Industrial Crops and Products 58 (2014) 335–339

Contents lists available at ScienceDirect

Industrial Crops and Products

journal homepage: www.elsevier.com/locate/indcrop

Manufacture of decyl pentosides surfactants by wood hemicelluloses transglycosidation: A potential pretreatment process for wood biomass valorization

Camille Ludot[a,b], Boris Estrine[a,*], Norbert Hoffmann[b], Jean Le Bras[b], Sinisa Marinkovic[a], Jacques Muzart[b]

[a] ARD Agro-industrie Recherches et Développements, Green Chemistry Department, Pomacle, France
[b] Institut de Chimie Moléculaire de Reims, UMR 7312, CNRS-Université de Reims Champagne-Ardenne, UFR des Sciences Exactes et Naturelles, Reims, France

ARTICLE INFO

Article history:
Received 6 February 2014
Received in revised form 17 April 2014
Accepted 22 April 2014
Available online 14 May 2014

Keywords:
Transglycosidation
Xylan
Poplar
Alkyl polyglycosides
Surfactant

ABSTRACT

We studied the reactivity of wood based hemicelluloses (beechwood xylan and poplar chips) in acid-catalyzed transglycosidation in decanol. Wood based hemicelluloses revealed to be more recalcitrant to transglycosidation than hemicelluloses from cereal origin (wheat straw, Oat spelt xylan). The chemical composition of the hemicelluloses, such as ash content or the level of arabinose and uronic acids in the polysaccharides structures, seems to influence the reactivity. The use of dimethylsulfoxide as solvent in the transglycosidation improved pentosides and glucosides yields for beechwood xylan, the more recalcitrant material. The surfactant properties of glycosides' compositions produced from poplar were studied and compared to those of glycosides' compositions obtained from pure monomeric carbohydrates or from wheat straw. The cellulose rich residue from poplar was hydrolyzed by concentrated acid saccharification yielding glucose in yields up to 55%.

1. Introduction

Hemicelluloses, the second most abundant type of polysaccharides from biomass next to cellulose, are increasingly considered as a promising alternative to fossil chemicals (Klass, 2004; Marinkovic et al., 2012). They are currently regarded as a renewable and cheap feedstock for the production of bio-based chemicals, biomaterials and biofuels. Their transformation into biodegradable surfactants is one possibility for their valorization (Martel et al., 2010). Most of the market available sugar surfactants are based on food related raw materials such as glucose from starch. This is the case for alkyl polyglucosides (APGlu), which combine high performance as non-ionic surfactants with low-skin irritation and high biodegradability (Balzer and Luders, 2000). They are usually produced by Fischer's glycosidation reaction of glucose with a long chain fatty alcohol. Some studies have been published for the conversion of biomass such as cellulose (Villandier and Corma, 2010) or starch (Roth et al., 1980) into APGlu but drastic conditions, long reaction times and several steps such as biomass fractionation, carbohydrates isolation and purification are required. Alternatively, pentose-based surfactants produced from agricultural wastes are gaining interest in the surfactant market for detergent and cosmetic applications, as they display high detergent properties and a good ecological profile; moreover they do not impact food supplies. New procedures have been recently developed for the high yield synthesis of long tailed alkyl polypentosides (APP) such as decyl and hexadecyl xylosides from wheat sourced hemicelluloses (Seguin et al., 2012) and oat spelt xylan (Bouxin et al., 2010) under mild conditions (Fig. 1). These procedures also provided pretreated biomass residue with residual amount of cellulose that can be further converted into glucose by enzymatic saccharification. Thus, transglycosidation process has the advantage, as a pretreatment step of biomass, to not degrade cellulose and to not use volatile solvents that cause problems of security and render the solvent recovery more complicated. It also offers more potential for valorization of the whole part of the lignocellulosic material. The weakness of this process lies in its singular advantage of converting directly hemicelluloses into valuable surfactants. The economics of the overall process are depending on the surfactant market, although the valorization of the cellulose as a feedstock for biofuel or chemicals would become more competitive. In this study we highlight the effect of botanical origin on the reactivity of hemicelluloses from wood and cereals in acid-catalyzed transglycosidation reaction. We

---

* Corresponding author. Tel.: +33 326 054 284; fax: +33 326 054 289.
E-mail address: b.estrine@a-r-d.fr (B. Estrine).

http://dx.doi.org/10.1016/j.indcrop.2014.04.039
0926-6690/

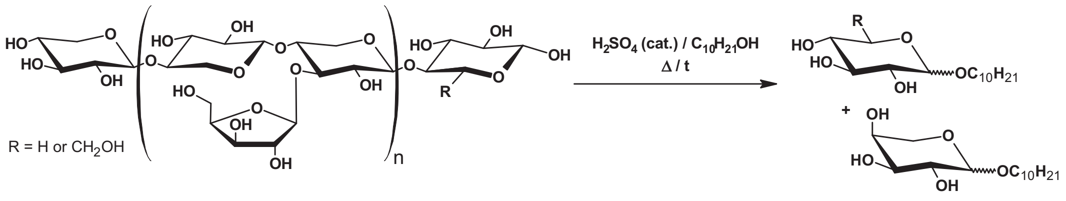

Fig. 1. Transglycosidation of hemicelluloses in decanol for the production of decyl-glycosides.

describe the direct synthesis of decyl glycosides surfactants from two wood-based materials: beechwood xylan and poplar wood chips. The surface active properties of the decyl glycosides have been evaluated and the valorization of the lignocellulosic residue into glucose by concentrated acid saccharification and enzymatic saccharification has been studied.

2. Experimental

2.1. Feedstocks

All required reagents are commercially available and used as received. Dimethylsulfoxide was from VWR; *n*-decyl alcohol was from Acros Organics; sulfuric acid was from Fischer Chemical, xylan *from Beechwood* was from Sigma; poplar was provided by Wageningen University (NL) in the framework of the EU Biosynergy project. Poplar chips were obtained by crushing into 2 mm particles. The dry matter contents of xylan and poplar are respectively 97.0% and 89.0%. Their carbohydrate contents were determined following NREL (National Renewable Energy Laboratory) analytical methods (Table 1) (Sluiter et al., 2008). The carbohydrate composition has been used for decyl monoglycosides yields calculation. For each decyl monoglycoside, yield is calculated as follow:

$$\text{Decyl monoglycosides yield} = \frac{\text{Moles of decyl monoglycosides}}{\text{Moles of corresponding carbohydrate in the starting material}} \times 100$$

Composition of wheat straw and oat spelt xylan have also been determined (Table 1) for comparison.

2.2. Transglycosidation pretreatment procedure

In a 100 mL round bottom flask, equipped with a magnetic stirring apparatus and a refluxing condenser, a mixture of beechwood xylan (10 g) or poplar chips (3.5 g) in decyl alcohol (30 g) and, for solvent-assisted reactions, DMSO (0.17–7.50 wt. eq. based on wood material weight), was progressively heated to the reaction temperature in an oil bath at atmospheric pressure. Distilled water and sulfuric acid were then added dropwise. The reaction was monitored by GC for 6 h. Only the maximum APG yields reached during the reaction and the time at which they have been reached are reported in tables. The remaining solid was filtered off using a sintered-glass filter. The residual material was washed by acetone, dried at 60 °C under vacuum and weighed. The filtrate was neutralized by caustic soda solution to pH 9 (measured in a 10 wt.% solution of water and isopropyl alcohol 1:1 v/v) and the alcohol was removed by distillation.

2.3. Concentrated acid and enzymatic saccharification procedure

2.3.1. Concentrated acid saccharification

In a typical experiment, a mixture of 10 g of the residual material obtained from poplar chips solvent-free transglycosidation (obtained from four repeats of the trial described in Table 2, entry 5) and sulfuric acid (40–120 wt.% based on poplar residue weight) was slowly stirred for about 30 min maintaining the temperature below 30 °C with an ice bath. After dilution with 75 g of distilled water the saccharification was pursued for 2 h in refluxing water. Acid insoluble material was obtained after filtration and hot water washing. Glucose and xylose productions were monitored by high performance liquid chromatography (HPLC) analysis of the filtrate.

2.3.2. Enzymatic saccharification

16 g of poplar chips or pretreated poplar chips recovered from transglycosidation trial, is loaded in a reaction vessel containing enzymes (total volume of 800 mL). Each reaction vessel was sterilized at 121 °C for 20 min prior to the addition of the enzymes and poplar or poplar residue. The enzymes were added at the following amounts: 3.7 g celluclast 1.5 L (60 FPU/g, 30 β-glucosidase IU/g) (Novozymes A/S), 0.8 g Novozyme 188 (500 β-glucosidase IU/g) (Novozymes A/S) and 0.8 g multifect xylanase (43 g protein/ml) (Genencor International Inc.). Enzymatic hydrolysis was performed at 40 °C for 72 h. The sample is immediately filtered through a 0.2 μm sterile filter and frozen to prevent further hydrolysis. Duplicate batches were run to verify the results.

2.4. Chemical analysis

For the pentosides and glucosides yields, in a typical GC analysis, a sample of 500 mg of the reaction medium was dissolved in 7 mL of anhydrous pyridine and then treated with 4 mL of 1,1,1,3,3,3-hexamethyldisilazane and 3 mL of trimethylsilyl chloride. Pyridium salts were removed by filtration on a 0.20 μm nylon filter. Analyses were performed with a Varian Bruker 450 Gas Chromatograph (temperature gradient from 150 °C to 300 °C, analysis time 84.5 min) or an Agilent 7890 A Gas Chromatograph (temperature gradient from 120 °C to 300 °C, analysis time 82 min), equipped

Table 1
Compositions[a] of lignocellulosic materials.

Component	Beechwood xylan	Poplar	Oat spelt xylan	Wheat straw
D-Xylose (%)	60.0	14.6	53	21.5
L-Arabinose (%)	1.6	0	7	2.4
D-Glucose (%)	2.7	41.7	7	35.8
Lignin (%)	0.7	24.8	0.3	21.7
Uronic acids (%)	5.7	3.6	4.2	1.9
Uronic acids/xylose ratio	0.10	0.25	0.08	0.09
Ash (%)	6.5	0.9	4	8.8

[a] Proteins, extractives, and D-mannose, D-galactose and L-rhamnose contents are not presented in the table.