

How to efficiently extract phenolic compounds from lignin bio-oil ?

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Assistant Professor

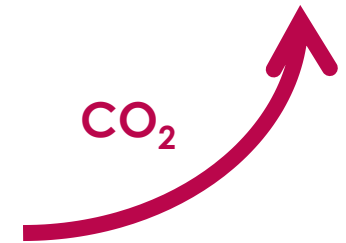
Laboratoire Réactions et Génie des Procédés, Nancy, France



Context



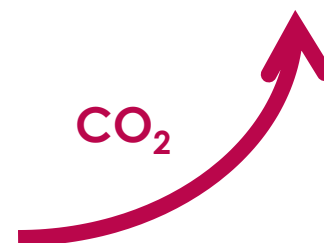
Global warming



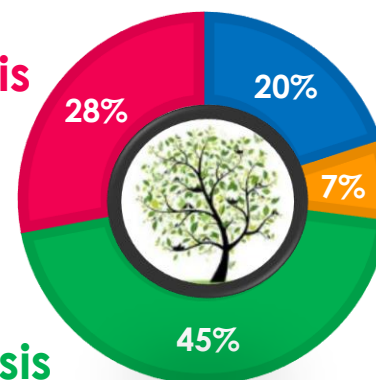
Context



Global warming



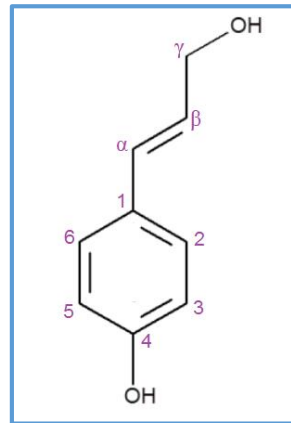
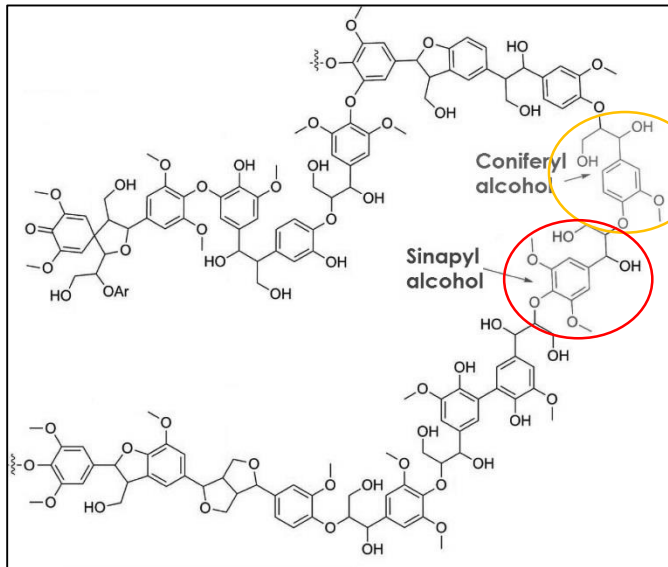
Hemicellulosis



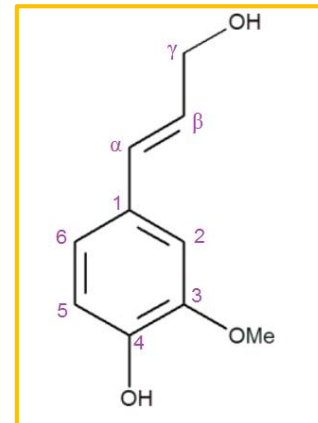
Lignin

Cellulosis

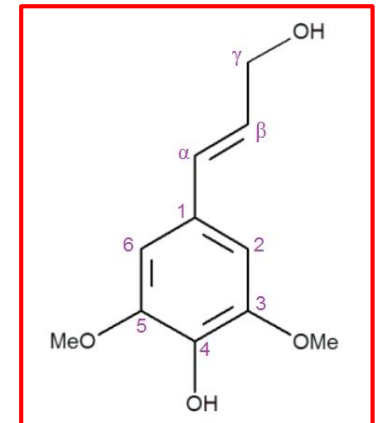
Lignin's structure



p-coumaryl alcohol

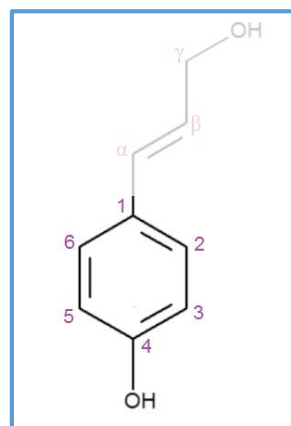
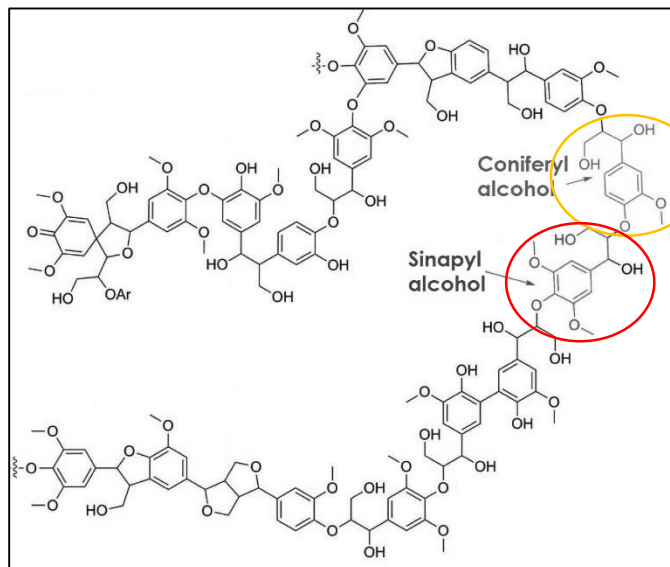


coniferyl alcohol



sinapyl alcohol

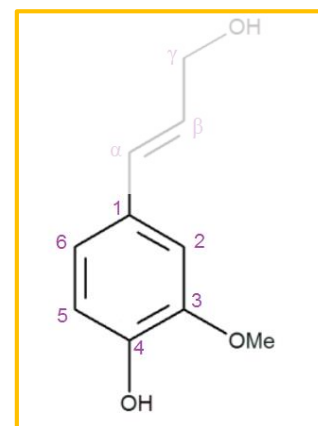
Lignin's structure



p-coumaryl alcohol



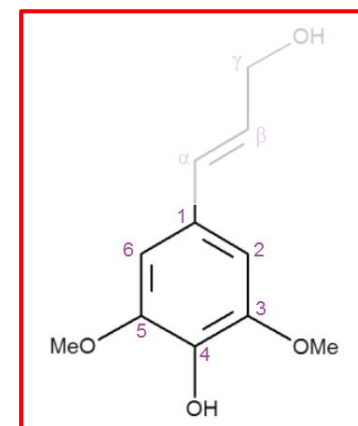
p-hydroxyphenyl unit



coniferyl alcohol



guaiacyl unit

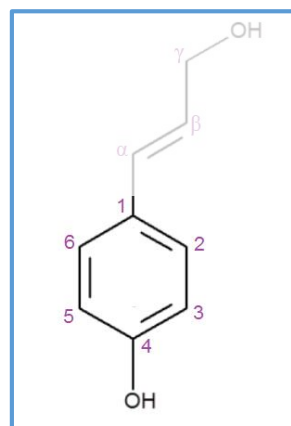
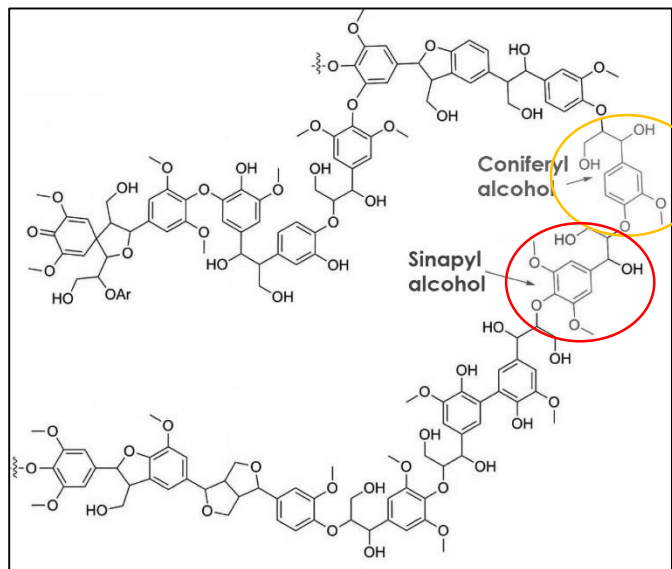


sinapyl alcohol



sinapyl unit

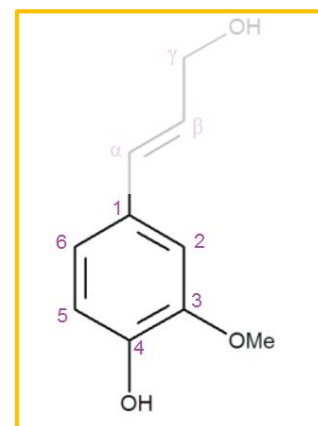
Lignin's structure



p-coumaryl alcohol



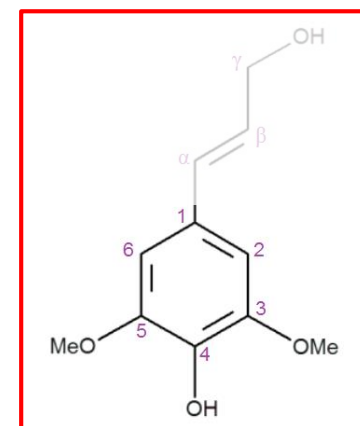
p-hydroxyphenyl unit



coniferyl alcohol



guaiacyl unit



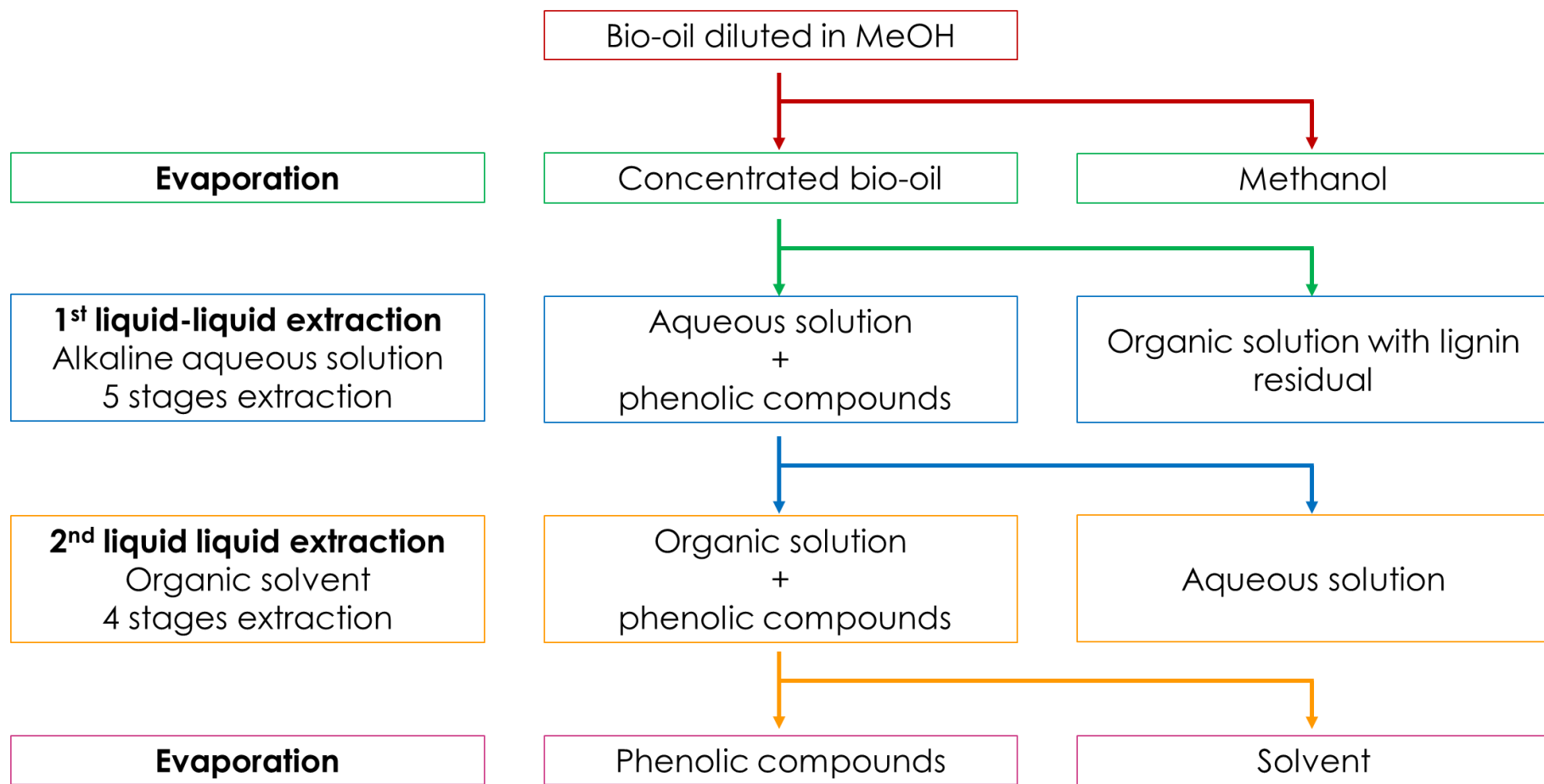
sinapyl alcohol



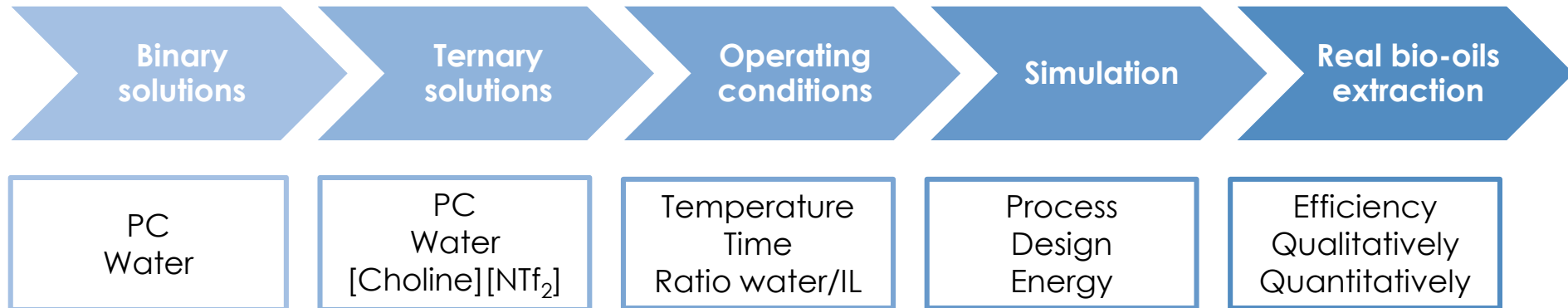
sinapyl unit

Flash pyrolysis
High temperature - Low residence time

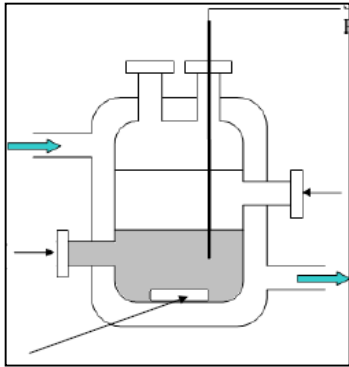
Extraction process



Plan



Binary solutions (PC + water)



Shake Flask method

Jacketed glass cell + Thermostatic bath
Stirring + Settling down
Analysis by UV spectroscopy

Solid-liquid equilibria

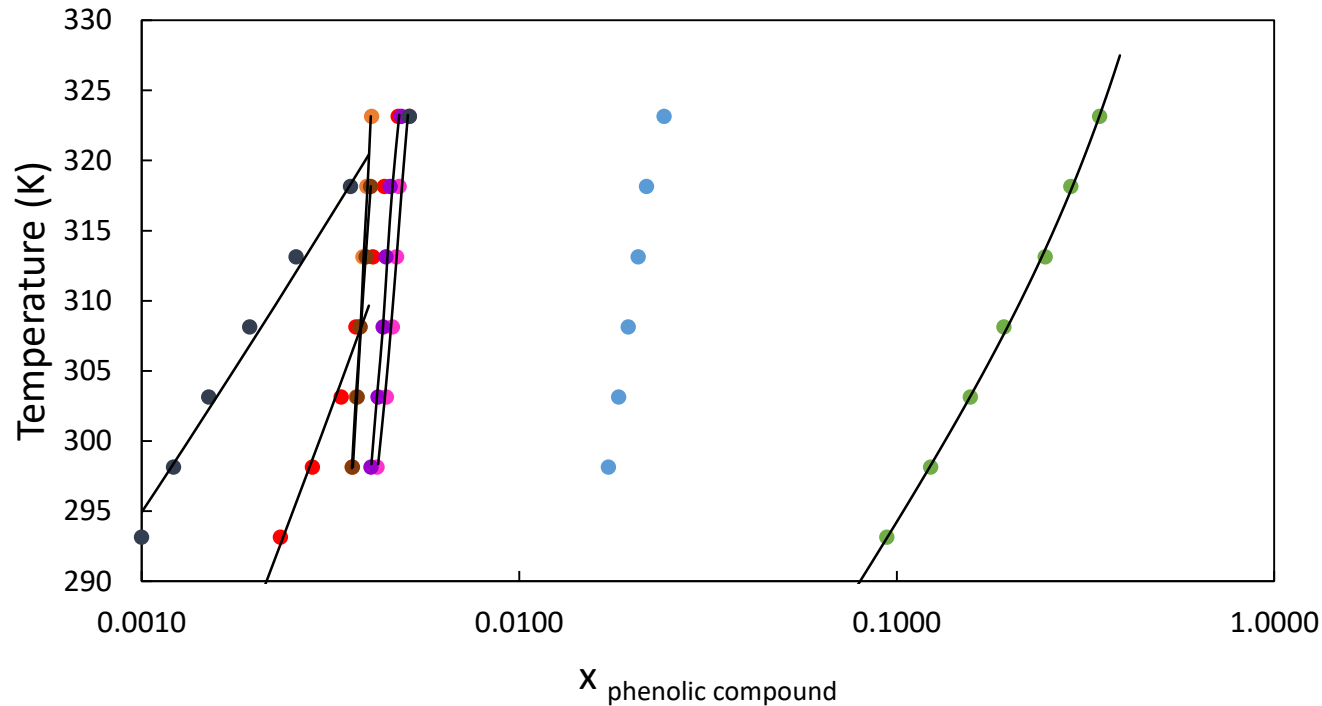
Syringol - water
Pyrocatechol - water
Vanillin - water

Liquid-liquid equilibria

Phenol - water
Guaiacol- water
O-cresol- water
M-cresol - water
P-cresol - water

Reference : Phase equilibria of phenolic compounds in water or ethanol; L Cesari,
S Namysl, L Canabady-Rochelle, F Mutelet; Fluid Phase Equilibria 453, 58-66

Binary solutions (PC + water)



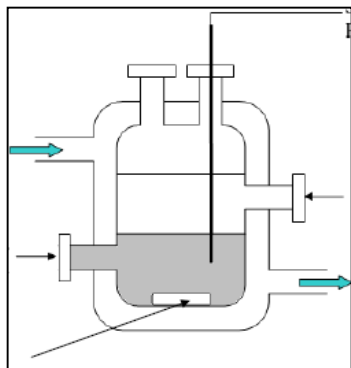
- Phénol
- Guaiacol
- Syringol
- Pyrocatechol
- O-crésol
- M-crésol
- P-crésol
- Vanilline



Logarithmic scale

Determination of the interaction parameters of the NRTL model
Relative deviation on $x < 1\%$

Ternary solutions (25°C)



Shake Flask method

Jacketed glass cell + Thermostatic bath
Stirring + Settling down

Analysis by gas chromatography

- Thermal Conductivity Detector
- Flame Ionization Detector

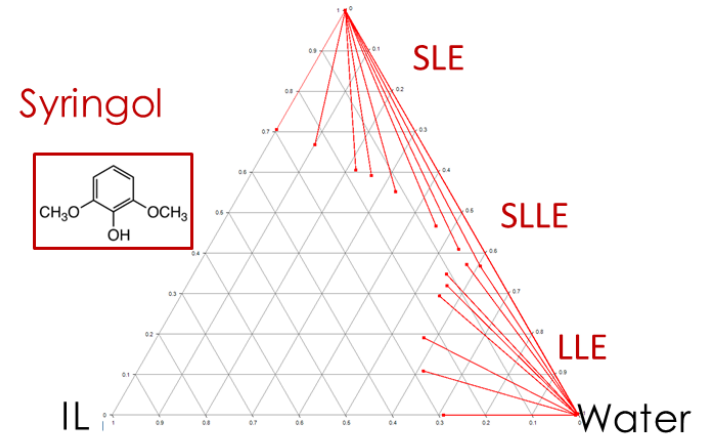
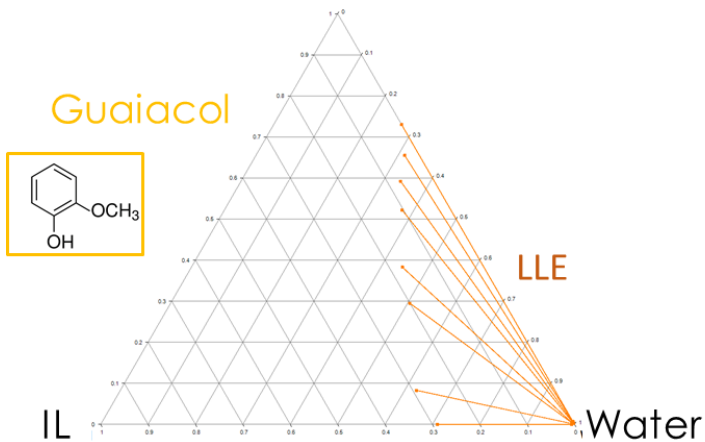
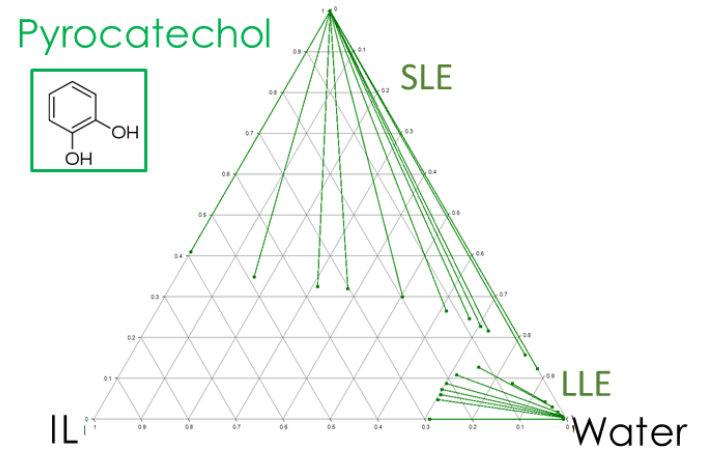
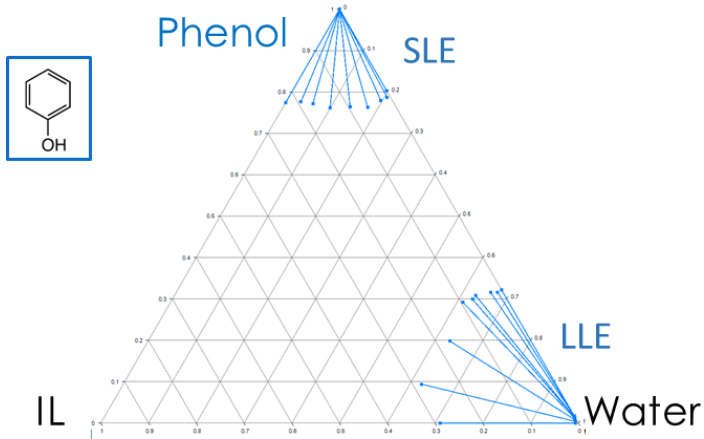


3 Compounds

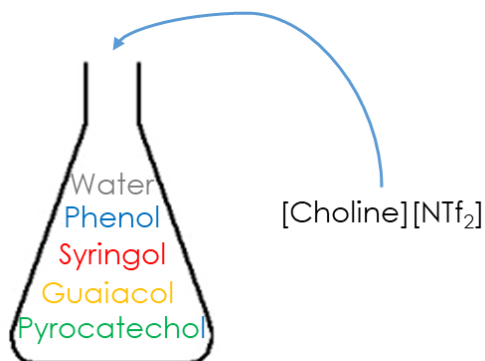
- Phenolic compound
- Water
- [Choline][Ntf2]

Reference : Extraction of phenolic compounds from aqueous solution using choline bis (trifluoromethylsulfonyl) imide; L Cesari, L Canabady-Rochelle, F Mutelet; Fluid Phase Equilibria 446, 28-35

Ternary diagrams (25°C)



Influence of parameters



Parameters :

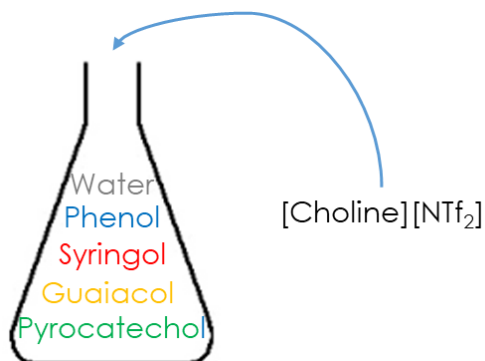
Time (0-6H)

Influence of **Temperature** (25-45°C)

Influence of **Ratio IL/water** (0.5-1-2)

% Extraction

Influence of parameters

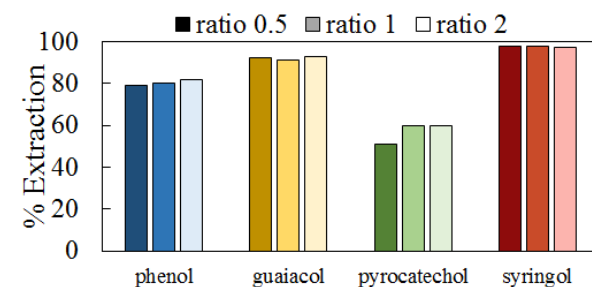
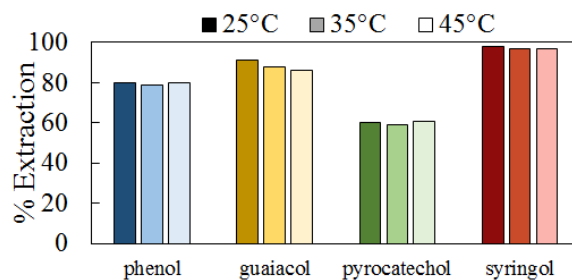
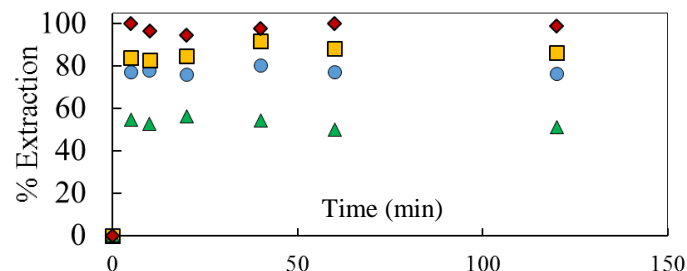


Parameters :

Time (0-6H)

Influence of **Temperature** (25-45°C)

Influence of **Ratio IL/water** (0.5-1-2)



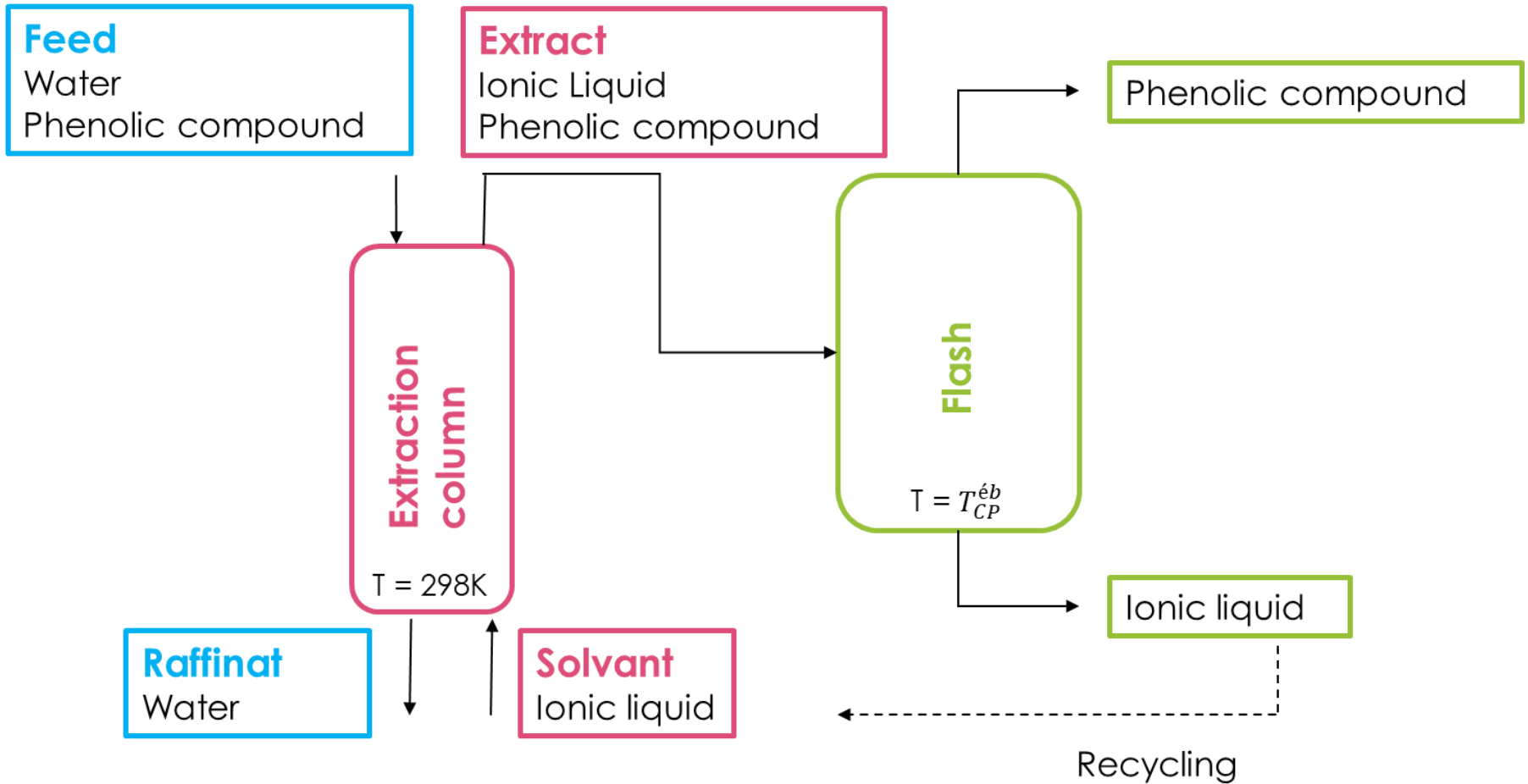
Results :

The liquid-liquid equilibria is reached quickly (< 5 minutes)

The temperature does not influence the LLE

The IL / water mass ratio has practically no influence on the extraction

Modelisation / Simulation



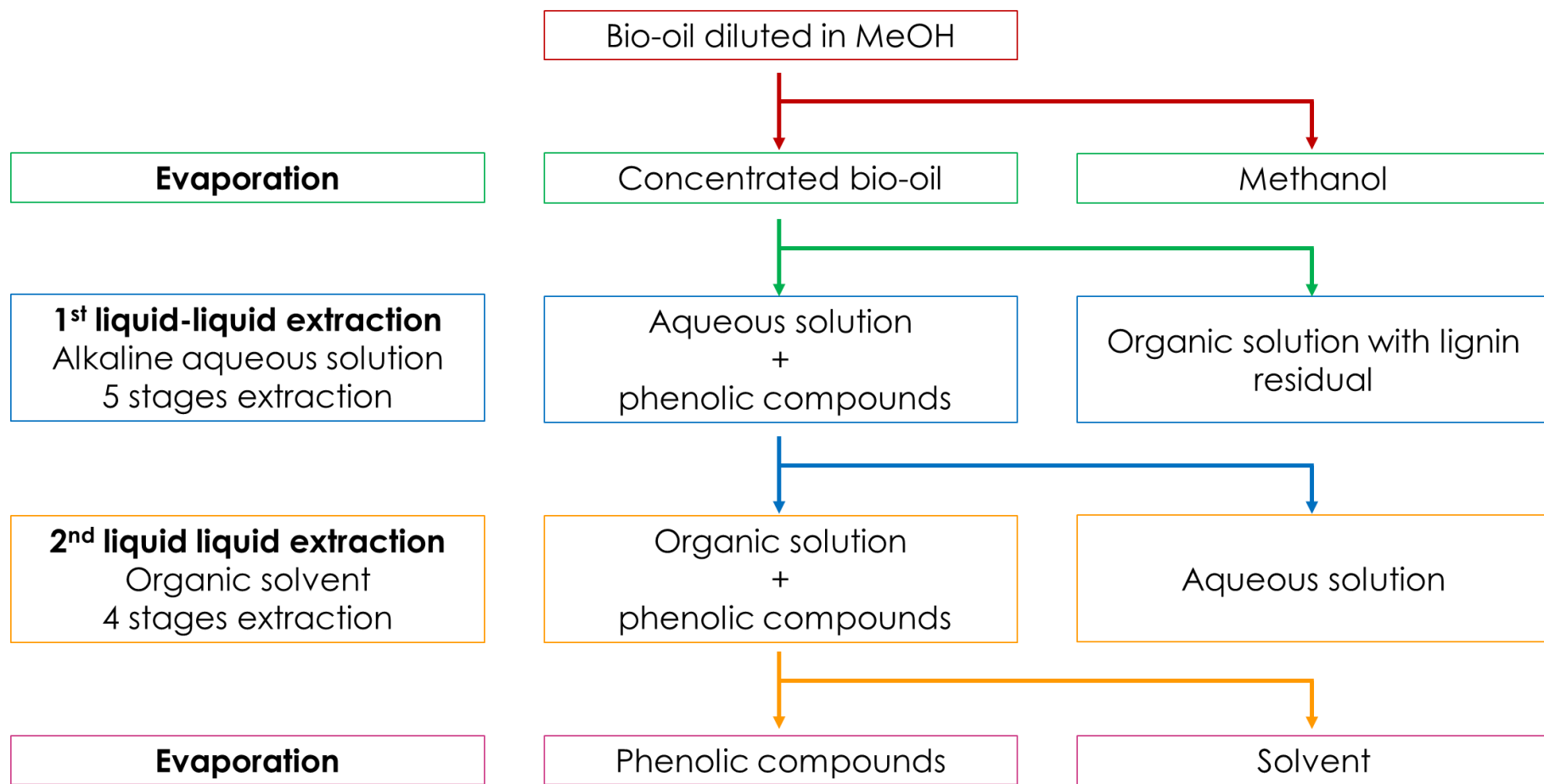
Modelisation

Hypothesis

- Counter-flow at 298.15K
- Mass fraction of phenolic compound in feed: 0.015
- Resulting extract and raffinate flows approximately equal the solvent and feed flows respectively
- Extraction effective at a 99.995% rate

Results				
Solvent	Compound	$\frac{\text{Solvent}}{\text{Feed}}$ ratio	Number of theoretical steps	Energy (MJ/kg compound)
[Choline][NTf ₂]	Phenol	0.3	7	10.75
	Guaiacol	0.3	4	3.41
	Syringol	0.1	7	6.57
	Pyrocatechol	1.3	7	45.64
Ethyl acetate	Guaiacol (X.Li et al. 2016)		3 (extraction) 8 (distillation)	12.42

Extraction process



Real bio-oils extractions



Solvent

Compounds

Phenol

O-cresol

P-cresol

Guaiacol

4-ethylphenol

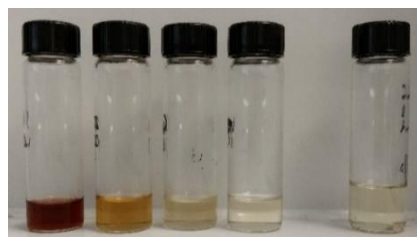
2-methoxy-3-methylphenol

2-methoxy-4-vinylphenol

Syringol

Separation of phenols from lignin pyrolysis oil using ionic liquid; L Cesari, L Canabady-Rochelle, F Mutelet;
Separation and Purification Technology 209, 528-534

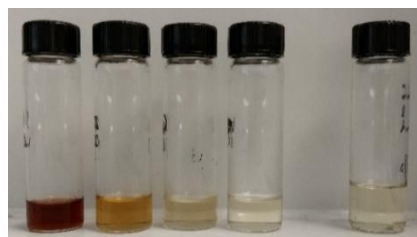
Real bio-oils extractions



Solvent	Ionic Liquid		
Compounds	1 st wash	2 nd wash	Total 2-stages
Phenol	69	21	90
O-cresol	55	13	68
P-cresol	63	13	76
Guaiacol	68	19	87
4-ethylphenol	92	n.d.	92
2-methoxy-3-methylphenol	41	n.d.	41
2-methoxy-4-vinylphenol	89	11	100
Syringol	80	20	100

Separation of phenols from lignin pyrolysis oil using ionic liquid; L Cesari, L Canabady-Rochelle, F Mutelet; Separation and Purification Technology 209, 528-534

Real bio-oils extractions



Solvent	Ionic Liquid			Ethyl acetate
Compounds	1 st wash	2 nd wash	Total 2-stages	Total 4-stages
Phenol	69	21	90	83
O-cresol	55	13	68	58
P-cresol	63	13	76	81
Guaiacol	68	19	87	89
4-ethylphenol	92	n.d.	92	70
2-methoxy-3-methylphenol	41	n.d.	41	28
2-methoxy-4-vinylphenol	89	11	100	96
Syringol	80	20	100	72

Separation of phenols from lignin pyrolysis oil using ionic liquid; L Cesari, L Canabady-Rochelle, F Mutelet;
Separation and Purification Technology 209, 528-534

Conclusion

Thermodynamique study

Experimental measurements

Determination of parameters for thermodynamic models

Extraction

Quick and efficient at room temperature

Requieres a few amount of ionic liquid

Process design

Creation of a simpler process

Design of smaller units

Lower energy consumption

Real study case

Confirmation of the [Choline][NTf₂] extraction efficiency

Thank you

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