Impact of steam explosion treatment on chemical configuration of Tall Fescue lignin : structural elucidation using NMR spectroscopy

G.Maniet, N. Jacquet , S. Gillet, A.Richel

Department of Industrial Biological Chemistry, Gembloux Agro-Bio Tech, Liège University

Background and Objectives

In the economic and energy context of our society, it is universally recognized that alternatives to petrochemicals products must be found. To overcome this problem, renewable lignocellulosic biomass could be used to produce high value products. To achieve this objective, pretreatment processes are required to allow the breakdown of lignocellulosic structure and increase accessibility of the material. In this way, steam explosion is a thermo-mechano-chemical pretreatment which allows the opening of lignocellulosic material structural components and includes modifications of the physical properties of the material, hydrolysis of hemicellulosic components and modification of the chemical structure of lignin [1].
This study is focused on the impact of various steam explosion treatments on the chemical configuration of tall fescue lignin. NMR analyses perform on the Festuca L. pretreated samples show variations of links with treatment intensity. Observations show double phenomen :re-polymerization and depolymerization of the lignin structure during steam explosion process [2]. In parallel, HPSEC analyses show modifications in the molecular weight of the lignin obtained after the steam explosion treatment.

Materials and Methods

Raw material

❖ *Tall fescue is a grass by poaceae family. It's actually used for feed but it presents a good potential for the second generation biomass development. Tall fescue is a pluriannual culture (6 to 10 years). It grows as march to oktober and it can measure 2 meters at flowering. Klason lignin contents is approximately of 15,6%±0,3.*

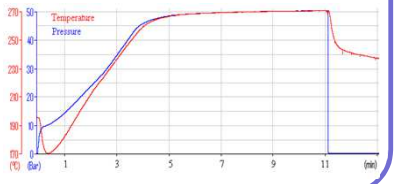
Steam explosion pretreatment

Pilot

Parameters

Severity factor	Maximum temperature in reactor
1,4	169,2
2,6	203,6
3,2	221,3
3,8	237,8
4,2	247,2

Process



Centrifugation
Centrifuge : Rousselet RC40VxR (18 liter bowl volume) at 3000rpm

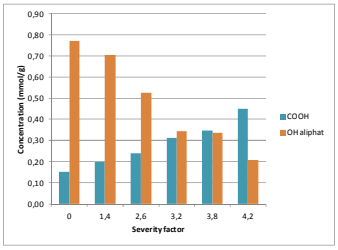
Organosolv process on solid
Acetic acid/Formic acid/water in 50/30/20 proportion 3h at107°C. 1/24 dry matter dilution

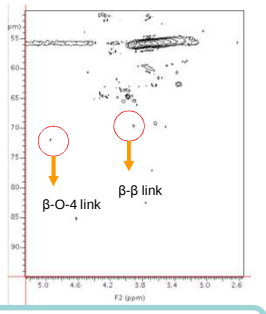
Black liquor filtration and recuperation
Filtration vacuum filter funnel with a fritted disk (40–100 µm pore size) and washing with acid solution

Lignin precipitation in black liquor and purification
Water pH 2 precipitation with 1/10 dilution, centifugation and freeze drying

Results

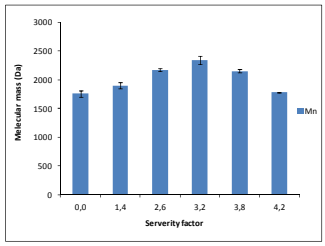
RMN lignin analysis (P_{31} and 2D HSQC)

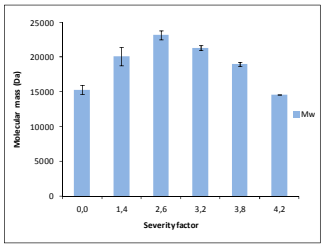




P_{31} RMN shows a decreasing of OH aliphatic groupments and a increasing of –COOH goupments with rising of steam explosion pretreatement intensity. RMN 2D HSQC shows decreasing of β-O-4 bounds and emergence of β-β bounds with rising of steam explosion pretreatement intensity

HPSEC Lignin analysis





HPSEC analysis of purified lignin shows in first time an increasing of molecular mass with serverity factor rising .It indicates polymerization process is dominant. In second time, molecular mass decreases and indicates lignin depolymerization is dominant.

Conclusions

❖ Presence of 2 phenomens in steam explosion process : polymerization and depolymerization [2]
❖ These 2 reactions have different kinetics with pretreatement intensity increasing
❖ Optimize pretreatment can focuse different products with variable mass and chemical structure

References
1. *Jacquet, N., Quievy, N., Vanderghem, C., Janas, S., Blecker, C., Wathelet, B., Devaux, J. and Paquot, M. Polymer Degradation ans Stability. 2011, 96, 1582-1588.*
2. *Jacquet N., Maniet G., Vanderghem C., Delvigne F., Richel A. , Application of the steam explosion as pretreatment on the lignocellulosic material: a review. Industrial & Engineering Chemistry Research, 2014.*