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Process Simulation and Life Cycle Assessment of Dilute Sodium Hydroxide Pretreatment of Wheat Straw

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Wheat straw is an abundant lignocellulosic residue from wheat cultivation. It is composed of cellulose, hemicellulose, and lignin and offers several possibilities for valorisation. Nowadays, a growing interest in lignocellulosic biomass fractionation and lignin utilisation is observed. Alkaline pretreatment with NaOH is often applied to obtain a high-quality lignin fraction under milder conditions. In this study, alkaline pretreatment of wheat straw using a NaOH solution is simulated in Aspen Plus to determine mass and energy balances producing a lignin fraction. These balances were used as input to perform a life cycle assessment to screen and estimate the environmental impacts underlying 12 different scenarios. According to the impact assessment results, pretreatment with 2 % NaOH solution, reactor temperature 105 ºC, and solid biomass as the thermal energy source, as described in the base case, is the best compromise between low Global Warming, Eutrophication, Human Toxicity potentials, Blue Water Consumption, and resource efficiency.

1. Introduction

Lignocellulosic biomass is the largest source of renewable organic material, mainly composed of three biological polymers: cellulose, hemicellulose, and lignin. Lignin is a natural hydrophobic polymer responsible for biomass rigidness and recalcitrance for further processing (Woiciechowski et al., 2020). It can be found in agricultural residues, forestry waste, or municipal and industrial waste (Wertz and Bédué, 2013). Wheat straw, rice straw, and corn stover are the most abundant agricultural residues and the primary lignocellulosic materials in this category. Most of the pretreatment processes applied to biomass focus on cellulose and hemicellulose fractions, but increasing interest in lignin as an abundant renewable resource with several applications is observed. Technologies for the fractionation of lignocellulosic biomass into its main constituents are divided into four categories: physical/mechanical, physicochemical, chemical, and biological treatments (Toquero and Bolado, 2014).To obtain lignin from lignocellulosic biomass, Organosolv or alkaline pretreatment is applied. While the Organosolv process uses harsh conditions (high temperature, low pH) leading to the formation of by-products, the use of alkaline solutions based on $Ca(OH)_2$ (lime) or NaOH allows having a process under mild conditions, avoiding lignin condensation and limiting the degradation of sugars to furfural and organic acids. Pretreatment of biomass of various types with sodium hydroxide is the most studied alkaline treatment (Harmsen et al., 2010). From an economic point of view, pretreatment is one of the most expensive steps within the biomass conversion process, and it can affect upstream and downstream operations. Besides process efficiency and economic considerations, the focus is nowadays on the (environmental) sustainability of pretreatment processes (Mussatto and Dragone, 2016). According to the International Organization for Standardization – the framework (2006a) and the guidelines (2006b), Life Cycle Assessment (LCA) is an international standardised method used to study the potential environmental impacts of a product or a product system (Klöpffer and Grahl, 2014).
This study aimed to develop a simulation model of the alkaline pretreatment of wheat straw using a NaOH solution and its underlying scenarios and finally assess the environmental impacts of the overall pretreatment process.

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2. Methodology

Process simulation in Aspen Plus (Aspen Plus V10, 2017) was used to calculate the mass and energy balances of lignin isolation from wheat straw, applying alkaline pretreatment with NaOH based on a lab-scale study taken from literature. The process flowsheet included wheat straw pretreatment, solid/liquid separation, washing, precipitation, and neutralisation steps. The obtained balances formed the basis for LCA analysis using the software GaBi (GaBi ts 9.1, 2019).

2.1 Process description

The core step of the investigated process is the reactor to fractionate wheat straw into its main constituents - lignin, cellulose and hemicellulose. Data for alkaline pretreatment with NaOH are taken from Barman et al. (2012), describing the dissolution of lignin and the remaining solid fraction of biomass as a function of the concentration of sodium hydroxide, at 105 °C, with a solid-liquid ratio for the extraction solution of 10 g wheat straw/100 mL NaOH solution, during a 10 min pretreatment time (Table 1). In the following step, the remaining solid phase, mainly consisting of cellulose, is separated from the liquid phase and then washed with water.

Table 1: NaOH concentration effect on lignin and hemicellulose removal (Barman et al., 2012)

NaOH conc. (wt%)	Lignin removal (%)	Hemicellulose removal (%)
0	13.7 ± 2.9	8.8 ± 2.8
0.5	32.1 ± 3.2	18 ± 3.1
1.0	37.2 ± 4.0	24.9 ± 3.2
1.5	56.2 ±3.7	46.1 ± 3.5
2.0	70.3 ± 2.9	68.2 ± 3.8

After cellulose separation, the resulting lignin-containing liquid phase is combined with the obtained washing solution. Lignin is precipitated by adding acidified water (5 % H_2SO_4) as a counter-solvent until a pH value of 2 is reached. Precipitated lignin is separated from the remaining solution, mainly containing hemicellulose. The solid lignin is washed. Finally, the washing solution and the remaining liquid solution from the solid-liquid separation step after lignin precipitation are neutralised with $Ca(OH)_2$ before going to a water treatment unit and being released into the environment.

2.2 Process simulation

Process simulation in Aspen Plus (Aspen Plus V10, 2017) is used to provide the mass and energy balances for LCA analysis. The process is scaled to 12.5 t/h wheat straw – based on an annual wheat straw production of 1,600 kt/y in Lower Austria, of which about 20 % is available for various use. To guarantee a stable wheat straw supply, 100 kt/y are assumed for lignin production at an operating time of the plant of 8,000 h/y. The composition of wheat straw used in the process simulation was the same as used by Paul (2018): 28.61 wt% cellulose, 19.76 wt% hemicellulose and 14.17 wt% lignin at a water content of 12 wt%. NRTL was set as the general property method, and the elecNRTL method was used to accurately calculate the pH value for the precipitation and neutralisation steps. An extended NREL database for biomass components is used to represent the key biomass components such as lignin, cellulose, and hemicellulose (Wooley and Putsche, 1996).

The pretreatment step is modelled as a stoichiometric reactor defining the dissolution of different constituents of wheat straw following Barman et al. (2012). For the base case of simulation (reaction temperature 105 °C, sodium hydroxide concentration 2 wt%, solid loading of 10 % w/v), 84.5 % of lignin is solubilised to allow a lignin recovery, as stated in Table 1. It is assumed that no cellulose is dissolved under these conditions.

The lignin precipitation step is modelled in a stoichiometric reactor. Due to lacking information about lignin solubility in a water-sodium hydroxide solution, it was assumed that the precipitation only depends on the solubility of lignin in water. 87 % of lignin precipitation is assumed following a correlation for lignin solubility in ethanol-water solutions at pH=2 (Santos, 2019) based on solubility data from Silva (2012) – recovery, and Huijgen et al. (2010) – fractionation.

Solid/liquid (S/L) separation to remove cellulose after the pretreatment step and solid lignin after the precipitation step is simulated using a simple splitter, assuming that all solid components are found in the solid stream at a dry matter content of 30 %. Both washing steps (cellulose, lignin) are implemented as mixer/splitter combinations assuming counter-current washing of the solids, replacing the solution in solids with an equal amount of water.

In the neutralisation step, the addition of calcium hydroxide until reaching pH 7 is controlled via a design specification. Calculation of pH (lignin precipitation, neutralisation) is based on the property method elecNRTL. The wastewater treatment step is not included in the Aspen Plus simulation but is considered in the GaBi model.

Figure 1 presents a summary of the process balance for the base case.

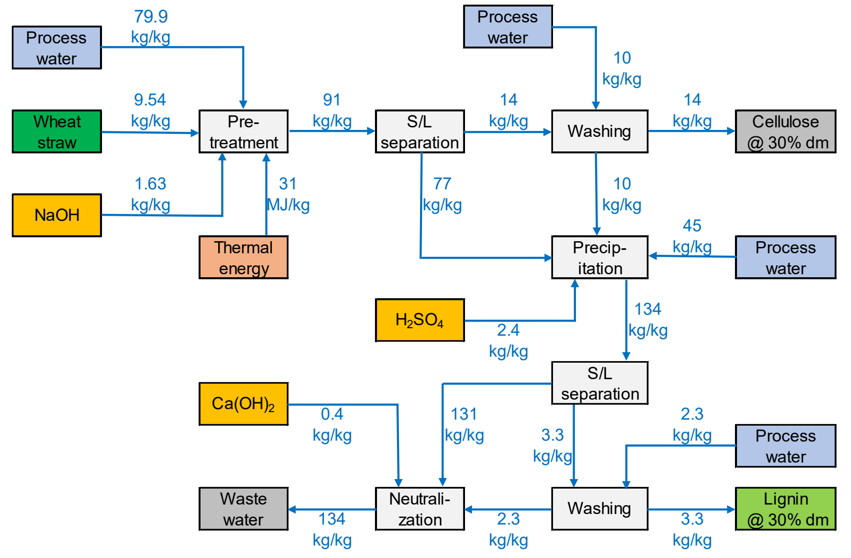

Figure 1: Process balance for a functional unit of 1 kg (dry matter) precipitated lignin at base case conditions (reaction temperature 105 °C, sodium hydroxide concentration 2 wt%, solid loading of 10 % w/v)

2.3 Life cycle assessment

The LCA was performed according to the ISO 14040 and ISO 14044 standards (International Organization for Standardization – the framework (2006a) and the guidelines (2006b). The technical system boundaries include the biorefinery process (see description in section 2.1), the provision of raw materials and utilities (wheat straw, NaOH, water, energy, H_2SO_4 and $Ca(OH)_2$), (by)-product streams (lignin, cellulose), process emissions and the residual stream from wastewater treatment.

The pretreatment process of wheat straw using a dilute sodium hydroxide solution and its underlying scenarios are assessed in a “cradle to gate” approach, not considering further processing of product streams and transport from the biorefinery. Since wheat straw is the stalk leftover after wheat harvesting and wheat grain is the most valuable product of this cultivation, the allocation between wheat grain and wheat straw used in this study was economic. Later, a comparison between economic and mass allocation is made to investigate its influence. The cellulose residue is considered a by-product of this process. Since its processing possibilities are not in the scope of this study, it will not be considered in further calculations. The functional unit (FU) is 1 kg (dry matter) of recovered lignin. It is important to note that the functional unit is fixed, but the raw material demand is dependent on the yield of the extraction.

Professional GaBi database (version 8.7, service pack 36) from Thinkstep AG provided the background data on wheat growth (including the use of fertilisers and pesticides) and harvesting processes, production of the chemicals used in the process, and the energy and water consumed according to the mass and energy balances obtained from the simulation.

The characterisation method CML 2001 (Jan 2016) was used to conduct the Life Cycle Impact Assessment (LCIA). Four impact categories were selected: (1) Global Warming Potential, (2) Eutrophication Potential, (3) Human Toxicity Potential, and (4) Blue Water Consumption. These are commonly used in literature for LCA of biorefinery concepts like Paul (2018), which assesses an Organosolv pretreatment of wheat straw.

2.4 Description of the case studies

Different scenarios are considered in process simulation and LCA to see their effect on the process, and consequently, their impacts on the environment. The base case scenario corresponds to lignin extraction from wheat straw using a 2 wt% NaOH solution at 105 °C, followed by lignin precipitation with 5 wt% H_2SO_4. Economic allocation between wheat straw and wheat grain, and solid biomass as the thermal energy source are assumed. Other investigated scenarios are divided into two main categories: process-performance related variations (extraction temperature, extraction solution, and concentration of precipitation agent) considered in process simulation and not performance-related variations (energy source, water demand, and feedstock allocation) considered only in LCA. The parameters selected in the first category follow a value range experimentally investigated in the literature. Since there was no literature on the quality of the antisolvent used after alkaline pretreatments, a different concentration was analysed in a designated scenario. For the second category, the goal was to assess how these changes would affect the overall system. Table 2 summarises the conditions used in the base case and the investigated scenarios.

Table 2: Summary of the scenarios

Scenario	Extraction Temperature	NaOH concentration, wt%	H_2O Cellulose washing	H_2SO_4 concentration, wt%	H_2O Lignin washing	Allocation	Thermal energy source
Base case	105	2	-	5	-	Economic	Solid biomass
Parameters	180 130	1.5 1.0 0.5	±50 %[1]	25	±50 %[1]	Mass[2]	Natural gas[2]

1 - ±50 % of the amount of water used in the base case. 2 - Simulated directly in GaBi.

3. Results and discussion

All twelve scenarios of lignin extraction through alkaline pretreatment of wheat straw are compared to the base case in a cradle-to-gate life cycle assessment. Each process contributor and its environmental impacts are presented in a hotspot analysis to give information about their influence and contribution to the overall result. The evaluation of the impact categories presented below provides insights into the environmental aspects and shows the trends for process variations, making the analysis of different scenarios possible. The relative difference between the total impacts of the scenarios and the base case is represented in Figure 2 and Figure 3, following different scales for the observed deviations in impacts. Total impacts for the base case: -1.02×10^1 [kg CO_2 eq.] (GWP), 8.72×10^{-3} [kg $(PO_4)^{3-}$ eq.] (EP), 6.06×10^1 [kg H_2O] (BWC), and 4.30×10^{-1} [kg DCB eq.] (HTP).

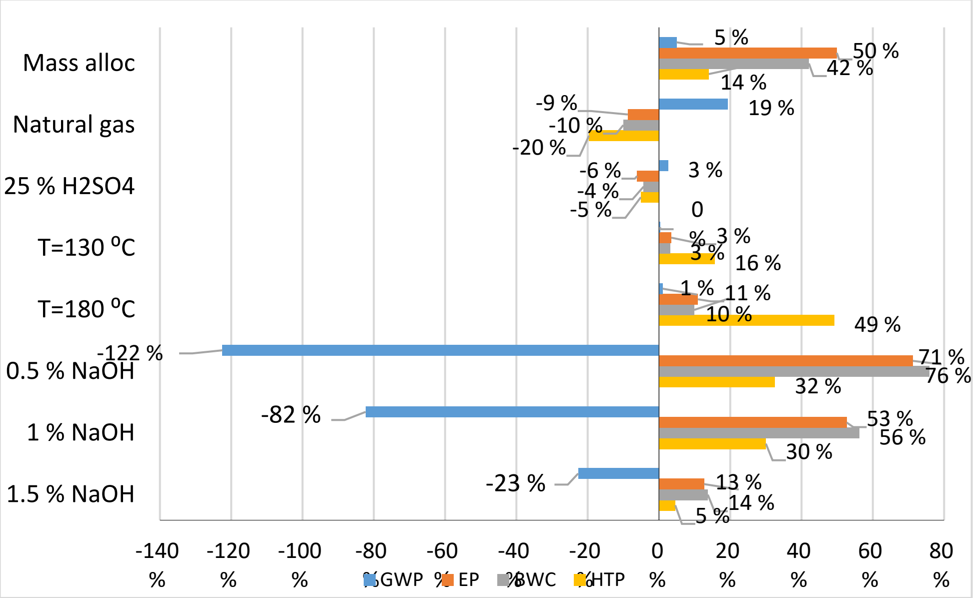

Figure 2: Relative difference between the total impacts of the base case and the scenarios for extraction temperature, NaOH concentration, H_2SO_4 concentration, feedstock allocation and thermal energy source

The first impact category considered is the **Global Warming Potential (GWP).** These results are a sum of the CO_2 credits and the emissions to the environment. Since the credits are higher than the emissions, in terms of absolute value, the total results are expressed as negative values and represent benefits to the environment. The main contributors to the emissions in this category are the chemicals NaOH and H_2SO_4, resulting from the high electricity consumption of their manufacturing processes. Wheat straw captures atmospheric CO_2 during its growth phase, reducing the net CO_2 emissions and contributing to lower global warming. It is beneficial to use it as feedstock. The lower the NaOH concentration, the higher the wheat straw needed to recover 1 kg of lignin, increasing the CO_2 credits and lowering the GWP at the cost of poor resource use.

The second impact category analysed, **Eutrophication Potential (EP)**, is related to the excess nutrients. The main process contributors affecting this category are wheat straw and thermal energy. Wheat straw cultivation is responsible for nitrogen oxides and nitrate emissions to air and freshwater, due to ploughing, drilling, the use of fertilisers and pesticides, the harvesting and drying of the straw (Smith et al., 1999). When decreasing the concentration of the sodium hydroxide solution, the total eutrophication impacts increase (Figure 2), since more mass of straw would be necessary to recover the same amount of lignin. The change in the source of thermal energy shows that renewable energy does not always mean a more environmentally friendly process, as the use of biomass to produce energy has the same magnitude of emissions contributing to eutrophication as natural gas.

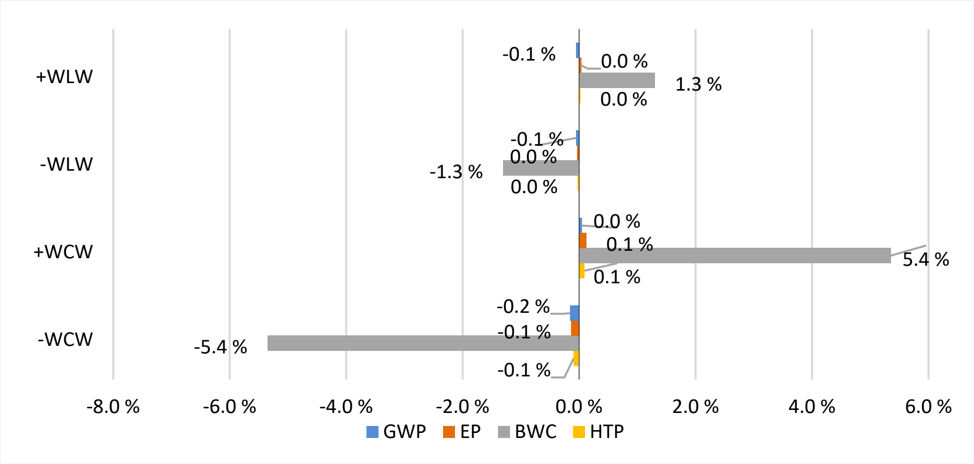

Figure 3: Relative difference between the total impacts of the base case and scenarios on water demand for cellulose and lignin washing

The main contributors to **Blue Water Consumption (BWC)** are process water demand and wastewater treatment. The first accounts for all the freshwater inputs in the process, while the latter accounts for the water recycled into the system after treatment. Wastewater treatment is beneficial to the whole process since it reduces the freshwater inputs. Wheat straw also contributes to the impacts (~20 %), as wheat cultivation requires water for irrigation. The base case counts 6.06 x 10^{1} kg H_2O of total BWC impacts. These impacts increase up to 80 % when decreasing the sodium hydroxide concentration to 0.5 %, because of higher water demand, especially preparing the extraction solution and the first washing step. As shown in Figure 3, using more or less water for the washing steps causes only a small contribution to the impact on this category.

For **Human Toxicity Potential (HTP)**, the total emissions in the base case correspond to 4.30 x 10^{-1} kg DCB eq. (1,4- dichlorobenzene equivalents). Thermal energy used to run the extraction step is the major contributor (corresponding to ca. 50 % of the total emissions), followed by the production of used chemicals. Solid biomass is the thermal energy source for all scenarios, except for the scenario represented by Natural gas. The sensitivity analysis reflects the share of thermal energy, as using a higher extraction temperature implies a significant increase in the total impacts (Figure 2). For the impacts caused due to the use of chemicals, the literature data analysis shows that the lower the concentration of sodium hydroxide, the higher the input for wheat straw, water, and thermal energy. Their respective emissions also increase. Thermal energy production from solid biomass emits various gases to the environment and requires large areas to grow the materials, limiting the location of the power plants. As a result, it requires transportation and fuel. The high need and continuous supply of resources may also lead to deforestation. According to (Singh et al., 2011), the infrastructure needed to produce thermal energy may emit hazardous substances, like heavy metals, from construction to use. The increase of the emissions in HTP due to wastewater treatment is a consequence of the rise in the water demand since it requires a higher need for treatment afterwards. Using a more concentrated antisolvent reduces the impacts caused by using calcium hydroxide prior to the wastewater treatment.

4. Summary and conclusion

LCA of NaOH pretreatment of wheat straw to produce lignin was performed based on mass and energy balances obtained from process simulation, assuming a functional unit of 1 kg (dry matter) of recovered lignin.

Results show that the base case represents the best combination of low impacts for the four analysed categories (-1.02 x 10^{1} kg CO_2 eq. (GWP), 8.72 x 10^{-3} kg $(PO_4)^{3-}$ eq. (EP), 6.06 x 10^{1} kg H_2O (BWC), and 4.30 x 10^{-1} kg DCB eq. (HTP)) and efficient resource use. The lower the NaOH concentration, the higher the resources demand to recover the same amount of lignin due to a lower yield. It consequently affects the whole process chain and the emissions to the environment.

The impact assessment shows that except for GWP, natural gas as the thermal energy source is responsible for fewer impacts, namely -9 %, -10 % and -20 % for EP, BWC and HTP, when compared to solid biomass, because the technologies used are already mature while renewable energy production is still in an early stage of development. Considering the fossil fuel dependency and climate change, it is reasonable to consider shifting to solid biomass as a thermal energy source. But it is crucial to optimise its extraction and processing to reduce the environmental burdens.

Although the focus of the sensitivity analysis was on single parameter variations, evaluating combined parameters such as NaOH concentration and temperature would be interesting. 2 % NaOH is the optimal concentration for lignin removal among the four concentrations used. It is expected that higher NaOH concentrations would increase lignin removal. But it may cause cellulose degradation since the pretreated sample with 2 % NaOH already presents the lowest crystalline index among the four. Temperature is a critical factor in lignocellulosic biomass pretreatment: high temperatures may also cause biomass degradation or even enhance the formation of inhibitory compounds, not to mention energy consumption. Future work should be focused on higher NaOH concentrations (up to 10 %) and lower extraction temperatures, with particular attention to the precipitation and antisolvent quality.

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