

1

Early-Stage Design and Analysis of Biorefinery Networks

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1.1 Introduction

The limited resources of fossil fuel as well as other important driving forces (e.g., environmental, social, and sustainability concerns) are expected to shape the future development of the chemical processing industries. These challenges motivate the development of new and sustainable technologies for the production of fuel, chemicals, and materials from renewable feedstock instead of fossil fuel. An emerging technology in response to these challenges is the biorefinery concept. The biorefinery is defined as the set of processes converting a bio-based feedstock into products such as fuels, chemicals, materials, and/or heat and power.

The design of a biorefinery process is a challenging task. First, several different types of biomass feedstock and many alternative conversion technologies can be selected to match a range of products, and therefore, a large number of potential processing paths are available for biorefinery development. Furthermore, being based on a natural feedstock, the economic and environmental viability of these processes is deeply dependent on local factors such as weather conditions, availability of raw materials, national or regional subsidies and regulations, etc. Therefore, the replication of a standard process configuration is often not convenient or impossible. Designing a biorefinery, therefore, requires screening among

a set of potential configurations in order to identify the most convenient option for the given set of conditions.

Detailed evaluation of each process alternative requires a substantial amount of information such as conversions and efficiencies for the different steps involved. Moreover, considerable time and resources are needed to execute the analysis, and it is therefore not practically possible to consider more than a handful of candidate processing paths. In order to partially overcome these drawbacks, a second level of decomposition is often employed based on the so-called *development funnel* approach (see Figure 1.1). The basic idea of the development funnel approach is to progressively reduce the number of candidate alternatives by employing simplified model and shortcut evaluation methods to identify nonconvenient or nonfeasible options and eliminate those from the set of candidate configurations.

One of the challenges associated with this development funnel approach lies in the ability of performing the early-stage screening in a project phase characterized by lack of detailed data. As a consequence, it is important to simplify and manage the complexity related to the vast amount of data that needs to be processed prior to identifying the optimal biorefinery processing path with respect to economics, consumption of resources, sustainability, and environmental impact.

In order to manage the complexity and perform synthesis and design of biorefineries, several publications have focused on simplification and different aspects of the problem: the study of Voll and Marquardt (2012) explored the use of reaction flux network analysis for synthesis and design of biorefinery processing paths, Pham and El-Halwagi (2012) proposed a systematic two-stage methodology to reduce the number of processing steps, Martin and Grossmann (2012) evaluated the heat integration on a biorefinery process flowsheet producing FT-diesel, Baliban et al. (2012) studied the heat and water integration and supply chain optimization of thermochemical conversion of biomass, Zondervan et al. (2011) studied the identification of the optimal processing paths of the biochemical platform, and finally, Cheali et al. (2014) presented a generic modeling framework to manage the complexity of the multidisciplinary data needed for superstructure-based optimization of biorefinery

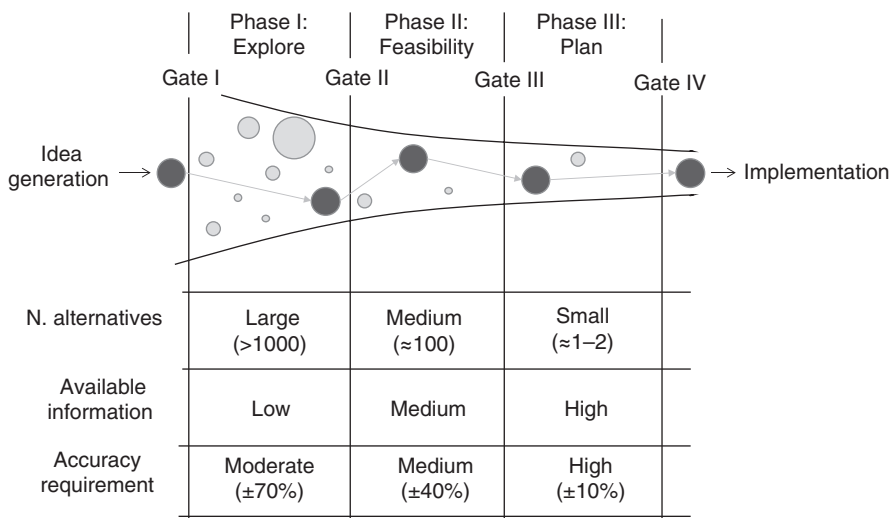


Figure 1.1 A schematic representation of the development funnel for a project in the processing industries. Reproduced from Alberto Quaglia, Ph.D. thesis, with permission

systems. A more detailed review of studies on the process synthesis of a biorefinery is given in Yuan et al. (2013).

While each of the abovementioned studies provided a valuable contribution, however, the scope of these studies was limited to one processing/conversion platform. Or, in other words, the studies focused either on biochemical, thermochemical, or biological platforms. In this contribution, as we focus on early-stage design and analysis of biorefinery systems, the scope of the biorefinery synthesis is broadened by considering a combination of thermochemical and biochemical platforms. In this way, the design space is extended significantly, meaning that more potential platforms and design alternatives can be compared resulting in a more robust and sustainable design solution. It is important to note that designing a biorefinery includes other challenges as well, such as the supply chain of the feedstock and land use, among others. These are beyond the scope of this study and will be considered in future work.

A methodology to generate and identify optimal biorefinery networks was developed earlier in our group (Zondervan et al., 2011; Quaglia et al., 2013). We present here the adaptation and extension of the methodology for the biorefinery problem. We expand the scope and the size of the biorefinery network problem by extending the database, the models, and the superstructure of the methodology with thermochemical biomass conversion routes. We then integrate the thermochemical superstructure with the superstructure of the biochemical conversion network. We then present a generic process modeling approach together with data collection and management for the multidisciplinary and multidimensional data related to different biorefinery processing steps. The optimal processing paths are then identified with respect to the given scenarios and specifications by formulating and solving an MILP/mixed-integer nonlinear programming problem (MINLP) problem using the GAMS optimization software. The resulting optimal biorefinery network is then further studied with respect to sustainability and environmental impact using two in-house software tools, SustainPro (Carvalho et al., 2013) and LCSOFT (Piyarak, 2012), respectively.

1.2 Framework

This study uses the integrated business and engineering framework (Figure 1.2) which was successfully applied to synthesis and design of a wide range of different processes (Quaglia et al., 2013). The framework uses a superstructure optimization-based process synthesis combined with a generic modeling approach, thus allowing the possibility of generating a larger design space, of managing the data and model complexity, and of identifying the optimal processing path with respect to technical and economic feasibility. The framework is integrated with the analysis and evaluation of sustainability and environmental impact.

A schematic representation of the framework is reported in Figure 1.2. The description of the framework is presented step by step in this chapter:

Step 1: Problem definition

The first step includes the definition of the problem scope (i.e., design a biorefinery network, wastewater treatment plant network, a processing network for vegetable oil production), the selection of suitable objective functions (i.e., maximum profit of the biorefinery, minimum total annualized cost (TAC) of the wastewater treatment plant), and optimization scenarios with respect to either business strategy, engineering performance, sustainability, or a combination of such objectives.

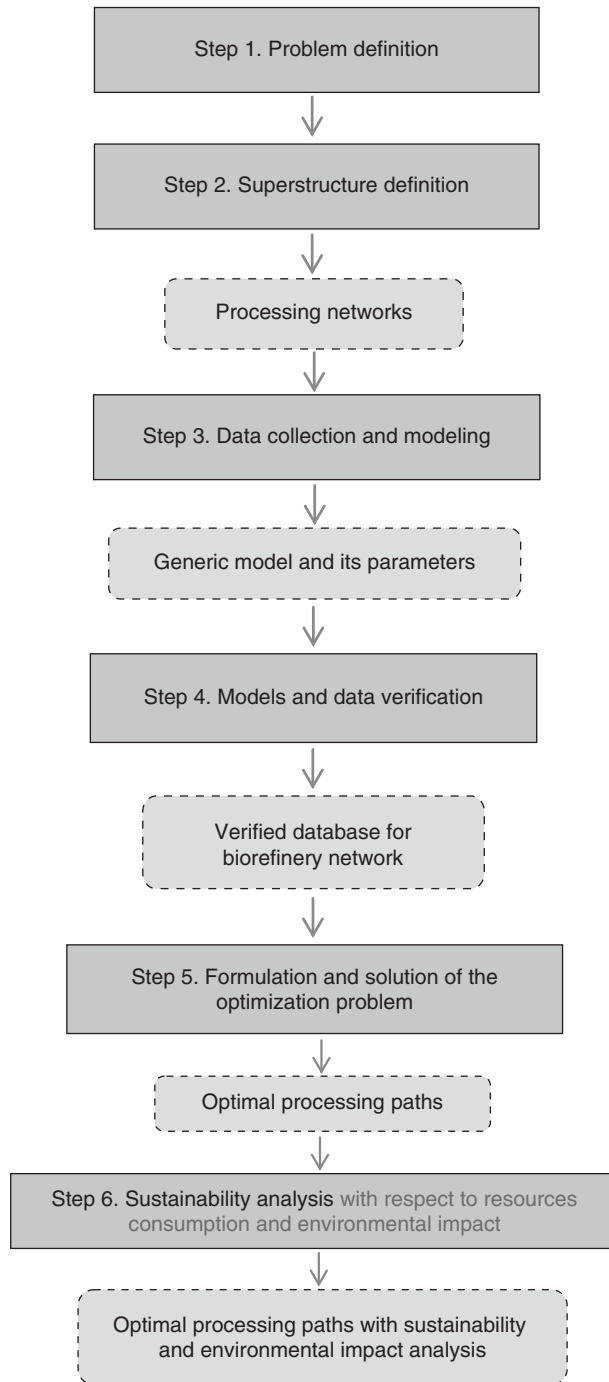


Figure 1.2 The integrated business and engineering framework adapted: the dashed boxes indicate the outcome of each step of the workflow

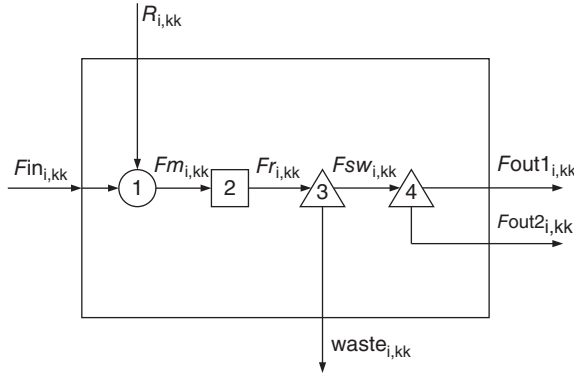


Figure 1.3 The generic process model block. Reproduced from Cheali et al. (2014), © 2014, American Chemical Society

Step 2: Superstructure definition

A superstructure representing different biorefinery concepts and networks is formulated by performing a literature review. A typical biorefinery network consists of a number of processing steps converting or connecting biomass feedstock to bioproducts such as pretreatment, primary conversion (gasification, pyrolysis), gas cleaning and conditioning, fuel synthesis, and product separation and purification. Each processing step is defined by one or several blocks depending on the number of unit operations considered in the step (several unit operations can be modeled using one process block). Each block incorporates the generic model to represent various tasks carried out in the block such as mixing, reaction, and separation (Figure 1.3).

Step 3: Data collection and modeling

Once the superstructure is defined, the data are collected and modeling is performed. Generally, the models for each processing technology are rigorous, nonlinear, and complex (e.g., kinetics, thermodynamics). However, in this step, a simple input–output-type generic model block is used, and this model is identified from the data generated from the aforementioned rigorous models. This generic model block thus consists of four parts of the typical simple mass balance equations: (i) mixing, (ii) reaction, (iii) waste separation, and (iv) product separation. The simple mass balance models representing each section of the generic model block are presented (Eqs. 1.1–1.7) and explained below:

$$Fm_{i,kk} = Fin_{i,kk} + Ri,kk \quad (1.1)$$

$$Ri,kk = (\mu_{i,j,kk} \times Fin_{i,kk} \times \alpha_{i,kk}) \quad (1.2)$$

$$Fr_{i,kk} = Fm_{i,kk} + MW_i \times \sum_{rr} (\gamma_{i,rr} \times \theta_{react,rr} \times Fm_{i,kk} / MW_{react}) \quad (1.3)$$

$$Fsw_{i,kk} = (1 - SW_{i,kk}) \times Fr_{i,kk} \quad (1.4)$$

$$waste_{i,kk} = SW_{i,kk} \times Fr_{i,kk} \quad (1.5)$$

$$Fout1_{i,kk} = split_{i,kk} \times Fsw_{i,kk} \quad (1.6)$$

$$Fout2_{i,kk} = (1 - split_{i,kk}) \times Fsw_{i,kk} \quad (1.7)$$

$$F1_{i,k,kk} \leq S_p^{k,kk} \times Fout1_{i,kk} \quad (1.8)$$

$$F2_{i,k,kk} \leq (S_p^{k,kk} - S^{k,kk}) \times Fout1_{i,kk} \quad (1.9)$$

$$Fin_{i,kk} = \sum_k (F1_{i,k,kk} + F2_{i,k,kk}) \quad (1.10)$$

The above equations (1.1–1.7) are the equations used for the generic model block to estimate the outlet mass flow ($Fout1_{i,kk}$, $Fout2_{i,kk}$) using simple mass balances. The subscripts i and j represent the components, whereas k and kk represent the upstream and downstream processing technologies, respectively. In Equations 1.1 and 1.2, the chemicals and utilities used ($R_{i,kk}$) for each processing technology are calculated by using the ratio ($\mu_{i,j,kk}$) to the inlet mass flow rate ($Fin_{i,kk}$). The parameter $\alpha_{i,kk}$ represents the amount of the utilities or chemicals carried to the outlets. In Equation 1.3, the reaction outlet mass stream ($Fr_{i,kk}$) is calculated based on stoichiometry, $\gamma_{i,rr}$, and conversion fraction, $\theta_{react,rr}$. In Equations 1.4 and 1.5, the waste stream ($waste_{i,kk}$) and the remaining stream ($Fsw_{i,kk}$) are calculated on the basis of the removal fraction, $SW_{i,kk}$. The product outlet streams are calculated in Equations 1.6 and 1.7 on the basis of a product separation fraction, $Split_{i,kk}$. Moreover, in order to connect each generic model block and thereby formulate the superstructure, Equations 1.8–1.10 are used. The mass outlet flows mentioned earlier ($Fout1_{i,kk}$, $Fout2_{i,kk}$) are called primary and secondary outlet flows, respectively. The primary and secondary outlet flows are connected to the next generic model blocks using binary variables (S_p , S), respectively. The outlet flows between the generic model blocks ($F1_{i,k,kk}$, $F2_{i,k,kk}$) of each stream (primary and secondary) are summed up as the input of the next generic model block. It is noted that recycle flows can be considered using Equations 1.8–1.10. There are two potential cases of recycle flows addressed: (i) recycle flows within the same processing step, that is, internal recirculation—the simulation of the recycle flows and their impact on process performance needs to be done prior to estimating the parameter values for the corresponding generic model block (e.g., processing step 2, 4)—and (ii) recycle between processing steps (e.g., processing step 4 to processing step 2 or 3), which is handled by using Equations 1.8 and 1.9.

The appropriate values for the aforementioned parameters can be collected in several ways including (i) literature sources or technical reports, (ii) experimental data, (iii) simulation results, or (iv) stream table or operating data of a designed flowsheet. The collected parameters are in the end organized in a multidimensional matrix form which represents the activities (chemicals/utilities used, reactions, separations, etc.) occurring in the processing alternatives.

Step 4: Models and data verification

After the superstructure is defined and the parameters are collected, a validation of the selected models and parameters needs to be performed for quality and consistency check. The verification can be performed in this step by fixing the decision variables in the MINLP problem formulation—that is, the vector y —and thereby to perform a simulation for each processing technology or path, followed by comparison of the simulation results against the available data. Such data can originate either from experiments or from the literature. All the necessary equations and constraints relevant to each processing technology are

also formulated in this step, prior to being solved as MILP or MINLP problems in GAMS. The output of this step is a verified database representing the biorefinery superstructure formulated in step 2 and stored in an Excel worksheet.

Step 5: Formulation and solution of the optimization problem

In this step, the optimization problem is formulated as MILP or MINLP problem depending on the objective function definition and constraints using appropriate software, in this case GAMS. The output is the optimal biorefinery configuration. The generic models and structure of the optimization problem (MIP/MINLP) organized and used in this study are presented and explained in the following text.

The optimization formulation (presented in Eqs. 1.11–1.16) consists of the objective function (e.g., minimize TAC; Eq. 1.11) subjected to process constraints, the process models and constraints (Eqs. 1.1–1.10) of the generic model block mentioned earlier (x is a process variable, the mass flow rate), structural constraints (Eqs. 1.12 and 1.13) representing the superstructure which allows selection of only one process alternative in each step, and cost functions (Eqs. 1.14–1.16) to calculate the operating and capital costs using cost parameters ($P1_{i,kk}^{\text{waste}}$, waste treatment cost; $P2_{i,kk}^{\text{utilities/chemicals}}$, utility or chemicals cost; $P3_a^{\text{kk}}$, reactor investment cost; $P3_b^{\text{kk}}$, separation investment cost; capex_{kk} , capital expenditures). The details on a related optimization problem can be found in the previous studies (Zondervan et al., 2011; Quaglia et al., 2013).

As an example, the objective function is formulated such as to minimize the TAC:

$$\text{OBJ} = \sum_{kk} \text{OPEX} - (\text{CAPEX}_1 + \text{CAPEX}_2) / t \quad (1.11)$$

Subject to the following constraints:

- i. Process models of the generic model block $h(\mu_{i,j,kk}, \alpha_{i,kk}, \gamma_{i,rr}, \theta_{\text{react},rr}, \text{MW}_i, \text{SW}_{i,kk}, \text{split}_{i,kk}) = 0$, as mentioned earlier, Equations 1.1–1.7 and 1.10
- ii. Process constraints $g(S_p^{k,kk}, S^{k,kk}) \leq 0$, as mentioned earlier, Equations 1.8 and 1.9
- iii. Structural constraints:

$$\sum_k y_k \leq 1 \quad (1.12)$$

$$y \in \{0;1\}^n \quad (1.13)$$

- iv. Cost constraints:

$$\text{OPEX}_{kk} = (P2_{i,kk}^{\text{utilities/chemicals}} \times R_{i,kk}) + (P1_{i,kk}^{\text{waste}} \times F_{i,kk}^{\text{waste}}) \quad (1.14)$$

$$\text{CAPEX}_{\text{thermochem}} = \sum_{kk} \text{capex}_{kk} \quad (1.15)$$

$$\text{CAPEX}_{\text{biochem}} = \sum_{kk} [P3_a^{\text{kk}} \times Fm_{i,kk}^{n1} + P3_b^{\text{kk}} \times Fr_{i,kk}^{n2}] \quad (1.16)$$

- v. Optimization constraints (big- M formulation):

$$\text{Process variables (e.g., } F_{i,kk} \text{)} \leq M \times y_{kk} \quad (1.17)$$

For the solution, GAMS retrieves the generic model parameters and other data appearing in the constraints (e.g., $\alpha_{i,kk}$, $\gamma_{i,rr}$, $\theta_{\text{react},rr}$, $P1_{i,kk}^{\text{waste}}$, $P2_{i,kk}^{\text{utilities/chemicals}}$) from the database. In this way, the overall MINLP problem formulation is separated into two parts: (i) data handling and representation (as described in this contribution, with help of a generic process model and its parameters stored in a database) and (ii) solution and analysis of the problem. This separation of the problem in two parts helps with the management of the complexity of formulating an MINLP-based optimization problem for biorefinery networks.

Step 6: Sustainability and environmental impact analysis

The presented framework has been integrated with the sustainability and environmental impact assessment. Both sustainability and environmental impact analysis are performed using two in-house software tools, SustainPro (Carvalho et al., 2013) and LCSofT (Kalakul et al., 2014), respectively. As a prerequisite for this step, some extra data are needed such as rigorous mass and energy balance, connectivity among the unit operations within the flowsheet, duty, and reaction data which are explained in more detail in the following text.

1.2.1 Sustainability Analysis

A sustainable process is characterized by the use of renewable resources as raw materials and as energy sources and utilities to produce biodegradable products while minimizing the production of waste, the use of nonenvironmentally friendly chemicals and the external dependence on energy and water. In this study, a generic and systematic approach of sustainability analysis developed by Carvalho et al. (2013) has been integrated with the business and engineering framework already proposed (see Figure 1.2). This integrated tool enables the user to evaluate the process in terms of raw material, water, and energy usage through the calculation of sustainability metrics (Azapagic, 2002) and by a set of previously defined indicators (Uerdingen et al., 2003). The sustainability-related methodology was adapted into Excel VBA-based software, resulting in the so-called SustainPro software tool, which contains four main parts as follows (see Table 1.1): (i) flowsheet decomposition into open path (OP) and closed path (CP), (ii) path flow assessment in terms of mass and energy indicators analysis, (iii) sustainability metrics calculation, (iv) and generation and comparison of new retrofit alternatives—note that this last stage is beyond the scope of this study.

The models used to perform the indicators analysis in SustainPro are presented below (Eqs. 1.18–1.22) (Uerdingen et al., 2003):

Material value added (MVA): The indicator that reflects the value added between the entrance and exit of a given compound in a certain path, and therefore, this indicator is only estimated for OPs. A high negative value of MVA indicates that the specific compound in that particular path is losing value along the process. Ideally, MVA should be close to zero. As mentioned before, the software defines paths or routes for each and every compound in the system, classifying a compound as OP, meaning that the compound enters and leaves the system, or CP, meaning that the compound is being recycled:

$$\text{MVA}_o^i = m_o^i \times \left[\text{PP}_o^i - \text{CA}_o^i \cdot \left(\sum_{m=1}^{\text{RM}} \frac{|U_o^{(m)}| \cdot M_o^{(m)}}{U_o^i \cdot M_o^i} \times \text{PR}_o^{(m)} \right) \right] \quad (1.18)$$

Table 1.1 The simplified explanation of each section in SustainPro

Part	Name	Description
Prerequisite	Input	<ul style="list-style-type: none"> • Mass and energy balance (stream table) • Component properties • Reactions • Duty of unit operations
(i)	Flowsheet decomposition (path decomposition)	Process streams are decomposed into: <ul style="list-style-type: none"> • Open path (OP): refers to a certain compound that enters and leaves the system, therefore characterizing a specific path • Closed path (CP): refers to a certain compound that is being recycled within the system, therefore characterizing a specific path
(ii)	Path flow assessment	The performance of each path flow is assessed through a set of indicators (MVA, EWC, RQ, AF, TVA) which are explained in Eqs. 1.18–1.22. Rank the paths from top to bottom, where the top are the worst in terms of the process sustainability, therefore identifying the process critical points (bottlenecks) with respect to energy and mass (raw materials and water)
(iii)	Evaluation	Sustainability metrics calculation with respect to energy, water, and raw material usage
(iv)	Generation and comparison of new alternatives	<ul style="list-style-type: none"> • Generation of retrofit alternatives according to the critical points identified by the application of the general known retrofit rules

where m_o^i is the flow rate of component i in the OP flow o , PP_o^i is the purchase price, CA_o^i is the cost allocation factor calculated by dividing the purchase price of the component i by the total purchase price of product, ν_o^i is the stoichiometric coefficient, M_o^i is the molecular weight, and $PR_o^{(m)}$ is the raw material price.

Energy and waste cost (EWC): The indicator of overall process costs related to utility consumption and waste treatment of a component path flow—for OP and CP. A high value of EWC means that the given path carries important units of energy that could be used for heat integration within the system but are being discarded instead:

$$EWC_k^i = \sum_{u=1}^U PE_u \times Q_u \times \frac{m_k^i \cdot A_{u,k}^i(T,p)}{\sum_{uk=1}^{UK} m_{uk} \cdot A_{u,uk}(T,p)} \quad (1.19)$$

where PE_u is the energy price of subunit operation u , Q_u is the subunit operation duty, m_k^i is the mass flow rate along the path flow k of the component i , and $A_{u,k}^i$ is the specific heat capacity.

Reaction quality (RQ): The indicator of the process productivity. A positive value (0–1) shows that a certain compound in a given path has a positive contribution to the process productivity. On the other hand, a negative value means that the given path has

a negative impact on the overall process productivity. This metric is also estimated for OP and CP:

$$RQ_k^i = \frac{\sum_{r=1}^R \sum_{rk=1}^{RK} \xi_{r,rk,k} \cdot E_{r,rk,k}^i}{\sum_{fp=1}^{FP} n^{(fp)}} \quad (1.20)$$

where $\xi_{r,rk,k}$ is the extent of reaction rk , $n^{(fp)}$ is the mole flow rate of a desired final product, and $E_{r,rk,k}^i$ represents the effect of the component i on reaction rk : +1 means component i is favored to the desired product, 0 means no effects, and -1 means that the compound i is inhibiting the formation of the desired product.

Accumulation factor (AF): The indicator that reflects the accumulation behavior of the compounds that are being recycled within the system, meaning that the recycle flow rate of a certain compound (a certain representative path in the system) is being evaluated regarding the amount of fresh compound that is being added to the system:

$$AF_z^i = \frac{m_z^i}{\sum_{i=l}^I \cdot \left(\sum_{a=1}^{EP} f_{i,a}^i + \sum_{op=1}^{OP} d_{i,op}^i \right)} \quad (1.21)$$

where m_z^i is the mass flow rate in cycle path flow z and $f_{i,a}^i$ and $d_{i,op}^i$ are the flow rates leaving the cycle path flow.

Total value added (TVA): The indicator that reflects the economic impact of a given path directly related to a certain compound in the system. Due to the aforementioned MVA and EWC constraints, a high negative value of TVA indicates that a given compound in a certain path is losing value along the process in terms of energy that is being wasted, raw material that is not being recycled, or even a valuable by-product that is being discarded:

$$TVA_k^i = MVA_k^i - EWC_k^i \quad (1.22)$$

1.2.2 Environmental Impact Assessment

Life cycle assessment (LCA) is a method to quantify the environmental impact of the designed process throughout the product–process life cycle. LCA is defined by the ISO14040 and ISO14044 standards as the evaluation of inputs, outputs, and the system during the lifetime of the process. It consists of a systematic framework including the following steps: (i) goal and scope definition, (ii) inventory analysis or life cycle inventory (LCI), (iii) impact assessment or life cycle impact assessment (LCIA), and (iv) interpretation.

Earlier in our group, an Excel VBA-based software tool—LCSoft—was developed according to the standard for the environmental impact and carbon footprint analysis (Piyarak, 2012). The tool contains three main parts: (i) LCI knowledge management, (ii) calculation factor estimation, and (iii) LCA calculation. It is noted that US EPA and IPCC emission factors are used to calculate the environmental impact for a given process. Figure 1.4 and Table 1.2 present the framework and a short description of each step of LCSoft.

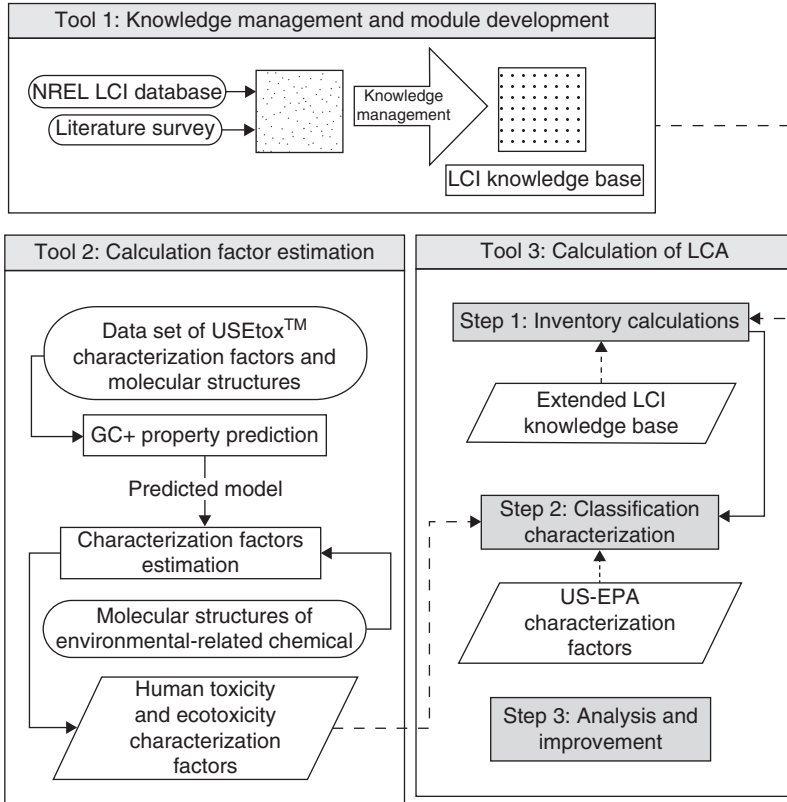


Figure 1.4 The framework of LCSoft (Kalakul et al., 2014)

In step 2 of Tool-3, the resources and energy consumption are calculated using the following equations (Eqs. 1.23–1.25):

$$R_{\text{total}} = R_{\text{renew}} + R_{\text{non-renew}} \quad (1.23)$$

$$R_{\text{renew}} = \frac{\left(\sum_{r,i} m_i^{\text{PI}} \times x_{r,i} \times \text{HV}_r \right)}{m_{\text{product}}} \quad (1.24)$$

$$R_{\text{non-renew}} = \frac{\left(\sum_{nr,i} m_i^{\text{PI}} \times x_{nr,i} \times \text{HV}_{nr} \right)}{m_{\text{product}}} \quad (1.25)$$

where r refers to the renewable resource used to produce input i , nr represents nonrenewable resource used to produce input i , $x_{r,i}$ is the mass of renewable resource r used to produce 1 kg of input i (kg), $x_{nr,i}$ is the mass of nonrenewable resource nr used to produce 1 kg of input i (kg), HV_r is the heating value of renewable resource r (MJ/kg_r), HV_{nr} is the heating value of nonrenewable resource nr (MJ/kg_{nr}), R_{total} is the total energy from resource consumption per

Table 1.2 *The simplified explanation of each section in LCSoft*

Part no.	Name	Description
Prerequisite	Input	<ul style="list-style-type: none"> • Mass and energy balance (stream table) • Duty of unit operations
Tool-1	LCI knowledge (LCI KB) management	<p>LCI data from NREL database and open literature are collected and used as input to LCI KB. The LCI KB is divided into two levels:</p> <p>The first level:</p> <ul style="list-style-type: none"> • Material: biomass, chemicals, fuels, plants, and others • Utility: hot utility, cold utility, electricity by fuel, electricity by country, and others • Transport: by mode (air, pipeline, rail, road, water) and by country <p>The second level (unit process):</p> <ul style="list-style-type: none"> • Inputs: activities, materials, and resources required in the unit operations • Outputs: emission to air, water, and soil
Tool-2	Calculation factor estimation	<p>Group-contribution+ (GC+) property models are used as the predictive models to calculate characterization factors (CFs) of 8 impacts:</p> <ul style="list-style-type: none"> • Human toxicity by ingestion (HTPI) • Human toxicity by exposure (HTPE) • Aquatic toxicity (ATP) • Terrestrial toxicity (TTP) • Global warming (GWP) • Ozone depletion (ODP) • Photochemical oxidation (PCOP) • Acidification (AP) <p>The USEtox database is also used to develop the predictive models to calculate CFs for 3 other impacts:</p> <ul style="list-style-type: none"> • Carcinogenic (HTC) • Noncarcinogenic (HTNC) • Freshwater ecotoxicity (ET)
Tool-3	Calculation of LCA	<p>This tool contains 3 steps:</p> <ul style="list-style-type: none"> • Step 1: to check the existence of LCI data and to retrieve LCI data from LCI KB • Step 2: to calculate resources and energy consumptions (Eqs. 1.22–1.24) and to calculate carbon footprint (Eq. 1.25) • Step 3: to assess and analyze the environmental impact (Eq. 1.27)

1 kg of product ($\text{MJ}/\text{kg}_{\text{product}}$), R_{renew} is the total energy from renewable resource consumption per 1 kg of product ($\text{MJ}/\text{kg}_{\text{product}}$), and $R_{\text{non-renew}}$ is the total energy from nonrenewable resource consumption per 1 kg of product ($\text{MJ}/\text{kg}_{\text{product}}$).

In this step, the carbon footprint is calculated by means of the following equation (Eq. 1.26):

$$\text{CO}_{2\text{eq}} = \frac{\left(m_{\text{GHG,air}}^{\text{PRO}} \times \text{CF}_{\text{GHG,air}}^{\text{GWP}}\right)}{m_{\text{product}}} \quad (1.26)$$

$$\text{Carbon footprint} = \sum \text{CO}_{2\text{eq}} \quad (1.27)$$

where GHG represents the greenhouse gases emitted to air from the process, $m_{\text{GHG,air}}^{\text{PRO}}$ is the mass flow rate of GHG emitted to air from the process, $\text{CF}_{\text{GHG,air}}^{\text{GWP}}$ is the characterization factor (CF) for the global warming effect of the greenhouse gas (GHG), and $\text{CO}_{2\text{eq}}$ represents the carbon dioxide equivalent per 1 kg of product.

In step 3, the environmental impact is calculated by the following equation (Eq. 1.28):

$$I^k = \sum_{i,c} \text{EM}_{i,c} \times \text{CF}_{i,c}^k \quad (1.28)$$

where i refers to a chemical emitted to compartment c , k represents the impact category, $\text{CF}_{i,c}^k$ is the CF of chemical n emitted to compartment c for impact category k , $\text{EM}_{i,c}$ is the mass of chemical i emitted to compartment c per 1 kg of product, and I^k is the potential environmental impact (PEI) of chemical i for a specific impact category of concern k .

1.3 Application: Early-Stage Design and Analysis of a Lignocellulosic Biorefinery

In this section, the application of the framework is shown and discussed. The superstructure of the biochemical and thermochemical processing networks and the combined network is presented. The data collection and verification are briefly illustrated; a more detailed study on data collection was presented in the previous work (Cheali et al., 2014). The optimal solutions are then identified with different optimization scenarios under techno-economic constraints, hence reflecting the CAPEX and OPEX costs. After the optimal solutions are identified with respect to techno-economic criteria, the solutions are further analyzed with respect to sustainability and environmental impact.

1.3.1 Biorefinery Networks and Identification of the Optimal Processing Paths

Step 1: Problem definition

Four optimization scenarios were studied for technical and economic feasibility on the basis of the extended superstructure which has extended capabilities to compare more potential processing technologies and platforms. The scenarios selected were as follows: (i) to maximize the production of FT-gasoline/diesel; (ii) to maximize FT-gasoline/diesel sales, min. operating cost, and min. investment cost; (iii) to maximize production of ethanol; and (iv) to maximize ethanol sales, min. operating cost, and min. investment cost.

Step 2: Superstructure definition

The superstructure of the biochemical conversion platform of biomass (corn stover) using biomass pretreatment, hydrolysis, and fermentation technologies was developed earlier to produce ethanol, butanol, succinic acid, and acetone with and without gasoline blend as presented in Figure 1.5 (Zondervan et al., 2011). Note that the short description of the processing blocks can be found in Zondervan et al. (2011) as well.

To increase the design space and the potential number of scenarios, the superstructure was extended by combining the biochemical conversion platform with a thermochemical conversion platform (Cheali et al., 2014). A literature review was performed to formulate

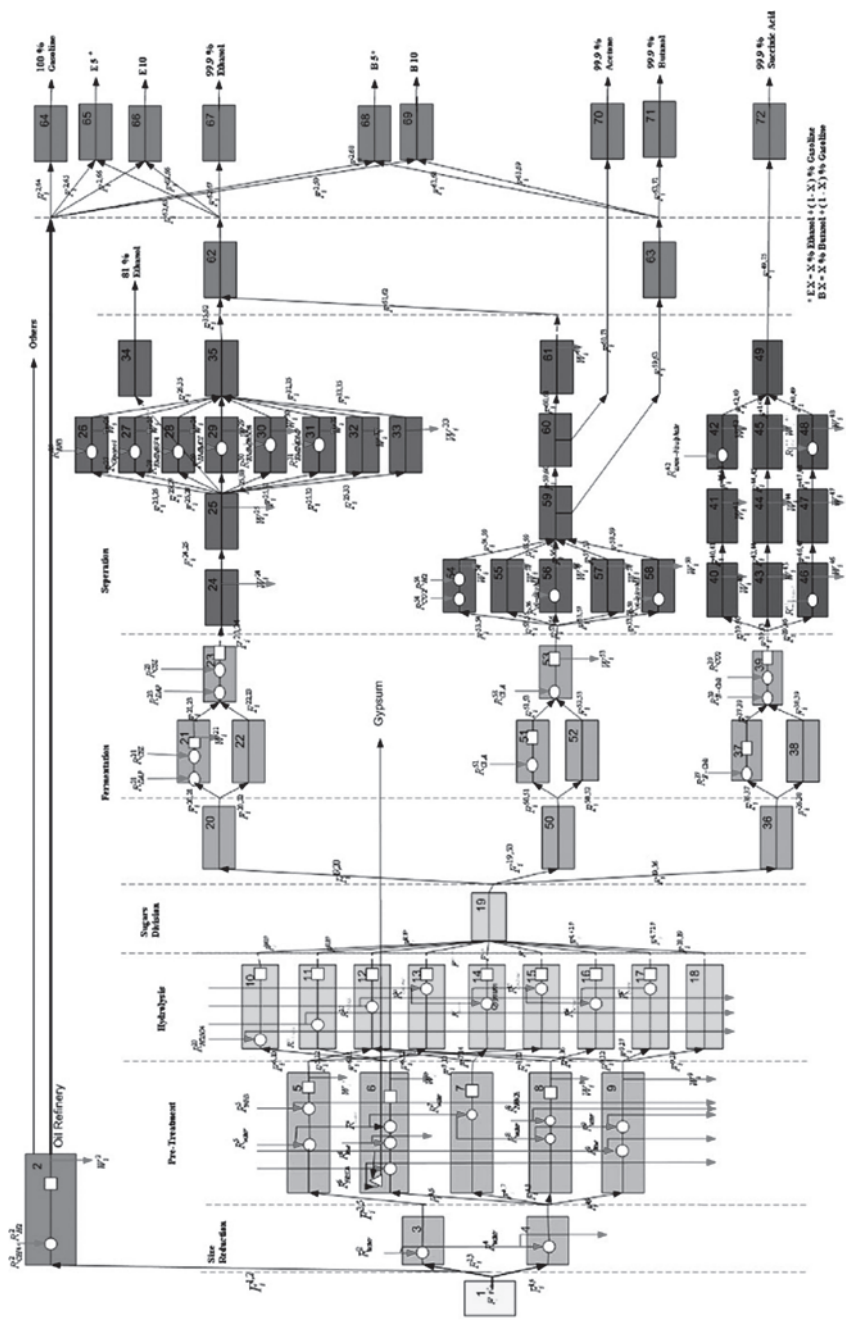


Figure 1.5 The superstructure of the biochemical conversion platform of biomass

the superstructure, and in particular, the simulation studies of the US National Renewable Energy Laboratory (NREL) (Phillips et al., 2007; Dutta and Philips, 2009; Dutta et al., 2011; Swanson et al., 2010; Wright et al., 2010) and the Pacific Northwest National Laboratory (PNNL) (Jones et al., 2009) were considered. Figure 1.6 illustrates the superstructure of the thermochemical conversion platform which is proposed based on NREL/PNNL studies. The superstructure consists of 7 sections: 1 feedstock section (source), 5 processing steps (processing tasks), and 1 product section (sink) resulting in a total of 27 process intervals.

As shown in Figure 1.6, corn stover (1) and woody biomass (2) were considered as alternative raw materials. For the thermochemical conversion platform, the processing techniques are generally divided into five processing tasks: (i) pretreatment (size reduction, dryer), (ii) primary conversion (gasification, pyrolysis), (iii) gas cleaning and conditioning (reformer, scrubber, acid gas removal, water–gas shift, PSA), (iv) product synthesis (Fischer–Tropsch (F-T), alcohol synthesis, hydroprocessing unit for pyrolysis oil), and (v) product separation and purification (hydroprocessing unit for F-T products, mol. sieve, and distillation). According to the considered raw materials and processing techniques, a number of products were considered: FT-gasoline, FT-diesel, ethanol, mixed alcohols, two waste heat streams from the gasification, and the reformer. Utilities and waste separation for each processing technology are presented in Figure 1.6. However, recycles which were also considered are not presented in the superstructure.

Then, the superstructure of thermochemical conversion was combined with the superstructure of biochemical conversion resulting in a superstructure with a total of 96 processing intervals, 3 raw materials, 79 processing technologies, and 14 products (main and by-products) as presented in Figure 1.7. The short description of each process interval of the combined superstructure can also be found in Table 1.3.

The extended biorefinery network (thermochemical and biochemical platforms) expands the design space significantly. This means that one can now screen among more potential processing paths and alternatives. The extended networks can also generate more scenarios and solutions and can serve more requirements and specifications of the end users (engineers,

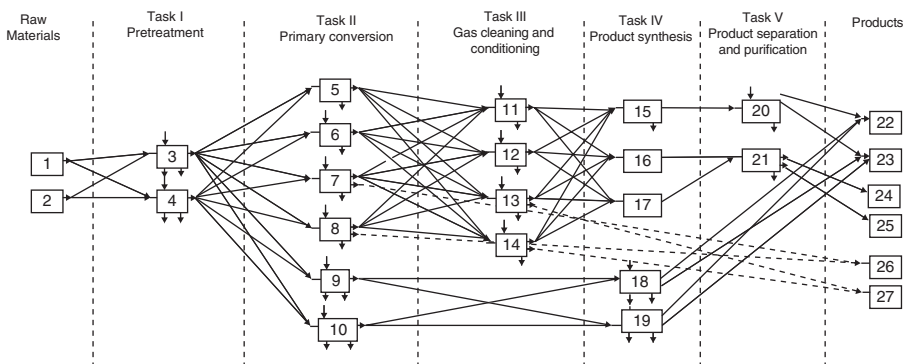


Figure 1.6 Combined superstructure of two biorefinery conversion platforms: thermochemical (top) and biochemical platform (bottom). Reproduced from Cheali et al. (2014), © 2014, American Chemical Society

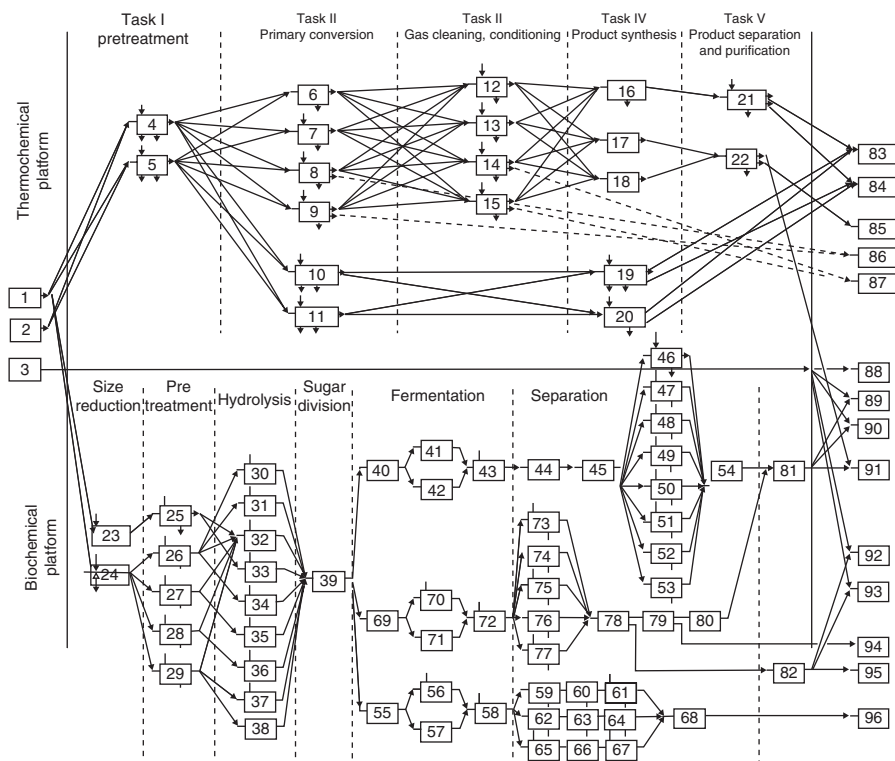


Figure 1.7 Combined superstructure of two biorefinery conversion platforms: thermochemical (top) and biochemical platform (bottom). Reproduced from Cheali et al. (2014), © 2014, American Chemical Society

researchers, managers, etc.). The expanded superstructure, alternatively, can also be used for the bottleneck studies in the existing processes, thereby helping end users (e.g., engineers) improve their processes.

Step 3: Data collection and modeling

The data and parameters required for the generic model blocks that are used to define the superstructure are presented here. When the reported data are available from experimental or pilot plant studies, the data were collected directly. If not, the data need to be obtained from simulations or should be estimated to obtain the parameters used in the general block using commercial process simulators such as ProII, Aspen, etc.

An example of data collection is presented below. Tables 1.4 and 1.5 and Figure 1.8 illustrate how the data were collected for the F-T process, which is one of the processing technologies to convert syngas to produce transportation fuels. The process requires a clean syngas to prolong the catalyst lifetime. There are no requirements for utilities and waste separation. The effluents are (i) unconverted gas which is recycled and (ii) liquid product which is discharged to a hydroprocessing unit. Generally, F-T catalytic synthesis is a well-known and commercial process producing a wide range of alkanes under a wide range of operating conditions and type of catalysts. Here, we have used the design data reported by

Table 1.3 The description of the process intervals presented in Figure 1.7**Raw materials**

1	Corn stover (33% moisture), 2000 tpd (dry)	3	Gasoline (for blending and comparing,
2	Wood (35% moisture), 2000 tpd (dry)		400 tpd)

Thermochemical conversion platform (processing technologies)

4	Size reduction, dryer (steam, indirect contact)	14	Steam reforming, WGS, acid gas removal—amine
5	Size reduction, dryer (flue gas, direct contact)	15	Steam reforming, WGS, acid gas removal—DEPG
6	Entrained-flow gasifier with size reduction	16	Fischer–Tropsch with special H ₂ S removal
7	Bubbling fluidized-bed gasifier	17	Alcohol synthesis (metal sulfide catalyst)
8	Indirectly heated with circulating gasifier	18	Alcohol synthesis (MoS ₂ catalyst)
9	Directly heated with bubbling gasifier	19	Hydroprocessing (H ₂ production)
10	Pyrolysis (bubbling fluidized bed)	20	Hydroprocessing (H ₂ purchasing)
11	Fast pyrolysis (fluidized bed)	21	Decanter with hydroprocessing unit
12	SWGS, acid gas removal—amine, PSA-H ₂	22	Molecular sieve, two distillation columns
13	Direct cooler, WGS, acid gas removal—amine		

Biochemical conversion platform (processing technologies)

23	Size reduction by 60% water	53	Molecular sieve
24	Size reduction by 54% water	54	Anhydrous ethanol
25	Ammonia fiber explosion	55	Fermentation feed handling
26	Pretreatment dilute acid	56	Seed production
27	Controlled pH pretreatment	57	Seed production bypass
28	Aqueous ammonia recycle pretreatment	58	Succinic acid fermentation by <i>E. coli</i>
29	Lime pretreatment	59	Filtration
30	Dilute acid hydrolysis	60	Evaporation
31	Concentrated acid hydrolysis	61	Crystallization
32	NREL enzyme hydrolysis	62	Water splitting electro dialysis
33	Spzyme hydrolysis from AFEX	63	Electro dialysis
34	Spzyme hydrolysis from dilute acid	64	Crystallization
35	Spzyme hydrolysis from controlled pH	65	Reactive distillation
36	Spzyme hydrolysis from APR	66	Vacuum distillation
37	Spzyme hydrolysis from lime	67	Crystallization
38	Hydrolysis bypass	68	Succinic acid storage
39	Sugar division	69	Fermentation feed handling
40	Fermentation feed handling	70	Seed production
41	Seed production	71	Seed production bypass
42	Seed production bypass	72	Butanol fermentation
43	Ethanol fermentation	73	Gas stripping
44	Flash	74	Adsorption

(continued overleaf)

Table 1.3 (continued)

45	Distillation column	75	Solvent extraction by oleyl alcohol
46	Solvent-based extraction by ethylene glycol	76	Pervaporation
47	Solvent-based extraction by ethylene glycerol	77	Membrane separation
48	Extraction with ionic liquid—EMIMBF ₄	78	Distillation for butanol
49	Extraction with ionic liquid—EMIMCl	79	Distillation for acetone
50	Extraction with ionic liquid—EMIM + EtSO ₄	80	Distillation for ethanol
51	Extraction with ionic liquid—EMIM + DMP	81	Total ethanol production
52	Membrane separation	82	Butanol storage
Products and by-products			
83	FT-gasoline	90	E10 (ethanol–gasoline blend)
84	FT-diesel	91	Ethanol (100%)
85	Higher alcohols (C ₃ -ol, C ₄ -ol, C ₅ -ol)	92	B5 (butanol–gasoline blend)
86	Hot flue gas from gasifier combustor	93	B10 (butanol–gasoline blend)
87	Hot flue gas from tar reformer combustor	94	Acetone
88	Gasoline (100%)	95	Butanol (100%)
89	E5 (ethanol–gasoline blend)	96	Succinic acid

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Table 1.4 The data collection example for Fischer–Tropsch reactor

Descriptions	Raw data from NREL study		Generic model block parameters	
Utilities	—			
Reaction	Stoichiometry	N/A	$\gamma_{i,rr}$	(Eq. 1.29)
	Conversion fraction of CO (once through)	0.4	$\theta_{react,rr}$	1
Waste separation	—			
Product separation	Gas product	Recycled	$split_{i,kk}$	0
	Liquid product	Main product	$split_{i,kk}$	1

the NREL study of Swanson et al. (2010) which uses an Anderson–Schulz–Flory chain-growth probability model to describe the product distribution. Based on the model mentioned, the chain-growth value (α) was selected, resulting in the product distribution as a function of chain-growth value (α) for F-T reaction. Figure 1.8 and Table 1.5 show the stoichiometry values estimated from the model.

Chain Anderson–Schulz–Flory chain-growth probability model:

$$\gamma_{C_n} = \alpha^{n-1} * (1 - \alpha) \quad (1.29)$$

The example mentioned in Table 1.4 shows how multidisciplinary data (simulation results, kinetics, separation efficiency, etc.) are converted into a generic form as a set of constant parameters. The collected data are then stored as a database in a multidimensional

Table 1.5 Example of the stream table of the Fischer–Tropsch reactor

Component	Chain-growth equation (Eq. 1.29)	$\gamma_{i,rr}$ (stoichiometric coefficient)	$\theta_{i,rr}$ (Conversion fraction)
CO	—	-1	1
H ₂	—	-2.1	—
C ₁	$\alpha^{1-1} \times (1-\alpha)$	0.010	—
C ₂	$\alpha^{2-1} \times (1-\alpha)$	0.009	—
C ₃	$\alpha^{3-1} \times (1-\alpha)$	0.0081	—
C ₄	$\alpha^{4-1} \times (1-\alpha)$	0.00729	—
C ₅	$\alpha^{5-1} \times (1-\alpha)$	0.00656	—
C ₆	$\alpha^{6-1} \times (1-\alpha)$	0.005905	—
C ₇	$\alpha^{7-1} \times (1-\alpha)$	0.005314	—
C ₈	$\alpha^{8-1} \times (1-\alpha)$	0.004783	—
C ₉	$\alpha^{9-1} \times (1-\alpha)$	0.004304	—
C ₁₀	$\alpha^{10-1} \times (1-\alpha)$	0.003874	—
C ₁₁	$\alpha^{11-1} \times (1-\alpha)$	0.003486	—
C ₁₂	$\alpha^{12-1} \times (1-\alpha)$	0.003138	—
C ₁₃	$\alpha^{13-1} \times (1-\alpha)$	0.002825	—
C ₁₄	$\alpha^{14-1} \times (1-\alpha)$	0.002542	—
C ₁₅	$\alpha^{15-1} \times (1-\alpha)$	0.002288	—
C ₁₆	$\alpha^{16-1} \times (1-\alpha)$	0.002059	—
C ₁₇	$\alpha^{17-1} \times (1-\alpha)$	0.001853	—
C ₁₈	$\alpha^{18-1} \times (1-\alpha)$	0.001668	—
C ₁₉	$\alpha^{19-1} \times (1-\alpha)$	0.001501	—
C ₂₀	$\alpha^{20-1} \times (1-\alpha)$	0.001351	—
Wax	$1 - \left(\sum_N^{20} \alpha^{N-1} \times (1-\alpha) \right)$	0.012158	—
H ₂ O	—	1	—

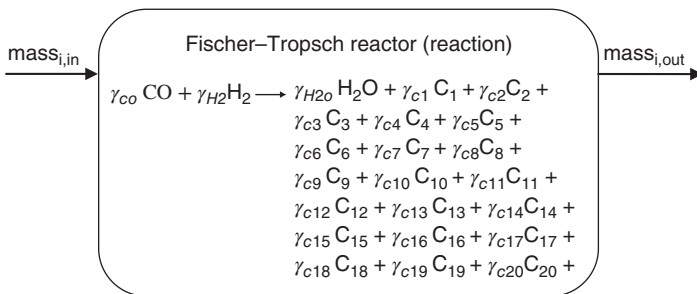


Figure 1.8 Process diagram showing mass inlet/outlet, the reaction, and its stoichiometry for the Fischer–Tropsch reactor

matrix (the database uses the Excel spreadsheet environment, but any other software environment would work, e.g., Matlab, MS Access, etc). In this way, storage of the data is flexible as it only requires simple column and row operations to add, modify, or update data in the database. At the same time, storing the data in matrix form provides a certain structure to organize the data and manage the complexity in a compact and efficient way.

The description and the data collection (plus parameter estimation where necessary) for the other process intervals included in the superstructure of the thermochemical platform (Figure 1.6) are summarized in Table 1.6 (Cheali et al., 2014). For each process interval, mixing parameters ($\mu_{i,j,kk}$, $\alpha_{i,kk}$), reaction parameters ($\gamma_{i,rr}$, $\theta_{react,rr}$), waste separation parameters ($SW_{i,kk}$), and a product separation parameter ($split_{i,kk}$) are provided.

Step 4: Models and data verification

After the data conversion (or estimation), the verification needs to be performed as a consistency check prior to performing the optimization. Seven processing paths based on five NREL reports and a PNNL report were used to verify the models and data used for each process interval and processing path. As explained earlier, the verification can be performed by fixing the processing path and comparing the simulation results with the NREL and PNNL studies. The full verification results were presented in the previous study (Cheali et al., 2014).

Here, an example of verification is presented. The data collected and modeled of the F-T reactor from the previous step were verified in this step. The simulation results of this study (implemented in GAMS) are necessary in order to verify the quality of the collected data and the models used in this study. In the previous section, the data collection was presented as examples for the entrained-flow gasifier. Here, the collected data for both examples are validated and presented in Table 1.7, respectively. The validation results confirm that the quality of the collected data is good and the data are consistent. The full simulation results (implemented in GAMS) can be found in the previous study (Cheali et al., 2014).

Step 5: Formulation and solution of the optimization problem

Four optimization scenarios selected in step 1 were formulated and solved in GAMS to identify the optimal biorefinery processing network. The optimization problem for scenario 2 resulted in 4,737,904 equations with 4,705,181 single variables (668 discrete variables). This problem was solved using the DICOPT solver using Windows 7 as operating system and an Intel® Core™ i7 CPU@ 3.4GHz, with 4GB RAM, resulting in an execution time of 12s. Table 1.8 presents the optimization results consisting of the processing paths; production rates; earnings before interest, taxes, depreciation, and amortization (EBITDA); investment costs; operating costs; and raw material costs for each of the scenarios.

The optimization problem for this study is formulated as follows:

The objective functions

Scenario 1:

$$\max .FT - \text{products} = F_{\text{gasoline},kk}^{\text{out}} + F_{\text{diesel},kk}^{\text{out}} \quad (1.30)$$

Scenario 2:

$$\max .EBITDA_{\text{gasoline, diesel}} = \sum_{i,kk} (P3_{i,kk} * F_{i,kk}^{\text{out}}) - \sum_{kk} \text{OPEX} - (\text{CAPEX}_1 + \text{CAPEX}_2) / t \quad (1.31)$$

Table 1.6 Summary table for the data collection (mixing, $\alpha_{i,kk}$, $\mu_{i,kk}$ reaction, $\gamma_{i,rr}$, $\theta_{\text{react},rr}$ waste, $SW_{i,kk}$ and product, $split_{i,kk}$, separation) for thermochemical processing networks (Cheali et al., 2014)

No.	Description	Mixing ($\alpha_{i,kk} = 1$)	$\mu_{i,kk}$	Reaction (stoichiometry, $\gamma_{i,rr}$)	$\theta_{\text{react},rr}$	Waste separation	$SW_{i,kk}$	Product separation (in primary outlet)	Split $_{i,kk}$
4	Hammer mill, rotary dryer (indirectly contact with steam)	<ul style="list-style-type: none"> Electricity to biomass ratio Steam to %moist ratio 	4 5.9	—	—	Moisture	0.6	Steam	0
5	Hammer mill and rotary dryer (directly contact with hot flue gas)	<ul style="list-style-type: none"> Electricity to biomass ratio Waste heat from process 	4	—	—	Moisture	0.96	Waste heat	0
6	Entrained-flow (free-fall) gasifier	<ul style="list-style-type: none"> O₂ to biomass ratio Steam to %moist ratio 	0.35 0.48	C + 0.13H ₂ O + 0.6O ₂ + 0.0017S → 0.13H ₂ + 0.0007N ₂ + 0.66CO + 0.34CO ₂ + 0.002H ₂ S + 0.07SOOT + 1.3SLAG	1	Ash, soot	0.99	One outlet stream	1
7	Bubbling fluidized-bed gasifier	<ul style="list-style-type: none"> O₂ to biomass ratio Steam to %moist ratio 	0.26 0.17	C + 0.11H ₂ O + 0.34H ₂ + 0.5O ₂ + 0.002S + 0.007N ₂ → 0.36CO + 0.41CO ₂ + 0.002H ₂ S + 0.01NH ₃ + 0.08CH ₄ + 0.01C ₂ H ₆ + 0.02C ₂ H ₄ + 1.2CHAR	1	Ash, char	0.99	One outlet stream	1
8	Indirectly heated with circulating FB gasifier	<ul style="list-style-type: none"> Air to biomass ratio Steam to %moist ratio Fresh olive to biomass ratio MgO to ash ratio 	2.2 0.38 0.003 0.004	C + 0.48H ₂ + 0.6O ₂ + 0.0006S + 0.001N ₂ → 0.37CO + 0.39CO ₂ + 0.12H ₂ O + 0.0006H ₂ S + 0.002NH ₃ + 0.13CH ₄ + 0.02C ₂ H ₆ + 0.03C ₂ H ₄ + 0.23TAR	1	Ash	0.99	H ₂ O CO ₂ O ₂ , N ₂ , Ar	0.75 0.25 0

(continued overleaf)

Table 1.6 (continued)

No.	Description	Mixing ($\alpha_{i,kk} = 1$)	$\mu_{i,kk}$	Reaction (stoichiometry, $\gamma_{i,rr}$)	$\theta_{\text{react},rr}$	Waste separation	$SW_{i,kk}$	Product separation (in primary outlet)	Split $\mu_{i,kk}$
9	Directly heated with bubbling gasifier	<ul style="list-style-type: none"> • O₂ to biomass ratio • Steam to %moist ratio • Fresh olive to biomass ratio • MgO to ash ratio 	0.22 0.2 0.003 0.004	$C + 0.47H_2 + 0.04H_2O + 0.4O_2 + 0.0006S + 0.001N_2 \rightarrow 0.19CO + 0.39CO_2 + 0.0006H_2S + 0.002NH_3 + 0.18CH_4 + 0.01C_2H_6 + 0.013C_6H_6 + 0.55TAR + CHAR$	1	Ash, char	0.99	Two product stream (same component)	0.6
10	Pyrolysis (bubbling fluidized bed)			$C + 0.3O_2 + 0.6H_2 + 0.007N_2 + 1.5ASH + -0.001S \rightarrow 0.05H_2O + 0.05CO + 0.07CO_2 + 0.01CH_4 + 4.5CHAR + 15PYRO - OIL$	1	Ash, char	0.85	H ₂ , O ₂ , N ₂ , CO, CO ₂ , CH ₄ , H ₂ O	0 0.63
11	Fast pyrolysis (fluidized bed)			$C + 0.5O_2 + 0.7H_2 + 0.45ASH + -0.0001S \rightarrow 1.4H_2O + 0.002CO + 0.25CO_2 + 15PYRO - OIL$	1	Ash, char	1	H ₂ , O ₂ , N ₂ , CO ₂ , H ₂ O, CO	0 0.15 0.01
12	SWGS, acid gas removal—amine, PSA-H ₂	Steam to inlet flow	0.14	$CO + H_2O \rightarrow CO_2 + H_2$	0.3	H ₂ O, N ₂ , CO ₂ , NH ₃ , H ₂ S, COS	1	One outlet stream	1
13	Direct cooler, SMR, WGS, acid gas removal—amine	Steam to inlet flow	0.36	<ul style="list-style-type: none"> • CH₄ + 0.1C₂H₆ + 0.2C₂H₄ + 1.6H₂O → 4.4H₂ + 1.6CO • CO + H₂O → CO₂ + H₂ 	0.35 0.25	NH ₃ , TAR, Ash, Char, H ₂ O, H ₂ S, CO ₂	0.99	One outlet stream	1

14	Tar reformer, scrubber, acid gas removal—amine	Air to inlet flow	1.2	TAR + 0.7CH ₄ + 0.015C ₂ H ₆ + 0.15C ₃ H ₈ + O ₂ → 1.5H ₂ + CO + 0.3CO ₂ + 0.4H ₂ O	1	H ₂ O H ₂ S CO ₂	0.98 0.8 0.6	Ar, N ₂ H ₂ O, CO ₂	0 0.5
15	Tar reforming, scrubber, acid gas removal—DEPG	Air to inlet flow	1	TAR + 0.8CH ₄ + 0.02C ₂ H ₆ + 0.14C ₃ H ₈ + 0.8O ₂ + 0.2CH ₄ O → 2.5H ₂ + 1.3CO + 0.5CO ₂ + 0.1H ₂ O	1	NH ₃ , H ₂ O, TAR, Ash, Char H ₂ S CO ₂	1 0.65 0.6	Ar, O ₂ , N ₂ H ₂ O CO ₂	0 0.6 0.4
16	Fischer–Tropsch	—	—	CO + 2.1H ₂ → 10.8C ₁ + 9.8C ₂ + 8.8C ₃ + 7.9C ₄ + 7.1C ₅ + 6.4C ₆ + 5.7C ₇ + 5.2C ₈ + 4.6C ₉ + 4.2C ₁₀ + 3.7C ₁₁ + 3.4C ₁₂ + 3C ₁₃ + 2.7C ₁₄ + 2.5C ₁₅ + 2.2C ₁₆ + 2C ₁₇ + 1.8C ₁₈ + 1.6C ₁₉ + 1.5C ₂₀ + 13Wax + H ₂ O	0.4	—	—	One outlet stream	1
17	Alcohol synthesis (modified F-T catalyst, MoS2)	—	—	CO + H ₂ + 0.006H ₂ O → 0.36CO ₂ + 0.06CH ₄ + 0.04CH ₃ O + 0.24C ₂ H ₆ O + 0.026C ₃ H ₈ O	0.4	—	—	One outlet stream	1
18	Alcohol synthesis (metal sulfide synthesis catalyst)	—	—	CO + 1.2H ₂ → 0.07H ₂ O + 0.07CO ₂ + 0.1CH ₄ + 0.1CH ₃ O + 0.2C ₂ H ₆ O + 0.017C ₃ H ₈ O	0.26	—	—	H ₂ , N ₂ , CO, CH ₄ H ₂ O, alcohols CO ₂	0.01 1 0.08

(continued overleaf)

Table 1.6 (continued)

No.	Description	Mixing ($\alpha_{i,kk} = 1$)	$\mu_{i,kk}$	Reaction (stoichiometry, $\gamma_{i,rr}$)	$\theta_{\text{react,rr}}$	Waste separation	$SW_{i,kk}$	Product separation (in primary outlet)	Split _{i,kk}
19	Hydroprocessing (H ₂ production)	<ul style="list-style-type: none"> O₂ to biomass ratio Steam to %moist ratio 	1.87 0.37	Pyro –oil + 0.02H ₂ O + 0.01O ₂ → 0.02CO ₂ + 0.0014gasoline + 0.0007diesel	1	—	—	H ₂ O, O ₂ , CO ₂	0
20	Hydroprocessing (H ₂ purchasing)	H ₂ to inlet flow ratio	0.05	Pyro –oil + 0.014H ₂ O + 0.027H ₂ → 0.003CO ₂ + 0.003CH ₄ + 0.002gasoline + 0.0012diesel	1	—	—	H ₂ O, O ₂ , CO ₂ , CH ₄	0
21	Hydroprocessing unit	H ₂ to wax ratio	0.0257	Wax + 5.4H ₂ + 0.5C ₅ + 0.48C ₆ + 0.44C ₇ + 0.35C ₉ + 0.32C ₁₀ + 0.28C ₁₁ + 0.25C ₁₂ + 0.23C ₁₃ + 0.2C ₁₄ + 0.18C ₁₅ + 0.15C ₁₇ + 0.14C ₁₈ + 0.12C ₁₉ + 0.11C ₂₀ → 2gasoline + 2.76diesel	1	—	—	H ₂ O, H ₂ , CO, CO ₂ , light hydrocarbon	0
22	Mol.sieve and distillations	—	—	—	—	H ₂ , N ₂ , CO, CH ₄ , H ₂ O	1 0.8	CH ₄ C ₂ H ₆ Higher alcohols	0.07 0.99 0.05

Table 1.7 Summary of the verification results for the Fischer–Tropsch reactor

	Inlet flow	The reported results from NREL report (Swanson et al., 2010)				The simulation results of this study					
		Recycles	R(i)	Waste (i)	Fout1	Fout2	Recycles	R(i)	Waste (i)	Fout1	Fout2
Total (tpd)	3376	1292	0	0	427	4237	1292	0	0.03	427	4237
H ₂ O	45					642					642
H ₂	288	81				225	81				225
O ₂											
N ₂											
S											
C											
ASH											
CO	1818	500				1391	500				1391
CO ₂	190	106				296	106				296
H ₂ S	0.03							0.03			
NH ₃											
COS	1.2	0,68				1,88	0.6				1.8
AR	544	305				850	305				850
CH ₄	63.4	38.6				107	38.6				107
C ₂ H ₆	106.9	65				180	65				180
C ₂ H ₄		86					86				
C ₆ H ₆		101.9					102				
C ₃	141.56	1.5				239	1.5				239
C ₄	167.55	0.7				283	0.7				283
C ₅	2.29	0.72			15.49	3.87	0.7		15.4	3.8	
C ₆	2.46	0.72			16.65	4.16	0.7		16.6	4	
C ₇	1.15	0.72			17.54	1.95	0.7		17.5	1.9	
C ₈	1.18	0.71			17.99	2	0.7		18	2	
C ₉	1.11	0.33			18.1	2.01	0.3		18	2	
C ₁₀	1.16	0.32			18.12	2.01	0.3		18	2	
C ₁₁	0.83	0.31			17.62	1.96	0.3		17.6	1.9	
C ₁₂	0.13	0.29			17.25	0.91	0.25		17.2	0.9	
C ₁₃	0.02	0.28			16.7	0.88	0.25		16.5	0.8	
C ₁₄					16.16	0.85			16	0.8	
C ₁₅					15.57	0.82			15.5	0.8	
C ₁₆					14.93	0.79			15	0.8	
C ₁₇					14.75				14.7		
C ₁₈					14.05				14		
C ₁₉					13.35				13.3		
C ₂₀					12.64				12.6		
Waxes					170				170		

Table 1.8 The optimization results and comparison. Highlighted in bold are the processing networks for each task

Scenario	Objective function	Processing path	EBITDA (MM\$/a)	Fuel production (tpd)	Investment cost (MM\$/a)	Operating cost (MM\$/a)	Feedstock cost (MM\$/a)
1	Max. FT-products	2 4 6 15 16 21 83 84	207	171 (gasoline), 403 (diesel)	11.5	18.6	60
2	Max. FT-product sales, min. investment, and operating cost	2 5 6 14 16 21 83 84	210	170 (gasoline), 400 (diesel)	9	17	60
3	Max. ethanol	2 4 6 15 18 91	100	602	10.5	12	60
4	Max. ethanol sales, min. investment cost, and operating cost	2 5 9 14 17 91	100.5	589	10.4	10	60

Note the number of process intervals refer to Figure 1.7.

Scenario 3:

$$\max .\text{Ethanol} = F_{\text{ethanol,kk}}^{\text{out}} \quad (1.32)$$

Scenario 4:

$$\max .\text{EBITDA}_{\text{ethanol}} = \sum_{i,kk} \left(P3_{i,kk} \times F_{i,kk}^{\text{out}} \right) - \sum_{kk} \text{OPEX} - (\text{CAPEX}_1 + \text{CAPEX}_2) / t \quad (1.33)$$

Subject to the following constraints are (i) process models, material balances of the generic model block (Eqs. 1.1–1.7); (ii) process constraints, rules defining the superstructure together with binary variables ($S_p^{k,kk}, S^{k,kk}$) and the flow constraints (Eqs. 1.8–1.10); (iii) structural constraints using $\sum_k y_k \leq 1$ with binary variable ($y \in \{0;1\}^n$), to define the extended superstructure (Eqs. 1.12 and 1.13); (iv) cost constraints, to calculate capital and operating cost regarding the estimated mass flow rate (Eqs. 1.14–1.16); and (v) optimization constraints using big-M formulation, where M was set to 10,000 in this study which is about three times higher than the maximum flow rate (Eq. 1.17).

As can be seen, for the gasoline and diesel cases, a higher production, 171 tpd-gasoline and 403 tpd-diesel, was found (scenario 1) as well as the higher EBITDA in scenario 2. For the ethanol production cases, a higher ethanol production, 600 tpd, was also found

Table 1.9 The top five ranked solutions identified in scenario 2: max. FT-product sales, min. operating cost, and investment cost. Highlighted in bold are the processing networks for each task

Rank no.	Process interval selection	EBITDA (MM\$/a)	Production (tpd)	EBITDA (MM \$/year)	TAC (MM \$/year)
1	2 5 6 14 16 21 83 84	210	170 ^a , 400 ^b	170	86
2	2 4 6 15 16 21 83 84	206	171 ^a , 403 ^b	158	90
3	2 5 11 20 83 84 (Jones et al., 2009)	148	245 ^a , 311 ^b	148	133
4	2 5 8 15 16 21 83 84	93	141 ^a , 334 ^b	93	108
5	2 4 8 14 16 21 83 84	93	138 ^a , 327 ^b	93	101

^a FT-gasoline.^b FT-diesel.

(scenario 3). The results show that the thermochemical conversion platform is able to produce a higher amount of ethanol compared to the biochemical platform under the considered design space of alternatives. Furthermore, the entrained-flow gasifier and reformer are found to be the best technical alternatives to produce higher FT-gasoline and FT-diesel. The results indicate a higher potential of the thermochemical platform due to a relatively lower investment cost (in agreement with Foust et al., 2009) and a higher ethanol production of the optimized thermochemical processing path.

We further analyzed the results obtained from scenario 2 with respect to the top five ranking solutions. The results are given in Table 1.9 which features the objective function value, production rates, EBITDA, and TAC for the top five solutions. Analyzing the solutions in Table 1.9 reveals the following: (i) wood and entrained-flow gasifier are the most favorable ones, and (ii) no processing paths of the biochemical platform were selected in this top five. The difference in the objective function value is reflected in the selection of particular processing technologies. For example, the differences between the first- and second-ranked solutions are the selection of a dryer using process waste heat (5) and a steam reformer with amine-based acid gas removal (14) instead of a dryer using steam (4) and a catalytic reformer with DEPG acid gas removal, respectively. The changes of these processing technologies cause the changes in operating and capital cost resulting in a better EBITDA. The simplified flow diagrams for the first and the second processing path are presented in Figures 1.9 and 1.10, respectively.

Moreover, the top two optimal processing paths were then selected to perform further analysis on sustainability and environmental impact in the next section in order to create sufficient data to perform multicriteria evaluation.

1.3.2 Sustainability Analysis with Respect to Resource Consumption and Environmental Impact

Step 6: Sustainability analysis with respect to resource consumption and environmental impact

In this section, the two highest ranking optimal processing paths identified with respect to the techno-economical metrics presented in Figures 1.9 and 1.10 were selected for further analysis with respect to the following sustainability metrics, resource consumption and environmental impact, using two software tools, SustainPro and LCSof, respectively.

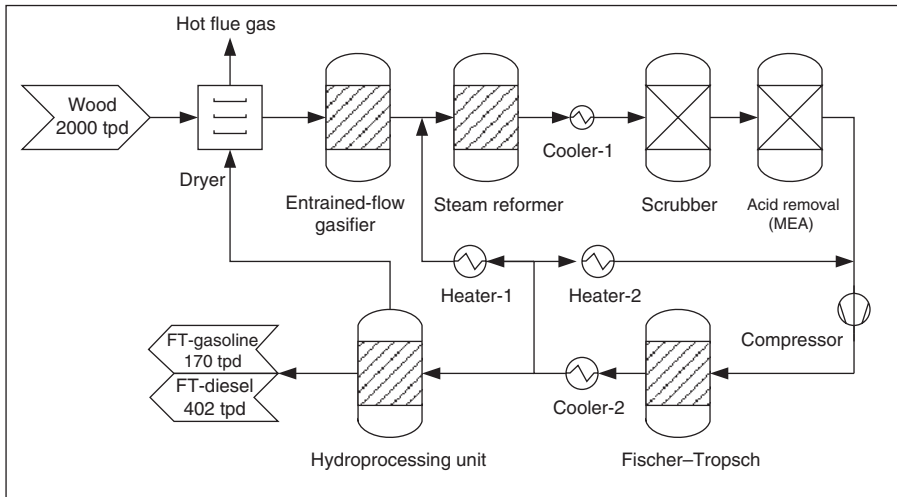


Figure 1.9 The simplified process flow diagram of the second best optimal processing path of scenario 2 (as presented in Table 1.9)

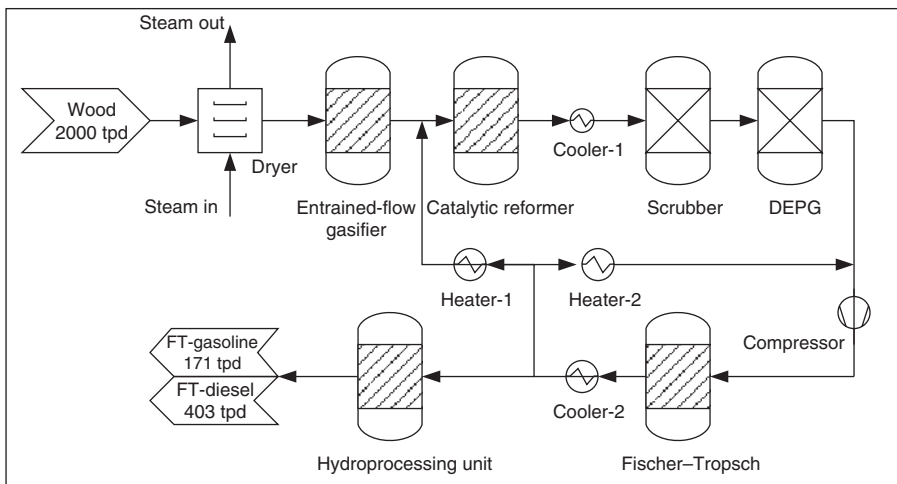


Figure 1.10 The simplified process flow diagram of the best optimal processing path of scenario 2 (as presented in Table 1.9)

1.3.2.1 Resource consumption analysis

The simulation results obtained from the sustainability analysis for two processing paths are presented in Tables 1.10, 1.11, 1.12, and 1.13. Tables 1.10 and 1.11 present the potential of improvement and the path flow details of the first optimal processing path (Figure 1.9), respectively. Tables 1.12 and 1.13 present the potential of improvement and the path flow details of the second optimal processing path (Figure 1.10). The potential of improvement is here related to the ability to change the process path flow with the aim of increasing the process sustainability.

Table 1.10 Identified process critical points for the first processing path, regarding the open and closed paths, respectively

Open path	MVA	EWC	TVA	Probability
OP 2	-40,951	3	-40,954	High
Closed path	EWC	Probability	AF	Probability
CP97	1125	Check AF	3,277	High
CP99	61,37	Check AF	0,6	High

Table 1.11 Path flow details on the critical points identified for the first processing path indicated in Table 1.10

Open path	Component	Path stream			Flow rate (kg/h)
OP 2	H ₂ O	FT—out	Hot flue gas—out	—	10,992
Closed path	Component	Path stream			Flow rate (kg/h)
CP97	H ₂	Gasifier—out	Acid—out	FT-out	38,348
CP99	O ₂	Gasifier—out	Acid—out	FT-out	30,737

Table 1.12 Identified process critical points for the second processing path, regarding the open and closed paths, respectively

Open path	MVA	EWC	TVA	Probability
OP 2	-1,952,512	2,956	-1,952,515	High
Closed path	EWC	Probability	AF	Probability
CP50	1,433	Check AF	3,892	High

Table 1.13 Path flow details on the critical points identified for the second processing path indicated in Table 1.12

Open path	Component	Path stream			Flow rate (kg/h)
OP 2	H ₂ O	Steam—in	Steam—out	—	636,038
Closed path	Component	Path stream			Flow rate (kg/h)
CP50	H ₂	Gasifier—out	Acid—out	FT—out	45,539

As mentioned before (Table 1.1), SustainPro decomposes the flowsheet into OP and CP. An OP corresponds to the mass or energy entering and exiting the system boundaries, and a CP reflects the recycle routes for mass or energy. After establishing each path flow rate, the software estimates the mass and energy indicators that reflect a complete analysis of the process. The software tool then ranks the OP and CP, from top to bottom, according to the respective impact on the overall process sustainability. In other words, the top indicators stand for the paths (and respective compounds) that have the highest impact on the process with respect to the resource consumption and the respective economic impact.

Tables 1.10 and 1.11 show the top indicators obtained through SustainPro for the optimal processing path (read as biorefinery network) obtained from the previous steps. OP2 was identified as a possible bottleneck due to the high negative value of MVA. It reflects the water vapor flow rate that is discarded from the F-T reactor to the dryer, being discarded as hot flue gas (waste) instead of being used/recycled. A possible solution to this is to recycle

this water flow, hence decreasing the net amount of freshwater that will be added to the system, and it needs to be analyzed in more detail. Moreover, CP97/CP99, which stand for the recycling of H₂ and O₂, respectively, are also identified as possible critical points, due to the fact that they carry high units of energy. This points toward the possibility of using these streams as potential heating source for heat integration. Therefore, by decreasing the external dependence on energy from fossil sources, the user achieves an improvement of the overall process sustainability and environmental impact.

For the second optimal processing path, there are two main paths (presented in Table 1.12 and 1.13, respectively) that were indicated as holding a high potential of improving the process sustainability if changes were performed in the mentioned paths. OP2 (steam used to dry biomass) presents a highly negative MVA. This is due to the fact that the process is discarding the steam after it is being used, and therefore, it is losing value along the way. In other words, this is a critical point in the process that clearly indicates that the process sustainability (in terms of natural resource usage) could be significantly improved if this steam was recycled, pressurized, and then reused resulting in an improvement on the process sustainability, decreasing the freshwater consumption and external dependence. Moreover, CP50, in which H₂ is being recycled from the F-T reactor to the gasifier, also indicates that this path carries more units of energy that are not being efficiently used. Therefore, there is a possibility of improving the process sustainability and of decreasing the external dependence by using this path as heating source through heat integration (HEN).

As mentioned previously, SustainPro also estimates the sustainability metrics. This is a valuable feature that allows the user to compare several processes in order to assess their degree of sustainability, presenting a complete evaluation with respect to water, energy, and raw material consumption. Table 1.14 presents both results from the first and the second processing path.

Sustainability metrics indicate that both the first and second processing paths have the same energy consumption per kg of product that is being produced. Nevertheless, the first process has a higher net primary energy usage per unit value added, which means that

Table 1.14 *Sustainability metrics for the first and second processing path*

	First path	Second path
Energy		
Total net primary energy usage rate (GJ/y)	414,301	414,301
% Total net primary energy sourced from renewables	0.9989	0.9989
Total net primary energy usage per Kg product (kJ/kg)	991.06	991.06
Total net primary energy usage per unit value added (kJ/\$)	0.215	0.0738
Raw materials		
Total raw materials used per kg product (kg/kg)	3.256	16.85
Total raw materials used per unit value added (kg/\$)	0.0007	0.00125
Fraction of raw materials recycled within company	0.9627	0.1936
Fraction of raw materials recycled from consumers	0	0
Hazardous raw material per kg product	0	0
Water		
Net water consumed per unit mass of product (kg/kg)	35.09	48.69
Net water consumed per unit value added (kg/\$)	0.0076	0.0036

the total MVA (see Eq. 1.18) is lower than the one characterizing the second process. This means that the first process uses energy more efficiently.

With respect to water and raw material consumption, one can see from Table 1.14 that the first processing route shows a better performance, also including a higher percentage of raw materials that are being recycled. For this particular analysis, the optimal biorefinery concept identified with respect to techno-economic criteria was found to perform better with respect to utilization of resources too. In addition to the retrofitting options mentioned previously, further process improvements and integration scenarios can be generated using formal chemical engineering techniques such as pinch analysis. However, this is beyond the scope of this study.

1.3.2.2 Environmental impact assessment

For each optimal path previously selected, the output data from the different subprocesses in the network is combined and presented as total emissions of a compound. To perform that analysis, the impact assessment requires component-specific CFs, which are estimated based on a methodology implemented in LCSofT, in particular Tool-2 (Table 1.2) using group-contribution+ (GC+) property models together with the US EPA USEtox™ database.

The results of the environmental impact analysis for the two mentioned processing paths are presented in the following text. With respect to the total carbon footprint, one can see (Table 1.15) that the second optimal processing path emits approximately 7% more CO₂, expressed as kg of CO₂ eq. per kg of ethanol being produced, than the first optimal process. Table 1.16 presents the list of PEIs also estimated by LCSofT for each one of the options. Also for this analysis, the first path has also been reported as the best one, having the lower environmental impact.

After the environmental impact assessment, one can see (Tables 1.15 and 1.16) that the first processing path is a better solution with respect to environmental impact since it has a lower total carbon footprint and lower values for the PEI metrics. This is due to the fact that the first process uses a waste heat stream as internal utility instead of using an external utility. Moreover, even when including a high electricity consumer such as the compressor, the first processing path includes coproduction of electricity that fully satisfies the electricity demands.

Table 1.15 Total carbon footprint for first and second processing path

Unit operations/processes	Duty/work (GJ/h)	First path	%	Second path	%
Biomass dryer	0.069	1.62E-09	0	7.58E-04	0
Entrained-flow gasifier	0.291	6.83E-09	0	0.0032	0.1
Cooler-1 prior to acid gas removal	1.981	0.0086	0.2	0.0029	0.1
Compressor to F-T	15.03	1.742	44.3	1.738	41.1
Fischer-Tropsch	0.146	0.0006	0,0	0.0002	0
Cooler-2 after Fischer-Tropsch	484.5	2.108	53.6	2.199	52
Heater-1 for recycles	17	0.0739	1.9	0.0248	0.6
Heater-2 for recycles	20	4.69E-07	0	0.2196	5.2
Hydroprocessing unit	3.88	9.11E-08	0	0.0426	1
Total carbon footprint (kg CO ₂ eq.)	—	3.93	100	4.23	100

Table 1.16 *Potential environmental impacts for first and second processing path*

Environmental impact	Unit	First path	Second path
Human toxicity by ingestion (HTPI)	1/Lethal dosage (LD ₅₀)	5.23E-07	4.75E-05
Human toxicity by exposure (HTPE)	1/Time-weighted average (TWA)	2.93E-04	3.65E-04
Global warming potential (GWP)	CO ₂ eq.	3.93	4.23
Ozone depletion potential (ODP)	CFC-11 eq.	5.24E-12	1.8E-06
Photochemical oxidation (PCOP)	C ₂ H ₂ eq.	5.86E-09	1.05E-05
Acidification (AP)	H ⁺ eq.	0.033	7.02E-03
Aquatic toxicity (ATP)	1/LC ₅₀	1.89E-06	1.98E-05
Terrestrial toxicity (TTP)	1/LD ₅₀	5.23E-07	4.75E-05
Carcinogenics (HTC)	kg benzene eq.	0.042	0.049
Noncarcinogenics (HTNC)	kg toluene eq.	5.37E-05	0.071
Freshwater ecotoxicity (ET)	kg 2,4-dichlorophenol eq.	3.35E-07	7.43E-06

In summary, the framework presented is a promising tool to represent the ever-increasing number of biorefinery alternatives with their competing technologies and routes and help evaluate them at their optimality for early-stage design and analysis purposes in terms of techno-economic analysis. Sustainability analysis and environmental impact assessment are included in the framework which enables a more detailed and comprehensive analysis of the biorefinery alternatives. The framework helps formulate a multicriteria evaluation (techno-economic, environmental impact, and sustainability analysis) of the biorefinery concept.

1.4 Conclusion

A systematic framework with a superstructure-based optimization approach was presented for the early-stage design and analysis of biorefinery alternatives. In the description of the framework, we have especially highlighted the use of the superstructure to represent many competing biorefinery alternatives (from thermochemical to biochemical), and we have used generic and simple models to describe the processing steps in the biorefinery. These generic models are coupled to a data structured to manage the multidisciplinary data needed to solve the problem, and we cast the resulting optimization problem as an MINLP and solve the problem to identify optimal processing paths for a given objective function definition. To further complement the analysis, we then analyze the results in terms of sustainability and environmental impact.

The integration of the sustainability and environmental impact analysis to the framework provides a more comprehensive decision making and multicriteria evaluation to enable the users to screen for economic but sustainable biorefinery concepts early on in the project development life cycle.

The framework was evaluated with a case study focusing on design of a lignocellulosic biorefinery. The results showed that the tool could find new optimal processing paths for different scenarios (objective functions) which provide a better, more efficient production process and less utility, waste, investment, and operating costs using the expanded biorefinery network. The optimal biorefinery pathways were further analyzed with respect to sustainability and environmental impact, which revealed further options for sustainability

improvement in the optimal biorefinery pathway. The results presented in this chapter convincingly demonstrate the promising potential of the framework as a decision support tool for analyzing biorefinery concepts early on for technical, economical, as well as sustainability and environmental impact-related aspects.

Nomenclature

Indexes

i	Component
k	Process interval (origin)—optimization model
kk	Process interval (destination)
react	Key reactant
rr	Reaction

Sustainability analysis model

o	Open path flow—sustainability model
rm	Raw material—sustainability model
RM	Total number of raw materials—sustainability model
k	Component path flow—sustainability model
z	Component cycle path flow—sustainability model
u	Subunit operation—sustainability model
U	Total number of subunit operations—sustainability model
uk	All component path flows in a given subunit operation—sustainability model
m	Mean value—sustainability model
rk	Reaction—sustainability model
r	Reactive unit operations—sustainability model

LCA model

c	Compartment (air, water, and soil)
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Parameters

MW_i	Molecular weight
$P1_{i,kk}$	Raw material prices
$P2_{i,kk}$	Utility prices
$P3_{i,kk}$	Product prices
$SW_{i,kk}$	Waste fraction
$S_{k,kk}$	Superstructure (binary)
$S^p_{k,kk}$	Superstructure (binary)
a_{kk}	Coefficient for capital cost estimation
n_{kk}	Coefficient for capital cost estimation
$\alpha_{i,kk}$	Specific utility consumption
$\gamma_{i,kk,rr}$	Reaction stoichiometry
$Split_{i,kk}$	Split factors

$\theta_{\text{react,kk,rr}}$	Conversion of key reactant
$\mu_{i,kk}$	Fraction of utility mixed with process stream
t	Time

Sustainability analysis model

PP_o^i	Purchase price of component i in the open path flow
$PR_o^{(rm)}$	Raw material price of component i in the open path flow
CA_o^i	Cost allocation factor of component i in the open path flow
ν_o^i	Stoichiometry of component i in the open path flow
M_o^i	Molecular weight of component i in the open path flow
PE_u	Energy price of subunit operation u
Q_u	The duty of subunit operations
$A_{u,k}^i$	Specific heat capacity of component i in the path flow k in a given subunit operation
$\xi_{r,rk,k}$	The extent of reaction rk
$n^{(fp)}$	Mole flow rate of a desired final product
$E_{r,rk,k}^i$	Effect of the component i to reaction rk
AF_z^i	Accumulation factor of component i in the cycle path flow z

LCA model

HV_r	Heating value of renewable resource r
HV_{nr}	Heating value of nonrenewable resource nr
$CF_{GHG,air}^{GWP}$	Characterization factor value regarding the global warming of greenhouse gas (GHG)
$EM_{i,c}$	Mass of chemical i emitted to compartment c per 1 kg of product
$CF_{i,c}^k$	Characterization factor of chemical n emitted to compartment c for impact category k

Variables

$F_{i,k,kk}$	Component i flow from process intervals k to process intervals kk
$F_{i,kk}^M$	Component flow after mixing
$R_{i,kk}$	Utility flow
$F_{i,kk}^R$	Component flow after reaction
$F_{i,kk}^{out}$	Component flow after waste separation
$waste_{i,kk}$	Component flow of waste stream after waste separation
$F_{i,kk}^{out1}$	Component flow leaving process intervals kk through primary outlet
$F_{i,kk}^{out2}$	Component flow leaving process intervals kk through secondary outlet
y_{kk}	Selection of process intervals (binary)
$w_{j,kk}$	Selection of a piece of the piecewise linearization (linear)

Sustainability analysis model

MVA_o^i	Mass Value Added (MVA) of component i in the open path flow o
m_o^i	Flow rate of component i in the open path flow o

EWC_k^i	Energy and waste cost of component i in the path flow k
m_k^i	Mass flow rate along the path flow k of the component i
RQ_k^i	Reaction quality of component i in the path flow k
$f_{i,a}^i, d_{i,op}^i$	The flow rate leaving the cycle path flow

LCA model

R_{renew}	Total energy from renewable resource consumption per 1 kg of product
$R_{non-renew}$	Total energy from nonrenewable resource consumption per 1 kg of product
R_{total}	Total energy from resource consumption per 1 kg of product
$x_{r,i}$	Mass of renewable resource r used to produce 1 kg of input i
$x_{nr,i}$	Mass of nonrenewable resource nr used to produce 1 kg of input i
CO_{2eq}	Carbon dioxide equivalent per 1 kg of product
$m_{GHG,air}^{PRO}$	Mass flow rate of greenhouse gas (GHG) emitted to air from the process
I^k	The potential environmental impact of chemical i for a specific impact category of concern k

Abbreviations

CAPEX	Capital investment
EBITDA	Earnings before interest, taxes, depreciation, and amortization
LB	Lower bound of the objective function
UB	Upper bound of the objective function

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