Attachment C: EXTENDED ABSTRACT

1. State of the art

The activities of the Ph.D. Thesis deal with the modeling, simulation and optimization of the innovative GREG™ (GReen Ethylene Glycol) process for the production of second generation bio-based glycols, currently under development at Biochemtex S.p.A. Two main topics have been addressed: the GREG™ downstream MINLP process optimization, and the kinetic modeling of biomass thermochemical conversion processes for the supply of hydrogen to the catalytic section of the process.

The GREG™ technology allows to produce simultaneously ethylene (EG) and propylene (PG) glycols from C5 sugars with a two-step catalytic conversion process. Purified pentose sugars, resulting from the depolymerization of the hemicellulose fraction of the lignocellulosic biomass, are converted to polyols, mainly xylitol, in the hydrogenation reactor (HN) and then they are further converted to glycols and other polyols in the hydrogenolysis reactor (HL). Xylitol conversion is greater than 90 %, while EG, PG, butanediols and glycerol yields are 28 %, 42 %, 8 % and 5 % respectively, with traces of lactate, arabitol, threitol, sorbitol.
The GREG™ process layout is reported in Figure 1. Three main sections allows to pretreat the raw C5 sugar stream (upstream section), to catalytically convert it to glycols (catalytic section), and, finally, to purify valuable products (downstream section). At the outlet of the HL reactor, unreacted hydrogen is easily separated and recycled, while the liquid stream is purified in a downstream section in order to produce high purity glycols. The purification is achieved in three main steps: dewatering; separation of the heavy cut; final purification of glycols. The dewatering partially occurs in a flash drum followed by a distillation column. Separation of the heavy cut is accomplished by using an Agitated Thin-Film Evaporator (ATFE). Finally, distillation of the raw glycols stream allows to separate pure products. Structured packing are employed, due to the separation difficulty (azeotropes and low relative volatility).

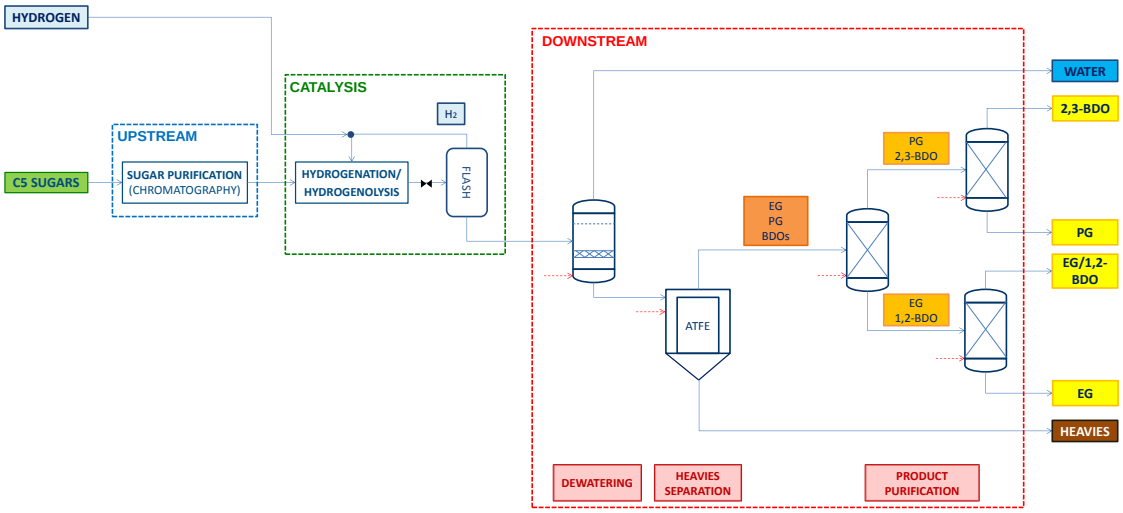

Figure 1: GREG™ process layout: upstream, catalysis and downstream sections.

The downstream processing of the aqueous solution involves distillation, leading to high operating costs motivated by the high heat of vaporization of water (Chen, 2009; Xiu & Zeng, 2008). For this reason, attempts to optimize and thermally integrate the purification step (Ahmetovic et al., 2010; Dias et al., 2009) result in a relevant lowering of the production costs that reduces the economic gap with respect to equivalent cheaper fossil-based products. In addition, the optimization of the downstream processes involves a highly nonideal liquid mixture that demand rigorous thermodynamic models. In this context, process simulators offer a reliable and rigorous modeling environment that rely on extensive thermodynamic properties databanks and tailored distillation algorithms, in contrast with equation-oriented optimization tools that are usually based on shortcut models (Navarro-Amoros et al., 2013).

Unfortunately, it has been demonstrated that the optimization tools available within commercial simulation packages are not as effective and flexible as it would be required (Biegler, 1985), due to the high nonlinearity of the equation systems, and to the impossibility to optimize structural decision variables. This was the motivation for several authors to develop ad-hoc interfaces for the process simulator-based optimization with MINLP algorithms. Recently, (Caballero et al., 2005) proposed an optimization algorithm for the rigorous design of single distillation columns using Aspen HYSYS. (Brunet et al., 2012) applied the same methodology to assist decision makers in the design of environmentally conscious ammonia-water absorption machines. (Navarro-Amoros et al., 2014) proposed a new algorithm for the structural optimization of process superstructures within the Generalized Disjunctive Programming framework. During the visiting period at Carnegie Mellon University, a new MINLP decomposition algorithm has been developed, coupling the process simulator PRO/II (SimSci, Schneider Electric) with the optimization environment of GAMS for the optimization of the GREG™ downstream process.

The hydrogen supply for the catalytic section by biomass thermochemical conversion processes is addressed developing proper simulation tools and kinetic models. The remarkable interest on coal and/or biomass gasifiers is well testified by the massive recent literature. Several papers propose mathematical models in order to understand the complex phenomena occurring in gasifiers, with an interest towards the design, simulation and optimization of the gasification processes. These papers mainly refer to mathematical models based on thermodynamic equilibrium and/or strongly simplified kinetics. It is clear that thermodynamic models are very useful tools for preliminary process assessments, but they are not able to give information on reaction intermediates and formation of tar (He et al., 2015; Mendiburu, Carvalho, & Coronado, 2014; Soltani et al., 2015). Other papers discuss mathematical models of the gasifier with a particular attention to CFD simulations with pyrolysis and secondary gas phase reactions, often very simplified. The novelty introduced in this Thesis consists in a greater detail of the kinetics of solid fuel thermal degradation with the definition of an updated kinetic model of biomass pyrolysis (Corbetta, Frassoldati, et al., 2014b; Ranzi et al., 2011). Multi-step kinetic models were embedded within a particle model, along with gas-solid reactions and secondary gas-phase reactions in order to simulate gasifiers at the reactor scale and to assess their performance in syngas production.

2. Objectives and methods

One of the targets of this Thesis was to propose a new algorithm for the topological and parameter optimization of complex process superstructures based on rigorous thermodynamic models, with special emphasis on distillation downstream processes in the biorefining area. Both continuous and integer decision variables are optimized under the Generalized Disjunctive Programming framework, using the rigorous process modeling environment of SimSci PRO/II, and the optimization environment of GAMS. The optimization algorithm basically requires a superstructure, the propositional logic to define the topology of the superstructure, selected flowsheets implemented in PRO/II, a set of bounded continuous and integer decision variables, nonlinear constraints, and an economic objective function. The most general superstructure that can be handled by this algorithm is based on the interconnection of permanent units with elementary conditional unit&trays modules. While permanent units are present in each possible optimal flowsheet originated from the superstructure, the elementary conditional unit&trays modules are introduced in the superstructure to describe the conditional units that are not necessarily present in the final optimized flowsheet. Conditional trays are introduced within the conditional unit&trays module for the rectification and stripping sections of the distillation columns eventually present (Figure 2).

When the target is to address the synthesis of biorefinery downstream processes, it is worth mentioning that predictive thermodynamic models, such as UNIFAC, frequently fail. Developing reliable VL(L)E thermodynamic models based on nonlinear regression of (UNIQUAC) binary interaction parameters on experimental data (Pirola et al., 2014) plays a major role in correctly predicting the distillation behavior.

Once the process simulator is set up with a proper thermodynamic model, the convergence of a flowsheet provides the value of the implicit variables for the evaluation of the economic objective function and for measuring the violation of nonlinear constraints.

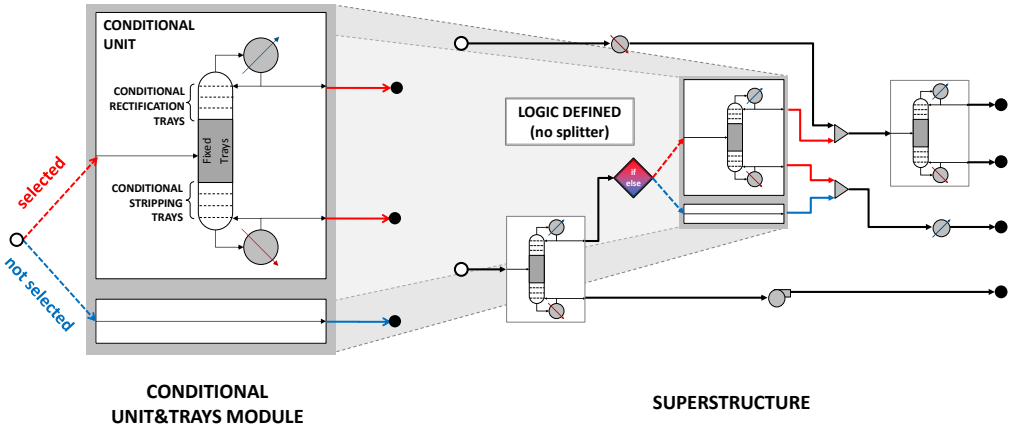

Figure 2: Representations of the conditional unit&trays elementary module and of a typical downstream process superstructure.

The optimization problem is formulated within the Generalized Disjunctive Programming framework (Ignacio E. Grossmann & Trespalacios, 2013), in which also implicit variables ($\mathbf{x_I}$) are assumed, along with continuous decision variables ($\mathbf{x}$) and Boolean decision variables ($\mathbf{Y}$), as outlined in Eq.(1).

$$
\begin{aligned}
&\min Z = \sum_{k\in K} TAC_k + f\left(\mathbf{x},\mathbf{x_I}\right) \\
&\text{s.t. } \mathbf{x_I} = \left[\mathbf{x_I}'\ \mathbf{x_I}''\right] \\
&\quad \mathbf{x_I}' = f_I'\left(\mathbf{x}\right) \\
&\quad g_n\left(\mathbf{x},\mathbf{x_I}\right) \le 0 \qquad n \in G \\
&\quad \begin{bmatrix} Y_k \\ \begin{bmatrix} Y_j \\ TAC_j = \gamma_j \end{bmatrix} \vee \begin{bmatrix} \neg Y_j \\ TAC_j = 0 \end{bmatrix} \\ x_{I,k}'' = f_I''\left(\mathbf{x}\right) \\ g_n\left(\mathbf{x},\mathbf{x_I}\right) \le 0 \\ TAC_k = \sum_{j\in CT_k} \gamma_j(\mathrm{x},\mathrm{y},\mathrm{x_I}) \end{bmatrix} \vee \begin{bmatrix} \neg Y_k \\ x_{I,k}'' = 0 \\ TAC_k = 0 \end{bmatrix} \qquad j \in CT_k,\ n \in G_k,\ k \in K \\
&\quad \Omega_{topology}\left(Y_k\right) = true \\
&\quad \neg Y_k \Rightarrow \neg Y_j \qquad\qquad k \in K,\ j \in CT_k \\
&\quad \dot{\vee} Y_i \qquad\qquad i \in RCT \\
&\quad \dot{\vee} Y_i \qquad\qquad i \in SCT \\
&\quad \mathbf{x^L} \le \mathbf{x} \le \mathbf{x^U} \\
&\quad \mathbf{x} \in \mathbb{R}^n,\ \mathbf{x_I} \in \mathbb{R}^{n_I},\ \mathbf{c} \in \mathbb{R}^m,\ \mathbf{Y} \in \{true; false\}^m
\end{aligned}
\tag{1}
$$

These implicit variables are evaluated by the process simulator, which is treated as a black-box and it is represented by the implicit function (f_I) that links implicit variables with decision variables. Nonlinear constraints (g) can be both global (set G) and conditional (set G_k). The mathematical programming formulation involves the definition of a set K of disjunctions, corresponding to conditional unit&trays modules, for which additional constraints, equations, and cost contributions are defined. Each disjunction involves only two terms, corresponding to the selection or not of a conditional unit (Y_k), with embedded disjunctions for the conditional trays (Y_j) belonging to each elementary module (set of CT_k conditional trays). Topology logic defines the interconnection between conditional units, while the three subsequent sets of logic constraints are required to ensure that no conditional trays are selected if the conditional unit is not selected, at most only one Boolean variable should be true for the rectification (RCT) and for the stripping (SCT) conditional trays.

The optimization problem is solved with a decomposition strategy based on the Logic-Based Outer Approximation (LBOA) algorithm (Turkay & Grossmann, 1996). The algorithm involves NLP subproblems that arise from fixed values at the Boolean variables, and MILP master problems that correspond to a linear approximation at the GDP in Eq.(1). NLP subproblems are solved with the BzzMath Derivative Free Optimizer (Buzzi-Ferraris, 1967; Buzzi-Ferraris & Manenti, 2012), and MILP master problems are solved with Branch & Cut methods (GAMS/CPLEX).

Moving to the second main topic, the complexity of the detailed description of a solid fuel gasification processes is mainly due to the coupling of the kinetics and transport phenomena occurring in this multi-component, multi-phase, and multi-scale system (Corbetta, Bassani, et al., 2015; Corbetta, Frassoldati, et al., 2014a; Ranzi et al., 2014).
The chemical evolution of the system during the gasification process requires a kinetic description at three different levels: solid fuel devolatilization and pyrolysis; residual solid gasification and combustion with steam, CO_2 and oxygen; secondary gas-phase reactions of released volatiles. The model adopted for biomass pyrolysis is based on the kinetic scheme found in Ranzi et al. (Ranzi et al., 2014), which has been updated in the present Thesis (Corbetta, Frassoldati, et al., 2014a). This is a multi-component mechanism whereby biomass pyrolysis is described by the superposition of different sub-mechanisms for each biomass pseudocomponent: cellulose, hemicellulose and lignin. 20 representative species are considered to describe the volatiles. Simplified mechanisms are presented for each component and they are derived from semi-detailed kinetic schemes. Depending on temperature and residence time, secondary gas-phase reactions are responsible for the successive pyrolysis and oxidation of gases and heavy tar species. The POLIMI_1411 kinetic scheme is used for this purpose (Ranzi et al., 2012), which involves more than 450 species and about 15,000 reactions.

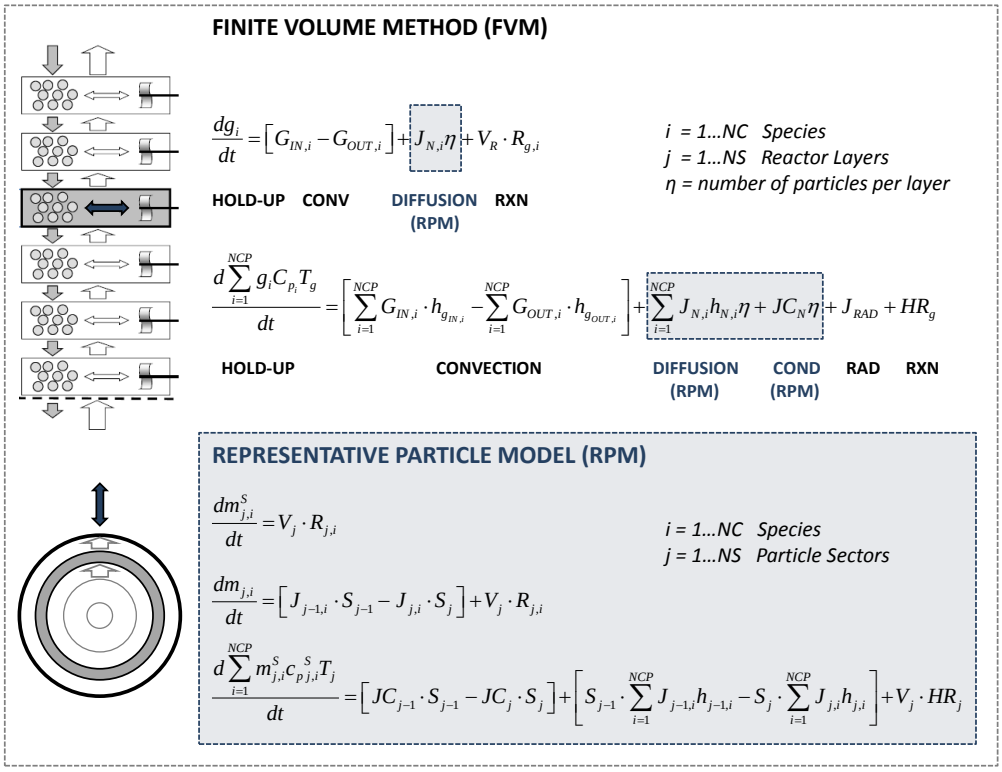

Figure 3: Mass and energy balance equations at the reactor and particle scales.

In order to model and simulate a gasifier, it is necessary to properly describe also transport processes at the reactor scale with dynamic mass and heat balances. The comprehensive mathematical model of the gasifiers implements a Finite Volume Method (FVM) with a Representative Particle Model (RPM), with two levels of spatial discretization. The first one is the particle radial discretization, depending on the number of particle sectors, while the second is the reactor axial discretization, depending on the number of reactor layers. Thus, the counter-current fixed bed (updraft) gasifier is modeled through a cascade of elementary

reactor layers. The solid fuel is fed from the top of the reactor where it encounters the rising gas stream, fed from the bottom of the tower. Figure 3 reports the mass and energy balances at the particle scale, as well as the ones at the elementary reactor layer scale. The dimension of the resulting Differential Algebraic Equation (DAE) system easily overcomes several thousands of equations and it is solved with the BzzMath library (Buzzi-Ferraris & Manenti, 2012).

3. Results and discussion

The requisite for a good downstream process optimization is the definition of a reliable thermodynamic model. The VLE of the glycol mixture is described with an ideal gas phase and a UNIQUAC liquid activity model because of the low pressures and the strong nonideality of the GREG™ aqueous solution. A literature survey (Yang et al., 2014; Zhang et al., 2013; Y. Zhong et al., 2014) and the collection of new experimental data at the Biochemtex laboratory allowed to perform a nonlinear regression on the UNIQUAC binary interaction parameters. Some of the comparisons between experimental data and model predictions are summarized in Figure 4. Moreover, a new set of batch distillation runs has been performed at the Biochemtex pilot plant, and some of the comparisons with the simulations in Aspen Batch Distillation with the new thermodynamic models are proposed in Figure 7, confirming their suitability to describe the GREG™ downstream process.

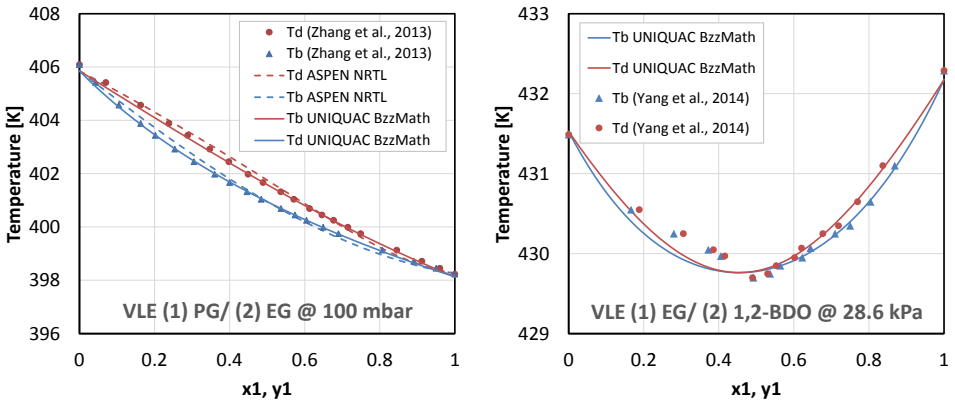

Figure 4: VLE Txy plots of glycols and butanediols. Experimental data and model predictions.

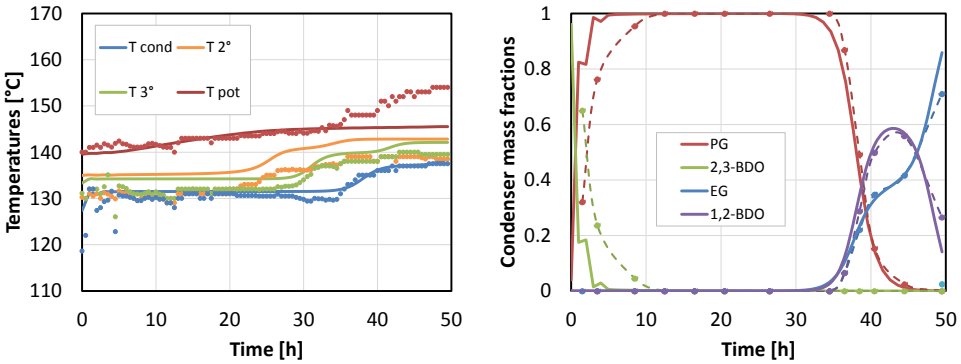

Figure 5: Experimental data (symbols) and model predictions (solid lines) with the new VLE model of a batch distillation run with a real mixture. Dynamic profiles of the temperature at the pot, 1/3 H, 2/3 H and condenser, and of the condenser mass fractions.

After the validation of the thermodynamic models, a process optimization has been performed based on the rigorous process simulation. Two different process technologies for the dewatering step are assessed. Namely, simple distillation at atmospheric pressure (column LP1) and multieffect distillation with two heat integrated distillation columns operating at different pressures (columns LP2 and HP2). The optimization targets are to select the proper technology, and to optimize the selected columns in terms of both structural and operating parameters. A glycols recovery and water purity specifications are considered as global constraints, while a conditional constraint related to the feasibility for the heat integration between HP2 and LP2 columns applies only to the second disjunction. It turns out that the multieffect distillation is

the most favorable technology. Interestingly, the two heat integrated distillation columns have similar topology and the same number of optimal stages. The split ratio between LP2 and HP2 is close to 50 %, while the HP2 condenser pressure is in the order of 10 bar. The heat integration between HP2 condenser and LP2 reboiler is greater than the 99.9 % ($Q_R^{LP} \approx Q_C^{HP}$), and it allows to save steam utility costs of 122,289 $/y, while TAC of LP2 and HP2 are 169,813 and 163,997 $/y.

The second downstream operation, i.e. heavies removal, has been addressed with the development of a first-principle rate-based model (Rossi et al., 2015). In Figure 6 the comparisons of experimental data obtained at the Biochemtex pilot plant are compared to the aprioristic predictions of the ATFE model. Moreover, a sensitivity analysis study allowed to assess the role of the main design (e.g. blades rotation speed) and operating (e.g. pressure, jacket steam pressure) parameters on product recoveries and efficiencies of the unit. Figure 6 shows that temperatures and flowrates are well reproduced, while glycols recovery is slightly over-predicted.

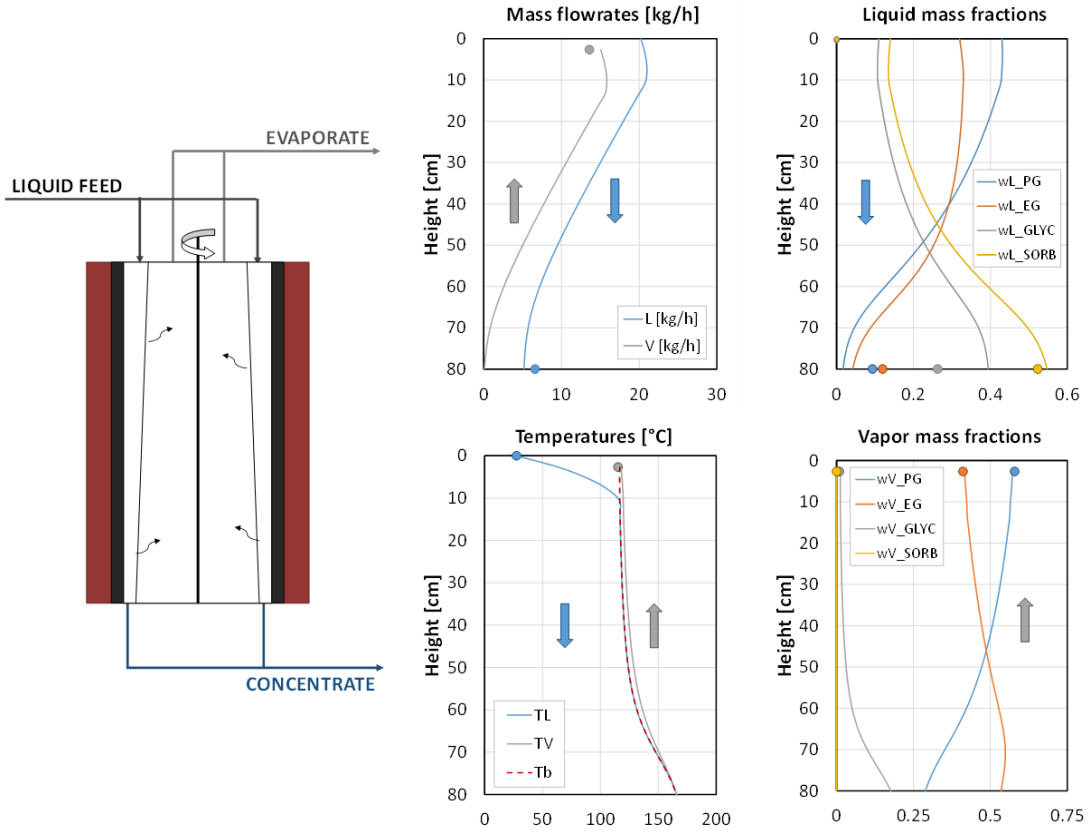

Figure 6: Comparisons between experimental data and model predictions on mass flowrates, temperatures, and liquid/vapor mass fraction axial profiles.

Successively, the rigorous design of the distillation sequencing for the glycols final purification step has been addressed. The test feed mixture is composed by 50 wt.% PG, 40 wt.% EG, and 10 wt.% of mixed butanediols (BDOs) at the bubble point. The design is achieved by considering a superstructure for the quaternary mixture (in which one pseudo-component, C, is the azeotrope) with 10 atmospheric distillation columns (Figure 7), and optimizing both the selection of the columns and their conditional trays, as well as two continuous decision variables to specify the operation of each active column. In this case, the reflux ratio and the bottom total molar flowrate are selected as continuous decision variables to help the convergence of the columns by providing exact estimates for reflux ratio and product flowrates. Four implicit inequality constraints are considered for the purity specifications (mole fractions) and for the mass recoveries of the two main products (i.e. EG and 1,2-PG). The selected configuration is the sequence of columns 2/8/10 that first realize the central cut between 1,2-PG and EG and then purify the two main products from butanediols. Considering the set covering problem, keeping the same total number of trays, the configurations 1/4/10, 1/5/9, 3/6/9, 3/7/8 have 24 %, 96 %, 67 % and 64 % higher extra TAC. For the optimized columns topology, the cost distribution among the selected columns is 54 %, 29 % and 18 % for columns 2, 8 and 10, respectively.

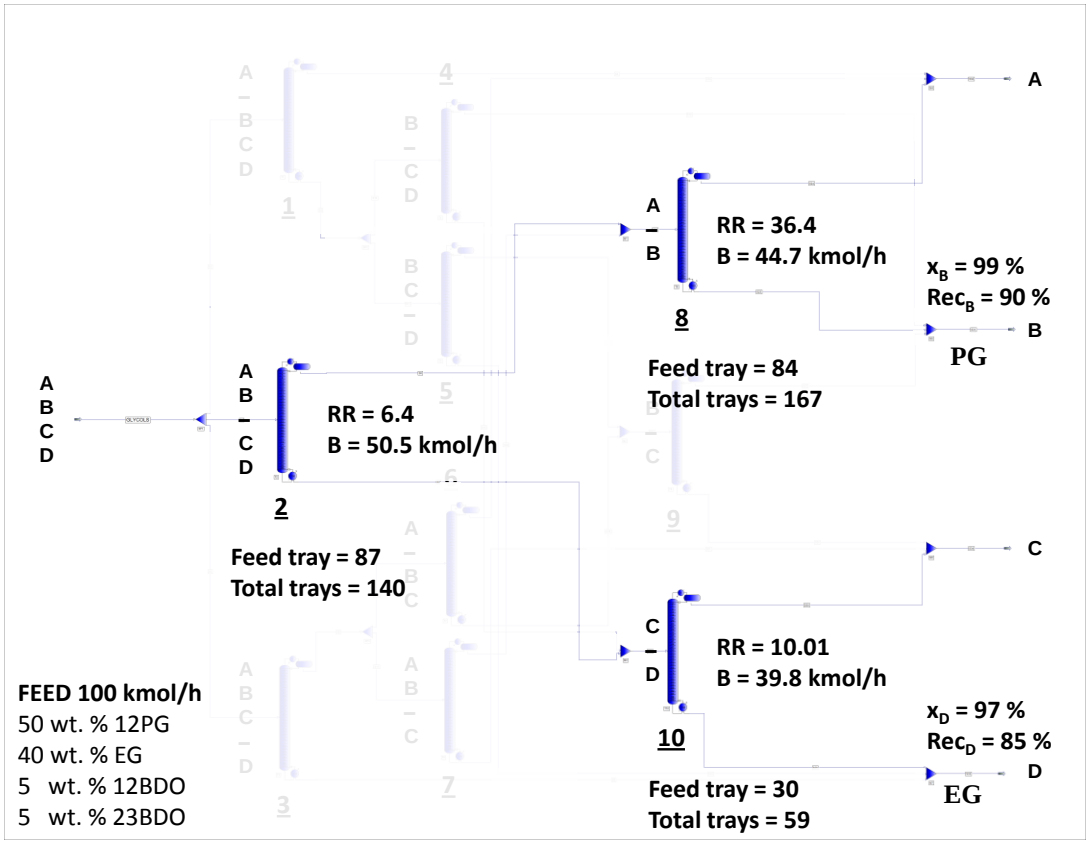

Figure 7: Superstructure of the distillation sequencing and optimal flowsheet.

In the following, results obtained in the field of solid fuels thermochemical conversion processes are briefly reported and summarized. First of all, comparisons of biomass pyrolysis experiments with the prediction of the kinetic model are proposed. Successively, results at the scale of the gasifier for the production of hydrogen are reported.

Results of the updated kinetic model of biomass pyrolysis (Corbetta, Frassoldati, et al., 2014a) are compared to experimental results of three independent sets of centimeter-scale experiments (Bennadji et al., 2013; Gauthier et al., 2013; Park et al., 2010). Temperatures, mass losses, and rate of production of several gaseous and light tar species are included in the comparisons. Predictions and experiments agree qualitatively, and in most cases have reasonable quantitative agreement, as outlined in Figure 8.

The mathematical model of the updraft gasifier is validated against experimental data referring to the lab scale gasifier reported in (Grieco & Baldi, 2011). The comprehensive mathematical model provides detailed information on chemical and physical phenomena occurring inside the gasifier. Figure 9 shows the axial temperature and composition profiles of both the solid and the gas phase. Panel (a) of Figure 9 shows the schematic of the chemical phenomena involved in the countercurrent gasification process. Moving from the top downward, solid particles are dried, pyrolyzed, gasified and burnt. The temperatures at the bottom of the gasifier overcome 1500-1600 K. In the bottom layer the hot residual char and ash heat up the rising oxidizer stream completing the solid phase combustion. Further oxidation reactions in the gas phase are responsible for the relevant production of CO_2 and for the temperature peak that overcomes the solid temperature. At these high temperatures, the endothermic gasification reactions of both steam and CO_2 contribute to CO and H_2 production. Carbon dioxide is initially produced in the bottom reactor layers and it is then consumed by the gasification reactions, while it is slightly produced in the upper reactor zone due to secondary gas phase oxidation reactions. A significant steam increase is observed in the top reactor layer, mainly due to the drying of wet coal. Methane is produced in the upper part of the gasifier due to coal devolatilization and secondary gas phase pyrolysis reactions. These reactions are also responsible for the final inflection of the CO profile. Panel (d) shows the char formation and successive transformations along the reactor. The char presence in the first layer of the gasifier indicates the occurring of a relevant coal devolatilization.

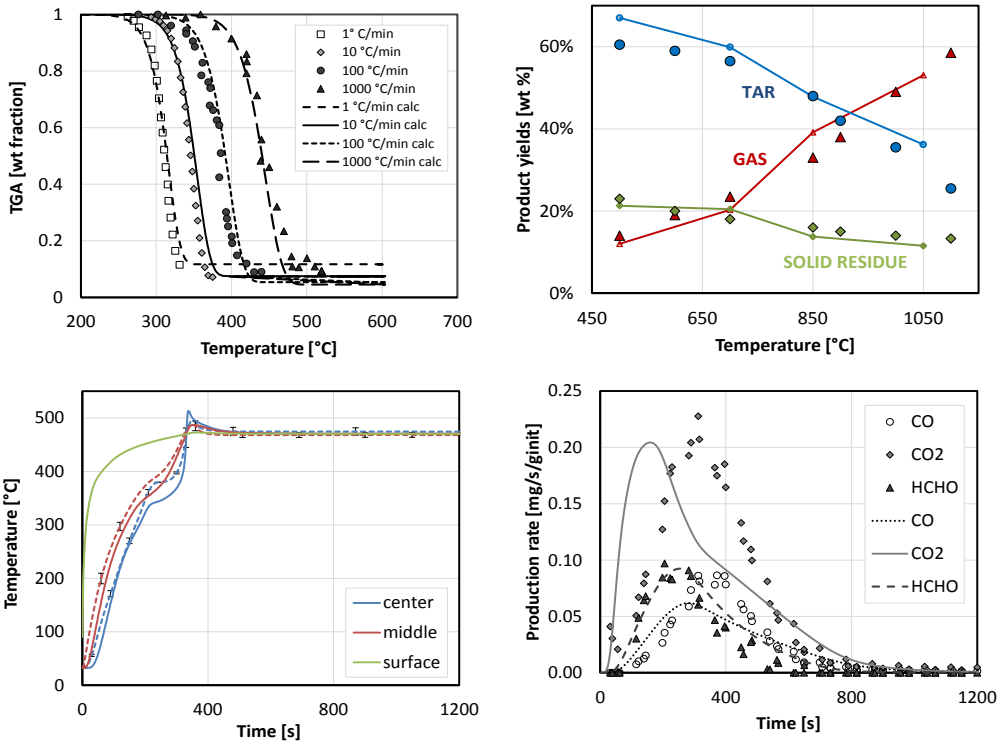

Figure 8: Comparisons between experimental data and model prediction of the kinetic model of biomass pyrolysis on TGA, thick particle temperature dynamic profiles, and average product yields as a function of pyrolysis temperature and main gases.

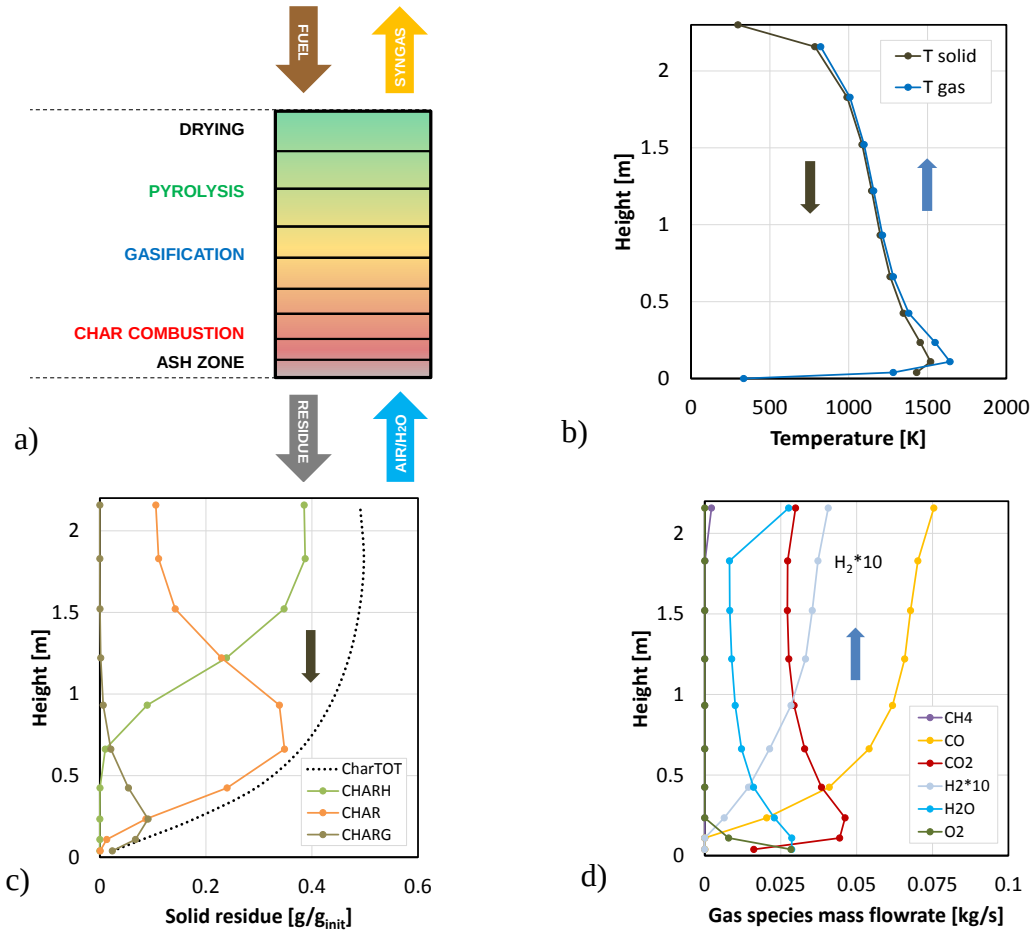

Figure 9: Panel (a) Schematic of chemical phenomena occurring within the updraft gasifier. Thermal profiles (b), residual solid composition (c), and mass flowrate of key gas components (d) along the gasifier axial length (Corbetta, Bassani, et al., 2015).

4. Conclusions

During the Doctoral studies several subjects in the biorefinery field have been addressed, especially focusing on the downstream (bio)process optimization and on the multi-scale kinetic modeling of solid fuels (e.g. biomass) thermochemical conversion processes (e.g. gasification).

This Thesis proposed a new methodology for the optimal synthesis of downstream processes based on the rigorous models embedded within the process simulator SimSci PRO/II, and on a deterministic Mixed-Integer Nonlinear Programming algorithm (Outer Approximation), implemented in C++ and GAMS. The effectiveness of this procedure is demonstrated with several case studies in the field of biorefining. For instance, the optimization of the GREG™ downstream process allowed to demonstrate the viability of the approach and to define an optimal process layout of the new technology. The model-based optimization is strengthen by the experimental feedback of the Biochemtex laboratory for the definition of reliable thermodynamic models and on the comparisons with distillation and evaporation experimental runs at the Biochemtex pilot plant.

Furthermore, a general and comprehensive kinetic model of biomass pyrolysis, including the effect of secondary gas phase reactions, has been updated and validated against a wide set of experiments. The model is at least partially predictive, both for thermal aspects and for the characterization of the released species. The same kinetic model is tested against TGA experiments with small particles as well as against thick-particle pyrolysis tests. Experiments involve a wide range of temperatures, and the model is able to cope with physical and chemical phenomena. The detailed kinetic mechanisms have been subsequently embedded in a multi-scale model of an updraft gasifier. Simulations are analyzed and compared with experiments with a reasonable agreement. The best feature of the model relies on the flexibility to handle different feedstocks with a fairly accurate prediction of the H_2 production potential.

5. References

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