Solvent Recovery from Fibers in a Lignocellulose Biorefinery: An Experimental Feasibility Study

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In a lignocellulose biorefinery, the complex structure of lignocellulosic biomass has to be disrupted for full valorization. This fractionation into the main constituents (lignin, hemicelluloses, and cellulose) can be achieved with organic solvents like alcohols and acetone. Recovery of the solvent is one of the main challenges of this process. Especially when using the cellulose-rich fraction directly as fiber fraction, solvent remaining in this fraction has to be removed for environmental and safety reasons. Currently, the solvent removal is based on flash evaporation and washing, resulting in excessive amounts of washing liquor with low solvent concentration. This research investigated vacuum drying and steam stripping in a paddle mixer as alternative methods for recovering solvent from the fiber fraction. Vacuum drying could lower the acetone content of stone groundwood fibers from 1,450.6 g/kg dry matter to around 0.10 g/kg dry matter within 8 min; steam stripping decreased the acetone content from 1,118.8 g/kg dry matter to around 0.17 g/kg dry matter within 12 min. Furthermore, both the drying and stripping experiments showed higher energy efficiencies than the corresponding simulation cases of conventional solvent recovery (except the cooling efficiency for steam stripping), although the simulation cases were ideal cases with maximum washing and rectification efficiency.

1. Introduction

Biobased economy or bioeconomy is considered as the transition from the current fossil-based economy to the exclusive usage of renewable resources. Kamm et al. (2015) use a pillar model to describe this necessary transition to biobased products as one of the three pillars and biorefineries as a part of the basement in the pillar model as well as a tool for this transition. Biorefineries convert renewable biomass to valuable fuels and products, similar to petroleum refineries which use crude oil as raw material (Kamm et al., 2015). Biorefineries can be divided into first-generation biorefineries (food crops, animal fats, etc., as feedstock), second-generation biorefineries (lignocellulosic biomass as feedstock), and third- or fourth-generation biorefineries (algae, etc., as feedstock). Compared to first-generation biorefineries, lignocellulose biorefineries use lignocellulosic biomass like straw or wood, but no feedstocks to produce food or feed (Ng et al., 2017). Using lignocellulosic feedstock in biorefineries therefore offers the opportunity to overcome the "food vs. fuel" issue. For full valorization, the complex structure of lignocellulosic biomass, mainly consisting of lignin, hemicelluloses, and cellulose, has to be disrupted (Hassan et al., 2019). These constituents can be separated with organic solvents like alcohols and acetone, leading to multiple product streams containing value-added components like cellulose fibers, lignin, hemicellulosic sugars, acetic acid, and furfural (Zhao et al., 2017). The resulting cellulose-rich fraction can be hydrolyzed to sugars using enzymes or used directly for dissolving pulp production as well as fiber fraction, i.e., for manufacturing paper, which is the most abundant application of cellulose (Zhang et al., 2016). However, one of the main challenges when fractionating biomass with organic solvents is still their recovery. They are expensive and there are environmental and safety issues since most organic solvents are toxic (Nanda et al., 2021), volatile, and flammable (Liu et al., 2019). Especially when using cellulose as fiber fraction, a big drawback of applying organic solvents in a lignocellulose biorefinery is remaining solvent in the fiber fraction. With established methods, like flash evaporation, most of the solvent remaining in the solid cellulose-rich fraction can be recovered, provided that the fractionation temperature and/or pressure is high enough. Nevertheless, complete solvent removal requires an additional washing step (Zhao et al., 2017). The method of choice is still

a single- (González Alriols et al., 2008) or multi-stage washing (da Silva et al., 2018) of the pulp with water, resulting in excessive amounts of washing liquor with low solvent concentration. The disadvantage of this process is, that solvent recovery from washing liquor is one of the most energy-intensive steps of biorefineries using organic solvents for fractionating lignocellulosic biomass (Viell et al., 2013). There is thus still a need for alternative methods for removing the organic solvent from the solid cellulose-rich fraction of a lignocellulose biorefinery.

This work aimed to investigate removing the solvent via evaporation, applying vacuum drying and steam stripping in a paddle mixer. Vacuum drying has a similar effect as flash evaporation due to the pressure drop at the beginning of the drying sequence, which is already used for solvent removal (Zhao et al., 2017). It has the advantage of lower drying temperatures for solvent evaporation. Lower temperatures facilitate not only energy integration but also decrease hornification effects. Hornification occurs when fibers are dried or dewatered, leading to the formation of irreversible or partially reversible hydrogen bonding and a reduction of swelling capacity. This results in a loss of fiber elasticity and decreased strength after resuspending (Fernandes Diniz et al., 2004). Lower hemicellulose and lignin content of the cellulose-rich fiber fraction (Rebuzzi et al., 2005) and particularly increasing drying temperatures (Kucner et al., 2014) significantly increase hornification. In contrast to vacuum drying, steam stripping evaporates the solvent by means of thermal energy provided by injecting steam into the cellulose-rich fiber fraction. Steam stripping was already successfully applied for removing volatile organic substances from solids like contaminated soils (Hassan et al., 1992). However, applications for solvent recovery from the solid fraction of a lignocellulose biorefinery have been very limited and were therefore investigated within this work. Main performance indicators of this feasibility study were the residual solvent content of the solid fraction and the thermal energy demand.

2. Material and methods

2.1 Materials

Stone groundwood (SGW) was chosen as cellulose-rich fiber fraction for the solvent recovery experiments in this work. The SGW raw material was softwood harvested in Central Europe, consisting of 95 wt% spruce and around 5 wt% pine. The wood fibers were never dried after the grinding and filtration process and remained as water-suspension with 8 wt% dry matter content (DMC) until feedstock preparation for the solvent recovery experiments. Acetone (VWR, 99 %) was used as organic solvent in this work.

2.2 Feedstock preparation

SGW-water-suspension with 8 wt% was dewatered in several batches at 16 bars in a 7.9 L stainless steel pressing basket (perforation Rv 3-5 mm according to DIN 24041) using a hydraulic shop press. The dewatered SGW had a DMC of around 30 wt% and was mixed with acetone using a spiral agitator to achieve acetone concentrations in the liquid phase of 70 – 80 wt%. The SGW-acetone-suspensions were filled into closed barrels for 24 h at room temperature to ensure concentration equilibrium of the entire liquid phase due to diffusion without changing the composition of the SGW significantly. The suspensions were then dewatered in the same way as the SGW-water-suspension giving a crumbled press cake in the shape of small chunks < 10 mm. The mean DMC of the dewatered acetone-containing SGW was 33 – 42 wt%. The initial water and acetone contents of the SGW were 603.6 g/kgDM (per kg dry matter) and 1,450.6 g/kgDM for the drying experiments and 275.3 g/kgDM and 1,118.8 g/kgDM for the stripping experiments.

2.3 Solvent recovery experiments

The acetone-containing SGW press cake - prepared as described in Chapter 2.2 and showing a bulk density of 216 g/l for the drying experiments and 166 g/l for the stripping experiments - was directly used as feedstock for the solvent recovery experiment.

Vacuum drying

The drying experiments were carried out in a 10 L horizontal paddle mixer with a heating mantle. The temperature of the heating mantle was adjusted to 80 °C. For each drying experiment 1,543 g feedstock was filled into the vacuum dryer and heated to 50 °C at atmospheric pressure for simulating elevated temperatures when leaving a biorefinery. Afterwards, the pressure was rapidly decreased to 100 or 50 mbar absolute pressure and dried between 6 and 38 min, depending on the experiment.

Steam stripping

The stripping experiments were carried out in a 130 L horizontal paddle mixer with a heating mantle. The temperature of the heating mantle was adjusted to 100 °C to avoid condensation on the inner stripper walls. For each stripping experiment, 8,180 g or 10,000 g feedstock (depending on the desired steam load) was filled into

the steam stripper and heated to 50 °C at atmospheric pressure for simulating elevated temperatures when leaving a biorefinery. Afterwards, the pressure was decreased to 945 mbar absolute pressure, and the steam injection started. The stripping steam was injected as saturated steam with 3 bar absolute pressure with a mass flow rate of 0.2 kg/min. Depending on the experiment, an additional chopper was used for chopping the SGW chunks during stripping.

2.4 Measurement and analytics

The DMC of the SGW before and after solvent removal was determined by drying the samples at 105 °C for 24 h. The temperature during drying/stripping was measured with a thermal sensor in the formed fluidized bed. The residual acetone content of the SGW was determined by using headspace gas chromatography (HS-GC). For each analysis 0.2 – 0.4 gDM sample was filled into a 20 ml HS-GC vial. The standards were prepared by filling around 0.4 gDM air-dried SGW into HS-GC vials and spiking them with acetone-water-solutions to achieve acetone contents of 0.1 – 9 mg/gDM and a water content of approximately 300 mg/gDM (for analyzing dried SGW) or 600 mg/gDM (for analyzing stripped SGW).

2.5 Calculation of energy demand and energy efficiency

In the case of vacuum drying, the energy demand for vaporization/condensation of solvent solution $q_{dry,vapor/condens}$ was approximated by heat demand to remove water and acetone mass during experiment (Eq.(1)). In the case of steam stripping, the thermal energy demand was approximated with the enthalpy of the stripping steam ($q_{strip,vapor}$, Eq.(2)) and the energy demand for condensation of removed water and acetone vapor ($q_{strip,condens}$, Eq.(3)). As reference for calculating the energy efficiency (Eq.(5)), the minimum energy demand for evaporating/condensing assuming the solvent acetone solely (Eq.(4)) was used. The enthalpy of vaporization of acetone was taken from Matyushov et al. (1994) (501 kJ/kg), the enthalpy of vaporization of water was taken from Majer et al. (1978) (2,256 kJ/kg), and the enthalpy of saturated steam with 3 bars absolute pressure was taken from Liley et al. (1997) (2,724 kJ/kg).

$$q_{dry,vapor/condens} = (m_{SGW acetone,end} - m_{SGW acetone,start}) \cdot \Delta H_{v,acetone} + (m_{SGW water,end} - m_{SGW water,start}) \cdot \Delta H_{v,water} = q_{approx} \tag{1}$$

$$q_{strip,vapor} = m_{steam} \cdot h_{steam,sat,3bar} = q_{approx} \tag{2}$$

$$q_{strip,condens} = (m_{SGW acetone,end} - m_{SGW acetone,start}) \cdot \Delta H_{v,acetone} + (m_{steam} - (m_{SGW water,end} - m_{SGW wc}) \cdot \Delta H_{v,water} = q_{approx} \tag{3}$$

$$q_{min} = (m_{SGW acetone,end} - m_{SGW acetone,start}) \cdot \Delta H_{v,acetone} \tag{4}$$

$$\eta_{heat/cool} = \frac{q_{min}}{q_{approx}} \tag{5}$$

2.6 Simulation

As reference case for the drying and stripping experiments, solvent recovery by washing the acetone-containing SGW with water and rectifying the washing liquor was simulated. The washing step was idealized by assuming countercurrent washing (liquid to DM ratio of 10) with infinite stages and 100 % acetone recovery efficiency. The heat demand of the rectification step for recovering acetone from the washing liquor was estimated with Aspen Plus (V10, Aspen Technology Inc., 2017) by using the short-cut model DSTWU (the properties were calculated with the NRTL model and verified with the work of Gmehling et al. (1977)). The residual acetone mass in the bottom product was adjusted to obtain similar acetone recoveries as in the drying/stripping experiment. The simulation was run with an acetone concentration in the top product equivalent to the calculated vapor condensate concentration obtained at the corresponding experiment (assuming 100 % condensation), except the stripping experiments where the calculated vapor condensate concentration was lower than the minimum acetone concentration in the top product due to the vapor-liquid equilibrium (VLE).

3. Results and discussion

Results of the vacuum drying experiments show similar residual specific acetone contents at 50 and 100 mbar final pressure at around the limit of quantitation (LOQ) of approximately 0.1 mg/gDM with very low standard deviations (SD) for the residual acetone content (Figure 1). Lowering the pressure from 100 to 50 mbar does not show significant advantages, but complicates technical realization. At 100 mbar a significant decrease in

the residual acetone content (from 1,450.6 mg/gDM to approximately 0.1 mg/gDM) up to a drying time of 8 min was observed and stayed almost constant for the remaining time of the experiment near LOQ, indicating an optimum drying time below 10 min. For vacuum drying at 50 mbar this decrease is not visible in the experimental results because the first sample was taken after 8 min.

Steam stripping experiments were carried out with and without the use of an additional chopper during the stripping process. Figure 2 compares these results at a constant specific steam mass flow of 48 g/kgDM/min. Results show a high residual acetone content after 7 min stripping with chopping (around 4 mg/gDM) compared to results of vacuum drying (below 1 mg/gDM) and high SDs, suggesting a higher residual acetone content with uneven distribution in the SGW. Further stripping experiments were therefore carried out with longer stripping times of 12 – 22 min. Stripping more than 12 min delivered residual acetone contents at around the LOQ of approximately 0.1 mg/gDM, independent of whether a chopper was used or not. Using an additional chopper was thus found to not significantly influence the residual acetone content, but increase the process's investment and operating costs. To give further insight to the process without using a chopper, additional experiments were carried out at higher specific steam flow rates. Figure 3 compares the experiments without chopper at specific steam mass flows of 48 g/kgDM/min and 59 g/kgDM/min for stripping times between 12 and 22 min. Both steam mass flows resulted in similar residual specific acetone contents at around the LOQ of approximately 0.1 mg/gDM. The final temperature approached 96 °C and the DMC decreased with increasing stripping time.
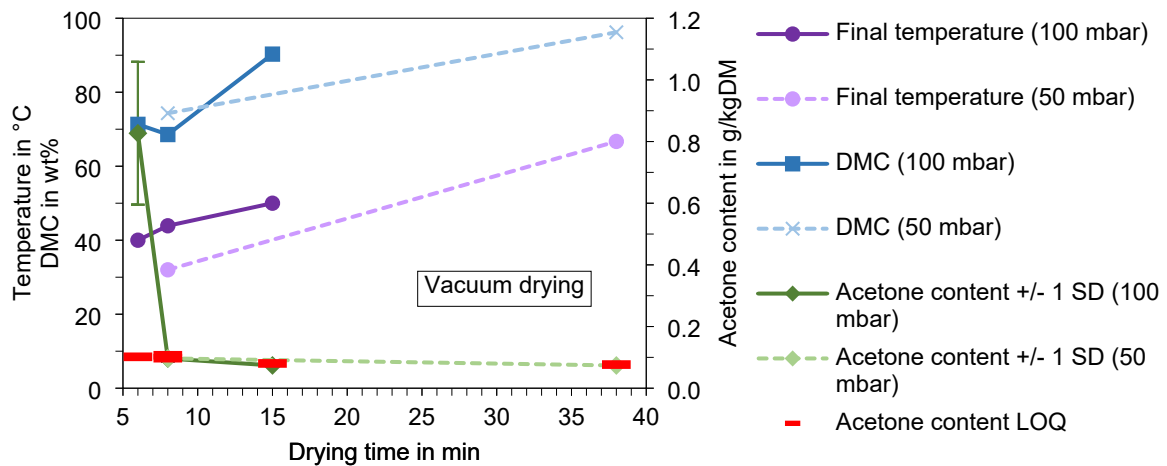

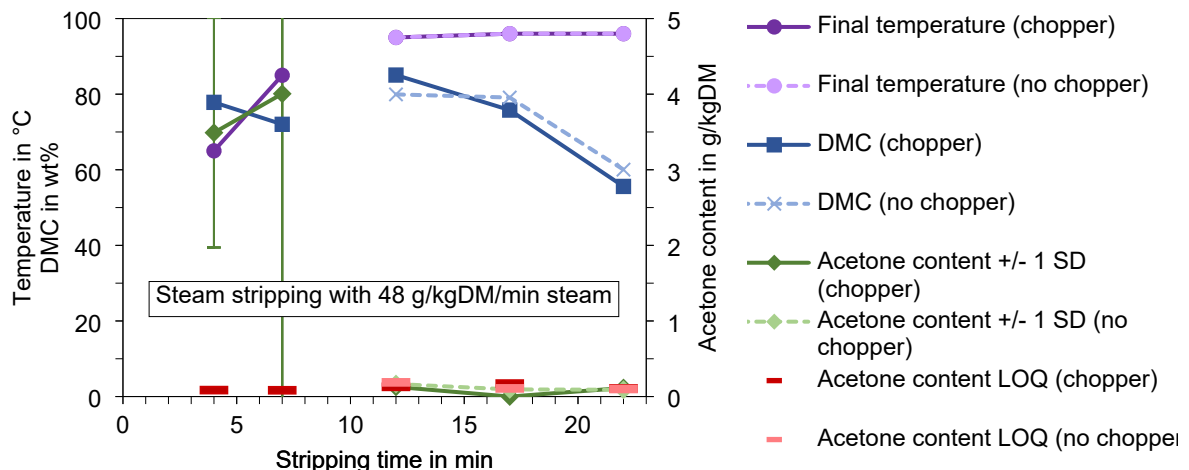Figure 1: Vacuum drying experiments (6 – 15 min with 50 mbar and 8 – 38 min with 100 mbar)

Figure 2: Steam stripping experiments with 48 g/kgDM/min steam mass flow (4 – 7 min without chopper and 12 – 22 min with and without chopper)
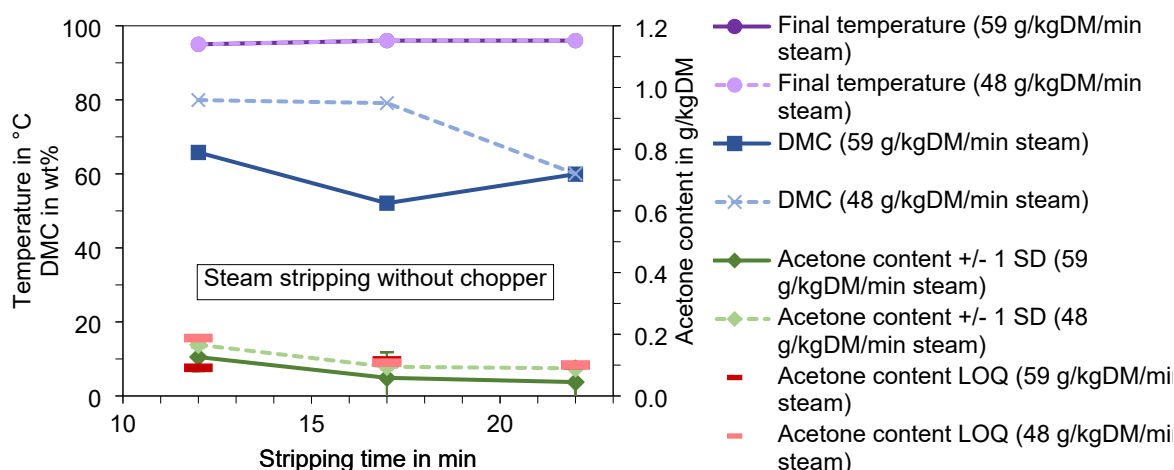
Figure 3: Steam stripping experiments without a chopper (12 – 22 min with 48 g/kgDM/min and 59 g/kgDM/min steam mass flow)

For both the drying and stripping experiments, one selected experiment case (shortest drying/stripping time for lowering the acetone content to the LOQ) was used as the basis for the simulation of the solvent removal via washing step and rectification of washing solution. The selected drying experiment was drying 8 min at 100 mbar, the selected stripping experiment was stripping 12 min with a steam mass flow of 48 g/kgDM/min without using a chopper. Figure 4 illustrates the selected experimental cases and the corresponding simulation cases. Energy efficiency was calculated against the minimum energy demand as described in equation (5). Although the simulations of washing and rectification were ideal cases with maximum efficiency and minimum energy demand, they delivered lower energy efficiencies than the experiment cases, except the cooling efficiency for steam stripping. The best energy efficiencies were obtained with vacuum drying, which also showed the highest condensate acetone concentration.
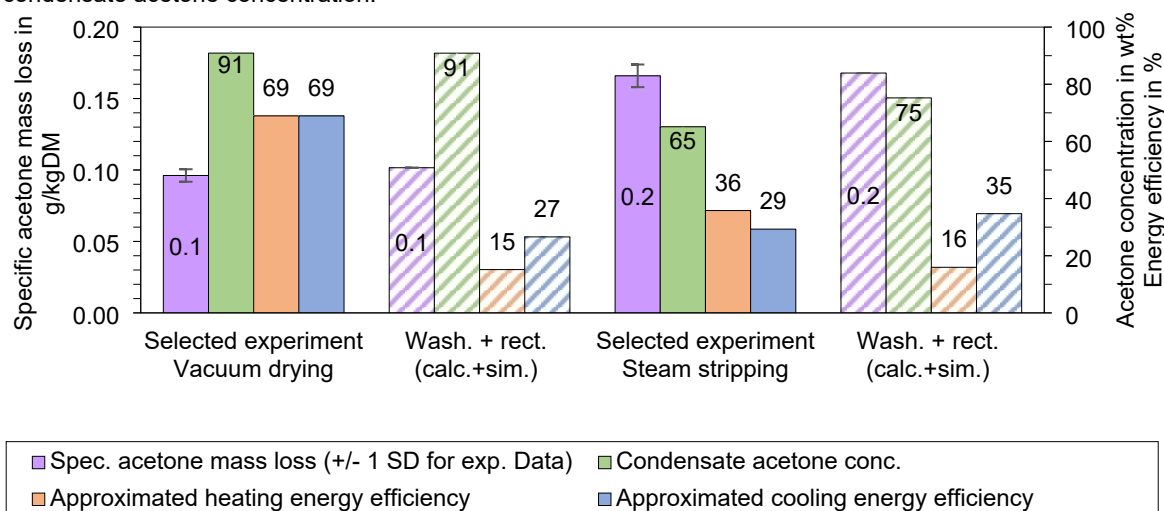

Figure 4: Comparison of the selected experiment cases with the corresponding simulation data

4. Conclusion

The experiments showed that vacuum drying and steam stripping are suitable alternatives for recovering solvent from the cellulose-rich fiber fraction of a biorefinery. Vacuum drying with 100 mbar absolute pressure could lower the residual acetone content of the SGW fibers to around 0.10 g/kgDM after 8 min. Decreasing the pressure to 50 mbar did not show significant advantages. Steam stripping could reduce the acetone content to around 0.17 g/kgDM after 12 min. The use of an additional chopper during steam stripping did not exhibit favorable influence on the stripping process. Vacuum drying, as well as steam stripping, were therefore proven as feasible methods for recovering solvent from the cellulose-rich fiber fraction of a lignocellulose biorefinery.

Vacuum drying had the highest heating and cooling energy efficiencies (69 %), but requires the lowest condensation temperatures due to the low pressure. Except for the cooling efficiency for steam stripping, all the simulation cases had lower energy efficiencies, although the simulation cases were ideal cases with maximum washing and rectification efficiency for vaporizing and condensing the solvent. For optimization and economic considerations, further experiments with more parameter variations, equal sampling times, and varying fiber properties and solvent contents will be carried out. Additionally, hornification effects will be investigated by means of mechanical analyses, particularly by measuring the water retention values (WRV) as an indicator for the irreversible hornification (Fernandes Diniz et al., 2004).

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