**From laboratory scale to innovative spruce-based biorefinery. Note I: Conceptual process design and simulation**

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Abstract

This paper presents the conceptual design and simulation of a biorefinery process converting Norway spruce (*Picea abies*) into ethanol, via fermentation of hydrolysed hemicellulose and cellulose sugar fractions, and into bio-oil, via pyrolysis of the lignin fraction. The conceptual design of the biomass pretreatment and fractioning (i.e., steam explosion and enzymatic saccharification) as well as the thermochemical conversion (i.e., fast pyrolysis) was assembled by translating laboratory-scale process steps into industrial unit/series operations. The process design was complemented with downstream processing for both ethanol purification and bio-oil subsequent stabilization and distillation. The experimental observations at the laboratory scale were used to tune the data-driven models for the steam explosion and enzymatic saccharification process units and to validate kinetic models retrieved from existing literature for fast pyrolysis. After establishing flowsheet implementation of the complete model of a wood-to-fuels biorefinery in COFE v3.6 (AmsterCHEM), the CAPE-open simulation environment, we scaled up the process to a relevant industrial scale (treating 100,000 tons of dry wood annually).

**Keywords**: biorefinery simulation and design, bio-oil, bioethanol, biorefinery scale-up, CAPE-open tool

* 1. Introduction

Tackling climate change requires decarbonization of fuels, leading to a shift from a fossil- to a bio-based economy. In this context, the biorefinery is a sustainable pathway to produce fuels, such as bioethanol, bio-oil and biochar, and high-added-value bioproducts with properties like the corresponding fossil-based ones, while replacing fossil feedstocks with green sources (Katakojwala and Mohan, 2021). A biorefinery producing bioethanol and bio-oil embraces a complex series of operations where, in our case, the cellulosic fraction is turned into ethanol via enzymatic saccharification and fermentation, while the lignin fraction undergoes pyrolysis to produce bio-oil and, optionally, biochar. Before deployment at scale, scale-up and techno-economic assessments (TEA) of the operations, both individually and in a process concept, are key steps to demonstrate process feasibility and sustainability. Simulation of process units includes the development and validation of process models and is intensified by the complexity of the feedstock and bioproducts. Process steps and process streams often incorporate thousands of reactions and species respectively, which require simplified models to characterize the system reasonably accurately while reducing the enormous computational effort (Vikram et al., 2021). In this work, we present the design, simulation and scale-up of a process to convert Norwegian spruce into bioethanol and bio-oil based on simplified models for the complex reaction schemes using COFE v3.6 (AmsterCHEM), a CAPE-open simulation software.

* 1. Process layout and implemented sub-models

The simplified layout of the biorefinery is shown in Figure 1. The laboratory-scale experimental setup by Hansen et al. (2022) was used as a basis for upscaling to a plant processing 100,000 tons of spruce/year. We developed dedicated sub-models for each unit operation and then integrated those into the COFE v3.6. The core of the process involves the following steps: (1) steam explosion of the feedstock; (2) saccharification of the pretreated feedstock with lytic polysaccharide monooxygenase (LPMO)-containing cellulase cocktail to break cellulose and hemicellulose into simple sugars; (3) fermentation of those sugars into bioethanol; (4) rectification of bioethanol to 96% (v/v) purity; (5) pyrolysis of the residual lignin-rich fraction from the saccharification step and separation of formed biochar; (6) the stabilization of the crude pyrolysis bio-oil via hydrodeoxygenation (HDO) to reduce oxygenated compounds; with (7) subsequent distillation to recover vacuum gas oil (VGO), diesel-like and gasoline-like fractions. The light tail gas is recovered from the top section and (8) burnt for steam generation.

A diagram of a chemical process

Description automatically generated

**Figure 1:** Simplified Block Flow Diagram of the biorefinery.

Biomass composition was defined by Wang et al. (2018). In the model, cellulose and hemicellulose were approximated as dimers, the corresponding monomers as their depolymerization products, and lignin as in Dussan et al. (2019), which considers four “building blocks” for lignin. The optimal linear combination of these four building blocks was determined previously as the best fit for Norway spruce (Bisotti et al., 2023). The main thermodynamic properties needed to close the material and energy balances (i.e., enthalpy of formation, heat capacities, vapour pressure for cellulose, hemicellulose, and lignin constituents) were estimated using the method by Constantinou and Gani (1994).

***Steam explosion:*** Based on the above-mentioned compounds, we set up a simplified kinetics scheme for the steam explosion as proposed by Lam et al. (2009). This model is considered valid for softwood, such as *Picea abies* (spruce). Briefly, the model describes (hemi)cellulose decomposition to its sugar monomers and estimates the partial conversion of these sugars to furfural and 5-hydroxymethylfurfural (HMF) and subsequent polymerization thereof into pseudo-lignin. In addition, the formation of acetic acid, a by-product of steam explosion, was incorporated in the model, based on the work by Chadni et al. (2019). Following the setup by Hansen et al. (2022), operating temperature and residence time were set to 220°C and 10 min, respectively.

***Enzymatic saccharification:*** For the enzymatic saccharification with LPMO-containing enzyme cocktail, a data-driven soft model was tuned to the experimental data published by Hansen et al. (2022). The model estimates the sugar yield as a function of residence time, enzyme concentration and steam explosion temperature. Details are available in Gilardi et al. (2023).

***Fermentation and ethanol recovery:*** The fermentation step was designed according to a technical report by the National Renewable Energy Laboratory (Humbird et al., 2011). The retrieved parameters included the operating temperature (33°C), residence time (48 h), microbial strain consumption (0.1 g/gsugar), glucose and xylose conversions (90% and 85%, respectively), as well as consumables (such as diammonium phosphate and corn steep liquor). Ethanol was recovered using extractive distillation with ethylene glycol using the non-random two-liquid model, as in Li and Bai (2012).

***Pyrolysis:*** The pyrolysis chamber was modelled as a fluidized bed reactor operated isothermally at 550°C. Given the complexity of the system, a lumped kinetic model was adopted. The kinetics for cellulose and hemicellulose conversion were adapted from Ranzi et al. (2008), while the updated model by Dussan et al. (2019) was implemented for lignin conversion. Further details are reported by Bisotti et al. (2023).

***Pyrolysis oil stabilization and formulation:*** The crude bio-oil is stabilized in a two-step HDO treatment. In the first step, at milder conditions (250°C, 100 bar), aldehydes, ketones and carboxylic acids are deoxygenated to prevent coke formation. In the second step, at around 400°C, hydrogen is added to produce a hydrocarbon-rich oil (Xu et al., 2013). Here, paraffines are formed from alcohols, while aromatics are mainly decomposed into phenol, which turns into saturated cyclohexanol and cyclohexane. The kinetic constants for the HDO reactions involving alcohols, carbonyl groups and carboxylic species were retrieved from Grilc et al. (2014); the hydrogenation of aromatics and dehydration of phenols were adopted from Venkatesan et al. (2021) and Yu et al. (2021), respectively. In the subsequent step, the separation of upgraded crude oil into gaseous and liquid fuel fractions by distillation was predicted by the Predictive Redlich-Kwong-Soave equation of state. First, the upgraded crude bio-oil (available at 400°C) is cooled down to 180°C to condense the vacuum gas oil (VGO) in a flash chamber. Then, uncondensed gas is conveyed to a distillation unit with fractions withdrawn at 120°C and 60°C, representing the intermediate and low-boiling point bio-oil fractions. The tail gas leaves at the top of the column and is burnt to produce steam (see Note II for more detail). The above-mentioned sub-models were integrated to build a comprehensive biorefinery flowsheet in COFE v3.6. The simulations gave estimations for ethanol and bio-oil production per unit of biomass and energy requirements, used for the TEA described in Note II.

* 1. Results

Table 1 summarizes the results of the simulation of the biorefinery sketched in the block flow diagram in Figure 1 in terms of productivity, energy demand and consumables, as well as the main key performance indicators (KPIs) enabling a preliminary feasibility assessment. These results were used for the techno-economic assessment (TEA) in Note II. The intermediate results for the individual process units have been presented earlier by Gilardi et al. (2023) and Bisotti et al. (2023).

**Table 1**: Simulation results and main KPIs (acronyms – CW: cooling water; BM: biomass)

| **Entity** | **Value** | **Note/comments** |
| --- | --- | --- |
| **Feedstock and products** | |  |
| Biomass feedstock  (5% moisture) | 100,000 ton/year | 12.5 ton/h assuming 8,000 operating hours per year |
| Bioethanol | 2.68 ton/h | 99.9 vol% (fuel grade) |
| Bio-oil total production | 3.03 ton/h |  |
| VGO cut (dry) | 0.64 ton/h | Boiling point 180°C |
| Diesel/naphtha cut (dry) | 1.60 ton/h | Boiling point 120°C |
| Light gasoline cut (dry) | 0.79 ton/h | Boiling point 70°C |
| Biochar | 1.69 ton/h | Solid produced during pyrolysis |
| Light gas | 1.35 ton/h |  |
| **Utilities and consumables** | |  |
| Steam for steam explosion | 12.5 ton/h | Steam at 220°C and 22.5 bar produced by tail gas combustion |
| Steam for ethanol purification | 17.8 ton/h | External utility |
| Hydrogen | 230 kg/h | Needed in the HDO phase |
| Cooling water | 405 ton/h | Total cooling water demand assuming inlet temperature 20°C and maximum outlet 35°C |
| 2-naphthol | 295 kg/h | Biomass impregnation based on (Pielhop et al., 2017) |
| Cellulase cocktail | 57.1 kg/h | For saccharification |
| Fermenting strain | 565 kg/h | For anaerobic fermentation |
| **Energy demand** |  |  |
| Duty for ethanol purification (col-1) | 6.55 MW | Column-1 (col-1) is a distillation tower to remove water and get azeotrope at the top stage, column-2 is an absorber, column-3 (col-3) is a distillation column to split ethylene glycol-water. Absorber (col-2) does not need a reboiler and condenser. |
| Cooling condenser (col-1) | 3.43 MW |
| Duty for ethanol purification (col-3) | 0.57 MW |
| Cooling condenser (col-3) | 0.57 MW |
| Pyrolysis  (pre-heating and process) | 2.98 MW | Pre-heating heat considers energy to heat up biomass before pyrolysis |
| H2 compression (HDO) | 0.65 MW |  |
| H2 compression intercooling (HDO) | 0.38 MW |  |
| HDO pre-heating | 0.91 MW | Pre-heating before the second HDO reactor |
| HDO heating | 0.66 MW | Re-heating after light gas removal upstream first HDO |
| HDO pump | 0.17 MW | Oil pumping to HDO operating pressure after pyrolysis |
| HDO cooler | 1.45 MW | Cooling system for HDO |
| Cooling for crude bio-oil distillation | 1.23 MW |  |
| Water pump | 0.13 MW | Needed in the steam generation loop when light gas is burnt |
| **KPIs (Key Performance Indicators)** | |  |
| Process weight yield (including biochar) | 59.3% kgproduct/kgBM | Light gas is excluded. The mass yield refers to the treated biomass |
| Process weight yield (excluding biochar) | 45.7% kgproduct/kgBM | Light gas is excluded |
| Bioethanol yield | 0.21 tonethanol/tonBM | Water/moisture is not included in the mass used to calculate these yields |
| Bio-oil yield | 0.24 tonbio-oil/tonBM |
| Biochar yield | 0.14 tonbiochar/tonBM |
| Light gas yield | 0.11 tontail gas/tonBM |
| Total specific steam demand | 2.43 tonsteam/tonBM | 40% of the steam demand (pre-treatment and ethanol purification) is covered by light gas combustion |
| Cooling water demand | 32.4 tonCW/tonBM |  |
| Pyrolysis specific energy | 1.65 MJ/kgdry BM  0.46 MWhth/tonBM | In line with Daugaard and Brown (2003) |
| Total specific thermal duty | 0.98 MWhth/tonBM | Includes all the thermal duties (supplied heat) |
| Specific cooling duty | 0.56 MWhth/tonBM | Includes all cooling duties (removed heat) |
| Specific electricity | 1.45 MWhel/tonBM | Simulations assume 70% efficiency for pumps and compressors. Auxiliary pumps are neglected. |

* 1. Conclusions and developments

The present work focuses on a full industrial-scale biorefinery converting softwood into fuel-grade bioethanol and three fuel-grade cuts of the upgraded pyrolysis oil. Here we present the simulation in COCO simulation software (COFE v3.6) of the biochemical and thermochemical conversion steps of the feedstock and product recovery and purification as well as a preliminary assessment of the energy and material balances. The overall product (i.e., biofuel) yield of the process was 46% (w/w; per unit of treated biomass) including ethanol as well as the VGO and gasoline- and diesel-like fractions. This yield reached 60% (w/w) when including biochar as a product. Pyrolysis was the most energy-intensive process, with 47% (0.46 MWhth/tBM) of the total thermal energy demand (0.98 MWhth/tBM). The specific energy demand aligns with the literature, and it confirms the adequacy of the defined/assigned thermodynamic properties and the kinetic model provided as inputs to COFE v3.6. While the product yields are reasonable, to achieve process feasibility at a commercial scale, this simulation needs to be complemented with energy integration, steam generation and minimization of waste streams, which are explored in Note II.

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