Hemicellulose Pre-Extraction of Hardwood

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ABSTRACT

A Southern US hardwood mixture was subjected to pre-extraction with water at 150 ºC. Well closed material balances were obtained for lignin-free yield, xylan and glucomannan when comparing the solid and liquid phases. Xylan initially dissolves as oligosaccharides and then slowly depolymerizes into monomeric xylose. The residual xylan in wood is only slightly deacetylated. The methyl-glucoronic anhydride/ xylose ratio in wood decreases significantly with increasing extraction time. A smaller amount of glucomannan is removed as oligosaccharides. Approximately 1% as cellulose dissolves mostly in polymeric form. Arabinan and galactan are completely removed from wood as monomers at the end of the extraction process. Initially all acetyl groups are removed while still bound to oligosaccharides. Then acetic acid is released by deacetylation of the dissolved oligosaccharides. A significant amount of lignin (up to 5% based on wood) is extracted, part of which is still covalently bound to hemicelluloses.

INTRODUCTION

Wood, the most abundant renewable raw materials on earth, primarily consists of cellulose, hemicelluloses and lignin with minor amounts of extractives and ash. The percentages of these components vary depending on wood species. Generally, about 70% of all wood consists of polysaccharides (cellulose and hemicelluloses) (Sjostrom, 1993). The objective during wood pulping is to retain the polysaccharides while removing the lignin. During kraft pulping of softwoods about 15-20% of the wood weight as hemicellulose (25-30% in wood) ends up in black liquor. For hardwoods, about half of the hemicellulose (27-33% in wood) is removed during kraft cooking. The degraded hemicellulose dissolved in the waste pulping liquor is then burned during the kraft recovery process. However, the heating value of wood carbohydrates is approximately half of that of lignin. Hence, it would be beneficial to develop a more economical use of wood hemicelluloses. One such technique would be to extract the hemicelluloses as oligo- or polysaccharides prior to pulping, and then convert them to higher value-added products such as ethanol, polymers and chemicals.

PRE-EXTRACTION OF HARDWOOD

Hemicelluloses were pre-extracted with water using different extraction times at 150 ºC in a modified Dionex ASE-100 extractor. The liquor to wood ratio (L/W) was approximately 3.7:1. The use of the ASE-100 equipment simplified the extraction process due to the elevated pressures used. Penetration of the voids inside and outside wood particles by extraction liquor is mostly completed in a short time at the high pressure (100-150 atm.) used by the ASE-100. The Dionex ASE-100 was modified to stabilize the pressure at the set point by introducing a pressurized expansion tank between the static valve and the extraction cell. This modification allows the ASE-100 to operate at constant volume during extraction regardless of thermal expansion. The Modified ASE-100 is schematically represented in figure 2. A heat exchanger after the extraction cell was also introduced to condense any volatile products such as methanol, which may form during the extraction.

Figure 1. Modified Accelerated Solvent Extractor (ASE-100)

Red lines indicate modifications

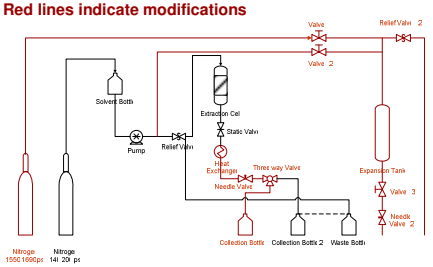

Figure 2. Schematic representation of Modified ASE-100

EXPERIMENTAL PRECEDURE

The experimental analysis scheme for the hemicellulose pre-extraction of the southern hardwood mixture is summarized in figure 3. The solid phase was analyzed for cellulose, hemicellulose, lignin, 4-*O*-Methyglucoronic anhydride (4-O-MGA), acetyl groups and ash content, while the liquid phase was analyzed for cellulose, hemicellulose, lignin, furfural and acetic acid concentration.

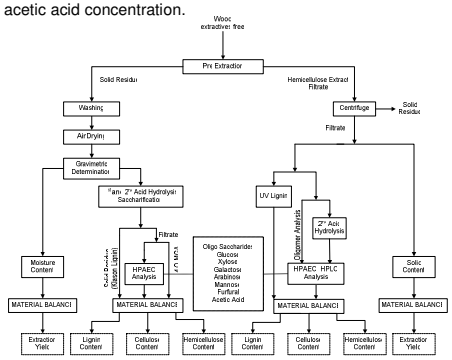

Figure 3. Experimental design for pre-extraction of hemicellulose

RESULTS

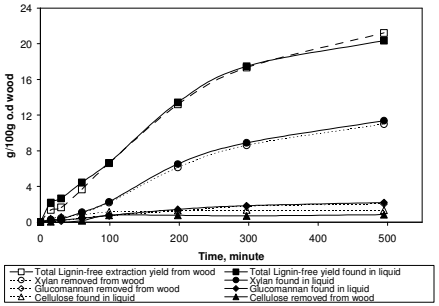

Figure 4. Total lignin-free, xylan and glucomannan extraction yields versus time

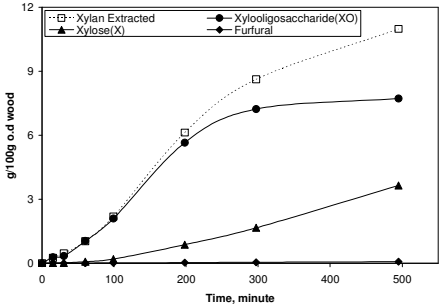

Figure 5. Kinetic of Xylan dissolution of Southern Hardwood Mixture with water

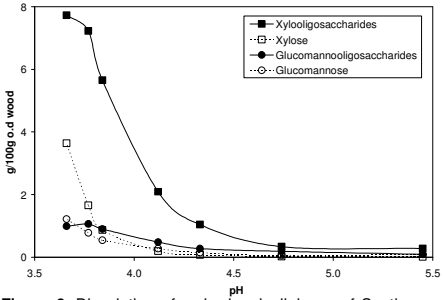

Figure 6. Dissolution of major hemicelluloses of Southern Hardwood Mixture with water versus pH

Table 1. The chemical composition of original extractives-free SHM (% on wood)

Monomeric Anhydro-monosugar								
Ara.	Gal.	Glu.	Xyl.	Man.	Cellulose	Hemicelluloses	Lignin	Ash
0.5	1.0	42.2	16.7	2.0	41.0	29.6	29.0	0.4

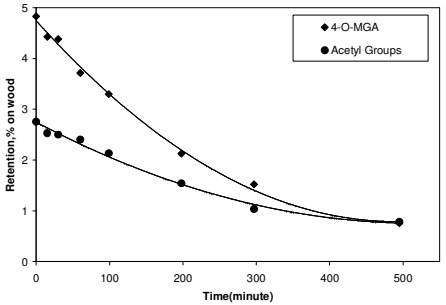

Figure 7. Acetyl groups and 4-O-MGA retentions of Southern Hardwood Mixture with water versus time

Table 2. Mole ratio of retained acetyl groups and 4-O-MGA to 10 mole xylan in wood

Time (min.)	Acetyl Groups/10 Xylose	4-O-MGA/10 Xylose
wood	5.1	2.2
15	4.7	2.1
30	4.7	2.1
60	4.7	1.8
99	4.5	1.7
198	4.5	1.5
297	4.0	1.5
495	4.2	1.0

CONCLUSIONS

Hemicelluloses are predominantly removed during pre-extraction of SHM with water at 150 ºC. Xylan dissolves as oligosaccharides and then it depolymerizes slowly into monomeric xylose at longer extraction times (up to 500 minutes). No significant amount of furfural, was generated under the present extraction conditions. The xylan that remains in the wood is only slightly deacetylated. The percentage of 4-O-MGA in xylan retained in wood decreases significantly with increasing extraction time. A much smaller amount of glucomannan is initially removed as oligosaccharides. Further hydrolysis into monosugars is faster than found for dissolved xylan. Approximately 1% of cellulose (based on wood) dissolves mostly in polymeric form. This most likely represents low molecular weight cellulose in SHW. Arabinan and galactan are completely removed from wood as monomers at the end of the extraction process. The acidity of the hemicellulose extract increases with time due to release of acetyl groups from SHM. The extraction of the hemicelluloses increases rapidly when the extract pH is below 4.3.

REFERENCES

Sjostrom, E., 1993. Wood Chemistry Fundamentals and Applications, 2nd Edition, Academy Press Inc.

ACKNOWLEDGMENTS

This research has been made possible by financial support of the US Department of Energy and International Paper Corporation under contract FC36-04GO14306