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Actually, biorefinery is increasingly considered as a promising alternative to petroleum chemistry, since it aims at not only the replacement of fossil energy but also the development of chemicals from biomass, with applications such as detergents, phytopharmaceutics, solvents, plastics, etc.

The valorisation of carbohydrates from renewable raw materials¹ is currently the subject of numerous researches². In this context, the synthesis of new surfactants derived from the sugars issued from the lignocellulose hydrolysis was undertaken by chemical or enzymatic routes. Hereafter, the examples of glucose, cellobiose and uronic acids³ will be discussed.

Enzymatic modification of Glc and Cel

Several sugars from lignocellulose were submitted to β -glucosidase modification with *n*-hexanol. The best yields were obtained with Cel and Glc for which further investigations were performed.

Different synthesis media were tested as described below :

reaction conditions	48h yield
biphasic media water/ <i>n</i> -hexanol 1/9	20%
<i>n</i> -hexanol saturated with phosphate buffer 92mM pH 5.7	60%
<i>n</i> -hexanol saturated with saturated NaCl solution	2%

The use of a solvent-free system with *n*-hexanol pre-saturated overnight with a phosphate buffer was the best choice.

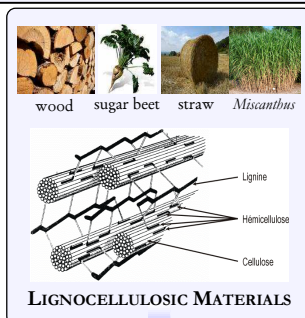
We then investigated the sugar and hexanol concentrations on the rate and yield of the synthesis.

That temperature of the reaction was optimized at 50°C.

We then added co-solvents to the media with the aim of improving the yields. DMF, pyridine and *t*-BuOH were therefore used

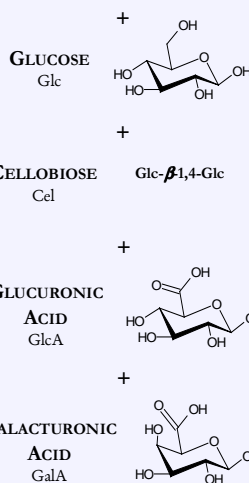
It revealed that for both Glc and Cel, the addition of co-solvent does not improved yields but on the contrary decreases the synthesis efficiency.

Finally, the best conditions for Glc (2.7mM) and Cel (10 mM) modification is the use of *n*-hexanol saturated with phosphate buffer, that leads to conversion of 72 % for Glc and 65 % for Cel at 50°C.



PRETREATMENTS HYDROLYSIS

NUMEROUS SUGARS



Enzymatic modification of GlcA

Esterification of GlcA catalyzed by Novozym 435

The Novozym 435 in *t*-BuOH was proved to be the most efficient system for GlcA esterification, with C6-C14 alcohols. No reaction was observed with GalA although it differs only by the orientation of the OH at C4. This highlights the importance of the C4-orientation for substrate recognition.

The influence of initial GlcA and alcohol concentrations was investigated.

Influence of initial concentrations in GlcA and tetradecanol on yields and initial rates.

Increase of the initial tetradecanol concentration leads to higher initial rates, and 48h-yield decreases in the meantime.

With GlcA, initial rates are hardly influenced, since these concentrations are lower than the solubility measured to be 4mM. As for yields, they are higher at low [GlcA]₀ (same amount of ester produced for less reactants).

The ester synthesis thus carried out at 0.04M GlcA and 0.25M tetradecanol results in a 48h-molar yield of 30% with a initial rate of 0.12 g/L/h/100mg of enzyme. The steady state is reached after 9 days, with a yield of 50%.

Several co-solvent were tested to improve the GlcA solubility, and pyridine revealed to be the best one: with alcohol from C6 et C14, 5 to 10% (V/V) of pyridine lead to great higher initial rates and yields.

Addition of co-solvent for esterification of GlcA with octanol and tetradecanol

Synthesis of GlcA or GalA esters and amides.

Chemical modification of GlcA and GalA

Routes for the formation of esters or thioesters of GlcA and GalA

Note that protection of the hydroxyl groups is required to avoid any side reaction and to ensure solubilization of the uronic compounds in the organic media.

This route involves an acyl chloride intermediate (a) or Steglich-type (thio)esterification with DCC and catalytic amounts of 4-dimethylaminopyridine (b).

To summarize, the different sugars selected and which derive from renewable resources can be enzymatically and/or chemically modified to lead to amphiphilic molecules. Moreover, the range of the alkyl chain lengths is large which provides numerous surfactants with various hydrophilic/lipophilic ratio. The properties of these molecules is under investigation.

1 Lichtenthaler, F.W. *Carbohydrates as Renewable Raw Materials: a Major Challenge of Green Chemistry* IN: *Methods and Reagents for Green Chemistry: an introduction*; Tundo, P., Perosa, A., Zecchini, F. Eds.; Wiley-Interscience, John Wiley & Sons, Inc., Hoboken, New Jersey, 2007, 23-63 ;
 2 Queneau, Y. et al. *Carbohydr. Res.*, **2008**, 343 (12), 1999 – 2009
 3 Blecker, C. et al. *J. Coll. Interf. Sc.*, **2008**, 321 (1), 154 – 158

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