



Research paper

Application potential of a carbocation scavenger in autohydrolysis and dilute acid pretreatment to overcome high softwood recalcitrance



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ABSTRACT

Both autohydrolysis and acidic pretreatments have already been commercialised to allow for the bioconversion of lignocellulosic biomass to valuable products. Recent fundamental research has shown that the pretreatment of lignocellulosic biomass can be enhanced by the suppression of lignin repolymerisation. This work evaluates the application potential of a carbocation scavenger additive that prevents lignin repolymerisation for the autohydrolysis and acidic pretreatment of woody biomass. The results show that the enhancing effect of the scavenger is strongly dependent on the type of biomass. While it proved hardly beneficial in the pretreatment of hardwoods, the pretreatment of recalcitrant softwoods could be greatly enhanced. Softwood has an exceptionally high recalcitrance to biochemical conversion compared to other biomass types, though the reasons for this behaviour have hardly been understood so far. Our study revealed that lignin repolymerisation is a major factor accounting for the exceptional softwood recalcitrance. A sensitivity analysis of pretreatment temperature and time showed that the scavenger can enhance the enzymatic digestibility of softwood cellulose by up to 113% in autohydrolysis and up to 142% in dilute acid pretreatments. The scavenger proved effective for both softwood sawdust and wood chips. Its mode of action in pretreatment was shown to be particularly suitable for the implementation in two-stage pretreatments, which are of high commercial relevance.

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1. Introduction

The bioconversion of cellulose and hemicellulose from lignocellulosic biomass to their sugars is an intensively studied subject. Among the potential feedstocks, woody raw materials possess characteristics that make them particularly interesting for biorefinery concepts. Unlike agricultural biomass, woody raw materials offer more flexible harvesting times and avoid long latency periods of storage [1,2]. The higher density of woody biomass significantly reduces its transportation costs [2], which account for a major portion of the feedstock supply cost and energy consumption. Compared to other lignocellulosic biomass, wood also possesses a much lower ash content (close to zero) and – especially softwood species – less pentoses [1,2]. The very low ash content eliminates dead load in transportation and processing [3] and

reduces waste product formation. A low pentose content facilitates the fermentation to ethanol [1]. For the above described reasons, it is supposed that woody biomass will make up a critical part of the supply mix in the future bioeconomy. Prior to this however, a way for surmounting its comparatively high recalcitrance to biochemical conversion must be found [1,2].

In particular softwood biomass poses high obstacles to bioconversion. While hardwood recalcitrance may be overcome via cost-effective autohydrolysis/hydrothermal pretreatment methods like liquid hot water and steam pretreatment, these methods are not effective for softwood. Despite intensive research no economically feasible process has been developed for bioconverting softwood so far [4–6]. This is why softwood is currently processed only via thermochemical technologies such as gasification and catalytic pyrolysis on a commercial scale [7], where its recalcitrance to biological conversion does not play a role. Finding a method for reducing the high softwood recalcitrance via cost-effective pretreatment methods would therefore be of great benefit.

The difficulties in the biological conversion of softwood are

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attributed to its lignin type and content, though the reasons for its exceptional resistance are not well understood [8–10]. Lignin is the most important but at the same time the most unknown factor in governing the digestibility of lignocellulose [11]. Elucidating the hindering effect of lignin is further complicated by the fact that the lignin content or its native structure are not necessarily the key factor, but also the way its structure is modified during pretreatment [12].

This is in accordance with our recent observation, revealing that the suppression of lignin repolymerisation in lignocellulose pretreatment can significantly enhance its enzymatic cellulose digestibility [13]. This can be achieved by the addition of a carbocation scavenger that reacts with carbocations which are formed in the lignin polymer under acidic conditions. Those carbocations are supposed to be responsible for repolymerisation reactions, as they can react with the electron rich aromatic rings present in lignin [14,15]. The use of a carbocation scavenger in softwood autohydrolysis pretreatment was shown to increase glucose yields in hydrolysis by up to 64%. It was revealed that the resulting less repolymerised lignin has a lower specific surface area, which reduces the adsorption and deactivation of cellulolytic enzymes and thus increases glucose yields in hydrolysis [13].

2-Naphthol has proven as a very effective carbocation scavenger to prevent lignin repolymerisation. It was first introduced by Wayman and Lora in the late 1970's in an autohydrolysis process to enhance the extractability of lignin by organic solvents [14,16]. Our recent studies have revealed that its use in autohydrolysis pretreatment can as well enhance the enzymatic cellulose digestibility. The 2-naphthol additive is nearly completely consumed in pretreatment and integrated into the lignin structure. Its residual concentration was shown to not hinder fermentation organisms such as *Saccharomyces cerevisiae* [13]. Next to 2-naphthol, further effective lignin carbocation scavengers such as dimethylphloroglucinol have been discovered and several potentially effective additives have been suggested lately [17].

Currently, the full potential of carbocation scavengers for enhancing softwood pretreatments still remains to be clarified, as they only have been studied in the autohydrolysis of spruce wood under limited pretreatment conditions. The present work therefore aims at evaluating this approach for other softwoods and pretreatments. The scavenger approach is tested in various autohydrolysis conditions and for the first time also in a dilute acid pretreatment. Acidic pretreatments are seen as the most suitable pretreatment method for softwood [18] and pretreatments like acid impregnated steam explosion have already been advanced to commercial scale [19]. Since the formation of lignin carbocations is acid-catalysed, we hypothesized that those pretreatments are accompanied by extensive lignin repolymerisation and the use of a carbocation scavenger can be particularly effective.

Next to the focus on obtaining a well digestible cellulose fraction from softwood, this work as well aims at further elucidating the underlying effects of the exceptionally high softwood resistance to biochemical conversion. Therefore, the effect of a carbocation scavenger is also studied in the pretreatment of hardwoods, which hold a much lower recalcitrance. Comparing the effects of a carbocation scavenger on the pretreatment of soft- and hardwood species can allow to obtain a better understanding of the high softwood recalcitrance.

2. Materials and methods

2.1. Autohydrolysis pretreatment

Spruce (*Picea abies*), pine (*Pinus sylvestris*), beech (*Fagus sylvatica*) and poplar (*Populus tremula*) were cut in spring 2012 in Villigen (canton of Aargau, Switzerland). The trees were debarked,

split with an axe, chipped and air dried for 4 weeks. The chips were then knife milled (SM200 cutting mill; Retsch) through a 1 mm screen size. The material was sieved to less than 1 mm and greater than 0.18 mm (AS200 vibratory sieve shaker; Retsch). Particles smaller than 0.18 mm were discarded. In a separate experimental set for studying the effect of biomass particle size on pretreatment, 8 fractions of different particle sizes were prepared from spruce as well. Therefore, spruce chips were knife milled through a 3 mm screen size and fractioned by sieving with mesh sizes of 2.8, 2, 1.4, 1, 0.63, 0.355, 0.18, 0.124 and 0.063 mm.

Dry matter, ethanol extractives and the content of glucan, mannan, acid-soluble lignin (ASL) and acid-insoluble lignin (AIL) were determined by standard National Renewable Energy Laboratory (NREL) methods [20,21]. All biomass analyses were done in triplicate and single standard deviations are reported with the mean in this work.

An overview of the various autohydrolysis pretreatments and experimental conditions is included in Table 1. Pretreatment experiments were carried out in a batch screening reactor (MRS 5000; Parr Instruments). The reactor was loaded with 2.5 g of wood and 39.2 g of water. In experiments with scavenger, 2-naphthol was added at a concentration of 0.205 mol/mol lignin C₉ unit, assuming a molecular weight 185 g mol⁻¹ of the C₉ unit. This corresponds to 118.5, 123.6, 101.7 and 91 mg for spruce, pine, beech and poplar wood, respectively. In a separate experimental set to study the influence of 2-naphthol concentration on the pretreatment of spruce wood, 2-naphthol was added at different concentrations of 0.05, 0.1, 0.21, 0.41 and 0.82 mol/mol lignin C₉ unit.

The loaded reactor was purged three times with nitrogen (10 bar) and the stirring speed was set to 400 min⁻¹. The pretreatment was carried out at different temperatures of 185, 195, 210 and 225 °C and different times of 0, 10, 20, 60, 120 and 240 min. A pretreatment time of 0 means the reactor was heated up to the corresponding pretreatment temperature and immediately cooled down again. The heating interval from 100 °C to the reaction temperatures of 185, 195, 210 and 225 °C took about 10, 11, 12 and 13 min, respectively. Submerging the reactor in a water bath at the end of the pretreatment allowed for fast cooling below 100 °C in less than 1 min. The pretreatment severity R₀ was calculated according to Overend et al. [22], including the heat-up phase to pretreatment temperature [13]. The contents of the reactor were vacuum filtered, recording volume and pH of the filtrate. The solids were washed with 300 ml of boiling water and the moisture of the recovered biomass was recorded. Further details of the pretreatment procedure and severity calculation are provided elsewhere [13].

2.2. Dilute acid pretreatment

Sawdust from a roughly 30 year old, debarked spruce (*Picea abies*), cut in winter 2012 in Bueren a.A., Switzerland, was milled, sieved to 0.18–1 mm and analysed analogue the wood chips in autohydrolysis pretreatment.

An overview of the different dilute acid pretreatments and experimental conditions is included in Table 1. The dilute acid pretreatment was carried out similarly as the autohydrolysis pretreatment and only the modifications of this procedure are reported in the following. Additionally to biomass and water, 0.333 mL of 72%w/w H₂SO₄ were added to the reactor. This corresponds to a concentration of 1%w/w H₂SO₄ in the liquid, also taking into account the biomass moisture. Water and acid were mixed in the reactor prior to adding the biomass. Optionally, 100 mg of 2-naphthol were added corresponding to a concentration of 0.205 mol/mol lignin C₉ unit. The biomass was soaked for 90 min at room temperature under stirring at 400 min⁻¹ in the reactor to ensure a thorough penetration of the biomass with acid.

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