

# Toward a Computer-Aided Synthesis and Design of Biorefinery Networks: Data Collection and Management Using a Generic Modeling Approach

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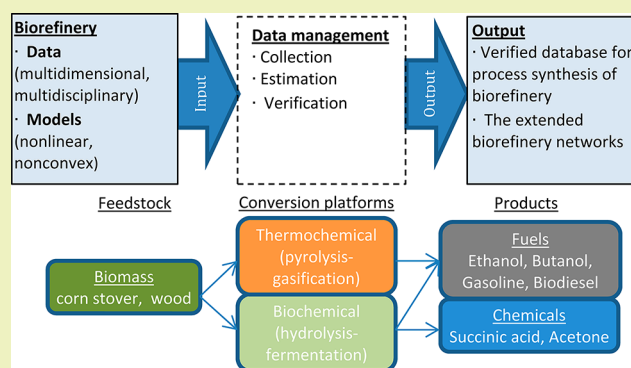
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## S Supporting Information

**ABSTRACT:** Recent research into biorefineries resulted in many competing concepts and technologies for conversion of renewable biobased feedstock into an array of promising products including fuels, chemicals, materials, etc. The topic of this study is collection and management of the complex biorefinery data that are needed among others to support the superstructure-based optimization studies. To this end, we first formulate an integrated thermochemical and biochemical biorefinery superstructure and then use a generic modeling approach to represent each processing technology in the superstructure. The generic model parameters includes reaction yield, utility consumption, and separation efficiency among others, which are identified on the basis of input–output data (generated from rigorous models) collected from detailed biorefinery case studies reported in the open literature. The outcome is a verified database for the extended biorefinery networks combining thermochemical and biochemical platforms that represents 2882 potential biorefinery routes. The validated biorefinery database is made public and can be used to cross-validate and benchmark new biorefinery technologies and concepts as well as in superstructure-based optimization studies.

**KEYWORDS:** Process synthesis, Superstructure, Biorefinery, Thermochemical conversion, Data management



## INTRODUCTION

The limited resources of fossil fuel feedstock form a serious challenge to the future growth of the processing and chemical industries. This motivates the development of new and more sustainable technologies for processing renewable feedstocks, with the aim of bridging the gap for fuel, chemicals, and material production. In a biorefinery, a biobased feedstock is processed to produce various products such as fuel, chemicals, or power/heat. As there are several feedstock sources, as well as many alternative conversion technologies to choose from to match a range of products, this creates a large number of potential processing paths for biorefinery development.<sup>3,7,10</sup> The characterization of each process alternative requires a substantial amount of information: parameters, variables, models of known reactions, thermodynamic properties, process efficiencies, and experimental data.<sup>1,2,4</sup> In order to manage the complexity of designing a biorefinery, several publications have focused on simplification, i.e., (i) to find an optimal processing route considering only the reaction,<sup>21,22</sup> (ii) to limit the number of processing steps to five steps,<sup>11</sup> or (iii) to develop a systematic study of the superstructure of integrated biorefi-

neries by using a combined process and economic modeling.<sup>16</sup> Clearly, in the early stage of biorefinery planning and design—a phase that is often characterized by lack of detailed data—it is important to simplify and manage the complexity related to the huge amount of data that is to be processed prior to identifying the optimal biorefinery processing path with respect to economics, consumption of resources, and sustainability.

A methodology to generate and identify optimal biorefinery networks was developed earlier.<sup>15,24</sup> The methodology is based on superstructure optimization and consists of tools and methods including databases, models, a superstructure, and solution strategies to represent, describe, and evaluate various processing network alternatives. The data collection and the modeling form a significant part of this methodology, which is the subject of this contribution.

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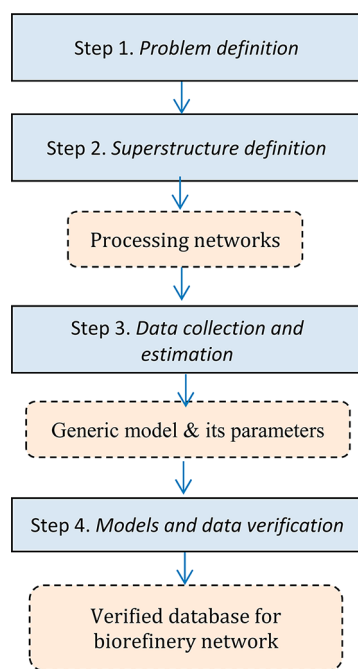
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In this study, we expand the scope and the size of the biorefinery network problem by extending the database, models, and superstructure of the methodology with thermochemical biomass conversion routes and integrate them with the superstructure of the biochemical conversion network.<sup>24</sup> In particular, in this paper, we present a generic process modeling approach to collect and manage multidisciplinary and multidimensional data related to process alternatives in a biorefinery process network. We then perform a verification of the generic models and its parameters against the actual data source for quality control purposes. We also briefly introduce the MINLP-based problem formulation to indicate how the generic model and data developed in this contribution are embedded in the optimization problem setting. The solution and analysis of the optimization problem itself, including the effect of data uncertainties, is however beyond the scope of this contribution and subject to further work.

The paper is organized as follows: (i) the overall methodology used in this study is briefly introduced and (ii) the methodology is applied to the expanded biorefinery network, where the superstructure definition, data collection, and data validation are presented.

## ■ FRAMEWORK FOR SYNTHESIS AND DESIGN OF BIOREFINERY

This study uses an earlier developed framework,<sup>15</sup> the so-called integrated business and engineering framework (Figure 1). In

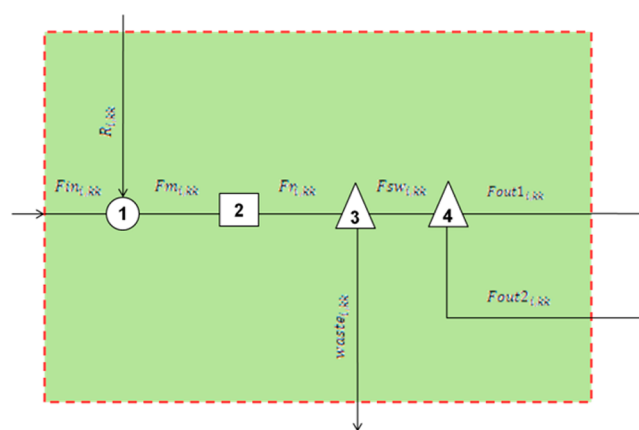


**Figure 1.** Steps taken in the data management and collection framework: Dashed boxes indicate the outcome of each step of the workflow.

particular, we highlight the data management and collection efforts with a generic process modeling approach<sup>13</sup> to collect and manage the complexity of multidisciplinary and multidimensional data related to the different process alternatives in a biorefinery process network. The different steps that are part of the framework (Figure 1) will be explained briefly.

**Step 1: Problem Definition.** The first step includes the definition of the problem scope, selection of suitable objective functions, and optimization scenarios with respect to either business strategy, engineering performance, sustainability, or a combination of such objectives.

**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 feedstocks 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 2).<sup>15</sup> Detailed presentation of the generic model itself is given below.



**Figure 2.** Generic process block model.

**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 models (e.g., kinetics, thermodynamics). In this step, however, a simple input–output type generic block model is used that is identified from the data generated from the above-mentioned complex model. This generic block thus consists of four parts of the typical simple mass balance equations: (i) mixing, (ii) reaction, (iii) waste separation, and (iv) product separation.

$$Fm_{i,kk} = Fin_{i,kk} + R_{i,kk} \quad (1)$$

$$R_{i,kk} = (\mu_{i,j,kk} \times Fin_{i,kk} \times \alpha_{i,kk}) \quad (2)$$

$$Fr_{i,kk} = Fm_{i,kk} + MW_i \times \sum_{rr} (\gamma_{i,rr} \times \theta_{react,rr} \times Fm_{i,kk}/MW_{react}) \quad (3)$$

$$Fsw_{i,kk} = (1 - SW_{i,kk}) \times Fr_{i,kk} \quad (4)$$

$$waste_{i,kk} = SW_{i,kk} \times Fr_{i,kk} \quad (5)$$

$$Fout1_{i,kk} = Split_{i,kk} \times Fsw_{i,kk} \quad (6)$$

$$Fout2_{i,kk} = (1 - Split_{i,kk}) \times Fsw_{i,kk} \quad (7)$$

$$F1_{i,k,kk} \leq S_p^{k,kk} \times Fout1_{i,kk} \quad (8)$$

$$F2_{i,k,kk} \leq (S_p^{k,kk} - S^{k,kk}) \times Fout1_{i,kk} \quad (9)$$

$$Fin_{i,kk} = \sum_k (F1_{i,k,kk} + F2_{i,k,kk}) \quad (10)$$

Equations 1–7 are the equations used for the generic block to estimate the outlet mass flow ( $Fout1_{i,kk}$ ,  $Fout2_{i,kk}$ ) using simple mass balances. In eqs 1 and 2, the chemicals and utilities used ( $R_{i,kk}$ ) for each processing technology are calculated by using the ratio ( $\mu_{i,kk}$ ) to the inlet mass flow rate ( $Fin_{i,kk}$ ). The parameter  $\alpha_{i,kk}$  represents the consumption of the utilities or chemicals: 0 corresponds to no consumption while 1 corresponds to 100% consumption. In eq 3, the reaction outlet mass stream ( $Fr_{i,kk}$ ) is calculated based on stoichiometry,  $\gamma_{i,rr}$  and conversion fraction,  $\theta_{react,rr}$ . In eqs 4 and 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 eqs 6 and 7 on the basis of a product separation fraction,  $Split_{i,kk}$ . Moreover, in order to connect each generic block and thereby formulate the superstructure, eqs 8–10 are used. The mass outlet flows mentioned earlier ( $Fout1_{i,kk}$ ,  $Fout2_{i,kk}$ ) are called primary and secondary outlet flow, respectively. The primary and secondary outlet flows are connected to the next generic blocks using binary variables ( $S_p$ ,  $S$ ), respectively. The outlet flows between the generic 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 block. Note as well that recycle flows can be considered using eqs 8–10. There are two potential cases of recycle flows addressed: (i) recycle flows within the same processing step, i.e., 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 steps 2 and 4), and (ii) recycle flows to the previous processing step, which is handled by using eqs 8 and 9. The appropriate values for the above-mentioned 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 data are in the end organized in a multidimensional matrix form that represents processing steps, alternatives, and components, among others.

**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 validation can be performed in this step by fixing the decision variables in the MINLP problem formulation, i.e., the vector  $y$  (see below), and thereby 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 be 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. To further highlight the use of this database, a simple optimization problem (MINLP) is briefly presented

below to indicate how the generic models and parameters are embedded in the optimization problem formulation. The optimization formulation is presented in eqs 11–16 that consists of the objective function (e.g., total annualized costs, eq 11) subjected to process constraints, process models and constraints (eqs 1–10) of the generic block mentioned earlier ( $x$  is a process variable, e.g. the mass flow rate), structural constraints (eqs 12 and 13) representing the superstructure that allows selection of only one process alternative in each step, and cost functions (eqs 14–16) to calculate the operating and capital costs using cost parameters ( $P1_{i,kk}^{waste}$ , waste treatment cost,  $P2_{i,kk}^{utilities/chemicals}$ , utility or chemicals cost,  $P3_a^{kk}$ , reactor investment cost,  $P3_b^{kk}$ , separation investment cost, and  $capex_{kk}$ , capital expenditure).

As an example, the objective function is formulated such as to minimize total annualized costs (TAC)

$$OBJ = \sum_{kk} OPEX - (CAPEX_1 + CAPEX_2)/t \quad (11)$$

Subject to (i) process models of the generic block  $h(\mu_{i,kk}, \alpha_{i,kk}, \gamma_{i,rr}, \theta_{react,rr}, MW_i, Split_{i,kk}) = 0$ , as mentioned earlier (eqs 1–7 and 10), (ii) process constraints ( $g(S_p^{k,kk}, S^{k,kk}) \leq 0$ , as mentioned earlier (eqs 8 and 9), (iii) structural constraints (eqs 12 and 13), and (iv) cost constraints (eqs 14–16).

$$\sum_k y_k \leq 1 \quad (12)$$

$$y \in \{0; 1\}^n \quad (13)$$

$$OPEX_{kk} = (P2_{i,kk}^{utilities/chemicals} \times R_{i,kk}) + (P1_{i,kk}^{waste} \times F_{i,kk}^{waste}) \quad (14)$$

$$CAPEX_{thermochem} = \sum_{kk} capex_{kk} \quad (15)$$

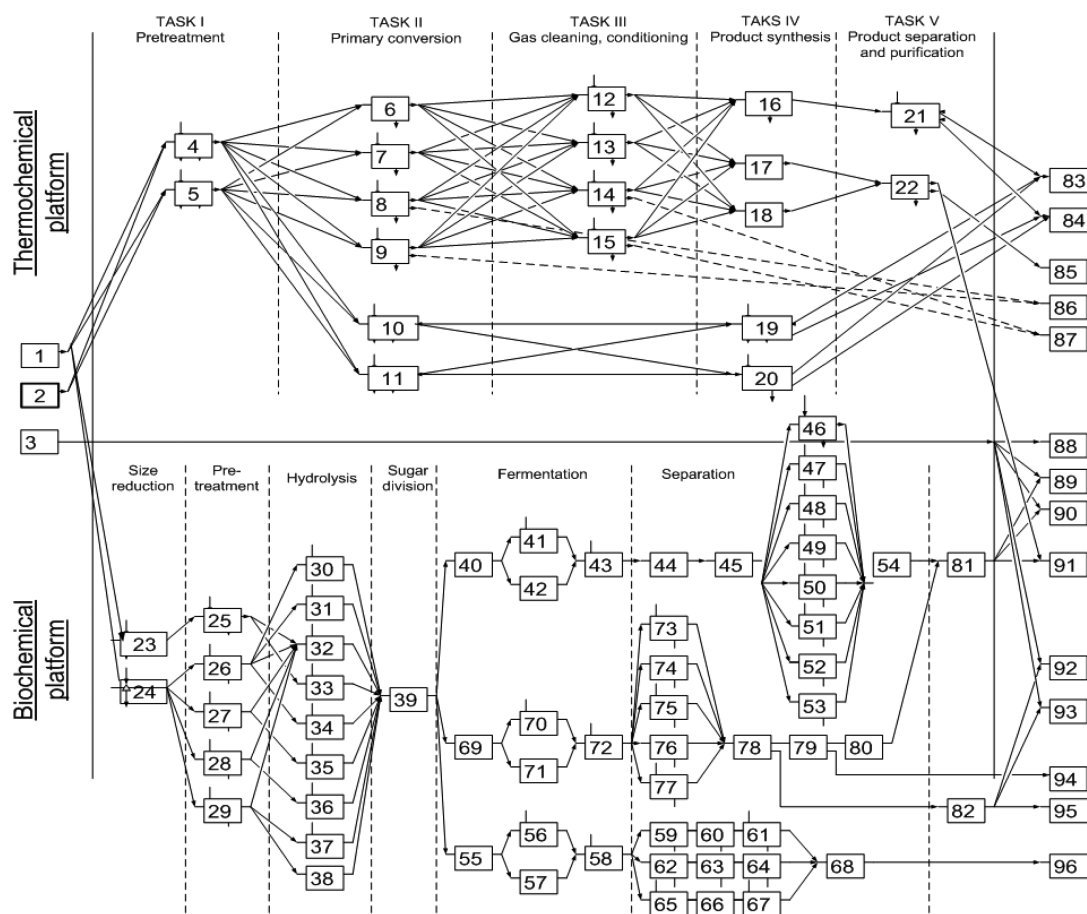
$$CAPEX_{biochem} = \sum_k [P3_a^{kk} \times Fm_{i,kk}^{n1} + P3_b^{kk} \times Fr_{i,kk}^{n2}] \quad (16)$$

The problem can be formulated and solved using appropriate software (e.g., GAMS), and the generic model parameters and other data appearing in the constraints (e.g.,  $\alpha_{i,kk}$ ,  $\gamma_{i,rr}$ ,  $\theta_{react,rr}$ ,  $P1_{i,kk}^{waste}$ ,  $P2_{i,kk}^{utilities/chemicals}$ , etc.) can be accessed from the database. In this way, the overall MINLP problem formulation is separated into two parts: (1) data handling and representation (as described in this contribution, with help of a generic process model and its parameters stored in a database) and (2) 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.

## ■ DATA MANAGEMENT, COLLECTION, VERIFICATION, AND DISCUSSION

**Step 1: Problem Definition.** The problem to be addressed is the design of an optimal biorefinery network consisting of a thermochemical platform integrated with a biochemical platform, which is indeed rather data intensive. The availability of data is however critically important for the quality of decisions to be generated using the decision support tool. Details about data collection and validation are therefore presented below.

**Step 2: Superstructure Definition.** The thermochemical biomass conversion routes were reviewed to formulate the superstructure (Figure 3, top). The data and models of



**Figure 3.** Combined superstructure of two biorefinery conversion platforms: thermochemical (top) and biochemical platform (bottom).

thermochemical conversion were collected from several U.S. National Renewable Energy Laboratory (NREL) technical reports<sup>5,6,12,18,23</sup> and one U.S. Pacific North National Laboratory (PNNL) report.<sup>9</sup> On the basis of these NREL reports, the superstructure was defined. The proposed processing network for thermochemical conversion consists of 27 process intervals: 2 raw materials, 19 processing technologies, 3 main products, and 3 byproducts, resulting in 156 parameters, 619,364 variables, and 26 discrete variables.

The proposed superstructure of thermochemical conversion was then combined with the superstructure of biochemical conversion<sup>24</sup> resulting in a superstructure with a total of 96 processing intervals<sup>4</sup>: 3 raw materials, 79 processing technologies, and 14 products (Figure 3) with 576 parameters, 4,705,181 variables, and 668 discrete variables.

The above-mentioned studies contain the complex, non-linear, rigorous models resulting in the simulated mass flow rate for each designed process stream. This information provides an adequate basis for estimating the parameters of each generic block using input–output information. Further explanation and examples are presented in the next section.

**Step 3: Data Collection and Estimation.** The data and parameters required for the generic blocks that are used to define the superstructure (Section 3.1) are presented here and in Tables 1–5. 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

**Table 1.** Data Collection Example for Entrained Flow Gasifier

descriptions	raw data from NREL study <sup>18</sup>		generic block model parameters	
utilities	steam to biomass ratio	0.48	mixing: steam ratio	0.48
	O <sub>2</sub> to biomass ratio	0.35	mixing: O <sub>2</sub> ratio	0.35
reaction	stoichiometry	N/A	reaction: stoichiometry was estimated from stream table (Table 2)	(eq 17)
	conversion fraction of C	1	reaction: conversion fraction	1
waste separation	char, ash, soot, slag removal	99%	SW <sub>i,kk</sub>	0.99
	ash removal	95%	SW <sub>ash,kk</sub>	0.95
product separation	stream separation	1 outlet stream	Split <sub>i,kk</sub>	1

general block using commercial process simulators such as ProII, Aspen, etc.

Here, two examples are presented. Tables 1 and 2 and Figure 4 illustrate how the data were collected for the entrained flow gasifier, which is one of the processing steps in the combined superstructure. The entrained flow gasifier is used to convert solid fuels (coal, biomass) into raw syngas. It requires a special size reduction equipment, steam, and O<sub>2</sub>. Char, ash, soot, and slag are collected at the bottom as wastes. It is normally operated at high temperature (1300 °C), and the reactions during the gasification are complex. We have used the design



**Table 2. Example of Stream Table of Entrained Flow Gasifier<sup>18</sup>**

component	gasifier inlet flow (tpd)	gasifier outlet flow (tpd)	$\gamma_{i,rr}$ (stoichiometry)	$\theta_{i,rr}$ (conversion fraction)
H <sub>2</sub> O	1182	988	-0.13	-
H <sub>2</sub>	101	123	0.13	-
C	945	-	-1	1
S	4.4	-	-0.0017	-
N <sub>2</sub>	16	17.7	0.0007	-
O <sub>2</sub>	1512.6	-	0.6	-
ash	120	-	-	-
CO	-	1457	0.66	-
CO <sub>2</sub>	-	1184	0.34	-
H <sub>2</sub> S	-	4.5	0.002	-
soot	-	6	0.07	-
slag	-	100	1.3	-

data reported by a NREL study<sup>18</sup> for estimating generic process block parameter values for steam and O<sub>2</sub> ratio, conversion fraction, and char and ash removal efficiencies. On the other hand, the complete stoichiometry of the reaction is not available. Thus, the stoichiometry of the reaction needs to be estimated, in this case by using eq 17 combined with the reported mass inlet and outlet streams of the processing unit shown in Table 2. The resulting estimated stoichiometry is given in Table 2 as well, and the reaction stoichiometry is shown in Figure 4. We note that there is no recycle stream for the entrained flow gasifier as a consequence of the very high conversion efficiency of biomass in such an entrained flow gasifier.

$$\gamma_{i,rr} = \frac{-(mass_{(i,rr)-out} - mass_{(i,rr)-in})/MW_i}{(mass_{(reactant,rr)-out} - mass_{(reactant,rr)-in})/MW_{reactant}} \quad (17)$$

Another example of the data collection is the gas cleaning and conditioning step (task 3 in Figure 3). This step has a major function and is used to (i) remove solid particles, (ii) convert the remaining hydrocarbons including tar into syngas, (iii) adjust the H<sub>2</sub>/CO ratio, and (iv) remove CO<sub>2</sub> and H<sub>2</sub>S, which will otherwise have a negative effect on the catalysts in the next processing step. There are several unit operations that can be used in this step such as a tar reformer, steam reformer, water-gas shift reactor, pressure-swing adsorption, venturi and water scrubber, and acid removal. Here, one of the gas cleaning and conditioning steps of the NREL studies<sup>12</sup> is selected as the second illustrative example. It consists of three main processing sections: tar reformer, venturi scrubber, and acid removal. The function of the tar reformer is to convert tar and hydrocarbons into syngas, and the process consists of two reactors: the reformer and combustor that requires air as utility. The function of the venturi scrubber is mainly to remove solid particles and water, and the acid removal process is necessary to remove CO<sub>2</sub> and H<sub>2</sub>S using aqueous solutions of amines, 35 wt

% monoethanol amine (MEA). Tables 3 and 4 and Figure 5 illustrate the data collection for these processes. With regard to recycle streams, this had been modeled using eqs 8 and 9.

**Table 3. Data Collection Example for Processing Units for Gas Cleaning and Conditioning: Tar Reformer, Venturi Scrubber, and Acid Removal**

descriptions	raw data from NREL study	generic block model parameters
utilities	air required for combustion (tpd)	3123 air to inlet flow ratio 1.2
reaction	stoichiometry	N/A stoichiometry was estimated from stream table (Table 4 and Figure 5)
	conversion fraction of tar	1 conversion fraction 1
waste separation	water removal	50% $SW_{i,kk}$ 0.5
	CO <sub>2</sub> removal	36% $SW_{ash,kk}$ 0.36
	H <sub>2</sub> S removal	85% $SW_{H2S,kk}$ 0.85
product separation	stream separation	2 outlet streams $Split_{i,kk}$ (Table 4)

The two examples above show how the complex 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 matrix (database uses 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 from the database. At the same time, storing the data in the matrix form provides a certain structure to organize the data and manage the complexity in a compact and efficient way.

The description and data collection (plus parameter estimation where necessary) for the other process intervals included in the superstructure of the thermochemical platform (Figure 3, top) are summarized in Table 5. For each process interval, mixing parameters ( $\mu_{i,j,kk}$ ,  $\alpha_{i,kk}$ ), reaction parameters ( $\gamma_{i,rr}$ ,  $\theta_{i,rr}$ ), waste separation parameters ( $SW_{i,kk}$ ), and product separation parameter ( $Split_{i,kk}$ ) are provided. These values are then validated by comparing the simulation results with the reported results of the NREL/PNNL reports.<sup>5,6,9,12,18,23</sup> The validation is presented in the next section, and the full simulation results are presented in the Appendix. Note that the process intervals that are feedstocks and products are presented here as follows: (i) feedstocks: 1-corn stover, 2-wood, and 3-gasoline (for blending) and (ii) products: 83-FT gasoline, 84-FT diesel, 85-mixed alcohols, 86-waste heat from gasifier, 87-waste heat from reformer, 88-gasoline (100%), 89-bioethanol (5%), 90-bioethanol (10%), 91-bioethanol (100%), 92-biobutanol (5%), 93-biobutanol (10%), 94-acetone, 95-biobutanol (100%), and 96-succinic acid. Specifically, for the

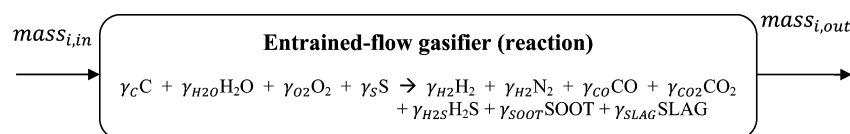
**Figure 4.** Process diagram showing the mass inlet/outlet, reaction, and its stoichiometry for the entrained flow gasifier.

Table 4. Stream Table of the Tar Reformer<sup>12</sup>

component	inlet stream (tpd)	recycle stream (tpd)	air inlet (tpd)	outlet stream (tpd)	$\gamma_{irr}$	$\theta_{irr}$	primary outlet (tpd)	$Split_{i,rr}$
H <sub>2</sub> O	901	0.35	60.9	1128	0.4	—	523.9	0.46
H <sub>2</sub>	37.7	68.8	—	168.75	1.48	—	168.75	1
N <sub>2</sub>	—	43.1	2312	2360.3	—	—	45.4	0.019
O <sub>2</sub>	—	—	708.6	86.4	-0.98	—	0	0
CO	874	903.5	—	2345.7	0.94	—	2345.7	1
CO <sub>2</sub>	408	1153.8	1.53	1873.6	0.29	—	978	0.52
H <sub>2</sub> S	1.75	0.29	—	2.04	—	—	2.04	1
NH <sub>3</sub>	3.8	0.27	—	0.3	—	—	0.3	1
AR	—	—	39.4	39.4	—	—	0	0
tar	19.8	—	—	—	-1	1	—	—
CH <sub>4</sub>	180	84.9	—	43	-0.7	—	43	1
C <sub>2</sub> H <sub>6</sub>	5.2	3.52	—	0.08	-0.015	—	0.08	1
C <sub>2</sub> H <sub>4</sub>	86.7	6.6	—	6.9	-0.15	—	6.9	1
C <sub>2</sub> H <sub>2</sub>	8.2	0.6	—	0.65	-0.0159	—	0.65	1
C <sub>6</sub> H <sub>6</sub>	6.6	—	—	0.04	-0.0042	—	0.04	1
C <sub>3</sub>	—	17.4	—	17.4	—	—	17.4	1
C <sub>4</sub>	—	3.2	—	3.2	—	—	3.2	1
C <sub>5</sub>	—	0.6	—	0.6	—	—	0.6	1
C <sub>1</sub> -ol	—	4.3	—	4.3	—	—	4.3	1
C <sub>2</sub> -ol	—	11.6	—	11.6	—	—	11.6	1
C <sub>3</sub> -ol	—	0.67	—	0.67	—	—	0.67	1

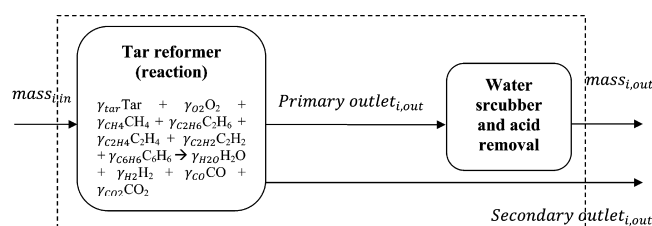


Figure 5. Process diagram showing mass inlet/outlet, reaction, and its stoichiometry for the gas cleaning and conditioning step (modified according to NREL report<sup>12</sup>).

biochemical platform (Figure 3, bottom), the detailed description can be found in a previous study.<sup>24</sup>

Another important aspect to consider when collecting data is that there are uncertainties that could be related to technical, economical, and environmental parameters. It is important therefore to address uncertainties in data, which is needed for making decisions under uncertainty when applying the computer-aided synthesis and design approach.<sup>14</sup> In order to exploit this feature, sources of uncertainties in the data need to be identified and characterized. In this study, the feedstock cost and product price are considered to have significant uncertainty associated with their reported range. After identifying the uncertain parameters, data were then collected for statistical analysis. For estimating the uncertainty on product prices, namely, gasoline, diesel, and ethanol prices, historical data (year 2012) have been used.<sup>19,20</sup> The historical data were statistically analyzed using the Matlab statistical toolbox that returned the correlation matrix (given in Table 6a) as well as empirical distribution functions (shown in Figure 6). On the basis of the empirical distribution function, a uniform distribution is selected to be appropriate to describe the uncertainty range for these data together with upper and lower range as reported in Table 6b. For the characterization of uncertainty on the feedstocks, as no historical data was available for these, instead the open literature was reviewed to find out lower and upper bound and reported in Table 6b. Further, a uniform

distribution was assumed for these parameters, which is common practice in the uncertainty and sensitivity analysis field to use noninformative priors in case of no data availability.<sup>8,17</sup>

**Step 4: Models and Data Verification.** Seven processing paths based on five NREL reports<sup>5,6,12,18,23</sup> and a PNNL report<sup>9</sup> were used to validate the models and data used for each process interval and processing path. As explained in Section 2.4, the verification can be performed by fixing the processing path and comparing the simulation results with the NREL and PNNL studies. Table 7 summarizes the short descriptions, processing paths, and the amount of biofuel products generated for each of the seven base cases used in this study. The simulation results of each processing path were validated by comparing with the detailed results published in NREL-PNNL reports.

The verification between the reported results from NREL-PNNL reports and the simulation results of this study (implemented in GAMS) is necessary in order to validate 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 (i) the entrained-flow gasifier and (ii) gas cleaning and conditioning processes. Here, the collected data for both examples are validated and presented in Tables 8 and 9, 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 Tables S1–S7 of the Supporting Information.

The expanded network provides an expanded space for optimization studies meaning that it can generate more scenarios to compare a large number of processing alternatives before generating an optimal decision for biorefinery designs.

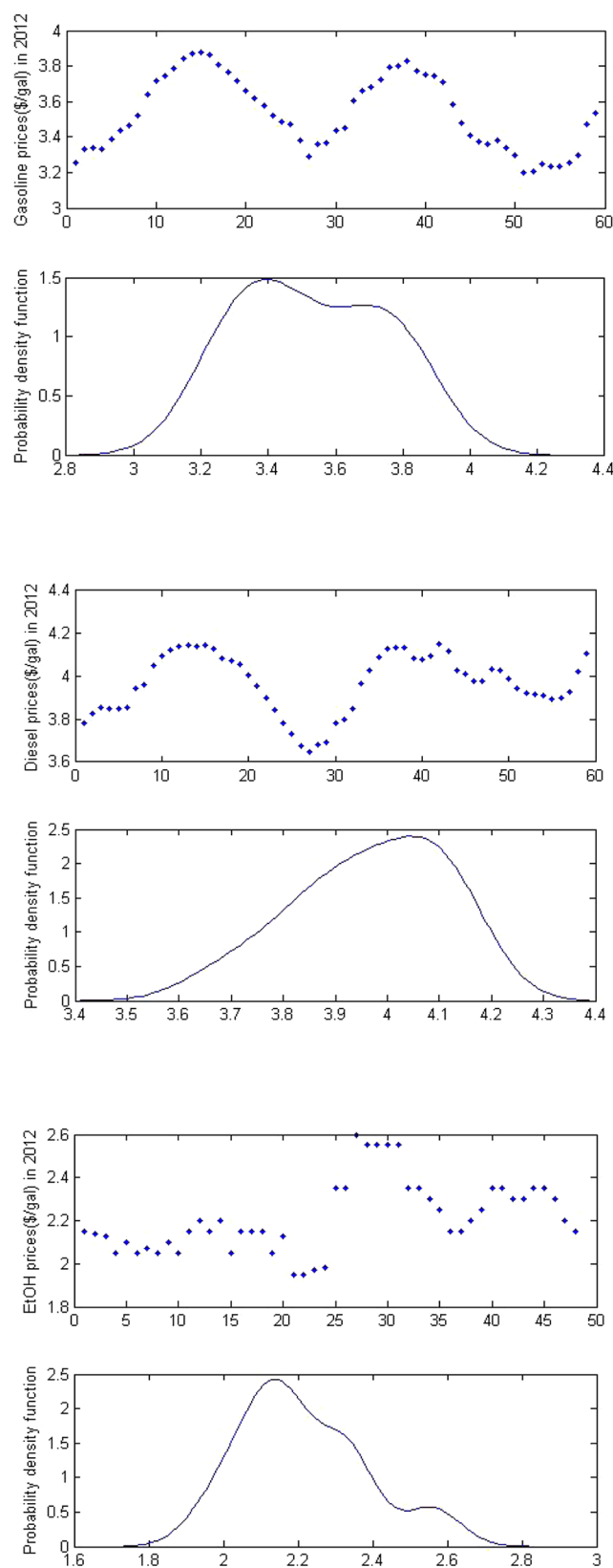
Because the problem of optimal biorefinery design is data intensive with several categories of data (thermodynamic properties, kinetics, operating conditions, or processing technologies), it is therefore important to organize the data in a compact and generic way. This is achieved by defining and using a generic process block model. In this way, it becomes

**Table 5. Summary Table for the Data Collection (mixing,  $\alpha_{i,ikk}$ ,  $\mu_{i,ikk}$  reaction,  $\gamma_{i,rrr}$ ,  $\theta_{react,rrr}$ ; waste separation,  $SW_{i,ikk}$  product separation,  $Splitt_{i,k}$ ) for Thermochemical Processing Networks**

no.	description	mixing ( $\alpha_{i,ikk} = 1$ )	$\mu_{i,ikk}$	reaction (stoichiometry, $\gamma_{i,rrr}$ )	$\theta_{react,rrr}$	waste separation	$SW_{i,ikk}$	product separation (in primary nutlet)	$Splitt_{i,k}$	
4	hammer mill, rotary dryer (indirectly contact with steam)	electricity to biomass ratio; steam to % moist ratio	4; 5.9	—	—	moisture removal	0.6	steam	0	
5	hammermill and rotary dryer (directly contact with hot flue gas)	electricity to biomass ratio; waste heat from process contact with hot flue gas	4	—	—	moisture removal	0.96	waste heat	0	
6	entrained-flow (free-fall) gasifier	O <sub>2</sub> to biomass ratio; steam to % moist ratio	0.35; 0.48	$C + 0.13H_2O + 0.6O_2 + 0.0017S \rightarrow 0.13H_2 + 0.0007N_2 + 0.66CO + 0.34CO_2 + 0.002H_2S + 0.07SOOT + 1.3SLAG$	1	ash, soot removal	0.999	one outlet stream	1	
7	bubbling fluidized bed gasifier	O <sub>2</sub> to biomass ratio; steam to % moist ratio	0.26; 0.17	$C + 0.11H_2O + 0.34H_2 + 0.5O_2 + 0.002S + 0.007N_2 \rightarrow 0.36CO + 0.41CO_2 + 0.002H_2S + 0.01NH_3 + 0.08CH_4 + 0.01C_2H_6 + 0.02C_2H_4 + 1.2CHAR$	1	ash, char removal	0.999	one outlet stream	1	
8	indirectly heated with circulating FB gasifier	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	$C + 0.48H_2 + 0.6O_2 + 0.0006S + 0.001N_2 \rightarrow 0.37CO + 0.39CO_2 + 0.12H_2O + 0.0006H_2S + 0.002NH_3 + 0.13CH_4 + 0.02C_2H_6 + 0.03C_2H_4 + 0.23TAR$	1	ash removal	0.999	H <sub>2</sub> O in primary outlet; CO <sub>2</sub> in primary outlet; O <sub>2</sub> , N <sub>2</sub> , Ar in primary outlet	0.75;	
9	0.25; 0	O <sub>2</sub> to biomass ratio; steam to % moist ratio; fresh olive to biomass ratio; MgO to ash ratio	directly heated with bubbling gasifier	$O_2$ to biomass ratio; steam to % moist ratio; fresh olive to biomass ratio; MgO to ash ratio	0.22; 0.2;	0.00;3 0.004	C +	0.47H <sub>2</sub> + 0.04H <sub>2</sub> O + 0.4O <sub>2</sub> + 0.0006S + 0.001N <sub>2</sub> → 0.19CO + 0.39CO <sub>2</sub> + 0.0006H <sub>2</sub> S + 0.002NH <sub>3</sub> + 0.18CH <sub>4</sub> + 0.01C <sub>2</sub> H <sub>6</sub> + 0.013C <sub>2</sub> H <sub>4</sub> + 0.55TAR + CHAR	0.47H <sub>2</sub> + 0.04H <sub>2</sub> O + 0.4O <sub>2</sub> + 0.0006S + 0.001N <sub>2</sub> → 0.19CO + 0.39CO <sub>2</sub> + 0.0006H <sub>2</sub> S + 0.002NH <sub>3</sub> + 0.18CH <sub>4</sub> + 0.01C <sub>2</sub> H <sub>6</sub> + 0.013C <sub>2</sub> H <sub>4</sub> + 0.55TAR + CHAR	1
10	pyrolysis (bubbling fluidized bed)	steam to inlet flow	0.14	$C + 0.3O_2 + 0.6H_2 + 0.007N_2 + 1.5ASH + -0.001S \rightarrow 0.05H_2O + 0.05CO + 0.07CO_2 + 0.01CH_4 + 4.5CHAR + 1.5PYRO-OIL$	1	ash, char removal	0.85	H <sub>2</sub> , O <sub>2</sub> , N <sub>2</sub> , CO, CO <sub>2</sub> , CH <sub>4</sub> , H <sub>2</sub> O	0; 0.63	
11	fast pyrolysis (fluidized bed)	steam to inlet flow	0.14	$C + 0.5O_2 + 0.7H_2 + 0.45ASH + -0.0001S \rightarrow 1.4H_2O + 0.002CO + 0.25CO_2 + 1.5PYRO-OIL$	1	ash, char removal	1	H <sub>2</sub> , O <sub>2</sub> , N <sub>2</sub> , CO <sub>2</sub> , H <sub>2</sub> O, CO	0; 0.15; 0.01	
12	SWGS, acid removal-amine, PSA-H2	steam to inlet flow	0.14	$CO+H_2O \rightarrow CO_2+H_2$	0.3	H <sub>2</sub> O, N <sub>2</sub> , CO <sub>2</sub> , NH <sub>3</sub> , H <sub>2</sub> S removal; COS removal	1 0.7	one outlet stream	1	
13	direct cooler, SMR, WGS, acid removal-amine	steam to inlet flow	0.36	$-CH_4 + 0.1C_2H_6 + 0.2C_2H_4 + 1.6H_2O \rightarrow 4.4H_2 + 1.6CO - CO + H_2O \rightarrow CO_2 + H_2$	0.35; 0.25	NH <sub>3</sub> , tar, ash, char, H <sub>2</sub> O removal; H <sub>2</sub> S removal; CO <sub>2</sub> removal	0.99; 0.95; 0.9	one outlet stream	1	
14	tar reformer, scrubber, acid removal-amine	air to inlet flow	1.2	$TAR + 0.7CH_4 + 0.015C_2H_6 + 0.15C_2H_4 + O_2 \rightarrow 1.5H_2 + CO + 0.3CO_2 + 0.4H_2O$	1	H <sub>2</sub> O removal; H <sub>2</sub> S removal; CO <sub>2</sub> removal	0.98; 0.8; 0.6	Ar, N <sub>2</sub> in primary outlet; H <sub>2</sub> O, CO <sub>2</sub> in primary outlet	0; 0.5	
15	tar reforming, scrubber, acid removal-DEPG	air to inlet flow	1	$TAR + 0.8CH_4 + 0.02C_2H_6 + 0.14C_2H_4 + 0.8O_2 + 0.2CH_4O \rightarrow 2.5H_2 + 1.3CO + 0.5CO_2 + 0.1H_2O$	1	NH <sub>3</sub> , H <sub>2</sub> O, tar, ash, char removal; H <sub>2</sub> S removal; CO <sub>2</sub> removal	1 0.65 0.6	Ar, O <sub>2</sub> , N <sub>2</sub> in primary outlet; H <sub>2</sub> O, N <sub>2</sub> in primary outlet; CO <sub>2</sub> in primary outlet	0; 0.6; 0.4	
16	Fischer-Tropsch	—	—	$CO + 2.1H_2 \rightarrow 10.8C_1 + 9.8C_2 + 8.8C_3 + 7.9C_4 + 7.1C_5 + 6.4C_6 + 5.7C_7 + 5.2C_8 + 4.6C_9 + 4.2C_{10} + 3.7C_{11} + 3.4C_{12} + 2.7C_{13} + 2.5C_{15} + 2.2C_{16} + 2C_{17} + 1.8C_{18} + 1.6C_{19} + 1.5C_{20} + 13Wax+H_2O$	0.4	—	—	one outlet stream	1	

Table S. continued

no.	description	mixing ( $\alpha_{i,ik} = 1$ )	$\mu_{i,ik}$	reaction (stoichiometry, $\gamma_{i,pr}$ )	$\theta_{i,react}$	waste separation	$SW_{i,ik}$	product separation (in primary outlet)	$Spl_{i,ik}$
17	alcohol synthesis (modified FT catalyst, MoS <sub>2</sub> )	-	-	$CO + H_2 + 0.006H_2O \rightarrow 0.36CO_2 + 0.06CH_4 + 0.04CH_4O + 0.24C_2H_6O + 0.026C_3H_8O$	0.4	-	-	one outlet stream	1
18	alcohol synthesis (metal sulfide synthesis catalyst)	-	-	$CO + 1.2H_2 \rightarrow 0.07H_2O + 0.07CO_2 + 0.1CH_4 + 0.1CH_4O + 0.2C_2H_6O + 0.017C_3H_8O$	0.26	-	-	H <sub>2</sub> , N <sub>2</sub> , CO, CH <sub>4</sub> in primary outlet; H <sub>2</sub> O, alcohols in primary outlet; CO <sub>2</sub> in primary outlet	0.01; 1; 0.08
19	hydroprocessing (H <sub>2</sub> -production)	O <sub>2</sub> to biomass ratio; steam to % moist ratio	1.87; 0.37	Pyro-oil + 0.02H <sub>2</sub> O + 0.01O <sub>2</sub> → 0.02CO <sub>2</sub> + 0.0014gasoline + 0.0007diesel	1	-	-	H <sub>2</sub> O, O <sub>2</sub> , CO <sub>2</sub> in primary outlet	0
20	hydroprocessing (H <sub>2</sub> -purchasing)	H <sub>2</sub> to inlet flow ratio	0.05	Pyro-oil + 0.014H <sub>2</sub> O + 0.027H <sub>2</sub> → 0.003 CO <sub>2</sub> + 0.003CH <sub>4</sub> + 0.002gasoline + 0.0012diesel	1	-	-	H <sub>2</sub> O, O <sub>2</sub> , CO <sub>2</sub> , CH <sub>4</sub> in primary outlet	0
21	hydroprocessing unit	H <sub>2</sub> to wax ratio	0.0257	Wax + 5.4H <sub>2</sub> + 0.5C <sub>3</sub> + 0.48C <sub>6</sub> + 0.44C <sub>7</sub> + 0.35C <sub>9</sub> + 0.32C <sub>10</sub> + 0.28C <sub>11</sub> + 0.25C <sub>12</sub> + 0.23C <sub>13</sub> + 0.2C <sub>14</sub> + 0.18C <sub>15</sub> + 0.15C <sub>17</sub> + 0.14C <sub>18</sub> + 0.12C <sub>19</sub> + 0.11C <sub>20</sub> → 2Gasoline + 2.76Diesel	1	-	-	H <sub>2</sub> O, H <sub>2</sub> , CO, CO <sub>2</sub> in primary outlet, light hydrocarbon	0
22	mol sieve and distillations	-	-	-	-	H <sub>2</sub> , N <sub>2</sub> , CO, CH <sub>4</sub> removal; H <sub>2</sub> O removal	1 0.8	CH <sub>4</sub> O in primary outlet; C <sub>2</sub> H <sub>6</sub> O in primary outlet; higher alcohols in primary outlet	0.07; 0.99; 0.05



**Figure 6.** Fuel price (\$/gal) in 2012 and corresponding probability density function for gasoline (top), diesel (middle), and ethanol (bottom).

relatively easy to collect and summarize different types of data (kinetics, experimental data, thermodynamics properties, simulation results, operating conditions, etc.) from many



**Table 6a. Correlation Matrix between Uncertain Data**<sup>19,20</sup>

correlation matrix	stover cost	wood cost	gasoline price	diesel price	ethanol price
stover cost	1	0	0	0	0
wood cost	0	1	0	0	0
gasoline price	0	0	1	0.71	0.12
diesel price	0	0	0.71	1	0.36
ethanol price	0	0	0.12	0.36	1

**Table 6b. Input Uncertainty for Feedstocks and Products**

input uncertainty	min.	max.	refs
corn stover cost (\$/dry ton)	60	100	NREL <sup>18</sup>
wood cost (\$/dry ton)	60	100	NREL <sup>5</sup>
	mean	std.	refs
gasoline price (\$/gal)	3.53	0.21	U.S. EIA
diesel price (\$/gal)	3.97	0.14	U.S. EIA
ethanol price (\$/gal)	2.24	0.18	U.S. Department of Agriculture

**Table 7. Seven Processing Paths Used as Base Cases**

cases	descriptions	processing path	biofuels production (tpd)
1	corn stover, entrained flow gasifier, hot gas cleaning, Fischer–Tropsch <sup>18</sup>	1 4 6 12 16 21 83 84	111 <sup>a</sup> , 262 <sup>b</sup>
2	corn stover, fluidized bed gasifier, cold gas cleaning, Fischer–Tropsch <sup>18</sup>	1 4 7 13 16 21 83 84	87 <sup>a</sup> , 206 <sup>b</sup>
3	wood, fluidized bed gasifier, tar reformer, alcohol synthesis <sup>12</sup>	2 5 8 14 17 22 85 91	429 <sup>c</sup>
4	wood, fluidized bed gasifier, tar reformer, alcohol synthesis <sup>6</sup>	2 5 9 14 17 22 85 91	526 <sup>c</sup>
5	wood, fluidized bed gasifier, tar reformer, alcohol synthesis <sup>5</sup>	2 5 8 15 18 22 85 91	549 <sup>c</sup>
6	corn stover, fast pyrolysis <sup>23</sup>	1 4 10 19 83 84	160 <sup>a</sup> , 160 <sup>b</sup>
7	wood, fast pyrolysis <sup>9</sup>	2 5 11 20 83 84	245 <sup>a</sup> , 311 <sup>b</sup>

<sup>a</sup>FT-gasoline. <sup>b</sup>FT-diesel. <sup>c</sup>bioethanol.

resources (literatures, reports, etc.) following the generic data structure. Indeed, the generic model reduces the data needs to six parameters representing mixing ( $\mu_{ij,kk}$ ,  $\alpha_{i,kk}$ ), reaction ( $\gamma_{i,rr}$ ,  $\theta_{i,rr}$ ), and waste ( $SW_{i,kk}$ ) and product separation ( $Split_{i,kk}$ ), which are obtained from experimental and rigorous simulation studies reported. Second, the resulting database and its structure can be used for cross-checking and validating data.

Of course, availability of informative data resources is important, also with the use of the generic model blocks, because the quality of the results strongly depends on the quality of the input data. In this study, therefore, peer-reviewed sources and reports from national and renowned institutes such as NREL-PNNL studies were used for several reasons: (1) The data are in general considered to be objective and of high quality as the data source (i.e., NREL-PNNL) confirms to quality check and assurance and remains impartial to technology developers. (2) The studies are easily accessible through public resources (open literature, books, reports). (3) The commercial technologies together their improved process designs (heat integration, techno-economic analysis, etc.) are represented in the alternatives. For these reasons, the superstructure defined and data collected represents a technically realistic and validated database of biorefinery relevant processing technologies. The database can be accessed from the following link: [http://www.capec.kt.dtu.dk/documents/biorefinery/InputData\\_biorefinery\\_for\\_public.xls](http://www.capec.kt.dtu.dk/documents/biorefinery/InputData_biorefinery_for_public.xls).

The database also features an option to include uncertainties for data by defining an appropriate statistical distribution function together with their parameters (e.g., lower and upper bounds for uniform distribution). This provides a means to assess quality of the data source—the larger the uncertainty, the lower the reliability of the data hence the performance of the included technical alternatives. In this study, we considered raw material costs and product prices to be major sources of uncertainty and provided a corresponding uncertainty characterization. Such uncertainty information is valuable for making robust decisions as discussed elsewhere.<sup>14</sup>

The database will be maintained and expanded with more biorefinery relevant technology development efforts to keep it

**Table 8. Summary of Validation Results for Entrained Flow Gasifier**

	inlet flow	reported results from NREL report <sup>18</sup>				simulation results of this study			
		R(i)	waste(i)	Fout1	Fout2	R(i)	waste(i)	Fout1	Fout2
total (tpd)	2222.22	1704	106	3819	0	1704	106	3818	0
H <sub>2</sub> O	222.22	960		988.4		960		988	
H <sub>2</sub>	101.2			122.8				123	
O <sub>2</sub>	812.6	700		0		700		0.1	
N <sub>2</sub>	16			17.7				17.7	
S	4.4			0				0.1	
C	945.6			0				0.1	
ash	120			0				0.1	
CO				1457				1457	
CO <sub>2</sub>				1184				1184	
H <sub>2</sub> S				4.5				4.5	
NH <sub>3</sub>				0.1				—	
COS				0.3				—	
AR		43.7		43.7		43.7		43.7	
CH <sub>4</sub>									
slag			100				100		
soot			6				6		
char									

Table 9. Summary of Validation Results for Gas Cleaning and Conditioning Step of Case 3: Tar Reformer, Water Scubber, and Acid Removal<sup>12</sup>

	inlet flow	reported results from NREL report					simulation results of this study				
		recycle	R(i)	waste(i)	Fout1	Fout2	recycle	R(i)	waste(i)	Fout1	Fout2
total (tpd)	2534	2302	3123	1089	3063	3940	2302	3123	1089	3063	3940
H <sub>2</sub> O	901.3	68.8	60.9	514.7	9.2	604	68.8	60.9	515	9.2	604
H <sub>2</sub>	37.7				168.7					168.7	
O <sub>2</sub>		43.1	708.6			86.4	43.1	708.6			86
N <sub>2</sub>			2313		45.4	2315		2313		45.4	2315
CO	874.3	903.6			2346		903.6			2346	
CO <sub>2</sub>	408	1153.8	1.5	572.7	405.3	895.6	1153.8	1.5	573	405.3	896
H <sub>2</sub> S	1.8			1.3					1.3		
NH <sub>3</sub>	3.9										
TAR	19.8									0.1	
COS											
AR			39.4			39.4		39.4			39.4
CH <sub>4</sub>	180.5	84.9			43.0		84.9			43	
C <sub>2</sub> H <sub>6</sub>	5.2	3.5			0.1		3.5			0.1	
C <sub>2</sub> H <sub>4</sub>	86.8	6.6			6.9		6.6			6.9	
C <sub>2</sub> H <sub>2</sub>	8.2	0.6			0.7		0.6			0.7	
C <sub>6</sub> H <sub>6</sub>	6.6	–					–			0.1	
C <sub>3</sub>		17.4			17.4		17.4			17.4	
C <sub>4</sub>		3.2			3.2		3.2			3.2	
C <sub>5</sub>		0.6			0.6		0.6			0.6	
C <sub>1</sub> -ol		4.3			4.3		4.3			4.3	
C <sub>2</sub> -ol		4.3			11.6		4.3			11.6	
C <sub>3</sub> -ol		11.6			17.4		11.6			17.4	

up-to-date and use it in our research for identifying optimal biorefinery concepts with respect to technical, economic, and environmental objectives using computer-aided synthesis and design toolbox.

### CONCLUSIONS AND FUTURE WORK

The development of a superstructure and database for thermochemical conversion and its integration with a biochemical conversion route were presented. The intensive data requirement of the biorefinery network design problem was addressed by using a structured and generic model to represent process alternatives. The structured and generic approach is important to manage and check the quality and consistency of multidimensional data. In the future, the database will be maintained and expanded with more biorefinery pathways and process alternatives and will be used to perform multicriteria evaluation to identify optimal biorefinery concepts under various applications and optimization scenarios including sustainability metrics. The biorefinery database features also characterize important sources of uncertainties in data, which is valuable for assessing risk associated with biorefinery design as well as supporting risk-based decision making during early project planning/development stages.

### ASSOCIATED CONTENT

#### Supporting Information

Summary table of the simulation results (seven cases) verified by NREL technical reports. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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#### Notes

The authors declare no competing financial interest.

### ABBREVIATIONS

#### INDEXES

- i*, component
- j*, component
- k*, process interval (origin)
- kk*, process interval (destination)
- react*, key reactant
- rr*, reaction number

### PARAMETERS

- $\mu_{i,j,kk}$  ratio of utility or chemical mixed with inlet process stream
- $\alpha_{i,kk}$  specific consumption of utility or chemical
- $MW_i$  molecular weight
- $\gamma_{i,rr}$  reaction stoichiometry
- $\theta_{react,rr}$  conversion fraction
- $SW_{i,kk}$  waste separation fraction
- $Split_{i,kk}$  fraction of component in primary outlet stream
- $P1_{i,kk}^{waste}$ , waste treatment cost
- $P2_{i,kk}^{utilities/chemicals}$ , utility or chemicals costs
- $P3_a^{kk}, n1$ , investment cost parameter for reactor
- $P3_b^{kk}, n2$ , investment cost parameter for separation
- $S_p^{k,kk}$ , superstructure split factor for primary outlet
- $S^{k,kk}$ , superstructure split factor for all outlets
- $OPEX_{kk}$  operating cost

CAPEX<sub>kk</sub> capital cost

## VARIABLES

$F_{in,i,kk}$  component flow of inlet process stream  
 $R_{i,kk}$  component flow of utility or chemical  
 $F_{m,i,kk}$  component flow after mixing  
 $Fr_{i,kk}$  component flow after reaction  
 $F_{sw,i,kk}$  component flow after waste separation  
 $waste_{i,kk}$  component flow of waste stream  
 $F_{out1,i,kk}$  component flow of primary outlet stream  
 $F_{out2,i,kk}$  component flow of secondary outlet stream

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