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Stabilising mannose using sodium dithionite at alkaline conditions

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Abstract: The kraft process remains the dominant chemical pulping process but still struggles with extensive hemicellulose degradation. Such degradation has previously been mitigated through the use of anthraquinone; but due to it recently being found to have carcinogenic properties, anthraquinone is now being phased out. One alternative, sodium dithionite, was initially investigated in the 1950s but was found to be unviable. The present study investigated whether sodium dithionite could be made viable through the use of different processing parameters, using mannose as a model compound and measuring the yield of mannitol in the various systems using gas chromatography with flame ionization detection (GC-FID) and nuclear magnetic resonance (NMR). Alkalinity was found to be crucial; at pH 14 as well as pH 7, dithionite indeed proved unviable, but if pH was kept at either 8 or 10 significant reduction was seen to occur. The best results were obtained at pH 10 when a lower temperature (70°C) was used to compensate for alkaline degradation of the mannose reactant.

Keywords: glucomannan, mannose, peeling reaction, reductive reaction, sodium dithionite

Introduction

The kraft process remains the dominant chemical pulping process worldwide thanks to the economic advantages of its chemical recovery system as well as the superior strength properties of the obtained pulps

compared to competing alternatives (Ragnar et al. 2014). The kraft process is, however, not without its own set of disadvantages.

One such problem is the extensive hemicellulose degradation that occurs due to the use of alkali in the process. This is especially true for glucomannans, which, lacking OH-2 substitution, have a low prevalence of natural stopping reactions (Johansson and Samuelson 1977; Sjöström 1977), making this degradation particularly concerning for softwood, which on average is composed of 19% glucomannans (Teleman 2009). Chemically, this degradation occurs through a combination of alkaline peeling and alkaline hydrolysis (Davidson 1934; Franzon and Samuelson 1957; Christofferson and Samuelson 1960). While alkaline hydrolysis cannot be mitigated by chemical means, peeling can be prevented by chemical modification of the reducing end of carbohydrates (Peckham and May 1960; Sjöström 1977). This is possible because such modification prevents or mitigates the tautomerisation steps that initiate peeling (Whistler and BeMiller 1958), see Figure 1.

Protecting carbohydrates from peeling in this manner is not a new concept. In particular, anthraquinone was introduced in the 1970s as a redox mediator that could efficiently protect carbohydrates while also improving delignification (Basta and Samuelson 1978). Unfortunately, toxicological studies have found anthraquinone to be carcinogenic (National Toxicology Program 2005), with the result that anthraquinone is gradually being phased out in the industry. In addition to anthraquinone, established technologies for protecting carbohydrates include using polysulphides or amines as additives as well as performing the cooking reaction at elevated alkalinities, known as high-alkali cooking. Polysulphides can be added at the beginning of the impregnation stage at a low temperature and a low liquid to wood ratio (Lindström and Wilgotson 2017). These can then protect carbohydrates by oxidation (Peckham and May 1960; Ahlgren and Teder 1967). However, adding polysulphides in this manner can disturb the sulphur balance in the mill. Various amines have been investigated as additives for cooking, with ethylenediamine and urea being particularly promising (Kubes et al. 1980; Santiago and Pascoal Neto 2007). These amines have been found to improve delignification as well as reduce degradation of carbohydrates. The cause of the

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Figure 1: Reaction scheme depicting primary peeling of mannan as well as various options to prevent peeling from occurring, including the naturally occurring stopping reaction.

latter effect has been suggested to stem from a combination of carbamation and Maillard reactions (Ershova et al. 2012). High-alkali cooking, on the other hand, utilises the fact that the glucomannan stopping reaction is favoured at alkalinities >0.5 M NaOH, resulting in higher glucomannan yields when using such alkalinities (Brännvall and Lindström 2007; Wigell et al. 2007). Unfortunately, the same is not true for xylan, the dissolution of which is continuously increased with higher alkali concentrations (Brännvall and Lindström 2007).

In light of this, it is of interest to find alternative means that can provide similar protection to that previously gained using anthraquinone. Any additive used to replace anthraquinone should preferably fulfil three criteria: first, it should be available at a low cost (or, alternatively, be recoverable from the process at acceptable costs); second, it should not include any non-process elements (i.e. it should be based only on sodium, oxygen, carbon, hydrogen and sulphur), so as to minimise scaling; third, it should be a reductant, as reduction has been suggested to provide stronger protection against peeling than oxidation does (Wang et al. 2015).

One alternative that fulfils all these criteria is sodium dithionite: it is already bought in bulk by the industry for the purpose of bleaching mechanical pulp, the only elements in the compound are sodium, sulphur and oxygen, all of which are process elements and it functions as a reductant. Specifically, it is the degradation products of dithionite that perform the reduction. Although the degradation pathway of dithionite is not fully elucidated and is dependent on alkalinity and the presence of other sulphur species, it is generally agreed that the sulphur dioxide dianion radical (SO_2^{2-}) is the main reductant (Malkavaara et al. 2000; Makarov 2001). The dianion radical also reacts with oxygen, making inert atmospheres preferable when working with dithionite. As this reaction consumes oxygen (Watson et al. 1977; Makarov and Silaghi-Dumitrescu 2013), an excess of dithionite could be used to form such an inert atmosphere in a closed vessel.

Using sodium dithionite as an additive in pulping is, however, not a novel idea as such. Sodium dithionite has been used for bleaching of mechanical pulp since the 1930s (Bajpai 2014) and has been extensively studied as such. A study investigating optimal bleaching parameters

for bagasse pulp found optimum conditions at a pH of 6–7 and temperatures of 60°C (El-Sakhawy 2005), which is close to the parameters currently used in the industry. It is, however, generally known that sodium dithionite has a higher reductive power at basic alkalinities (Gassman et al. 1981). This discrepancy could be due to the fact that alkaline darkening is initiated at higher alkalinities, which then competes with the brightness increase from the reduction of chromophores.

Additionally, the concept of using sodium dithionite as an additive was extensively investigated in the 1950s by the German scientists Jayme and Wörner over a series of papers where they discussed a variety of concepts, including an actual pulping process using dithionite as the main pulping agent (Jayme and Wörner 1952a,b,c,d). In 1957, however, the papers in question were reviewed and criticised by Professor Regnfors, who argued that sodium dithionite would rapidly degrade under the conditions used in Jayme and Wörner's work. Regnfors further measured the effects of adding sodium dithionite, sodium sulphite and sodium thiosulphate to standard white liquor on pulping and found no increases in strength. Regnfors concluded that neither sodium dithionite nor any of its degradation products are viable as pulping additives under normal pulping conditions (Regnfors 1957).

Sodium borohydride has also been suggested as a reducing additive for preventing carbohydrate degradation (Akgül et al. 2007). Sodium borohydride has the advantage of being a stronger reducing agent than sodium dithionite. Additionally, unlike dithionite, borohydride is stabilised at $\text{pH} \geq 13$ (Churikov et al. 2012). However, sodium borohydride risks introducing the non-process element boron into the chemical recovery system and has been found to have reproductive toxicity (Weir and Fisher 1972), causing it to be labelled as a carcinogenic, mutagenic and reprotoxic (CMR) substance.

The present work set out to test the boundaries of that final statement by Regnfors: whether sodium dithionite can or cannot be used as a reducing agent to achieve protection at the reducing end as well as which processing parameters need to be used in order to achieve such protection. To this end, the monosaccharide mannose was used to test the reducing power of sodium dithionite at varying alkalinities, temperatures and dithionite concentrations. Reduction yield was quantified by measuring the amount of mannose which was reduced to mannitol using gas chromatography with flame ionization detection (GC-FID) as well as quantitative carbon-13 nuclear magnetic resonance (^{13}C -NMR). While a polysaccharide model compound might have been preferred for mimicking industrial conditions, using mannose maximised the

number of reducing end groups per weight and kept the molecular weight (and thus, the boiling points of the acetylated derivative) low, which was necessary in order to use the aforementioned analysis methods. If the chemistry of the reducing end groups is assumed to be the same in both cases, this study on mannose should be illustrative of the polysaccharide behaviour as well.

Materials and methods

Materials: D-(+)-Mannose from wood $\geq 99\%$ and D-mannitol $\geq 99\%$ as well as Glycine ReagentPlus[®] $\geq 99\%$ and Deuterium Oxide 99.9 atom% were procured from Sigma Aldrich Co. (St. Louis, MO, USA). Sodium hydrosulphite ca. 85% technical grade was procured from Acrös Organics (NJ, USA). Sodium hydrogen carbonate AnalaR NORMAPUR was procured from VWR International BVBA (Leuven, Belgium). Ethanol absolute AnalaR NORMAPUR was procured from VWR International (Fontenay-sous-Bois, France).

Reduction of mannose using sodium dithionite: Samples of mannose were reduced with sodium dithionite in batches using different processing parameters in a system inspired by the conditions and setup of de Vries and Kellogg (1980) for the reduction of aldehydes; samples of mannose and varying amounts of dithionite depending on the experiment were added to a round bottom flask in which deionised water at an alkalinity set by the specific experiment (using one of the buffers detailed below) had been added. The round bottom flask with buffer was placed in an oil bath and preheated to the requisite temperature before the mannose and dithionite were added. The mannose concentration was 25 mg ml^{-1} . The solution was bubbled continuously with nitrogen during the reaction to keep an inert atmosphere. Aliquots were collected after 0 min, 15 min, 30 min, 60 min and 120 min, which were acetylated and analysed using GC-FID. Later experiments used a different setup; mannose and varying amounts of dithionite and buffer were added to vials, to which solutions of 10% deuterated water and 90% deionised water were added. The mannose concentration was 60 mg ml^{-1} . The vials were sealed with Teflon tape (but could not be bubbled continuously for an inert atmosphere) and placed in an oil bath for 120 min. After the reaction, the solutions were cooled. Ethanol was added as a standard after which the solution was analysed using inverse gate ^{13}C -NMR.

For either reaction system, three variables were varied: temperature, alkalinity and equivalents of dithionite to mannose. The temperatures used were 70°C, 85°C or 100°C. Alkalinity was set to pH 7 (using no buffer), pH 8 (using a sodium bicarbonate buffer, unadjusted), pH 10 (using a glycine buffer, adjusted using NaOH) or pH 14 (using 1 M NaOH). The dithionite to mannose ratio was 0.5:1, 1:1, 2:1 or 4:1, molar basis.

Rather than performing a full analysis of variance, a reduced set of experiments was performed, where each variable was varied individually from a common baseline. For clarity, the full set of experiments is detailed in Table 1. Each experiment was performed twice.

Quantification using GC-FID: Aliquots of each sample were acetylated and dissolved in ethyl acetate. The acetylated samples were then

Table 1: Full description of the processing parameters for each experiment in the study.

Experiment	Alkalinity (pH)	Temperature (°C)	Dithionite: mannose GC-FID (mol mol ⁻¹)	Dithionite: mannose NMR (mol mol ⁻¹)
Centre experiment, bicarbonate	8	85	1:1	2:1
High temperature, bicarbonate	8	100	1:1	2:1
Low temperature, bicarbonate	8	70	1:1	2:1
High dithionite, bicarbonate	8	85	2:1	4:1
Low dithionite, bicarbonate	8	85	0.5:1	1:1
Centre experiment, glycine	10	85	–	2:1
High temperature, glycine	10	100	–	2:1
Low temperature, glycine	10	70	–	2:1
High dithionite, glycine	10	85	–	4:1
Low dithionite, glycine	10	85	–	1:1
Centre experiment, none	7	85	1:1	–
Centre experiment, hydroxide	14	85	1:1	–

analysed on an Agilent 7890 (Agilent Technologies, Santa Clara, CA, USA) instrument with a split injector, an HP-5 column [30 m, 320 mm inner diameter (I.D.) and 0.25 mm thickness], a flame ionisation detector and the OpenLab CDS ChemStation software (Agilent Technologies, Santa Clara, CA, USA). The oven was set to 80°C and held at 1 min followed by a ramping of 30°C min⁻¹ to 200°C, followed by a ramping of 5°C min⁻¹ to 230°C, followed by a ramping of 30°C min⁻¹ to 250°C, held for 3 min. Meso-erythritol was used as internal standard for the quantification.

Select acetylated samples were also analysed on a ThermoQuest TRACE 2000 GC (ThermoQuest Corporation, Austin, TX, USA) instrument with a split injector, a DB-5MS column (30 m, 320 mm I.D. and 0.25 mm thickness), a Finnigan TRACE MS (Finnigan Corporation, San Jose, CA, USA) mass spectrometer (MS) and the Xcalibur software (Finnigan Corporation, San Jose, CA, USA). The oven was set to the same temperature ramping program as for the GC-FID analysis mentioned above.

Using the weight of the molecular ions and the fragmentation patterns observed in GC-MS as well as corroborating suggestions from the NIST library, the peak at a retention time of 9.7 min with a molecular ion of 375 m/z was identified as acetylated mannitol, while peaks at retention times of 9.0 min, 9.1 min and 9.4 min with molecular ions of 331 m/z were identified as isomers of acetylated mannose. Quantification was done by normalising the sum of the respective integrals to the meso-erythritol standard and comparing with a standard curve. See Figure 2 for an example spectrum from the Centre, bicarbonate experiment.

Quantification using ¹³C-NMR: Deuterated samples with ethanol added as the internal standard were analysed on a Bruker 400 DMX (Bruker Corporation, Billerica, MA, USA) instrument equipped with a 10 mm Bruker BBO probe (Bruker Corporation, Billerica, MA, USA) by applying the carbon inverse gate zgig pulse program, with p1=8 µs (resulting in a 50° tip angle); d1=20 s; aq=1.6 s; ns>3100; rg=32 k; pl12=10 dB. Finally, each FID was processed with 3.0 Hz exponential apodisation, manual phase adjustment and automatic baseline correction using a third order polynomial function. This processing was done using the software MestReNova (Mestrelab Research, Santiago de Compostela, Galicia, Spain).

An example spectrum from the Centre, bicarbonate experiment is shown in Figure 3. The peaks at 61.0 ppm and 63.2 ppm

Figure 2: Example spectrum for quantification of mannose and mannitol using GC-FID, using the parameters for Centre experiment, bicarbonate (85°C, pH 8, 1:1 dithionite mannose ratio, 2 h). Spectrum is cut for brevity. Select peaks were identified from similarly acquired GC-MS spectra using their molecular ions and suggestions from the NIST library.

were identified as the C6 peak of mannose and the overlapping C1/C6 peaks of mannitol, respectively, by comparison to spectra of pure standards. The peaks at 57.4 ppm and 16.9 ppm originate from ethanol. Quantification was done by comparing the specified mannose and mannitol integrals with the 16.9 ppm ethanol integral and multiplying with the molar amount of added ethanol.

In order to validate the selection of relaxation delay time, a relaxation delay study was performed. Mannose, mannitol and ethanol were dissolved in high concentration in deuterated solvent and subjected to the t1irpg pulse program with p1=14 µs; d1=60 s; vdlst=[0.1; 0.3; 0.5; 0.7; 0.9; 1.5; 2.0; 3.0; 5.0; 7.0; 10; 15; 25; 35; 45; 55]s; aq=1.6s; ns=64 (at each level of vd); rg=32 k; pl12=10 dB. The resulting stack of spectra is shown in Supplementary Figure S16 together with their respective variable delays.

Figure 3: Example spectrum for quantification of mannose and mannitol using NMR, using the parameters for Centre experiment, bicarbonate (85°C, pH 8, 2:1 dithionite mannose ratio, 2 h).

By fitting the relaxation delay data obtained from the t1lrp experiment to $\ln(I_0 - I_t) = \ln\left(2I_0 - \frac{t}{T_1}\right)$, which can be derived from

the Bloch equations [see (Traficante 1992)], the T_1 relaxation delay times for the respective nuclei of interest were found to be 0.4 s for the C6 mannose peak, 0.4 s for the C6 mannitol peak and 6.3 s for the aliphatic ethanol peak. Ninety-nine percent relaxation in the quantification experiment is therefore achieved after $6.3 \cdot \ln(100 - 99 \cos(50^\circ)) = 22.6$ s. While this is higher than the pulse repetition time (21.6 s) used in the experiment, the difference is lower than 0.25% of relaxation.

Results and discussion

Yields of mannitol at varying temperatures, concentrations and alkalinities

The viability of sodium dithionite as a reductant of mannose was determined by applying dithionite to mannose using a variety of processing parameters as shown in Table 1 in the Experiment section. Yields of mannitol and conversions of mannose were then determined using GC-FID as well as NMR.

The starting point for the study was to vary alkalinity, temperature and dithionite concentration independently and measure the effects on mannitol formation using GC-FID. For each experiment, aliquots were collected and analysed after 0 min, 15 min, 30 min, 60 min and 120 min.

It was found that alkalinity is crucial to the viability of the reaction. Comparing the GC-FID results obtained by varying alkalinity while keeping the other parameters constant, one can find that only small amounts (less than 1% reduction yield) of mannitol are formed at pH 7 and that

Figure 4: Yield of mannitol formed at various time intervals by varying alkalinity, with GC-FID used for quantification. All experiments were done using a temperature of 85°C and a 1:1 molar ratio of dithionite to mannose. Error bars depict standard deviations of double tests.

no mannitol (0% reduction yield) is formed at pH 14 (see Figure 4) – at the latter pH, the mannose reactant is also seen to completely degrade (see Supplementary Figures S12–S15). This observation is in agreement with the conclusions of Regnfors (1957), who stated that sodium dithionite would be unviable at pulping conditions while further predicting degradation at lower alkalinities, with later studies finding “mildly basic” alkalinities in general and a sodium bicarbonate buffer specifically to be preferable when working with dithionite (de Vries and Kellogg 1980). At pH 8 in this study, however, a reduction is seen to take place, and non-negligible amounts of mannitol are formed with a final yield of 17%. The full GC-FID results for these experiments are presented in Figure 4 and the corresponding chromatograms after 120 min are presented in Supplementary Figures S2, S3, S12–S15. Supplementary Figure S1 is also provided for reference.

From the initial GC-FID experiments, it was also found that yield of mannitol at pH 8 is improved by increasing the temperature (although the difference between 85°C and 100°C was not statistically significant after the full 120 min) as well as by increasing the dithionite concentration. Just as for alkalinity, aliquots were procured and analysed multiple times during each reaction, where it was found that an increase in temperature had a particularly large effect at shorter reaction times, see Figure 5. This temperature asymptote could suggest that all dithionite has been consumed or degraded after 30 min of reaction at 100°C. Such an explanation is corroborated by the study by Lakshmi Veguta et al (2017), where the

Figure 5: Yield of mannitol formed at various time intervals by varying temperature, with GC-FID used for quantification. All experiments were done at pH 8 and a 1:1 molar ratio of dithionite to mannose. Error bars depict standard deviations of double tests.

inorganic stability of the sodium dithionite salt was investigated, and remaining dithionite was found to decrease from 50% to 20% when the temperature was increased from 80°C to 100°C at pH 9. Differences in yield at varying dithionite concentrations, as seen in Figure 6, are less pronounced, with no significant differences in the yield between the 1:1 and 2:1 experiments until the final time point. The 0.5:1 experiment, on the other hand, shows a significantly lower yield throughout. The corresponding

Figure 6: Yield of mannitol formed at various time intervals by varying molar ratios of dithionite to mannose, with GC-FID used for quantification. All experiments were done using a temperature of 85°C and a pH of 8. Error bars depict standard deviations of double tests.

chromatograms for all of these experiments after 120 min are presented in Supplementary Figures S4–S11. Supplementary Figure S1 is also provided as a reference.

Having identified alkalinity as a crucial parameter, the next step was to investigate the yield of mannitol formation at an intermediate alkalinity between pH 8 and pH 14. It has previously been shown by Lakshmi Veguta et al. (2017) that the stability of the dithionite salt increases with pH until it reaches a maximum between pH 11 and pH 13. In order to investigate if the higher stability of dithionite at these alkalinities could improve reduction efficiency, a new set of experiments was performed. These experiments used the same conditions as the GC-FID experiments, except that the dithionite to mannose ratios were doubled, the pH 7 and pH 14 experiments were obviated and inverse gate ^{13}C -NMR was used for quantification. In addition, five more experiments were added to this new series, using the same variations in temperature and dithionite to mannose ratios but conducted at pH 10 rather than pH 8. The results of all these experiments are presented in Table 2 together with the previous GC-FID results. The corresponding spectra for all NMR experiments are presented in Supplementary Figures S18–S37, with Supplementary Figure S17 also provided as a reference for the chemical shifts. As previously mentioned, GC-FID chromatograms are provided in Supplementary Figures S2–S15, with Supplementary Figure S1 provided for reference.

Comparing the NMR results at pH 8 and pH 10 at a standard temperature and dithionite concentration, the yields are seen to be similar (16% and 18%, respectively), while the losses of mannose are seen to be higher at pH

Table 2: Yield of mannitol and losses of mannose after 120 min for each of the experiments done in the study.

Experiment	GC-FID yield (mol%)	NMR yield (mol%)	GC-FID losses (mol%)	NMR losses (mol%)
Centre experiment, bicarbonate	17	16	56	42
High temperature, bicarbonate	20	12	80	73
Low temperature, bicarbonate	6	15	44	41
High dithionite, bicarbonate	25	17	40	46
Low dithionite, bicarbonate	7	16	67	38
Centre experiment, glycine	–	18	–	73
High temperature, glycine	–	20	–	76
Low temperature, glycine	–	26	–	55
High dithionite, glycine	–	21	–	78
Low dithionite, glycine	–	16	–	73
Centre experiment, none	1	–	35	–
Centre experiment, hydroxide	0	–	100	–

Losses of mannose were calculated as the differences between the respective conversion of mannose and yield of mannitol.

Figure 7: Schematic illustration of how mannose could behave in the presence of dithionite as performed in this study.

Upon ring-opening of the molecule, two reaction paths are possible, one in which the saccharide is reduced to its alditol form and one in which the saccharide is fragmented and lost. As dithionite is stabilised by alkali, and degradation is induced by alkali, the kinetics of both paths can be expected to depend on a combination of alkalinity and temperature.

10 (42% and 73%, respectively). Increasing the dithionite concentration at either alkalinity is seen to give marginal increases in yield, with the pH 8 experiments giving a 17% yield at a 4:1 ratio of dithionite to mannose while the pH 10 experiments gave a 21% yield at a 4:1 ratio of dithionite to mannose. This would suggest that a 2:1 ratio of dithionite to mannose is sufficient for the reaction. Crucially, the low temperature pH 10 experiment is seen to have the highest yield out of all the NMR experiments at a 26% yield and 55% losses. It is our hypothesis that the system in the present study can be seen as a reaction system where mannose can either be degraded by the alkali – the kinetics of which is increased with alkalinity and temperature – or reduced by the dithionite – the kinetics of which is also increased with alkali and temperature. The exact nature of the observed alkaline degradation in this study is unknown, but alkaline degradation of monosaccharides is generally accepted to proceed through the formation of multiple enediol intermediaries which are further degraded through a combination of benzylic acid rearrangement, α -dicarbonyl cleavage and retro-aldolisation (de Wit et al. 1979; de Bruijn et al. 1986; Yang and Montgomery 1996). This generally accepted system is illustrated schematically in Figure 7. This scheme does not, however, account for further reaction of the degradation products with sodium dithionite or other high molecular-weight degradation products in alkali which to this day remain unknown (Liggett and Deitz 1954; de Bruijn et al. 1986).

According to such a reaction system, the increase in pH from 8 to 10 would increase the kinetics of reduction due to the increased stability of dithionite but would also increase degradation of mannose. When a lower temperature is used, however, the reaction with lower activation energy would be promoted. If the activation energy of reduction is lower than that of the degradation, this would explain the maxima observed in the data.

Comparing analysis methods, NMR yields are seen to be lower than GC-FID yields when the same experimental parameters are used. At a 2:1 ratio of dithionite to mannose at pH 8 and 85°C, the yield is 25% for GC-FID and 16% for NMR, and at a 1:1 ratio at the same conditions, the yield is 17% for GC-FID and 16% for NMR. The deviation at the 1:1 ratio is not statistically significant. However, while part of the deviation at the 2:1 ratio could be attributed to the high standard deviation of 3.2% at that GC-FID data point (the corresponding value for the NMR data point is 1.2%), there is still a significant difference in yield at the 2:1 ratio. This might be due to the fact that the NMR experiments could not be done in an oxygen-free atmosphere. This might have caused additional degradation of dithionite, as previously detailed by de Vries and Kellogg (1980).

Relevance of results to the industrial scale

These results show that sodium dithionite could indeed be used to protect carbohydrates, although not at pulping alkalinities. Interestingly, one of the buffers used in this study – sodium bicarbonate – is also present in green liquor (in the form of sodium carbonate). One possible industrial concept would therefore be to use part of this liquor as buffer in order to perform the reduction in a pre-impregnation step. If needed, the alkalinity could be further increased by adding white liquor. Possible temperatures for the impregnation step could be 100°C using a pH of 8 or 70°C using a pH of 10 depending on whether kinetics or reduction yield is being optimised. Oxygen levels in the wood chips could be lowered by steaming, with the remainder being consumed using a slight excess of dithionite.

The preferred dithionite charge in such a pre-impregnation merits a discussion of its own. In this study, 2:1 molar amounts of dithionite to mannose were seen to provide good results. As the molecular weight of sodium dithionite is close to that of mannose, charges of dithionite between approximately 50 w% and 400 w% were used in this study. In an industrial scenario on wood chips, however, the charges would need to be adjusted with consideration to the relative amount of glucomannan as well as the average molecular weight of the glucomannan.

Normal softwood contains 19% (galacto)glucomannan by weight with an average molecular weight of 14.7 kDa (Teleman 2009). For such a material, a 2:1 dithionite charge would require: $w\% = 2 \times 0.19 \times \frac{174.1}{14\,700} = 0.45\%$ (4.5 g kg⁻¹) on wood. This does not take diffusion gradients or loss of dithionite due to reduction of other substances into consideration, of course, but could serve as a starting point for further optimisation.

Conclusions

- When alkalinity was kept at pH 8 or pH 10, sodium dithionite was successfully used to reduce mannose to mannitol. At pH 7 and pH 14, no such reduction was seen to occur in this study.
- When alkalinity was kept at pH 8, increases in temperature and dithionite concentration were both seen to be beneficial for reduction yields. The effects of increasing temperature were especially pronounced at lower reaction times.

- When alkalinity was kept at pH 10, a maximum yield of mannitol was found when a lower temperature of 70°C was used. This can be explained by the higher stability of dithionite at pH 10 compared to pH 8 in combination with the lower temperature mitigating alkaline degradation at that alkalinity.
- A sodium dithionite treatment might be considered for inclusion in different pulping and biorefinery concepts. Such a treatment could be performed using green liquor as a buffer in a pre-impregnation step, potentially using white liquor to raise the alkalinity further. A starting point for sodium dithionite charge could be 4.5 g kg⁻¹ of wood.

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