University of Milano-Bicocca
Department of Earth and Environmental Sciences

Characterization of lignocellulosic materials during the biorefinery process of *Arundo donax* for “Fine” chemicals production

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BIOREFINERY

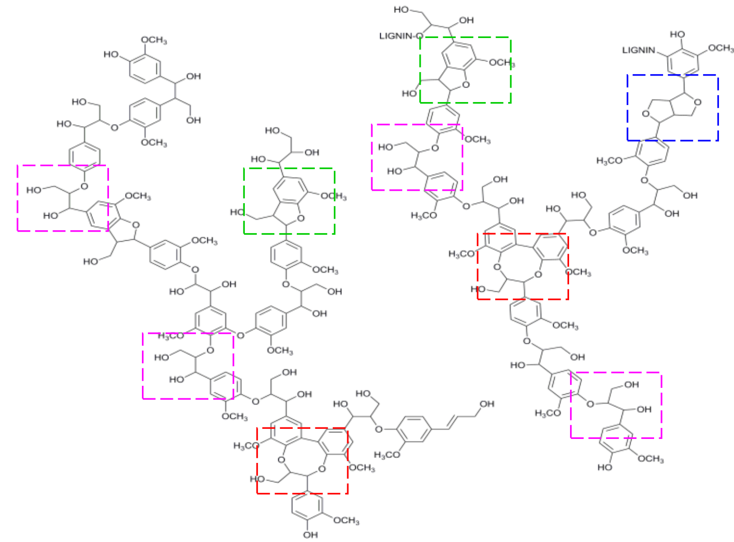
Biorefinery is a process to obtain biofuel, power, heat, value-added chemicals based on ***cyclic, renewable, biodegradable*** feedstock (biomass).
We studied *Arundo Donax* as Feedstock for the isolation of High-Value Biomaterials: a simple process has been applied to obtain Cellulose nanocrystal and Lignin, followed by GPC.

ARUNDO DONAX (Giant Cane)

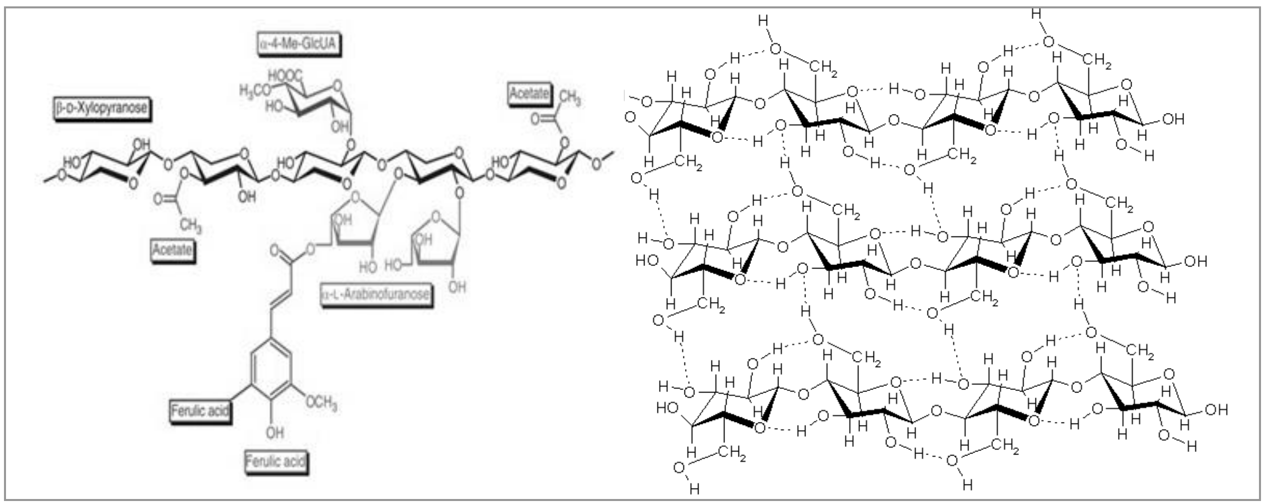
Annual renewability
Large annual biomass stock
Widespread availability
Ability to grow in different soil types and climatic conditions
(550 mln tons/year)

ARUNDO DONAX (composition)

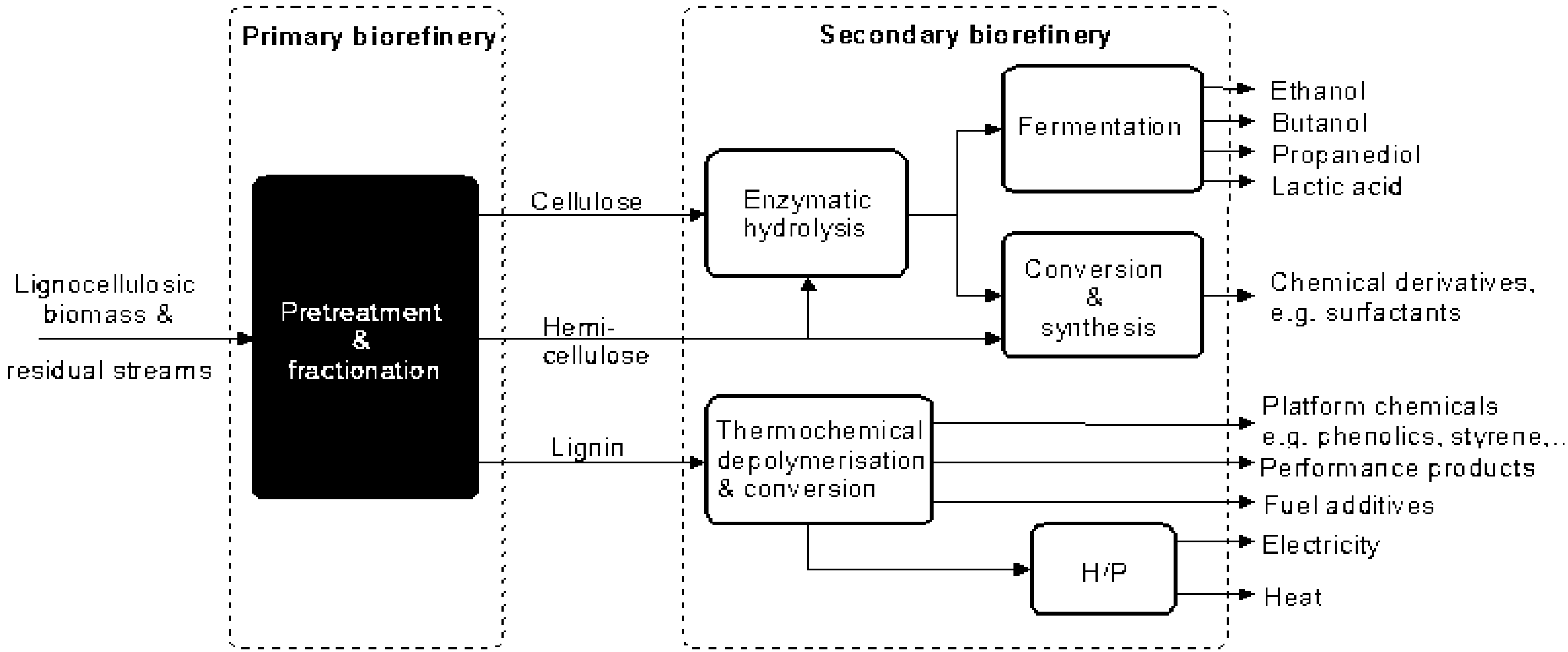
	%
Lignin	28
Hemicellulose	29
Cellulose	36
Ashes	4



β-O-4 β-β β-5 5-5’-O-4

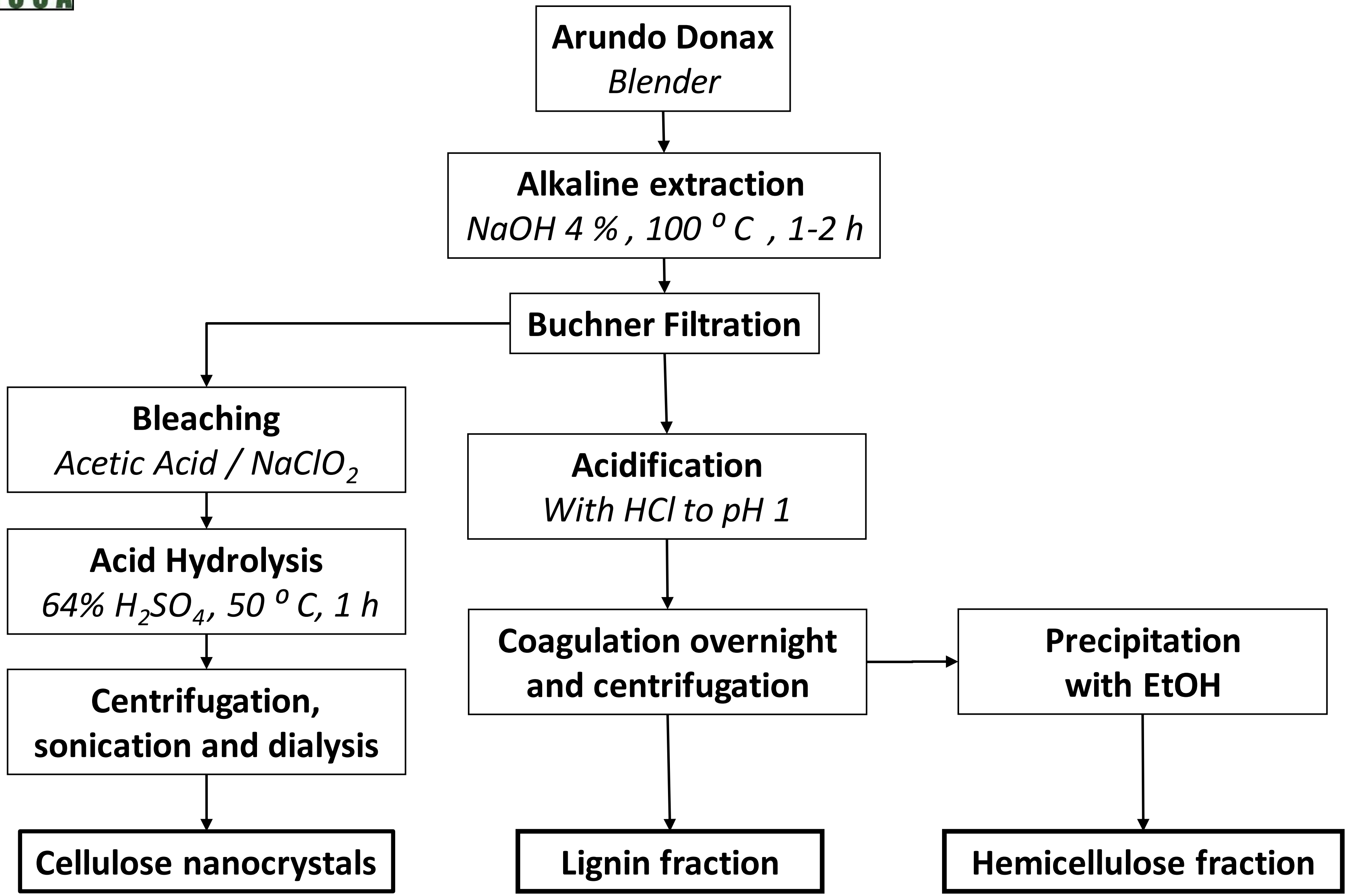


SCHEME OF BIOREFINERY PLANT



lignocellulose pretreatment to fractionate the recalcitrant lignocellulose structure; enzymatic hydrolysis of the isolated cellulose moiety, by which cellulases hydrolyze reactive intermediates to fermentable sugars; and fermentation, which produces cellulosic ethanol or other bio-based chemicals

BIOREFINERY PROCESS



ANALYTICAL PROBLEMS

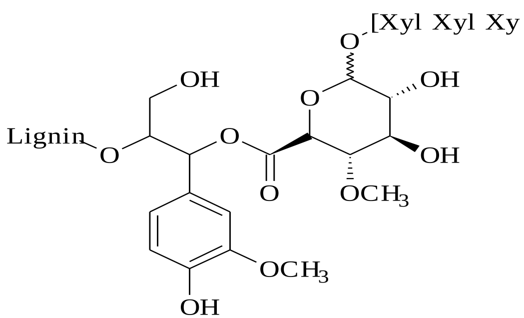
•Qualitative analysis of different fractions

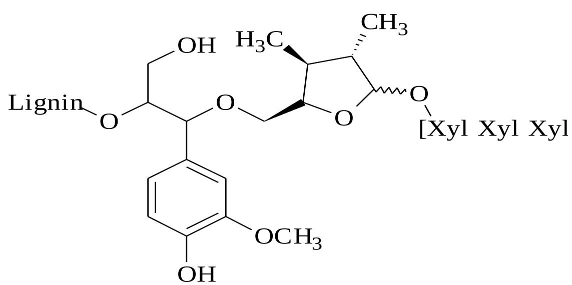
•complete solubilization of the materials under investigation and a homogeneous derivatization reaction

•Qualitatative analysis of LCC Present in different fractions

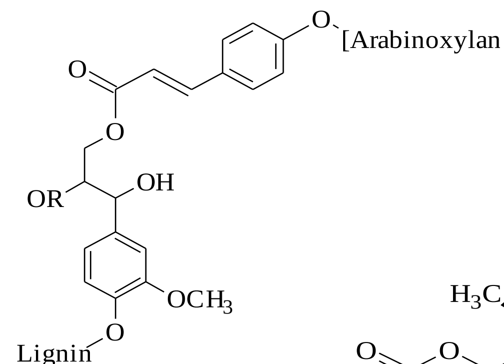
LIGNIN-CARBOHYDRATE COMPLEXES (LCCs)

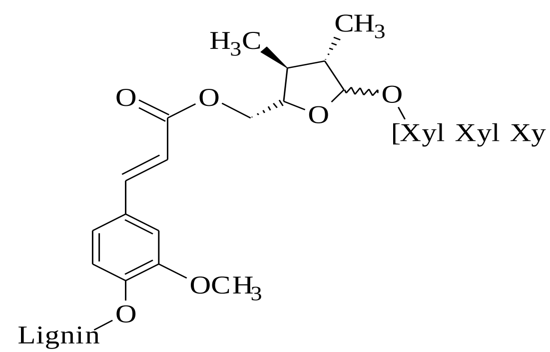
In wood, LCCs mainly consist of ester and ether linkages connecting sugar hydroxyls of hemicellulose to the α-carbanol of phenylpropane subunits in lignin.





In herbaceous plants, lignin and hemicellulose are connected through a phenolic bridge. Ferulic and p-coumaric acids are esterified to hemicelluloses and lignin, respectively.

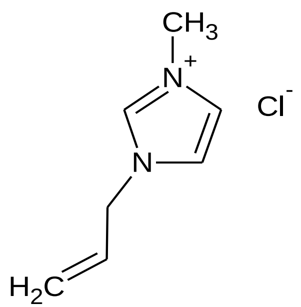




Crestini C.; Argyropoulos D.S. Structural Analysis of Wheat Straw Lignin by Quantitative ^{31}P and 2D NMR Spectroscopy. The Occurrence of Ester Bonds and β-O-4 Substructures. *J. Agric. Food Chem*. **1997**, 45, 1212-1219

The complex structure and the tridimensional lignin network that binds lignocellulosic components together makes it practically impossible to dissolve lignocellulosic materials in their native form in conventional solvents

IONIC LIQUIDS (ILs)



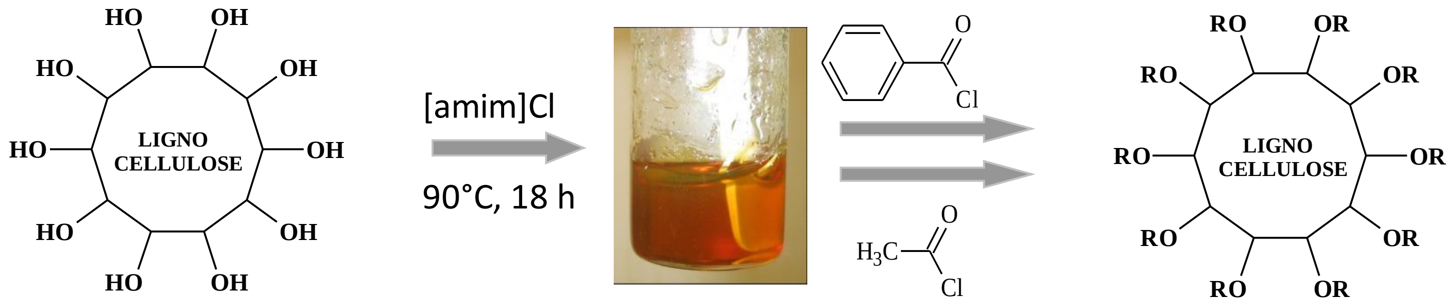
1-allyl-3-methylimidazolium chloride - [amim]Cl

- ✓ The aromatic electronrich cationic moiety creates strong interactions for polymers which undergoes π-π stacking (lignin)
- ✓ The chloride anion is the most efficient in disrupting the extensive inter- and intramolecular H-bonding interactions present in wood (cellulose) allowing the IL to diffuse into the interior of the material

t_0 **20 min** **50 min** **2 h**

Fluorescence images of a stem of switchgrass treated with ionic liquid. The organized cell wall structure has been completely broken down.

BENZOYLATION AND ACETYLATION OF MILLED NATIVE SUBSTRATES IN IONIC LIQUID FOR GPC-UV ANALYSES



Aliphatic and aromatic hydroxyls from cellulose, hemicellulose and lignin

R = CH_3CO, PhCO

ACETYLATION vs **BENZOYLATION**

ACETYLATION

GPC-UV (280 nm)

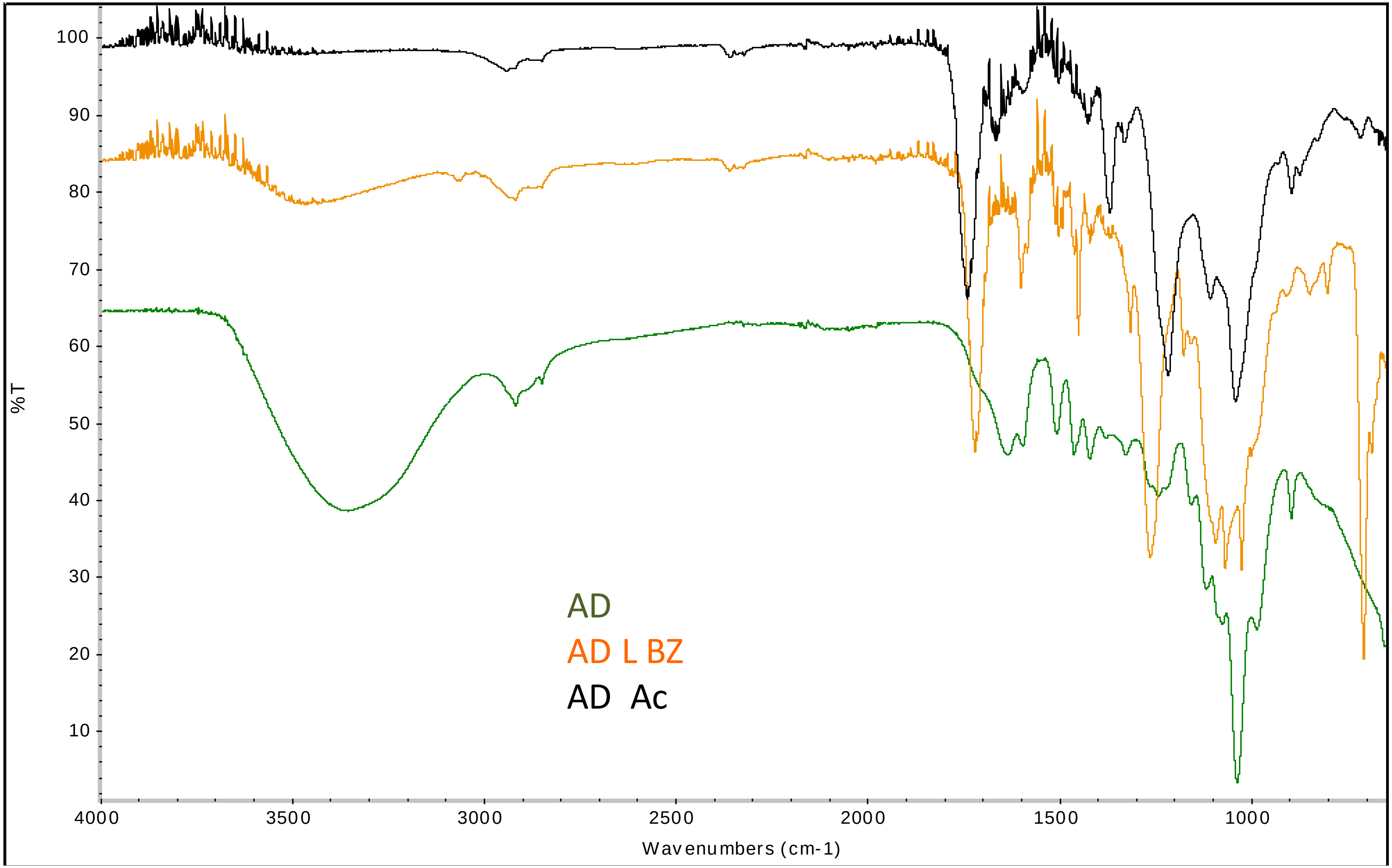
- ACETYLATED FREE LIGNIN: RESPONSE (aromatic rings)
- ACETYLATED LCCs: RESPONSE (aromatic rings)
- ACETYLATED FREE POLYSACCHARIDES: **NO RESPONSE** (none aromatic rings)

BENZOYLATION

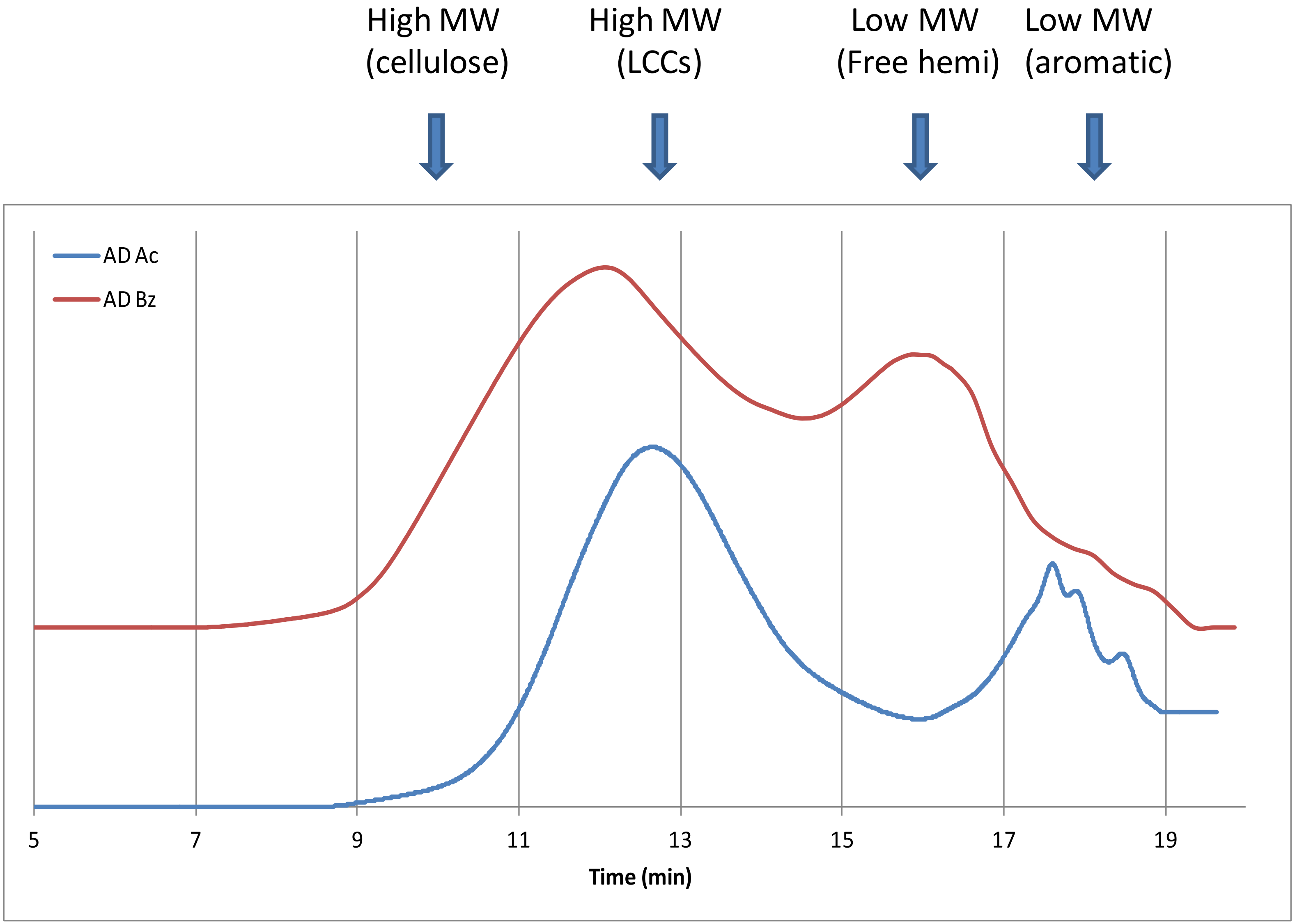
GPC-UV (240 nm)

- BENZOYLATED FREE LIGNIN: RESPONSE (more aromatic rings)
- BENZOYLATED LCCs: RESPONSE (more aromatic rings)
- BENZOYLATED FREE POLYSACCHARIDES: RESPONSE (aromatic rings)

BENZOYLATION AND ACETYLATION OF MILLED NATIVE SUBSTRATES IN IONIC LIQUID FOR GPC-UV ANALYSES

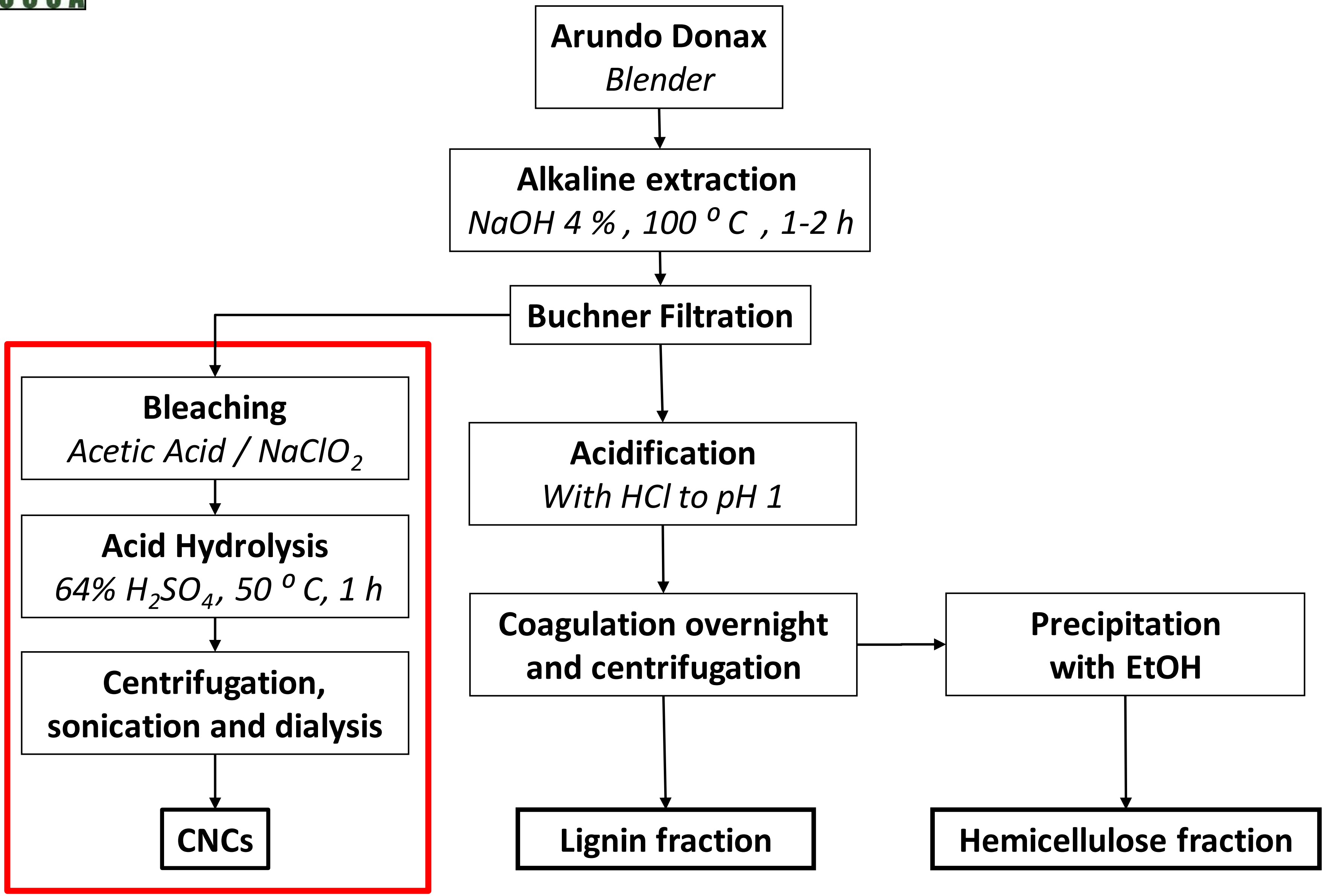


ARUNDO DONAX CHARACTERIZATION BY GPC



A. Salanti, L. Zoia, E-L Tolppa, and M.Orlandi Biomacromolecules (2012), 13, 445-454

ARUNDO DONAX CHARACTERIZATION: CNCs ISOLATION



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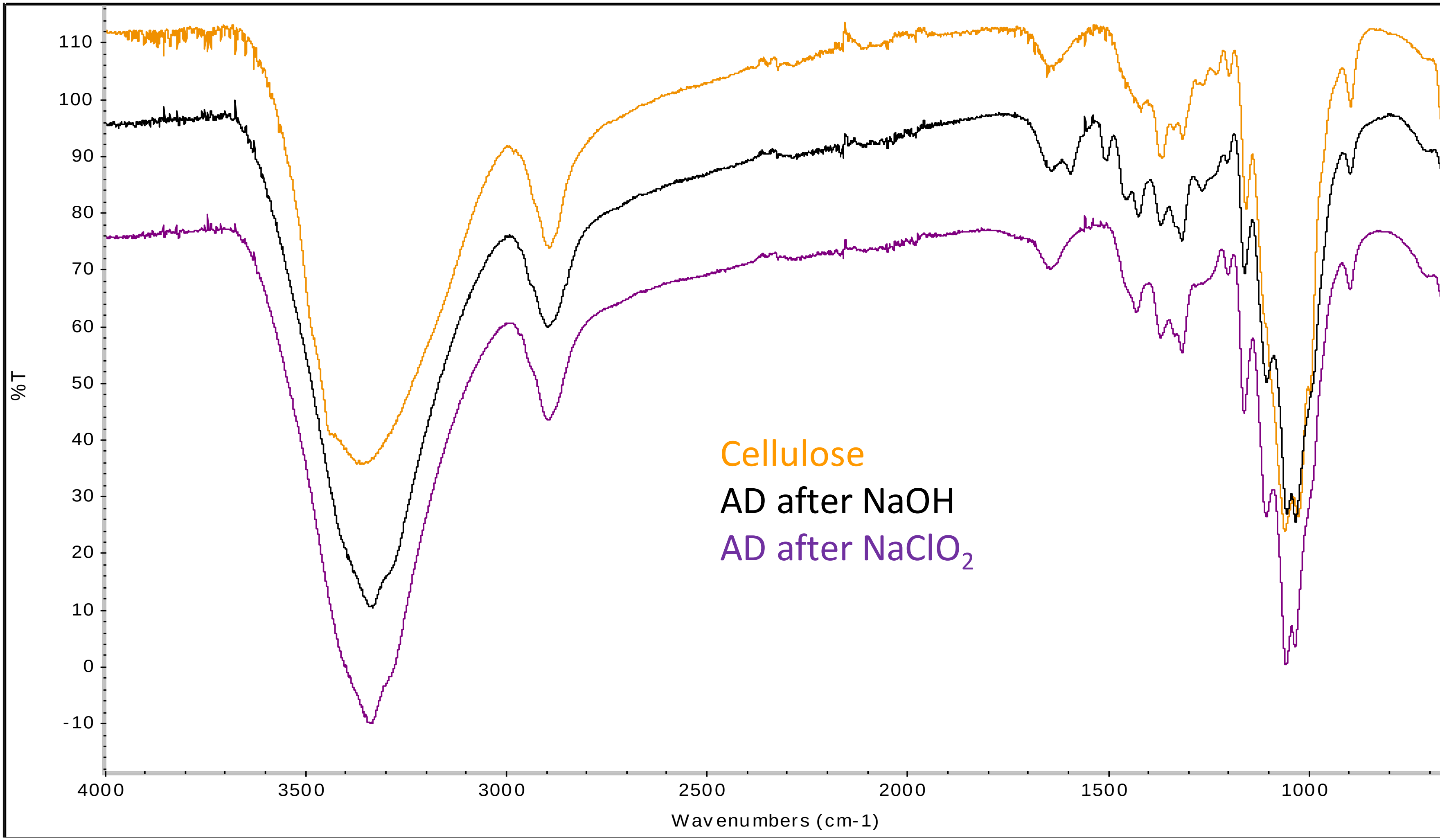
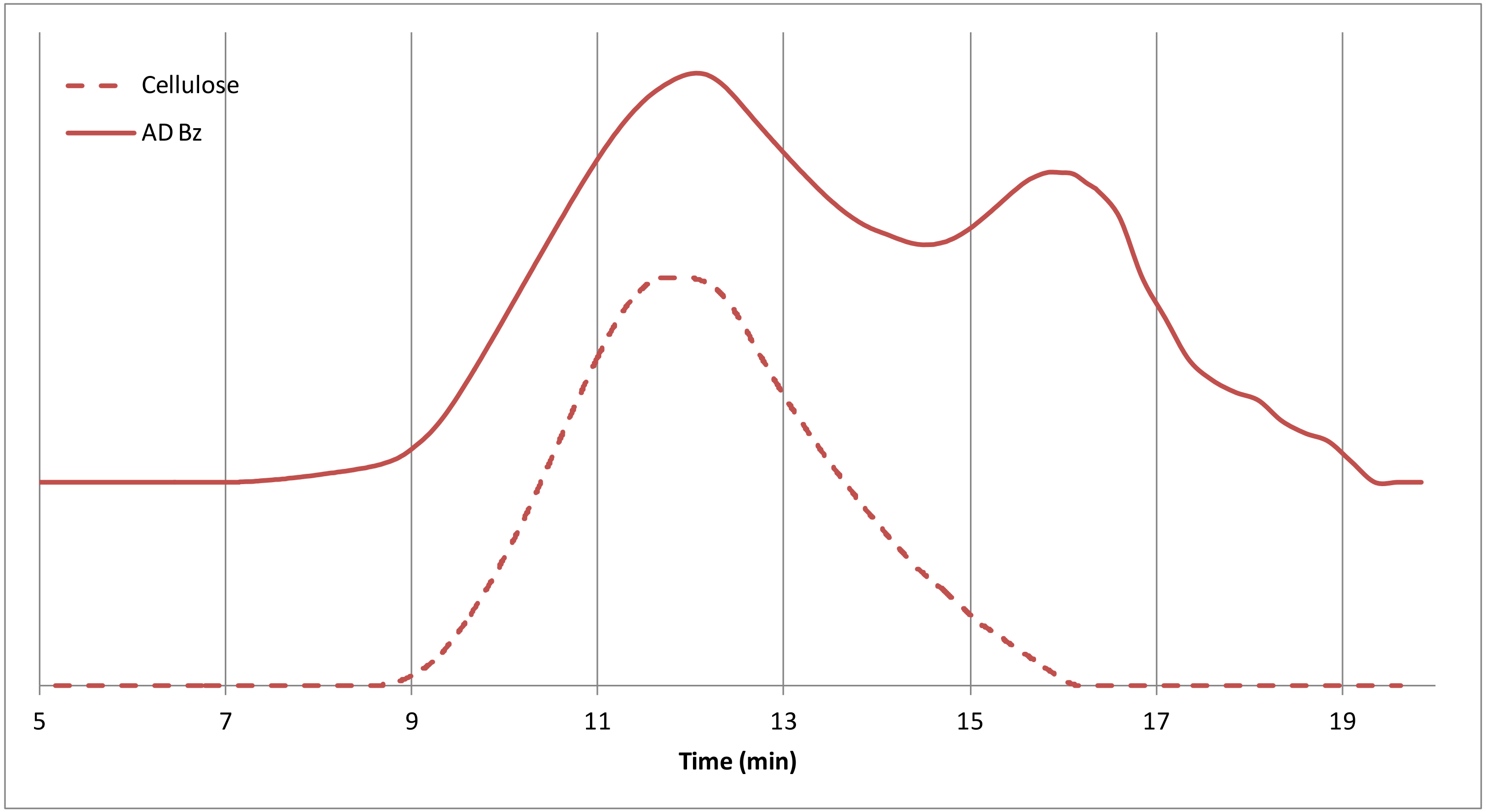


ARUNDO DONAX CHARACTERIZATION: CNCs ISOLATION

AD benzoylated vs AD after $NaClO_2$ benzoylated (cellulose)



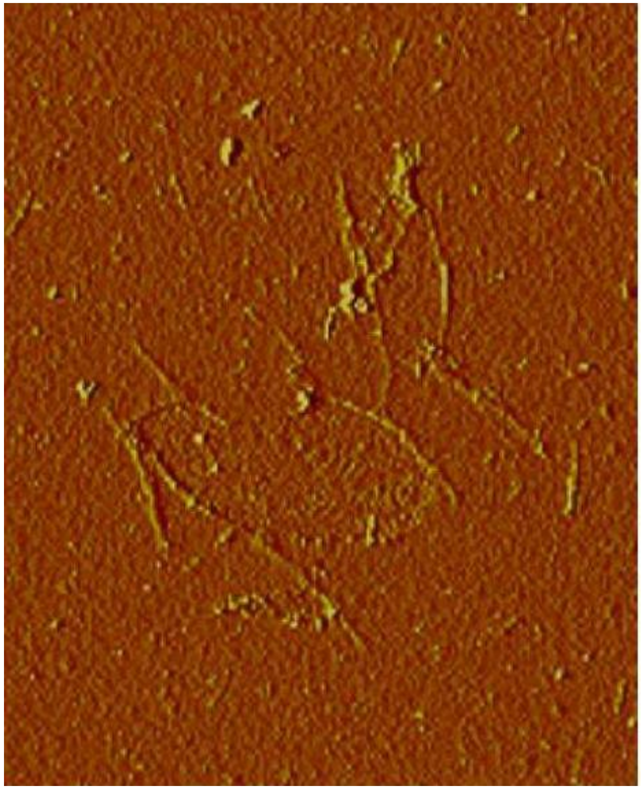
ARUNDO DONAX CHARACTERIZATION: CNCs ISOLATION

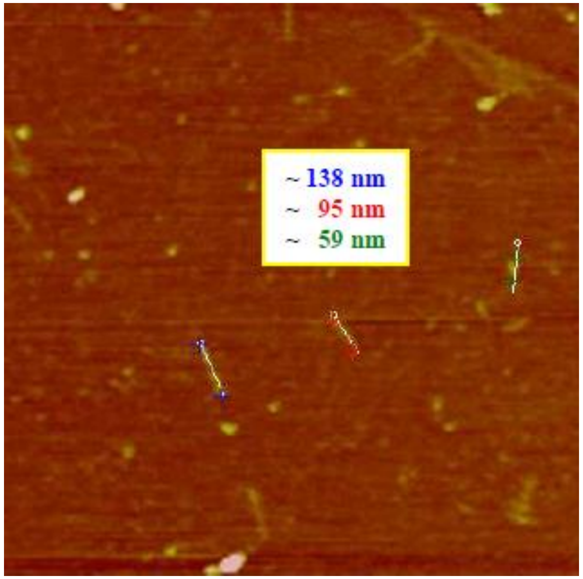
	Weight (g)
Starting AD	10
After NaOH	4,5
After $NaClO_2$	4
CNCs	0,8

200 ml of a stable suspension 0,4 % w/v of CNCs has been obtained

ARUNDO DONAX CHARACTERIZATION: CNCs ISOLATION

AFM Analyses

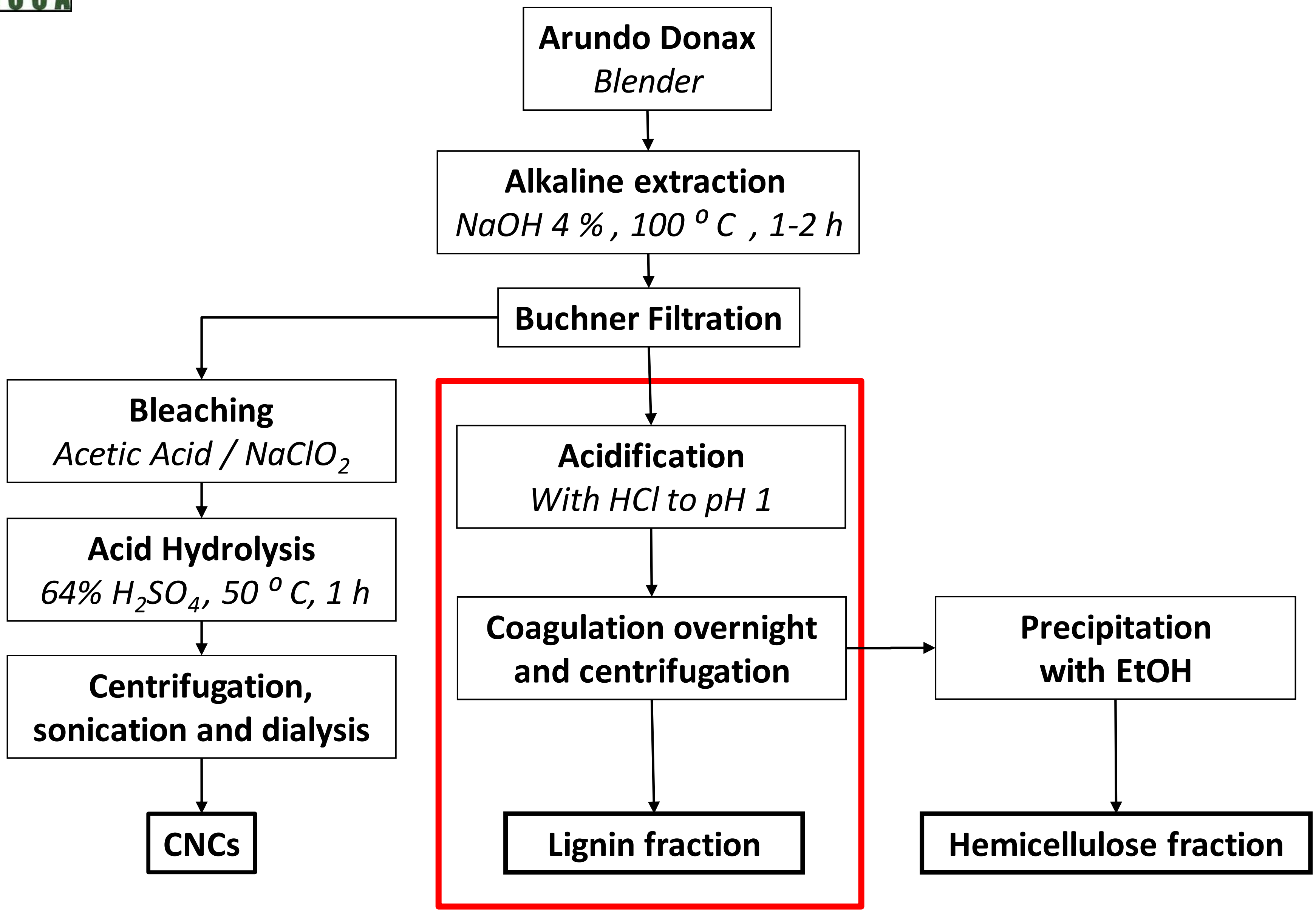




SEM and TEM characterizations are on going.

CNCs have great potential as reinforcing agents in nanocomposites due to their size and the possibility of chemically modifying their surface.

ARUNDO DONAX CHARACTERIZATION: LIGNIN RECOVERY



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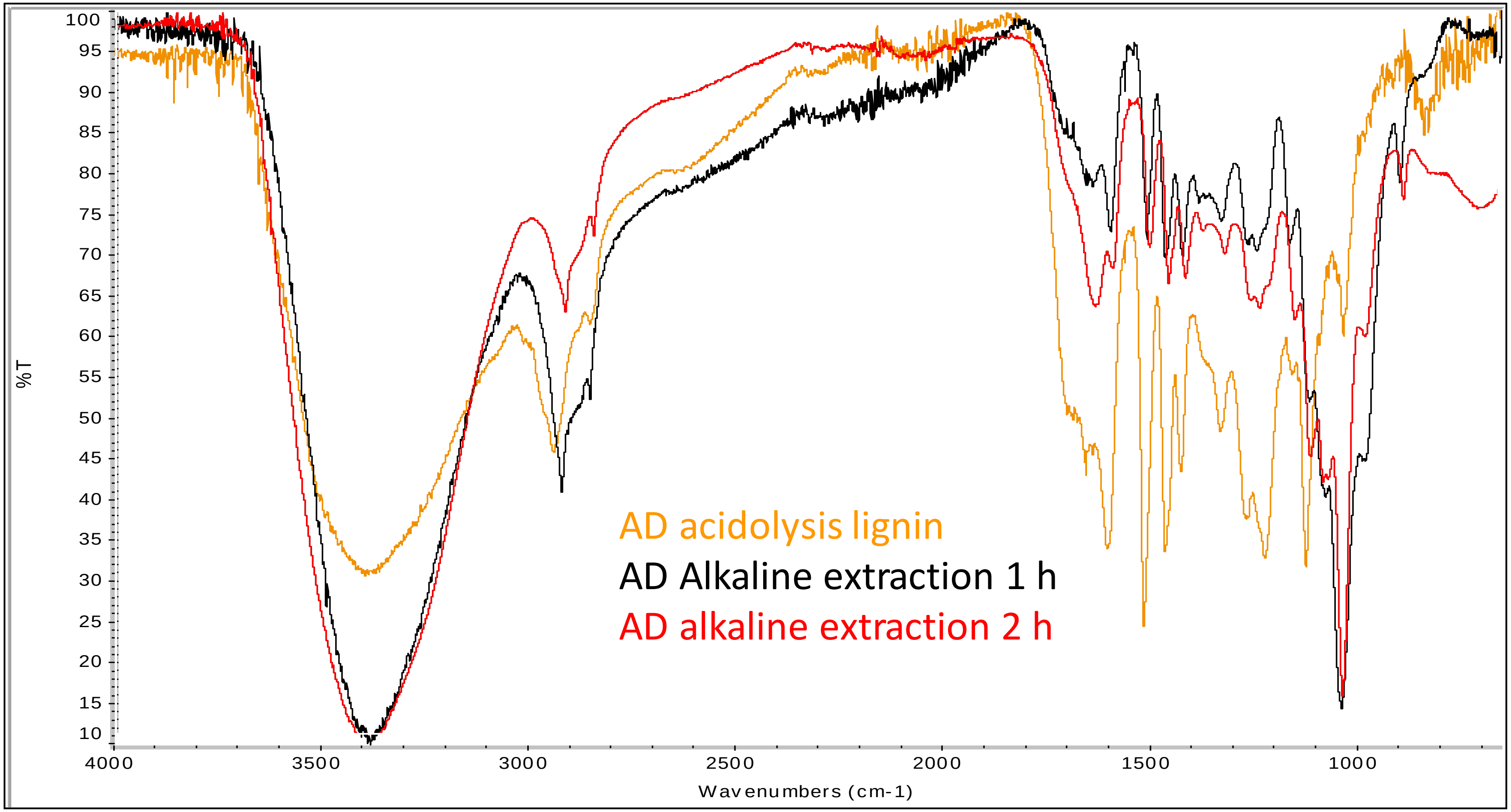

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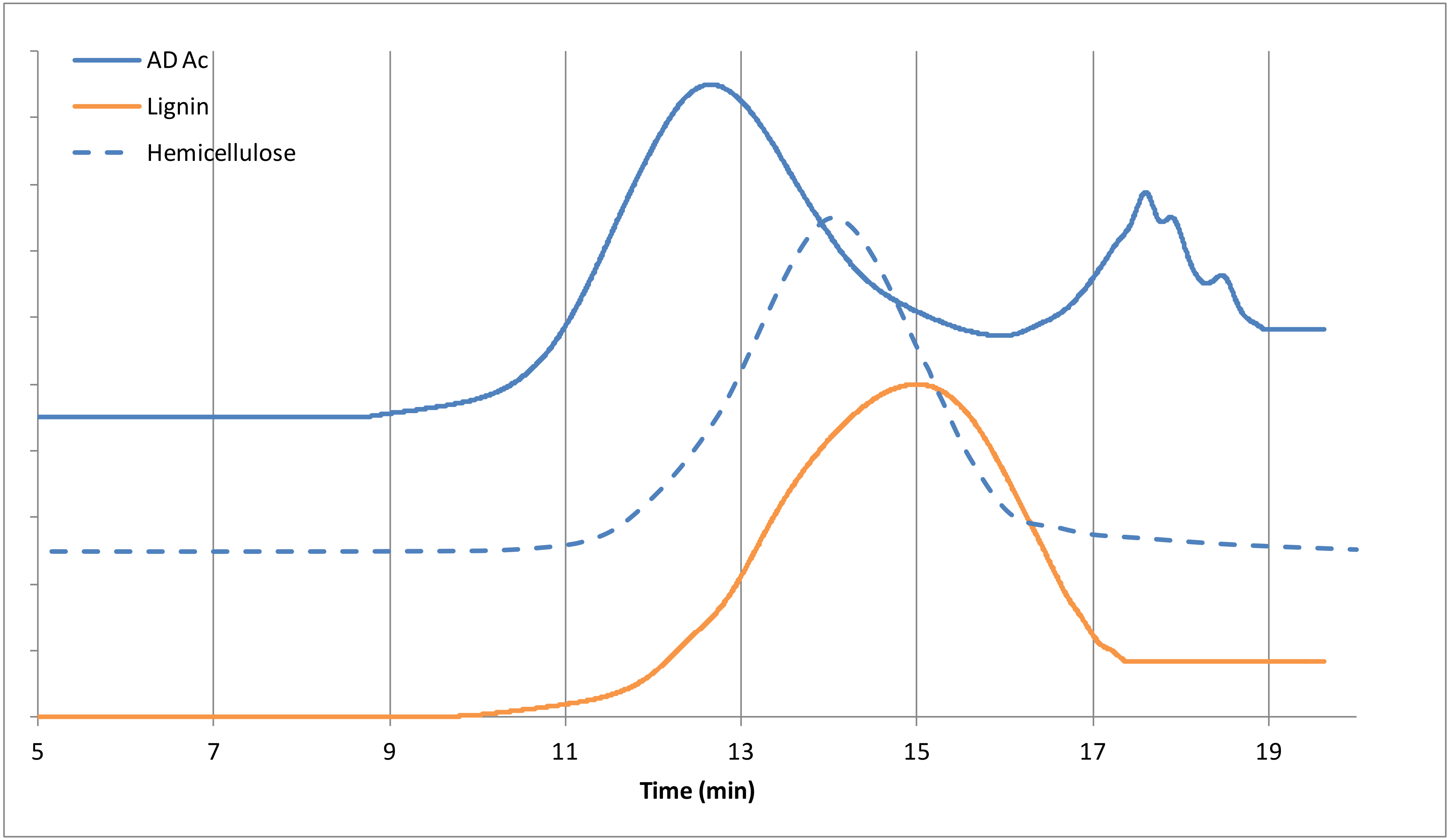

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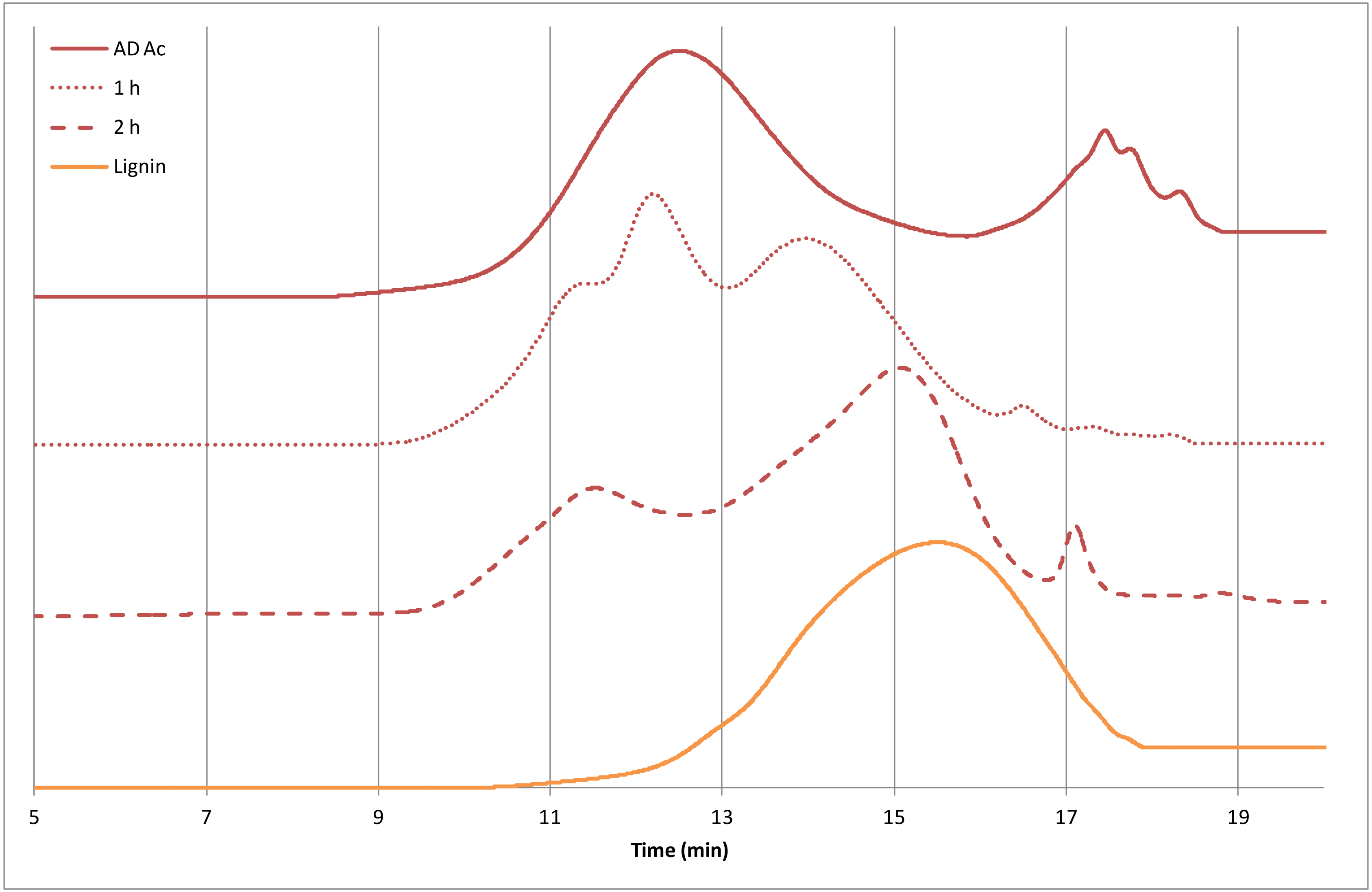

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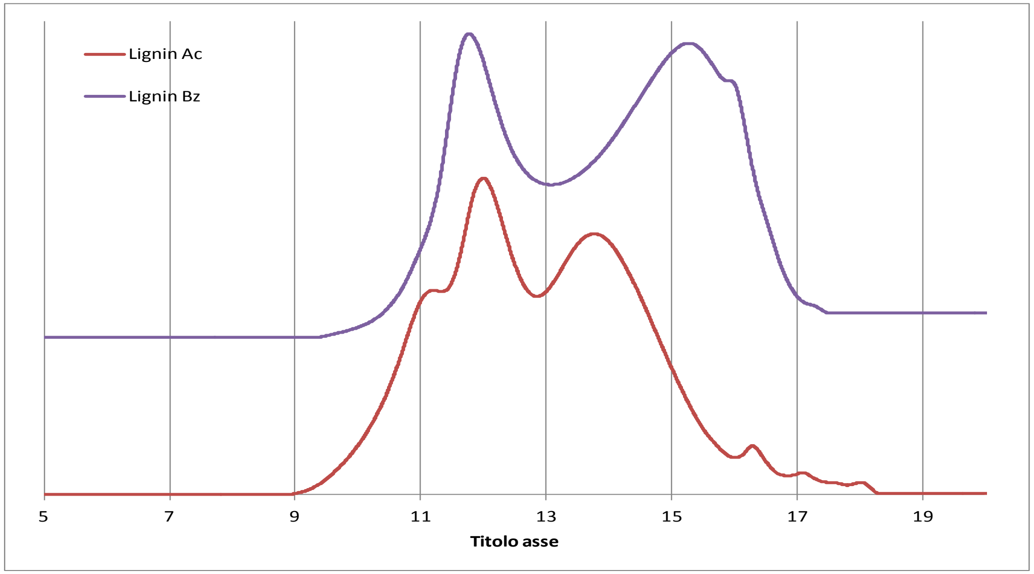
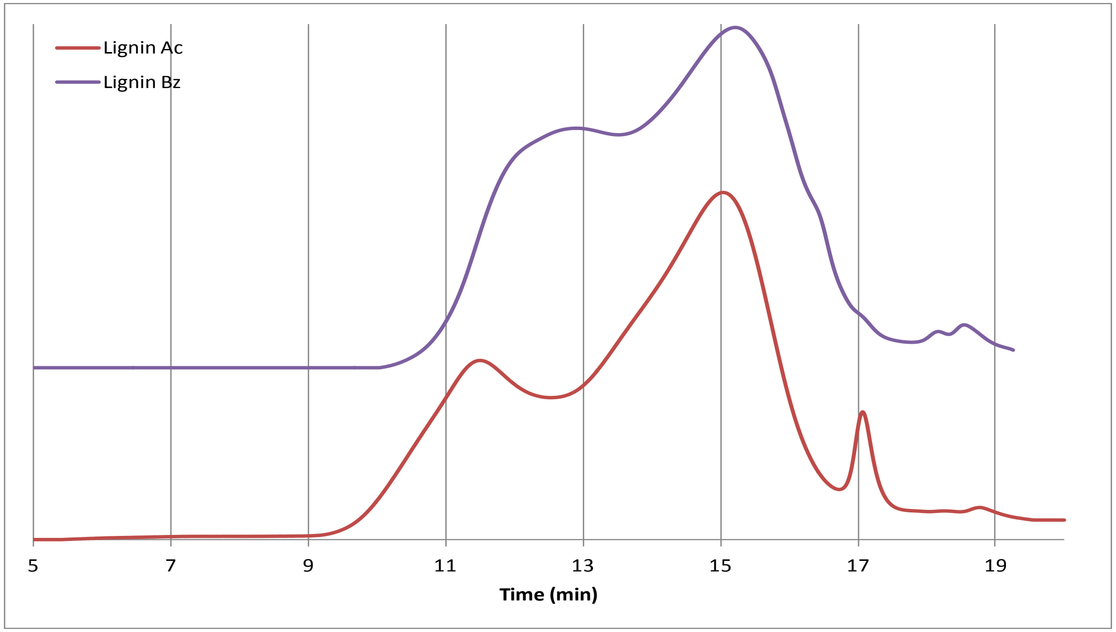


Lignin fraction 1 h

Lignin fraction 2 h



ARUNDO DONAX CHARACTERIZATION: LIGNIN RECOVERY

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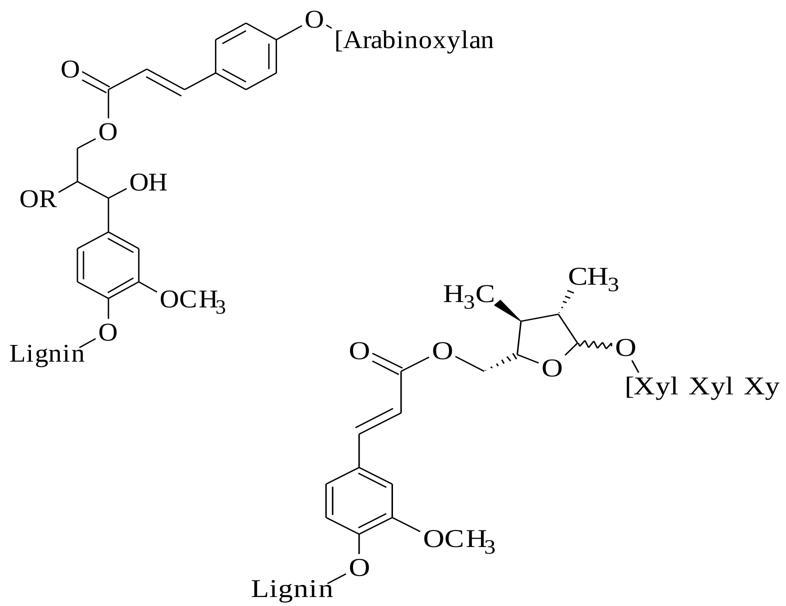
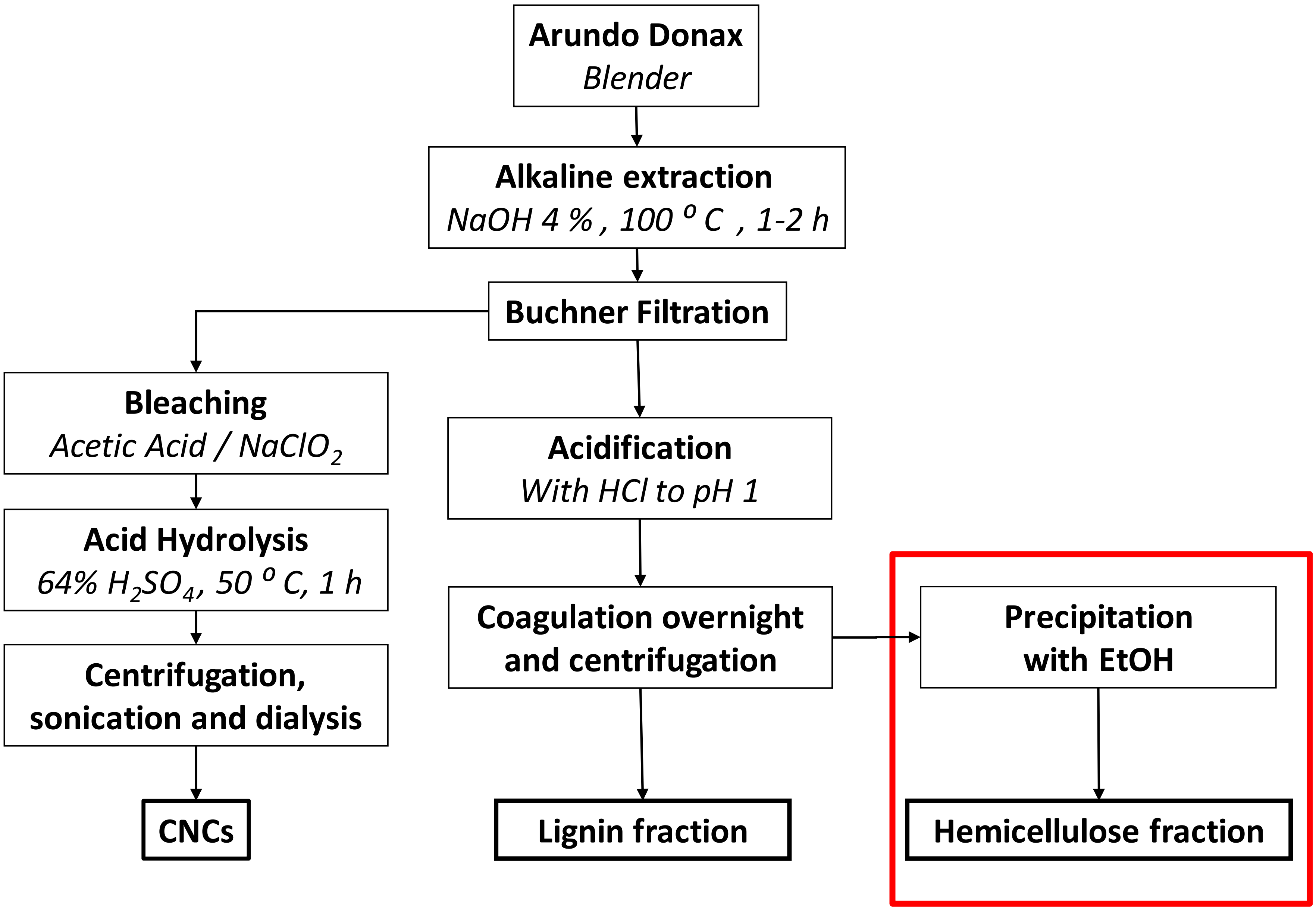
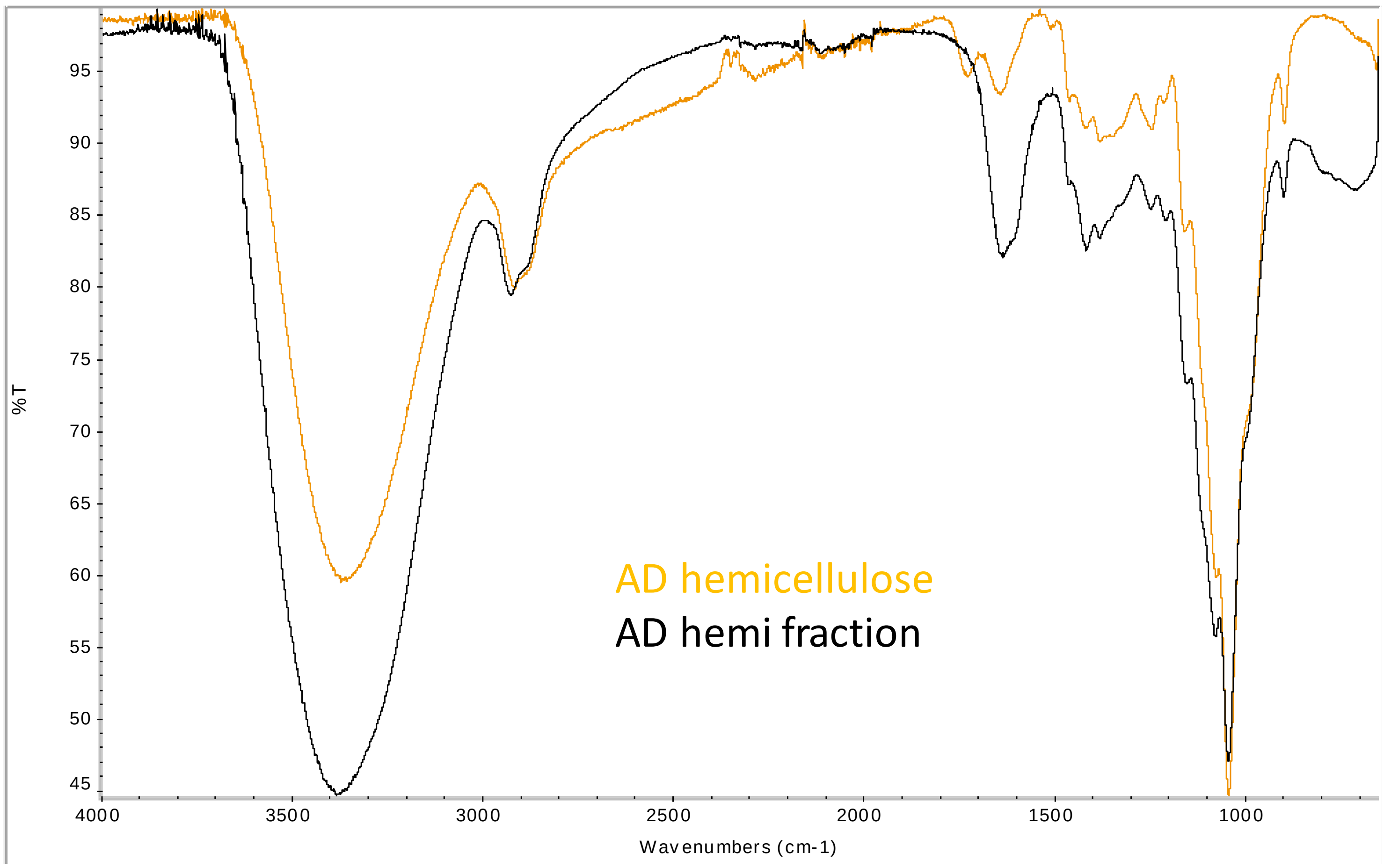


ARUNDO DONAX CHARACTERIZATION: HEMICELLULOSE RECOVERY



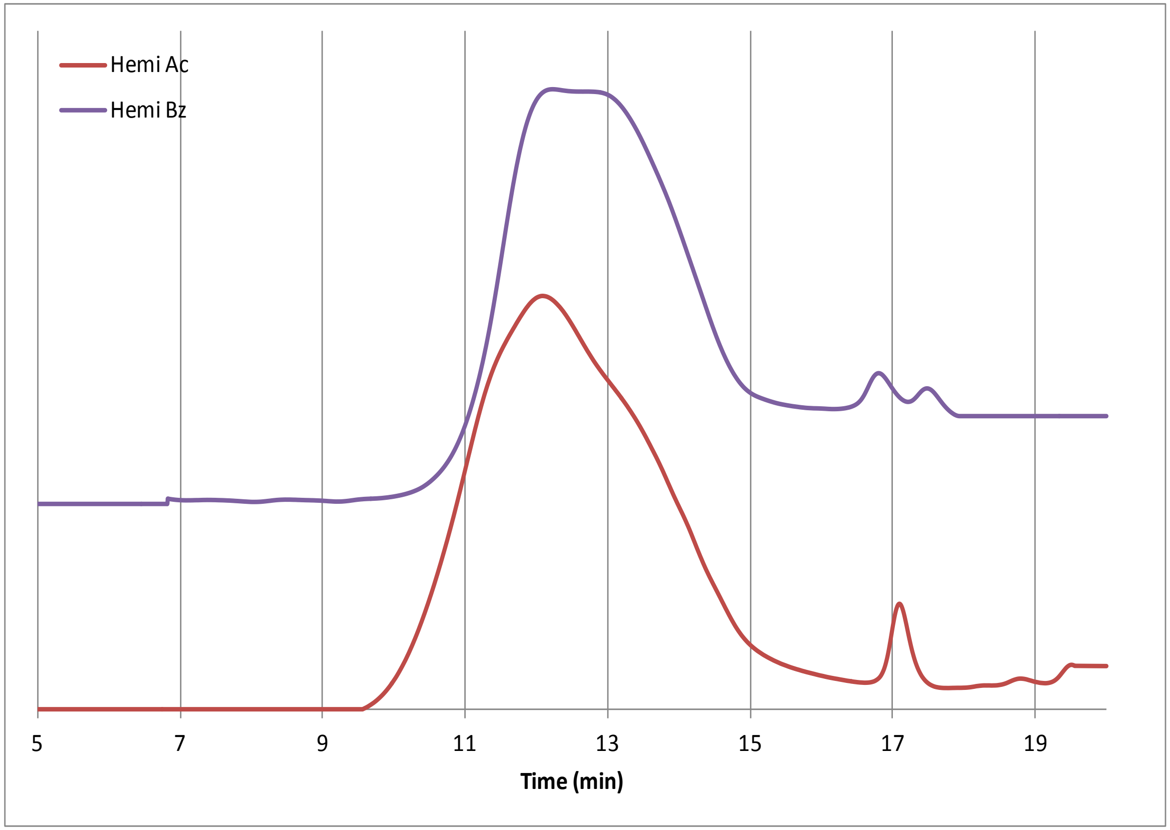
ARUNDO DONAX CHARACTERIZATION: HEMI RECOVERY

After lignin precipitation (2 h sample) :
10 Fold dilution with EtOH and centrifugation (1 g)



ARUNDO DONAX CHARACTERIZATION: HEMI RECOVERY

After lignin precipitation:
1- 10 Fold EtOH and centrifugation



Recovery of LCCs and hemicellulose

CONCLUSION REMARKS

With the simple process used, it was possible to recovery from 10 g of blended *Arundo donax*:

- 0,8 g of CNCs (from around 3 g of cellulose);
- 1 g of hemicellulose (from around 3 g of hemicellulose);
- 2,5 g of lignin (from 2 g of lignin in the starting AD);

By GPC it was possible to follow the process:

- The use of Ionic liquid permits the complete solubilization of the materials under investigation and a homogeneous derivatization reaction;
- Homogeneous derivatization reaction gives high solubility of all the samples in THF (chromatographic solvent);
- Different derivatizations permit to obtain information about the connection between the different lignocellulosic fraction;
- NaOH treatment solubilized almost all the hemicellulose and lignin.
- The connections between hemi and lignin were partially broken during the process.