Function

The objective function is to maximize the total potential profit (Eq.5.13).

$$maximize \quad Profit = \quad Revenue - Cost^{Total} \qquad Eq.5.13$$

The total revenue depends on the material flows that go to the consumers (Eq.5.14).

$$Revenue = \sum_{m} \sum_{j \in J^B} \sum_{n} sp_j \cdot F_{mj}^{IN} \qquad Eq.5.14$$

The total cost includes the capital and the operating cost (Eq.5.15).

$$Cost^{Total} = Cost^{CI} + Cost^{OP} \qquad Eq.5.15$$

The operating cost is the cost of the supplied materials and energy (Eq.5.16).

$$Cost^{OP} = Cost^{M} + Cost^{W} + Cost^{E} \qquad Eq.5.16$$

The cost of the materials depends on the total flow coming from the suppliers (Eq.5.17).

$$Cost^{M} = \sum_{m} \sum_{i \in I^S} \sum_{n} pp_n \cdot \bar{F}_{min}^{OUT} \qquad Eq.5.17$$

The cost of waste depends on the total flow going to the waste treatment units (Eq.5.18).

$$Cost^{W} = \sum_{m} \sum_{j \in J^W} \sum_{n} tp_n \cdot \bar{F}_{mjn}^{IN} \qquad Eq.5.18$$

The cost of the energy utilities is the cost of the hot and cold energy requirements (Eq.5.19).

$$Cost^{E} = \sum_{n} pp_n \sum_{m} (Q_{mn}^{H} + Q_{mn}^{C}) \qquad Eq.5.19$$

The capital cost includes the annualized, piecewise linearized cost of the process units (Eq.5.20).

$$Cost^{CI} = \sum_{m} Cost_m \qquad Eq. 5.20$$

5.5 Results

In addition to screening the product portfolio, the selection of a suitable biomass pretreatment technology is also necessary. This work studies twelve pretreatment and nine conversion processes. The operating factor is set at 8,000 hr/yr, the depreciation factor at 35%, and the life of investment at 15 years. Prices refer to $ in 2016 and are updated using inflation indicators from the chemical engineering plant cost index (CEPCI) (Compass International, 2018). Prices in euros (€) are converted into United States dollars (USD $) according to the 2016 year average exchange range (ECB, 2018). Biomass availability is set at 2Mtn/yr dry biomass. Three different synthesis options are studied for a network that demands minimum ethanol production of 80ktn/yr. The same process network is used for all three cases. First, the processes of the network are screened based on dry mass calculations, as it is used in the literature. Then quality constraints regarding the humid content of the feed are taken into account. Finally, enablers are activated to estimate the additional link cost.

5.5.1 Case Study Description

This work studies a network that needs to produce at least 80kt/yr fuel ethanol and needs to choose amongst twelve options for biomass pretreatment and nine options for value chain technologies (Figure 5.2).

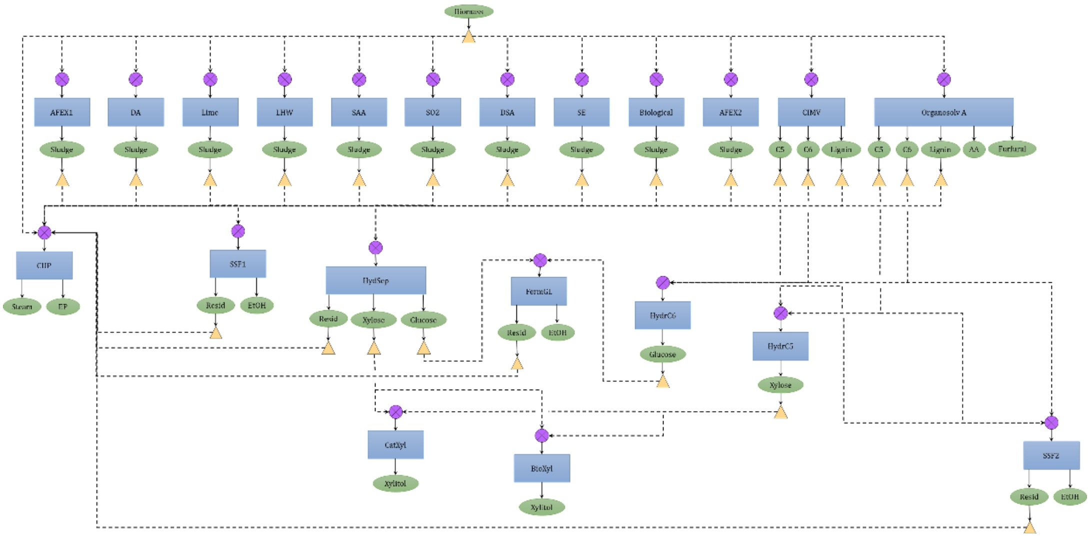

Figure 5.2. Case Study Network

The design of each process is based either on literature data (reference noted), or on models developed for the needs of this thesis based on experimental data provided by CIMV (no reference). Biomass pretreatment options include:

1. CIMV organosolv, which produces C5 syrup, C6 pulp, and lignin
2. Organosolv A (Kautto et al., 2013), which produces C5 syrup, C6 pulp, lignin, acetic acid (AA), and furfurals

3. Ammonia fiber expansion (AFEX1) (Tao et al., 2011), which produces a slurry mix of sugars and lignin
4. Diluted acid (DA) (Tao et al., 2011), which produces a slurry mix of sugars and lignin
5. Steam explosion with lime (Lime) (Tao et al., 2011), which produces a slurry mix of sugars and lignin
6. Liquid hot water (LHW) (Tao et al., 2011), which produces a slurry mix of sugars and lignin
7. Soaking in aqueous ammonia (SAA) (Tao et al., 2011), which produces a slurry mix of sugars and lignin
8. Sulfite pulping (SO2) (Tao et al., 2011), which produces a slurry mix of sugars and lignin
9. Dilute sulfuric acid (DSA) (Baral & Shah, 2017), which produces a slurry mix of sugars and lignin
10. Steam explosion (SE) (Baral & Shah, 2017), which produces a slurry mix of sugars and lignin
11. Biological (Baral & Shah, 2017), which produces a slurry mix of sugars and lignin
12. Ammonia fiber expansion (AFEX2) (Baral & Shah, 2017), which produces a slurry mix of sugars and lignin

Options for value chain technologies include

1. Simultaneous saccharification fermentation of sludge (SSF1) to ethanol (EtOH) and solid residue (SolidRes)
2. Simultaneous saccharification fermentation of C6 pulp and C5 syrup (SSF2) to ethanol and solid residue
3. Hydrolysis of C6 pulp (HydrC6) to glucose
4. Hydrolysis of C5 syrup (HydrC5) to xylose
5. Fermentation of glucose (FermGL) to ethanol and solid residue
6. Hydrolysis of sludge and separation of the produced glucose, xylose, and solid residue (HydrSep)
7. Catalytic conversion of xylose to xylitol (CatXyl) (Mountraki et al., 2017)
8. Biotechnological conversion of xylose to xylitol (BioXyl) (Mountraki et al., 2017)
9. Combined heat and power unit (CHP), which may use biomass, sludge, solid residue and/or lignin to produce steam and electric power (EP)

Table 5.1 shows the sinks and sources attributed per process.

Table 5.1. Sinks and sources per process

M	N in	J	I	N out
CIMV	Biomass	J1	I1	Lignin
			I2	C6
			I3	C5
AFEX1	Biomass	J2	I4	Sludge
DA	Biomass	J3	I5	Sludge
Lime	Biomass	J4	I6	Sludge
LHW	Biomass	J5	I7	Sludge
SAA	Biomass	J6	I8	Sludge
SO2	Biomass	J7	I9	Sludge
SE	Biomass	J8	I10	Sludge
Biological	Biomass	J9	I11	Sludge
DSA	Biomass	J10	I12	Sludge
AFEX2	Biomass	J11	I13	Sludge

organosolvA	Biomass	J12	I14	Lignin
			I15	C6
			I16	C5
			I17	AA
			I18	Furfural
SSF1	Sludge	J13	I19	EtOH
			I20	SolidRes
SSF2	C5 & C6	J14	I21	EtOH
			I22	SolidRes
HydrSep	Sludge	J15	I23	Glucose
			I24	Xylose
			I25	SolidRes
HydC5	C5	J16	I26	Xylose
HydC6	C6	J17	I27	Glucose
FermGL	Glucose	J18	I28	EtOH
			I29	SolidRes
CatXyl	Xylose	J19	I30	Xylitol
BioXyl	Xylose	J20	I31	Xylitol
CHP	Biomass/Sludge /SolidRes	J21	I32	Steam
	Lignin	J22	I33	EP

In the literature, pretreatment processes are designed to produce ethanol as their main product. To enable options for a multi-product biorefinery design, the original design is cut into discrete processing steps. The yields of those processing steps are approximated by following backwards calculations: starting from the ethanol produced, how many sugars are required. The data of the discretized processes are presented in Tables B.1 to B.3 in the Appendix B. Table 5.2 presents the costing data. The purchase/ selling prices are provided by CIMV. The treatment cost for water and solids is an approximation based on Mountraki et al. (2016), while the treatment cost for ethanol, furfural, and acetic acid is postulated to be half of its buying price. The treatment cost has been introduced as a penalty for the discharged streams.

Table 5.2. Costing data ($2016)

N	**pp/ sp** [$/tn] or [$/kWh]	**tp** [$/tn]
Biomass	100.00	0.41
Slurry		0.41
SolidRes		0.41
Lignin	800.00	0.41
C5	400.00	0.41
C6	250.00	0.41
Xylose	600.00	0.41
Glucose	400.00	0.41
EtOH	502.23	251.12
Xylitol	900.00	0.41
Furfural	950.00	475.00
AA	492.93	246.47
H2O	0.53	0.31
solids		0.41
Steam	0.048	
Electricity	0.040	

5.5.2 Nominal Parameter Design

The first case study screens the processing options based on whether the main component is present or not (nominal screening). Figure 5.3 summarizes the resulted network. CIMV is the sole pretreatment technology selected, and lignin is sold as product. All the C5 syrup produced are hydrolyzed to xylose and then converted to xylitol through the catalytic path. Part of the C6 pulp is sold as it is, another part is hydrolyzed to glucose, and a small part goes to SSF2 ethanol production. Part of the glucose produced is also fermented into ethanol to satisfy the market demand.

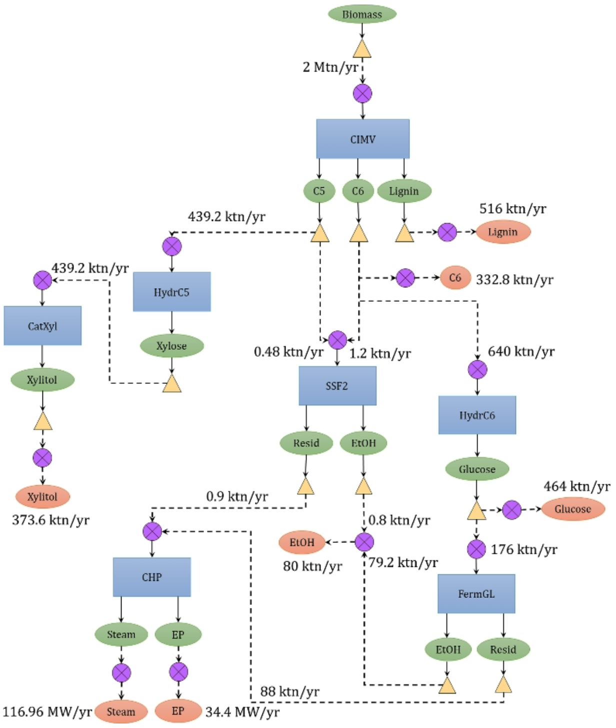

Figure 5.3. Network solution – dry basis

Table 5.3 summarizes the cost calculations. The material cost makes the biggest contribution in the cost function, followed by the capital investment cost.

Table 5.3. Costing results (MM$ 2016/yr) – dry basis calculations

Profit	**Revenue**	**$Cost^{Total}$**	**$Cost^{UM}$**	**$Cost^{UE}$**	**$Cost^{CI}$**
769.7	1064.9	295.3	200.0	0.2	95.1
			67.7%	0.1%	32.2%

It is also interesting to track the revenue sources (Table 5.4). Despite the moderate selling price, lignin makes the greatest contribution in the revenue, followed by xylitol. Ethanol, whose production is imposed, contributes only by 4%.

Table 5.4. Revenue (MM$ 2016/yr) – dry basis calculations

Revenue	**C6**	**Lignin**	**Glucose**	**EtOH**	**Xylitol**	**Steam**	**EP**
1064.9	83.2	412.8	185.6	40.2	336.2	5.6	1.4
	7.8%	38.8%	17.4%	3.8%	31.6%	0.5%	0.1%

5.5.3 Variable Parameter Design

The second case study takes into account potential quality restrictions about the humid content of the incoming stream, focusing mainly on the sugar streams. Humidity standards are set at minimum 40 Brix for the sugar products. The new conversion and capital cost data are adapted from the previous data on dry basis. The prices of the products are considered the same as those of the dry basis, since products have humidity standards in real markets. Data for the calculations on humid basis are presented in Tables B4 to B6, in the Appendix B. Figure 5.4 presents the resulted network. C5 syrup produced by CIMV is more condensed than the minimum standards (65% wt.) and thus is mixed with the C5 syrup produced by organosolv A (25% wt.) increasing the acceptable product (58%-65% wt.). Sugars from CIMV are too concentrated for fermentation, while sugars from organosolv A are too dilute. Sugars produced by both organosolvs are mixed to give an appropriate stream for the SSF2 unit (20% wt.). The excess of C6 pulp that cannot be used at the SSF2 can be hydrolyzed to glucose. However, a small portion is disposed to waste, because the increase in the production was not sufficient to cover the capital investment due to the capacity bounce.

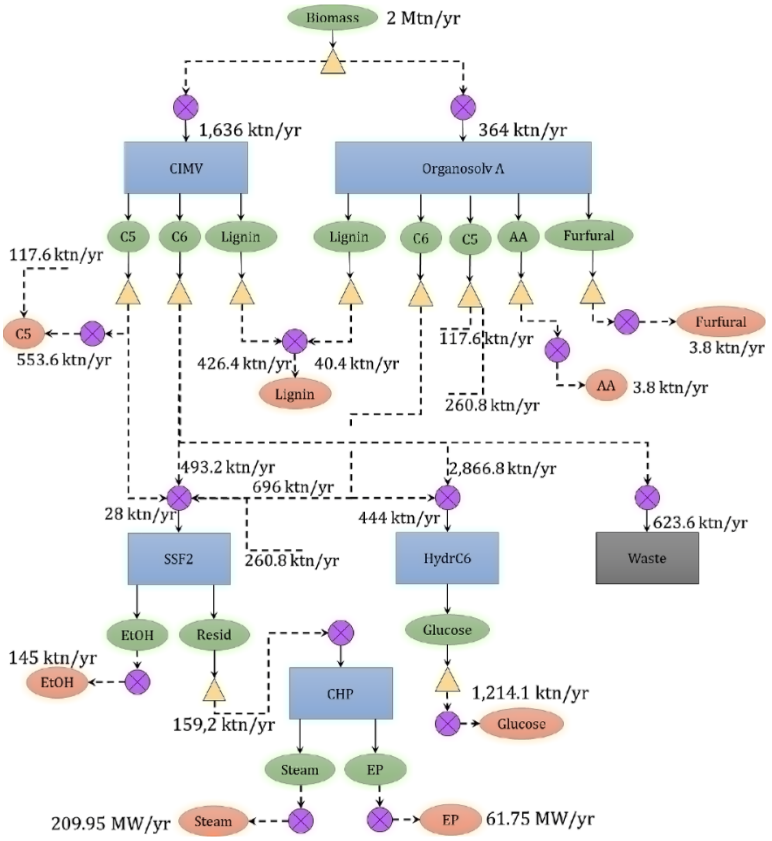

Figure 5.4. Network solution – humid basis

Table 5.5 summarizes the cost calculations. The material cost makes the biggest contribution in the cost function, followed by the capital investment cost.

Table 5.5. Costing results (MM$ 2016/yr) – humid basis calculations

Profit	**Revenue**	**Cost^{Total}**	**Cost^{UM}**	**Cost^{UE}**	**Cost^{CI}**	**Cost^{W}**
933.8	1,218.4	284.6	200.0	0.3	84.1	0.2
			70.3%	0.1%	29.5%	0.1%

Table 5.6 shows the revenue sources. Glucose makes the greatest contribution in the revenue, followed by lignin.

Table 5.6. Revenue (MM$ 2016/yr) – humid basis calculations

Revenue	**C5**	**Lignin**	**Glucose**	**EtOH**	**AA**	**Furfural**	**Steam**	**EP**
1,218.4	268.5	373.4	485.6	72.8	1.9	3.6	10.1	2.5
	22.0%	30.7%	39.9%	6.0%	0.1%	0.3%	0.8%	0.2%

5.5.4 Inclusion of Enablers

New process units are activated to enable the exploitation of streams that previously did not meet the quality standards. Water is now available to dilute where necessary, while concentration units are deployed to make all produced sugars ready-to-sell. Data for the operation of the enablers are presented in Tables B7 to B9 in the Appendix B. Figure 5.5 shows the resulted network. Model seems to dilute products and streams to the minimum concentration allowed, while no enabler for evaporation is activated.

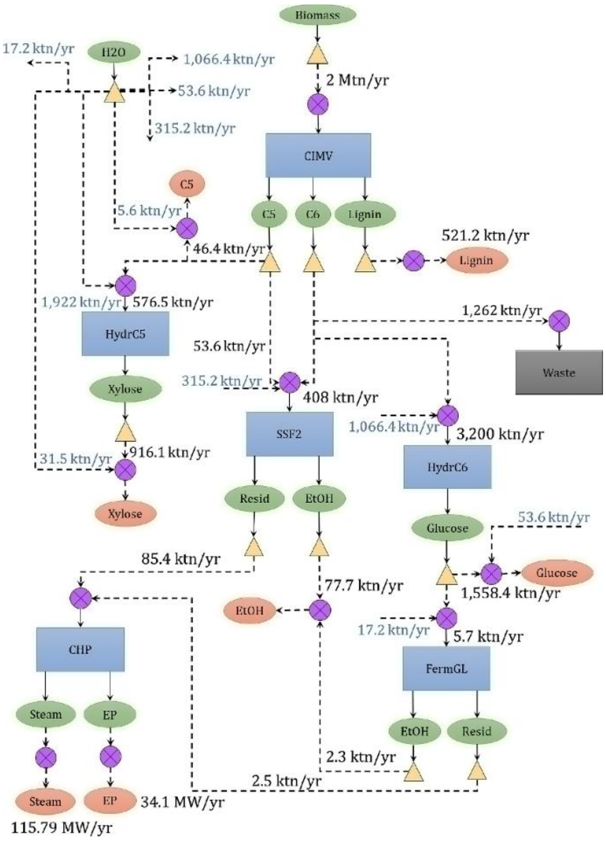

Figure 5.5. Network solution with enablers

Table 5.7 summarizes the cost calculations. The material cost makes the biggest contribution in the cost function, followed by the capital investment cost.

Table 5.7. Costing results with enablers (MM$ 2016/yr)

Profit	**Revenue**	**$Cost^{Total}$**	**$Cost^{UM}$**	**$Cost^{UE}$**	**$Cost^{C}$**	**$Cost^{W}$**
1,399.8	1,698.5	298.7	201.8	0.4	96.1	0.4
			67.6%	0.1%	32.2%	0.1%

Table 5.8 shows the revenue sources. Glucose and xylose makes the greatest contribution in the revenue, followed by lignin.

Table 5.8. Revenue with enablers (MM$ 2016/yr)

Revenue	**C5**	**Lignin**	**Glucose**	**Xylose**	**EtOH**	**Steam**	**EP**
1,698.5	20.8	417.8	645.0	568.7	40.2	5.6	1.4
	1.2%	24.5%	38.0%	33.5%	2.4%	0.3%	0.1%

5.6 Discussion

This chapter presents a new method for the modular synthesis of biorefineries. Each process is considered as a modular unit: an autonomous unit that includes information about the feed transformation and controls its connection to other modules. The method is applied to a network of twenty-one processes (twelve pretreatment and nine processing) to select the optimum configuration for the production of 80kt/yr fuel ethanol. The first case study screens the processing paths based only on the existence of the main component. CIMV organosov is selected as the biomass pretreatment technology, while other value chain technologies are selected in addition to ethanol production. The second case study results in a synergistic scheme between CIMV and organosolv A, because their product streams can be combined together and provide ready-to-use streams that can either be sold as final products or be further valorized. Finally, the last case study activates options for the dilution and the concentration of the streams. The final network has only CIMV as the biomass pretreatment technology, while no enabler for evaporation is activated.

In all three cases, ethanol makes a little contribution in the overall revenue, while the major income comes from components of higher value (lignin, xylitol, or xylose). The selling price is also an important factor. Even though the selling prices were the same for all three cases, results show that is important to have products able to come with a high marge of profit. For example xylitol is the second highest revenue contributor in the first case, but it is not even selected in the third case. Xylose stream is produced at 20% w/w, while the incoming stream in catalytic xylitol process requires feed at 90% w/w. The cost to evaporate this great amount of water has caused model to search for alternatives. The processing capacity per module is another issue that came up. In case studies 2 and 3, the cellulosic pulp is suitable for hydroxylation. Instead, a part of it is discharged to waste treatment. The extra glucose production is not sufficient to cover the extra cost due to the capacity leap. Of course, the selling price of the products has an important role too. Water and energy consumption may have little impact on the overall cost, but they have significant impact as environmental indicators. Even though the objective function used in those cases does not contain environmental penalties, the use of streams quality control in synthesizing processes gives an indication. Enablers show the economic and environmental cost when linking two processes. In all cases, the revenues from selling the produced steam were greater than the energy cost. Therefore, a premature conclusion could be that those networks have energy independence. Nevertheless, energy integration analysis is necessary in order to come to a safer conclusion.

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Chapter VI

Utility Network Optimization

This chapter presents a new targeting tool for the simultaneous optimization of the utility and the capital cost. This work extends existing methods to multiple-utility networks, accounting for alternative design options. The approach introduces the concept of interconnected superstructures formulated as hypergraphs.

6.1 Motivation and Challenges

Chemical and biochemical supplies have a significant share in the material cost. The amount of water being used in bioprocesses is enormous. Nevertheless, the key-factor for the viability of the biorefineries is the energy consumption. Moreover, each utility may have multiple technological options for its regeneration. But each technological selection results in a different utility network configuration with a different thermal profile for the energy network. Furthermore, practical reasons (control, operation, etc.) may impose an intermediate storage stage. The optimal use of each utility is a complicated design problem that calls for a systematic approach. Existing methods consider only the simultaneous use of water and energy (or one main component and energy), handling any other substance as a contaminant. However, when multiple utilities need to be considered, current techniques are challenged by the complexity introduced. None of the known approaches can hitherto address the simultaneous problem of multiple utility use and process design optimization. The combinatorial nature of the utility network design calls for the development of a systematic methodology that can deal with the high dimensionality of the design problem.

The proposed method aims at the simultaneous optimization of the utility consumption (mass and energy), while including alternative technological options for the regeneration design and while considering different temperature levels for any intermediate storage. This research extends existing methods to multiple-utility networks, accounting for multiple upgrade units with the option of parallel regeneration for several utilities. The approach introduces the concept of interconnected superstructures, which are modeled as hypergraphs. Network design does not pivot on a central component (water, H_2, etc.), but the role of each, a priori peer, component is defined by its impact on the objective function. At first, the proposed framework is discussed. Then the mathematical formulation of the model is introduced. The problem is nonlinear by nature, but assumptions and piecewise linearization techniques are adopted to keep it linear. Next, the method is applied for the design of the utility network of a real life biorefinery process. Results start with the description of the case study. Case 0 presents the results of sequential optimization combined with heuristics rules. Case 1 applies the proposed simultaneous method. Case 2 imposes central management for the solvent mixture. Finally, Case 3 studies the separate impact of the treatment cost, the investment cost, and the ΔT_{min} on the design of the utility network.

6.2 Problem Statement

The problem can be stated as one where given is a set of

- utilities that relate to mass (e.g. water, solvents) or energy (e.g. steam, cooling water)
- sink and source locations that relate to mass exchange
- sink and source locations that relate to energy exchange
- process units that relate to source and/or sink locations and can be essential or auxiliary. The units may also relate to utility supply, treatment, storage, or upgrade.
- temperature intervals that relate to the temperatures on the energy sources and sinks

Mass sources and sinks physically relate to process units that feature utility production at a given concentration, or utility requirements at minimum/maximum concentration. Energy sources and sinks physically relate to the hot and cold streams of the plant. Given are the operating temperatures of each process. However, the flowrate and the overall heat capacity of each stream remain a variable and a degree of freedom. The systems approach is to determine the configuration of the utility network that minimizes its operating and capital cost but satisfies the utility demands on both mass and energy utilities.

The systems approach is organized in two interconnected sections:

Part A: The mass exchange section

1. Identification of the mass sinks and sources.
2. Association of the process units with the mass sinks and sources.

Part B: The energy exchange section

1. Identification of the energy sinks and sources.
2. Association of the process units with the energy sinks and sources.
3. Association of the mass exchange locations with the energy exchange locations.

6.3 Methods

Utility network optimization (UNO) model is based on a joint bipartite graph (Bretto, 2013; Diestel, 2017) accounting for two interconnected graphs:

- A MEN superstructure of mass source (I^M) and sink (J^M) vertices:
$$\boldsymbol{G}^M = (I^M \cup J^M, S^M)$$
- A HEN superstructure of energy source (I^E) and sink (J^E) vertices:
$$\boldsymbol{G}^E = (I^E \cup J^E, S^E)$$

Process units keep information about the layout of the network and can either be processing or auxiliary. The role of the auxiliary units is to support the processing units. A process unit, physically, can be a piece of equipment or a whole process section, but, in this work, it is decided to use process sections for clarity reasons.

Five different types are introduced:

1. *Processing* units, which are essentials and whose design is given
2. *Supply* units, which are auxiliaries that supply makeup utilities
3. *Storage* units, which are auxiliaries that store utilities
4. *Upgrade* units, which are auxiliaries that upgrade the quality of the incoming streams (e.g. regeneration)
5. *Treatment* units, which are auxiliaries that treat the discharged streams

Connectivity in the MEN is determined by the type of the process units the exchange locations are associated with (Figure 6.1):

Sources associated with the:
  - processing units can be linked to all sinks
  - supply units can feed storage and processing sinks
  - storage units can only be linked to processing sinks
  - upgrade units can be linked to all sink locations but other upgrade sinks

Sinks associated with the:
  - processing units can be linked to all sources
  - storage units can be linked to all source locations, but other storage sources
  - upgrade units can only be linked to processing sources

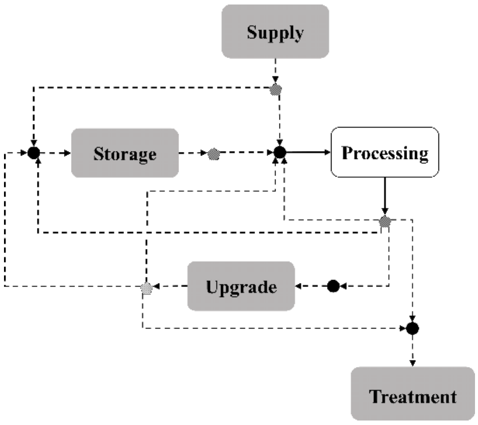

Figure 6.1. MEN Connectivity

Connectivity in the HEN follows the criteria for thermal exchange over temperature intervals (Papoulias & Grossmann, 1983; Yee & Grossman, 1991; Navarro-Amorós et al., 2013). The energy exchange locations are classified into

- sinks, if the initial temperature is lower than the target temperature ($T_s^{IN} > T_s^{OUT}$)
- sources, if the initial temperature is greater than the target temperature ($T_s^{IN} < T_s^{OUT}$)

The energy sinks and sources may be related to processing (essential) units, to auxiliary units, or to mass streams created by matching mass sources and sinks (Figure 6.2).

Energy exchange locations associated to:

- Processing units have fixed heat loads
- auxiliary units have variable heat load, which depends on the throughput of the unit
- mass streams have variable heat load, which depends on the mass flow between the mass sources and sinks (stream mass flow).

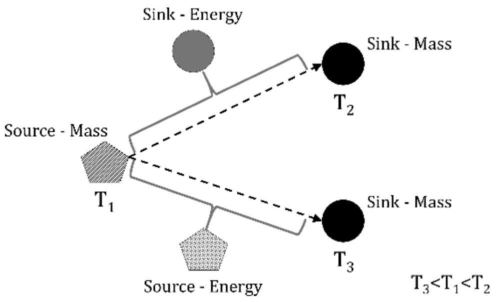

Figure 6.2. Illustration of mass and energy locations in UNO

For a given ΔT_{min}, the shifted temperatures are extended to k temperature intervals, starting from the maximum (k=1) and ending with the minimum temperature ($k=k_{end}$). It is postulated that only isothermal mixing is allowed and that all temperatures are known, based on the operating conditions. Therefore, the energy cascade is projected to constant temperature intervals. However, the energy transshipment includes streams with both fixed and variable flowrates. Streams with fixed flowrates have a fixed contribution in the energy cascade (solid line), while the thermal contribution of streams with variable flowrates is left as a degree of freedom (dotted line), so multiple energy cascades are created at the same time (Figure 6.3).

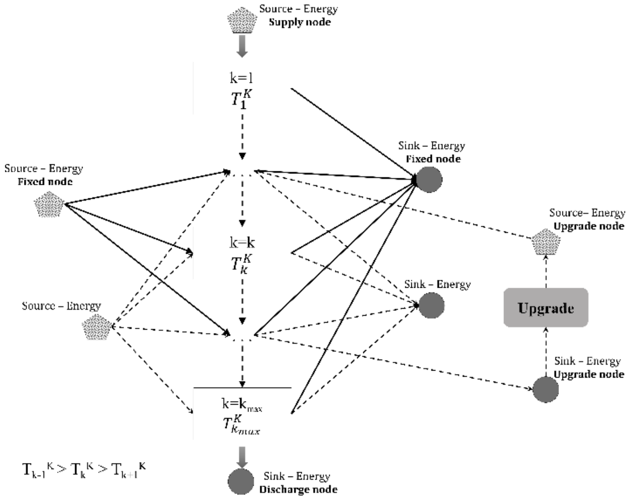

Figure 6.3. Illustration of energy cascade in UNO

6.4 Mathematical Formulation

UNO minimizes the objective function of the reuse/recycle network cost and considers alternative design options for storage, regeneration (upgrade), and treatment, while respecting the mass balances, the energy transshipment, the imposed constraints (logical and technological), and factors for network flexibility. But mass exchange units introduce nonlinearities in the mass superstructure when they have both flows and compositions as variables. Moreover, when both flowrates and temperatures are variables, the energy superstructure is also described by non-linear equations. To keep the model linear, a reasonable set of assumptions could be that

- the process operates at a continuous, steady-state, and fixed performance mode
- all the temperatures are known, based on the operating conditions
- there is only isothermal mixing
- information about total inflow and/or quality constraints are available on the sinks
- the compositions and total available flows are known on the sources, based on the fixed performance
- Contaminants/neutrals are considered utilities with zero availability in the supply units
- Piecewise linearized models can be used for the estimation of equipment cost

The upgrade units are mass exchange units and, thus, they introduce non-linear terms in the mathematical formulation of both mass and energy network. To preserve the linearity of the model the upgrade units are linearized assuming that they operate at constant separation factors. For example, a distillation column has both sink and source locations. It is postulated that, inside the distillation unit, each mass sink is linked to a mass source through a separation factor, and that the operating conditions are already optimized (Figure 6.4). The compositions on the source locations are considered fixed, since the distillation column has to produce two streams of certain quality, but they can also be estimated if the recovery ratios are modeled as a function of the utilities. It is also postulated that a distillation column stands for two energy exchange locations: one source for the condenser ($\Delta T=1$) and one sink for the reboiler ($\Delta T=-1$). The different impact of each incoming stream on the energy requirements of the column can be expressed through a different specific heat capacity coefficient linked to the identity of the incoming stream. According to our calculations, this linearization approach overestimates the energy requirements of the column by +5%.

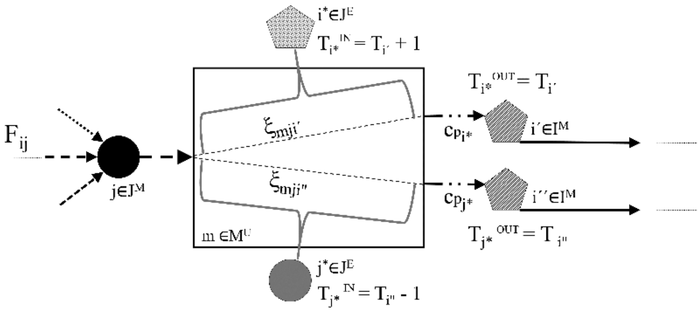

Figure 6.4. Illustration of a linearized distillation column

The cost (operating and capital) and the balances (mass and energy) of the treatment units are presented as linear/linearized models. But the treatment and the supply units, can either be a direct investment (decentralized management) or be part of the industrial site infrastructures (centralized management). Nevertheless, the scope of this work is to highlight the complexity of the design problem for a utility network of a process. Thus, the impact of supply and treatment units is introduced as cost of the makeup utilities and as treatment cost, respectively.

The following sets are denoted:

N={n| utilities that can be mass N^M or energy N^E} = {$N^M \cup N^E$}
    where the energy utilities may be hot N^{EH} or cold N^{EC}, N^E = {$N^{EH} \cup N^{EC}$}
I= {i| sources that are related to mass $i \in I^M$ or energy $i \in I^E$} = {$I^M \cup I^E$}
J= {j| sinks that are related to mass $j \in J^M$ or energy $j \in J^E$} = {$J^M \cup J^E$}
M= {m| process units that are related to I and/or J and can be essentials $m \in M^P$ or auxiliary $m \in M^N$} = {$M^P \cup M^N$}
    where units may also be for supply M^S, treatment M^D, storage M^B, or upgrade M^U
K= {k| temperature intervals}

Let

S= {$s_{i,j}$| streams representing all possible matches in the MEN, $i \in I^M$, $j \in J^M$}

Figure 6.5 presents the interactions amongst the sets. Sinks interact with sources, on the HEN and/or the MEN, but they also interact with the process units.

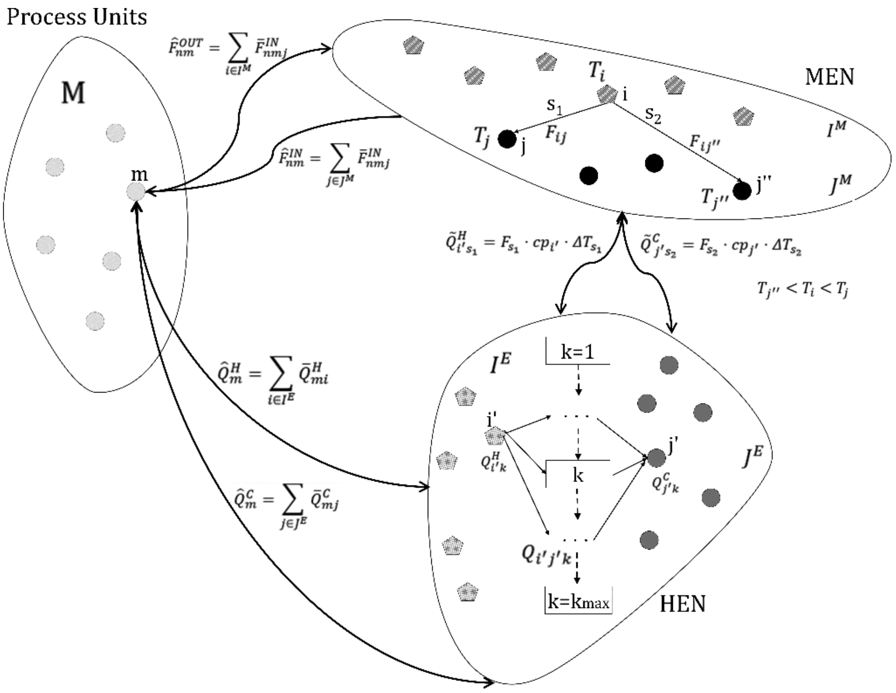

Figure 6.5. Interaction of sets in UNO

The continuous variables of the problem are:

For the MEN [ktn/yr]

F_{ij}	Mass flow between mass sources and sinks, $i \in I^M, j \in J^M$
$\bar{F}_{ijn}$	Utility mass flow from source i to sink j, $i \in I^M$, $j \in J^M$, $n \in N^M$
$F^{OUT}_{mi}, F^{IN}_{mj}$	Mass flow from unit m to source i or from sink j to unit m, $i \in I^M$, $j \in J^M$, $m \in M$
$\bar{F}^{OUT}_{nmi}, \bar{F}^{IN}_{nmj}$	Utility n from unit m to source i or from sink j to unit m, $j \in J^M$, $n \in N^M$, $m \in M$
$\hat{F}^{OUT}_{nm}, \hat{F}^{IN}_{nm}$	Utility n from or to unit m, $n \in N^M$, $m \in M$

For the HEN [MW/yr]

R_{ik}	Heat residual from energy source i per temperature interval k, $i \in I^E$
Q_{ijk}	Heat flow between source i and sink j over the temperature interval k, $i \in I^E$, $j \in J^E$
Q^H_{ik}, Q^C_{jk}	Heat content of source i or sink j per temperature interval k, $i \in I^E$, $j \in J^E$
$\bar{Q}^H_{mi}, \bar{Q}^C_{mj}$	Heat content of source i or sink j per process unit m, $i \in I^E$, $j \in J^E$, $m \in M$
$\hat{Q}^H_m, \hat{Q}^C_m$	Hot or cold energy utilities per process unit m, $m \in M$
$\tilde{Q}^H_{is}, \tilde{Q}^C_{js}$	Heat content of source i or sink j per mas stream s, $i \in I^E$, $j \in J^E$

For the costing [M$/yr]

$Cost_m$	Annualized equipment purchase cost of process unit m

$Cost^{Total}, Cost^{CI}, Cost^{OP}, Cost^{TR}, Cost^{UT}, Cost^{UM}, Cost^{UE}$ Cost for total, capital, operating, treatment, utility, mass utility, and energy utility

The binary variables of the problem are:

Y^M_{ij}	the matching between a source and a sink in MEN, $i \in I^M, j \in J^M$
Y^E_{ij}	the matching between a source and a sink in HEN, $i \in I^E, j \in J^E$
Z_m	the existence of a process unit, $m \in M^N$

The parameters of the problem include economic, operational, and bounds information:

Economic

ap_{ij}	Cost of the match i,j, i∈I, j∈J [M$/yr]
pp_n	Purchase cost of utilities, n∈N [M$/ktn or M$/MW]
tp_n	Treatment cost of utilities, n∈N^M [M$/ktn]

Operational

ξ_{mji}	Separation factor of sink j to source i for unit m, i∈I^M, j∈J^M, n∈N^U [ktn/ktn]
c_{in}	Concentration on the mass sources, i∈I^M, n∈N^M [ktn n/ktn]
$T_i, T_j,$	Temperatures, i∈I^M, j∈J^M [K]
cp_i^H, cp_j^C	Specific heat capacity, i∈I^E,j∈J^E [MW ktn^{-1} K^{-1}]
h_{mi}^H, h_{mj}^C	Specific enthalpy of energy sources or sinks in process unit m, i∈I^E,j∈J^E [MW/ktn]

Bounds

c_{jk}^{UB}, c_{jk}^{LB}	Upper and lower concentration boundaries on the mass sinks, i∈I^M, k∈K^M
${F_{mi}^{OUT}}^*, {F_{mj}^{IN}}^*$	Available and required mass flow per unit m, i∈I^M, j∈J^M, m∈(M^P ∪ M^S)
${\bar{Q}_{mi}^{H}}^*, {\bar{Q}_{mj}^{C}}^*$	Heat content of source i or sink j per existing unit m, i∈I^E, j∈J^E, m∈M^P
LU	big number

6.4.1 Mass Balances

<u>>Over MEN</u> (*DoF: (i,j) matching*)

The summation of mass utilities equals the total flow (Eq.6.1).

$$F_{ij} - \sum_{n\in N^M} \bar{F}_{ijn} = 0 \qquad i \in I^M, \;\; j \in J^M \qquad Eq.6.1$$

Constraints

Link (i,j) exists only if there is mass flow coming from source i to sink j (Eq.6.2).

$$F_{ij} - LU \cdot Y_{ij}^M \leq 0 \qquad i \in I^M, \; j \in J^M \qquad Eq.6.2$$

<u>>Connect process units with MEN</u> (*DoF: splitting/mixing*)

The utilities from a source are distributed to sinks (Eq.6.3 & Eq.6.4).

$$F_{mi}^{OUT} - \sum_{j\in J^M} F_{ij} = 0 \qquad i \in I^M, \;\; m \in M \qquad Eq.6.3$$

$$F_{mi}^{OUT} \cdot c_{in} - \sum_{j\in J^M} \bar{F}_{nmj}^{IN} = 0 \qquad i \in I^M, \;\; m \in M\,, \;\; n \in N^M \qquad Eq.6.4$$

Eq.6.5 and Eq.6.6 calculate the utilities per sink.

$$F_{mj}^{IN} - \sum_{i\in I^M} F_{ij} = 0 \qquad j \in J^M, \;\; m \in M \qquad Eq.6.5$$

$$\bar{F}_{nmi}^{OUT} - \sum_{i\in I^M} F_{ij} \cdot c_{in} = 0 \qquad j \in J^M, \;\; n \in N^M, \;\; m \in M \qquad Eq.6.6$$

Constraints

Utilities are limited by availability in the supply (Eq.6.7 & Eq.6.8) and the processing units (Eq.6.9 & Eq.6.10).

$$F_{mi}^{OUT^*} - \sum_{j \in J^M} F_{ij} \geq 0 \qquad i \in I^M, \quad m \in M^S \qquad Eq.6.7$$

$$F_{mi}^{OUT^*} \cdot c_{in} - \sum_{j \in J^M} \bar{F}_{nmj}^{IN} \geq 0 \qquad i \in I^M, \quad m \in M^S \ , \ n \in N^M \qquad Eq.6.8$$

$$F_{mi}^{OUT^*} - \sum_{j \in J^M} F_{ij} = 0 \qquad i \in I^M, \quad m \in M^P \qquad Eq.6.9$$

$$F_{mi}^{OUT^*} \cdot c_{in} - \sum_{j \in J^M} \bar{F}_{nmj}^{IN} = 0 \qquad i \in I^M, \quad m \in M^P \ , \ n \in N^M \qquad Eq.6.10$$

Processing units have fixed inflow requirements (Eq.6.11).

$$F_{mj}^{IN^*} - \sum_{i \in I^M} F_{ij} = 0 \qquad j \in J^M \ , \ m \in M^P \qquad Eq.6.11$$

Sinks have permitted composition boundaries (Eq.6.12 & Eq.6.13).

$$F_{mj}^{IN} \cdot c_{jn}^{UB} - \bar{F}_{nmj}^{IN} \geq 0 \qquad j \in J^M, \ n \in N^M, \ m \notin M^D \qquad Eq.6.12$$

$$F_{mj}^{IN} \cdot c_{jn}^{LB} - \bar{F}_{nmj}^{IN} \leq 0 \qquad j \in J^M, \ n \in N^M, \ m \notin M^D \qquad Eq.6.13$$

<u>>Balances over process units</u> (*DoF: Throughput in units*)

The throughput in a process unit is the summation of the associated sinks (Eq.6.14)

$$\hat{F}_{nm}^{IN} = \sum_{j \in J^M} \bar{F}_{nmj}^{IN} \qquad n \in N^M, \ m \in M \qquad Eq.6.14$$

The outflow from a process unit is the summation of the associated sources (Eq.6.15)

$$\hat{F}_{nm}^{OUT} = \sum_{i \in I^M} \bar{F}_{nmj}^{IN} \qquad n \in N^M, \ m \in M \qquad Eq.6.15$$

The outflow of the upgrade units depends on the throughput (Eq.6.16).

$$F_{mi}^{OUT} - \sum_{j \in J^M} F_{mj}^{IN} \cdot \xi_{mji} = 0 \qquad i \in I^M, \ m \in M^U \qquad Eq.6.16$$

Constraints

Zero accumulations around upgrade and storage units (Eq.6.17 and Eq.6.18).

$$\sum_{i \in I^M} F_{mi}^{OUT} - \sum_{j \in J^M} F_{mj}^{IN} = 0 \qquad m \in (M^U \cup M^S) \qquad Eq.6.17$$

$$\sum_{i \in I^M} F_{mi}^{OUT} \cdot c_{in} - \sum_{j \in J^M} \bar{F}_{nmj}^{IN} = 0 \qquad m \in (M^U \cup M^S), \ n \in N^M \qquad Eq.6.18$$

6.4.2 Energy Balances

The transshipment model is based on the extended formulation (Yee & Grossman, 1991), because, when necessary, constraints on the thermal matches can be specified (Eq.6.19 to Eq.6.21).

>Over HEN (*DoF: (i,j) matching*)

$$R_{ik} - R_{ik-1} + \sum_{j\in J_k^E} Q_{ijk} = Q_{ik}^H \qquad i \in I_k^E \qquad Eq. 6.19$$

$$\sum_{i\in I_k^E} Q_{ijk} = Q_{jk}^C \qquad j \in J_k^E \qquad Eq. 6.20$$

$$R_{i0} = R_{ik_{max}} = 0 \qquad i \in I_k^E \qquad Eq. 6.21$$

Where

I_k^E energy sources supply heat at temperature interval k, or higher
J_k^E energy sinks supplied heat by temperature interval k, or lower

The heat content of the energy sources is the summation of the heat content of the existing units, the auxiliary units, and the process streams that are created by the matching of a mass sink and a mass source (Eq.6.22).

$$\sum_k Q_{ik}^H = \sum_{m\in M^P} \bar{Q}_{mi}^{H\,*} + \sum_{m\in M^N} \bar{Q}_{mi}^H + \sum_{s\in S^M} \tilde{Q}_{is}^H \qquad i \in I_k^E \qquad Eq. 6.22$$

Accordingly for the energy sinks (Eq.6.23).

$$\sum_k Q_{jk}^C = \sum_{m\in M^P} \bar{Q}_{mj}^{C\,*} + \sum_{m\in M^N} \bar{Q}_{mj}^C + \sum_{s\in S^M} \tilde{Q}_{js}^C \qquad j \in J_k^E \qquad Eq. 6.23$$

Constraints

The thermal match exists only if the match exchanges enthalpy (Eq.6.24).

$$\sum_k Q_{ijk} - LU \cdot Y_{ij}^E \leq 0 \qquad i \in I_k^E,\ j \in J_k^E \qquad Eq. 6.24$$

>Connect process units with HEN (*DoF: split of heat content*)

Eq.6.25 and Eq.6.26 estimate the heat load of sources and sinks respectively.

$$R_{ik} - R_{ik-1} + \sum_{j\in J_k^E} Q_{ijk} = \bar{Q}_{mi}^H \qquad i \in I_k^E\ ,\ m \in M^S \qquad Eq. 6.25$$

$$\sum_{i\in I_k^E} Q_{ijk} = \bar{Q}_{mj}^C \qquad j \in J_k^E\ ,\ m \in M^S \qquad Eq. 6.26$$

The heat load due to energy sources in the auxiliary units is calculated by Eq.6.27 and Eq.6.28.

$$\bar{Q}_{mi}^H = \sum_{j\in J^M} F_{mj}^{IN} \cdot h_{mi}^H \qquad i \in I^E\ ,\ m \in M \qquad Eq. 6.27$$

$$\bar{Q}_{mj}^C = \sum_{j'\in J^M} F_{mj'}^{IN} \cdot h_{mj}^C \qquad j \in J^E\ ,\ m \in M \qquad Eq. 6.28$$

>Balances over process units (*DoF: heat content of units*)

Eq.6.29 and Eq.6.30 calculate the total hot and cold utilities.

$$\hat{Q}^{H}_{m} = \sum_{i\in I^{E}} \bar{Q}^{H}_{mi} \qquad m \in M \qquad Eq.6.29$$

$$\hat{Q}^{C}_{m} = \sum_{j\in J^{E}} \bar{Q}^{C}_{mj} \qquad m \in M \qquad Eq.6.30$$

>Interconnect HEN with MEN (*DoF: heat content of streams*)

The heat content due to matching mass sources and sinks is calculated by Eq.6.31 and Eq.6.32.

$$\tilde{Q}^{H}_{is} = F_{s} \cdot cp^{H}_{i} \cdot \Delta T_{s} \qquad s \in S^{M},\ i \in I^{E} \qquad Eq.6.31$$

$$\tilde{Q}^{C}_{js} = F_{s} \cdot cp^{C}_{j} \cdot \Delta T_{s} \qquad s \in S^{M},\ j \in J^{E} \qquad Eq.6.32$$

Where

$$F_{s} = F_{ij} \quad and \quad \Delta T_{s} = \left|T_{j} - T_{i}\right| \quad for \quad s \in S^{M},\ i \in I^{M},\ j \in J^{M}$$

6.4.3 Investment Cost

A process unit exists if it has inflow (Eq.6.33).

$$\sum_{j\in J^{M}} F^{IN}_{mj} - LU \cdot Z_{m} \leq 0 \qquad m \in M^{N} \qquad Eq.6.33$$

The equipment purchase cost is annualized with respect to the chosen depreciation factor and life of investment and is a function of the throughput of the process unit (Eq.6.34).

$$Cost_{m} = a_{m} \sum_{j\in J^{M}} F^{IN}_{mj} + \beta_{m} \cdot Z_{m} \qquad m \in M^{N} \qquad Eq.6.34$$

Where α is the slope and β is the fixed parameter for each process unit m.

6.4.4 Objective Function

The objective function is to minimize the total cost by taking into account the operating and the capital cost (Eq.6.35).

$$minimize \quad Cost^{Total} = Cost^{CI} + Cost^{OP} \qquad Eq.6.35$$

The capital cost includes the annualized, piecewise linearized cost of the auxiliary units and the cost of the mass and energy matches (Eq.6.36).

$$Cost^{CI} = \sum_{m\in M^{N}} Cost_{m} + \sum_{j\in J^{M}} \sum_{i\in I^{M}} ap_{ij} \cdot Y^{M}_{ij} + \sum_{j\in J^{E}} \sum_{i\in I^{E}} ap_{ij} \cdot Y^{E}_{ij} \qquad Eq.6.36$$

The operating cost includes the cost for utilities and treatment (Eq.6.37).

$$Cost^{OP} = Cost^{UT} + Cost^{TR} \qquad Eq.6.37$$

The treatment cost is the cost of treating discharged utilities (Eq.6.38).

$$Cost^{TR} = \sum_{n\in N^{M}} tp_{n} \sum_{m\in M^{D}} \hat{F}^{IN}_{nm} \qquad Eq.6.38$$

The utility cost includes the cost for mass and energy utilities (Eq.6.39).

$$Cost^{UT} = Cost^{UM} + Cost^{UE} \qquad Eq. 6.39$$

The mass utility cost is the cost of the mass utility flow coming from the supply units (Eq.6.40).

$$Cost^{UM} = \sum_{n \in N^M} pp_n \sum_{m \in M^S} \hat{F}_{nm}^{OUT} \qquad Eq. 6.40$$

The energy utility cost is the cost of hot and cold energy utility requirements (Eq.6.41).

$$Cost^{UE} = \sum_{n \in N^E} pp_n \sum_{m \in M^S} (\hat{Q}_{nm}^H + \hat{Q}_{nm}^C) \qquad Eq. 6.41$$

6.5 Results

CIMV, as most organosolv fractionation technologies, has high demands for both mass and energy utilities. The capacity is set at 300kt/yr dry poplar with bark, at 34.8% w/w humidity before drying and 15% w/w after drying. It is postulated that the process operates 8,000 hr/yr and the ΔTmin used for the heat integration is 10K. The depreciation factor is set at 35%, and the life of investment at 15 years. Prices refer to $ in 2016 and are updated using inflation indicators from the chemical engineering plant cost index (CEPCI) (Compass International, 2018). Prices in euros (€) are converted into United States dollars (USD $) according to the 2016 year average exchange range (ECB, 2018). Case 0 shows the results of the sequential optimization of CIMV process, starting with the solvent, following with the water, and finishing with the energy consumption. Case 1 applies the UNO model, accounting simultaneously for the mass and energy utility, the treatment, and the annualized investment in auxiliary units cost. Case 2 imposes centralized management for the solvent in the UNO model. Case 3 run a sensitivity analysis on how UNO is affected when the different factors of the objective function vary.

6.5.1 Case Study Description

The CIMV process consists of eight *processing units* (Figure 6.6): 1) biomass handling 2) biomass extraction 3) delignification 4) de-acidification 5) washing of the cellulosic pulp 6) concentration of the extraction liquor 7) treatment of lignin, and 8) concentration of the sugar syrup. The raw materials (lignocellulosic biomass) are converted to products (C6, C5, and lignin) by following the sequence of the processing units. The utilities (H_2O, AA, FA, steam, and cooling water) come from the *supply units*, enter the process as makeup streams, and exit as discharged streams going into a *treatment unit*. The configuration of the processing units is fixed, but the *auxiliary units* (supply, storage, upgrade, treatment) are left as a degree of freedom, as the energy and mass streams are variables. Three different technological options are tested for the regeneration of the organic solvent: 1) single effect distillation (D1) 2) double effect distillation (D2), and 3) liquid-liquid extraction (LLE). Each network scenario forms a different set of hot and cold streams, whose potential for energy integration, can be described by conventional energy integration techniques.

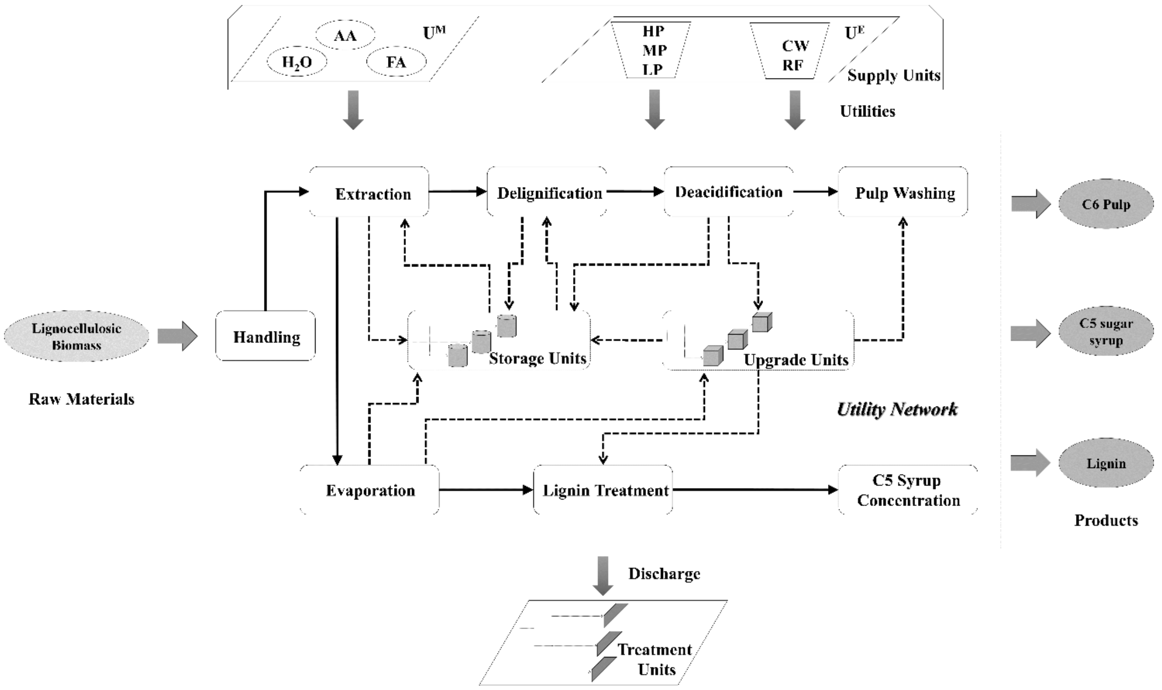

Figure 6.6. Utility network of CIMV process (permission CIMV)

Starting with the MEN (Figure 6.7), eight essential units can exchange mass utilities through eighteen mass exchange locations:

1. The handling unit (m^p_1) preheats and dries wood biomass until reaching a specific humidity content (15% w/w). The evaporated water can be reused through splitter i_4.
2. The extraction unit (m^p_2) requires solvent mixture on two different locations (j_1, j_2) and accepts solids up to 3% w/w.
3. The delignification unit (m^p_3) requires solvent mixture, which contains up to 3% w/w solids (j_3) and produces two possibly recyclable streams (i_5, i_6), rich in water and solvent with dissolved solids.
4. The condensates coming from the deacidification unit (m^p_4) contain water and acids (i_7).
5. The pulp washing unit (m^p_5) requires water on two locations (j_4, j_5) and produces one stream rich in water, acids, and solids (i_8). The first mixer (j_4) accepts water with acids up to 3% w/w, while the second one (j_5) needs pure water because it is located on the final product washing stage.
6. The evaporation unit (m^p_6) produces two streams that contain solvent mixture and water, which are recyclable (i_9, i_{10}).
7. The lignin treatment unit (m^p_7) requires water on two locations (j_6, j_7), while the condensates from lignin drying (i_{11}) contain mainly water and a small amount of acids. The first sink location (j_6) accepts water with acids up to 6% w/w, while the second one (j_7) needs pure water because it is located on the final product washing stage.
8. The C5 treatment unit (m^p_8) requires LP steam (j_8) and produces two streams that contain water and acids, which can be recycled (i_{12}, i_{13}).

The supply of makeup utilities and the treatment of the waste streams (no direct investment) are studied only as decentralized design, while the storage and upgrade units are studied as direct investment. In total, eight auxiliary units are used:

1. A supply unit (m^n_1) provides the process with water, AA, and FA (i_1, i_2, i_3).
2. A treatment unit (m^n_2) accepts all the waste streams (j_9).

3. A storage unit (m^n_3) stores pure aqueous solvent mixture (Slv) (j_{10}, i_{14}).
4. A storage unit (m^n_4) stores impure solvent mixture (Slv2) (j_{11}, i_{15}).
5. A storage unit (m^n_5) stores pure water (WT) (j_{12}, i_{16}).
6. An upgrade unit of single effect distillation, D1 unit (m^n_6), accepts aqueous solvent mixtures, without solids, at three different qualities (j_{13}, j_{14}, j_{15}), and from each sink location streams of different qualities with upgraded water (i_{17}, i_{19}, i_{21}), while the regenerated solvent and water are redistributed (i_{18}, i_{20}, i_{22}) to the network.
7. An upgrade unit of double effect distillation, D2 unit (m^n_7), also accepts aqueous solvent mixtures, without solids, at three different qualities (j_{16}, j_{17}, j_{18}). There are five upgraded streams with purified water (i_{23}, i_{25}, i_{27}, i_{28}, i_{30}) and three streams with purified acid solvent (i_{24}, i_{26}, i_{29}).
8. An upgrade unit of liquid liquid extraction, LLE unit (m^n_8), accepts aqueous solvent mixtures, without solids, at two different qualities (j_{19}, j_{20}) and produces two streams with upgraded water (i_{31}, i_{33}) and two streams with the regenerated solvent (i_{32}, i_{34}).

In the Appendix C, Table C.1 summarizes the associated process units and mass exchange locations, and Table C.2 summarizes the separation factors of the auxiliary units.

For the setup of the HEN, only isothermal mixing is allowed, so a heat exchanger is postulated before each mixer (mass sink) for each stream coming from a splitter (mass source) (Figure 6.7). The process has source locations, which may provide reusable utilities in either the vapor (V) or the liquid phase (L). For safety reasons, it is decided that all sources containing acids must provide flows only in the liquid phase, while those with pure water can provide either LP steam or liquid water. Mass source i_4 produces a pure water stream at vapor phase. If stream coming from i_4 is to be distribute at liquid phase then first it has to be condensed first (heat exchanger after splitter). Mass sink j_8 requires LP vapor. If the incoming stream is at the liquid phase, it first need to come at the required temperature (heat exchanger – L) and then to be vaporized (heat exchanger - V). Therefore, the link (i_4, j_8) can either pass through three heat exchangers (condensation – temperature change – vaporization) or just one (temperature change at the vapor phase).

The energy network exchanges heat through hot (energy source) and cold (energy sink) streams:

- with fixed flowrates (Table C.3)
- whose flowrate is a degree of freedom and depends on the throughput of the auxiliary units (Table C.4)
- whose flowrate is a degree of freedom and depends on the mass streams

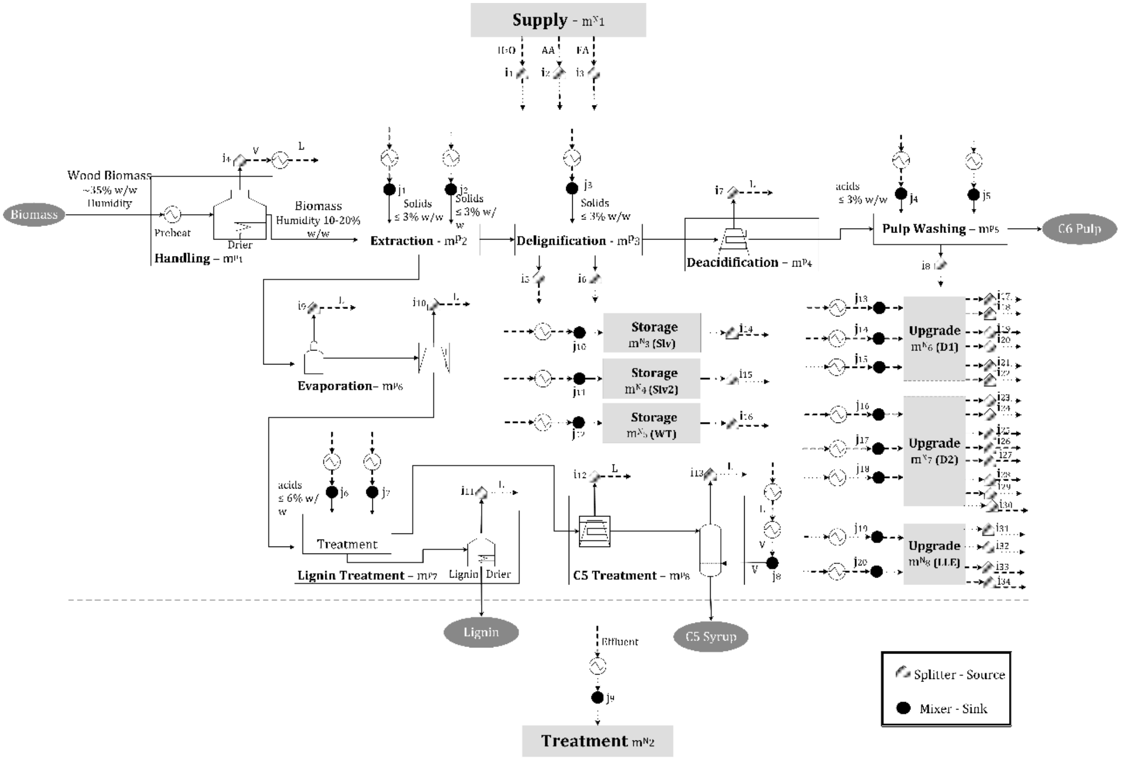

Figure 6.7. Utility Network superstructure for the CIMV process

The evaporated water (i_4) can be re-used either as LP steam (V), creating one thermal stream (one cp active), or as condensates (L), creating one thermal stream for condensation and another for the thermal change (two cp_s active). According to CIMV's experiments, the process maintains its efficiency for a range of 50-58% wt. of FA and 28-32%wt of AA. Therefore, it is decided to constrain the solvent composition at 54-55% wt. FA and 29-31% wt AA. The specifications used on the mass source and sink locations are presented in the Appendix C in Table C.5 and Table C.6, respectively.

Table 6.1 presents the costing data. The prices for the mass and energy utilities are provided by CIMV. The treatment cost for water and solids is an approximation based on Mountraki et al. (2016), while the treatment cost for AA and FA is postulated to be half of its buying price. The treatment cost is introduced as an extra penalty for the discharged streams because the industrial effluents must be treated. The cost of materials that do not participate in the recycle/reuse network, for example reactants, is omitted.

Table 6.1. Costing data ($2016)

Mass Utilities		
	Purchase Price [$/tn]	Treatment Cost [$/tn]
Water	0.53	0.31
AA	492.93	246.47
FA	793.18	396.59
solids		0.41

Energy Utilities			
	Tin (°C)	Tout (°C)	Cost [$/kWh]
Steam	176	175	0.048
Cooling Water	15	25	0.018

6.5.2 Case 0: Sequential Optimization

For the sequential approach, the recycling/reuse of the solvent is first set up. Next, follows the water network setup, treating the acid solvent as impurities. Part of the vapor fraction coming out of the splitter i_4 is arbitrarily used to cover the requirements in LP process steam in j_8. The solvent mixture is temporarily stored in two storage tanks, where makeup and recycled acids are mixed until reaching the desirable composition for the processing units. After a comparison analysis of the standalone design and integration of D1, D2, and LLE, D2 is chosen as the upgrade technology. Finally, heat integration is applied to the total process. Figure 6.8 shows the configuration of the utility network for Case 0. Normally, the D2 unit has only three source streams (two of upgraded water and one of upgraded solvent), but for consistency reasons the linearized approach is employed. The resulted mass network of Case 0 has 30 mass source-sink matches (Table C.7).

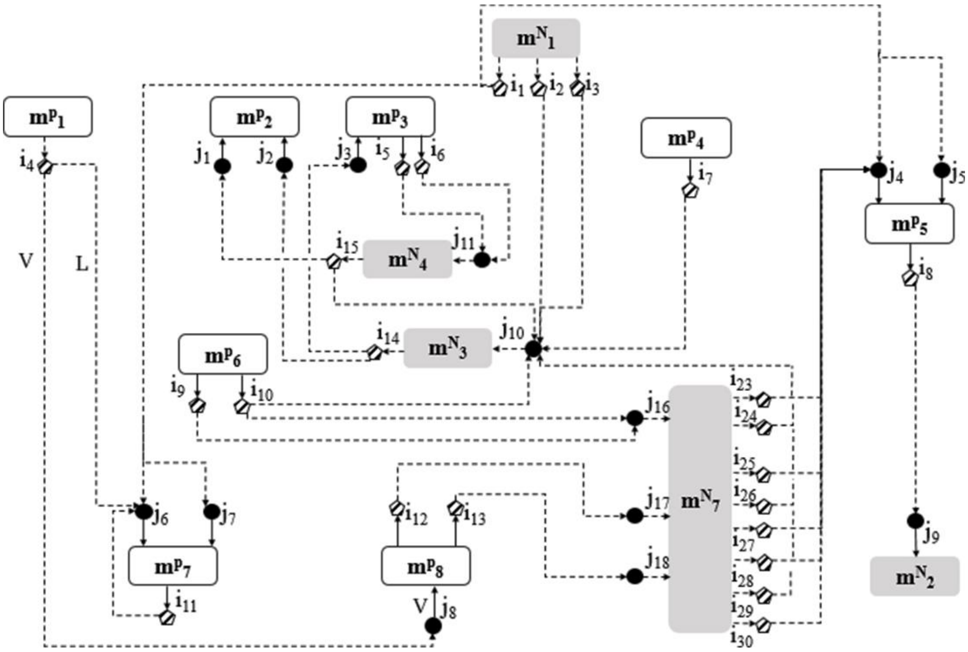

Figure 6.8. CIMV utility network – Case 0

The original mass network with no recycles and requires 191.8 tn/hr water, 75.3 tn/hr AA, and 138.0 tn/hr FA. The mass network with recycles requires 82.50 tn/hr water, 1.14 tn/hr AA, and 1.33 tn/hr FA. Case 0 managed to save the 57% of water, the 98.5% of AA, and the 99.0% of FA. In total, 117.51 tn/hr go to treatment, 114.78 tn/hr go to upgrade, and 250.90 tn/hr are shortly stored in the storage units.

Before applying energy integration, the utility network requires 194.2 MW for cooling and 206.8 MW for heating. It is interesting to note that only 38% of the heating requirements (79.4MW) are due to the fixed heat sink/sources in the processing units. Heat exchange locations due to process streams, by linking a mass source and a sink, control 4% of the total heating requirements (8.9MW), while streams in the auxiliary units control the 57% (118.5 MW). After applying heat integration, Case 0 requires 65.4 MW for cooling and 71.4 MW for heating (Figure 6.9). Energy PINCH managed to reduce energy requirements by 66%.

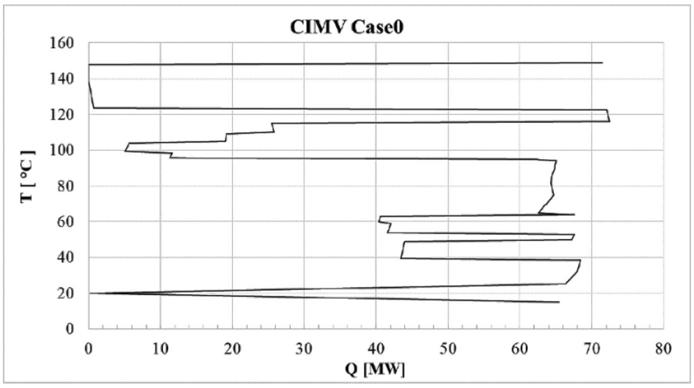

Figure 6.9. GCC– Case 0

Table 6.2 summarizes the annual costs for Case 0. The cost of the energy utilities is the 82% of the total annual cost. It is also interesting to note that the 71MW required for heating, after PINCH, are meant for the upgrade unit (D-2), which upgrades the quality of 114.79 tn/hr.

Table 6.2. Cost Summary – Case 0

M$ 2016/yr				
$Cost^{Total}$	**$Cost^{UM}$**	**$Cost^{UE}$**	**$Cost^{TR}$**	**$Cost^{C}$**
130,531.9	13,284.8	107,376.0	3,693.4	6177.8
	10.2%	82.3%	2.8%	4.7%

6.5.3 Case 1: Simultaneous Optimization (UNO)

Case 1 applies the simultaneous optimization approach. UNO model searches for the mass network configuration with the minimum annual cost, considering the mass and energy utility cost, the treatment cost of the effluents, and the annualized investment cost in auxiliary units. Figure 6.10 shows the resulted network, which has 36 mass source-sink matches (Table C.8). The final network requires 99.51 tn/hr water, 1.45 tn/hr AA, and 0.01tn/hr FA. In total, 131.33 tn/hr go to treatment and 64.91 tn/hr go to upgrade, while no intermediate storage is used.

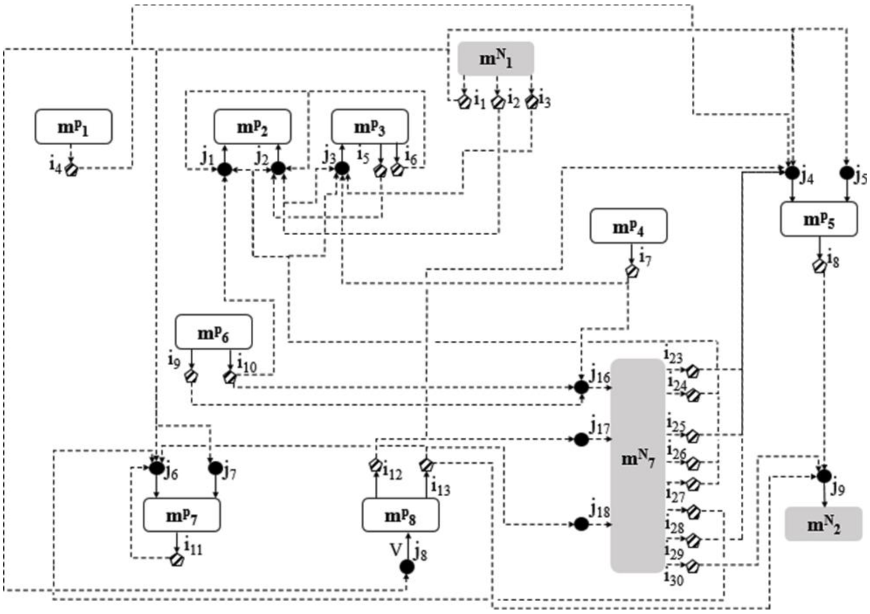

Figure 6.10. CIMV utility network – Case 1

Figure 6.11 shows the GCC of the process with the resulted network. The integrated process requires 39.6 MW for heating and 33.4 MW for cooling. The energy required for heating, after PINCH, is meant for the upgrade unit (D-2), which upgrades the quality of 64.91 tn/hr.

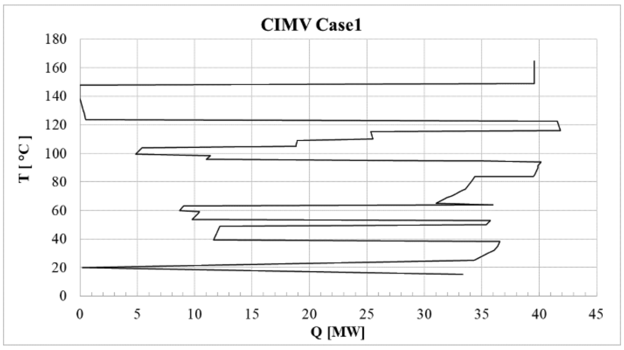

Figure 6.11. GCC– Case 1

Table 6.3 summarizes the annual costs for Case 1. The cost of the energy utilities is the 50% of the total annual cost.

Table 6.3. Cost Summary – Case 1

M$ 2016/yr				
Cost^{Total}	**Cost^{UM}**	**Cost^{UE}**	**Cost^{TR}**	**Cost^{C}**
39,711.7	6,199.1	20,000.3	9,067.8	4,444.5
	15.6%	50.4%	22.8%	11.2%

6.5.4 Case 2: UNO and Centralized Solvent Management

Case 2 postulates that the solvent is distributed through a central tank, for safety reasons. Therefore, the total inflow in splitter j_{11} must be equal with the summation of utility requirements on j_1, j_2, and j_3 (250.90tn/hr). Figure 6.12 shows the resulted network, which has 33 mass source-sink matches (Table C.9). Case 2 requires 79.44 tn/hr water, 1.25 tn/hr AA, and 0.01 tn/hr FA. In total, 118.96 tn/hr go to treatment, 112.30 tn/hr go to upgrade, and 250.90 tn/hr are shortly stored in one storage unit.

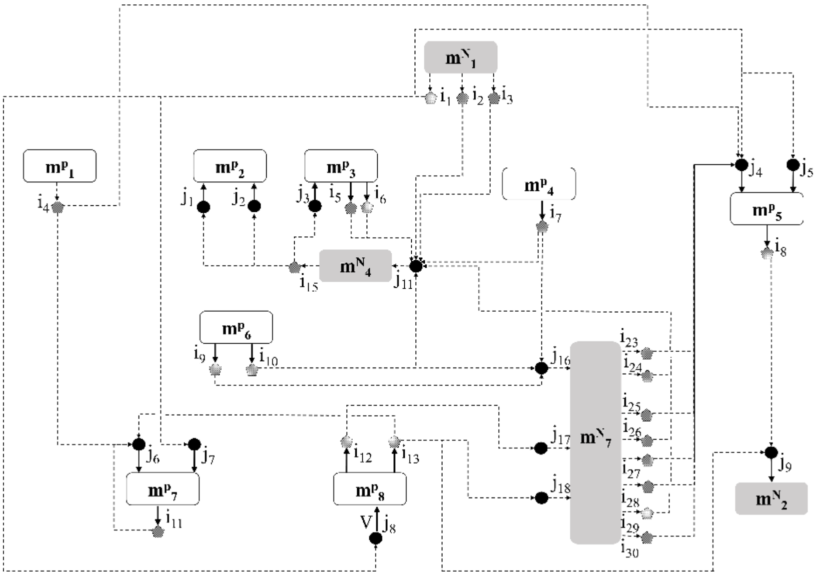

Figure 6.12. CIMV utility network – Case 2

Figure 6.13 shows the GCC of the process with the resulted network. The integrated process requires 70.0 MW for heating and 66.9 MW for cooling. The energy required for heating, after PINCH, is meant for the upgrade unit (D-2), which upgrades the quality of 112.30 tn/hr.

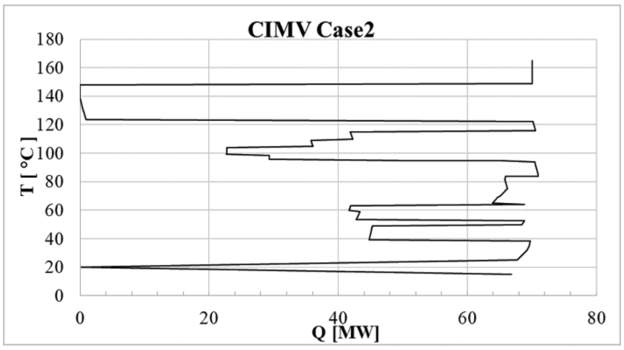

Figure 6.13. GCC– Case 2

Table 6.4 summarizes the annual costs for Case 2. The cost of the energy utilities is the 65% of the total annual cost.

Table 6.4. Cost Summary – Case 2

M$ 2016/yr				
$\mathbf{Cost^{Total}}$	$\mathbf{Cost^{UM}}$	$\mathbf{Cost^{UE}}$	$\mathbf{Cost^{TR}}$	$\mathbf{Cost^{C}}$
56,098.5	9,229.8	36,525.6	4,245.7	6,097.4
	16.5%	65.1%	7.6%	10.8%

6.5.6 Case 3 UNO and Sensitivity Analysis

Case 3 studies how UNO model respond when different cost factors vary.

Treatment Price

Figure 6.14 shows how different costs change when the treatment price changes. It is postulated that there is a flat price, no matter the quality of the effluents. It would be expected that when the treatment price went up, the material cost would go down. But the upgrade process causes a significant increase in the energy cost, and the investment cost. This is why they seem to stay at the same level as the treatment price rises.

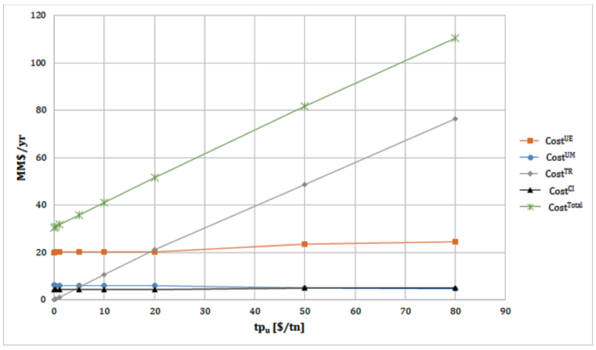

Figure 6.14. Costs as a function of treatment cost

The situation looks more complicated when the treatment cost depends on the quality of the effluents (Figure 6.15). In that case, treatment and mass utility cost try to equilibrate with energy cost, and it is only after the 8 times amplification when the treatment cost dominates. The 8x point is an equivalent of 45$/tn flat treatment cost, comparing the total cost.

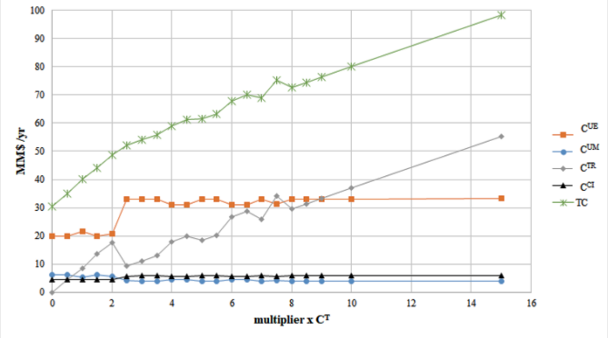

Figure 6.15. Costs as a function of C^T amplification

Figure 6.16 shows that for a flat treatment cost range 0 to 80 $/tn the treatment cost contribution rises from 0% to 77%. The contribution of the energy cost is decreased from 66% to to 22%, but it is only after the cost of 20 $/tn where the treatment cost becomes important and the energy cost falls under the 50%.

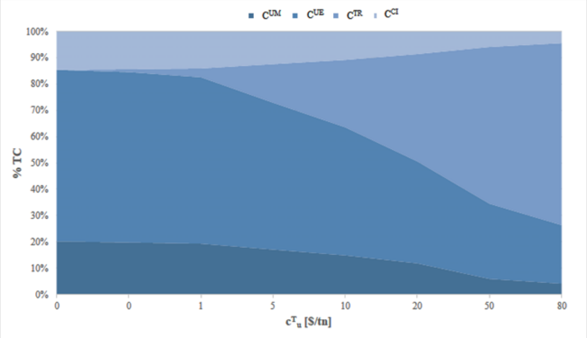

Figure 6.16. Shares of TC as a function of treatment cost

Figure 6.17 shows that, when the quality of the effluents is taken into account, the treatment cost C^{TR} is important (>15%) until the 2.5x point, which is the equivalent of 15$/tn flat treatment cost. The energy cost to reduce the effluents is more important than the cost of the effluent treatment.

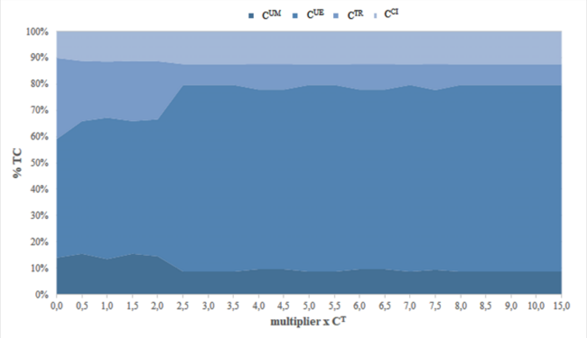

Figure 6.17. Shares of TC as a function of C^T amplification

Auxiliary Investment Cost

Figure 6.18 shows how different costs change when the investment cost for the auxiliary units changes. As the investment cost goes up, the rest of the cost contributors do not seem to change significantly. It is only after the 10x point when UNO reduces the inflow in the upgrade unit, reducing that way the investment and the energy cost, but increasing, at the same time, the mass utility and the treatment cost.

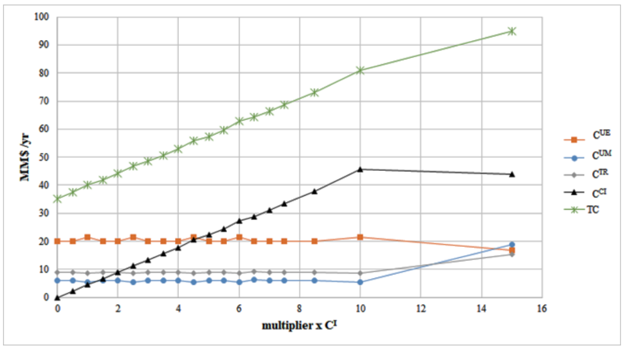

Figure 6.18. Costs as a function as a function of C^{CI} amplification

Figure 6.19 shows that the investment cost becomes more important than the energy cost after the 5x point, but it is only after the 10x point when it forces UNO to sacrifice material and treatment cost.

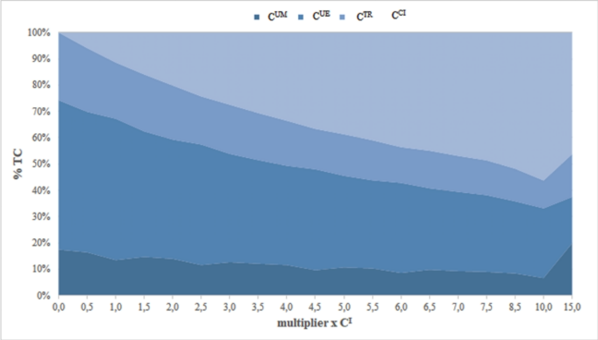

Figure 6.19. Shares of TC as a function of C^I amplification

Mass Utility Cost

To examine the effect of the mass utility cost, it is postulated that all mass utilities have the same price. When the prices are still low (< 5 $/tn) UNO seems to decrease the energy cost, while allowing relatively high treatment cost (Figure 6.20). As the prices go up, UNO tries to reduce the need in makeup material utilities, so the treatment cost goes down and the energy cost goes up, mainly due to the bigger inflow in the upgrade unit. The investment cost in auxiliary units remains relatively constant, since all the available flows are driven for upgrade after a while.

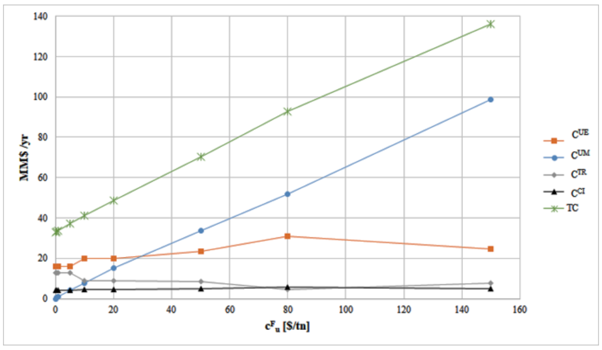

Figure 6.20. Costs as a function of mass utility purchase price

Figure 6.21 shows that as the contribution of the mass utilities increases, the contribution of the energy utilities decreases (from 50% to 18%). Treatment cost is affected the most, and its contribution goes from 40% to 6% as the mass utility cost rises from 0% to 72%. The contribution of the auxiliary investment cost is reduced from 12% to 4%.

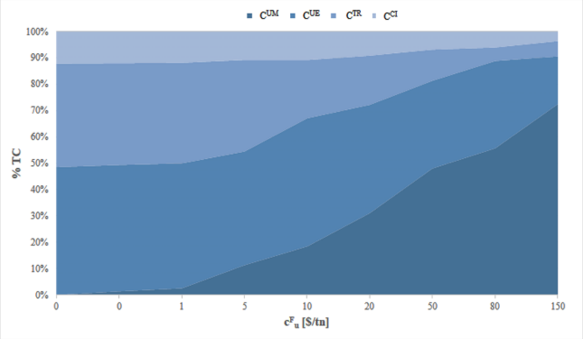

Figure 6.21. Shares of TC as a function of mass utility purchase price

Energy Utility Cost

Figure 6.22 shows how different costs change when the energy utility cost changes. For both, hot and cold utilities, UNO reaches a minimum consumption, after which other costs remain stable. After the price of 0.5 $/kWh for the hot utilities and the price of 0.1 $/kWh for the cold ones, no retrenchment can set back the linear increase of the total cost. When either the hot or the cold utilities have zero purchase cost, the cost for mass utilities and treatment reach their minimum, while the investment in auxiliary is at its maximum.

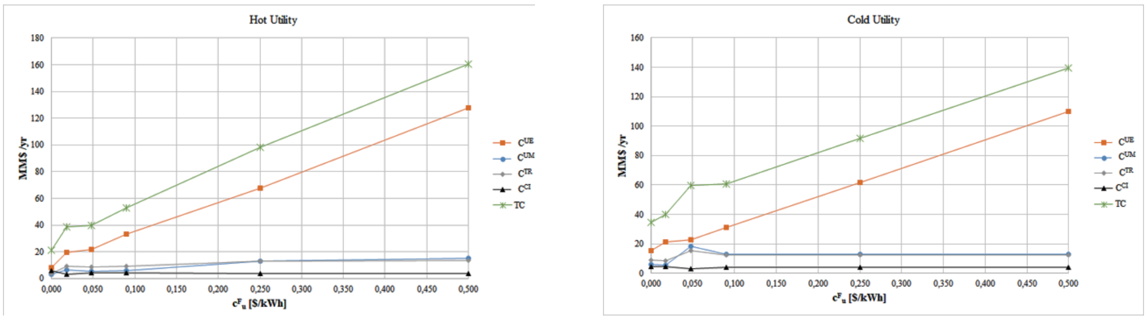

Figure 6.22. Costs as a function of energy utility purchase price

Figure 6.23 shows that even when ignoring the cost of one of the energy utilities, the energy cost still dominates. Starting with a contribution around 40% and reaching the 80%, UNO sacrificed part of the material cost only to reduce the cold utility cost (0.048$/kWh).

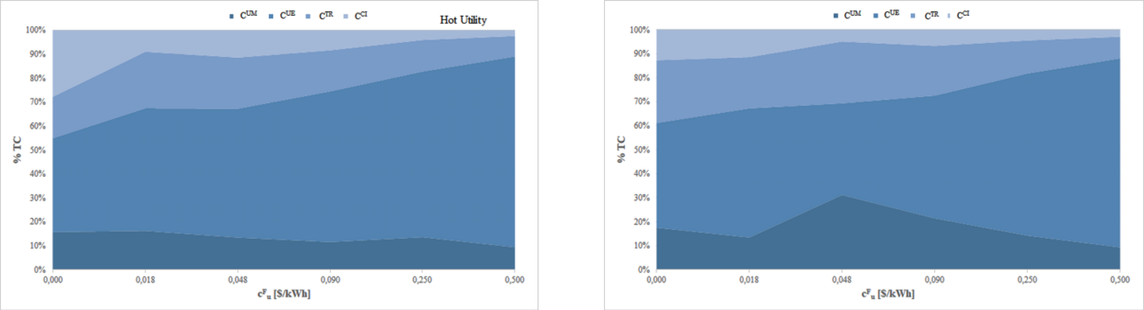

Figure 6.23. Shares of TC as a function of mass utility purchase price

ΔTmin

In energy PINCH, the ΔTmin chosen is to balance between the energy savings and the heat exchange surface investment. Figure 6.24 shows how different costs change when ΔTmin changes, without considering the investment in heat exchange area. ΔTmin seems to affect total cost only after 16K, where the additional energy requirements cannot be offset by further reducing the cost for treatment and mass utilities.

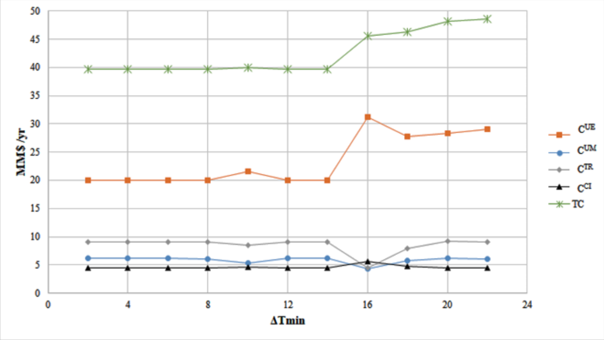

Figure 6.24. Costs as a function as a function of ΔTmin

Figure 6.25 shows that UNO manages to eliminate the increased energy requirements imposed by lower ΔTmins, until the 16K, where drastic cuts the cost for mass utilities and effluent treatment are required.

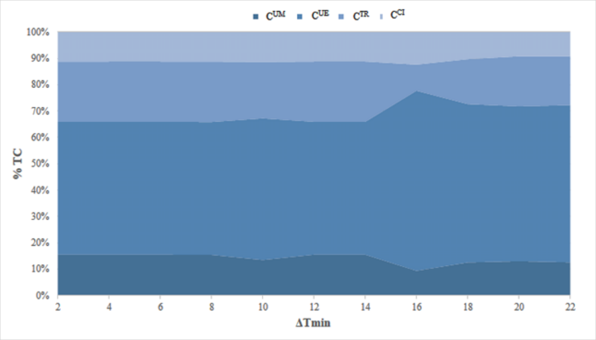

Figure 6.25. Shares of TC as a function of ΔTmin

6.6 Discussion

Solvent and water networks are interconnected. The utility network of CIMV has a single pure water source in the case of wood drying. The results of UNO were verified with Aspen simulation model. To sum up, Case 0 presents CIMV's utility network as a result of applying heuristic and sequential optimization techniques. Compared to the non-integrated design with no recycles, Case 0 decreased the solvent needs by 99% and the energy requirements by 66%. Case 1 applies simultaneous UNO and results indicate 70% reduction of the total cost compared to Case 0. This is achieved mainly due to 50% reduction in the mass utility cost, by minimizing the inflow of the most expensive mass utility (FA). The treatment cost has almost tripled because the inflow in the upgrade unit is reduced by 40%, but at the same time the energy requirements are reduced by 80% and the investment cost by 28%. Case 2 imposes central solvent management. All streams with solvent mix have to pass through a central storage tank before entering the main processing units. The results show that the total cost can be further reduced by 57% by cutting down on the mass and energy utility consumption without increasing significantly the complexity of the network. Table 6.5 summarizes the results of the three case studies.

Table 6.5. Results Summary

	[tn/hr]			**[MWh]**		**#**	**[2016 M$/yr]**				
	H2O	**AA**	**FA**	**QH**	**QC**	**IJ**	**$Cost^{Total}$**	**$Cost^{UM}$**	**$Cost^{UE}$**	**$Cost^{TR}$**	**$Cost^{C}$**
Open	191.80	75.30	138.00	206.8	194.2						
Case 0	82.50	1.14	1.33	71.4	65.4	30	130,531.9	13,284.8	107,376.0	3,693.4	6,177.8
Case 1	99.51	1.45	0.01	39.6	33.4	36	39,711.7	6,199.1	20,000.3	9,067.0	4,444.5
Case 2	79.44	1.25	0.01	70.0	66.9	33	56,098.5	9,229.8	36,525.6	4,245.7	6,097.4

Sensitivity analysis shows how UNO responds to different costs variations. Treatment cost has an important impact on the configuration of the utility network, forcing the system to minimize makeup supplies and maximize the reuse/recycling of the mass utilities. When the treatment cost depends on the quality of the effluents, then the system appears to have more options to balance the investment and energy cost with material and effluent reduction. This analysis highlights the impact of the environmental policies on the design of a process. When the target is the quality and not the quantity of the effluents, the system seems to have more options to counterbalance the environmental penalty. Regarding the investment cost in auxiliary units, the impact on the network appears to be small. This is because the upgrade unit is the main contributor in the investment cost and when the upgrade unit gets smaller, the energy consumption lessens, but the mass utility and effluent treatment cost increases. On the other hand, the cost of mass utilities has an important impact on the configuration of the utility network. When the purchase price is different, UNO searches for the configuration that favors the minimization of the consumption of the most expensive mass utility (Cases 1 and 2). But, when all makeup supplies have the same price, then the target is simply to balance the inflow, with the effluents and the energy consumption.

All results support the fact that energy has the most important role in the utility network. Even when one of the two energy utilities has zero purchase price, the energy cost is the 40% of the total cost. The network is sensitive to the purchase price of energy utilities. When energy is cheap, D1 is chosen as the upgrade unit, but in all other cases D2 is a steady choice. Storage units were chosen when the system wanted to increase the cooling requirements. However, the system seems to reach a minimum energy consumption that is able to satisfy the demand to the sinks. Further decrease in the energy consumption causes a drastic increase in the makeup supply and the effluent treatment cost, which is more important than the energy cost raise. In other words, it is still better to pay for energy than satisfying the demand with makeup supplies and treating all the effluents. It should also be noted that in the current case study UNO controlled 62% of the heat flowrates, which provides a significant flexibility in searching for alternative designs. Lastly, ΔTmin is important for the design of HENs, but UNO rearranges the flows so as to counterbalance the elevated energy requirements as ΔTmin increases.

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Chapter VII

Utility Network Optimization with Synergistic Revamp

This chapter extends the targeting model presented in Chapter VI to revamp biorefinery installations while considering options for industrial synergies. The method systematizes the combined grassroots-retrofit problem and integrates synthesis tools to screen the value-chain and look for potential synergies.

7.1 Motivation and Challenges

The potential to cut down on the utility consumption is the driving force behind process retrofitting. Second generation (2G) biorefineries can be used to upgrade, rather than eliminate existing first generation (1G) plants. As they process different feedstock, the integration of different generation biorefineries has attracted attention (e.g. Dias, 2008; Naik et al., 2010; Palacios et al., 2012; Dias et al., 2014; Lennartsson et al. 2014). However, the revamp of biorefineries subsumes the inherent value chain problem with the additional complication of endogenous synergies between the existing and the candidate units. Nevertheless, existing studies undertake the problem as a grassroots design problem. While first generation installations are nascent plants, still possible to amend and modify, second generation upgrades account for new technology and investment very flexible to adjust so that the upgrades are best. An additional challenge with the particular integration is that first and second generation technologies hide inner trade-offs (Mountraki et al., 2016a).

This chapter presents a combined grassroots-retrofit approach for the systematic upgrade of existing biorefineries. The proposed methodology equilibrates the benefit of the proposed modification with its cost of implementation while considering possible symbiotic options. Utility network optimization with synergistic revamp (UNOSR) model combines process integration with process synthesis. The optimization method is applied to a 1G sugarcane biorefinery using CIMV process as the 2G revamp technology. Two case studies demonstrate the importance of synergies in the revamping procedure. Case 1 studies the technological revamp without the synergistic options, using the 2G technology only to increase the ethanol production. Case 2 takes into account the value chain synthesis, scoping for the best valorization of all product streams.

7.2 Problem Statement

The problem can be stated as one where given is a set of

- utilities that relate to materials or energy (e.g. steam, cooling water)
- sink and source locations that relate to mass exchange
- sink and source locations that relate to energy exchange
- process units that relate to source and/or sink locations and can be existing or new. The units may also relate to supply, treatment, buying, or processing.
- temperature and enthalpy intervals that relate with the temperatures of the energy sources and sinks

Mass sources and sinks physically relate to process units that feature material production at a given concentration, or requirements at minimum/maximum concentration. Energy sources and sinks physically relate to the hot and cold streams of the plant. Given are the configurations of the existing units and streams and all the operating temperatures. The systems approach is to determine which of the existing units to retain or revamp and in which new units to invest.

The systems approach involves four steps and requires data pretreatment for the existing design:

Step I: Flowsheeting Analysis
    Collect all the necessary information
Step II: Mass exchange network (MEN) setup
    Identify and associate sink, sources, and process units
Step III: HEN exchange network (HEN) setup
    Identify and associate streams and process units
    Calculate targets for the existing design
Step IV: Import information in the optimization model
    Solve the MILP to provide information about the designs and the connections.

7.3 Methods

The utility network optimization with synergistic revamp (UNOSR) model employs the same interconnected superstructures as the grassroots UNO model (Chapter VI), including options to retain, revamp, or replace the existing units. UNOSR includes raw material and product streams. The following process unit types are used in UNOSR:

i. *Supply* units to supply makeup utilities, including raw materials
ii. *Treatment* units to treat the discharged streams
iii. *Buying* units to buy the product streams
iv. *Processing* units to transform the incoming streams, which can be new or existing units to retain, retrofit, or replace with new ones.

Connectivity in the MEN is controlled by the type of the process units the exchange locations are associated with (Figure 7.1). The design of the supply, buying, treatment, and grassroots processing units is a degree of freedom. Three design options are set for the existing units: (a) maintain the design as its, imposing its utility requirements as fixed or within strict boundaries, (b) opt for process modifications, if the utility requirements are within appointed boundaries, or (c) replace the existing equipment with new one.

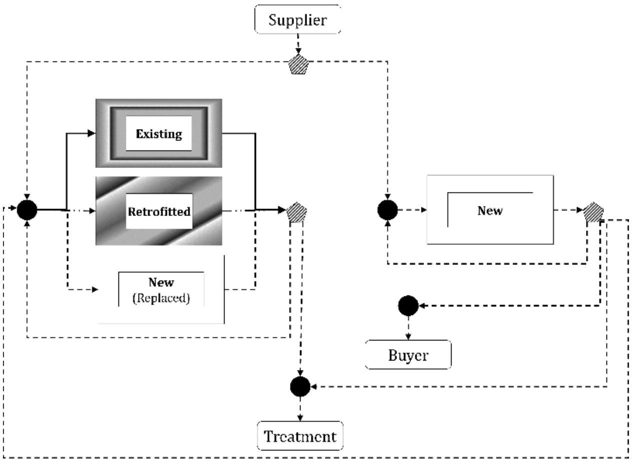

Figure 7.1. MEN Connectivity

HEN design is as described in Chapter V for UNO, employing also the area target model (ATM) (Briones & Kokossis, 1999a ,b) to screen promising grassroots and retrofit options. The ATM includes targeting expressions for the heat transfer area and addresses issues of dissimilar heat transfer coefficients.

7.4 Mathematical Formulation

The model minimizes the objective function of the total cost, which includes options for preserving, revamping, or investing in new pieces of equipment, while respecting the mass balances, the energy transshipment, and the constraints (logical and technological).

To keep the model linear, a reasonable set of assumptions could be that

- The process operates at a continuous, steady-state, and fixed performance mode
- All the temperatures are known, based on the operating conditions
- There is only isothermal mixing
- Information about total inflow and/or quality constraints are available on the sinks
- The compositions and total available flows are known on the sources, based on the fixed performance
- A stream/unit can be retained if its flow/throughput is within ±10% of the original
- A stream/unit can be modified if its flow/throughput is more than 10% but less than 30% of the original
- A stream/unit needs to be replaced if its flow/throughput is more than 30% of the original
- Piecewise linearized models can be used for the estimation of equipment cost
- Detailed modifications in equipment are not examined, but a retrofit approach can be adopted depending the type of the equipment (e.g. Liu & Jobson, 2004)

The following sets are denoted:

N= {n| utilities that can be mass N^M or energy N^E} = {$N^M \cup N^E$}
where the energy utilities may be hot N^{EH} or cold N^{EC}, $N^E = \{N^{EH} \cup N^{EC}\}$
I= {i| sources that are related to mass $i \in I^M$ or energy $i \in I^E$} = {$I^M \cup I^E$}
J= {j| sinks that are related to mass $j \in J^M$ or energy $j \in J^E$} = {$J^M \cup J^E$}
M= {m| process units that are related to I and/or J and can be existing $m \in M^F$ or new $m \in M^N$} = {$M^F \cup M^N$}
where units may also be for supply M^S, treatment M^D, buyers M^B, or processing M^P
K= {k| intervals for temperature $k \in K^T$ or enthalpy $k \in K^E$} = {$K^T \cup K^E$}

Let

S= {$s_{i,j}$| streams representing all possible matches in the MEN $i \in I^M$, $j \in J^M \subseteq s \in S^M$ or the HEN $i \in I^E$, $j \in J^E \subseteq s \in S^E$}
where the streams may also be existing (S^F) or new (S^N)

The continuous variables of the problem are:

For the MEN [ktn/yr]

F_{ij}	Flow between mass sources and sinks, $i \in I^M, j \in J^M$
$\bar{F}_{ijn}$	Utility n from mass source i to sink j, $i \in I^M$, $j \in J^M$, $n \in N^M$
$F_{mi}^{OUT}, F_{mj}^{IN}$	Flow from unit m to source i or from sink j to unit m, $i \in I^M$, $j \in J^M$, $m \in M$
$\bar{F}_{nmi}^{OUT}, \bar{F}_{nmj}^{IN}$	Utility n from unit m to source i or from sink j to unit m, $j \in J^M$, $n \in N^M$, $m \in M$

For the HEN [MW/yr]

R_{ik}	Heat residual from source i per interval k, $i \in I^E$
Q_{ijk} , Q_{sk}	Heat exchange between source i and sink j over the interval k, $i \in I^E$, $j \in J^E$
Q_{ik}^H, Q_{jk}^C	Heat content of source i or sink j per temperature interval k, $i \in I^E$, $j \in J^E$
$\bar{Q}_{mi}^H, \bar{Q}_{mj}^C$	Heat content of source i or sink j per process unit m, $i \in I^E$, $j \in J^E$, $m \in M$
$\hat{Q}_m^H, \hat{Q}_m^C$	Hot or cold energy utilities per process unit m, $m \in M$
$\tilde{Q}_{is}^H, \tilde{Q}_{js}^C$	Heat content of source i or sink j per mas stream s, $i \in I^E$, $j \in J^E$

For the ATD [m^2]

ATD_{sk}	Area target deviations for stream s in enthalpy interval k, $s \in S^E$, $k \in K^E$

For the costing [M$/yr]

$Cost_m$	Annualized equipment cost of process unit m
$Cost^{Total}, Cost^{CI}, Cost^{OP}, Cost^{TR}, Cost^{M}, Cost^{E}$	Cost for total, capital, operating, treatment, materials, and energy
$Revenue$	Earnings from selling product streams
$Profit$	Potential profit

The binary variables of the problem are:

Y_s^M	the existence of stream s in the MEN, $s \in S^M$
Y_s^{MN}	the existence of a new stream in the MEN, $s \in (S^M \cap S^N)$
Y_s^{NF}, Y_s^{NR}	the existence of a retained or a revamped stream in the MEN, $s \in (S^M \cap S^F)$
Y_s^E	the existence of stream s in the HEN, $s \in S^E$
Y_s^{EN}	the existence of a new stream in the HEN, $s \in (S^E \cap S^N)$
Y_s^{EF}, Y_s^{ER}	the existence of a retained or a revamped stream in the MEN, $s \in (S^E \cap S^F)$
Z_m	the existence of a processing unit, $m \in M^P$
Z_m^N	the existence of a new processing unit, $m \in (M^P \cap M^N)$
Z_m^F, Z_m^R	the existence of a retained or a revamped processing unit, $m \in (M^P \cap M^F)$

The parameters of the problem include economic, operational, and bounds information:

Economic

ap_s^N, ap_s^R	area deviation price of the new ($s \in S^N$) and revamped ($s \in S^{NR}$) energy matches, $s \in S^E$ [M$ yr^{-1} m^{-2}]
bp_s^N, bp_s^R	cost of setting up a new ($s \in S^N$) or revamped ($s \in S^{NR}$) stream, $s \in S$ [M$/yr]
pp_n	purchase price of utilities, $n \in N$ [M$/ktn or M$/MW]
sp_j	selling price of material streams, $j \in (J^M \cap J^B)$ [M$/ktn]
tp_n	treatment cost of utilities, $n \in N^M$ [M$/ktn]

Operational

ξ_{mji}	Separation factor of sink j to source i for unit m, $i \in I^M$, $j \in J^M$, $n \in N^U$ [ktn/ktn]
c_{in}	Concentration on the mass sources, $i \in I^M$, $n \in N^M$ [ktn n/ktn]
$T_i, T_j,$	Temperatures, $i \in I^M$, $j \in J^M$ [K]
cp_i^H, cp_j^C	Specific heat capacity, $i \in I^E$,$j \in J^E$ [MW ktn^{-1} K^{-1}]
h_{mi}^H, h_{mj}^C	Specific enthalpy of energy sources or sinks in process unit m, $i \in I^E$,$j \in J^E$ [MW/ktn]
$LMTD_{sk}$	Actual logarithmic mean temperature difference, $s \in S^E$, $k \in K^E$
U_s	Overall heat transfer coefficient, $s \in S^E$ [W m^{-2} K^{-1}]

Bounds

c_{jk}^{UB}, c_{jk}^{LB}	Upper and lower concentration boundaries on the mass sinks, $i \in I^M$, $k \in K^M$
F_{mi}^{OUT*}	Available supply of materials per unit m, $i \in I^M$, $m \in M^S$
F_{mj}^{IN*}	Throughput in existing processing units, $j \in J^M$, $m \in (M^P \cup M^F)$
$F_{ij}{}^{*}$	Flow between existing sources and sinks, $i \in I^M, j \in J^M$, $i,j \in S^F$
$ATD_{sk}{}^{*}$	Area target deviations for the existing streams, $s \in (S^E \cap S^F)$, $k \in K^E$
Q_{sk}^{T}	Target heat exchange, $s \in S^E$, $k \in K^E$
$LMTD_{sk}^{T}$	Target logarithmic mean temperature difference, $s \in S^E$, $k \in K^E$
LU	big number

7.4.1 Mass Balances

The summation of the mass utilities equals the total flow (Eq.7.1).

$$F_{ij} - \sum_{n \in N^M} \bar{F}_{ijn} = 0 \qquad i \in I^M, \;\; j \in J^M \qquad Eq.7.1$$

The utilities from a source are distributed to sinks (Eq.7.2 & Eq.7.3).

$$F_{mi}^{OUT} - \sum_{j \in J^M} F_{ij} = 0 \qquad i \in I^M, \;\; m \in M \qquad Eq.7.2$$

$$F_{mi}^{OUT} \cdot c_{in} - \sum_{j \in J^M} \bar{F}_{nmj}^{IN} = 0 \qquad i \in I^M, \;\; m \in M\,, \;\; n \in N^M \qquad Eq.7.3$$

Eq.7.4 and Eq.7.5 calculate the utilities per sink.

$$F_{mj}^{IN} - \sum_{i \in I^M} F_{ij} = 0 \qquad j \in J^M, \;\; m \in M \qquad Eq.7.4$$

$$\bar{F}_{nmi}^{OUT} - \sum_{i \in I^M} F_{ij} \cdot c_{in} = 0 \qquad j \in J^M, \;\; n \in N^M, \;\; m \in M \qquad Eq.7.5$$

The outflow of the process units depends on the throughput (Eq.7.6).

$$F_{mi}^{OUT} - \sum_{j \in J^M} F_{mj}^{IN} \cdot \xi_{mji} = 0 \qquad i \in I^M, \;\; m \in M^P \qquad Eq.7.6$$

Sinks have permitted composition boundaries (Eq.7.7 & Eq.7.8).

$$F_{mj}^{IN} \cdot c_{jn}^{UB} - \bar{F}_{nmj}^{IN} \geq 0 \qquad j \in J^M, \;\; n \in N^M, \;\; m \notin M^D \qquad Eq.7.7$$

$$F_{mj}^{IN} \cdot c_{jn}^{LB} - \bar{F}_{nmj}^{IN} \leq 0 \qquad j \in J^M, \;\; n \in N^M, \;\; m \notin M^D \qquad Eq.7.8$$

Utilities are limited by the availability in the supply units (Eq.7.9 & Eq.7.10).

$$F_{mi}^{OUT*} - \sum_{j \in J^M} F_{ij} \geq 0 \qquad i \in I^M, \;\; m \in M^S \qquad Eq.7.9$$

$$F_{mi}^{OUT*} \cdot c_{in} - \sum_{j \in J^M} \bar{F}_{nmj}^{IN} \geq 0 \qquad i \in I^M, \;\; m \in M^S\,, \;\; n \in N^M \qquad Eq.7.10$$

Stream s_{ij} exists only if there is mass flow coming from the related source i to sink j (Eq.7.11).

$$F_{ij} - LU \cdot Y_s^M \leq 0 \qquad i,j \in S^M \qquad Eq.7.11$$

A new stream exists only if its flow exists (Eq.7.12).

$$F_{ij} - LU \cdot Y_s^{MN} \leq 0 \qquad i,j \in (S^M \cap S^N) \qquad Eq.7.12$$

An old stream is retained only if the flow is within ±10% of its original flow (Eq.7.13 & Eq.7.14).

$$F_{ij} - 1.1 \cdot F_{ij}{}^* \cdot Y_s^{MF} \leq 0 \qquad i,j \in (S^M \cap S^F) \qquad Eq.7.13$$

$$F_{ij} - 0.9 \cdot F_{ij}{}^* \cdot Y_s^{MF} \geq 0 \qquad i,j \in (S^M \cap S^F) \qquad Eq.7.14$$

An old stream is modified if the flow is greater than ±10% but less than ±30% of the original flow (Eq.7.15 to Eq.7.18).

$$F_{ij} - 1.1 \cdot F_{ij}{}^* \cdot Y_s^{MR} > 0 \qquad i,j \in (S^M \cap S^F) \qquad Eq.7.15$$

$$F_{ij} - 1.3 \cdot F_{ij}{}^* \cdot Y_s^{MR} \leq 0 \qquad i,j \in (S^M \cap S^F) \qquad Eq.7.16$$

$$F_{ij} - 0.9 \cdot F_{ij}{}^* \cdot Y_s^{MR} < 0 \qquad i,j \in (S^M \cap S^F) \qquad Eq.7.17$$

$$F_{ij} - 0.7 \cdot F_{ij}{}^* \cdot Y_s^{MR} \geq 0 \qquad i,j \in (S^M \cap S^F) \qquad Eq.7.18$$

An old stream is replaced by a new one if its flow is greater than ±30% of the original (Eq.7.19 & Eq.7.20).

$$F_{ij} - 1.3 \cdot F_{ij}{}^* \cdot Y_s^{MN} > 0 \qquad i,j \in (S^M \cap S^F) \qquad Eq.7.19$$

$$F_{ij} - 0.7 \cdot F_{ij}{}^* \cdot Y_s^{MN} < 0 \qquad i,j \in (S^M \cap S^F) \qquad Eq.7.20$$

An existing stream can either be retained, modified, or replaced (Eq.7.21)

$$1 - Y_s^{MF} - Y_s^{MR} - Y_s^{MN} \geq 0 \qquad s \in (S^M \cap S^F) \qquad Eq.7.21$$

The total number of streams is logically controlled by Eq.7.22.

$$Y_s^M - Y_s^{MN}|_{s \in S^N} - Y_s^{MN}|_{s \in S^F} - Y_s^{MR}|_{s \in S^F} - Y_s^{MF}|_{s \in S^F} = 0 \qquad s \in S^M \qquad Eq.7.22$$

7.4.2 Energy Balances

The energy balances are based on the extended energy transshipment with some retrofit modifications (Ciric & Floudas, 1989; Yee & Grossman, 1991) (Eq.7.23 to Eq.7.25).

$$R_{ik} - R_{ik-1} + \sum_{j \in J_k^E} Q_{ijk} = Q_{ik}^H \qquad i \in I_k^E \qquad Eq.7.23$$

$$\sum_{i \in I_k^E} Q_{ijk} = Q_{jk}^C \qquad j \in J_k^E \qquad Eq.7.24$$

$$R_{i0} = R_{ik_{max}} = 0 \qquad i \in I_k^E \qquad Eq.7.25$$

Where

I_k^E energy sources supply heat at temperature interval $k \in K^T$, or higher

J_k^E energy sinks supplied heat by temperature interval $k \in K^T$, or lower

The heat content of the energy sources is the summation of the heat content of the units and the new material streams that are formatted by the matching of a mass sink and a mass source (Eq.7.26).

$$\sum_k Q_{ik}^H = \sum_{m \in M^N} \bar{Q}_{mi}^H + \sum_{s \in (S^M \cap S^N)} \bar{Q}_{is}^H \qquad i \in I_k^E \qquad Eq.7.26$$

Accordingly, for the energy sinks (Eq.7.27).

$$\sum_{k} Q_{jk}^{C} = \sum_{m \in M^{N}} \bar{Q}_{mj}^{C} + \sum_{s \in (S^{M} \cap S^{N})} \tilde{Q}_{js}^{C} \qquad j \in J_{k}^{E} \qquad Eq.7.27$$

The heat load of sources and sinks is estimated by Eq.7.28 and Eq.7.29 respectively.

$$R_{ik} - R_{ik-1} + \sum_{j \in J_{k}^{E}} Q_{ijk} = \bar{Q}_{mi}^{H} \qquad i \in I_{k}^{E}\ ,\ m \in M^{S} \qquad Eq.7.28$$

$$\sum_{i \in I_{k}^{E}} Q_{ijk} = \bar{Q}_{mj}^{C} \qquad j \in J_{k}^{E}\ ,\ m \in M^{S} \qquad Eq.7.29$$

The heat load due to energy sources in the units is calculated by Eq.7.30 and Eq.7.31.

$$\bar{Q}_{mi}^{H} = \sum_{j \in J^{M}} F_{mj}^{IN} \cdot h_{mi}^{H} \qquad i \in I^{E}\ ,\ m \in M \qquad Eq.7.30$$

$$\bar{Q}_{mj}^{C} = \sum_{j' \in J^{M}} F_{mj'}^{IN} \cdot h_{mj}^{C} \qquad j \in J^{E}\ ,\ m \in M \qquad Eq.7.31$$

The heat content due to matching mass sources and sinks is calculated by Eq.7.32 and Eq.7.33.

$$\tilde{Q}_{is}^{H} = F_{s} \cdot cp_{i}^{H} \cdot \Delta T_{s} \qquad s \in S^{M},\ i \in I^{E} \qquad Eq.7.32$$

$$\tilde{Q}_{js}^{C} = F_{s} \cdot cp_{j}^{C} \cdot \Delta T_{s} \qquad s \in S^{M},\ j \in J^{E} \qquad Eq.7.33$$

Where

$$F_{s} = F_{ij} \quad and \quad \Delta T_{s} = \left|T_{j} - T_{i}\right| \quad for \quad s \in S^{M},\ i \in I^{M},\ j \in J^{M}$$

Eq.7.34 and Eq.7.35 calculate the total hot and cold utilities.

$$\hat{Q}_{m}^{H} = \sum_{i \in I^{E}} \bar{Q}_{mi}^{H} \qquad m \in M \qquad Eq.7.34$$

$$\hat{Q}_{m}^{C} = \sum_{j \in J^{E}} \bar{Q}_{mj}^{C} \qquad m \in M \qquad Eq.7.35$$

The thermal match exists only if the match exchanges enthalpy (Eq.7.36).

$$\sum_{k} Q_{ijk} - LU \cdot Y_{s}^{E} \leq 0 \qquad i \in I_{k}^{E},\ j \in J_{k}^{E}\ \ ,\ i,j\ \in S^{E} \qquad Eq.7.36$$

7.4.3 Area Target Deviation

Hypertargets (Briones & Kokossis, 1999a ,b) are adopted for the auditing of the HEN. The target load, Q_{sk}^{T} and driving forces, $LMDT_{sk}^{T}$ and $LMTD_{sk}$, are calculated for each potential match according to the driving force algorithm (Briones & Kokossis, 1999a). Eq.7.37 calculates the area target deviation.

$$ATD_{sk} - \frac{1}{U_{s}}\left(\frac{Q_{sk}}{LMTD_{sk}} - \frac{Q_{sk}^{T}}{LMTD_{sk}^{T}} Y_{s}^{E}\right) = 0 \qquad s \in S^{E},\ k \in K^{E} \qquad Eq.7.37$$

If the ATD is within ±10% of the existing, the match is retained (Eq.7.38 & Eq.7.39).

$$\sum_{k \in K^{E}} ATD_{sk} - 1.1 \cdot ATD_{s}{}^{*} \cdot Y_{s}^{EF} \leq 0 \qquad s \in (S^{E} \cap S^{F}) \qquad Eq.7.38$$

$$\sum_{k\in K^E} ATD_{sk} - 0.9\cdot ATD_s{}^* \cdot Y_s^{EF} \geq 0 \qquad s\in (S^E \cap S^F) \qquad Eq.7.39$$

If the ATD is greater than ±10% but lower than ±30% of the existing, the match is modified (Eq.7.40 to Eq.7.43).

$$\sum_{k\in K^E} ATD_{sk} - 1.1\cdot ATD_s{}^* \cdot Y_s^{EM} > 0 \qquad s\in (S^E \cap S^F) \qquad Eq.7.40$$

$$\sum_{k\in K^E} ATD_{sk} - 1.3\cdot ATD_s{}^* \cdot Y_s^{EM} \leq 0 \qquad s\in (S^E \cap S^F) \qquad Eq.7.41$$

$$\sum_{k\in K^E} ATD_{sk} - 0.9\cdot ATD_s{}^* \cdot Y_s^{EM} < 0 \qquad s\in (S^E \cap S^F) \qquad Eq.7.42$$

$$\sum_{k\in K^E} ATD_{sk} - 0.7\cdot ATD_s{}^* \cdot Y_s^{EM} \geq 0 \qquad s\in (S^E \cap S^F) \qquad Eq.7.43$$

If the ATD is greater than ±30% of the existing, the match is replaced (Eq.7.44 & Eq.7.45).

$$\sum_{k\in K^E} ATD_{sk} - 1.3\cdot ATD_s{}^* \cdot Y_s^{EN} > 0 \qquad s\in (S^E \cap S^F) \qquad Eq.7.44$$

$$\sum_{k\in K^E} ATD_{sk} - 0.7\cdot ATD_s{}^* \cdot Y_s^{EN} < 0 \qquad s\in (S^E \cap S^F) \qquad Eq.7.45$$

An existing stream can either be retained, modified, or replaced (Eq.7.46)

$$1 - Y_s^{EF} - Y_s^{ER} - Y_s^{EN} \geq 0 \qquad s\in (S^E \cap S^F) \qquad Eq.7.46$$

A new stream exists if it has an ATD (Eq.7.47).

$$ATD_{sk} - \frac{1}{U_s}\left(\frac{Q_{sk}}{LMTD_{sk}} - \frac{Q_{sk}^T}{LMTD_{sk}^T} Y_s^{EN}\right) = 0 \qquad s\in (S^E \cap S^N),\ \ k\in K^E \qquad Eq.7.47$$

The total number of streams is logically controlled by Eq.7.48.

$$Y_s^E - Y_s^{EN}|_{s\in S^N} - Y_s^{EN}|_{s\in S^F} - Y_s^{ER}|_{s\in S^F} - Y_s^{EF}|_{s\in S^F} = 0 \qquad s\in S^E \qquad Eq.7.48$$

7.4.4 Investment Cost

The capital cost is annualized with respect to the chosen depreciation factor and life of investment and is a function of the throughput of the process unit (Eq.7.49).

$$Cost_m = a_m \sum_{j\in J^M} F_{mj}^{IN} + \beta_m \cdot Z_m \qquad m\in M^P \qquad Eq.7.49$$

Where α is the slope and β is the fixed parameter for each process unit m.

A processing unit exists if it has inflow (Eq.7.50).

$$\sum_{j\in J^M} F_{mj}^{IN} - LU\cdot Z_m \leq 0 \qquad m\in M^P \qquad Eq.7.50$$

Existing units can be retained if their inflow is within ±10% of the original throughput (Eq.7.51 & Eq.7.52).

$$1.1 \cdot F_{mj}^{IN^*} \cdot Z_m^F - \sum_{i \in I^M} F_{ij} \geq 0 \qquad j \in J^M,\ m \in (M^P \cap M^F) \qquad Eq.7.51$$

$$0.9 \cdot F_{mj}^{IN^*} \cdot Z_m^F - \sum_{i \in I^M} F_{ij} \leq 0 \qquad j \in J^M,\ m \in (M^P \cap M^F) \qquad Eq.7.52$$

Existing units can be modified if their inflow is greater than ±10% but less than ±30% of the original throughput (Eq.7.53 to Eq.7.56).

$$1.1 \cdot F_{mj}^{IN^*} \cdot Z_m^R - \sum_{i \in I^M} F_{ij} < 0 \qquad j \in J^M,\ m \in (M^P \cap M^F) \qquad Eq.7.53$$

$$1.3 \cdot F_{mj}^{IN^*} \cdot Z_m^R - \sum_{i \in I^M} F_{ij} \geq 0 \qquad j \in J^M,\ m \in (M^P \cap M^F) \qquad Eq.7.54$$

$$0.9 \cdot F_{mj}^{IN^*} \cdot Z_m^R - \sum_{i \in I^M} F_{ij} > 0 \qquad j \in J^M,\ m \in (M^P \cap M^F) \qquad Eq.7.55$$

$$0.7 \cdot F_{mj}^{IN^*} \cdot Z_m^R - \sum_{i \in I^M} F_{ij} \leq 0 \qquad j \in J^M,\ m \in (M^P \cap M^F) \qquad Eq.7.56$$

New investment is required if the inflow is greater than ±30% of the original throughput (Eq.7.57 & Eq.7.58).

$$1.3 \cdot F_{mj}^{IN^*} \cdot Z_m^N - \sum_{i \in I^M} F_{ij} < 0 \qquad j \in J^M,\ m \in (M^P \cap M^F) \qquad Eq.7.57$$

$$0.7 \cdot F_{mj}^{IN^*} \cdot Z_m^N - \sum_{i \in I^M} F_{ij} > 0 \qquad j \in J^M,\ m \in (M^P \cap M^F) \qquad Eq.7.58$$

An existing unit can either be retained or modified or replaced (Eq.7.59).

$$1 - Z_m^F - Z_m^R - Z_m^N \geq 0 \qquad m \in (M^P \cap M^F) \qquad Eq.7.59$$

A new processing unit exists if it has inflow (Eq.7.60).

$$\sum_{j \in J^M} F_{mj}^{IN} - LU \cdot Z_m^N \leq 0 \qquad m \in (M^P \cap M^N) \qquad Eq.7.60$$

The total number of units is logically controlled by Eq.7.61.

$$Z_m - Z_m^N|_{m \in M^N} - Z_m^N|_{m \in M^F} - Z_m^R|_{m \in M^F} - Z_m^F|_{m \in M^F} = 0 \qquad m \in M^P \qquad Eq.7.61$$

7.4.5 Objective Function

The objective function is to maximize the total potential profit (Eq.7.62).

$$\text{maximize } \ Profit = Revenue - Cost^{Total} \qquad Eq.7.62$$

The revenue is calculated by the total flow that goes to consumers (Eq.7.63).

$$Revenue = \sum_{j \in J^M} sp_j \sum_{m \in M^B} F_{mj}^{IN} \qquad Eq.7.63$$

The total cost includes the capital and the operating cost (Eq.7.64).

$$Cost^{Total} = Cost^{CI} + Cost^{OP} \qquad Eq. 7.64$$

The operating cost includes the treatment cost and the cost of the supplied utilities (mass and energy) (Eq.7.65).

$$Cost^{OP} = Cost^{M} + Cost^{E} + Cost^{TR} \qquad Eq. 7.65$$

The treatment cost is calculated by the total utility flow that goes to treatment (Eq.7.66).

$$Cost^{TR} = \sum_{n \in N^M} tp_n \sum_{j \in J^M} \sum_{m \in M^D} \bar{F}^{IN}_{nmj} \qquad Eq. 7.67$$

The cost of materials is calculated by the total flow coming from the supply units (Eq.7.68).

$$Cost^{M} = \sum_{n \in N^M} pp_n \sum_{m \in M^S} \sum_{i \in I^M} \bar{F}^{OUT}_{nmi} \qquad Eq. 7.68$$

The cost of energy utilities is the cost of the hot and cold energy requirements (Eq.7.69).

$$Cost^{E} = \sum_{n \in N^E} pp_n \sum_{m \in M^S} \left(\hat{Q}^{H}_{nm} + \hat{Q}^{C}_{nm}\right) \qquad Eq. 7.69$$

The capital cost includes the annualized, piecewise linearized cost of the new and modified processing units, the area target deviations, the mass and the energy streams (Eq.7.70).

$$\begin{aligned} Cost^{CI} = {} & \sum_{m \in M^P} Cost_m + \sum_{s \in (S^E \cap S^N)} ap^N_s \cdot ATD_s + \sum_{s \in (S^E \cap S^F)} ap^R_s \cdot ATD_s + \sum_{s \in (S^E \cap S^N)} bp^N_s \cdot Y^{EN}_S \\ & + \sum_{s \in (S^E \cap S^F)} bp^R_s \cdot Y^{ER}_S + \sum_{s \in (S^M \cap S^N)} bp^N_s \cdot Y^{MN}_S + \sum_{s \in (S^M \cap S^F)} bp^R_s \cdot Y^{MR}_S \qquad Eq. 7.70 \end{aligned}$$

7.5 Results

CIMV process is used as a second generation (2G) technological option to revamp a first generation (1G) sugarcane bioethanol process, treating 600kt/yr dry sugarcane, at 70% w/w humidity. It is postulated that the processes operate at 8,000 hr/yr and the ΔTmin used for the heat integration is 10K. The cost estimation of the existing units is based on the assumption that modification costs 50% and replacement costs 90% of the related new installation cost. The depreciation factor is set at 35%, and the life of investment at 15 years. Prices refer to $ in 2016 and are updated using inflation indicators from the chemical engineering plant cost index (CEPCI) (Compass International, 2018). Prices in euros (€) are converted into United States dollars (USD $) according to the 2016 year average exchange range (ECB, 2018). Two case studies demonstrate the importance of synergies in the revamping procedure. Case 1 studies the technological revamp without the synergistic options, using the 2G technology to increase the production of fuel ethanol. Case 2 uses the 2G technology as a synergistic revamp option, considering the possibility to further invest in value chain processes scoping for the best valorization of all product streams.

7.5.1 Case Study Description

The design of the autonomous distillery (Figure 7.2) is based on literature (Dias, 2008) and is organized into four process sections: 1) pretreatment, where (a) sugarcane is cleaned to remove part of the dirt, (b) sugars are extracted by using mills, and (c) the sugar juice is concentrated and sterilized, 2) fermentation, 3) ethanol purification, where ethanol is recovered from the fermentation broth to 92% w/w purity, and 4) ethanol dehydration, where pressure swing distillation is used to recover fuel ethanol (99.9% w/w). The data for the sink and source locations are presented in Tables D1 to D4, in the Appendix D.

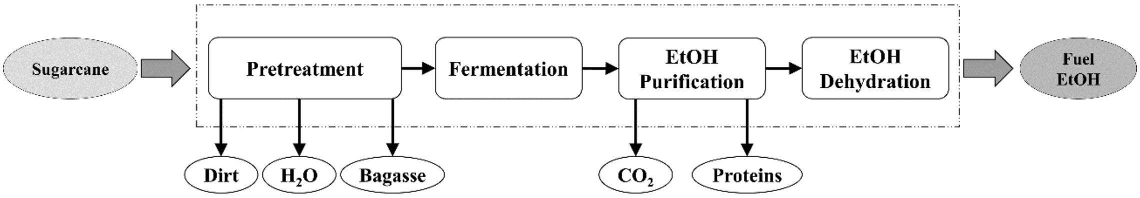

Figure 7.2. Ethanol 1G process

The design of the lignocellulosic process is based on the organosolv biorefinery of CIMV as described in Chapter IV. Additional options for the valorization of the 2G products include the separate hydrolysis of C5 and C6 sugars, their simultaneous saccharification co-fermentation (SScF) to ethanol, and the ethanol dehydration by molecular sieves (Figure 7.3).

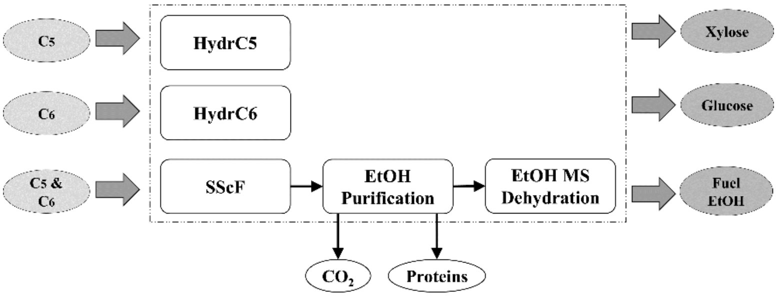

Figure 7.3. Valorization options for the 2G sugars

Figure 7.4 shows the UNOSR superstructure with options to retain, revamp, and invest in new equipment. The network of internal flows is omitted for clarity reasons.

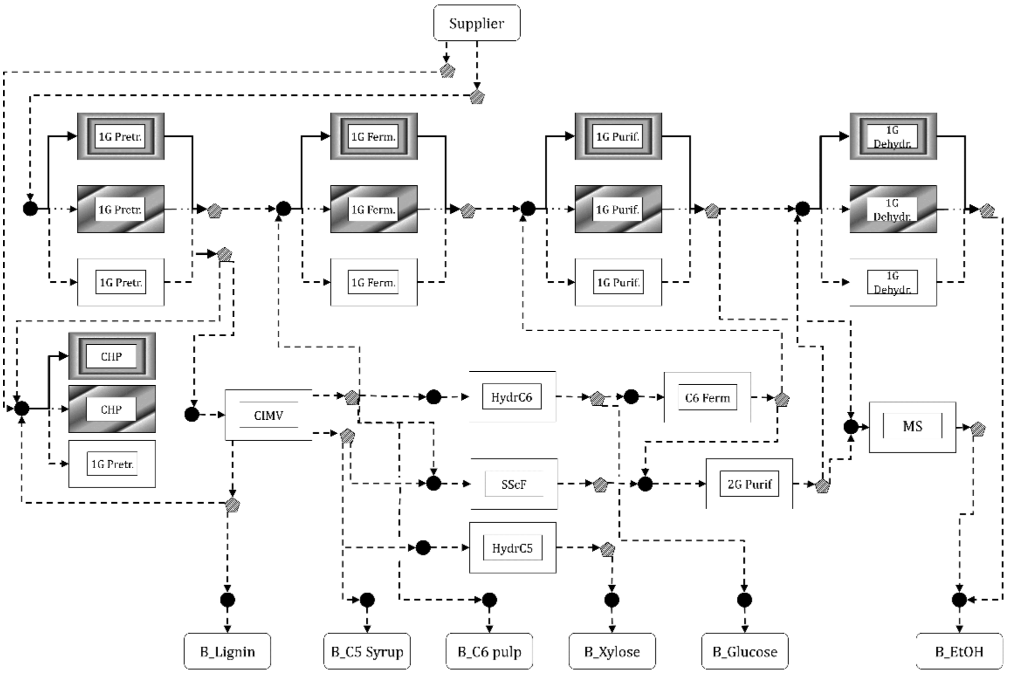

Figure 7.4. 1G-2G Synergistic Revamp Network

It is postulated that the cost of modifying an existing installation is the 50% of the related cost for a new unit and that the replacement of an existing unit with a new one costs 90% of the grassroots cost. Table 7.1 shows the costing data. The prices for the products, the mass, and the energy utilities are provided by CIMV. The treatment cost for water and solids is an approximation based on Mountraki et al. (2016b), while the treatment cost for AA and FA is postulated to be half of its buying price. The treatment cost has been introduced as an extra penalty for the discharged streams because the industrial effluents must be treated. The cost of materials, which do not participate in the recycle/reuse network, for example reactants, has not been considered. No treatment cost is accounted for the CO_2 because it can be considered as "green", but also it can be used as a raw material for other industrial applications.

Table 7.1. Costing data ($2016)

Mass Utilities			
	Purchase Price [$/tn]	Treatment Cost [$/tn]	
Water	0.53	0.31	
AA	492.93	246.47	
FA	793.18	396.59	
solids		0.41	
Products			
EtOH	502.23		
C5 syrup	500.00		
C6 pulp	250.00		
Xylose	700.00		
Glucose	500.00		
Lignin	900.00		
Energy Utilities			
	Tin (°C)	Tout (°C)	Cost [$/kWh]
Steam	176	175	0.048
Cooling	15	25	0.018

The calorific value of wet bagasse (50% moisture) is 2.58 MWh/tn (Nassar et al., 1996) and for dry lignin 5.55 MWh/tn (>7% moisture) (Zhao & Liu, 2010). The thermal efficiency of the CHP unit is 51%.

7.5.2 Case 1: Revamp

The first case deals with the most common revamp scenario in the literature, where the 2G technology is used to increase the production of fuel ethanol. A common case in the literature is to feed C5 and lignin in the CHP unit. For demonstration reasons, the linking options amongst the process units are imposed (Figure 7.5). The first scenario feeds C5 syrup and lignin in the CHP unit, while the second one sells them as marketable products. The optimization problem is to determine the utility consumption.

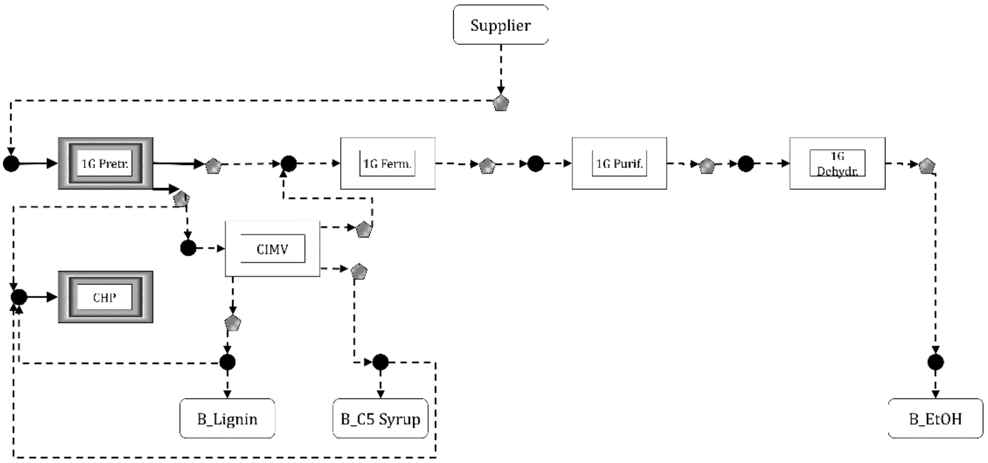

Figure 7.5. Revamped 1G-2G Network

The heat integration of the two technologies resulted in 254MW heating and 242MW cooling requirements (Figure 7.6).

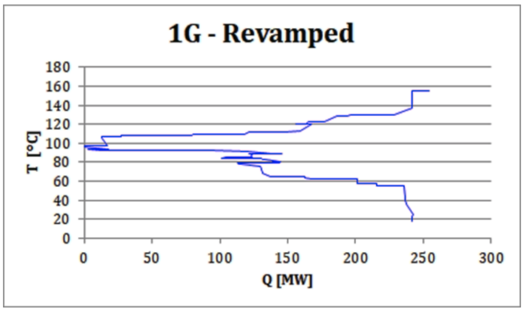

Figure 7.6. GCC of 1G-2G Revamped

Table 7.2 summarizes the results of scenario 1, where lignin and C5 syrup feed the CHP unit, producing 12MWh. It seems that the revamp attempt is not profitable. The greatest cost is the investment cost, which is the installation cost for the new 2G unit, holding 98.8% of the total cost. In the operating cost, the treatment cost seems to be greater than then energy cost. This is mainly due to the fact that 1G process has effluents with high solids concentration (sugarcane washing etc.).

Table 7.2. Cost Summary – Case 1 with CHP (C5 & Lignin)

MM$ 2016/yr						
Profit	**Revenue**	**$Cost^{Total}$**	**$Cost^{CI}$**	**$Cost^{UE}$**	**$Cost^{UM}$**	**$Cost^{TR}$**
-10.81	79.12	89.94	88.90	0.12	0.28	0.62
			98.9%	0.1%	0.3%	0.7%

In the second scenario, lignin and C5 sugars are sold as products. In this case, the revamp seems to be a profitable venture (Table 7.3). The integrated process has revenues 79.12MM$/yr from selling the ethanol (1G), 65.72 from the C5 syrup (2G), and 33.12 MM$/yr from the lignin (2G).

Table 7.3. Cost Summary – Case 1 – no CHP

MM$ 2016/yr						
Profit	**Revenue**	**$Cost^{Total}$**	**$Cost^{CI}$**	**$Cost^{UE}$**	**$Cost^{UM}$**	**$Cost^{TR}$**
88.02	177.96	89.94	88.90	0.13	0.28	0.62
			98.8%	0.2%	0.7%	0.3%

7.5.3 Case 2: Revamp with Synergies

Case 2 deals with the full problem presented in Figure 7.4. The optimization problem is to setup the utility and the process network. Figure 7.7 shows the selected process units. The 1G process is kept as it was, feeding the bagasse to the 2G process. C5 sugars and C6 pulp are hydrolyzed to xylose and glucose respectively. No CHP unit is activated.

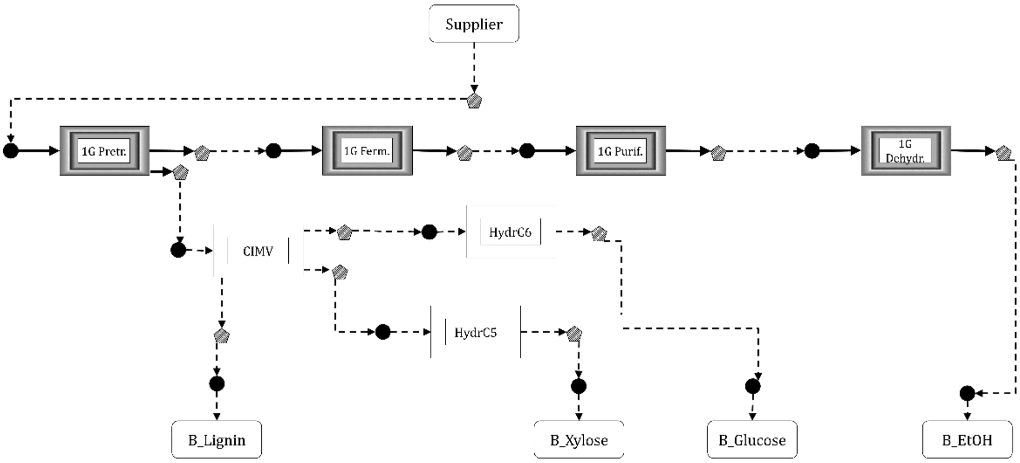

Figure 7.7. 1G-2G Revamp Network

The integrated processes requires 258MW for heating and 223MW for cooling (Figure 7.8).

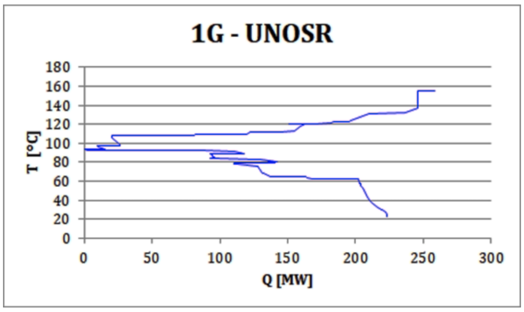

Figure 7.8. 1G-2G Revamp Network

Table 7.4 summarizes the results. The revamp venture is profitable. The greatest cost is the investment cost, while treatment cost has the greater impact on the operating cost.

Table 7.4. Cost Summary – Case 2

MM$ 2016/yr						
Profit	**Revenue**	**$Cost^{Total}$**	**$Cost^{CI}$**	**$Cost^{UE}$**	**$Cost^{UM}$**	**$Cost^{TR}$**
152.64	232.80	80.16	79.42	0.10	0.28	0.36
			99.1%	0.1%	0.4%	0.4%

7.6 Discussion

This chapter presents the utility network optimization with synergistic revamp (UNOSR) model, which combines process integration with process synthesis to revamp processes. The optimization method is applied to a 1G sugarcane biorefinery using CIMV process as the 2G revamp technology. The first case study devoted the 2G process to increase the ethanol production of the existing 1G plant. Results show that the venture is profitable only if CIMV sells lignin and C5 syrup. The second case study leaves the selection of the process units as a degree of freedom by activating the synergistic process synthesis. In that case, CIMV is used only as a symbiotic process to treat the bagasse. No CHP unit is activated as the energy cost is less than the potential profit of the streams used as energy source. Even though case 2 has two additional process sections for hydrolyzing the sugars, the venture is more profitable than case 1. To be fair, the relevant cases studied in the literature use more simple 2G technologies (mainly steam explosion), and it is only logical that a sophisticated 2G technology, like CIMV organosolv, cannot be used only to produce bulk products. UNOSR seems to invest in producing more valuable products than modifying the existing installation only for the production of fuel ethanol. Nevertheless, the revamp of existing biorefineries is not a straight forward process, since synergistic and value chain synthesis options coexist in addition to the complicated retrofit problem.

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Chapter VIII

Integrated Waste Management

This chapter extends the systematic approach to integrated waste management systems. The proposed framework can address both, the generation of waste streams depending the selected process units and the treatment technologies. The integrated system includes options for alternative treatment technologies and decentralized and centralized management strategies.

8.1 Motivation and Challenges

The concept of circular economy conceives a system of producers and consumers with minimal losses of materials and energy through extensive reuse, recycling, and recovery (Korhonen et al., 2018). Following this concept, waste can be seen as a potential feedstock and not as a material that need pretreatment before disposal. The biorefinery capacity and/or its value chain paths are often degrees of freedom. The valorization of the waste streams can also be seen as a degree of freedom, since there are several candidate technologies for waste treatment. Moreover, the strategy for decentralized or centralized waste management is a design decision. Other than selecting isolated treatment technologies, one is faced with options to either deploy a particular technology on several streams or, on the contrary, treat a single stream using several technologies. It is important to holistically address both the waste streams as well as the waste treatment technologies. To evaluate the potential benefits of waste treatment it is necessary to follow an integrated design with the main process. A systems approach holds the potential to assess the extent to which the biorefinery is able to 'integrate' its production with its waste management. The proposed methodology highlights a systematic and generic approach. The potential of the work is illustrated with a real-life lignocellulosic biorefinery consisted by 11 valorization paths. Waste streams are first mapped to treatment options. Next, the proposed mapping is structured as a synthesis problem that is formulated and optimized in the form of an MINLP. The optimization selects technologies; optimal solution determines the technology to use.

8.2 Problem Statement

The problem can be stated as one where given is a set of

- Biorefinery processes
- waste streams and waste management technologies
- engineering economics and costing models for each technology
- design specifications including environmental regulations and constraints

The systems approach is accordingly required to determine

- which treatment technologies are appropriate to deploy
- whether each waste stream should be treated by single or multiple technologies
- whether waste streams should be treated jointly or separately

The stages of the systems approach are:

1. Classification of the treatment technologies
2. Development of surrogates
3. Classification of the waste streams and allocation to the appropriate technology
4. Synthesis based on bipartite graphical superstructure models
5. Formulation and solving of the mathematical optimization problem

8.3 Methods

Waste streams are first classified and mapped onto lists of eligible technologies. Next, the proposed mapping is structured as a synthesis problem that is formulated and optimized in the form of an MINLP. The optimization selects technologies; optimal solution determines which technology to use.

8.3.1 Treatment Technologies Classification

The treatment technologies follow the classification proposed by Woodard (2001), based on the characteristics of the treated waste and the required processing intensity (e.g. chemicals, physicals, thermochemical). The technologies studied during this research include:

- Gaseous emissions
  - Calcinations-loop (Ca-loop)
  - Membrane reactor (MR)
  - Cryogenic methods (CR)
  - Chemical absorption using monoethanolamine (MEA) or N-methyl diethanolamine (MDEA) as solvent
  - Physical absorption using Rectisol (RCT) or Selexol (SLX)

- Liquid effluents
  - Anaerobic Digestion (AD)
  - Activated Sludge (AS)
  - Trickling Filter (TF)
  - Rotating Biological Contactors (RBC)
  - Aerated Lagoon (AL)
  - Stabilization pond (SP)

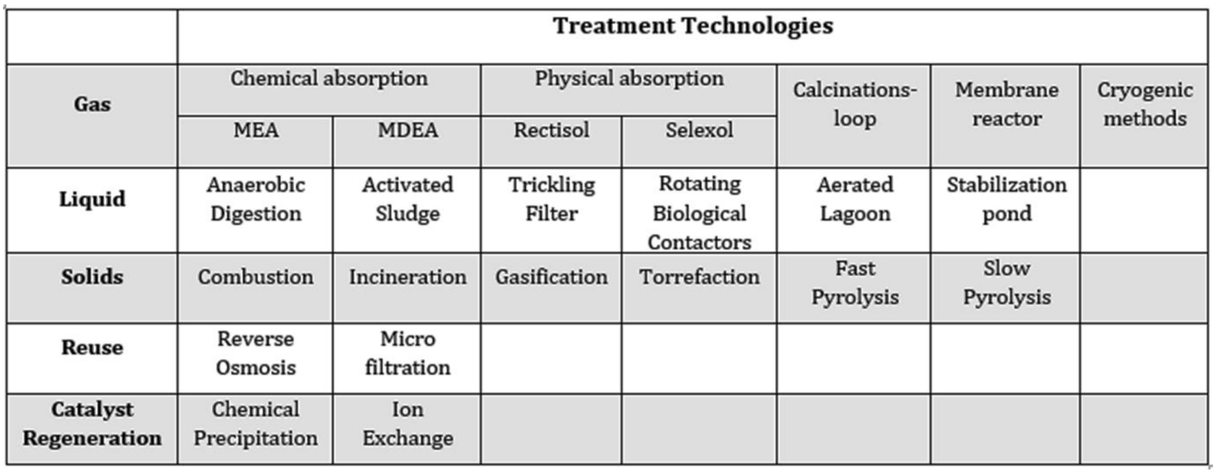
- Solid waste
  - Combustion (COM)
  - Incineration (INC)
  - Gasification (GSF)
  - Torrefaction (TOR)
  - Pyrolysis slow (SPY) or fast (FPY)

- Reuse of liquid streams
  - Reverse osmosis (RO)
  - Micro filtration (MF)

- Catalyst regeneration
  - Chemical precipitation (CPR)
  - Ion exchange (IE)

Table 8.1 summarizes the classification of the waste treatment technologies. All treatment models can be replaced without complications to the approach. By a similar token the types of technologies can be adjusted.

Table 8.1. Classification of treatment technologies.



	Treatment Technologies						
Gas	Chemical absorption		Physical absorption		Calcinations-loop	Membrane reactor	Cryogenic methods
	MEA	MDEA	Rectisol	Selexol			
Liquid	Anaerobic Digestion	Activated Sludge	Trickling Filter	Rotating Biological Contactors	Aerated Lagoon	Stabilization pond	
Solids	Combustion	Incineration	Gasification	Torrefaction	Fast Pyrolysis	Slow Pyrolysis	
Reuse	Reverse Osmosis	Micro filtration					
Catalyst Regeneration	Chemical Precipitation	Ion Exchange					

8.3.2 Surrogates for Treatment Technologies

Shortcut models that are useful for mass and energy balances as well as costing and economics are presented in Mountraki et al. (2016). The models are regressed using simulation studies and involve conditional terms (i.e. different models are applies for different ranges of design parameters). For each waste treatment process j, models are developed to relate inlet flows and inlet conditions with product outflows (P_j), energy use (E_j), solvents' requirements (R_{sj}), capital costs (C_j^f), and operating costs (C_j^{op}). Different treatment technologies are studied separately for gas, liquid and solid waste. All model parameters are presented in the Appendix E. Nonlinearities are accounted using polynomial expressions that are discussed in detail in the following sections. The extent of linearization was set to restrict model deviations to less than 15%.

- Gaseous emissions

Gases are treated to reduce COx, NOx and SOx at acceptable levels. Byproducts include gas streams of acceptable environmental limits. The output is calculated with respect to the inlet stream flow (S_j) and its CO_2 content, R_{CO2j}, expressed in kg/day. The model calculates the products (P_j), the energy required (E_j), the capital investment (C_j^f), the operating cost (C_j^{op}) and the quantity of the solvent ($R_{s\,j}$) as required by the treatment technologies. Figure 8.1 illustrates the input-output structure of the models of gas treatment.

Figure 8.1. Input-output structure: gas treatment

- Chemical absorption (MEA & MDEA)

Surrogates are produced by using established literature (Appels et al., 2008; Panteli, 2014; Papoutsi,2014). P_j and C_j^f are functions of S_j based on Eq.8.1 and Eq.8.2 respectively. R_{sj}, E_j and C_j^{op} depend on R_{CO2j} as follows.

$$P_j = \alpha_{1\,j} \cdot S_j + \alpha_{2\,j}\ ,\ \text{j = MEA/MDEA} \qquad Eq. 8.1$$

$$C_j^{\,f} = c_{1\,j} \cdot S_j + c_{2\,j}\ ,\ \text{j = MEA/MDEA} \qquad Eq. 8.2$$

$$R_{s\,j} = \beta_{1\,j} \cdot R_{co2ij}\ ,\ \text{j = MEA/MDEA} \qquad Eq. 8.3$$

$$E_j = e_{1\,jp} \cdot R_{co2ij}\ ,\ \text{j = MEA/MDEA} \qquad Eq. 8.4$$

$$C_j^{\,op} = c_{1\,j} \cdot R_{co2ij}\ ,\ \text{j = MEA/MDEA} \qquad Eq. 8.5$$

The regression parameters of the models are presented in Tables E.1 and E.2.

- Physical absorption (RCT & SLX)

The analysis is based on detailed design assuming literature models that postulate 30% CO_2 in the inflow stream (Papoutsi, 2014). R_{sj} is function of $R_{CO2\ j}$ and follows Eq.8.3. E_j is required to regenerate the solvent and, for practical reasons, it is calculated as a function of R_{CO2j} using Eq.8.4. C_j^f is a function of S_j, while C_j^{op} is modeled with respect to $R_{CO2\ j}$, following the chemical absorption Eq.8.2 and Eq.8.5. Regression parameters are presented in Tables E.3 and E.4.

- Calcinations-loop (Ca-loop) & Cryogenic methods (CR)

The model makes use of available literature (Papoutsi, 2014) that requires 30% CO_2 content in the incoming flow. Cryogenic purification separates gas mixtures using fractional distillation and condensation at low temperature. The CO_2 is liquified and condensed from high concentration (> 90%) streams offering advantages as the captured CO_2 can be directly transported and/or sold. The models make similar use of available literature (Appels et al., 2018). Both models follow those equations used in physical absorption. Regression parameters are presented in Tables E.5 and E.6.

➢ Liquid effluents

Liquids are treated to reduce the BOD and the suspended solids at acceptable levels. Byproducts include liquid streams of acceptable environmental limits, energy, and compost. The output has been modeled based on the basis of total inlet flows (S_j), total suspended solids (TSS_j), and the BOD of the inlet stream (BOD_j). Figure 8.2 illustrates the presumed input-output structure of the models.

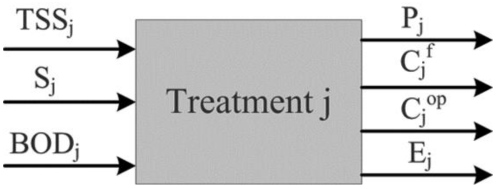


Figure 8.2. Input-output structure: liquid treatment

- Anaerobic Digestion (AD)

Biodegradable material is biologically converted into compost, water and biogas. Biogas is postulated to contain 70% methane (Van Haandel & Van der Lubbe, 2007; Appels, 2008). The regression ranged from 25-1100 kg/m³. P_j is modeled as function of S_j. C_j^f and C_j^{op} are modeled as functions of the BOD_j. Accordingly,

$$P_j = \mathrm{f}\left(S_j\right) \cong \sum_k P_{jk} = \sum_k \left(\alpha_{1\,jk} \cdot S_j + \alpha_{2\,jk} \right)\ ,\ \text{j = AD} \qquad \text{Eq. 8.6}$$

$$\mathrm{C}_{\mathrm{j}}^{\mathrm{f}} = \mathrm{f}\left(BOD_j\right) \cong \sum_k {C_{jk}}^{f} = \sum_k \left(f_{1\,jk} \cdot BOD_{jk}\right)\ ,\ \mathrm{j} = \mathrm{AD} \qquad \text{Eq. 8.7}$$

$$\mathrm{C}_{\mathrm{j}}^{\mathrm{op}} = \mathrm{f}\left(BOD_j\right) \cong \sum_k {C_{jk}}^{op} = \sum_k \left(c_{1\,jk} \cdot BOD_{jk}\right)\ ,\ \mathrm{j} = \mathrm{AD} \qquad Eq. 8.8$$

k denotes linearization intervals. The regression parameters of the models are presented in Table E.7.

– Activated Sludge (AS)

Micro-organisms metabolize the suspended and soluble organic matter in aeration basins. Sludge is the main product. The regression ranged from 120-380 kg/m^3. P_j is modeled as a function of S_j following Eq 8.6 (j=AS). The energy required for aeration, E_j, and the costs C_j^f and C_j^{op}, are modeled as functions of S_j following,

$$E_j = \mathrm{f}\left(S_j\right) \cong \sum_k E_{jk} = \sum_k \left(e_{1\,jkp} \cdot S_j + e_{2\,jkp}\right)\ ,\ \mathrm{j} = \mathrm{AS} \qquad Eq. 8.9$$

$$\mathrm{C}_{\mathrm{j}}^{\mathrm{f}} = \mathrm{f}\left(S_j\right) \cong \sum_k {C_{jk}}^{f} = \sum_k \left(\mathrm{f}_{1\,jk} \cdot S_j + \mathrm{f}_{2\,jk}\right)\ ,\ \mathrm{j} = \mathrm{AS} \qquad Eq. 8.10$$

$$\mathrm{C}_{\mathrm{j}}^{\mathrm{op}} = \mathrm{f}\left(S_j\right) \cong \sum_k {C_{jk}}^{op} = \sum_k \left(c_{1\,jk} \cdot S_j + c_{2\,jk}\right)\ ,\ \mathrm{j} = \mathrm{AS} \qquad Eq. 8.11$$

k denotes linearization intervals. The regression parameters of the models are presented in Table E.8.

– Trickling Filter (TF)

TFs are used to remove organic matter from wastewater. The regression ranged from 120- 520 kg/m^3. P_j is modeled as function of S_j following Eq.8.6 (j=TF). Energy is required for the sludge aeration and the rotation of distributor arms. E_j is modeled as function of S_j and based on Eq.8.9. C_j^f is modeled as polynomial function of S_j; the costs C_j^{op} are modeled as power function of S_j.

$$\mathrm{C}_{\mathrm{j}}^{\mathrm{f}} = \mathrm{f}\left(S_j\right) \cong \sum_k {C_{jk}}^{f} = \sum_k \left(\mathrm{f}_{1\,jk} \cdot \left(S_j\right)^2 + f_{2\,jk} \cdot S_j + \mathrm{f}_{3\,jk}\right)\ ,\ \mathrm{j} = \mathrm{TF} \qquad \text{Eq. 8.12}$$

$$\mathrm{C}_{\mathrm{j}}^{\mathrm{op}} = \mathrm{f}\left(S_j\right) \cong \sum_k {C_{jk}}^{op} = \sum_k \left(c_{1\,jk} \cdot \left(S_j\right)^{c_{2\,jk}}\right)\ ,\ \mathrm{j} = \mathrm{TF} \qquad Eq. 8.13$$

k denotes linearization intervals. The regression parameters of the models are presented in Table E.9.

– Rotating Biological Contactors (RBC)

RBC involves a number of rotating discs attached on a shaft that is submerged in a tank and is partially or completely filled with by the treated liquid. In many respects, RBC is similar to TF. The regression ranged from 100 - 380 kg/m^3. Costs C_j^f and C_j^{op}, are modeled as functions of S_j following respectively Eq.8.10 and Eq.8.11 (j=RBC). P_j is modeled as function of TSS_j.

$$P_j = \mathrm{f}\left(\mathrm{TS}S_j\right) \cong \sum_k P_{jk} = \sum_k \left(\ \alpha_{1\,jk} \cdot TSS_j +\ \ \alpha_{2\,jk}\right)\ ,\ \mathrm{j} = \mathrm{RBC} \qquad Eq. 8.14$$

k denotes linearization intervals. The regression parameters of the models are presented in Table E.10.

– Aerated Lagoon (AL) & Stabilization pond (SP)

ALs are ponds with artificial aeration to promote biological oxidation. Capable to perform at shock (peak) loads, they feature low maintenance cost. The regression ranged from 4000 - 150000 kg/day. P_j is modeled as function of TSS_j following Eq.8.14. E_j, C_j^f and C_j^{op}, are modeled as functions of S_j respectively following Eqs.8.9, 8.10, and 8.11 (j=AL). SPs are large shallow excavations that drain sewage from various systems. The regression ranged from 80 - 290 kg/m^3. P_j is modeled as functions of TSS_j using Eq.8.14 (j=SP). C_j^f is modeled as function of S_j following Eq.8.11 (j=SP). As SPs do not need aeration the operating cost is assumed negligible. The regression parameters of the models are presented in Tables E.11 and E.12.

- Solid waste

Main products include ash and thermal energy. Each treatment output is modeled as a function of the inlet flow (S_j), and the energy required (E_j). Figure 8.3 illustrates the input-output structure of the models of solid treatment.

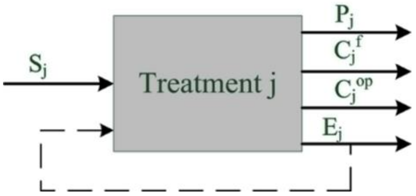


Figure 8.3. Input-output structure: solid treatment

– Combustion (COM), Incineration (INC), & Gasification (GSF)

Combustion produces energy turning solids to energy and ash (assumed 15% of the solids). The energy depends on the total inlet flow, its LHV and the combustion technology. P_j is modeled as a function of S_j based on Eq.8.6. The regression considered LHV values from 2.5 - 40 MJ/kg. Costs C_j^f and C_j^{op} are modeled as functions of S_j following Eq.8.10 and Eq.8.11 respectively. Gasification operates at high temperatures (>700°C) converting organics into carbon monoxide, hydrogen and carbon dioxide. P_j, C_j^f and E_j are expressed as functions of S_j respectively following Eq.8.1, Eq.8.15, and Eq.8.16 (j= GSF). Incineration uses excess of oxygen and produces ash, flue gas, and heat. P_j and C_j^f are modeled as functions of S_j. based on Eq8.1 and Eq.8.15, (j= INC).

$$C_j{}^{f} = f_{1\,j} \cdot S_j + f_{2\,j}\ ,\ \ \text{j} = \text{GSF , INC} \qquad Eq.8.15$$

$$E_j = e_{1\,jp} \cdot S_j + e_{2\,jp}\ ,\ \ \text{j} = \text{GSF} \qquad Eq.8.16$$

The regression parameters of the models are presented in Tables E.13, E.14, and E.15.

– Fast Pyrolysis (FPY), Slow Pyrolysis (SPY) & Torrefaction (TOR)

Fast pyrolysis operates at 650- 1000°C, while slow pyrolysis requires lower temperatures (~400°C) and longer residence times. Products include oil (50%), char (20%), and gas (30%) (Van Haandel & van der Lubbe, 2007; Atsonios et al., 2013). P_j, E_j and C_j^{op} depend on S_j and are modeled following Eq.8.1, Eq.8.16 and Eq.8.2 respectively. In fast pyrolysis C_j^f is calculated as power function of E_j following Eq.8.17; slow pyrolysis models costs follow instead Eq.8.15.

$$C_j{}^{fixed} = c_{1\,j} \cdot E_j{}^{c_{2\,j}}\ ,\qquad \text{j} = \text{FPY, SPY} \qquad Eq.8.17$$

Torrefaction is a thermo-chemical process which operates under anaerobic conditions at 250 to 300°C. The end product is a stable, homogeneous, high quality biofuel with upgraded energy density and calorific value. The models of P_j and E_j, follow those in fast pyrolysis (j=SPY). C_j^{op} is modeled as linear functions of E_j and C_j^f.

$$C_j{}^{oper} = c_{1\,j}\ \cdot E_j\ ,\ \ \text{j} = \text{TOR} \qquad Eq.8.18$$

$$C_j{}^{fixed} = cc_{1\,j}\ \cdot \left(S_j\right)^{cc_{2\,j}},\ \ \text{j} = \text{TOR} \qquad Eq.8.19$$

The regression parameters of the models are presented in Tables E16, E.17 and E.18.

8.3.3 Allocation Maps

Waste streams are characterized as liquids, solids or gases. Depending on their water content, they are classified as liquids (higher than 50% water content) or solids (less than 50% H2O). Streams with water content close to 50% can be treated as liquids as well as solids, so we will call them mixed streams. Liquid streams with water content higher than 99,5% are considered recyclable; if water content is between 97-99,5% they can be reused after treatment. If the effluent stream contains a catalyst, it is treated for its recovery and regeneration. A more detailed classification depends on the C/N content, their Lower Heating Value (LHV), and their BOD concentration. Gaseous waste streams are classified as rich in carbon dioxide. Those lower than 4% carbon dioxide content may be released into the environment. The effluent gas streams are sufficiently rich to carbon dioxide, which can be considered "green", as product of fermentation processes. In this work, the scenarios of CO_2 capture examine the commercial applications of this product and therefore the possibility of profit from its sale.

Following established literature (Cavin et al., 2001; Muñoz et al., 2013a,b), different allocation maps are developed for each case (Mountraki et al., 2016).

- Gaseous emissions

The allocation diagram for gas emissions is shown on Figure 8.4.

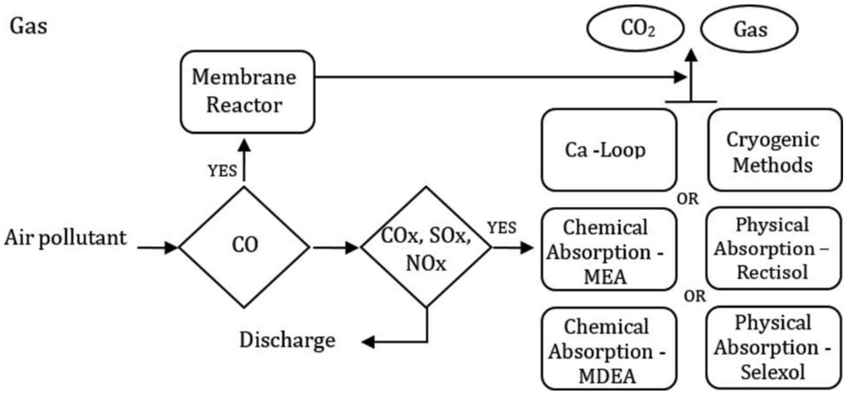


Figure 8.4. Allocation maps – Gaseous emissions.

- Liquid effluents

Allocation relates to the capacity, the organic content (expressed as BOD), and the nitrogen content. The allocation map is sketched in Figure 8.5. Reuse technologies are restricted by the amount of suspended solids (TSS) that they hold. Regeneration depends on the substance regenerated following Figure 8.6.

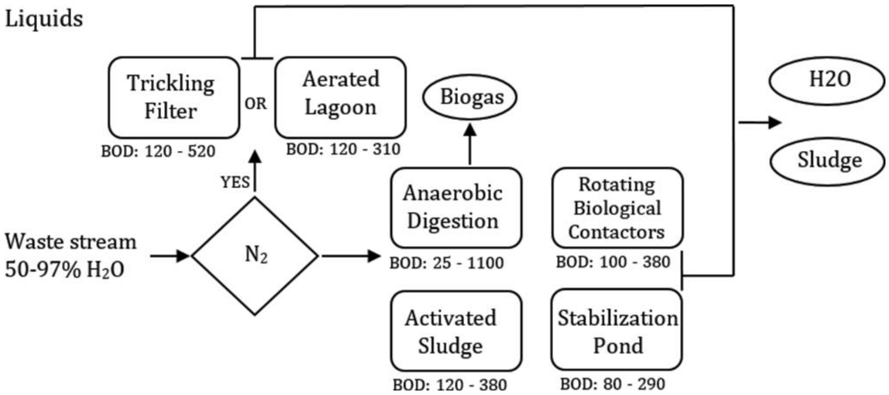


Figure 8.5. Allocation maps – Liquids (a)

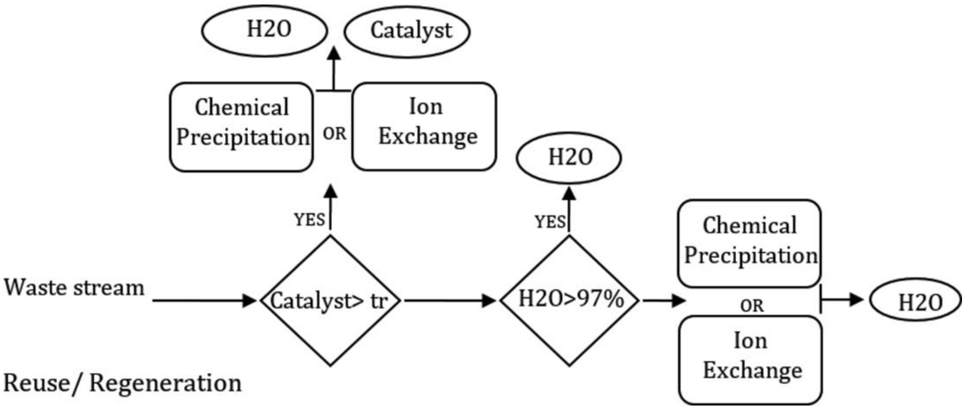


Figure 8.6. Allocation maps – Liquids Reuse/ Regeneration (b)

- Solid waste

The allocation of the solid streams follows the diagram of Figure 8.7. Streams are candidates as fuels provided that they contain H2O less than 40%; otherwise, they are desiccated. If nitrogen, cells, sugars or yeasts are present, then the streams can be used for animal feed or fertilizer.

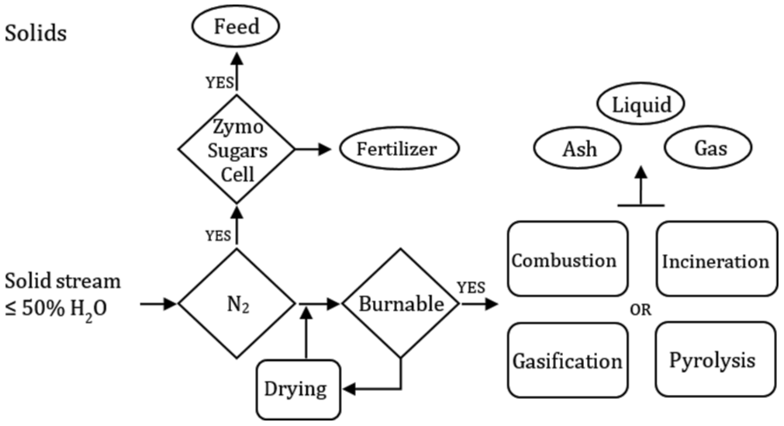


Figure 8.7. Allocation maps – Solids.

8.3.4 Synthesis Models

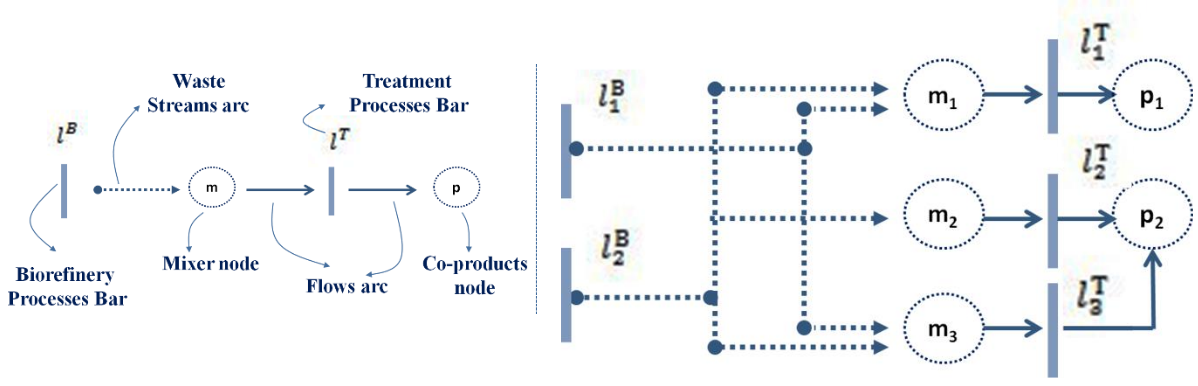
Synthesis blocks are based on the *bipartite biomass graph representation* (BBR) introduced by Kokossis et al (2015). The BBR has been introduced as a weighted graph that takes the form:

$$BBR = (\widetilde{M}, \widetilde{T}, \tilde{P}, w)$$

where $\widetilde{M}$ accounts for graph *places* (graph nodes) and includes raw materials, intermediates, and products, $\widetilde{T}$ accounts for transitions (graph bars) and consists of technologies/processing units, $\tilde{P}$ accounts for arcs (connections), and w stand for weights that amy be assigned to binary variables in the formulation

For the purpose of waste treatment, $\widetilde{M}$ (graph *places*) is extended to include additional lists of end-products, such as biogas and bioenergy. $\widetilde{T}$ (transitions and graph bars) are similarly extended to account for treatment technologies and their preceding mixers. The set $\tilde{P}$ (connections) requires the use of *direct* and *indirect* allocation. In *direct* allocations the connections follow the single rules of assignment introduced by Kokossis et al (2015). However, the allocation of waste streams to technologies requires the use of specific properties of the waste streams (e.g. content, composition, flows etc.).

Figure 8.8 (left) explains the graph places (biorefinery processes, treatment processes) and their connections (arcs). Graph properties dictate connections, and they integrate to networks. A set of basic connections relates the raw materials, the intermediates, and the products. In other words, raw materials/intermediates are feeding/produced by processing technologies; connections process outputs to process inputs (simple allocation). The network of Figure 8.8 (right) connects the waste streams flowing out of the biorefinery processes as feed to the treatment technologies.



a) b)

Figure 8.8. A BBR graph representation

Figure 8.9 is accordingly the superstructure representation that corresponds to the BBR network of Figure 8.8 (right-hand). Figure 8.10 represents a real-life treatment network following the connections of Figure 8.9.

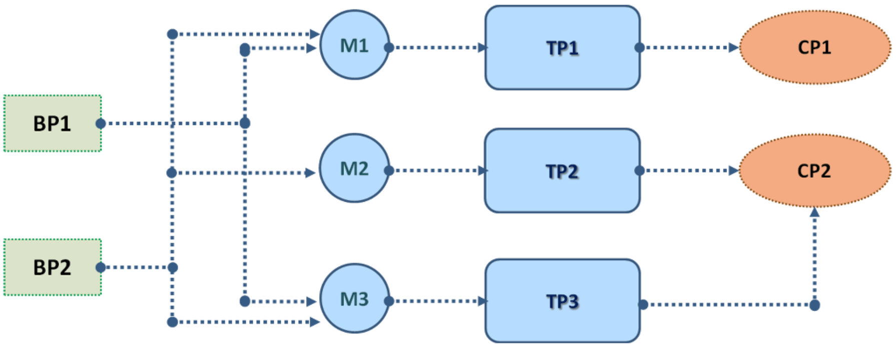


Figure8.9. Superstructure corresponding to Figure 8.8b

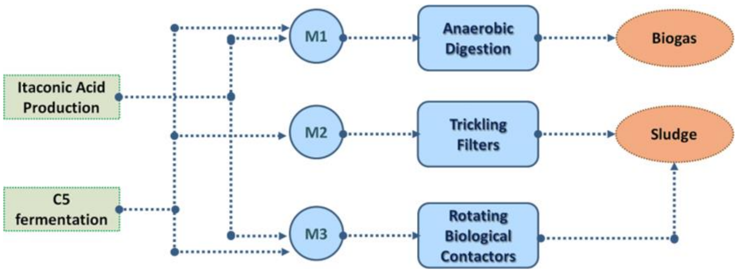


Figure 8.10. Treatment configuration

8.4 Mathematical Formulation

The optimization model includes integer and continuous variables and is formulated as a mixed-integer nonlinear programming problem (MINLP). Binaries are assigned to determine the type of treatment technologies to select and the type of model that is applicable to use. The model includes basic mass and energy balances, expressions that account for the economic flows, and a set of logical constraints.

The following sets are denoted:

$I = \{i|\ i\ waste\ streams\}$

$J = \{j|\ j\ treatment\ technologies\}$

$P = \{p|\ p\ waste\ products\}$

$K = \{k|k\ discretization\ intervals\}$

The continuous variables are:

R_{ij} : waste stream i in technology j

R_{pij} : component p of waste stream i in technology j

S_j : total inlet to technology j

M_{jk} : total waste from technology j going to discretization k

BOD_{jk} : total BOD from technology j going to discretization k

TSS_j total TSS to technology j

L_j : total TSS from technology j going to discretization k

Pr_{jp}^{out} , Pr_p^t: product p from technology j / from all the waste management processes

E_j , E^t: energy needs of technology j / total energy needs of treatment processes

$\mathrm{C_j^f}$, $\mathrm{C_t^f}$: installation cost of technology process j / of biorefinery [M$ per year]

$\mathrm{C_j^o}$: operational cost of technology process j [M$ per year]

$\mathrm{C_j^e}$, $\mathrm{C_t^e}$: energy cost of technology process j / total energy cost of biorefinery [M$ per year]

RV_j, RV_j^t : revenue from technology j / total revenue from waste management [M$ per year]

C_j^t : total cost from waste management treatment [M$ per year]

Binary variables are assigned to the type of treatment technologies and to type of model that is appropriate to use as different models are valid as the conditions vary:

z_{jk} : modeling variable of technology j and interval k

y_{ij} : modeling variable of waste stream i and the technology j

The parameters of the problem include treatment yields, stream compositions, and cost information. They are presented in the Appendix E.

$a_{1\ jkp}$, $\alpha_{2\ jkp}$: discretization parameters for product p produced by technology j

$e_{1\ jkp}$, $e_{2\ jkp}$: discretization parameters for energy needs produced by technology j

$f_{1\ j}$, $f_{2\ j}$: discretization parameters for fixed cost of technology j

$c_{1\ j}$, $c_{2\ j}$: discretization parameters for operating cost of technology j

$\beta_{1\ jkp}$: parameter for the estimation of solvent p (component) required by technology j

$\mathrm{p_p}$, $\mathrm{p_e}$: product/energy price

LHV_i : lower heatig value of waste liquid stream i

LH_{pi} : latent heat of component p in waste liquid stream i

N: number of technologies

$\overline{BOD_i}$: BOD of waste liquid stream i

F_i : flow of waste liquid stream i [kg/day]

$\overline{TSS_i}$: TSS of waste liquid stream i [kg/day]

BOD_k^{max} , BOD_k^{min} : maximum / minimum BOD going to discretization k [kg/day]

LU^F, LU^R: upper bounds for logical constraints

8.4.1 Mass Balances

The mass balances around the mixers of the waste streams are calculated be Eqs. 8.20-8.23.

$$\sum_{i\in I} R_{ij} \cdot \overline{BOD}_i = \sum_{k\in K} M_{jk} \cdot BOD_{jk}, \qquad \forall j \in J \qquad \text{Eq. 8.20}$$

$$\sum_{i\in I} R_{ij} \cdot \overline{TSS}_i = \sum_{k\in K} M_{jk} \cdot TSS_j, \qquad \forall j \in J \qquad \text{Eq. 8.21}$$

$$\sum_{i\in I} R_{ij} = \sum_{k\in K} M_{jk}, \qquad \forall j \in J \qquad \text{Eq. 8.22}$$

$$F_i = \sum_{j\in J} R_{ij}, \qquad \forall i \in I \qquad \text{Eq. 8.23}$$

8.4.2 Energy Balances

The energy requirements of the treatment technologies are estimated by Eqs 8.24 and 8.25.

$$E_j = \sum_{k\in K} (e_{1\,jkp} \cdot M_{jk} + e_{2\,jkp} \cdot z_{jk}), \qquad \forall j \in J \qquad \text{Eq. 8.24}$$

$$E^t = \sum_{j\in J} E_j \qquad \text{Eq. 8.25}$$

8.4.3 Constraints

Design Constraints

The design constraints depend on the waste products of each treatment technology.

$$Pr_{jp}^{out} = \sum_{k\in K} (a_{1\,jkp} \cdot M_{jk} + a_{2\,jkp} \cdot z_{jk}), \qquad \forall p \in P, \quad j = AD, AS, TF \qquad \text{Eq. 8.26}$$

$$Pr_{jp}^{out} = \sum_{k\in K} (a_{1\,jkp} \cdot L_j + a_{2\,jkp} \cdot z_{jk}), \qquad \forall p \in P, \quad j = RBC, AL, SP \qquad \text{Eq. 8.27}$$

$$Pr_p^t = \sum_{j\in J} Pr_{jp}^{out}, \qquad \forall p \in P \qquad \text{Eq. 8.28}$$

Logical Constraints:

A basic set of constraints relates binary and continues variables.

$$M_{jk} - z_{jk} \cdot LU^F \leq 0, \qquad \forall \; j \in J, k \in K \qquad \text{Eq. 8.29}$$

$$R_{jk} - y_{jk} \cdot LU^R \leq 0, \qquad \forall \; i \in I, k \in K \qquad \text{Eq. 8.30}$$

$$BOD_{jk} - z_{jk} \cdot BOD_k^{max} \leq 0, \qquad \forall \; j \in J, k \in K \qquad \text{Eq. 8.31}$$

$$BOD_{jk} - z_{jk} \cdot BOD_k^{min} \leq 0, \qquad \forall \; j \in J, k \in K \qquad \text{Eq. 8.32}$$

Additional logical constraints include exclusivity constraints on the selection of treatment technologies and constraints to enforce appropriate linearization intervals,

$$\sum_{j\in J} y_{ij} = 1, \qquad \forall \; i \in I \qquad \text{Eq. 8.33}$$

$$\sum_{k\in K} z_{jk} \leq 1, \qquad \forall \; j \in J \qquad \text{Eq. 8.34}$$

and contingency constraints and bounds on the number of technologies to use,

$$\sum_{i \in I} y_{ij} \geq z_{jk}, \qquad \forall\ j \in J,\ \forall\ k \in K \qquad \text{Eq. 8.35}$$

$$\sum_{k \in K} z_{jk} \geq y_{ij}, \qquad \forall\ i \in I,\ \forall\ j \in J \qquad \text{Eq. 8.36}$$

$$\sum_{i \in I} \sum_{j \in J} y_{ij} \leq N, \qquad \forall\ i \in I,\ \forall\ j \in J \qquad \text{Eq. 8.37}$$

8.4.4 Cost and revenues

These include cost models as presented by Eqs 8.2, 8.5, 8.7, 8.11, 8.14 and 8.16,

$$C_j^f = \sum_{k \in K} (f_{1\,j} \cdot M_{jk} + f_{2\,j} \cdot z_{jk}), \qquad j = \mathrm{AS, TF, RBC, AL, SP} \qquad \text{Eq. 8.38}$$

$$C_j^f = \sum_{k \in K} (f_{1\,j} \cdot BOD_{jk} + f_{2\,j} \cdot z_{jk}), \qquad j = \mathrm{AD} \qquad \text{Eq. 8.39}$$

$$C_t^f = \sum_{j \in J} C_j^f \qquad \text{Eq. 8.40}$$

$$C_j^e = E_{jp} \cdot p_e, \qquad j \in J, p \in P \qquad \text{Eq. 8.41}$$

$$C_t^e = \sum_{j \in J} C_j^e \qquad \text{Eq. 8.42}$$

$$RV_j = Pr_{jp}^{out} \cdot p_p, \qquad j \in J, p \in P \qquad \text{Eq. 8.43}$$

$$RV^t = \sum_{j \in J} RV_j \qquad \text{Eq. 8.44}$$

The mathematical formulation yields a MINLP problem with nonlinearities mostly in the form of bilinear terms. The bilinear terms have resulted from the surrogates for the treatment technologies, where polynomial expressions have been applied to regress simulation data. The MINLP was solved using GAMS/BARON and the quality of solutions has been verified using different initial points.

8.4.5 Objective Function

The objective is the maximization of the total annualized cost with the latter expressed by

$$C_j^t = \sum_{j \in J} \left(C_t^f + C_t^e - RV^t \right) \qquad \text{Eq. 8.45}$$

Negative energy costs indicate operational profits in processing waste.

8.4 Results

The methodology is illustrated using the real-life lignocellulosic biorefinery of CIMV organosolv. The multiproduct biorefinery scheme includes 54 streams, 14 production processes, and 12 products (cellulosic pulp, glucose, lignin powder, C5 sugar syrup, xylose, itaconic acid, xylitol, PF resin, polyurethanes, ethylene, PVC, ethanol). The coproducts consist of biogas, electric and/or thermal energy, sludge, cleaned water, compressed CO2, and the regenerated catalyst. 2007 is set as the economic year. The BBR representation is adopted and the total network along with the waste streams and the treatment technologies are shown in Figure 8.11. The superstructure produced based on the graph representation is illustrated in Figure 8.12.

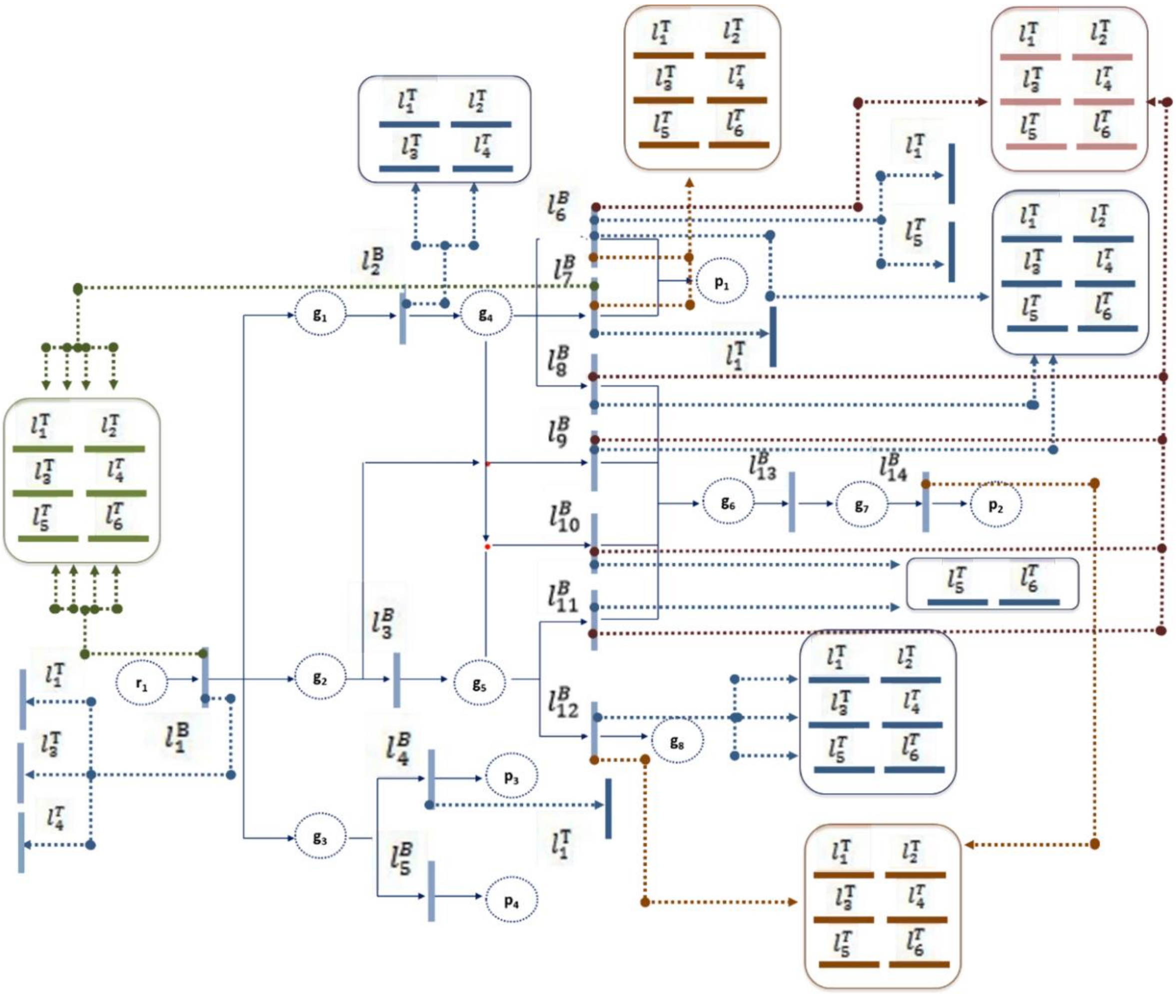


Figure 8.11. BBR graph of multiproduct biorefinery

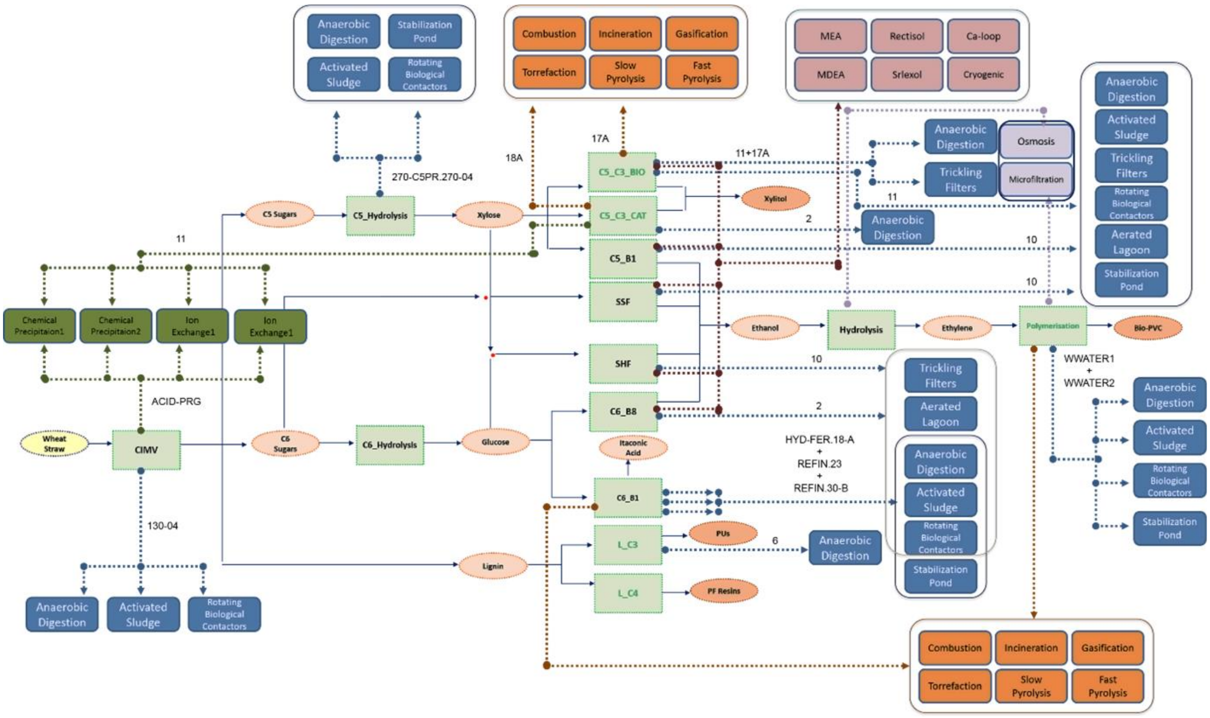


Figure 8.12. Superstructure of the multiproduct biorefinery

Results are obtained in the background of two different biorefinery portfolios:

Portfolio I: xylitol, cellulosic ethanol, and lignin-based polyurethanes;
Portfolio II: xylitol, cellulosic PVC, and lignin-based polyurethanes

On the basis of the two portfolios, three different examples are presented:

Example 1: Evaluation of trade-offs between centralized and decentralized treatment (liquid streams)
Example 2: Integrated treatment of solid and gas byproducts
Example 3: Retrofitting existing installations

8.4.1 Waste Allocation

The selected biorefinery scheme has 29 waste streams. Table 8.2 summarizes the results of the allocation maps.

Table 8.2. Waste streams from each production processes

Production Process	Gas	Liquid	for Reuse	Solid	Catalyst regeneration
CIMV		1			1
C5 to xylose		1			
to xylitol bio	1	1+1*		1*	
to xylitol cat		1		1	1
to ethanol	1	1			
C6 to glucose			1		
to Itaconic Acid		3		1	
to ethanol	1	1			
Lignin to PF					
to PU		1			
SSH ethanol	1	1			
SHF ethanol	1	1			
Ethanol to ethylene			1		
Ethylene to PVC		3		2	

*Binary stream

8.4.2 Evaluation of trade-offs between centralized and decentralized treatment (liquid streams)

Portfolio I is selected as a basis. The problem involves five liquid streams, for which the treatment technologies include:

- anaerobic digestion (AD)
- activated sludge (AS)
- tricking filters (TF)
- rotating biological contractors (RBC)
- aerated lagoons (AL)
- stabilization ponds (SP)

Figure 8.13 illustrates the liquid streams following the BBR representation. The graph properties, in conjunction with the allocation maps, give rise to the superstructure of Figure 8.14. Centralized treatment corresponds to the case where the number of units (N) is set to 1. As N increases, options for decentralized treatment are possible. The solutions produced by the optimization models are presented and discussed separately for each case

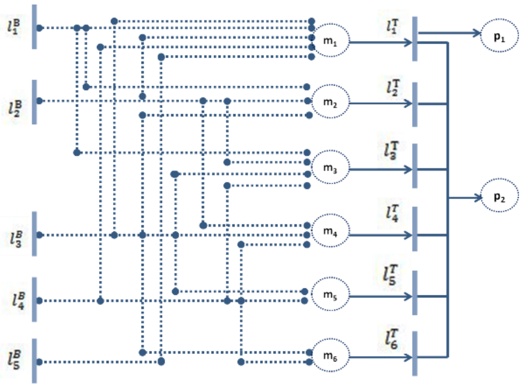


Figure 8.13. BBR representation - Example 1

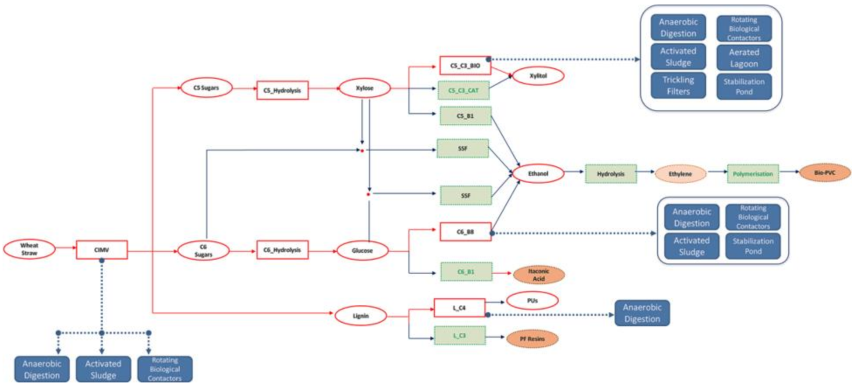


Figure 8.14. Superstructure - Example 1

(i). Centralized Management

By restricting the approach to the use of a single technology (N = 1), the optimization selected the anaerobic digestion (AD). The total installation cost is 15 $M/yr and the revenues from the production of biogas is 1.5 $M/yr. The selection of AD is essentially forced as AD is the only technology suitable for all streams; no other technology can stand as an alternative option.

(ii). Decentralized Management

As N increases, the optimization is able to introduce options for decentralized management. Results are presented for N = 2 and N = 3. The optimization effort is similar for higher values of N; still, higher values for N are considered less realistic.

For N = 2, the selected technologies include AD and RBC. The installation cost is 4.2 $M/yr. In comparison with the previous case, distributed treatment saves 33% of the cost. Table 8.3 presents the allocation of streams across treatment technologies and the cost distribution in the selected technologies. The BBR with the optimal solution is illustrated in Figure 8.15.

Table 8.3. Results summary – Example 1 (N=2)

	Liquid 1	**Liquid 2**	**Liquid 3**	**Liquid 8**	**Liquid 11**	**Total M$/yr**
Technology	RBC	RBC	RBC	AD	AD	
Fixed Cost	0.185			4.722		4.907
Energy Cost	0.172					0.172
Revenue					0.845	0.845
Total Cost M$/yr	4.234					

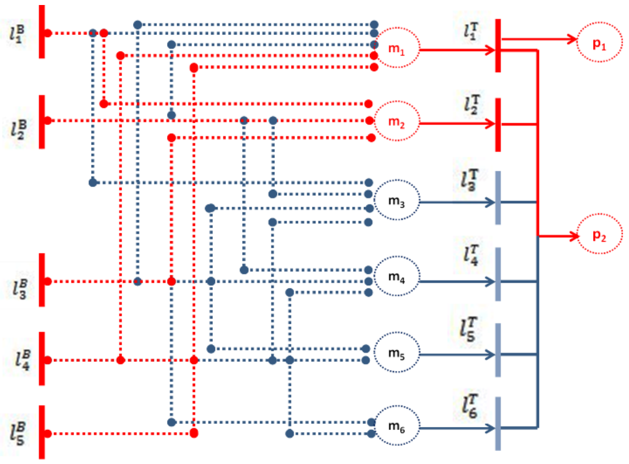


Figure 8.15. BBR of Example 1 - DC optimal solution for N=2

For N = 3 the selected treatment includes AD, RBC, and SP. The installation cost is 0.42 $M/yr, namely a 10-fold decrease as compared with the previous case. Table 8.4 presents the allocation of streams across treatment technologies and the cost distribution. Figure 8.16 illustrates the optimal solution. Integration options are important, and liquid 8 is forced to split into SP and AD.

Table 8.4. Results summary Example 1 (N=3)

	Liquid 1	**Liquid 2**	**Liquid 3**	**Liquid 8**		**Liquid 11**	**Total $M/yr**
Technology	RBC	SP	SP	SP	AD	AD	
Fixed Cost	0.139	0.029			0.136		0.304
Energy Cost	0.129						0.129
Revenue						0.013	0.013
Total Cost (M$/yr)	0.420						

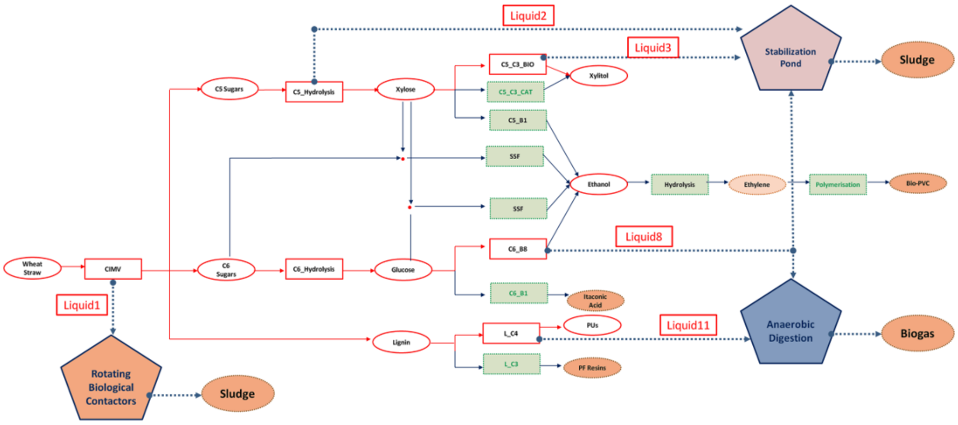


Figure 8.16. Optimal Solution - Example 1 (N=3)

According to the results, the integrated approach and the use of distributed treatment lead to a significant decrease in cost, and, essentially, it reduces the burden by 1 or 2 orders of magnitude.

8.4.3 Integrated treatment of solid and gas byproducts

Two different biorefineries are presented for the treatment of solid and gas waste. The treatment of solids is based on Portfolio II, whereas the treatment of gases uses Portfolio I.

(i). Solids

Solid streams can be treated by all six technologies:

- combustion (COM)
- incineration (INC)
- gasification (GSF)
- torrefaction (TOR)
- slow pyrolysis (SPY)
- fast pyrolysis (FPY)

The superstructure integrates solid streams, according to Figure 8.17. Results are summarized in Table 9.5. Still, the optimization selects a single treatment (e.g. combustion) as the better choice, even when N is relaxed at higher values. A single treatment is the optimal solution and central management emerges as the better choice to handle solids. The optimization produces negative values for the objective (see Table 8.5), essentially indicating that the treatment of solids is economically profitable.

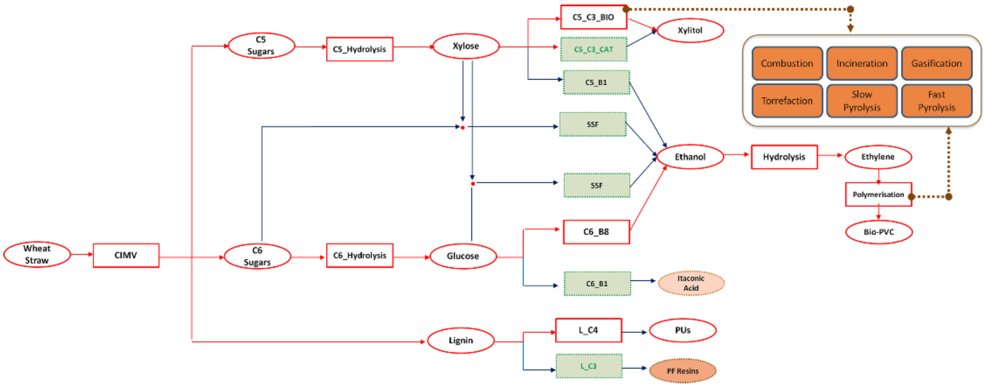


Figure 8.17. Superstructure - Example 2 (solids)

Table 8.5. Results summary - Example 2 (solids)

	Solid 1	Solid 2
Technology	Combustion	Combustion
Fixed Cost	0.784	
Revenue	2.577	
Total Cost (M$/yr)	-1.809	

(ii). Gases

Gas streams can be treated by the following technologies:

- Calcinations-loop (Ca-loop)
- Membrane reactor (MR)
- Cryogenic methods (CR)
- Chemical absorption using monoethanolamine (MEA)
- Chemical absorption using N-methyl diethanolamine (MDEA)
- Physical absorption using rectisol (RCT)
- Physical absorption using Selexol (SLX)

The superstructure integrates gas streams according to Figure 8.18. Results are summarized in Table 8.6. Unlike the case for solids, the optimization selected two different technologies, indicating benefits in the distributed management of waste and the use of Ca-loops (even though MEA offers 80% lower costs than the Ca-loop).

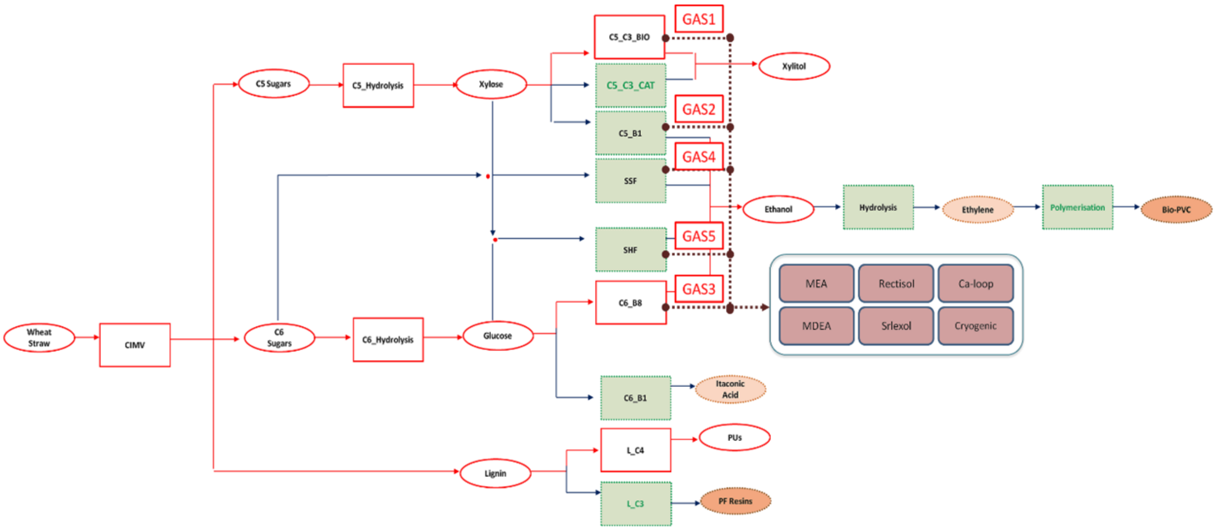


Figure 8.18. Superstructure - Example 2 (gas)

Table 8.6. Results summary - Example 2 (gases)

	Gas 1	Gas 2
Technology	MEA	Ca-loop
Fixed Cost	0.006	0.031
Total Cost (M$/yr)	0.038	

8.4.4 Retrofitting existing installations

The example assumes a bioethanol plant that already uses a small anaerobic digestion (AD) unit to treat its waste. The plant is upgraded into a second generation biorefinery using the products of Portfolio I. Options stand to (a) upgrade treatment adhering to anaerobic technology, now using a larger unit, and (b) combine the existing unit with one or more new units (e.g., new additional units, not excluding options to purchase other small AD units).

The fixed cost of case (a) is estimated at 14.9 $M/yr; the annualized fixed costs account for 16.4 $M/yr and revenue of 1.474 $M/yr available from the biogas that is produced.

In case (b) it is postulated that:

- the set of treatment options remains as discussed in Example 1, and
- the existing unit does not incur payback costs (e.g., it only contributes to energy balances/costs yielding revenues in producing biogas).

The purpose of the optimization remains to identify treatment technologies that could be combined with the existing unit to improve the economic performance of case (a).

In the case where a single technology (N = 1) is allowed to be selected, the best solution is shown in Figure 8.19. The additional unit is, also, an AD process. Table 8.7 presents the cost distribution and the allocation of streams between the existing and the new unit.

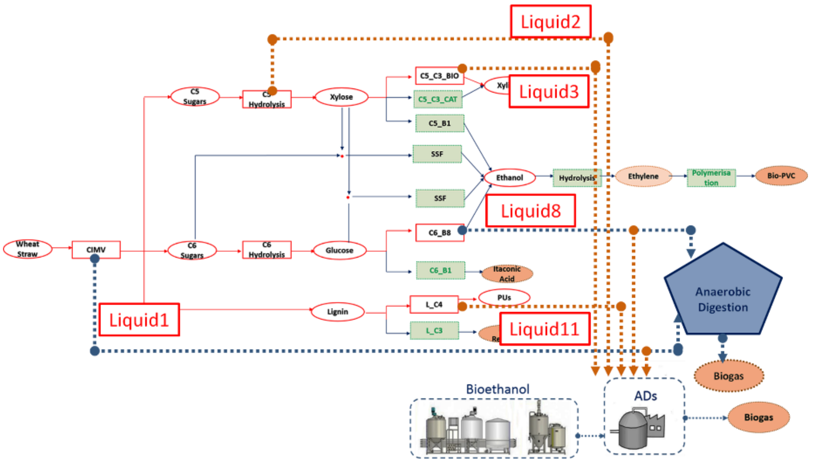


Figure 8.19. Optimal Solution – Example 3 (N=1)

Table 8.7. Costing features comparison

	AD costing	AD+ ADs costing	
	(all liquid streams)	Liquid 1+8	Liquid 1+2+3+8+11
Technology	AD	AD	ADs
Fixed Cost	16,404	5.712	0
Revenue	1,474	0.479	0.998
Total Cost (M$/yr)	14,930	4,234	

For N = 2 the technologies selected include RBC and SP; none involves an anaerobic unit. The result is counterintuitive since, in all previous cases studied, the design options have been dominated by AD units. Figure 8.20 illustrates the optimal solution. Table 8.8 summarizes results, explaining the stream and the cost allocation between the 3 technologies available. Moreover, the overall objective has now turned negative (−0.104 $M/yr), indicating a profitable process in operation. This is a significant improvement over the results of the nominal case (purchase of new and/or complementary AD units) that required 14.9 and 4.234$M/yr, respectively (Table 8.7).

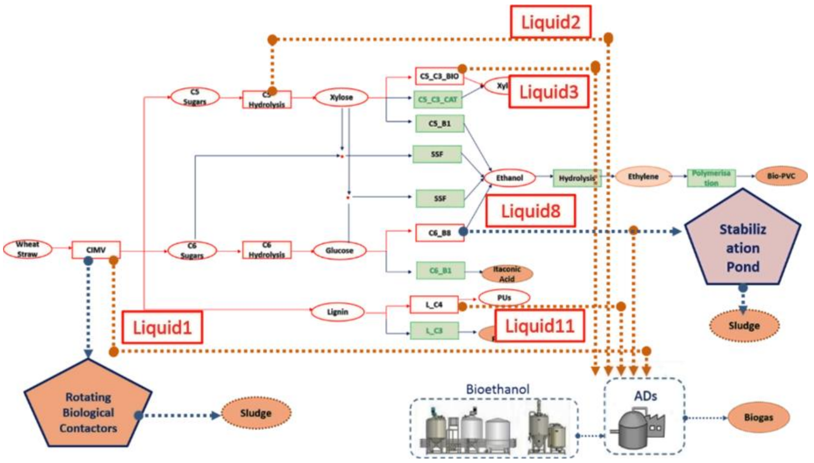


Figure 8.20. Optimal Solution – Example 3 (N=2)

Table 8.8. Costing features comparison.

	AD costing	RBC	SP	ADs
	(all liquid streams)	Liquid 1	Liquid 8	Liquid 1+2+3+8+11
Fixed Cost	16,404	0.082	0.025	0
Revenue	1,474	0.077		1.225
Total Cost (M$/yr)	14,930	-0.1040		

8.5 Discussion

The integration of technologies is systematically leading to the holistic evaluation of options and the development of designs that are economic and efficient. The methodology can be adjusted to restrict the level of integration by constraints on the number of technologies (either per plant or per stream) that are allowed to integrate. The approach is further applicable in retrofitting applications, where the integrated designs essentially convert operating costs into clean profits for the plant. Results generally demonstrate that integration is exceptionally important, often leading to significant savings and cost reductions, even able to turn treatment costs into profits. The integrated approach may yield significant savings in using decentralized treatment and nonconventional solutions.

8.6 References

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Chapter IX

Conclusions

This final chapter extracts the conclusions and the significance of this thesis and sketches directions for future research.

9.1 Conclusions

Sustainable biorefineries must satisfy the economic, environmental, and social demands. Due to the size and the complexity of the problem, the design and optimization of sustainable biorefineries cannot be addressed by a single model; thus, it remains an open field of research. Following the research needs for the industrial development of a real-life biorefinery technology developed in France (CIMV), this thesis proposes a systematic framework to assist in the design decisions about the optimal use of resources, while considering synergies and technological integrations. Focusing mainly on the factors affecting the economic domain and its intersection with the environmental domain, the framework renders generalization in various design scales and combines tools for modeling, integration, and synthesis. The main objective is the cost reduction, while environmental issues are also incorporated as the cost for the utilities and the waste treatment. Challenges include (i) the management of the data acquired by various sources (literature or experimental) and at different accuracy levels due to different TRLs (pilot, laboratory, or theoretical stage), (ii) the systematic screening of possessing paths while considering the technological attributes, (iii) the impact of alternative designs on the utility consumption (mass and energy), (iv) the endogenous symbiotic options when revamping existing installations, and (v) the integrated waste management. The complexity and the size of the problem do not allow the development of a single optimization method. Therefore, the problem is decomposed to smaller sub-problems, and different tools are developed to deal with each "sub-challenge".

The first challenge is to identify and improve the accuracy levels of the data used for the analysis. Surrogate-based optimization emerges as the key producers of harmonized data. The proposed approach makes use of components, thermodynamic, and unit operation models available in existing libraries. Results from Chapter IV confirm the twofold role surrogates can support: a) assist in the systematic development of fine models, searching systematically for shortcomings in the process and property systems, but also b) serve as reliable shortcut models. However, the framework is limited by the availability of process and property models in the libraries of the software selected to develop the fine model.

The second challenge is to assess the market potential of a process in comparison with the competitive technologies. Chapter V introduces a new method for the conditional synthesis of value chains based on a modular superstructure formulation. This modular approach takes into account the product-feed compatibility of each candidate process in order to detect potential relationships amongst the processes. Results verify that different technologies may collaborate or compete to provide products of a certain quality. The first case study, focused mainly on the humid continent, shows that is preferable to discharge the dilute products that spending large amounts of energy to concentrate them. Even though this analysis provides an insight about the environmental cost of linking different technologies and evaluates the readiness of the produced streams, we need to note that this method is short-sighted to the synthesis of individual process units. Integration tools may identify possibilities to provide this energy from different sources.

The third challenge is about the utility consumption and the impact of different design options. Chapter VI introduces the utility network optimization method to optimize simultaneously the use of multiple utilities, while design options are screened as integer options. The approach introduces the concept of interconnected superstructures through hypergraphs. Results support that energy is the most important factor in the utility network. Yet, half of the energy requirements were for the regeneration of the solvent (prior to heat integration). The aquatic mixture of organic solvents needed to be regenerated and recycled for both economic and environmental reasons. The technological choice for the solvent regeneration affects both the investment and the operating cost. However, due to the size and the complexity of the problem, the proposed method had to make some compromises to keep the formulation simple and linear. The method postulates steady state operation and known operating efficiency.

The fourth challenge is to evaluate the potential of CIMV technology as a revamp option for first generation installations. Even though 1G-2G integration studies were already published in the literature, every revamp case is unique. Moreover, the revamp with a second generation process incorporates the inherent value chain synthesis problem, while it may also hide potential synergies. The method presented in Chapter VII systematizes the combined grassroots-retrofit problem and integrates synthesis tools to screen the portfolio of products and look for synergies. Results show that the second generation process should be used as a symbiotic process that valorizes the lignocellulosic biomass discharged by the first generation. Results suggest that the new process should produce valuable 2G products instead of bulk 1G ethanol. Yet the method is restricted to steady state operation at known operating efficiencies. Moreover, revamp problems require a vast amount of detailed data, which need pretreatment and harmonization.

Last but not least is the challenge about the waste management. Every industry needs to treat its effluents. Yet, moving towards the era of circular economy, waste treatment is not the end of the line. Waste streams can be seen as potential raw materials and treatment paths may give different portfolio of products. Chapter VIII presents a systematic method for the integrated waste management. Decision trees are developed to drive streams to different technologies based on their quality. Surrogates are developed to produce data for the treatment technologies. A synthesis problem is formulated in the form of a mixed-integer nonlinear programming problem (MINLP) to select technologies, and the optimal management strategy. Results generally demonstrate that integration is exceptionally important, often leading to significant savings and cost reductions, even able to turn treatment costs into profits. However, the method is limited to the waste streams whose quality is within the limits of the decision maps.

9.2 Significance

This thesis contributes to the scientific community by expanding existing and devising new methodologies for the integrated design of biorefineries but also by producing new knowledge for the industrial development of a real-life biorefinery technology. Starting with the scientific findings, a new use is revealed for the surrogates. Not only can they be used as reliable data sources, but they can also drive improvements in the fine models. Next, the representation of the superstructure as a network of modular sinks and sources automates the alternative space and offers both flexibility and controllability in the system. UNO expands simultaneous mass and energy optimization to systems with multiple components including technological options for process modifications. UNOSR combines grassroots-retrofit and process synthesis tools, in search for industrial synergies. Finally, decision maps and surrogates are developed for the waste treatment technologies, while an optimization method selects the technologies and the management strategy.

Moving to the industrial development of CIMV process, this thesis revealed that the technology is a strong candidate for the design of a multi-product biorefinery, but integration is essential for its sustainability. Surrogate-based optimization revealed shortcomings in the description of the property system and gave valuable insight into how to develop a more flexible and reliable fine model that will allow the safe extrapolation of the resulted surrogates to different operating scenarios. CIMV provides products ready-to-use are different valorization processes. Even though the market prices have significant impact on the selected products, CIMV can provide a wide range of bulk and specialties. Utility consumption is its main drawback, as in all organosolv processes, but with the appropriate integration strategy it can host a number of valorizing processes without increasing its energy consumption. CIMV can also be used to revamp existing installations and profit from the integrated utility network, but also to take the leap and produce in specialties. Finally, the integrated design of waste management reveals strategies for potential profitable uses of the waste streams.

9.3 Future Research

The methods presented in this thesis have not reached their full potential yet. The surrogate-based optimization framework can be integrated with artificial intelligence tools to automatize the search but also the link with the process and property models used from the commercial databanks. The conditional synthesis approach can be enriched with more criterial to verify the technological compatibility among processes, while pure environmental indicators (LCA) can be integrated to assess the environmental impact of both the link and the integrated configuration. Future work in the utility network optimization framework, for both grassroots and retrofit models, can incorporate options for the energy and treatment systems. The methods can also be used to analyze total site networks. A challenge would also be to address the non-linearized formulation by considering the mass exchange units and their energy consumption. The version for the retrofitting can also be integrated with artificial intelligence tools for a more sophisticated search of potential synergies. Mass exchange networks and artificial intelligence can assist in the development of the waste management framework. The approach can be expanded to other waste types, while also considering the process design of the treatment technologies.

In closing, it is important to note that the design of sustainable integrated biorefineries is an interdisciplinary task. Engineers, technicians, chemists, biologists, agricultural economists, market analysts etc. are deployed to reveal which conditions and uncertainties may have a significant impact on the decision making process and how the technology can be improved and resilient to changes. Multiscale modeling and systems engineering tools in collaboration with artificial intelligence techniques have still a lot to offer in this direction.

APPENDICES

Appendix A

A.1 Summary

Appendix A includes the data tables and the list of mathematical symbols for Chapter IV. Tables A1 to A3 present the data used for the modeling of the biomass component. Tables A4 to A12 describe the property system of the final run. Tables A13 to A24 present the parameters of the surrogates of CIMV process for six different biomass types: wheat straw, rice straw, poplar, sugarcane bagasse, banana stem, and miscanthus.

A.2 Biomass Modeling

Table A1. Wheat straw composition – version 01

	Wheat straw input in ASPEN			
	MIXED	**Type**	**Name**	**wt.%**
	H2O	Conventional	WATER	10.00
	CISOLID			
C5	Xylan	Solid	GLUTARIC-ACID	13.07
	Arabinan	Solid	GLUTARIC-ACID	1.97
C6	Glucan	Solid	DILACTIC-ACID	45.25
	Galactan	Solid	DILACTIC-ACID	1.60
Lignin	Lignin	Solid	LIGNIN-1	25.31
Minerals	Ash-insoluble	Solid	SiO2	3.50
	Acetyl*	Solid	ACETIC-ACID	2.18
	Ash-soluble	Solid	KCL	0.31
Other	Rest-soluble	Solid	CITRIC-ACID	5.60
	Rest-insoluble	Solid	CITRIC-ACID	1.21

**The solid state of AA introduces an "error" in the thermodynamic calculations that predicts correctly the properties of the acetyl group, according to Wooley and Putsche (1996)*

Table A2. Pulp description as a nonconventional component (after extraction)

Pulp					
PROXANAL	**%**	**SULFANAL**	**%**	**ULTANAL**	**%**
Moisture	15.00				
Ash	4.90	Pyritic	0.08	Ash	4.90
Volatile	81.30	Sulfate	0.06	C	41.27
Fixed Carbon	13.80	Organic	0.01	H	6.19
				N	0.19
				Cl	0.32
				S	0.15
				O	46.98
sum	100.00	sum	0.15	sum	100.00

Table A3. Glucan description as a nonconventional component (after delignification)

<table>
<tr><th colspan="6">Glucan</th></tr>
<tr><th>PROXANAL</th><th>%</th><th>SULFANAL</th><th>%</th><th>ULTANAL</th><th>%</th></tr>
<tr><td>Moisture</td><td>15.00</td><td></td><td></td><td></td><td></td></tr>
<tr><td>Ash</td><td>0.74</td><td>Pyritic</td><td>0.08</td><td>Ash</td><td>0.74</td></tr>
<tr><td>Volatile</td><td>88.30</td><td>Sulfate</td><td>0.06</td><td>C</td><td>43.07</td></tr>
<tr><td>Fixed Carbon</td><td>10.96</td><td>Organic</td><td>0.01</td><td>H</td><td>6.47</td></tr>
<tr><td></td><td></td><td></td><td></td><td>N</td><td>0.20</td></tr>
<tr><td></td><td></td><td></td><td></td><td>Cl</td><td>0.33</td></tr>
<tr><td></td><td></td><td></td><td></td><td>S</td><td>0.15</td></tr>
<tr><td></td><td></td><td></td><td></td><td>O</td><td>49.04</td></tr>
<tr><td>sum</td><td>100.00</td><td>sum</td><td>0.15</td><td>sum</td><td>100.00</td></tr>
</table>

A.3 Property System – Final Version

Table A4. Property System – Extraction section

<table>
<tr><th colspan="5">Conventional</th></tr>
<tr><td>H2O</td><td>AA</td><td>FA</td><td></td><td></td></tr>
<tr><th colspan="5">Nonconventional</th></tr>
<tr><td>Biomass</td><td colspan="2">Pulp</td><td colspan="2"></td></tr>
<tr><td colspan="5">g_c</td></tr>
<tr><td colspan="5">NRTL-RK</td></tr>
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Table A5. Property System – Delignification section

<table>
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<tr><th colspan="5">Nonconventional</th></tr>
<tr><td colspan="2"></td><td>Pulp</td><td colspan="2">Glucan</td></tr>
<tr><td colspan="5">g_c</td></tr>
<tr><td colspan="5">NRTL-RK</td></tr>
</table>

Table A6. Property System – Deacidification section

<table>
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<tr><td colspan="2"></td><td></td><td colspan="2">Glucan</td></tr>
<tr><td colspan="5">g_c</td></tr>
<tr><td colspan="5">Regressed</td></tr>
</table>

Table A7. Property System – Pulp section

<table>
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<tr><td>H2O</td><td>AA</td><td>FA</td><td></td><td>NaOH</td></tr>
<tr><th colspan="5">Nonconventional</th></tr>
<tr><td colspan="2"></td><td></td><td colspan="2">Glucan</td></tr>
<tr><th colspan="5">Mixture of pseudo-components</th></tr>
<tr><td colspan="2"></td><td>C6 pulp</td><td colspan="2"></td></tr>
<tr><td colspan="2"></td><td>C6</td><td colspan="2"></td></tr>
<tr><td colspan="2"></td><td>C5</td><td colspan="2"></td></tr>
<tr><td colspan="2"></td><td>Lignin</td><td colspan="2"></td></tr>
<tr><td colspan="2"></td><td>SiO2</td><td colspan="2"></td></tr>
<tr><td colspan="2"></td><td>Mineral</td><td colspan="2"></td></tr>
<tr><td colspan="2"></td><td>Other</td><td colspan="2"></td></tr>
<tr><td colspan="5">g_c</td></tr>
<tr><td colspan="5">NRTL-RK</td></tr>
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Table A8. Property System – Evaporation section

<table>
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<tr><th colspan="7">Mixture of pseudo-components</th></tr>
<tr><th colspan="2">C5 syrup</th><td colspan="2"></td><th colspan="3">BioLignin</th></tr>
<tr><td colspan="2">C5</td><td colspan="2"></td><td colspan="3">Lignin</td></tr>
<tr><td colspan="2">C6</td><td colspan="2"></td><td colspan="3">C6</td></tr>
<tr><td colspan="2">Lignin</td><td colspan="2"></td><td colspan="3">C5</td></tr>
<tr><td colspan="2">SiO2</td><td colspan="2"></td><td colspan="3">SiO2</td></tr>
<tr><td colspan="2">Mineral</td><td colspan="2"></td><td colspan="3">Mineral</td></tr>
<tr><td colspan="2">Other</td><td colspan="2"></td><td colspan="3">Other</td></tr>
<tr><td colspan="2"></td><td colspan="2"></td><td colspan="3"></td></tr>
<tr><th colspan="7">g_c</th></tr>
<tr><td colspan="7">Regressed</td></tr>
</table>

Table A9. Property System – Lignin treatment section

<table>
<tr><th colspan="7">Conventional</th></tr>
<tr><td>H2O</td><td colspan="2">AA</td><td colspan="2">FA</td><td></td><td></td></tr>
<tr><th colspan="7">Mixture of pseudo-components</th></tr>
<tr><td colspan="2"></td><td colspan="2"></td><th colspan="3">BioLignin</th></tr>
<tr><td colspan="2"></td><td colspan="2"></td><td colspan="3">Lignin</td></tr>
<tr><td colspan="2"></td><td colspan="2"></td><td colspan="3">C6</td></tr>
<tr><td colspan="2"></td><td colspan="2"></td><td colspan="3">C5</td></tr>
<tr><td colspan="2"></td><td colspan="2"></td><td colspan="3">SiO2</td></tr>
<tr><td colspan="2"></td><td colspan="2"></td><td colspan="3">Mineral</td></tr>
<tr><td colspan="2"></td><td colspan="2"></td><td colspan="3">Other</td></tr>
<tr><td colspan="2"></td><td colspan="2"></td><td colspan="3"></td></tr>
<tr><th colspan="7">g_c</th></tr>
<tr><td colspan="7">NRTL-RK</td></tr>
</table>

Table A10. Property System – C5 Concentration section

<table>
<tr><th colspan="7">Conventional</th></tr>
<tr><td>H2O</td><td colspan="2">AA</td><td colspan="2">FA</td><td></td><td></td></tr>
<tr><th colspan="7">Nonconventional</th></tr>
<tr><td colspan="2">Biomass</td><td colspan="2">Pulp</td><td colspan="3">Glucan</td></tr>
<tr><th colspan="7">Mixture of pseudo-components</th></tr>
<tr><th colspan="2">C5 syrup</th><th colspan="2">C6 pulp</th><th colspan="3">BioLignin</th></tr>
<tr><td colspan="2">C5</td><td colspan="2">C6</td><td colspan="3">Lignin</td></tr>
<tr><td colspan="2">C6</td><td colspan="2">C5</td><td colspan="3">C6</td></tr>
<tr><td colspan="2">Lignin</td><td colspan="2">Lignin</td><td colspan="3">C5</td></tr>
<tr><td colspan="2">SiO2</td><td colspan="2">SiO2</td><td colspan="3">SiO2</td></tr>
<tr><td colspan="2">Mineral</td><td colspan="2">Mineral</td><td colspan="3">Mineral</td></tr>
<tr><td colspan="2">Other</td><td colspan="2">Other</td><td colspan="3">Other</td></tr>
<tr><td colspan="2"></td><td colspan="2"></td><td colspan="3"></td></tr>
<tr><th colspan="7">g_c</th></tr>
<tr><td colspan="7">NRTL-RK</td></tr>
</table>

Table A11. Property System – Solvent regeneration section

<table>
<tr><th colspan="5">Conventional</th></tr>
<tr><td>H2O</td><td>AA</td><td>FA</td><td></td><td></td></tr>
<tr><th colspan="5">g_c</th></tr>
<tr><td colspan="5">Regressed</td></tr>
</table>

Table A12. Property System – Storage Tank section

<table>
<tr><th colspan="5">Conventional</th></tr>
<tr><td>H2O</td><td>AA</td><td>FA</td><td></td><td></td></tr>
<tr><th colspan="5">Mixture of pseudo-components</th></tr>
<tr><td>C5</td><td></td><td colspan="3"></td></tr>
<tr><td>C6</td><td></td><td colspan="3"></td></tr>
<tr><td>Lignin</td><td></td><td colspan="3"></td></tr>
<tr><td>SiO2</td><td></td><td colspan="3"></td></tr>
<tr><td>Mineral</td><td></td><td colspan="3"></td></tr>
<tr><td>Other</td><td></td><td colspan="3"></td></tr>
<tr><td></td><td></td><td colspan="3"></td></tr>
<tr><td colspan="5">g_c</td></tr>
<tr><td colspan="5">NRTL-RK</td></tr>
</table>

A.4 Parameters for the Surrogates

Table A13. Surrogate parameters (wheat straw)*

n=Wheat straw/ p=CIMV organosolv										
q	**C6 Pulp**		**C5 syrup**		**Biolignin**		**Silica**		**Losses**	
wt.%	α_1	α_2	α_1	α_2	α_1	α_2	α_1	α_2	α_1	α_2
F^{OUT}	0.487		0.220		0.258		0.018		0.017	
c=C6		0.978		0.012		0.000				0.008
c=C5		0.334		0.555		0.072				0.037
c=Lignin		0.024				0.963				0.012
c=Mineral		0.017		0.869		0.044				0.068
c=SiO2		0.018		0.253		0.019		0.692		0.015
c=Other				1.000						

*(AA/FA/H_2O = 30/55/15)

Table A14. Streams composition (wheat straw)

wt.%	Wheat Straw	C6 pulp	C5 syrup	Biolignin	Silica	Losses
C6	42.6%	85.6%	2.5%	0.03%		20.89%
C5	18.8%	12.9%	47.5%	5.3%		41.19%
Lignin	25.1%	1.25%		93.73%		18.17%
Minerals	4.3%	0.15%	17.00%	0.74%		17.41%
SiO_2	2.6%	0.1%	3.00%	0.2%	100.00%	2.34%
Other	6.6%		30.00%			

Table A15. Surrogate parameters (rice straw)*

n=Rice straw/ p=CIMV organosolv								
q	**C6 Pulp**		**C5 syrup**		**Biolignin**		**Losses**	
wt.%	α_1	α_2	α_1	α_2	α_1	α_2	α_1	α_2
F^{OUT}	0.5165		0.1962		0.2577		0.0296	
c=C6		0.9791		0.0132		0.0002		0.0075
c=C5		0.3358		0.5565		0.0738		0.0339
c=Lignin		0.0245				0.9656		0.0099
c=Minerals		0.0200		0.6367		0.0350		0.3083
c=Other				1.0000				

*(AA/FA/H_2O = 30/55/15)

Table A16. Streams composition (rice straw)

wt.%	Rice Straw	C6 pulp	C5 syrup	Biolignin	Losses
C6	46.84%	88.79%	3.16%	0.04%	11.82%
C5	15.04%	9.78%	42.66%	4.31%	17.23%
Lignin	25.31%	1.2%		94.84%	8.45%
Minerals	6,00%	0.23%	19.47%	0.81%	62.5%
Other	6.81%		34.71%		

Table A17. Surrogate parameters (poplar with bark)*

n=Poplar/ p=CIMV organosolv								
q	**C6 Pulp**		**C5 syrup**		**Biolignin**		**Losses**	
wt.%	α_1	α_2	α_1	α_2	α_1	α_2	α_1	α_2
F^{OUT}	0.4890		0.1717		0.3108		0.0285	
c=C6		0.9591		0.0351		0.0002		0.0056
c=C5		0.3095		0.5914		0.0942		0.0049
c=Lignin		0.0205				0.9564		0.0231
c=Minerals		0.0713		0.4851		0.0276		0.4160
c=Other				1.0000				

*(AA/FA/H_2O = 55/30/15)

Table A18. Streams composition (poplar with bark)

wt.%	Poplar	C6 pulp	C5 syrup	Biolignin	Losses
C6	44.76%	87.79%	9.14%	0.03%	8.77%
C5	16.25%	10.29%	55.97%	4.92%	2.81%
Lignin	30.76%	1.29%		94.66%	24.91%
Minerals	4.35%	0.63%	12.29%	0.39%	63.51%
Other	3.88%		22.6%		

Table A19. Surrogate parameters (sugarcane bagasse)*

n=Sugarcane bagasse/ p=CIMV organosolv								
q	**C6 Pulp**		**C5 syrup**		**Biolignin**		**Losses**	
wt.%	α_1	α_2	α_1	α_2	α_1	α_2	α_1	α_2
F^{OUT}	0.5187		0.2208		0.2434		0.0171	
c=C6		0.9832		0.0136		0.0005		0.0027
c=C5		0.3348		0.5755		0.0734		0.0163
c=Lignin		0.0250				0.9608		0.0142
c=Minerals		0.0204		0.6565		0.0374		0.2857
c=Other				1.0000				

*(AA/FA/H_2O = 55/30/15)

Table A20. Streams composition (sugarcane bagasse)

wt.%	Bagasse	C6 pulp	C5 syrup	Biolignin	Losses
C6	43.38%	82.22%	2.67%	0.08%	7.02%
C5	25.63%	16.54%	66.8%	7.72%	24.56%
Lignin	23.24%	1.12%		91.74%	19.3%
Minerals	2.94%	0.12%	8.74%	0.46%	49.12%
Other	4.81%		21.79%		

Table A21. Surrogate parameters (banana stem)*

n=Banana stem/ p=CIMV organosolv								
q	**C6 Pulp**		**C5 syrup**		**Biolignin**		**Losses**	
wt.%	α_1	α_2	α_1	α_2	α_1	α_2	α_1	α_2
F^{OUT}	0.4809		0.3690		0.1168		0.0333	
c=C6		0.9775		0.0106		0.0005		0.0114
c=C5		0.3371		0.5586		0.0743		0.0300
c=Lignin		0.0527				0.9391		0.0082
c=Minerals		0.0239		0.6085		0.0408		0.3268
c=Other				1.0000				

*(AA/FA/H_2O = 55/30/15)

Table A22. Streams composition (banana stem)

wt.%	Banana stem	C6 pulp	C5 syrup	Biolignin	Losses
C6	43.6%	88.63%	1.25%	0.17%	15.02%
C5	14,00%	9.81%	21.19%	8.9%	12.61%
Lignin	11,00%	1.21%		88.44%	2.7%
Minerals	7.1%	0.35%	11.71%	2.49%	69.67%
Other	24.3%		65.85%		

Table A23. Surrogate parameters (miscanthus)*

n=Miscanthus/ p=CIMV organosolv								
q	C6 Pulp		C5 syrup		Biolignin		Losses	
wt.%	α_1	α_2	α_1	α_2	α_1	α_2	α_1	α_2
F^{OUT}	0.5352		0.1816		0.2640		0.0192	
c=C6		0.9705		0.0090		0.0007		0.0198
c=C5		0.3370		0.5585		0.0824		0.0221
c=Lignin		0.0269				0.9585		0.0146
c=Minerals		0.0472		0.8208		0.0472		0.0848
c=Other				1.0000				

*(AA/FA/H_2O = 55/30/15)

Table A24. Streams composition (miscanthus)

wt.%	Miscanthus	C6 pulp	C5 syrup	Biolignin	Losses
C6	45.76%	82.98%	2.26%	0.11%	47.4%
C5	24.87%	15.66%	76.69%	7.77%	28.65%
Lignin	25.32%	1.27%		91.93%	19.27%
Minerals	1.06%	0.09%	4.51%	0.19%	4.68%
Other	2.99%		16.54%		

A.5 List of Symbols

Latin Symbols

D	set of real data ($\tilde{x}, \tilde{y} \in D$)
F	flow
f	function for the surrogate
g	thermodynamic models
H	property system
S	process system
u	operating parameters
x	incoming information (materials, energy, etc.)
y	output information
z	binary to select the thermodynamic model

Greek Symbols

α	configuration of the process system (unit operation models and connectivity)
δ	acceptable margin of error
ε	error between the estimated value and the experimental data
ψ	feasibility function

Subscripts and superscripts

c	components
i	iteration for the property system
j	iteration for the process system
k	iteration for the thermodynamic models
m	unit operation models
n	feedstock type
p	process units
q	product stream

Superscripts

L	lower bound
U	upper bound

Appendix B

B.1 Summary

Appendix B includes the data tables and the list of mathematical symbols for Chapter V. Tables B1 to B3 are the data for the calculations on dry basis. Tables B4 to B6 are the data for the calculations on humid basis. Finally, Tables B7 to B9 present the data for the enabler units.

B.2 Tables

Table B1. Separation factor of feed to product streams (Dry basis)

M	J	I	ξ
CIMV	J1	I1	0.2580
	J1	I2	0.4870
	J1	I3	0.2200
AFEX1	J2	I4	0.8010
DA	J3	I5	0.8010
lime	J4	I6	0.8010
LHW	J5	I7	0.8010
SAA	J6	I8	0.8010
SO2	J7	I9	0.8010
SE	J8	I10	0.7856
Biological	J9	I11	0.7856
DSA	J10	I12	0.7856
AFEX2	J11	I13	0.7856
organosolvA	J12	I14	0.1100
	J12	I15	0.4700
	J12	I16	0.2600
	J12	I17	0.0100
	J12	I18	0.0100
SSF1	J13	I19	0.2250
	J13	I20	0.5000
SSF2	J14	I21	0.4500
	J14	I22	0.5000
HydrSep	J15	I23	0.1500
	J15	I24	0.1100
	J15	I25	0.1000
HydC5	J16	I26	1.0000
HydC6	J17	I27	1.0000
FermGL	J18	I28	0.4500
	J18	I29	0.5000
CatXyl	J19	I30	0.8500
BioXyl	J20	I31	0.7300
CHP	J21	I32	1315.8000
	J21	I33	387.0000
	J22	I32	2805.0000
	J22	I33	825.0000

Table B2. Minimum and maximum composition on the process sinks (dry basis)

M	J	N	c^{LB}	c^{UB}
CIMV	J1	Biomass	1.00	1.00
AFEX1	J2	Biomass	1.00	1.00
DA	J3	Biomass	1.00	1.00
Lime	J4	Biomass	1.00	1.00
LHW	J5	Biomass	1.00	1.00
SAA	J6	Biomass	1.00	1.00
SO2	J7	Biomass	1.00	1.00
SE	J8	Biomass	1.00	1.00
Biological	J9	Biomass	1.00	1.00
DSA	J10	Biomass	1.00	1.00
AFEX2	J11	Biomass	1.00	1.00
organosolvA	J12	Biomass	1.00	1.00
SSF1	J13	Sludge	1.00	1.00
SSF2	J14	C6	0.60	0.70
	J14	C5	0.30	0.40
HydrSep	J15	Sludge	1.00	1.00
HydC5	J16	C5	1.00	1.00
HydC6	J17	C6	1.00	1.00
FermGL	J18	Glucose	1.00	1.00
CatXyl	J19	Xylose	1.00	1.00
BioXyl	J20	Xylose	1.00	1.00
CHP	J21	Biomass		1.00
	J21	Sludge		1.00
	J21	SolidRes		1.00
	J22	Lignin	1.00	1.00

Table B3. Heat requirements and equipment cost per process

M	q^H [kWh/tn feed]	**Investment** [MM$ 2016]	**Capacity 0** [kt/yr]
CIMV	1.7816	140.28	170.0
AFEX1	0.6250	31.96	700.5
DA	0.7808	46.40	700.5
Lime	0.6727	58.77	700.5
LHW	2.1887	20.63	700.5
SAA	1.0578	46.40	700.5
SO2	0.9044	36.08	700.5
SE	0.7415	23.67	666.3
Biological	0.0326	275.04	1675.4
DSA	0.9938	22.32	746.8
AFEX2	5.4390	16.52	818.7
organosolvA	0.4570	74.86	666.7
SSF1	1.9718	13.39	5.66
SSF2	1.7933	13.39	5.66
HydrSep	0.4653	87.08	708.00
HydC5	0.3660	3.49	1.76
HydC6	0.4185	5.62	3.90
FermGL	1.6853	5.08	3.90
CatXyl	0.2888	4.45	33.04
BiochXyl	0.0061	21.83	33.04

Table B4. Separation factor of the feed to product streams (with H2O)

M	J	I	ξ
CIMV	J1	I1	0.2606
	J1	I2	2.4350
	J1	I3	0.3385
AFEX1	J2	I4	0.8010
DA	J3	I5	0.8010
Lime	J4	I6	0.8010
LHW	J5	I7	0.8010
SAA	J6	I8	0.8010
SO2	J7	I9	0.8010
SE	J8	I10	0.7856
Biological	J9	I11	0.7856
DSA	J10	I12	0.7856
AFEX2	J11	I13	0.7856
organosolvA	J12	I14	0.1111
	J12	I15	3.1333
	J12	I16	1.0400
	J12	I17	0.0103
	J12	I18	0.0103
SSF1	J13	I19	0.2273
	J13	I20	0.5000
SSF2	J14	I21	0.1000
	J14	I22	0.1100
HydrSep	J15	I23	0.2500
	J15	I24	0.1833
	J15	I25	0.1000
HydC5	J16	I26	0.3667
HydC6	J17	I27	0.3667
FermGL	J18	I28	0.1000
	J18	I29	0.1100
CatXyl	J19	I30	0.5784
BiochXyl	J20	I31	0.0903
CHP	J21	I32	1315.8000
	J21	I33	387.0000
	J22	I32	2805.0000
	J22	I33	825.0000

Table B5. Minimum and maximum composition on the process sinks (with H2O)

M	J	N	c^{LB}	c^{UB}
CIMV	J1	Biomass	1.00	1.00
AFEX1	J2	Biomass	1.00	1.00
DA	J3	Biomass	1.00	1.00
lime	J4	Biomass	1.00	1.00
LHW	J5	Biomass	1.00	1.00
SAA	J6	Biomass	1.00	1.00
SO2	J7	Biomass	1.00	1.00
SE	J8	Biomass	1.00	1.00
Biological	J9	Biomass	1.00	1.00
DSA	J10	Biomass	1.00	1.00
AFEX2	J11	Biomass	1.00	1.00
organosolvA	J12	Biomass	1.00	1.00
SSF1	J13	Sludge	1.00	1.00
SSF2	J14	C6	0.09	0.14
	J14	C5	0.05	0.08
	J14	H2O	0.78	0.85
HydrSep	J15	Sludge	1.00	1.00
HydC5	J16	C5	0.15	0.22
	J16	H2O	0.78	0.85
HydC6	J17	C6	0.15	0.22
	J17	H2O	0.78	0.85
FermGL	J18	Glucose	0.15	0.22
	J18	H2O	0.78	0.85
CatXyl	J19	Xylose	0.58	0.66
	J19	H2O	0.34	0.42
BiochXyl	J20	Xylose	0.08	0.12
	J20	H2O	0.88	0.92
CHP	J21	Biomass		1.00
	J21	Sludge		1.00
	J21	SolidRes		1.00
	J22	Lignin	1.00	1.00

Table B6. Minimum and maximum composition on the consumers (with H2O)

J	N	c^{LB}	c^{UB}
B1	C5	0.58	0.65
B1	H2O	0.35	0.42
B2	C6	0.58	0.62
B2	H2O	0.38	0.42
B3	Lignin	0.99	1.00
B3	H2O		0.01
B4	Xylose	0.58	0.62
B4	H2O	0.38	0.42
B5	Glucose	0.58	0.62
B5	H2O	0.38	0.42
B6	EtOH	0.99	1.00
B6	H2O		0.01
B7	Xylitol	0.95	1.00
B7	H2O		0.05
B8	Furfural	0.95	1.00
B8	H2O		0.05
B9	Aacid	0.95	1.00
B9	H2O		0.05
B10	Steam	1.00	1.00
B11	Electricity	1.00	1.00

Table B7. Separation factor of the enabler units

M	**J**	**I**	**ξ**	**q^H** [kWh/tn feed]
EU1	En1	Eo1	0.3333	0.4185
	En1	Eo2	0.6667	
EU2	En2	Eo3	0.4167	0.3662
	En2	Eo4	0.5833	
EU3	En3	Eo5	0.2500	0.4709
	En3	Eo6	0.7500	

Table B8. Composition on the sources of the enable units

M	**I**	**N**	**c^{OUT}**
EU1	Eo1	C6	0.60
	Eo1	H2O	0.40
	Eo2	H2O	1.00
EU2	Eo3	C5	0.60
	Eo3	H2O	0.40
	Eo4	H2O	1.00
EU3	Eo5	C6	0.60
	Eo5	H2O	0.40
	Eo6	H2O	1.00

Table B9. Minimum and maximum composition on the sinks of the enable units

M	**J**	**N**	**c^{LB}**	**c^{UB}**
EU1	En1	C6	0.19	0.21
	En1	H2O	0.79	0.81
EU2	En2	C5	0.24	0.26
	En2	H2O	0.74	0.76
EU3	En3	C6	0.14	0.16
	En3	H2O	0.84	0.86

B.3 List of Symbols

Latin Symbols

c	concentration	[ktn ktn^{-1}]
Cost	cost	[M\$ yr^{-1}]
F	mass flow	[ktn yr^{-1}]
LU	large unit	
pp	purchase price	[M\$ ktn^{-1} or M\$ MW^{-1}]
Profit	profit	[M\$ yr^{-1}]
q	energy requirements (parameter)	[MW yr^{-1} kt^{-1}]
Q	energy requirements (variable)	[MW yr^{-1}]
RA	raw material availability	[ktn yr^{-1}]
Revenue	revenue	[M\$ yr^{-1}]
sp	selling price	[M\$ ktn^{-1} or M\$ MW^{-1}]
tp	treatment price	[M\$ ktn^{-1} or M\$ MW^{-1}]
Z	integer variable	

Greek Symbols

α	slope in the piecewise linearized cost function	$[\mathrm{M\$\ ktn^{-1}}]$
β	fixed parameter in the piecewise linearized cost function	$[\mathrm{M\$\ yr^{-1}}]$
ξ	conversion factor	$[\mathrm{ktn\ ktn^{-1}}]$

Subscripts and superscripts

i	sources
j	sinks
m	process units
n	raw materials and utilities

Superscripts

B	consumers
C	cold utilities (energy)
CI	capital investment
E	energy
H	hot utilities (energy)
IN	incoming
LB	lower bound
M	materials
OP	operating
OUT	outgoing
P	processes
S	suppliers
Total	total amount
UB	upper bound
W	waste treatment

Appendix C

C.1 Summary

Appendix C includes the list of mathematical symbols and tables of Chapter VI. Tables C1 to C6 present the data used to setup the problem. Tables C7 to C9 present the mass flow results.

C.2 Data Tables

Table C.1. Process units & Mass exchange locations

M	**$i \in I^M, j \in J^M$**
m^P_1 (Handling)	$\{i_{14}\}$
m^P_2 (Extraction)	$\{j_1, j_2\}$
m^P_3 (Delignification)	$\{i_5, i_6, j_3\}$
m^P_4 (Deacidification)	$\{i_7\}$
m^P_5 (Pulp)	$\{i_8, j_4, j_5\}$
m^P_6 (Evaporation)	$\{i_9, i_{10}\}$
m^P_7 (Lignin)	$\{i_{11}, j_6, j_7\}$
m^P_8 (C5)	$\{i_{12}, i_{13}, j_8\}$
m^N_1 (Supply)	$\{i_1, i_2, i_3\}$
m^N_2 (Treatment)	$\{j_9\}$
m^N_3 (Storage - Slv)	$\{i_{14}, j_{10}\}$
m^N_4 (Storage – Slv2)	$\{i_{15}, j_{11}\}$
m^N_5 (Storage – WT)	$\{i_{16}, j_{12}\}$
m^N_6 (Upgrade - D1)	$\{i_{17}, i_{18}, i_{19}, i_{20}, i_{21}, i_{22}, j_{13}, j_{14}, j_{15}\}$
m^N_7 (Upgrade - D2)	$\{i_{23}, i_{24}, i_{25}, i_{26}, i_{27}, i_{28}, i_{29}, i_{30}, j_{16}, j_{17}, j_{18}\}$
m^N_8 (Upgrade - LLE)	$\{i_{31}, i_{32}, i_{33}, i_{34}, j_{19}, j_{20}\}$

Table C.2. Separation factor of the auxiliary units

	m	**$j \in J^M$**	**$i \in I^M$**	**ξ**
Slv	m^N 3	j10	i14	1.000
Slv2	m^N 4	j11	i15	1.000
WT	m^N 5	j12	i16	1.000
D-1	m^N 6	j13	i17	0.083
	m^N 6	j13	i18	0.917
	m^N 6	j14	i19	0.824
	m^N 6	j14	i20	0.176
	m^N 6	j15	i21	0.851
	m^N 6	j15	i22	0.149
D-2	m^N 7	j16	i23	0.083
	m^N 7	j16	i24	0.917
	m^N 7	j17	i25	0.250
	m^N 7	j17	i26	0.177
	m^N 7	j18	i27	0.573
	m^N 7	j18	i28	0.192
	m^N 7	j18	i29	0.149
	m^N 7	J18	i30	0.659
LLE	m^N 8	j19	i31	0.083
	m^N 8	j19	i32	0.917
	m^N 8	j20	i33	0.870
	m^N 8	j20	i34	0.130

Table C.3. Steams with fixed flowrates

$i \in I^E$, $j \in J^E$	**Flowrate [tn/hr]**	**T_S^{IN} [°C]**	**T_S^{OUT} [°C]**	**cp [kW/K tn]**
j1	57.50	10.0	99.0	0.748
j2	57.50	99.0	100.0	147.016
j3	48.32	86.5	99.0	0.711
j4	48.32	104.0	105.0	135.762
j5	82.37	20.0	70.0	1.093
j6	146.32	64.0	65.0	1.203
j7	137.71	44.0	45.0	167.217
j8	19.57	49.9	99.0	0.728
j9	19.57	99.0	100.0	251.477
j10	54.10	58.0	59.0	495.534
i1	27.5	104.4	103.4	242.301
i2	8.61	65.0	64.0	217.271
i3	110.50	44.3	43.3	226.337
i4	8.09	100.6	99.6	607.342
i5	44.41	58.7	57.7	588.390
i6	8.89	70.0	69.0	570.011

Table C4. Streams with variable flowrates (auxiliary process units)

$i \in I^E$, $j \in J^E$	**T_S^{IN} [°C]**	**T_S^{OUT} [°C]**	**cp [kW/K tn]**
i7	144.7	143.7	585.763
i8	144.7	143.7	2,130.866
i9	144.7	143.7	2,270.975
i10	128.5	127.5	585.763
i11	128.5	127.5	891.040
i12	100.7	99.7	780.210
i13	111.0	80.0	0.510
i14	128.5	127.5	616.235
i15	100.7	99.7	869.615
i16	111.0	80.0	0.001
i17	134.6	133.6	799.835
i18	77.5	76.5	1,128.587
j11	158.8	159.8	646.582
j12	158.8	159.8	2,204.252
j13	158.8	159.8	2,355.303
j14	142.8	143.8	646.580
j15	142.8	143.8	391.920
j16	110.0	111.0	800.000
j17	142.8	143.8	634.230
j18	110.0	111.0	900.698
j19	148.4	149.4	852.247
j20	104.0	105.0	7,176.852
j21	25.0	60.0	0.027
j22	57.0	60.0	1.720
i19	76.5	55.0	1.650
*j23	78.6 (L)	78.7 (V)	6,429.076

*does not exist if (i4,j8) V-V link exist in the MEN

Table C.5 Data for the mass sources

	i∈I^M	T_i	cp	F_{mi}^{OUT*}	c_n			
		[°C]	**[kW/K tn]**	**[tn/hr]**	**H2O**	**FA**	**AA**	**solids**
I^F	i1	15.0	1.131	800.00	100.0%			
	i2	20.0	0.500	800.00			100.0%	
	i3	20.0	0.496	800.00		100.0%		
I^P	i4	100 (V-L)	628.613	13.40	100.0%			
		99 (L)	1.151					
		100 (V-V)	0.441					
	i5	86.5	0.767	27.00	20.7%	50.7%	27.6%	1.0%
	i6	86.5	0.749	76.63	18.5%	51.5%	28.1%	1.9%
	i7	103.4	0.017	27.35	18.5%	53.4%	28.1%	
	i8	70.0	1.090	117.51	88.6%	0.6%	0.5%	10.3%
	i9	64.0	0.722	8.61	15.6%	57.8%	26.6%	
	i10	43.3	0.716	110.50	16.8%	54.2%	29.0%	
	i11	99.6	1.177	8.09	96.7%	1.8%	1.5%	
	i12	69.0	1.104	8.89	83.1%	10.6%	6.3%	
	i13	57.7	0.554	44.41	85.6%	7.8%	6.6%	
I^B	i14	80.0	0.730		15.0%	55.0%	30.0%	
	i15	80.0	0.709		14.0%	54.0%	29.0%	3.0%
	i16	40.0	1.145		100.0%			
I^U	i17	143.7	1.187		99.2%	0.8%		
	i18	159.9	0.733		8.0%	63.0%	29.0%	
	i19	143.7	1.183		99.2%	0.05%	0.75%	
	i20	159.9	0.727		8.0%	59.8%	32.2%	
	i21	143.7	1.183		99.2%	0.77%	0.03%	
	i22	159.9	0.713		8.0%	52.1%	39.9%	
	i23	127.5	1.171		99.2%	0.8%		
	i24	143.9	0.718		8.0%	63.0%	29.0%	
	i25	127.5	1.171		99.2%	0.75%	0.05%	
	i26	143.9	0.713		8.0%	59.8%	32.2%	
	i27	99.7	1.133		99.2%	0.7%	0.1%	
	i28	127.5	1.172		99.2%	0.2%	0.6%	
	i29	143.9	0.699		8.0%	52.0%	40.0%	
	i30	99.7	1.156		99.2%		0.8%	
	i31	133.6	1.179		99.2%	0.8%		
	i32	149.6	0.724		8.0%	63.0%	29.0%	
	i33	53.0	1.286		97.1%	2.2%	0.7%	
	i34	105.0	0.0006		5.5%	49.1%	45.4%	

Table C.6. Data for the mass sinks

	$j \in J^M$	Tj	F_{mj}^{IN*}	c_{jn}^{UB}				c_{jn}^{LB}			
		[°C]	**[tn/hr]**	**H2O**	**FA**	**AA**	**solids**	**H2O**	**FA**	**AA**	**solids**
$\mathbf{J^P}$	j1	85.0	93.80	17.0%	55.0%	31.0%	3,0%	13.0%	54.0%	29.0%	
	j2	105.0	135.00	17.0%	55.0%	31.0%	3,0%	13.0%	54.0%	29.0%	
	j3	80.0	22.10	17.0%	55.0%	31.0%	3,0%	13.0%	54.0%	29.0%	
	j4	70.0	62.40	100.0%	3.0%	3.0%		97.0%			
	j5	30.0	37.50	100.0%				100.0%			
	j6	50.0	23.20	100.0%	6.0%	6.0%		94.0%			
	j7	50.0	23.20	100.0%				100.0%			
	j8	78.6 (L) 78.7 (V)	7.90	100.0%				100.0%			
$\mathbf{J^T}$	j9	37.0									
$\mathbf{J^B}$	j10	80.0		15.0%	55.0%	30.0%		15.0%	55.0%	30.0%	
	j11	80.0		14.0%	54.0%	29.0%	3,0%	14.0%	54.0%	29.0%	3.0%
	j12	40.0		100.0%				100.0%			
$\mathbf{J^U}$	j13	80.0		15.6%	57.8%	26.6%		15.6%	57.8%	26.6%	
	j14	70.0		83.1%	10.6%	6.3%		83.1%	10.6%	6.3%	
	j15	80.0		85.6%	7.8%	6.6%		85.6%	7.8%	6.6%	
	j16	80.0		15.6%	57.8%	26.6%		15.6%	57.8%	26.6%	
	j17	70.0		83.1%	10.6%	6.3%		83.1%	10.6%	6.3%	
	j18	70.0		85.6%	7.8%	6.6%		85.6%	7.8%	6.6%	
	j19	80.0		15.6%	57.8%	26.6%		15.6%	57.8%	26.6%	
	j20	60.0		85.2%	8.3%	6.5%		85.2%	8.3%	6.5%	

C.3 Results Tables

Table C.7. Matching in MEN – Case 0

#	$i \in I^M$	$j \in J^M$	Fij [tn/hr]
1	i1	j4	12.19
2	i1	j5	37.50
3	i1	j6	9.61
4	i1	j7	23.20
5	i2	j10	1.33
6	i3	j10	1.14
7	i4 (V)	j6 (L)	5.50
8	i4 (V)	j8 (V)	7.90
9	i5	j11	27.00
10	i6	j11	76.63
11	i7	j10	27.35
12	I8	j9	117.51
13	i9	j16	8.61
14	i10	j10	57.62
15	i10	j16	52.88
16	i11	j6	8.09
17	i12	j17	8.89
18	i13	j18	44.41
19	i14	j2	135.00
20	i14	j3	22.10
21	i15	j1	93.80
22	i15	j10	4.74
23	i23	j4	5.10
24	i24	j10	56.38
25	i25	j4	2.22
26	i26	j10	1.57
27	i27	j4	5.09
28	i28	j4	8.53
29	i29	j10	6.62
30	i30	j4	29.27

Table C.8. Matching in MEN – Case 1

#	**$i \in I^M$**	**$j \in J^M$**	**Fij [tn/hr]**
1	i1	j4	28.43
2	i1	j5	37.50
3	i1	j6	2.49
4	i1	j7	23.20
5	i1	j8	7.90
6	i2	j2	1.21
7	i2	j3	0.24
8	i3	j3	0.01
9	i4	j4	13.40
10	i5	j2	27.00
11	i6	j1	8.79
12	i6	j2	67.84
13	i7	j1	2.36
14	i7	j3	18.92
15	i7	j16	6.08
16	i8	j9	117.51
17	i9	j16	8.61
18	i10	j1	79.67
19	i10	j16	30.83
20	i11	j6	8.09
21	i12	j17	8.89
22	i13	j4	12.55
23	i13	j6	7.53
24	i13	j9	13.82
25	i13	j18	10.50
26	i23	j4	3.78
27	i24	j1	2.07
28	i24	j2	36.72
29	i24	j3	2.95
30	i25	j4	2.22
31	i26	j2	1.57
32	i27	j6	5.09
33	i28	j4	2.02
34	i29	j1	0.91
35	i29	j2	0.65
36	i30	j9	6.92

Table C.9. Matching in MEN – Case 2

#	$i \in I^M$	$j \in J^M$	Fij [tn/hr]
1	i1	j4	10.84
2	i1	j5	37.50
3	i1	j7	23.20
4	i1	j8	7.90
5	i2	j11	2.24
6	i3	j11	0.01
7	i4	j4	6.10
8	i4	j6	7.30
9	i5	j11	27.00
10	i6	j11	76.63
11	i7	j11	21.27
12	i7	j16	6.08
13	i8	j9	117.51
14	i9	j16	8.61
15	i10	j11	45.83
16	i10	j16	64.67
17	i11	j6	8.09
18	i12	j17	8.89
19	i13	j4	11.09
20	i13	j6	7.81
21	i13	j9	1.45
22	i13	j18	24.05
23	i15	j1	93.80
24	i15	j2	135.00
25	i15	j3	22.10
26	i23	j4	6.59
27	i24	j11	72.77
28	i25	j4	2.22
29	i26	j11	1.57
30	i27	j4	5.09
31	i28	j4	4.62
32	i29	j11	3.58
33	i30	j4	15.85

C.4 List of Symbols

Latin Symbols

ap	cost for source-sink matching	$[\text{M\$ yr}^{-1}]$
c	concentration	$[\text{ktn ktn}^{-1}]$
Cost	cost	$[\text{M\$ yr}^{-1}]$
cp	specific heat capacity	$[\text{MW ktn}^{-1}\ \text{K}^{-1}]$
F	mass flow	$[\text{ktn yr}^{-1}]$
G	graph	
h	specific heat enthalpy	$[\text{MW ktn}^{-1}]$
LU	large unit	
pp	purchase price	$[\text{M\$ ktn}^{-1}\text{ or M\$ MW}^{-1}]$
Q	heat flow (variable)	$[\text{MW yr}^{-1}]$
R	heat residual	$[\text{MW yr}^{-1}]$
T	temperature	[K]
tp	treatment price	$[\text{M\$ ktn}^{-1}\text{ or M\$ MW}^{-1}]$
Y	integer variable	
Z	integer variable	

Greek Symbols

α	slope in the piecewise linearized cost function	$[\text{M\$ ktn}^{-1}]$
β	fixed parameter in the piecewise linearized cost function	$[\text{M\$ yr}^{-1}]$
ξ	conversion factor	$[\text{ktn ktn}^{-1}]$

Subscripts

i	sources
j	sinks
k	temperature intervals
m	process units
n	utilities
s	streams

Superscripts

B	storage units
C	cold utilities (energy)
CI	capital investment
D	treatment units
E	energy
H	hot utilities (energy)
IN	incoming
LB	lower bound
M	materials
N	auxiliary units
OP	operating
OUT	outgoing
P	processing units (essential)
S	supply units
Total	total amount
TR	treatment
U	upgrade units
UB	upper bound
UT	utilities

Appendix D

D.1 Summary

Appendix D includes four tables to share the data used for the 1G technology in Chapter VII the list of mathematical symbols.

D.2 Tables

Table D.1. Process units & Mass exchange locations – 1G

M	**$i \in I^M$, $j \in J^M$**
m^P_1 (Pretreatment)	{ip_1, ip_2, ip_3, ip_4, ip_5, ip_6, ip_7, ip_8, jp_1, jp_2, jp_3}
m^P_2 (Fermentation)	{ip_9, jp_4}
m^P_3 (EtOH Purification)	{ip_{10}, ip_{11}, ip_{12}, ip_{13}, jp_5, jp_6}
m^P_4 (EtOH Dehydration)	{ip_{14}, jp_7}

Table D.2. Separation factor of the 1G units

M	**$j \in J^M$**	**$i \in I^M$**	**ξ**
mp1	jp1	ip1	7.7400
	jp1	ip2	0.3000
	jp1	ip3	0.0192
	jp1	ip4	0.0488
	jp1	ip5	0.0376
	jp1	ip6	0.4195
	jp1	ip7	0.2368
	jp1	ip8	0.4754
mp2	jp4	ip9	1.2694
mp3	jp5	ip10	0.0784
	jp5	ip11	0.9914
	jp5	ip12	0.0834
	jp5	ip13	0.1166
mp4	jp7	ip14	0.7861

Table D.3. Data for the mass sinks – 1G

$j \in J^M$	**Tj**	**c_{jn}^{LB}**						**c_{jn}^{UB}**					
	[°C]	**H2O**	**Sugarcane**	**Sugars**	**EtOH**	**CO2**	**Solids**	**H2O**	**Sugarcane**	**Sugars**	**EtOH**	**CO2**	**Solids**
jp1	25	0.70	0.30					0.70	0.3				
jp2	50	0.97						1.0					0.30
jp3	25	0.98						1.00					0.20
jp4	33	0.78		0.18				0.82		0.22			
jp5	33	0.64			0.07	0.07		0.80			0.08	0.09	0.22
jp6	33	1.00						1.00					
jp7	91	0.06			0.91			0.09			0.94		

Table D.4 Data for the mass source locations – 1G

$i \in I^M$	**T_i**	**cp**	**c_n**					
	[°C]	**[kW/K tn]**	**H2O**	**Bagasse**	**Sugars**	**EtOH**	**CO2**	**Solids**
ip1	25	0.0007	0.450					0.550
ip2	32	0.7429	0.500	0.500				
ip3	32	0.6723	0.500					0.500
ip4 (V-L)	100	628.6130	1.000					
ip4 (L)	99	1.1510						
ip5	54	0.7601	0.564					0.436
ip6	54	1.0684	0.960					0.040
ip7 (V-L)	100	628.6130	1.000					
ip7 (L)	99	1.1510						
ip8	33	0.9541	0.800		0.200			
ip9	33	2.6751	0.644			0.076	0.080	0.200
ip10	27	1.1927	0.016			0.007	0.977	
ip11	124	1.0445	0.921					0.079
ip12	114	1.2049	0.999					0.001
ip13	91	0.4819	0.080			0.920		
ip14	115	1.2379	0.001			0.999		

*The compositions of the streams are simplified.

D.3 List of Symbols

Latin Symbols

ATD	area target deviations	$[\mathrm{m^2}]$
bp	stream cost	$[\mathrm{M\$\ yr^{-1}}]$
c	concentration	$[\mathrm{ktn\ ktn^{-1}}]$
Cost	cost	$[\mathrm{M\$\ yr^{-1}}]$
cp	specific heat capacity	$[\mathrm{MW\ ktn^{-1}\ K^{-1}}]$
F	mass flow	$[\mathrm{ktn\ yr^{-1}}]$
h	specific enthalpy	$[\mathrm{MW\ ktn^{-1}}]$
LMTD	logarithmic mean temperature difference	
LU	large unit	
pp	purchase price	$[\mathrm{M\$\ ktn^{-1}}$ or $\mathrm{M\$\ MW^{-1}}]$
Profit	profit	$[\mathrm{M\$\ yr^{-1}}]$
Q	heat flow (variable)	$[\mathrm{MW\ yr^{-1}}]$
R	heat residual	$[\mathrm{MW\ yr^{-1}}]$
Revenue	revenue	$[\mathrm{M\$\ yr^{-1}}]$
sp	selling price	$[\mathrm{M\$\ ktn^{-1}}$ or $\mathrm{M\$\ MW^{-1}}]$
T	temperature	[K]
tp	treatment price	$[\mathrm{M\$\ ktn^{-1}}$ or $\mathrm{M\$\ MW^{-1}}]$
U	overall heat transfer coefficient	$[\mathrm{W\ m^{-2}\ K^{-1}}]$
Y	integer variable	
Z	integer variable	
αp	area deviation cost	$[\mathrm{M\$\ yr^{-1}\ m^{-2}}]$

Greek Symbols

α	slope in the piecewise linearized cost function	[M\$ ktn^{-1}]
β	fixed parameter in the piecewise linearized cost function	[M\$ yr^{-1}]
ξ	conversion factor	[ktn ktn^{-1}]

Subscripts

i	sources
j	sinks
k	intervals
m	process units
n	utilities
s	streams

Superscripts

B	buyers
C	cold utilities (energy)
CI	capital investment
D	treatment units
E	energy
F	existing units
H	hot utilities (energy)
IN	incoming
LB	lower bound
M	materials
N	new units
OP	operating
OUT	outgoing
P	processing units
S	supply units
Total	total amount
TR	treatment
UB	upper bound

Appendix E

E.1 Summary

Appendix E includes information for the waste treatment technologies presented in Chapter VIII. Tables E.1 to E.18 present the parameters of the surrogates for the treatment technologies. The equations associated with each unit are described in detail in Mountraki et al. (2016).

E.2 Gaseous Emissions Treatment Technologies

Table E.1 Parameters for the model of Chemical absorption (MEA)

Chemical absorption (MEA)			
Eq.	CO_2 captured	α_{1j}	0.0575
8.1	[kg/day]	α_{2j}	0.0000
8.2	Fixed Cost 10^{-6}	c_{1j}	0.70
	[M\$/yr]	c_{2j}	$7.6\ 10^{-6}$
8.3	Solvent [kg/day]	β_{1j}	0.0022
8.4	Energy [kWh/yr]	e_{1jp}	1037.70
8.5	Operating Cost 10^{-6} [M\$/yr]	f_{1j}	0.30

Table E.2 Parameters for the model of Chemical absorption (MDEA)

Chemical absorption (MDEA)			
Eq.	CO2 captured	α_{1j}	0.319
8.1	[kg/day]	α_{2j}	0.000
8.2	Fixed Cost 10^{-6}	c_{1j}	0.90
	[M\$/yr]	c_{2j}	$9.8\ 10^{-6}$
8.3	Solvent [kg/day]	β_{1j}	0.0011
8.4	Energy [kWh/yr]	e_{1jp}	477.78
8.5	Operating Cost 10^{-6} [M\$/yr]	f_{1j}	20

Table E.3 Parameters for the model of Physical absorption (Rectisol)

Physical absorption (Rectisol)			
Eq.	CO2 captured	α_{1j}	0.334
8.1	[kg/day]	α_{2j}	0.000
8.2	Fixed Cost 10^{-6}	c_{1j}	0.80
	[M\$/yr]	c_{2j}	$7.6\ 10^{-6}$
8.3	Solvent [kg/day]	β_{1j}	61.30
8.4	Energy [kWh/yr]	e_{1jp}	136 847.00
8.5	Operating Cost 10^{-6} [M\$/yr]	f_{1j}	0.0048

Table E.4 Parameters for the model of Physical absorption (Selexol)

Physical absorption (Selexol)			
Eq.	CO2 captured	$\alpha_{1\,j}$	0.334
8.1	[kg/day]	$\alpha_{2\,j}$	0.000
8.2	Fixed Cost 10^{-6}	c_{1j}	0.80
	[M$/yr]	c_{2j}	7.6 10^{-6}
8.3	Solvent [kg/day]	$\beta_{1\,j}$	185.85
8.4	Energy [kWh/yr]	$e_{1\,jp}$	227 093.00
8.5	Operating Cost 10^{-6} [M$/yr]	f_{1j}	0.0079

Table E.5 Parameters for the model of Ca-loop

Ca-loop			
Eq.	CO2 captured	$\alpha_{1\,j}$	0.319
8.1	[kg/day]	$\alpha_{2\,j}$	0.000
8.2	Fixed Cost 10^{-6}	c_{1j}	0.003
	[M$/yr]	c_{2j}	30 831.00
8.4	Energy [kWh/yr]	$e_{1\,jp}$	477.78
8.5	Operating Cost 10^{-6} [M$/yr]	f_{1j}	0.0092

Table E.6 Parameters for the model of Cryogenic methods

Cryogenic methods			
Eq.	CO2 captured	$\alpha_{1\,j}$	0.3433
8.1	[kg/day]	$\alpha_{2\,j}$	0.000
8.2	Fixed Cost 10^{-6}	c_{1j}	0.0005
	[M$/yr]	c_{2j}	10.472
8.4	Energy [kWh/yr]	$e_{1\,jp}$	36.725
8.5	Operating Cost 10^{-6} [M$/yr]	f_{1j}	1.00

E.3 Liquid Waste Treatment Technologies

Table E.7 Parameters for the model of AD

Anaerobic Digestion						
Eq.	(8.6)		(8.6)		(8.7)	(8.8)
	Compost [kg/day]		**Biogas[kg/day]**		**Fixed Cost [M$/yr]**	**Operating Cost [M$/yr]**
Regr. Param / BOD [kg/m^3]	$\alpha_{1\ j,k}$	$\alpha_{2\ j,k}$	$\alpha_{1\ j,k}$	$\alpha_{2\ j,k}$	$f_{1\ jk}$	$c_{1\ jk}$
[25,35]	0.10	0.00	0.0029	101.81	0.048	0.0037
(35,50]			0.004			
(50,75]			0.006			
(75,110]			0.0092			
(110,170]			0.00137			
(170,250]			0.02			
(250,350]			0.0028			
(350,500]			0.0405			
(500,740]			0.059			
(740,1100]			0.0875			

Table E.8 Parameters for the model of AS

Activated Sludge						
Eq.	**k** **BOD (kg/m^3)**		**[120,170]**	**(170,240]**	**(240,320]**	**(320,380]**
8.6	Sludge [kg/day]	$\alpha_{1\ j,k}$	0.056	0.08	0.11	0.1424
		$\alpha_{2\ j,k}$	3474.7			
8.9	Energy Needs [kWh/yr]	$e_{1\ jkp}$	41.3	59	81.125	59
		$e_{2\ jkp}$	22563			
8.10	Fixed Cost 10^{-6} [M$/yr]	$f_{1\ jk}$	72			
		$f_{2\ jk}$	368.043			
8.11	Operating Cost 10^{-6} [M$/yr]	$c_{1\ jk}$	4.58			
		$c_{2\ jk}$	36.295			

Table E.9 Parameters for the model of TF

Trickling Filters							
Eq.	**k** **BOD (kg/m^3)**		**[120,170]**	**(170,230]**	**(230,320]**	**(320,420]**	**(420,520]**
8.6	Sludge [kg/day]	$\alpha_{1\ j,k}$	0.058	0.08	0.11	0.148	0.188
		$\alpha_{2\ j,k}$	432.54				
8.9	Energy Needs [kWh/yr]	$e_{1\ jkp}$	17.864	24.64	33.88	45.584	57.904
		$e_{2\ jkp}$	104693				
8.12	Fixed Cost 10^{-6} [M$/yr]	$f_{1\ jk}$	-0,00007				
		$f_{2\ jk}$	56.89				
		$f_{3\ jk}$	244.791				
8.13	Operating Cost 10^{-6} [M$/yr]	$c_{1\ jk}$	278				
		$c_{2\ jk}$	0.505				

Table E.10 Parameters for the model of RBC

Rotating Biological Contactors			
Eq.	**k BOD (kg/m3)]**		**[100,380]**
8.14	Sludge [kg/day]	$\alpha_{1\ j,k}$	1.43
		$\alpha_{2\ j,k}$	-1.27
8.10	Fixed Cost 10^{-6} [M$/yr]	$f_{1\ jk}$	0.1605
		$f_{2\ jk}$	-448.27
8.11	Operating Cost 10^{-6} [M$/yr]	$c_{1\ jk}$	0.006
		$c_{2\ jk}$	2060.1

Table E.11 Parameters for the model of AL

Aerated Lagoon						
Eq.	**k TSS [kg/day]**		**[4000,8000]**	**(8000,12000]**	**(12000,135000]**	**>135000**
8.14	Sludge [kg/day]	$\alpha_{1\ j,k}$	0.555	0.80	1.38	0.95
		$\alpha_{2\ j,k}$	0			
8.9	Energy Needs [kWh/yr]	$e_{1\ jkp}$	104.37			
		$e_{2\ jkp}$	-554875			
8.10	Fixed Cost 10^{-6} [M$/yr]	$f_{1\ jk}$	0.184			
		$f_{2\ jk}$	118.06			
8.11	Operating Cost 10^{-6} [M$/yr]	$c_{1\ jk}$	3.93			
		$c_{2\ jk}$	-20877			

Table E.12 Parameters for the model of SP

Stabilization Pond							
Eq.	**k BOD (kg/m^3)]**		**[80,110]**	**(110,150]**	**(150,200]**	**(200,250]**	**(250,290]**
8.14	Sludge [kg/day]	$\alpha_{1\ j,k}$	1.66				
		$\alpha_{2\ j,k}$	0				
8.11	Fixed Cost10^{-6} [M$/yr]	$f_{1\ jk}$	0.4	0.6	0.8	1.0	2.0
		$f_{2\ jk}$	0.4	0.6	0.8	1.0	2.0

E.4 Solid Waste Treatment Technologies

Table E.13 Parameters for the model of Combustion

Combustion								
Eq.	**k LHV (MJ/kg)**		**[-2.5,-3.5]**	**(-3.5,-4.5]**	**(-4.5,-10]**	**(-10,-16]**	**(-16,-25]**	**(-25,-40]**
8.6	Ash [kg/day]	$\alpha_{1\ j,k}$	0.15					
		$\alpha_{2\ j,k}$	0.00					
8.6	Energy [kWh/yr]	$\alpha_{1\ j,k}$	2722.22	3500.00	5950.00	1.00	2.00	10111.11
		$\alpha_{2\ j,k}$	0.00					
8.10	Fixed Cost 10^{-6} [M$/yr]	$f_{1\ jk}$	9.26					
		$f_{2\ jk}$	0.00					
8.11	Operating Cost 10^{-6} [M$/yr]	$c_{1\ jk}$	4.71					
		$c_{2\ jk}$	-510.00					

Table E.14 Parameters for the model of Incineration

	Incineration		
Eq.	Ash	α_{1j}	0.20
8.1	[kg/day]	α_{2j}	0.00
8.1	Gas	α_{1j}	0.67
	[kg/day]	α_{2j}	-85.99
8.1	Energy	α_{1j}	125.65
	[kWh/yr]	α_{2j}	$2.00\ 10^{6}$
8.15	Fixed Cost 10^{-6}	f_{1j}	200.00
	[M$/yr]	f_{2j}	0.00

Table E.15 Parameters for the model of Gasification

	Gasification		
Eq.	Gas	α_{1j}	0.85
8.1	[kg/day]	α_{2j}	0.00
8.1	Liquid	α_{1j}	0.05
	[kg/day]	α_{2j}	0.00
8.1	Char	α_{1j}	0.10
	[kWh/yr]	α_{2j}	0.00
8.1	Energy (product)	cc_{1j}	28000.00
	[kWh/yr]	cc_{2j}	0.00
8.16	Energy (required) [kWh/year]	e_{1j}	5714.28
	[kWh/yr]	e_{2j}	0.00
8.15	Fixed Cost 10^{-6}	f_{1j}	185.51
	[M$/yr]	f_{2j}	-152.08

Table E.16 Parameters for the model of Fast Pyrolysis

	Fast Pyrolysis		
Eq.	Oil	α_{1j}	0.500
8.1	[kg/day]	α_{2j}	0.000
8.1	Char	α_{1j}	0.200
	[kg/day]	α_{2j}	0.000
8.1	Gas	α_{1j}	0.300
	[kg/day]	α_{2j}	0.000
8.16	Energy	e_{1jp}	0.040
	[kWh/yr]	e_{2jp}	0.000
8.2	Operating Cost 10^{-6}	c_{1j}	0.035
	[M$/yr]	c_{2j}	0.000
8.17	Fixed Cost	f_{1j}	0.042
	[M$/yr]	f_{2j}	0.670

Table E.17 Parameters for the model of Slow Pyrolysis

	Slow Pyrolysis		
Eq.	Oil	$\alpha_{1\,j}$	0.30
8.1	[kg/day]	$\alpha_{2\,j}$	0.00
8.1	Char	$\alpha_{1\,j}$	0.35
	[kg/day]	$\alpha_{2\,j}$	0.00
8.1	Gas	$\alpha_{1\,j}$	0.35
	[kg/day]	$\alpha_{2\,j}$	0.00
8.16	Energy	$e_{1\,jp}$	320.00
	[kWh/yr]	$e_{2\,jp}$	0.00
8.2	Operating Cost 10-6	c_{1j}	0.035
	[M$/yr]	c_{2j}	0.00
8.17	Fixed Cost	f_{1j}	0.01185
	[M$/yr]	f_{2j}	0.00

Table E.18 Parameters for the model of Torrefaction

		Torrefaction	
Eq.	Char	$\alpha_{1\,j}$	0.350
8.1	[kg/day]	$\alpha_{2\,j}$	0.000
8.16	Energy	$e_{1\,jp}$	0.002
	[kWh/year]	$e_{2\,jp}$	0.000
8.18	Operating Cost 10^{-6}	c_{1j}	0.00315
	[M$/yr]	c_{2j}	0.670
8.19	Fixed Cost	f_{1j}	0.035
	[M$/yr]	f_{2j}	0.000

E.5 References

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E.6 List of Symbols

Latin Symbols

P	Product flow	[kg day^{-1}]
E	Energy use	[kWh yr^{-1}]
R	solvent requirements	[kg day^{-1}]
C	cost	[M$ yr^{-1}]
S	Inlet stream flow	[kg day^{-1}]
c	discretization parameter for operating cost	
e	discretization parameter for energy	
f	discretization parameter for fixed cost	
RV	revenue	[M$ yr^{-1}]
z	binary variabley	
y	binary variabley	
N	number of technologies	
F	Flow of waste liquid stream	[kg day^{-1}]
LU	lower bound	

Greek Symbols

α	discretization parameter for products
β	parameter for the estimation of the solvent requirements

Subscripts

j	waste treatment processes
p	waste products
k	linearization intervals
i	waste streams

Superscripts

f	capital investment
op	operating

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Abbreviations

1G	First Generation [biorefineries]
2G	Second Generation [biorefineries]
3G	Third Generation [biorefineries]
4G	Fourth Generation [biorefineries]
AA	Acetic Acid
AD	Anaerobic Digestion
AFEX	Ammonia Fiber Expansion
AL	Aerated Lagoon
API	Application Programming Interface
AS	Activated Sludge
ATD	Area Target Deviations
ATM	Area Target Model
BBR	Bipartite Biomass Graph Representation
BFD	Block Flow Diagram
BioXyl	Biotechnological Xylitol
BK10	Braun K-10 [model]
BOD	Biochemical Oxygen Demand
BWR	Benedict - Webb – Rubin [model]
C5	Pentoses
C6	Hexoses
Ca-loop	Calcinations-loop
CatXyl	Catalytic Xylitol
CFD	Computational Fluid Dynamics
CHP	Cogeneration of Heat and Power
CIMV	Compagnie Industrielle de la Matière Végétale (Industrial Company of Vegetative Material)
COD	Chemical Oxygen Demand
COM	Combustion
COx	Carbon oxides
CP	Conversion processing
CPR	Chemical precipitation
CR	Cryogenic methods
D1	Single effect distillation
D2	Double effect distillation
DA	Diluted Acid
DoF	Degrees of Freedom
DSA	Dilute Sulfuric Acid
DSP	Downstream processing
EP	Electric Power
EtOH	Ethanol
EU	Enabler Unit
FA	Formic Acid
FermGL	Fermentation of Glucose
FP7	7th Framework Programme [European Research Funding]

FPY	Fast Pyrolysis
GERG	Groupe Européen de Recherches Gazières
GSF	Gasification
HEN	Heat Exchange Network
HF	Hydrogen Fluoride [model]
HydrC5	Hydrolysis of pentoses
HydrC6	Hydrolysis of hexoses
HydrSep	Hydrolysis – Separation
I.E.A.	International Energy Agency
IE	Ion exchange
INC	Incineration
LCA	Life-cycle Assessment
LHV	Lower Heating Value
LHW	Liquid Hot Water
LK	Lee – Kesler [model]
LKP	Lee – Kesler – Plocker [model]
LLE	Liquid-Liquid-Extraction
LP	Low Pressure (stream)
MDEA	Chemical absorption using N-methyl diethanolamine
MEA	Chemical absorption using monoethanolamine
MEN	Mass Exchange Network
MF	Micro filtration
MILP	Mixed Integer Linear Programming
MILP	Mixed Integer Linear Programming
MINLP	Mixed Integer Non Linear Programming
MR	Membrane reactor
MS	Molecular Sieves
NLP	Non Linear Programming
NOx	Nitrogen oxides
NPSH	Net Positive Suction Head
NRTL	Non-Random Two-Liquid [model]
NTUA	National Technical University of Athens
PF	Phenol-Formaldehyde (resins)
PFD	Process Flow Diagram
PR	Peng – Robinson [model]
PPMC	Property Process Modeling Cycle
PU	Polyurethane
PVC	Polyvinyl chloride
R&D	Research and Development
RBC	Rotating Biological Contactors
RCT	Physical absorption using Rectisol
REFPROP	REference Fluid PROPerties
RK	Redlich – Kwong [model]
RO	Reverse osmosis
SAA	Soaking in Aqueous Ammonia
SE	Steam Explosion
SHF	Separate Hydrolysis Fermentation
Slv	Solvent
SLX	Physical absorption using Selexol
SolidRes	Solid Residue

SOx	Sulfur oxides
SP	Stabilization pond
SPY	Slow Pyrolysis
SRK	Soave - Redlich – Kwong [model]
SScF	Simultaneous Saccharification co-Fermentation
SSF	Simultaneous Saccharification Fermentation
SWOT	Strengths, Weaknesses, Opportunities, and Threats [analysis]
TC	Total Cost
TF	Trickling Filter
TOR	Torrefaction
TRL	Technological Readiness Level
TSS	Total Suspended Solids
U.S.	United States [of America]
UNIFAC	UNIQUAC Functional-group Activity Coefficients [model]
UNIQUAC	UNIversal QUAsiChemical [model]
UNO	Utility Network Optimization
UNOSR	Utility Network Optimization with Synergistic Revamp
USP	Upstream processing
VLE	Vapor Liquid Equilibrium

Συνοπτική Μετάφραση στα Ελληνικά

Κεφάλαιο Ι: Εισαγωγή

Το πρώτο κεφάλαιο έχει ως στόχο να προετοιμάσει τον αναγνώστη να κατανοήσει το περιεχόμενο και τη δομή της διατριβής. Αρχικά, παρουσιάζεται το γενικό ερευνητικό πλαίσιο στο οποίο υπάγεται η διατριβή και αναγνωρίζονται στοιχεία που δέχονται βελτίωση. Έπειτα, αναφέρεται ο σκοπός και το πεδίο εφαρμογής της συγκεκριμένης έρευνας καθώς και η σημασία της. Τέλος, σκιαγραφείται η διάρθρωση της διατριβής ώστε να δει ο αναγνώστης πώς επιτυγχάνεται ο σκοπός της έρευνας.

Το γενικό ερευνητικό πλαίσιο είναι ο σχεδιασμός των βιοδιυλιστηρίων. Ο όρος «βιοδιυλιστήριο» περικλείει την ιδέα της βιώσιμης και συνεργατικής επεξεργασίας ανανεώσιμων πρώτων υλών σε ένα ευρύ φάσμα εμπορεύσιμων προϊόντων (χημικών και υλικών), τροφίμων, ζωοτροφών και ενέργειας (ηλεκτρική, θερμική, καύσιμα). Τα βιοδιυλιστήρια αναπτύχθηκαν ως το πράσινο ισοδύναμο των συμβατικών διυλιστηρίων πετρελαίου. Ανάλογα με τις πρώτες ύλες ταξινομούνται σε (α) πρώτης γενιάς, αν επεξεργάζονται εδώδιμες ύλες (π.χ. καλαμπόκι, ζαχαροκάλαμο, σπόρους, φυτικά έλαια, κλπ.), (β) δεύτερης γενιάς, αν χρησιμοποιούν μη εδώδιμες ύλες, όπως γεωργικά ή δασικά υπολείμματα (π.χ. λιγνοκυτταρινούχος βιομάζα), (γ) τρίτης γενιάς, αν χρησιμοποιούν μη συμβατικές πρώτες ύλες (π.χ. (μικρο)φύκια, αστικά απόβλητα) και (δ) τέταρτης γενιάς, αν χρησιμοποιούν το διοξείδιο του άνθρακα για τη μείωση των εκπομπών του. Η έρευνα για το σχεδιασμό βιώσιμων βιοδιυλιστηρίων εκτείνεται σε τρία πεδία: (i) το πεδίο της κοινωνικής αποδοχής και τον αντίκτυπο στο βιοτικό επίπεδο, (ii) το πεδίο της προστασίας του περιβάλλοντος και τον αντίκτυπο στη διατήρηση των φυσικών πόρων και τη βιοποικιλότητας και (iii) το πεδίο της οικονομίας και τον αντίκτυπο στην οικονομική ανάπτυξη. Δεδομένου ότι η κοινωνική αποδοχή αυξάνει με την βελτίωση της ενεργειακής και περιβαλλοντικής απόδοσης μιας βιομηχανίας, η παρούσα διατριβή στοχεύει στην ανάπτυξη μιας συστηματικής μεθοδολογίας για τη βελτιστοποίηση βιο-διεργασιών, με έμφαση κυρίως στους παράγοντες που επηρεάζουν την οικονομική και περιβαλλοντική τους απόδοση.

Ερέθισμα για την έναρξη της διατριβής αποτέλεσε το γεγονός πως ενώ υπάρχουν πολιτικές σε εθνικό αλλά και διεθνές επίπεδο που δίνουν κίνητρα για την εξέλιξη των βιοδιυλιστηρίων, η ανάπτυξή τους σε βιομηχανική κλίμακα γίνεται με πολύ αργούς ρυθμούς. Επιπλέον, τα ιδιωτικά κεφάλαια δυσπιστούν απέναντι σε μια τέτοια επένδυση, κυρίως επειδή τα εργαλεία που χρησιμοποιούνται για την οικονομική τους αξιολόγηση βασίζονται σε μεθόδους που αναπτύχθηκαν για τον σχεδιασμό συμβατικών διεργασιών. Μέχρι σήμερα, δεν υπάρχει επαρκής έρευνα που να συνδυάζει τις τεχνολογικές λεπτομέρειες με τις επιλογές προϊόντων από την αλυσίδα αξιών. Οι υπάρχουσες συστημικές μέθοδοι αντιμετωπίζουν τις επιλογές της αλυσίδας αξιών ως δεδομένες συνδέσεις, χωρίς περιορισμούς. Είναι σημαντικό να κατανοηθεί ο τρόπος με τον οποίο οι επιλογές για άμεση επένδυση ή για ανάπτυξη συνεργασιών επηρεάζουν το χάρτη επιλογών της αλυσίδας αξιών. Η παρούσα διατριβή έχει ως σκοπό την ανάπτυξη διαδικασιών για τη συστημική αντιμετώπιση των προβλημάτων λήψης αποφάσεων που προκύπτουν κατά την πορεία της βιομηχανικής ανάπτυξης των βιοδιυλιστηρίων δεύτερης γενιάς. Χρησιμοποιούνται μοντέλα που συνδυάζουν διαφορετικές σχεδιαστικές κλίμακες με σκοπό να διερευνηθούν οι συσχετίσεις μεταξύ του λειτουργικού κόστους και του κόστους επένδυσης σε όλο το δέντρο της αλυσίδας αξιών. Προβλέπονται επιλογές για διαφορετικές πρώτες ύλες, τεχνολογίες προεπεξεργασίας, χαρτοφυλάκια προϊόντων, τεχνολογικές διαδρομές παραγωγής και τεχνολογίες επεξεργασίας αποβλήτων. Η συγκεκριμένη εργασία δεν προτείνει μια ενιαία μέθοδο βελτιστοποίησης, αλλά αποσκοπεί στην ανάπτυξη και το συνδυασμό εργαλείων που μπορούν να βοηθήσουν μηχανικούς κι επενδυτές να θέσουν στόχους και να αξιολογήσουν τις σχεδιαστικές επιλογές που εμφανίζονται στις διάφορες φάσεις της βιομηχανικής ανάπτυξης μιας τεχνολογίας.

Η παρούσα διατριβή οργανώνεται σε οκτώ επιπλέον κεφάλαια:

Το κεφάλαιο II αναλύει την υπάρχουσα έρευνα πάνω στο συστημικό σχεδιασμό βιώσιμων βιοτεχνολογιών. Συγκεκριμένα, εστιάζει στις προσπάθειες της μηχανική συστημάτων διεργασιών να συμβάλει στην ανάπτυξη βιώσιμων βιοτεχνιών στους τομείς της σύνθεσης, της ολοκλήρωσης και της προσομοίωση διεργασιών. Ο στόχος είναι να αποκαλυφθούν τα κενά της υπάρχουσας γνώσης που η παρούσα διατριβή επιδιώκει να καλύψει.

Το κεφάλαιο III παρουσιάζει μια νέα συστημική προσέγγιση για τον αρθρωτό ολοκληρωμένο σχεδιασμό βιοδιυλιστηρίων πολλαπλών προϊόντων. Συγκεκριμένα, το μεθοδολογικό πλαίσιο ξεκινά με την αποδόμηση του προβλήματος στις διαφορετικές σχεδιαστικές κλίμακες. Στη συνέχεια, προτείνονται τρόποι οργάνωσης των δομικών στοιχείων κάθε κλίμακας, έτσι ώστε να αναπτυχθεί αυτόματα η υπερδομή των εναλλακτικών επιλογών. Τέλος, παρουσιάζεται ο τρόπος με τον οποίο συνδυάζονται τα εργαλεία μηχανικής συστημάτων με τις διάφορες σχεδιαστικές κλίμακες ώστε να επιτευχθεί ο αρθρωτός ολοκληρωμένος σχεδιασμός.

Το κεφάλαιο IV ασχολείται με τη διαχείριση των ακατέργαστων δεδομένων. Τα πρωτογενή δεδομένα που χρησιμοποιήθηκαν στην παρούσα έρευνα ελήφθησαν από διάφορες πηγές (βιβλιογραφικά ή πειραματικά) και είχαν διαφορετική ακρίβεια λόγω των διαφορετικών επιπέδων ωριμότητας της τεχνολογίας των εξεταζόμενων διεργασιών (πιλοτικό, εργαστηριακό ή θεωρητικό στάδιο). Η μέθοδος βελτιστοποίησης χρησιμοποιείται μοντέλα-υποκατάστατες για την παραγωγή αξιόπιστων και εναρμονισμένων δεδομένων.

Το κεφάλαιο V αξιολογεί σε πρώιμο στάδιο τα πλεονεκτήματα μιας τεχνολογίας σε σύγκριση με τον ανταγωνισμό. Το προτεινόμενο μοντέλο της σύνθετης διεργασιών χρησιμοποιεί την αρθρωτή δομή των διμερών γράφων που παρουσιάζονται στο κεφάλαιο III.

Το κεφάλαιο VI συσχετίζει την ανάγκη σε βοηθητικές παροχές με τις σχεδιαστικές επιλογές. Εισάγεται ένα νέο μοντέλο για την ταυτόχρονη βελτιστοποίηση του δικτύου πολλαπλών βοηθητικών παροχών και σχεδιαστικών επιλογών. Η μέθοδος προϋποθέτει λειτουργία σε μόνιμη κατάσταση και σταθερή απόδοση λειτουργίας.

Το Κεφάλαιο VII επεκτείνει το μοντέλο βελτιστοποίησης που παρουσιάζεται στο κεφάλαιο VI σε προβλήματα επανασχεδιασμού υφιστάμενων εγκαταστάσεων, λαμβάνοντας υπόψη τις επιλογές για βιομηχανικές συνέργειες. Η μέθοδος συνδυάζει μεθόδους για το σχεδιασμό νέων διεργασιών και υφιστάμενων εγκαταστάσεων και ενσωματώνει εργαλεία σύνθεσης για την αξιολόγηση επιλογών του χαρτοφυλακίου προϊόντων και την αναζήτηση συνεργειών.

Το κεφάλαιο VIII επεκτείνει το μεθοδολογικό πλαίσιο σε ολοκληρωμένα συστήματα διαχείρισης αποβλήτων, για την αντιμετώπιση τόσο της δημιουργίας των ρευμάτων όσο και της αξιολόγηση των επιλογών επεξεργασίας αποβλήτων. Το ολοκληρωμένο σύστημα περιλαμβάνει επιλογές εναλλακτικών τεχνολογιών επεξεργασίας και στρατηγικές αποκεντρωμένης και κεντρικής διαχείρισης.

Κεφάλαιο ΙΙ: Βιβλιογραφική Ανασκόπηση

Το δεύτερο κεφάλαιο παρέχει μια ανασκόπηση της βιβλιογραφίας των συστημικών μεθόδων που εφαρμόζονται για το σχεδιασμό βιώσιμων βιο-διεργασιών, βασισμένες σε οικονομικά και περιβαλλοντικά κριτήρια. Συγκεκριμένα, εξετάζονται οι συνεισφορές στους τομείς της σύνθεσης, της ολοκλήρωσης και της προσομοίωσης βιοδιυλιστηρίων. Ο στόχος είναι να αποκαλυφθούν οι περιορισμοί της υπάρχουσας γνώσης που η παρούσα διατριβή επιδιώκει να βελτιώσει.

Η ανάπτυξη σύγχρονων βιοδιυλιστηρίων αποτελεί σύνθετο σχεδιαστικό πρόβλημα. Η βιβλιογραφία φαίνεται να ακολουθεί μια ενιαία πρακτική αποδόμησης του σύνθετου προβλήματος σε στοιχεία (i) πρώτων υλών, (ii) διεργασιών, (iii) ενδιάμεσων και (iv) τελικών προϊόντων. Οι συνδυασμοί αυτών των δομικών στοιχείων θεωρητικά οδηγεί σε σχεδόν απεριόριστο αριθμό σχεδιαστικών επιλογών. Επιπλέον, κάθε χημικό μονοπάτι της αλυσίδας αξιών περικλείει έναν άλλο αριθμό τεχνολογικών μονοπατιών, τα οποία βρίσκονται σε διαφορετικό επίπεδο τεχνολογικής ωριμότητας. Το μέγεθος και η πολυπλοκότητα του προβλήματος απαιτούν μια συστημική προσέγγιση, ικανή να εξετάσει τις θεωρητικές και τεχνολογικές πτυχές των συστημάτων για την καλύτερη χρήση των πόρων, εξετάζοντας επίσης επιλογές για ενδογενείς και εξωγενείς συνεργίες.

Η μηχανική συστημάτων χρησιμοποιεί την ολοκλήρωση διεργασιών και τις τρεις συνιστώσες της, τη σύνθεση, την ανάλυση και τη βελτιστοποίηση, προκειμένου να αντιμετωπίσει συστηματικά τις προκλήσεις του σχεδιασμού διεργασιών. Η ολοκλήρωση διεργασιών είναι μια ολιστική προσέγγιση χρήσιμη για την ενσωμάτωση των περιβαλλοντικών κριτηρίων σε διάφορους σχεδιαστικούς στόχους, όπως η κερδοφορία, η απόδοση και η εξοικονόμηση πόρων. Η σύνθεση διεργασιών συνδυάζει κι ενσωματώνει μονάδες και ρεύματα για την επίτευξη των στόχων του σχεδιασμού. Η ανάλυση διεργασιών περιλαμβάνει την αποδόμηση του συνόλου σε στοιχεία για να μελετήσει την επίδρασή τους στη συμπεριφορά της διεργασίας. Η βελτιστοποίηση διεργασιών περιλαμβάνει την επιλογή της "βέλτιστης" λύσης ανάμεσα σε ένα σύνολο επιλογών.

Όσον αφορά τις μεθόδους που σχετίζονται με το σχεδιασμό και την αξιολόγηση των βιοδιυλιστηρίων, αναγνωρίζονται τρεις κύριες μεθοδολογικές τάσεις: (i) οι εννοιολογικές, (ii) της πρώιμης φάσης και (iii) της βελτιστοποίησης βασισμένη στην ιεραρχία ή την ολοκλήρωση των διεργασιών. Οι υπάρχουσες μέθοδοι συμβάλουν στη βελτιστοποίηση των αποδόσεων, της διαχείρισης πόρων και της μείωσης του κόστους, λαμβάνοντας υπόψη εξωτερικούς (πολιτικές, περιβαλλοντικές εκτιμήσεις και συνθήκες της αγοράς) κι εσωτερικούς περιορισμούς (αποδόσεις, προϋπολογισμός κλπ.). Ωστόσο, δεν αναλύονται ολιστικά οι συνεργίες ούτε οι τεχνολογικοί περιορισμοί στις συνδέσεις των διαφορετικών μονοπατιών της αλυσίδας αξιών.

Η σύνθεση διεργασιών παρέχει έναν συστημικό τρόπο αξιολόγησης επιλογών με τη μορφή ενός δικτύου που επιτυγχάνει τους οικονομικούς, περιβαλλοντικούς και / ή κοινωνικούς στόχους. Οι κύριες μεθοδολογικές τάσεις περιλαμβάνουν τους ευριστικούς κανόνες, τις τεχνικές αποδόμησης και τις μεθόδους βελτιστοποίησης. Οι ευριστικοί κανόνες περιορίζονται σε μια γειτονιά επιλογών προσθέτοντας ή τροποποιώντας διαδοχικά τις μονάδες μιας βασικής υπόθεσης εργασίας. Οι τεχνικές αποδόμησης αναλύουν ένα μεγάλο και πολύπλοκο πρόβλημα σε μικρότερα, ιεραρχικά υπο-προβλήματα. Οι μέθοδοι βελτιστοποίησης εξετάζουν αναλυτικά τις συσχετίσεις μεταξύ των υποσυστημάτων και αναζητούν, αυστηρά, μέσω ενός προτεινόμενου χώρου σχεδιασμού τη βέλτιστη λύση. Οι εφαρμογές σε προβλήματα βιοδιυλιστηρίων περιλαμβάνουν την παραγωγή ενός ή πολλαπλών προϊόντων, εστιάζοντας στο πρόβλημα της συνολικής αλυσίδας αξιών ή σε συγκεκριμένες διεργασίες. Τα μοντέλα είτε δημιουργούν στοχαστικά τον χώρο αναζήτησης είτε χρησιμοποιήσουν υπερδομές για να αξιολογήσουν και να αναζητήσουν τις καλύτερες επιλογές αξιοποίησης της βιομάζας. Ωστόσο, η ευελιξία στο σχεδιασμό και η αβεβαιότητα στην αλυσίδα αξιών δεν έχουν αντιμετωπιστεί επαρκώς. Επιπλέον, η ποιότητα των ενδιάμεσων και τελικών προϊόντων δεν λαμβάνεται υπόψη, αγνοώντας τις όποιες τεχνολογικές διαφορές.

Η ολοκλήρωση διεργασιών παρέχει έναν συστημικό τρόπο εξοικονόμησης πόρων και μείωσης του κόστους, παρέχοντας μια στρατηγική χαρτογράφησης που βασίζεται σε θερμοδυναμικά προερχόμενα όρια. Οι εφαρμογές σε προβλήματα βιοδιυλιστηρίων βασίζονται κυρίως σε σενάρια, μελετώντας την παραγωγή βιοαιθανόλης από αμυλώδη ή λιγνοκυτταρινούχα βιομάζα ή την παραγωγή βιοντίζελ με διεστεροποίηση με ετερογενή ή ομοιογενή κατάλυση (αλκαλικά, όξινα ή ένζυμα και τα δυο) ή την παραγωγή χαρτοπολτού. Ωστόσο, οι υπάρχουσες μέθοδοι εξετάζουν μόνο την ταυτόχρονη χρήση νερού και ενέργειας (ή ενός βασικού συστατικού και ενέργειας. Μέχρι σήμερα, καμία από τις υπάρχουσες μεθόδους δεν μπορεί να αντιμετωπίσει το ταυτόχρονο πρόβλημα για την αναγέννηση πολλαπλών συστατικών. Επιπλέον, οι πολλαπλές τεχνολογικές επιλογές για την αναγέννηση ενός συστατικού αυξάνουν την πολυπλοκότητα του προβλήματος. Επίσης, πρακτικοί λόγοι (έλεγχος, λειτουργία) μπορεί να επιβάλλουν ενδιάμεσο στάδιο αποθήκευσης. Κάθε σχεδιαστική επιλογή στο δίκτυο βοηθητικών παροχών δημιουργεί διαφορετικό θερμικό προφίλ. Το συνδυαστικό πρόβλημα της σχεδίασης του δικτύου βοηθητικών παροχών απαιτεί την ανάπτυξη μιας συστημικής προσέγγισης ικανής να αντιμετωπίσει την πολυπλοκότητα και το μέγεθος του σχεδιαστικού προβλήματος.

Η προσομοίωση διεργασιών οργανώνει απλές χημικές και φυσικές διεργασίες με βάση τις μαθηματικές περιγραφές των βασικών χημικών και φυσικών νόμων. Η συστημική ανάπτυξη ενός μοντέλου προσομοίωσης ξεκινά με τη συλλογή πληροφοριών για τα υπάρχοντα συστατικά, τις μονάδες επεξεργασίας και τις διασυνδέσεις τους, τις προδιαγραφές σχεδιασμού των πιέσεων λειτουργίας, τις θερμοκρασίες, τις ροές και τις συστάσεις. Στη συνέχεια, το φυσικό πρόβλημα προσδιορίζεται με την επιλογή των μεθόδων ιδιοτήτων και πρόσθετων δεδομένων για τα συστατικά και με τον υπολογισμό των ισοζυγίων θερμότητας και μάζας ανά μονάδα επεξεργασίας. Η μεγαλύτερη πρόκληση είναι η αναπαράσταση της σχεδιαστικής γνώσης, η οποία απαιτεί βαθιά κατανόηση της διεργασίας, των φυσικοχημικών φαινομένων της και των συστημάτων εξισώσεων, ειδικά όταν αφορά διαδικασίες (πολύ) χαμηλής τεχνολογικής ωριμότητας. Η συμφωνία μεταξύ του μοντέλου της προσομοίωσης και της πραγματικής διεργασίας είναι το βασικό κριτήριο ενός καλού μοντέλου. Η δυσκολία έγκειται στην επιλογή κατάλληλων μοντέλων αναπαράστασης των διεργασιών και στη λήψη κατάλληλων υποθέσεων για την αποφυγή της περιττής πολυπλοκότητας.

Η βιβλιογραφική ανασκόπηση κλείνει με αναφορά στην οπτική του καθηγητή Flouda σχετικά με τις δυνατότητες που προσφέρει η μηχανική συστημάτων στην αειφορία (Floudas et al., 2016). Αρχικά επισημαίνεται πως η προσομοίωση σε πολλαπλές σχεδιαστικές κλίμακες είναι κρίσιμη για την αντιμετώπιση μεγάλων και σύνθετων προβλημάτων, καθώς και για την πρόταση καινοτόμων λύσεων. Ένα άλλο ζήτημα είναι η εκτίμηση και η ανακάλυψη νέων υλικών προς μια επιλεκτική διεργασία με ευέλικτες αποδόσεις προϊόντων. Είναι επίσης σημαντικό να εκτιμηθεί η τεχνική εφικτότητα σε κλίμακα δικτύου παροχών. Ακόμα, οι αλυσίδες αξιών πρέπει να σχεδιάζονται στρατηγικά και να βελτιστοποιούνται σε μακροπρόθεσμο ορίζοντα. Τέλος, είναι σημαντικό να αντιμετωπιστούν συστημικά οι αβεβαιότητες ως προς τις τιμές, τη διαθεσιμότητα τροφοδοσίας, τις απαιτήσεις, τις παραμέτρους κόστους και τις παραμέτρους διεργασίας.

Παρά τη διαθεσιμότητα συστημικών μεθόδων, η βελτιστοποίηση βιοδιυλιστηρίων φαίνεται να βασίζεται σε προεπιλεγμένα σενάρια. Οι ολιστικές μέθοδοι αγνοούν τις συνέργιες, τα διαφορετικά επίπεδα τεχνολογικής ωριμότητας και τους περιορισμούς σύνθεσης λόγω τεχνολογικής ασυμβατότητας. Οι μελέτες ολοκλήρωσης επικεντρώνονται κυρίως στην κατανάλωση ενέργειας ή / και νερού, παραμελώντας την επίδραση άλλων βοηθητικών παροχών. Η προσομοίωση διεργασιών παραμένει μια πρόκληση λόγω της πολυπλοκότητας των συστατικών της βιομάζας και της χαμηλής τεχνολογικής ωριμότητας. Ωστόσο, η βιομηχανική ανάπτυξη των βιοδιυλιστηρίων απαιτεί έρευνα δύο κατευθύνσεων: i) εσωστρεφή έρευνα για την ανάπτυξη νέων και τη βελτίωση υφιστάμενων τεχνολογιών και ii) εξωστρεφή έρευνα για την αξιολόγηση της τεχνολογικής ολοκλήρωσης και των βιομηχανικών συνεργασιών. Η διατριβή αυτή προτείνει ένα νέο μεθοδολογικό πλαίσιο για την εσωστρεφή και εξωστρεφή ανάπτυξη των βιο-διεργασιών, λαμβάνοντας υπόψη την ανάγκη για διαφορετικά επίπεδα ακρίβειας ανά σχεδιαστική κλίμακα.

Συνοψίζοντας την επιστημονική συνεισφορά:

- Προτείνεται μια νέα συστημική προσέγγιση για τον αρθρωτό ολοκληρωμένο σχεδιασμό βιοδιυλιστηρίων πολλαπλών προϊόντων. Το μεθοδολογικό πλαίσιο είναι γενικεύσιμο σε διάφορες σχεδιαστικές κλίμακες και συνδυάζει εργαλεία για την προσομοίωση, ολοκλήρωση και σύνθεση διεργασιών. Οι προκλήσεις που απαντώνται είναι: i) η διαχείριση των πρωτογενών δεδομένων, ii) ο συστηματικός έλεγχος της ύπαρξης μονοπατιών λαμβάνοντας υπόψη τα τεχνολογικά χαρακτηριστικά, iii) η επίδραση των σχεδιαστικών επιλογών στην κατανάλωση βοηθητικών παροχών, iv) ο επανασχεδιασμός υφιστάμενων εγκαταστάσεων και v) η ολοκληρωμένη διαχείριση των αποβλήτων.
  - Χρησιμοποιείται η βελτιστοποίηση βάσει μοντέλων-υποκαταστάτες για την εναρμόνιση των πρωτογενών δεδομένων, αλλά και για τη συστημική ανάπτυξη των λεπτομερών μοντέλων. Προτείνεται ένα νέο μεθοδολογικό πλαίσιο για την υποβοηθούμενη επιλογή των συστημάτων ιδιοτήτων κι επεξεργασίας. Με δεδομένες βιβλιοθήκες συστατικών, θερμοδυναμικών μοντέλων και μοντέλων διεργασιών, ο στόχος είναι η ανάπτυξη μοντέλων-υποκατάστατες που ελαχιστοποιούν τις αποκλίσεις με τα δεδομένα της διεργασίας (βιβλιογραφική ή πειραματική).
  - Παρουσιάζεται μια νέα μέθοδος αρθρωτής σύνθεσης που επιτρέπει την αυτόματη δημιουργία του χώρου της εναλλακτικών επιλογών, η οποία βασίζεται στην αρχή της συμβατότητας "πηγής-στόχου". Οι υπερδομές διαμορφώνονται ως διμερείς Γράφοι πηγών και στόχων, οργανώνοντας τις διαδικασίες ως αρθρωτές μονάδες που μπορούν σχετικά εύκολα να τροποποιηθούν και / ή να αντικατασταθούν. Με δεδομένους τους διαθέσιμους πόρους, των θέσεων πηγών και στόχων και των μονάδων επεξεργασίας, η μέθοδος αναζητά ποια μονοπάτια αξιοποιούν καλύτερα τις διαθέσιμες πρώτες ύλες, λαμβάνοντας υπόψη τους τεχνολογικούς περιορισμούς.
  - Προτείνεται μια νέα μέθοδος για τον καθορισμό στόχων ταυτόχρονα για την κατανάλωση βοηθητικών παροχών μάζας και ενέργειας και για την επιλογή εναλλακτικών σχεδιασμών. Η μέθοδος επεκτείνει τις υπάρχουσες μεθόδους σε δίκτυα πολλαπλών συστατικών, συμπεριλαμβάνοντας πολλαπλές και παράλληλες μονάδες αναγέννησης πολλαπλών συστατικών, ενώ εισάγει την έννοια των διαδραστικών υπερδομών βασει υπεργράφων. Ο σχεδιασμός του δικτύου βοηθητικών παροχών δεν περιστρέφεται γύρω

από ένα κεντρικό συστατικό (νερό, H2, κ.λπ.), αλλά ο ρόλος τους καθορίζεται από την επίδρασή τους στην αντικειμενική συνάρτηση.

- Η προαναφερθείσα μέθοδος επεκτείνεται σε προβλήματα επανασχεδιασμού υφιστάμενων εγκαταστάσεων και αξιολογεί πιθανές συνεργίες (ενδογενείς ή εξωγενείς). Η προσέγγιση συνδυάζει τις βασικές τεχνικές βελτιστοποίησης με τα εργαλεία σύνθεσης για την τεχνολογική αναβάθμιση των υφιστάμενων διεργασιών. Η αρθρωτή αναπαράσταση επιτρέπει την αναζήτηση πιθανών αλληλεπιδράσεων μεταξύ των διαφόρων μονάδων επεξεργασίας.
- Προτείνεται μια νέα μεθοδολογία για την ολιστική αντιμετώπιση του προβλήματος διαχείρισης τόσο της παραγωγής όσο και των τεχνολογιών επεξεργασίας αποβλήτων. Η προτεινόμενη μεθοδολογία υπογραμμίζει μια συστημική και γενική προσέγγιση. Αρχικά, προτείνονται δέντρα αποφάσεων για την κατανομή των ροών αποβλήτων στις κατάλληλες τεχνολογίες επεξεργασίας. Στη συνέχεια, η προτεινόμενη χαρτογράφηση είναι δομημένη ως πρόβλημα σύνθεσης που διαμορφώνεται και βελτιστοποιείται με τη μορφή ενός μικτού ακέραιου μη γραμμικού προβλήματος προγραμματισμού. Η βελτιστοποίηση επιλέγει τεχνολογίες και η βέλτιστη λύση καθορίζει τη στρατηγική διαχείρισης (κεντρική και αποκεντρωμένη).

Ως βασική υπόθεση εργασίας χρησιμοποιείται μια πραγματική τεχνολογία βιοδιυλιστηρίου που αναπτύχθηκε από την Compagnie Industrielle de la Matière Végétale (CIMV). Τα αποτελέσματα της διατριβής συνεισέφεραν στις μελέτες για την κατασκευή της μονάδας βιομηχανικής κλίμακας.

Κεφάλαιο III: Προτεινόμενη Μεθοδολογία

Το τρίτο κεφάλαιο προτείνει μια νέα συστημική προσέγγιση για τη βιομηχανική ανάπτυξη βιοδιυλιστηρίων πολλαπλών προϊόντων. Αρχικά, περιγράφονται οι διαφορετικές σχεδιαστικές κλίμακες και τα δομικά τους στοιχεία. Στη συνέχεια, συζητείται πώς μπορούν να οργανωθούν τα στοιχεία κάθε κλίμακας έτσι ώστε να αναπτυχθεί αυτόματα η υπερδομή του χώρου εναλλακτικών επιλογών. Τέλος, παρουσιάζεται ο τρόπος συνδυασμού των διαφόρων εργαλείων συστημάτων για την ολοκλήρωση των σχεδιαστικών κλιμάκων, ώστε να προκύψει ο ολοκληρωμένων σχεδιασμός βιοδιυλιστηρίων δεύτερης γενιάς.

Η συστημική προσέγγιση συνδυάζει την προσομοίωση, τη σύνθεση και την ολοκλήρωση διεργασιών σε διαφορετικές σχεδιαστικές κλίμακες. Βασιζόμενη σε αρθρωτές μονάδες, το σύστημα που προκύπτει είναι ευέλικτο και τροποποιήσιμο. Οι τεχνολογικοί περιορισμοί και οι στόχοι αποδοτικότητας ορίζονται τόσο για τις αυτόνομες μονάδες, όσο και για τις ολοκληρωμένες. Το προτεινόμενο σχεδιαστικό αποτέλεσμα αξιολογείται από μια επαναληπτική διαδικασία.

Τα σύνολα που ορίζουν το πρόβλημα περιλαμβάνουν

- Στοιχεία (βιομάζα, χημικά προϊόντα, καύσιμα, ενέργεια κ.λπ.)
- Χημείες που χρησιμοποιούν ή παράγουν αυτά τα στοιχεία
- Τεχνολογίες σε διαφορετικά επίπεδα ωριμότητας, οι οποίες χρησιμοποιούν τις χημείες και δέχονται ή/ και παράγουν ροές των στοιχείων σε γνωστή ποιότητα

Ζητείται ο βέλτιστος σχεδιασμός ενός βιοδιυλιστηρίου πολλαπλών προϊόντων επιλέγοντας

- τα μονοπάτια της αλυσίδας αξιών (πρώτες ύλες, ενδιάμεσα προϊόντα, προϊόντα, χημείες και τεχνολογίες) που θα συνδυαστούν για την ανάπτυξη του βιοδιυλιστηρίου (άμεσες επενδύσεις)
- τα μονοπάτια της αλυσίδας αξιών με τα οποία μπορούν να αναπτυχθούν συνεργασίες (βιομηχανικές συνέργιες)
- τον βέλτιστο σχεδιασμό των επιλεγμένων τεχνολογιών

Για την αποδόμηση του προβλήματος σε επιλύσιμα υποσυστήματα, εφαρμόζονται τεχνικές δομημένου προγραμματισμού. Ακολουθείται η τεχνική της αμφίδρομης βελτίωσης: α) η καθοδική προσέγγιση ξεκινά από μια ασαφή περιγραφή για να καταλήξει σε μια λεπτομερή έκθεση, ενώ β) η ανοδική προσέγγιση ξεκινά από την αναλυτική περιγραφή για να καταλήξει στην πιο εμπειρικές λύσεις. Οι σχεδιαστικές κλίμακες περιλαμβάνουν (από κάτω προς τα πάνω) την μοριακή κλίμακα, τη φυσικοχημεία, τον εξοπλισμό, το τμήμα διεργασίας, την διεργασία, το εργοστάσιο, τη βιομηχανική περιοχή, τις βιομηχανικές συνεργίες και την ανάλυση της αγοράς. Η ανοδική και η καθοδική προσέγγιση είναι συμπληρωματικές μεταξύ τους, ενώ υπάρχει δυνατότητα εναλλαγής των δομικών τους στοιχείων. Εντούτοις, η ολοκλήρωση μοντέλων διαφορετικών κλιμάκων πρέπει να αντιμετωπίσει τη διαφορά στην ακρίβεια των δεδομένων που απαιτούνται ανά κλίμακα. Κάθε βήμα αποδόμησης πρέπει να συνοδεύεται από ένα βήμα επεξεργασίας δεδομένων.

Τα δομικά στοιχεία της προτεινόμενης μεθοδολογίας είναι τα συστατικά (N), οι μονάδες επεξεργασίας (M), οι πηγές (I) (παροχές) και οι στόχοι (J) (ανάγκες). Κάθε μονάδα επεξεργασίας απαιτεί και παρέχει συστατικά σε συγκεκριμένη ποιότητα.

Χρησιμοποιούνται σχεδιαστικά κριτήρια για την αναγνώριση την εφικτών συνδέσεων και όχι προκαθορισμένες συνδέσεις. Επομένως, μπορούν να συνδυαστούν διαφορετικές μονάδες με βάσει τη συμβατότητα μεταξύ των πηγών και των στόχων τους. Για κάθε επίπεδο αποδόμησης, το σχεδιαστικό πρόβλημα μπορεί να αναπαρασταθεί από ένα γράφο, χρησιμοποιώντας τις πληροφορίες του κατώτερου επιπέδου για να περιγράψει τα δομικά στοιχεία. Για παράδειγμα, στο επίπεδο του σχεδιασμού διεργασίες χρησιμοποιούνται τα τμήματα της διεργασίας ως δομικά στοιχεία. Κατά τη μετάβαση στο επίπεδο σχεδιασμού του τμήματος της διεργασίας δομικό στοιχείο γίνεται πλέον ο εξοπλισμός.

Ανάλογα με τις ιδιότητες της σύνδεσης «πηγών-στόχων», μπορούν να αναγνωριστούν διαφορετικές σχέσεις μεταξύ των μονάδων:

i. Οι μονάδες προς άμεση επένδυση έχουν αποκλειστική σχέση τύπου "προμηθευτή-αποδέκτη ".
ii. Οι μονάδες προς συνεργασία έχουν μη αποκλειστική σχέση τύπου "προμηθευτή-αποδέκτη".
iii. Οι ανταγωνιστικές μονάδες ανταγωνίζονται για τις ίδιες πηγές ή/ και στόχους.
iv. Οι ουδέτερες μονάδες δεν έχουν τίποτα κοινό.

Η μέθοδος ξεκινά με την επεξεργασία δεδομένων, να διασφαλιστεί η ομοιόμορφη και αξιόπιστη ροή πληροφορίας ανάμεσα στις διάφορες σχεδιαστικές κλίμακες. Στη συνέχεια, τίθενται οι στόχοι λειτουργίας (π.χ. ενέργεια, νερό, LCA κ.λπ.) για κάθε αυτόνομη μονάδας. Ακολουθεί το στάδιο της σύνθεσης, όπου αξιολογούνται οι αυτόνομες μονάδες και αναζητούνται οφέλη από πιθανές συνεργασίες. Επιστρέφοντας στην ολοκλήρωση διεργασιών, τίθενται νέοι στόχοι, αυτή τη φορά για τις ολοκληρωμένες μονάδες. Τέλος, το στάδιο προσομοίωσης ελέγχει την αξιοπιστία των αποτελεσμάτων και τα μεταφράζει σε σχεδιαστικές προτάσεις.

Στο επίπεδο στη προσομοίωσης, χρησιμοποιούνται υπολογιστικά πρότυπα υποκατάστασης για την επεξεργασία κι εναρμόνιση των δεδομένων (κεφάλαιο IV). Στο επίπεδο της σύνδεσης διεργασιών, η υπό όρους σύνθεση (κεφάλαιο V) καταδεικνύει την επίδραση των τεχνολογικών περιορισμών στην διαμόρφωση λύσεων της αλυσίδας αξιών. Συνδυάζοντας το επίπεδο ολοκλήρωσης με το επίπεδο μοντελοποίησης, τίθενται ταυτόχρονα στόχοι για την κατανάλωση και το σχεδιασμό του δικτύου βοηθητικών παροχών (κεφάλαιο VI). Το πρόβλημα επανασχεδιασμού υφιστάμενων εγκαταστάσεων αντιμετωπίζεται με συνδυασμό και των τριών επιπέδων, μοντελοποίηση, ολοκλήρωση και σύνθεση (κεφάλαιο VII). Τέλος, το συστημικό πλαίσιο επεκτείνεται σε προβλήματα ολοκληρωμένης διαχείρισης αποβλήτων (κεφάλαιο VIII).

Κεφάλαιο IV: Ανάπτυξη Μαθηματικών Προτύπων Υποκατάστασης

Το τέταρτο κεφάλαιο παρουσιάζει μια μεθοδολογία για την εναρμόνιση των δεδομένων που προέρχονται από διαφορετικές πηγές, αλλά και για την υποβοήθηση στη συστημική ανάπτυξη μοντέλων προσομοίωσης. Η προτεινόμενη προσέγγιση αξιοποιεί συστατικά, θερμοδυναμικά μοντέλα και μοντέλα διεργασιών που είναι διαθέσιμα σε υπάρχουσες βιβλιοθήκες.

Η ανάπτυξη ενός αξιόπιστου μοντέλου προσομοίωσης είναι το πρώτο βήμα σε μια σειρά μελετών αξιολόγησης και βελτιστοποίησης. Ωστόσο, ένα μοντέλο προσομοίωσης είναι ένα λεπτομερές και «ακριβό» μοντέλο, τόσο στον χρόνο ανάπτυξής του όσο και στο υπολογιστικό κόστος. Απλούστερα μετα-μοντέλα χρησιμοποιούνται συχνά, αλλά οι απλοποιημένες προσεγγίσεις παράγουν μοντέλα χαμηλής αξιοπιστίας, τα οποία δεν μπορούν να υποστηρίξουν μελέτες ολοκλήρωσης και βελτιστοποίησης ανώτερου επιπέδου. Τα μαθηματικά πρότυπα υποκατάστασης συνδυάζονται με προβλήματα τύπου «μαύρο κουτί» κι έχουν ελκυστική υπολογιστική απλότητα. Ένα «φτηνό» (απλοποιημένο) μοντέλο χρησιμοποιείται για να υποκαταστήσει ένα πιο «ακριβό» (λεπτομερές) μοντέλο. Μια ρουτίνα βελτιστοποίησης εφαρμόζεται απευθείας στο μοντέλο υποκαταστάτη, το οποίο αντικαθιστά το αρχικό μοντέλο. Ωστόσο, μέχρι σήμερα καμία μέθοδος δεν αμφισβητεί την εγκυρότητα του λεπτομερούς μοντέλου.

Έχοντας δεδομένη μια βιβλιοθήκη συστατικών, θερμοδυναμικών ιδιοτήτων και μοντέλων διεργασιών, ο στόχος είναι να αναπτυχθούν πρότυπα υποκαταστάτες με ελάχιστη απόκλιση από τα δεδομένα (βιβλιογραφικά ή πειραματικά). Τα πρότυπα υποκαταστάτες παράγονται ως τεχνητά υβριδικά που επεξεργάζονται μείγματα συστατικών τα οποία "προσομοιάζουν" πολύπλοκα συστατικά που σχεδιάζονται από μίγματα συμβατικών, η επιλογή και η σύνθεση των οποίων παραμένει βαθμός ελευθερίας και πρέπει να ταιριάζουν με τα πειραματικά δεδομένα. Η μεθοδολογία εφαρμόζεται για τη μοντελοποίηση μιας πραγματικής τεχνολογίας προεπεξεργασίας βιομάζας (CIMV). Αναπτύσσονται μοντέλα υποκαταστάτες για κάθε τμήμα της διεργασίας και η αξιοπιστία τους ελέγχεται με πειραματικά δεδομένα. Επίσης, διεξάγεται ανάλυση ευελιξίας για την αναζήτηση των αξιόπιστων ορίων εντός των οποίων μπορούν να χρησιμοποιηθούν τα μοντέλα αυτά.

Από συστημικής άποψης, ένα διάγραμμα ροής είναι ένας ιεραρχικός συνδυασμός μονάδων επεξεργασίας που μετατρέπει τα εισερχόμενα ρεύματα συστατικών, ενέργειας και πληροφοριών σε νέες ροές εξόδου οι οποίες συνδέονται με άλλες μονάδες επεξεργασίας. Μια μονάδα επεξεργασίας μπορεί να είναι ένα κομμάτι εξοπλισμού ή ένα κομμάτι διεργασίας που συνδυάζει τα συστήματα ιδιοτήτων και διεργασιών. Το σύστημα ιδιοτήτων αποτελείται από συστατικά και θερμοδυναμικά μοντέλα. Το σύστημα διεργασιών αποτελείται από μοντέλα διεργασιών, κανόνες συνδεσιμότητας και λειτουργικές παραμέτρους. Οι ροές που εισέρχονται σε μια μονάδα επεξεργασίας μετατρέπονται σε ροές εξόδου έπειτα από τη συνδυασμένη επίδραση των συστημάτων ιδιοτήτων και διεργασιών.

Η μέθοδος θεωρεί δεδομένα

- Ένα εργοστάσιο που αποτελείται από επιμέρους μονάδες επεξεργασίας
- Μια βιβλιοθήκη μοντέλων διεργασίας
- Μια βιβλιοθήκη συστατικών
- Μια βιβλιοθήκη θερμοδυναμικών μοντέλων
- Ένα σύνολο αξιόπιστων δεδομένων

Αναπτύσσονται μαθηματικά πρότυπα υποκατάστασης για κάθε μονάδα επεξεργασίας, σχετικά με

- Το σύστημα ιδιοτήτων: συστατικά και θερμοδυναμικά μοντέλα ως συνάρτηση των ενεργών συστατικών
- Το σύστημα διεργασιών: τα μοντέλα διεργασίας, οι κανόνες συνδεσιμότητάς τους και οι λειτουργικές τους παράμετροι ως συνάρτηση των ενεργών μοντέλων διεργασίας

Στόχος είναι η ελαχιστοποίηση της απόκλισης μεταξύ των προτύπων υποκατάστασης και των αξιόπιστων δεδομένων.

Το σύνθετο πρόβλημα αποικοδομείται σε δύο επιμέρους προβλήματα βελτιστοποίησης για το σύστημα ιδιοτήτων και το σύστημα διεργασιών. Ο έλεγχος της αξιοπιστίας των προτύπων υποκατάστασης και των λεπτομερών μοντέλων γίνεται με επαναληπτική διαδικασία. Ξεκινώντας με τα λεπτομερή μοντέλα, τα πρότυπα υποκατάστασης χρησιμοποιούνται για την επικύρωση των επιλογών των συστημάτων ιδιοτήτων και διεργασιών. Τα αποτελέσματα των προτύπων υποκατάστασης επαληθεύονται με τα πειραματικά προτού προχωρήσει η διαδικασία εκπαίδευσής τους για τη συνολική διεργασία.

Ο επιτυχής ορισμός του συστήματος ιδιοτήτων περιλαμβάνει:

(i) Επιλογή των συστατικών που είναι διαθέσιμα στη βάση δεδομένων
(ii) Περιγραφή των συστατικών και των παραμέτρων που δεν βρίσκονται στη βάση δεδομένων
(iii) Επιλογή του κατάλληλου θερμοδυναμικού μοντέλου
(iv) Επαλήθευση

Ο επιτυχής ορισμός του συστήματος διεργασιών περιλαμβάνει:

(i) Επιλογή των μοντέλων διεργασιών που είναι διαθέσιμα στη βάση δεδομένων και της συνδεσιμότητάς τους
(ii) Περιγραφή των μοντέλων διεργασιών που δεν βρίσκονται στη βάση δεδομένων
(iii) Βελτιστοποίηση των λειτουργικών παραμέτρων
(iv) Επαλήθευση

Μετά το στάδιο της επαλήθευσης, εφαρμόζεται ανάλυση σκοπιμότητας ώστε να βρεθεί η εφικτή περιοχή για την οποία μπορεί να χρησιμοποιηθεί το ίδιο μοντέλο προσομοίωσης.

Η προτεινόμενη μεθοδολογία εφαρμόζεται για την μοντελοποίηση της διεργασίας της CIMV. Ως περιβάλλον προσομοίωσης επιλέγεται το AspenPlus. Ο συντελεστής ετήσιας λειτουργίας ορίζεται σε 8.000 ώρες / έτος. Κατά τη διάρκεια του πρώτου κύκλου της επαναληπτικής διαδικασίας συγκεντρώθηκαν πληροφορίες για την ανάπτυξη του λεπτομερούς μοντέλου, το οποίο χρησιμοποιήθηκε έπειτα για την ανάπτυξη των προτύπων υποκατάστασης. Στο στάδιο της επαλήθευσης αποκαλύφθηκαν αδυναμίες στην περιγραφή των συστατικών της βιομάζας και των θερμοδυναμικών μοντέλων. Η ακολουθία των λύσεων έδωσε μια εικόνα για το πώς μεταμορφώνεται η βιομάζα ακολουθώντας τα διάφορα στάδια επεξεργασίας και συνεισέφερε στην επιλογή καταλληλότερων μοντέλων. Ως αποτέλεσμα, προέκυψαν αξιόπιστα πρότυπα υποκατάστασης και βελτιώθηκε η ακρίβεια και η ευελιξία του λεπτομερούς μοντέλου προσομοίωσης για διάφορους τύπους βιομάζας και δυναμικότητας.

Κεφάλαιο V: Σύνθεση Αλυσίδων Αξιών Υπό όρους

Το πέμπτο κεφάλαιο προτείνει ένα νέο μοντέλο για την υπό όρους σύνθεση της αλυσίδας αξιών. Πρότυπα υποκατάστασης που αναπτύχθηκαν με τη διαδικασία που περιγράφει το κεφάλαιο IV τροφοδοτούν την ανάλυση. Η σύνθεση διεργασιών οργανώνεται με βάση τον αρθρωτό γράφο πηγών-στόχων που περιγράφεται στο κεφάλαιο III. Οι μελέτες του συγκεκριμένου κεφαλαίου καταδεικνύουν την επίδραση της αρχής συμβατότητας πηγής-στόχου στη διαμόρφωση του χαρτοφυλακίου προϊόντων.

Η σύνθεση διεργασιών αξιολογεί ποια μονοπάτια είναι κατάλληλα για την παραγωγή ενός χαρτοφυλακίου προϊόντων σε σχέση με τις πρώτες ύλες. Οι υπάρχουσες μέθοδοι σύνθεσης βιοδιυλιστηρίων χρησιμοποιούν ένα δεδομένο δέντρο αλυσίδας αξιών με γνωστά μονοπάτια και χαρτοφυλάκια προϊόντων. Κοινή πρακτική αποτελεί η χρήση μιας βασικής τεχνολογίας (π.χ. για προ-επεξεργασία), στην οποία προστίθενται σταδιακά μονάδες προ-επεξεργασίας για την προετοιμασία των πρώτων υλών και μονάδες μετέπειτα επεξεργασίας για τον καθαρισμό και την αξιοποίηση των προϊόντων της. Παρόλο που οι υπάρχουσες προσεγγίσεις οδηγούν σε λειτουργικές προτάσεις, ενδέχεται να παρεμποδίζουν την διαμόρφωση καινοτόμων λύσεων. Η διαδικασία αξιολόγησης βασίζεται σε ιεραρχικές δομές "πρώτες ύλες προς ενδιάμεσα προϊόντα", αγνοώντας τις τεχνολογικές ασυμβατότητες που οφείλονται σε περιορισμούς ποιότητας των ρευμάτων. Κάθε τεχνολογία έχει διαφορετικά πρότυπα ποιότητας σχετικά με τα αποδεκτά όρια στις ροές τροφοδοσίας αλλά και για τα παραγόμενα ρεύματα.

Προτείνεται, λοιπόν, μια νέα μέθοδος για την υπό όρους σύνθεση των βιοδιεργασιών, όπου ο χώρος εναλλακτικών επιλογών και οι υπερδομές δημιουργούνται αυτόματα και διαμορφώνονται ως σύνθετα δίκτυα. Κάθε διεργασία δίνει στοιχεία για τις ροές που παρέχονται και απαιτούνται και περιλαμβάνει ένα σύνολο κανόνων μετασχηματισμού, περιγραφές των εισερχόμενων και εξερχόμενων ροών και συνθήκες ελέγχου συμβατότητας. Η μέθοδος εφαρμόζεται σε τρεις μελέτες εργασίας με σκοπό να αποδειχθεί η επίδραση των κανόνων συνδεσιμότητας στο τελικό σχεδιασμό του δικτύου. Η πρώτη περίπτωση αφορά τη σύνθεση με βάσει μόνο το κύριο συστατικού που παράγεται/ απαιτείται. Η δεύτερη περίπτωση λαμβάνει υπόψη την ποιότητα των ρευμάτων και τέλος, ενεργοποιούνται μονάδες που βελτιώνουν την ποιότητα των ροών και καθιστούν εφικτή τη σύνδεση όλων των μονάδων.

Τα σύνολα που ορίζουν το πρόβλημα περιλαμβάνουν

- βοηθητικές παροχές που σχετίζονται με μάζα (π.χ. βιομάζα, νερό) ή ενέργεια (π.χ. ατμός, νερό ψύξης)
- θέσεις πηγών και στόχων που σχετίζονται με ανταλλαγή ροών μάζας
- μονάδες επεξεργασίας που σχετίζονται με τοποθεσίες πηγής ή/ και στόχου. Οι μονάδες αυτές μπορούν επίσης να αφορούν προμηθευτές, μετατροπή, καταναλωτές ή εγκαταστάσεις επεξεργασίας αποβλήτων.

Δεδομένα είναι η διαθεσιμότητα των πρώτων υλών, οι αποδόσεις και οι ενεργειακές απαιτήσεις κάθε μονάδας επεξεργασίας. Ωστόσο, ο αριθμός και οι σχέσεις των ενεργών μονάδων επεξεργασίας καθώς και οι ροές του δικτύου είναι βαθμοί ελευθερίας. Σκοπός είναι να προσδιοριστεί η δομή του δικτύου βοηθητικών παροχών που μεγιστοποιεί το δυνητικό κέρδος για τη δεδομένη διαθεσιμότητα πρώτων υλών ενώ ικανοποιεί όλους τους περιορισμούς.

Το μαθηματικό μοντέλο διαμορφώνεται ως ένα πρόβλημα μικτού-ακέραιου γραμμικού προγραμματισμού (MILP). Οι ενεργές μονάδες επιλέγονται με τη βοήθεια των δυαδικών μεταβλητών. Το μοντέλο περιλαμβάνει ισοζύγια μάζας κι ενέργειας, σχέσεις που περιγράφουν τις οικονομικές ροές κι ένα σύνολο λογικών περιορισμών. Ωστόσο, όταν οι ροές και οι συστάσεις είναι μεταβλητές, το μοντέλο είναι μη γραμμικό. Για να διατηρηθεί η γραμμικότητα του μοντέλου, υιοθετείται ένα λογικό σύνολο υποθέσεων

- Οι διεργασίες βρίσκονται σε συνθήκη συνεχούς λειτουργίας και σταθερής απόδοσης
- Χρησιμοποιούνται γραμμικοποιημένα μοντέλα για την εκτίμηση του κόστους εξοπλισμού
- Οι τοποθεσίες στόχων έχουν γνωστά όρια για τη μαζική ροή, με βάση τα γραμμικοποιημένα μοντέλα κόστους αλλά και για την ποιότητα των ροών, βάσει της σταθερής απόδοσης
- Οι πηγές παράγουν ροές με σταθερές συστάσεις, βάσει της σταθερή απόδοση

Η μέθοδος εφαρμόζεται σε μελέτη εργασίας με δώδεκα διεργασίες προ-επεξεργασίας βιομάζας κι εννέα διεργασίες μετατροπής. Ο συντελεστής λειτουργίας ορίζεται σε 8.000 ώρες/ έτος, ο συντελεστής απόσβεσης σε 35% και η διάρκεια ζωής της επένδυσης σε 15 χρόνια. Οι τιμές αναφέρονται σε $ το 2016 κι επικαιροποιούνται με δείκτες πληθωρισμού. Οι τιμές σε ευρώ (€) μετατρέπονται σε δολάρια Ηνωμένων Πολιτειών (USD) σύμφωνα με το μέσο εύρος συναλλαγών του 2016. Η διαθεσιμότητα της βιομάζας ορίζεται σε 2Mtn/ έτος ξηρά βάση. Τρεις διαφορετικές επιλογές σύνθεσης μελετώνται για ένα δίκτυο που απαιτεί ελάχιστη παραγωγή αιθανόλης 80ktn/ έτος. Το ίδιο δίκτυο διεργασιών χρησιμοποιείται και για τις τρεις περιπτώσεις.

Στην πρώτη μελέτη εργασίας οι διεργασίες του δικτύου αξιολογούνται με βάση το κύριο συστατικό, όπως γίνεται στην υπάρχουσα βιβλιογραφία. Η διεργασία της CIMV επιλέγεται ως η κύρια τεχνολογία προ-επεξεργασίας βιομάζας, ενώ εκτός από την παραγωγή αιθανόλης επιλέγονται κι άλλα προϊόντα. Στη δεύτερη μελέτη εργασίας λαμβάνονται υπόψη οι περιορισμοί ποιότητας όσον αφορά τα ποσοστά υγρασία. Το δίκτυο καταλήγει σε ένα συνεργιστικό σχήμα μεταξύ CIMV και άλλης μιας διεργασίας, επειδή τα ρεύματά τους μπορούν να συνδυαστούν και να παράξουν ρεύματα έτοιμα προς χρήση είτε ως ενδιάμεσα είτε ως τελικά προϊόντα. Τέλος, ενεργοποιούνται μονάδες που βελτιώνουν την ποιότητα των ρευμάτων, ώστε να εκτιμηθεί το πρόσθετο κόστος σύνδεσης των αρχικά μη συμβατών διεργασιών. Το τελικό δίκτυο επιλέγει μόνο τη CIMV για την προ-επεξεργασία της βιομάζας, ενώ δεν ενεργοποιείται μονάδα συμπύκνωσης ρευμάτων.

Και στις τρεις περιπτώσεις, η αιθανόλη συμβάλλει ελάχιστα στα συνολικά έσοδα, ενώ το κύριο εισόδημα προέρχεται από συστατικά υψηλότερης αξίας (λιγνίνη, ξυλιτόλη ή ξυλόζη). Η τιμή πώλησης παίζει επίσης σημαντικό ρόλο. Παρόλο που οι τιμές πώλησης ήταν οι ίδιες και για τις τρεις περιπτώσεις, τα αποτελέσματα δείχνουν ότι είναι σημαντικό τα προϊόντα να μπορούν να έρθουν με υψηλό κέρδος. Για παράδειγμα, η ξυλιτόλη έχει τη δεύτερη υψηλότερη συνεισφορά εσόδων στην πρώτη περίπτωση, αλλά δεν επιλέχθηκε στην τρίτη περίπτωση. Το ρεύμα ξυλόζης παράγεται σε συγκέντρωση 20% w/w, ενώ το εισερχόμενο ρεύμα σε διαδικασία καταλυτικής ξυλιτόλης απαιτεί τροφοδοσία συγκέντρωσης 90% w/w. Το κόστος για την εξάτμιση αυτής της μεγάλης ποσότητας νερού είναι απαγορευτικό. Ακόμη ένας σημαντικός παράγοντας είναι η δυναμικότητα ανά μονάδα επεξεργασίας. Η κατανάλωση νερού κι ενέργειας μπορεί να έχουν μικρή επίπτωση στο συνολικό κόστος, αλλά έχουν σημαντικό ρόλο ως περιβαλλοντικοί δείκτες. Οι μονάδες βελτίωσης της ποιότητας των ρευμάτων εκτιμούν το οικονομικό και περιβαλλοντικό κόστος της σύνδεσης δύο διεργασιών. Σε όλες τις περιπτώσεις, τα έσοδα από την πώληση του παραγόμενου ατμού ήταν μεγαλύτερα από το κόστος ενέργειας. Ως εκ τούτου, ένα πρόωρο συμπέρασμα θα μπορούσε να είναι ότι τα δίκτυα αυτά έχουν ενεργειακή ανεξαρτησία. Εντούτοις, η ανάλυση ενεργειακής ολοκλήρωσης είναι απαραίτητη προκειμένου να καταλήξουμε σε ασφαλέστερο συμπέρασμα.

Κεφάλαιο VI: Βελτιστοποίηση Δικτύου Βοηθητικών Παροχών

Το έκτο κεφάλαιο παρουσιάζει ένα νέο εργαλείο για την ταυτόχρονη βελτιστοποίηση της του κόστους εξοπλισμού και βοηθητικών παροχών. Η έρευνα αυτή επεκτείνει τις υπάρχουσες μεθόδους σε δίκτυα πολλαπλών συστατικών, λαμβάνοντας υπόψη εναλλακτικές σχεδιαστικές επιλογές. Η προσέγγιση εισάγει την έννοια των διαδραστικών υπερδομών που διατυπώνονται ως υπεργράφοι.

Τα σύνολα που ορίζουν το πρόβλημα περιλαμβάνουν

- βοηθητικές παροχές που σχετίζονται με μάζα (π.χ. βιομάζα, νερό) ή ενέργεια (π.χ. ατμός, νερό ψύξης)
- θέσεις πηγών και στόχων που σχετίζονται με ανταλλαγή ροών μάζας
- θέσεις πηγών και στόχων που σχετίζονται με ανταλλαγή ροών ενέργειας
- μονάδες επεξεργασίας που σχετίζονται με τοποθεσίες πηγής ή/ και στόχου. Οι μονάδες αυτές μπορούν επίσης να αφορούν προμηθευτές, μετατροπή, αποθήκευση, αναγέννηση, επεξεργασία αποβλήτων

Οι θερμοκρασίες λειτουργίας κάθε διεργασίας θεωρούνται γνωστές. Ωστόσο, η παροχή και η συνολική θερμική ικανότητα κάθε ρεύματος είναι βαθμοί ελευθερίας. Σκοπός είναι να προσδιοριστεί η διαμόρφωση του δικτύου βοηθητικών παροχών που ελαχιστοποιεί το λειτουργικό και επενδυτικό κόστος, αλλά ικανοποιεί τις ανάγκες σε βοηθητικές παροχές μάζας κι ενέργειας.

Η συστημική προσέγγιση οργανώνεται σε δύο διασυνδεδεμένα τμήματα:

Μέρος Α: Τμήμα ανταλλαγής μάζας

i. Αναγνώριση των κόμβων πηγών και στόχων
ii. Συσχετισμός των μονάδων διεργασιών με τους κόμβους πηγών και στόχων

Μέρος Β: Το τμήμα ανταλλαγής ενέργειας

i. Αναγνώριση των ενεργειακών πηγών και στόχων
ii. Συσχετισμός των μονάδων διεργασιών με τους ενεργειακούς κόμβους πηγών και στόχων
iii. Συσχετισμός των κόμβων μάζας με τους κόμβους ενέργειας

Η ενεργειακή ολοκλήρωση περιλαμβάνει ρεύματα με σταθερές και μεταβλητές ροές. Τα ρεύματα με σταθερές ροές έχουν σταθερή συμβολή στον ενεργειακό καταρράκτη , ενώ η θερμική συμβολή ρευμάτων με μεταβλητές ροές είναι βαθμός ελευθερίας, με αποτέλεσμα να δημιουργούνται ταυτόχρονα πολλαπλοί ενεργειακοί καταρράκτες.

Για να διατηρηθεί η γραμμικότητα του μοντέλου, υιοθετείται ένα λογικό σύνολο υποθέσεων

- Οι διεργασίες βρίσκονται σε συνθήκη συνεχούς λειτουργίας και σταθερής απόδοσης
- Χρησιμοποιούνται γραμμικοποιημένα μοντέλα για την εκτίμηση του κόστους εξοπλισμού
- Οι τοποθεσίες στόχων έχουν γνωστά όρια για τη μαζική ροή, με βάση τα γραμμικοποιημένα μοντέλα κόστους αλλά και για την ποιότητα των ροών, βάσει της σταθερής απόδοσης
- Οι πηγές παράγουν ροές με σταθερές συστάσεις, βάσει της σταθερή απόδοση
- Οι θερμοκρασίες λειτουργίας είναι γνωστές
- Επιτρέπεται μόνη η ισοθερμοκρασιακή ανάμιξη των ρευμάτων

Η μέθοδος εφαρμόζεται για το σχεδιασμό του δικτύου βοηθητικών παροχών της CIMV. Ο συντελεστής λειτουργίας ορίζεται σε 8.000 ώρες/ έτος, ο συντελεστής απόσβεσης σε 35% και η διάρκεια ζωής της επένδυσης σε 15 χρόνια. Οι τιμές αναφέρονται σε \$ το 2016 κι επικαιροποιούνται με δείκτες πληθωρισμού. Οι τιμές σε ευρώ (€) μετατρέπονται σε δολάρια Ηνωμένων Πολιτειών (USD) σύμφωνα με το μέσο εύρος συναλλαγών του 2016. Η αρχική μελέτη εργασίας βελτιστοποιεί διαδοχικά το δίκτυ, χρησιμοποιώντας ευριστικούς κανόνες για την ιεράρχηση των βημάτων. Έπειτα εφαρμόζεται η προτεινόμενη μέθοδος ταυτόχρονης βελτιστοποίησης. Εξετάζεται και η περίπτωση όπου απαιτείται κεντρική διαχείριση του διαλύτη. Τέλος, γίνεται μια ανάλυση ευαισθησίας για να μελετηθεί πώς επηρεάζεται το μοντέλο σε σχέση με διάφορες λειτουργικές παραμέτρους.

Η σταδιακή βελτιστοποίηση μείωσε τις απαιτήσεις σε οργανικούς διαλύτες κατά 99% και σε ενέργεια κατά 66%, σε σχέση με το σενάριο μηδενικών ανακυκλώσεων. Το προτεινόμενο μοντέλο μείωσε το συνολικό κόστος κατά 70% σε σύγκριση με την αρχική υπόθεση. Αυτό επιτυγχάνεται κυρίως λόγω της μείωσης κατά 50% του κόστους των μαζικών παροχών. Το κόστος επεξεργασίας αποβλήτων ρευμάτων σχεδόν τριπλασιάστηκε, αλλά οι ενεργειακές απαιτήσεις μειώθηκαν κατά 80% και το κόστος εξοπλισμού μειώθηκε κατά 28%. Στην περίπτωση όπου επιβάλλεται η κεντρική διαχείριση των διαλυτών, όλα τα ρεύματα που περιέχουν μίγμα οργανικού διαλύτη πρέπει να περάσουν από μια κεντρική δεξαμενή αποθήκευσης πριν εισέλθουν στις κύριες μονάδες επεξεργασίας. Τα αποτελέσματα δείχνουν ότι το συνολικό κόστος μπορεί να μειωθεί περαιτέρω κατά 57%, χωρίς να αυξηθεί σημαντικά η πολυπλοκότητα του δικτύου. Όλες οι περιπτώσεις συμφωνούν πως η ενέργεια έχει τον σημαντικότερο ρόλο στα δίκτυα βοηθητικών παροχών. Αυτό μπορεί να συνδέεται και με το γεγονός πως στο συγκεκριμένο δίκτυο το 62% των ροών θερμότητας είναι μεταβλητές, το οποίο σημαίνει πως το μοντέλο είχε σημαντική ευελιξία στην αναζήτηση εναλλακτικών λύσεων. Ακόμα, το ΔTmin έχει σημαντικό ρόλο στο σχεδιασμό του δικτύου εναλλακτών, αλλά το μοντέλο αναδιατάσσει τις ροές έτσι ώστε να εξισορροπήσει τις αυξημένες ενεργειακές απαιτήσεις που προκύπτουν από την άνοδο του ΔTmin.

Κεφάλαιο VII: Βελτιστοποίηση Δικτύου Βοηθητικών Παροχών με Επανασχεδιασμό

Το έβδομο κεφάλαιο επεκτείνει το μοντέλο που παρουσιάζεται στο κεφάλαιο VI σε προβλήματα επανασχεδιασμού υφιστάμενων εγκαταστάσεων, εξετάζοντας παράλληλα επιλογές για βιομηχανικές συνέργειες. Η μέθοδος συστηματοποιεί το συνδυαστικό πρόβλημα σχεδιασμού νέων και υφιστάμενων διεργασιών, ενώ ταυτόχρονα ενσωματώνει εργαλεία σύνθεσης για την αξιολόγηση επιλογών της αλυσίδας αξιών και την αναζήτηση πιθανών συνεργειών.

Τα σύνολα που ορίζουν το πρόβλημα περιλαμβάνουν

- βοηθητικές παροχές που σχετίζονται με μάζα (π.χ. βιομάζα, νερό) ή ενέργεια (π.χ. ατμός, νερό ψύξης)
- θέσεις πηγών και στόχων που σχετίζονται με ανταλλαγή ροών μάζας
- θέσεις πηγών και στόχων που σχετίζονται με ανταλλαγή ροών ενέργειας
- μονάδες επεξεργασίας που σχετίζονται με τοποθεσίες πηγής ή/ και στόχου, οι οποίες μπορεί να είναι υπάρχουσες ή νέες. Οι μονάδες αυτές μπορούν επίσης να αφορούν προμηθευτές, αγοραστές, μετατροπή, αποθήκευση, αναγέννηση, επεξεργασία αποβλήτων
- διαστήματα θερμοκρασίας κι ενθαλπίας που σχετίζονται με τις θερμοκρασίες των κόμβων ενέργειας

Ο σχεδιασμός των υπαρχουσών μονάδων θεωρείται γνωστός. Σκοπός είναι να προσδιοριστεί ποιες από τις υπάρχουσες μονάδες να διατηρηθούν, να τροποποιηθούν ή να αντικατασταθούν και σε ποιες νέες μονάδες αξίζει να γίνει επένδυση.

Η συστημική προσέγγιση οργανώνεται σε τέσσερα στάδια και απαιτεί προ-επεξεργασία δεδομένων για τις υπάρχουσες μονάδες:

- Στάδιο I: Ανάλυση διαγράμματος ροής
  - Συλλογή και προ-επεξεργασία δεδομένων
- Στάδιο II: Δίκτυο ανταλλαγής μάζας
  - Αναγνώριση των κόμβων πηγών και στόχων
  - Συσχετισμός των μονάδων διεργασιών με τους κόμβους
- Στάδιο III: Δίκτυο ανταλλαγής ενέργειας
  - Αναγνώριση των κόμβων πηγών και στόχων
  - Συσχετισμός των μονάδων διεργασιών με τους κόμβους
  - Υπολογισμός στόχους για την υφιστάμενη διεργασία
- Στάδιο IV: Εισαγωγή δεδομένων στο μοντέλο βελτιστοποίησης
  - Επίλυση του μαθηματικού προβλήματος

Το μοντέλο ελαχιστοποιεί την αντικειμενική συνάρτηση συνολικού κόστους και περιλαμβάνει επιλογές για διατήρηση, ανακατασκευής ή επένδυσης σε νέες μονάδες. Οι περιορισμοί περιλαμβάνουν την ικανοποίηση των ισοζυγίων μάζας κι ενέργειας και των λογικών και τεχνολογικών απαιτήσεων.

Για να διατηρηθεί η γραμμικότητα του μοντέλου, υιοθετείται ένα λογικό σύνολο υποθέσεων

- Οι διεργασίες βρίσκονται σε συνθήκη συνεχούς λειτουργίας και σταθερής απόδοσης
- Χρησιμοποιούνται γραμμικοποιημένα μοντέλα για την εκτίμηση του κόστους εξοπλισμού
- Οι τοποθεσίες στόχων έχουν γνωστά όρια για τη μαζική ροή, με βάση τα γραμμικοποιημένα μοντέλα κόστους αλλά και για την ποιότητα των ροών, βάσει της σταθερής απόδοσης
- Οι πηγές παράγουν ροές με σταθερές συστάσεις, βάσει της σταθερή απόδοση
- Οι θερμοκρασίες λειτουργίας είναι γνωστές
- Επιτρέπεται μόνη η ισοθερμοκρασιακή ανάμιξη των ρευμάτων
- Μια υπάρχουσα ροή/ μονάδα μπορεί να διατηρηθεί εάν η ροή/ η απόδοσή της είναι εντός ± 10% της αρχικής
- Μια υπάρχουσα ροή/ μονάδα μπορεί να τροποποιηθεί εάν η ροή/ η απόδοσή της είναι μεγαλύτερη από το 10% αλλά μικρότερη από το 30% της αρχικής
- Μια υπάρχουσα ροή/ μονάδα πρέπει να αντικατασταθεί εάν η ροή/ η απόδοσή της υπερβαίνει το 30% της αρχικής
- Δεν εξετάζονται λεπτομερείς μετατροπές εξοπλισμού

Η μέθοδος εφαρμόζεται για τον επανασχεδιασμό βιοδιυλιστηρίου πρώτης γενιάς χρησιμοποιώντας τη διεργασία της CIMV ως τεχνολογία αναβάθμισης. Η πρώτη μελέτη εργασίας χρησιμοποιεί την νέα τεχνολογία (CIMV) για να αυξήσει την παραγωγή αιθανόλης του υπάρχοντος εργοστασίου πρώτης γενιάς. Τα αποτελέσματα δείχνουν πως το εγχείρημα είναι κερδοφόρο μόνο όταν τα προϊόντα λιγνίνη και πεντόζες σε σιρόπι πωλούνται ως προϊόντα. Η δεύτερη μελέτη εργασίας αφήνει την επιλογή των προϊόντων ως βαθμό ελευθερία ενεργοποιώντας τη συνεργατική σύνθεση διεργασιών. Σε αυτή την περίπτωση, η τεχνολογία δεύτερης γενιάς εμφανίζεται ως συμβιωτική διεργασία για την αξιοποίηση του λιγνοκυτταρινούχου κατάλοιπου της διεργασίας πρώτης γενιάς. Η μονάδα CHP δεν ενεργοποιείται, καθώς το ενεργειακό όφελος είναι μικρότερο από το όφελος πώλησης των ρευμάτων που χρησιμοποιούνται ως πηγή ενέργειας. Παρόλο που η δεύτερη μελέτη εργασίας έχει δύο επιπλέον τμήματα διεργασίας για την υδρόλυση των σακχάρων, το εγχείρημα είναι περισσότερο επικερδές από την πρώτη περίπτωση. Φαίνεται, λοιπόν, να προτιμάται η επένδυση σε παραγωγή προϊόντων με μεγαλύτερη αξία πώλησης, παρά την τροποποίηση της υπάρχουσας εγκατάστασης μόνο για την παραγωγή αιθανόλης καυσίμου.

Κεφάλαιο VIII: Ολοκληρωμένη Διαχείριση Αποβλήτων

Το όγδοο κεφάλαιο επεκτείνει τη συστημική προσέγγιση σε συστήματα ολοκληρωμένης διαχείρισης αποβλήτων. Το προτεινόμενο μεθοδολογικό πλαίσιο λαμβάνει υπόψη τόσο τη δημιουργία αποβλήτων ρευμάτων, ανάλογα με τις επιλεγμένες βιοδιυλιστηριακές μονάδες, όσο και τις τεχνολογίες επεξεργασίας τους. Το ολοκληρωμένο σύστημα περιλαμβάνει επιλογές εναλλακτικών τεχνολογιών επεξεργασίας αποβλήτων και στρατηγικές αποκεντρωμένης και κεντρικής διαχείρισης.

Η κυκλική οικονομία εστιάζει μακροπρόθεσμα στη μείωση της σπατάλης πόρων, δίνοντας έμφαση στην αξιοποίηση, την ανάκτηση και την επαναχρησιμοποίηση προϊόντων, αλλά και αποβλήτων. Με βάση αυτή τη λογική, τα απόβλητα μπορούν να θεωρηθούν ως πρώτη ύλη και όχι ως απορρίμματα. Η αξιοποίηση των αποβλήτων ρευμάτων μπορεί να θεωρηθεί βαθμός ελευθερίας, καθώς υπάρχουν αρκετές υποψήφιες τεχνολογίες για την επεξεργασία τους. Επιπλέον, η στρατηγική για την αποκεντρωμένη ή κεντρική διαχείριση είναι σχεδιαστική μεταβλητή. Για να αξιολογηθούν τα πιθανά οφέλη της επεξεργασίας αποβλήτων είναι απαραίτητος ο ολοκληρωμένος σχεδιασμός με την βασική διεργασία. Μια συστημική προσέγγιση μπορεί να εκτιμήσει σε ποιο βαθμό η διεργασία είναι σε θέση να ολοκληρώσει την παραγωγή της με τη διαχείριση των αποβλήτων της. Η προτεινόμενη μεθοδολογία αναδεικνύει μια συστημική και ολιστική προσέγγιση.

Τα σύνολα που ορίζουν το πρόβλημα περιλαμβάνουν

- διεργασίες του βιοδιυλιστηρίου
- μη αξιοποιήσιμα ρεύματα (απόβλητα) και τεχνολογίες για την επεξεργασία τους
- οικονομικά μοντέλα και μοντέλα κοστολόγησης για κάθε τεχνολογία
- σχεδιαστικές προδιαγραφές, συμπεριλαμβανομένων περιβαλλοντικών κανονισμών και περιορισμών

Σκοπός είναι να προσδιοριστεί

- ποιες τεχνολογίες επεξεργασίας είναι κατάλληλες
- εάν κάθε ρεύμα πρέπει να επεξεργάζεται από μια ή από πολλαπλές τεχνολογίες
- εάν τα ρεύματα αποβλήτων πρέπει να επεξεργάζονται από κοινού ή ξεχωριστά

Τα στάδια της συστημικής προσέγγισης είναι:

i. Ταξινόμηση των τεχνολογιών επεξεργασίας αποβλήτων
ii. Ανάπτυξη προτύπων υποκατάστασης των τεχνολογιών επεξεργασίας αποβλήτων
iii. Ταξινόμηση των μη αξιοποιούμενων ρευμάτων και συσχετισμό με τις τεχνολογίες επεξεργασίας αποβλήτων
iv. Σύνθεση τεχνολογιών βασισμένη σε υπερδομές διμερών γράφων
v. Διατύπωση κι επίλυση του μαθηματικού προβλήματος βελτιστοποίησης

Τα μη αξιοποιούμενα ρεύματα του δεδομένου βιοδιυλιστηρίου ταξινομούνται με βάση τη φυσική τους κατάσταση (υγρά, στερεά και αέρια) και στη συνέχεια συσχετίζονται με τις κατάλληλες τεχνολογίες επεξεργασίας τους με κριτήριο τα ποιοτικά χαρακτηριστικά των συστατικών τους. Η προτεινόμενη χαρτογράφηση διατυπώνεται ως πρόβλημα σύνθεσης στη μορφή ενός προβλήματος μεικτού ακέραιου μη γραμμικού προγραμματισμού. Η μέθοδος επιλέγει τεχνολογίες, ενώ η βέλτιστη λύση καθορίζει ποια τεχνολογία θα χρησιμοποιηθεί.

Η μέθοδος εφαρμόζεται για την επιλογή της στρατηγικής επεξεργασίας των αποβλήτων της διεργασίας της CIMV. Το βιοδιυλιστήριο περιλαμβάνει 54 ρεύματα, 14 διεργασίες βιοδιυλιστηρίου και 12 προϊόντα (κυτταρινικό πολτό, γλυκόζη, λιγνίνη, σιρόπι γλυκόζης, πεντόζες σε σιρόπι, ξυλόζη, ιτακονικό οξύ, ξυλιτόλη, φαινολικές ρητίνες, πολυουρεθάνες, αιθυλένιο, PVC, αιθανόλη). Τα προϊόντα από την επεξεργασία των αποβλήτων ρευμάτων περιλαμβάνουν βιοαέριο, ηλεκτρική ή/ και θερμική ενέργεια, λυματολάσπη, καθαρισμένο νερό, συμπιεσμένο CO_2 και αναγεννημένο καταλύτη.

Χρησιμοποιούνται δύο διαφορετικά χαρτοφυλάκια βιοδιυλίστηρίων:

Χαρτοφυλάκιο I: ξυλιτόλη, κυτταρινική αιθανόλη και πολυουρεθάνες με βάση την λιγνίνη.

Χαρτοφυλάκιο II: ξυλιτόλη, κυτταρινικό PVC και πολυουρεθάνες με βάση την λιγνίνη

Με βάση αυτά τα δύο χαρτοφυλάκια εξετάζονται τρία διαφορετικά σενάρια:

Σενάριο 1: Αξιολόγηση της κεντρικής και αποκεντρωμένης επεξεργασίας (ροές υγρών)

Σενάριο 2: Ολοκληρωμένη επεξεργασία στερεών και αερίων προϊόντων

Σενάριο 3: Επανασχεδιασμός υφιστάμενων εγκαταστάσεων

Η ολοκλήρωση των τεχνολογιών επεξεργασίας αποβλήτων οδηγεί συστηματικά στην ολιστική αξιολόγηση των εναλλακτικών επιλογών και συμβάλει στην ανάπτυξη διεργασιών με καλύτερη οικονομική και περιβαλλοντική απόδοση. Το ποσοστό της εξοικονόμησης από την εφαρμογή αποκεντρωμένης επεξεργασίας φτάνει μέχρι και 97%. Στην περίπτωση επανασχεδιασμού υφιστάμενων μονάδων επεξεργασίας, τα ολοκληρωμένα συστήματα ουσιαστικά μετατρέπουν το λειτουργικό κόστος σε κέρδη. Τα αποτελέσματα δείχνουν ότι η ολοκλήρωση είναι κρίσιμη για την αειφορία μιας διεργασίας, καθώς μπορεί να μειώσει το κόστος, ακόμη και να μετατρέψει το λειτουργικό κόστος σε κέρδη. Η ολοκληρωμένη προσέγγιση μπορεί να αποφέρει σημαντική εξοικονόμηση χάρη σε επιλογές αποκεντρωμένης επεξεργασίας και μη συμβατικών λύσεων.

Κεφάλαιο IX: Συμπεράσματα

Το ένατο κεφάλαιο εξάγει τα συμπεράσματα και τη σημασία αυτής της διατριβής και σκιαγραφεί κατευθύνσεις για μελλοντική έρευνα.

Τα βιοδιυλιστήρια πρέπει να ικανοποιούν τις οικονομικές, περιβαλλοντικές και κοινωνικές απαιτήσεις. Λόγω του μεγέθους και της πολυπλοκότητας του προβλήματος, ο σχεδιασμός και η βελτιστοποίηση βιώσιμων βιοτεχνολογιών απασχολούν ενεργά την έρευνα. Ακολουθώντας τις ερευνητικές ανάγκες για τη βιομηχανική ανάπτυξη μιας τεχνολογίας βιοδιυλιστηρίου που αναπτύχθηκε στη Γαλλία (CIMV), η διατριβή αυτή προτείνει ένα συστημικό πλαίσιο για να συμβάλει στη λήψη σχεδιαστικών αποφάσεων σχετικά με τη βέλτιστη χρήση πόρων, λαμβάνοντας υπόψη πιθανές βιομηχανικές συνέργειες και την τεχνολογική ολοκλήρωση. Εστιάζοντας κυρίως στους παράγοντες που επηρεάζουν τα οικονομικά και περιβαλλοντικά κριτήρια, το μεθοδολογικό πλαίσιο εκτείνεται σε διάφορες σχεδιαστικές κλίμακες και συνδυάζει εργαλεία για μοντελοποίηση, ολοκλήρωση και σύνθεση διεργασιών. Ο κύριος στόχος είναι η μείωση του κόστους, ενώ τα περιβαλλοντικά κριτήρια ενσωματώνονται ως κόστος των βοηθητικών παροχών και της επεξεργασίας αποβλήτων. Συστημικές προκλήσεις περιλαμβάνουν (i) τη διαχείριση δεδομένων που προέρχονται από διαφορετικές πηγές (βιβλιογραφία ή πειράματα), σε κάθε περίπτωση με διαφορετική ακρίβεια λόγω διαφορετικής πειραματικής προέλευσης και τεχνολογικής ωριμότητας (πιλοτική εγκατάσταση, εργαστήριο, θεωρητικό στάδιο), (ii) τη συστηματική σύγκριση εναλλακτικών επιλογών επεξεργασίας, λαμβάνοντας υπόψη τεχνολογικά χαρακτηριστικά, (iii) την επίδραση των σχεδιαστικών επιλογών στην κατανάλωση βοηθητικών παροχών (ενέργειας και μάζας), (iv) τις ενδογενείς συμβιωτικές επιλογές κατά την αναβάθμιση υφιστάμενων μονάδων με νέες τεχνολογίες και (v) την ολοκληρωμένη διαχείριση αποβλήτων. Η πολυπλοκότητα και το μέγεθος του προβλήματος καθιστούν ανέφικτη την ανάπτυξη ενός ενιαίου μοντέλου βελτιστοποίησης. Επομένως, το πρόβλημα αποικοδομείται σε μικρότερα προβλήματα και αναπτύσσονται διαφορετικά εργαλεία για την αντιμετώπιση κάθε υπο-προβλήματος.

Η πρώτη πρόκληση είναι να διασφαλιστεί η αξιοπιστία των δεδομένων. Η εναρμόνιση των δεδομένων γίνεται με τη βοήθεια προτύπων υποκατάστασης. Τα αποτελέσματα από το κεφάλαιο IV καταδεικνύουν ότι τα μοντέλα υποκατάστασης μπορούν να στηρίξουν δύο ρόλους: α) να βοηθήσουν στη συστημική ανάπτυξη λεπτομερών μοντέλων, αναζητώντας συστηματικά αδυναμίες στα συστήματα ιδιοτήτων και διεργασιών και β) χρησιμεύουν ως αξιόπιστα απλοποιημένα μοντέλα. Ωστόσο, το πλαίσιο περιορίζεται από την ύπαρξη διαθέσιμων μοντέλων ιδιοτήτων και διεργασιών στις βιβλιοθήκες του λογισμικού που επιλέχθηκε για την ανάπτυξη του λεπτομερούς μοντέλου.

Η δεύτερη πρόκληση είναι να εκτιμηθεί η δυναμική μιας διεργασίας σε σύγκριση με τον ανταγωνισμό. Το κεφάλαιο V εισάγει μια νέα μέθοδο για την υπό όρους σύνθεση αλυσίδων αξιών, η οποία λαμβάνει υπόψη τα ποιοτικά και τεχνολογικά χαρακτηριστικά των διεργασιών, προκειμένου να ανιχνεύσει πιθανές συνέργειες. Η ανάλυση εκτιμά, σε πρώιμο στάδιο, το περιβαλλοντικό κόστος της σύνδεσης διαφορετικών τεχνολογιών και αξιολογεί την ετοιμότητα των παραγόμενων ροών. Όμως, πρέπει να σημειωθεί ότι αυτή η μέθοδος περιορίζεται στη σύνθεση αυτόνομων μονάδων.

Η τρίτη πρόκληση αφορά την κατανάλωση βοηθητικών παροχών και την επίδραση των διαφορετικών σχεδιαστικών επιλογών. Το κεφάλαιο VI παρουσιάζει μια μέθοδο για τη βελτιστοποίηση του δικτύου ταυτόχρονης χρήσης πολλαπλών βοηθητικών παροχών. Τα αποτελέσματα καταδεικνύουν ότι η ενέργεια είναι ο σημαντικότερος παράγοντας, ωστόσο, οι μισές από τις ενεργειακές ανάγκες, πριν από την ολοκλήρωση θερμότητας, ήταν για την αναγέννηση του διαλύτη. Λόγω του μεγέθους και της πολυπλοκότητας του προβλήματος, η προτεινόμενη μέθοδος προϋποθέτει λειτουργία σε μόνιμη κατάσταση και με σταθερή απόδοση λειτουργίας, ώστε να διατηρηθεί η γραμμικότητα του μαθηματικού μοντέλου.

Η τέταρτη πρόκληση αφορά την αξιολόγηση των τεχνολογιών δεύτερης γενιάς ως επιλογές αναβάθμισης των εγκαταστάσεων πρώτης γενιάς. Παρόλο που έχουν ήδη δημοσιευθεί μελέτες ολοκλήρωσης 1G-2G στη βιβλιογραφία, κάθε περίπτωση επανασχεδιασμού είναι μοναδική. Η μέθοδος που παρουσιάζεται στο κεφάλαιο VII συστηματοποιεί το συνδυασμένο πρόβλημα ολοκλήρωσης νέων και υφιστάμενων διεργασιών, ενώ ταυτόχρονα ενσωματώνει εργαλεία σύνθεσης για την αξιολόγηση του χαρτοφυλακίου προϊόντων και την αναζήτηση συνεργιών. Τα αποτελέσματα δείχνουν ότι η διαδικασία δεύτερης γενιάς πρέπει να χρησιμοποιηθεί ως συμβιωτική διαδικασία που αξιοποιεί την λιγνοκυτταρινική βιομάζα που παράγεται από τη διεργασίας πρώτης γενιάς. Το ολοκληρωμένο σχήμα θα πρέπει να επενδύσει σε προϊόντα υψηλότερης αγοραστικής αξίας αντί να στοχεύσεις στην αύξηση της παραγωγής της αιθανόλης. Η μέθοδος περιορίζεται σε λειτουργία μόνιμης κατάστασης με σταθερές λειτουργικές αποδόσεις.

Η τελευταία πρόκληση αφορά τη διαχείριση αποβλήτων. Κάθε βιομηχανία πρέπει να επεξεργάζεται τα απόβλητά της. Ωστόσο, στην της εποχής της κυκλικής οικονομίας, η επεξεργασία των αποβλήτων δεν είναι το τέλος της γραμμής. Τα ρεύματα αποβλήτων μπορούν να θεωρηθούν ως πιθανές πρώτες ύλες και τα μονοπάτια επεξεργασίας τους μπορεί να δώσουν νέο χαρτοφυλάκιο προϊόντων. Το κεφάλαιο VIII παρουσιάζει μια συστημική μέθοδο για την ολοκληρωμένη διαχείριση των αποβλήτων. Προτείνονται δέντρα αποφάσεων που συσχετίζουν ροές και τεχνολογίες με βάση τα ποιοτικά χαρακτηριστικά τους. Αναπτύσσονται πρότυπα υποκατάστασης για την παραγωγή δεδομένων για τις τεχνολογίες επεξεργασίας. Τα αποτελέσματα δείχνουν ότι η ολοκλήρωση είναι εξαιρετικά σημαντική και οδηγεί συχνά σε σημαντικές μειώσεις του κόστους, ενώ μπορεί μετατρέψει το κόστος σε κέρδος. Ωστόσο, η μέθοδος περιορίζεται σε ρεύματα αποβλήτων των οποίων η ποιότητα βρίσκεται εντός των ορίων των δέντρων αποφάσεων.

Η διατριβή συμβάλλει στην επιστημονική κοινότητα με την επέκταση υπαρχουσών και την επινόηση νέων μεθοδολογιών για τον ολοκληρωμένο σχεδιασμό βιοδιυλιστηρίων. Επιπλέον, δημιούργησε νέα γνώση και συνεισέφερε στη βιομηχανική ανάπτυξη μιας πραγματικής τεχνολογίας. Ξεκινώντας από τα επιστημονικά ευρήματα, αποκαλύπτεται μια νέα χρήση για τα πρότυπα υποκατάστασης, τα οποία μπορούν να χρησιμοποιηθούν ως αξιόπιστες πηγές δεδομένων, αλλά μπορούν επίσης να οδηγήσουν σε βελτιώσεις των λεπτομερών μοντέλων. Στη συνέχεια, η αναπαράσταση της υπερδομής ως δίκτυο πηγών και στόχων αυτοματοποιεί την ανάπτυξη του χώρου εναλλακτικών επιλογών και προσφέρει μεγαλύτερη ευελιξία και καλύτερη δυνατότητα ελέγχου στο σύστημα. Το μοντέλο βελτιστοποίησης δικτύων βοηθητικών παροχών επεκτείνει υπάρχουσες μεθοδολογίες σε συστήματα πολλαπλών συστατικών και ταυτόχρονα προσθέτει την αξιολόγηση σχεδιαστικών επιλογών. Το μοντέλο για τον επανασχεδιασμό διεργασιών συνδυάζει την ολοκλήρωση νέων και υφιστάμενων διεργασιών και ταυτόχρονα περιλαμβάνει εργαλεία για τη σύνθεση διεργασιών, αναζητώντας βιομηχανικές συνέργειες. Τέλος, αναπτύσσονται χάρτες αποφάσεων και πρότυπα υποκατάστασης για τις τεχνολογίες επεξεργασίας αποβλήτων, ενώ μια μέθοδος βελτιστοποίησης επιλέγει τις τεχνολογίες και τη στρατηγική διαχείριση των αποβλήτων ρευμάτων.

Όσον αφορά τη διεργασία της CIMV, η διατριβή αποκάλυψε ότι η τεχνολογία μπορεί να στηρίξει ένα σχεδιασμό παραγωγής πολλαπλών προϊόντων. Η βελτιστοποίηση βάσει μοντέλων υποκατάστασης αποκάλυψε ελλείψεις στην περιγραφή του συστήματος ιδιοτήτων και συνεισέφερε στην ανάπτυξη ενός πιο ευέλικτου και αξιόπιστου μοντέλου προσομοίωσης. Παρόλο που οι τιμές της αγοράς έχουν σημαντική επίπτωση στην επιλογή του χαρτοφυλακίου προϊόντων, η CIMV μπορεί να στηρίξει μια μεγάλη γκάμα χημικών και προϊόντων ενέργειας. Η κατανάλωση ενέργειας είναι το κύριο μειονέκτημα της, όπως σε όλες τις διεργασίες με οργανικούς διαλύτες, αλλά με την κατάλληλη στρατηγική ολοκλήρωσης μπορεί να επενδύσει σε επιπλέον διεργασίες χωρίς περαιτέρω αύξηση στην κατανάλωση ενέργειας. Ακόμα, μπορεί να χρησιμοποιηθεί για την αναβάθμιση υφιστάμενων εγκαταστάσεων. Τέλος, ο ολοκληρωμένος σχεδιασμός διαχείρισης των αποβλήτων αποκαλύπτει στρατηγικές για επικερδείς χρήσεις των μη αξιοποιούμενων ρευμάτων.

Οι μεθοδολογίες που παρουσιάζονται σε αυτή τη διατριβή έχουν αρκετά περιθώρια βελτίωσης. Η μέθοδος με τα πρότυπα υποκατάστασης μπορεί να συνδυαστεί με εργαλεία τεχνητής νοημοσύνης για την αυτοματοποίηση της αναζήτησης αλλά και την αυτόματη σύνδεση με τις βάσεις δεδομένων για τα μοντέλα ιδιοτήτων και διεργασιών. Η υπό όρους σύνθεση μπορεί να εμπλουτιστεί με περισσότερα κριτήριο για την επαλήθευση της τεχνολογικής συμβατότητας και για την αξιολόγηση περιβαλλοντικών δεικτών. Λεπτομερείς επιλογές για τα συστήματα ενέργειας και επεξεργασίας αποβλήτων μπορούν να προστεθούν για τον ολιστικό σχεδιασμό των δικτύων βοηθητικών παροχών. Μια πρόκληση θα ήταν επίσης η αντιμετώπιση της μη γραμμικοποιημένης διατύπωσης των προβλημάτων. Η μέθοδος επανασχεδιασμού μπορεί να συνδυαστεί με εργαλεία τεχνητής νοημοσύνης για μια πιο εξελιγμένη αναζήτηση πιθανών συνεργειών. Η ολοκληρωμένη διαχείριση των αποβλήτων μπορεί να επεκταθεί και σε άλλους τύπους αποβλήτων, και παράλληλα να εξετάζεται και ο σχεδιασμός των διεργασιών του βιοδιυλιστηρίου.

Κλείνοντας, είναι σημαντικό να σημειωθεί ότι για το σχεδιασμό βιώσιμων βιοδιυλιστηρίων είναι απαραίτητη η συνεργασία διεπιστημονικών ομάδων. Μηχανικοί, τεχνικοί, χημικοί, βιολόγοι, γεωργοί, αναλυτές της αγοράς και άλλοι συνεργάζονται για να αποκαλύψουν ποιες συνθήκες και αβεβαιότητες μπορεί να έχουν σημαντικό αντίκτυπο στη διαδικασία λήψης αποφάσεων και πώς μπορεί να βελτιωθεί η τεχνολογία και να ανταπεξέλθει στις απρόσμενες αλλαγές. Η μηχανική συστημάτων και εργαλεία που συνδυάζουν διαφορετικές σχεδιαστικές κλίμακες, σε συνδυασμό με τεχνικές τεχνητής νοημοσύνης έχουν ακόμα πολλά να προσφέρουν.