



Universidad de Concepción



III Latin American Congress - Biorefineries - Ideas for a sustainable world

Fractionation of fast pyrolysis liquids for chemical applications: an exploratory study

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Why fast pyrolysis of biomass?

1. Thermochemical conversion of dry biomass particles in **a liquid product** with **high yield (bio-oil)** .
2. **Energy densification** of inherently distributed, heterogeneous, low-density solid biomass in a dense and uniform liquid improving logistics, handling and storage.
3. **Centralized processing** / upgrading to fuels and chemicals.
4. **Decoupling** in time and space of production and use of energy or bio-oil.
5. Opportunity of locally **recycling minerals** of biomass to soils as bio-char .

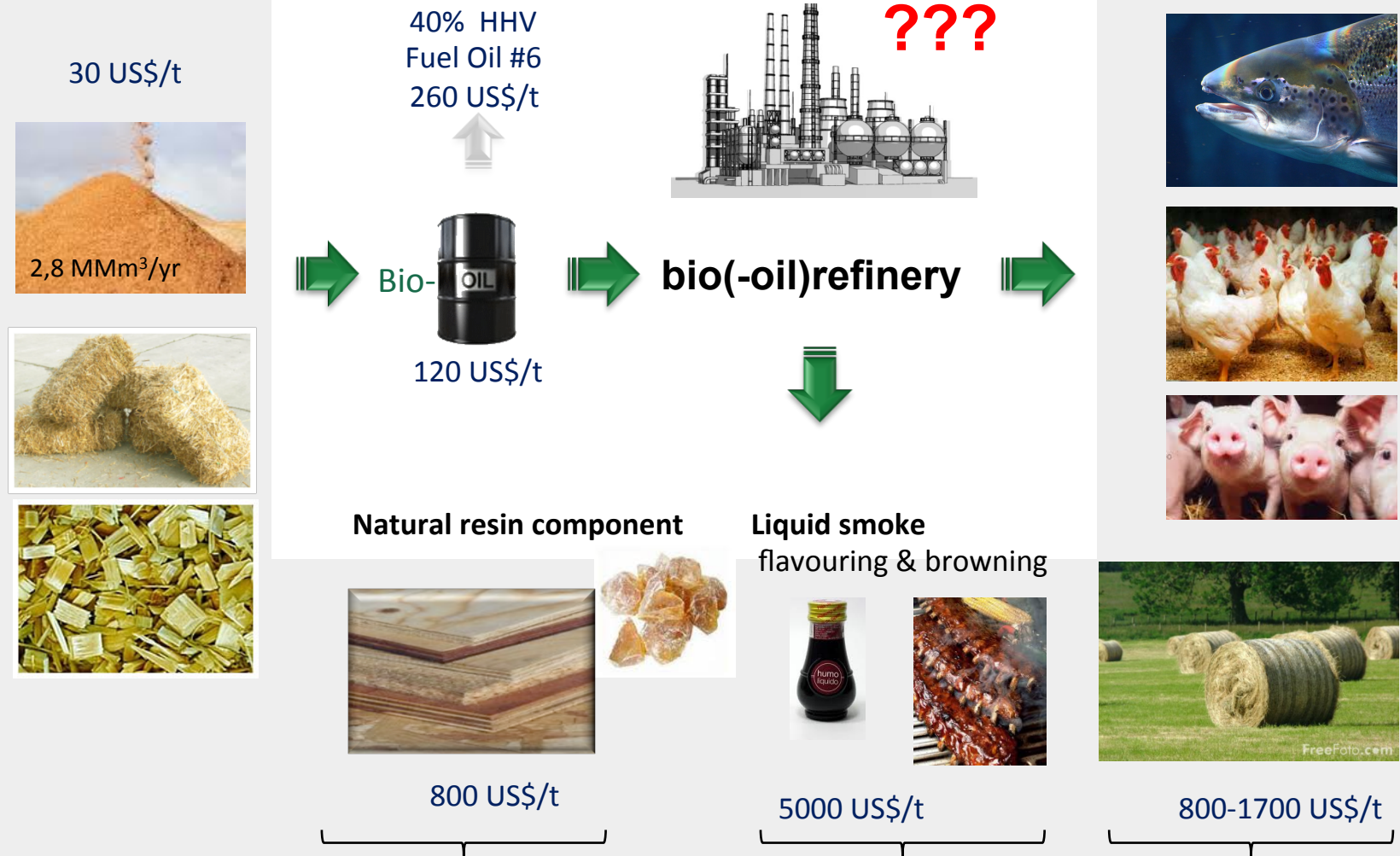


400- 600 °C

0.5 – 5 s

ϕ_2

How to add value to lignocelulosic residues or bio-oil?



Current stage of development: demonstration

commercial

laboratory/new



Objective

Development of an integrated bio-oil fractionation process with multiple products for chemical applications (maximize bio-oil value).

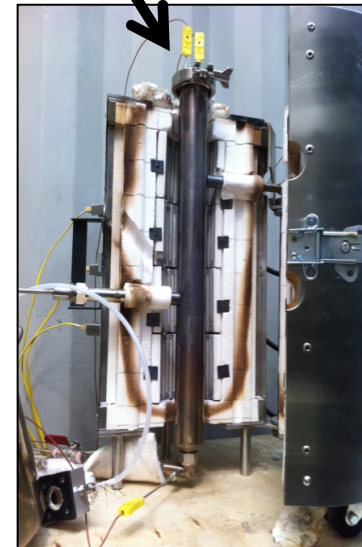
1. Production of bio-oil
2. Characterization of bio-oil and products
3. **Exploratory study of fractionation of bio-oil**
4. **Development of a separation process**
5. **Evaluation of potential application of bio-oil fractions**

1. Production of bio-oil: fast pyrolysis plants at UDT

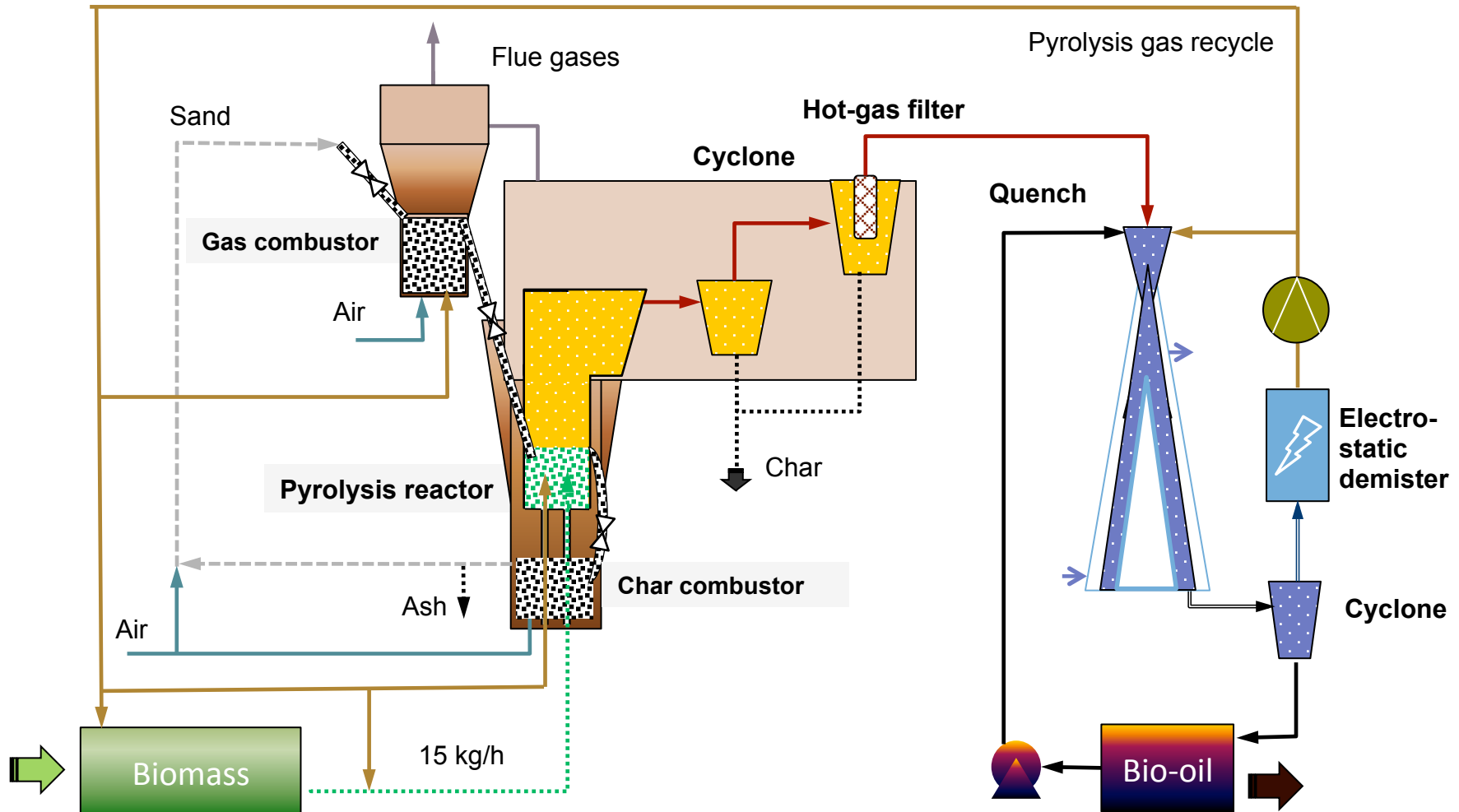
0.15 – 15 kg/h biomass



Design, construction U. Maine

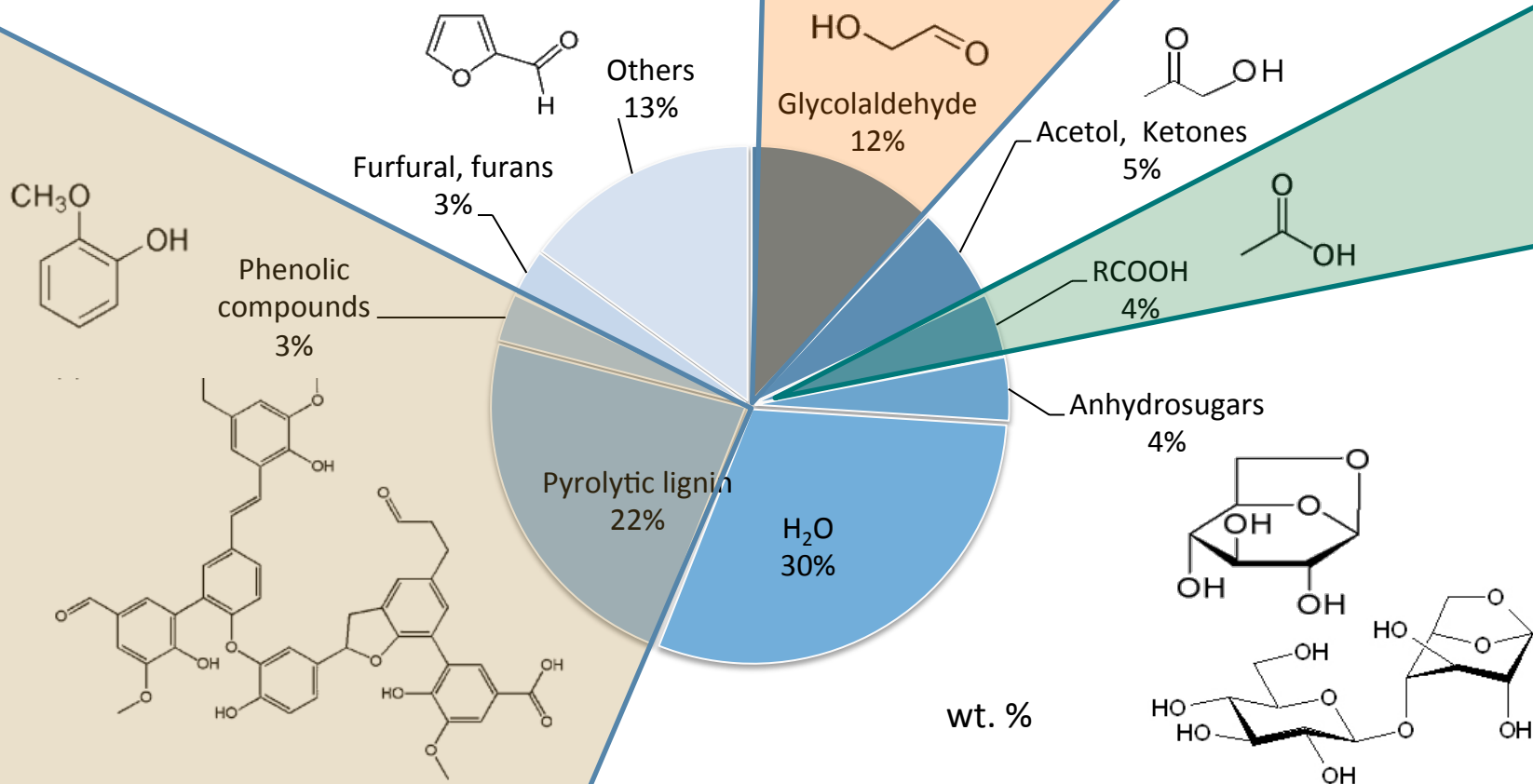


1. Production of bio-oil: basic flowsheet pilot plant, UDT



2. Bio-oil composition

(*pinus radiata* sawdust)

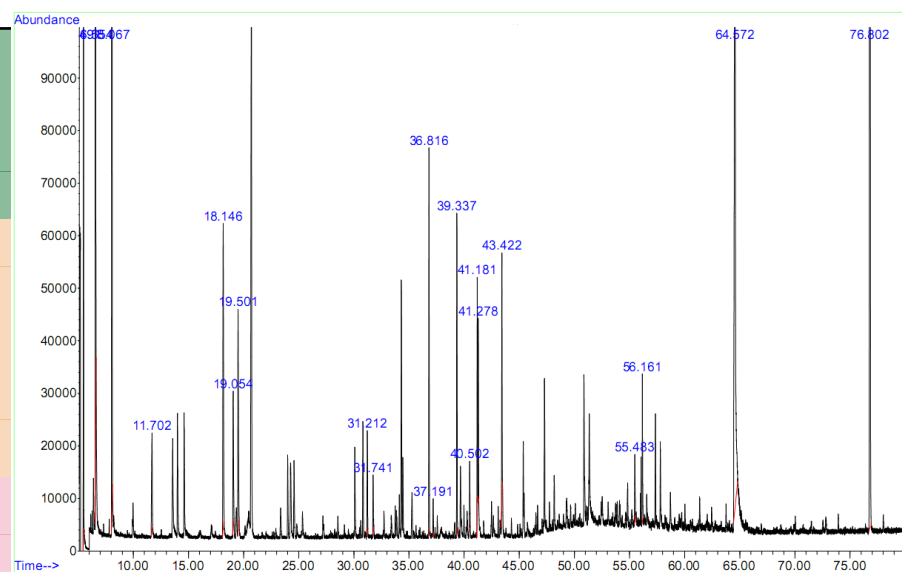


2. Bio-oil composition

(*pinus radiata* sawdust,)

Table 1 Concentrations of selected components in bio-oil by GC-MS

Bio-oil ID	J	L
Compound	(wt.%)	(wt.%)
Formic Acid¹	-	0.72
Acetic Acid	2.0	1.77
Propionic Acid	0.28	0.18
Lactic Acid	-	0.18
Glycolaldehyde	13.9	11.6
Formaldehyde²	2.0	1.8
Acetol	5.1	4.7
2-Furaldehyde	0.17	0.16
2(5H)-Furanone	0.15	0.27
Guaicacol	-	0.2
Vaniline	-	0.17
Levogluconan	2.3	1.89
Cellobiosan³	-	0.27
Water ⁴	34.0	31.3



- ¹ GC-MS previous derivatization with BTFSA
- ² measured by HS-SPME
- ³ measured by HPTLC
- ⁴ Karl-Fischer method

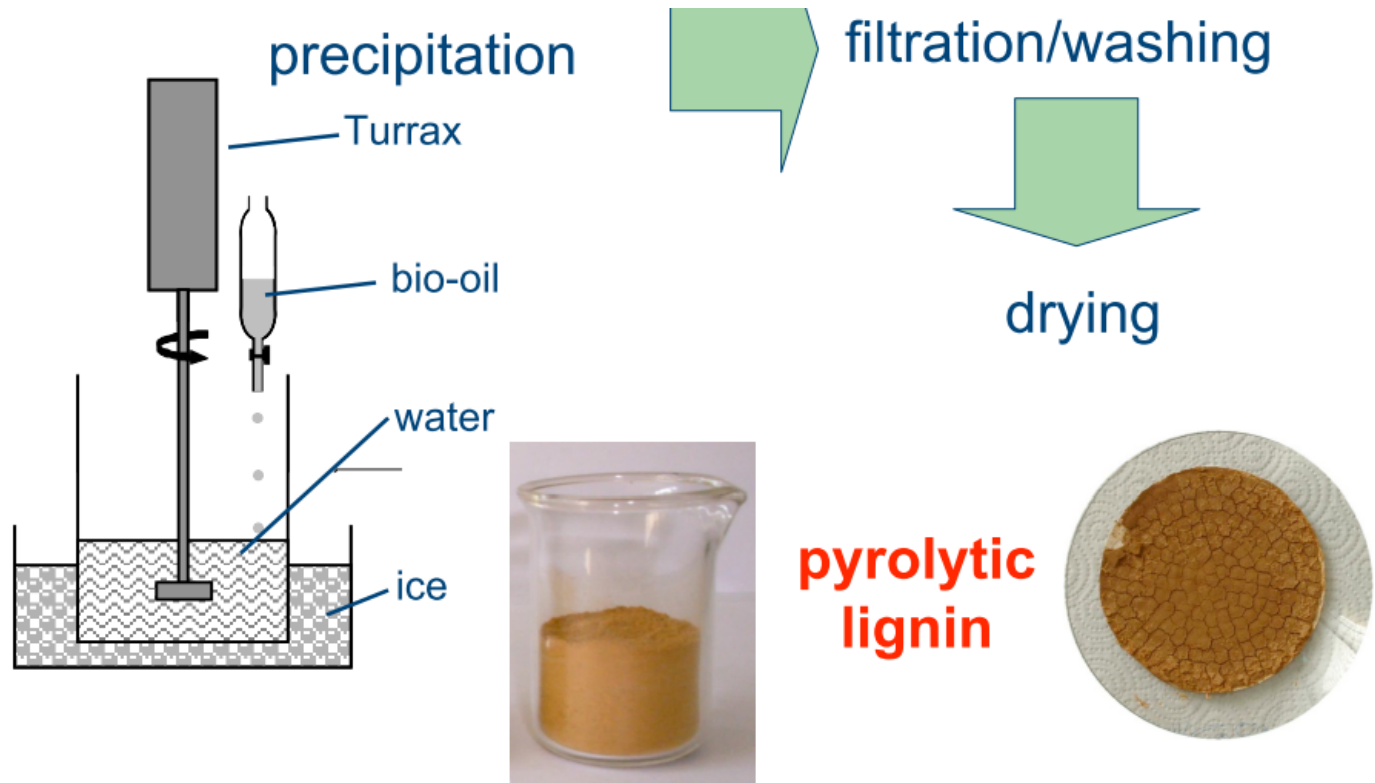
2. Bio-oil properties

Table 2 C,H,N analysis and properties of filtered bio-oil produced in bench-scale pyrolysis unit from sawdust of *pinus radiata*

Bio-oil ID	J	L
Carbon (wt. %)	38.07	39.27
Hydrogen (wt. %)	7.98	7.76
Nitrogen (wt. %)	0.26	0.09
Density (20 °C)	1163 kg/m ³	1182 kg/m ³
Dynamic viscosity (40 °C)	6.80 cSt	13.3 cSt
Ash content (wt. %)	0.07	NA
Ethanol insoluble solids (wt.%)	0.04	0.66
Water (wt. %)	34.0	31.3
Pyrolytic lignin (wt. %)	18.7	17.0
Total acid number	58 mg KOH/g	64 mg KOH/g
Carbonyl groups	5.0 mol/kg	4.9 mol/kg

Pyrolytic lignin content:

Dispersion of bio-oil sample in chilled water, filtration of water insolubles.

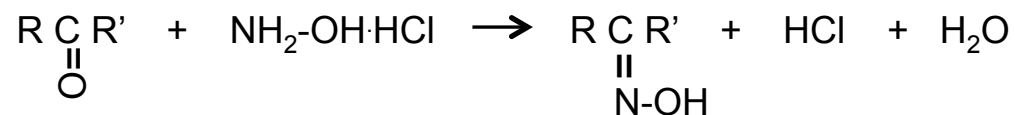


(Dietrich Meier, vTI - Institut of wood technology and wood biology, Hamburg)

Assessing bio-oil fractionation

Carbonyl groups:

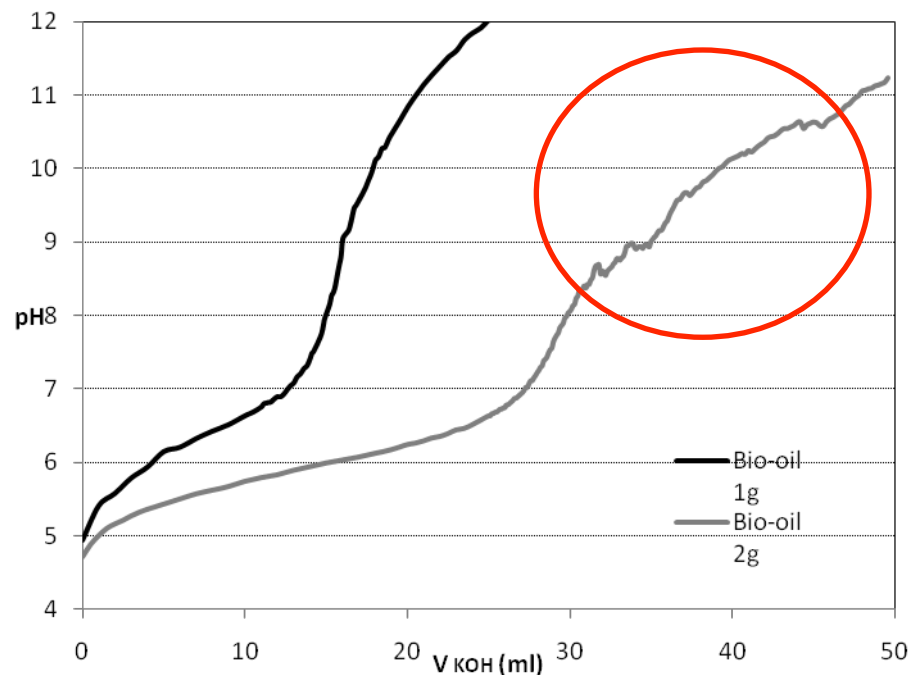
Quantitative microdetermination of aldehydes and ketones by oximation in presence of excess triethanolamine



Total acid content:

Fast titration of bio-oil sample in ethanol with KOH

Fig. 1 Titration of 1g (fast) and 2g(slow) of bio-oil dissolved in 50 ml ethanol with KOH (0,08N)



2. Bio-oil reactivity

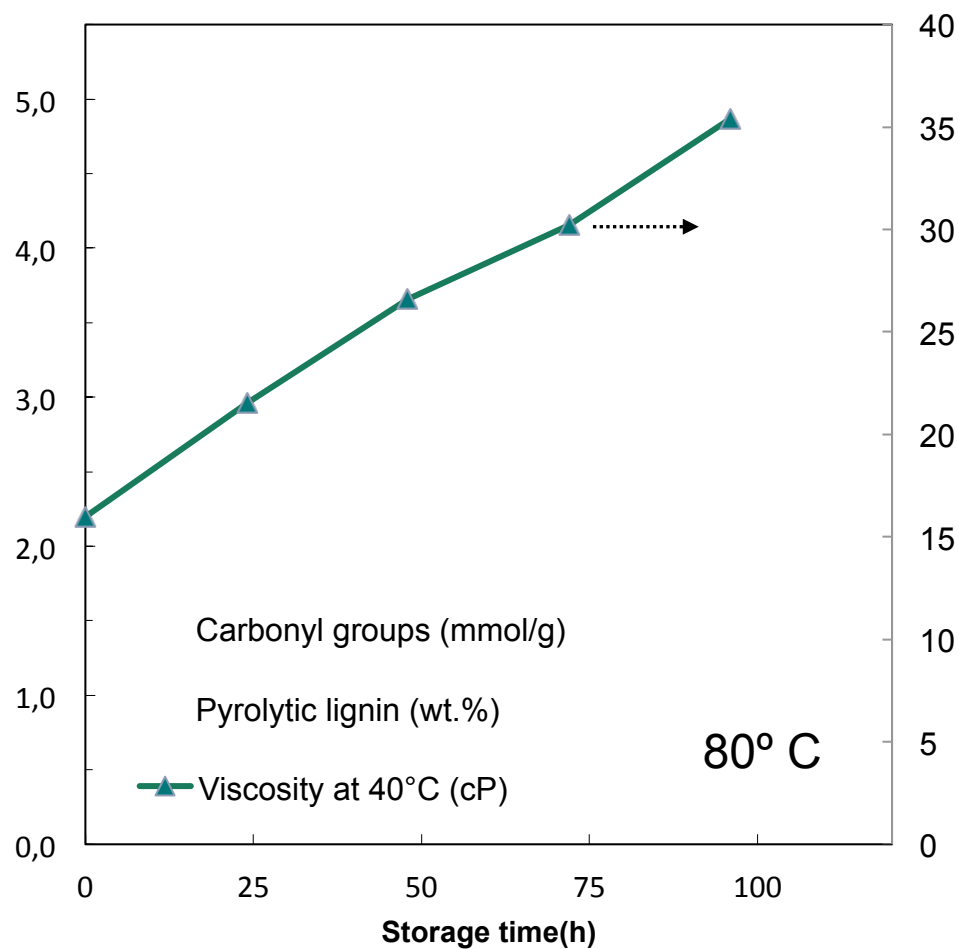


Fig. 2 Change in viscosity, carbonyl and pyrolytic lignin content of bio-oil L at 80°C

2. Bio-oil reactivity

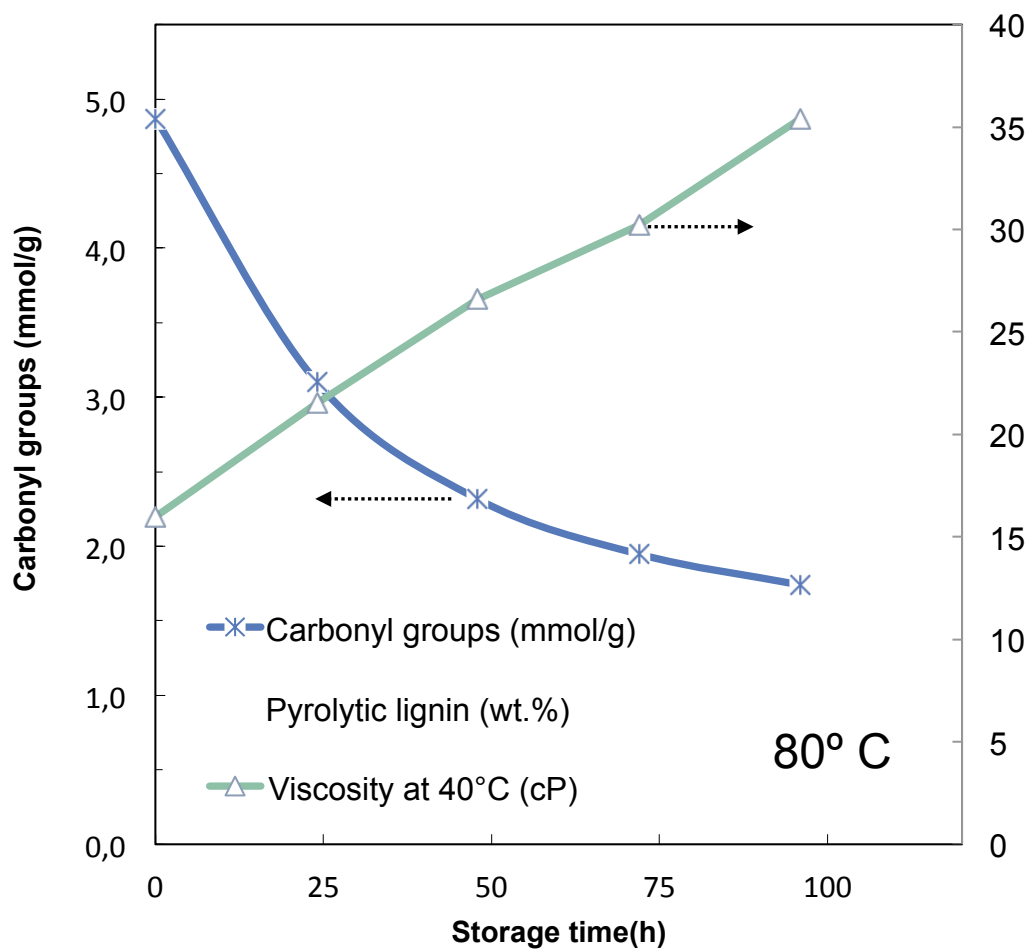


Fig. 2 Change in viscosity, carbonyl and pyrolytic lignin content of bio-oil L at 80°C

2. Bio-oil reactivity

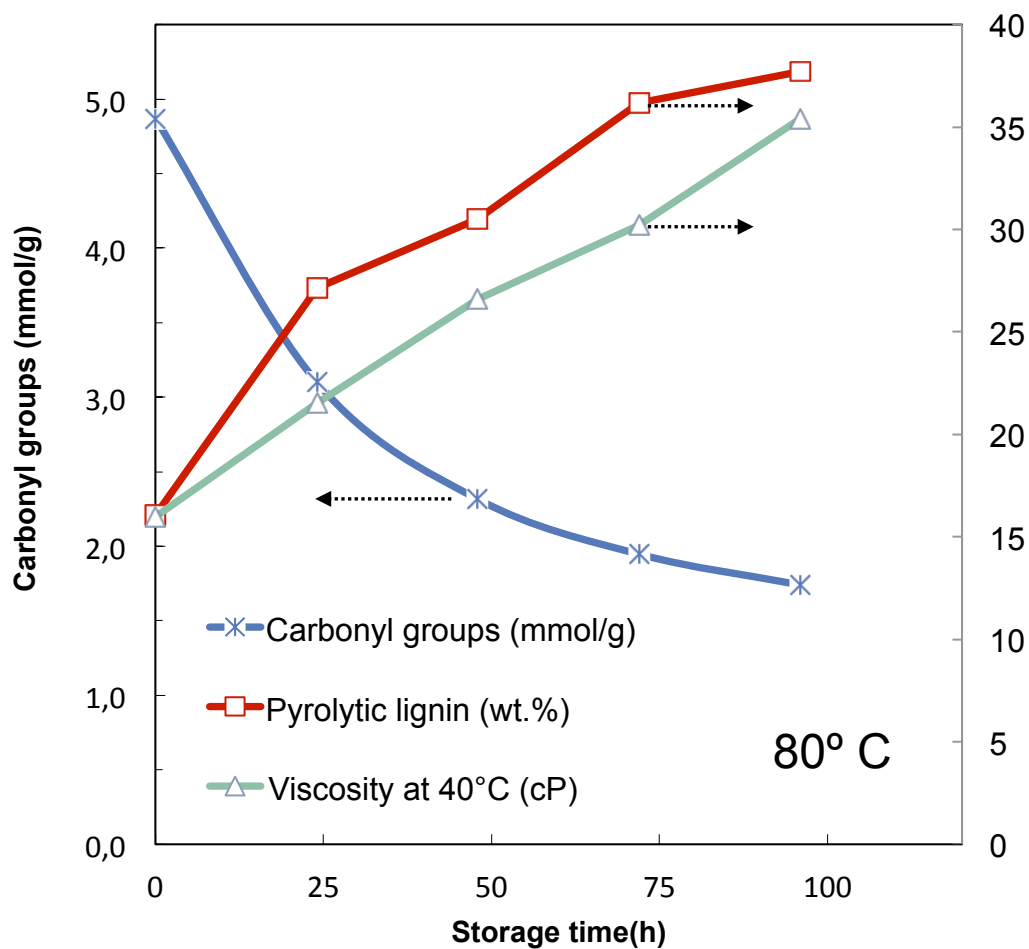


Fig. 2 Change in viscosity, carbonyl and pyrolytic lignin content of bio-oil L at 80°C

2. Bio-oil reactivity - carbonyls

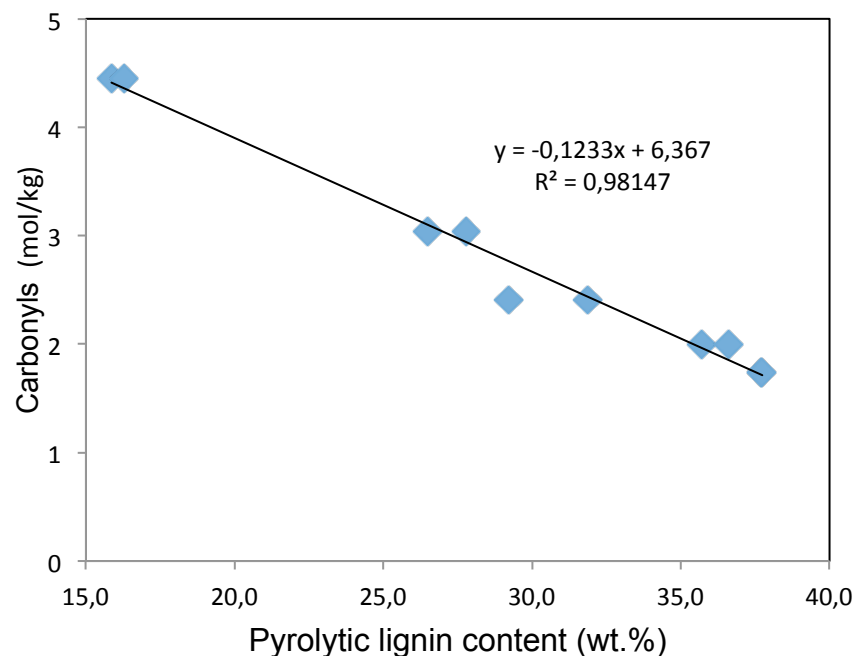


Fig. 3 Correlation of carbonyl and pyrolytic lignin content of bio-oil L during storage up to 96 h at 80°C

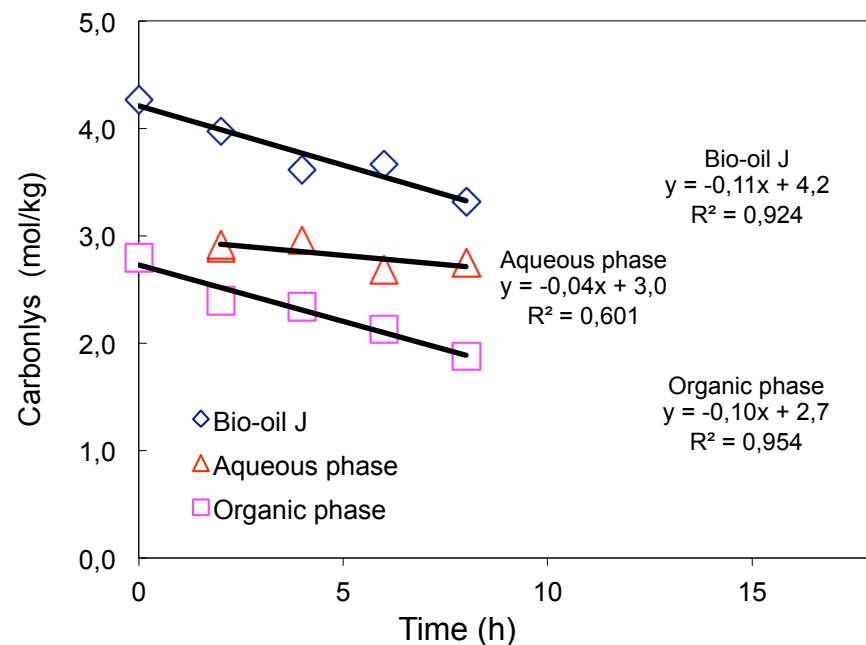


Fig. 4 Changes of carbonyl content at 85°C of bio-oil J, an organic and an aqueous phase of bio-oil J, produced by addition of water to bio-oil 1:1 by weight.

- Carbonyl compounds react in presence of compounds of organic phase of bio-oil, increasing the “pyrolytic lignin” content of bio-oil
- 90% of carbonyls of bio-oil are detected in the aqueous phase, less than 5% are extracted with ether (MTBE) from the aqueous phase (1:1 volume)

Bio-oil reactivity

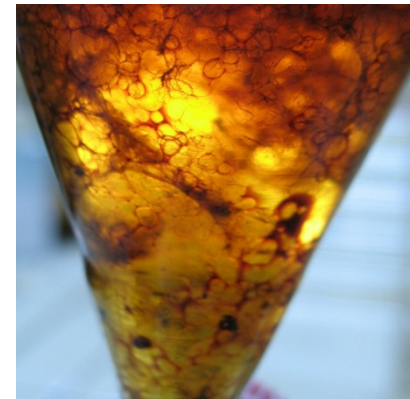
Storage of bio-oil L for 24h at 80°C

Glycolaldehyde	10.1% → 2.2%
Acetol	6.0% → 4.8%
Acetic Acid	3.6% → 4.8%

Table 3 Identification of reactive carbonyls by GC-MS

	Component bio-oil J	Mol weight	Concentration	Carbonyls
		g/mol	wt. %	mol/kg
80%	Glycolaldehyde	60.05	13.9	2.315
	Acetol	74.08	5.1	0.688
	Formaldehyde	30.00	1.97	0.667
	Butandial (succinaldehyde)	86.09	0.694	0.244
	Propionaldehyde, 3-hydroxy	74.08	0.389	0.080
	Butanone, 1-dihydroxy-2	90.08	0.444	0.075
	2-Furaldehyde	96.08	0.431	0.068
	Cyclopenten-3-one, 2-hydroxy-1-methyl-1-	110.08	0.386	0.053
	Cyclopenten-1-one, 2-	82.10	0.269	0.050
	Diacetone alcohol	116.16	0.268	0.035
2%	Furan-2-one, 3-methyl-, (5H)-	98.10	0.174	0.027
	Butyrolactone, γ-	86.09	0.144	0.025
	Cyclopenten-1-one, 2-methyl-2-	112.10	0.132	0.018
	Furanone, 2(5H)-	84.07	0.084	0.015
	Propanone, acetyloxy-2-	116.00	0.110	0.014
	Butanone, 2-	72.11	0.068	0.014
	Acetoin (Hydroxy-2-butanone, 3-)	88.11	0.080	0.014
	Furaldehyde, 5-methyl-2-	102.11	0.081	0.012
	Butandione, 2,3- (Diacetyl)	86.09	0.067	0.012
	Cyclopenten-1-one, 2-hydroxy-2-	132.00	0.078	0.009
8%	Furaldehyde, 3-	96.08	0.058	0.009
	Cyclopenten-1-one, 3-methyl-2-	96.08	0.054	0.009
	Cyclopentanone	83.11	0.038	0.007
	Pyrolytic lignin			0.39
Total				4.85
+ glyoxal ! + ?				~ 5

3. Exploratory study of bio-oil fractionation



3. Bio-oil fractionation: distillation

- Bio-oil distilled at atmospheric pressure, boiling temperature is initially around 105°C and mainly water is removed; residue is very viscous; further distilling temperature rises sharply and residue becomes carbonaceous.
- Vacuum distillation (50 mbar)
- Adequate for removal of volatiles with pungent odor (2-butenal)
- Loss of carbonyl compounds in distillate and by reaction (5-10%)
- Condensate is biphasic (see figure) only if distilled with reflux
- Steam distillation effect (removal of higher boiling and water insoluble compounds)

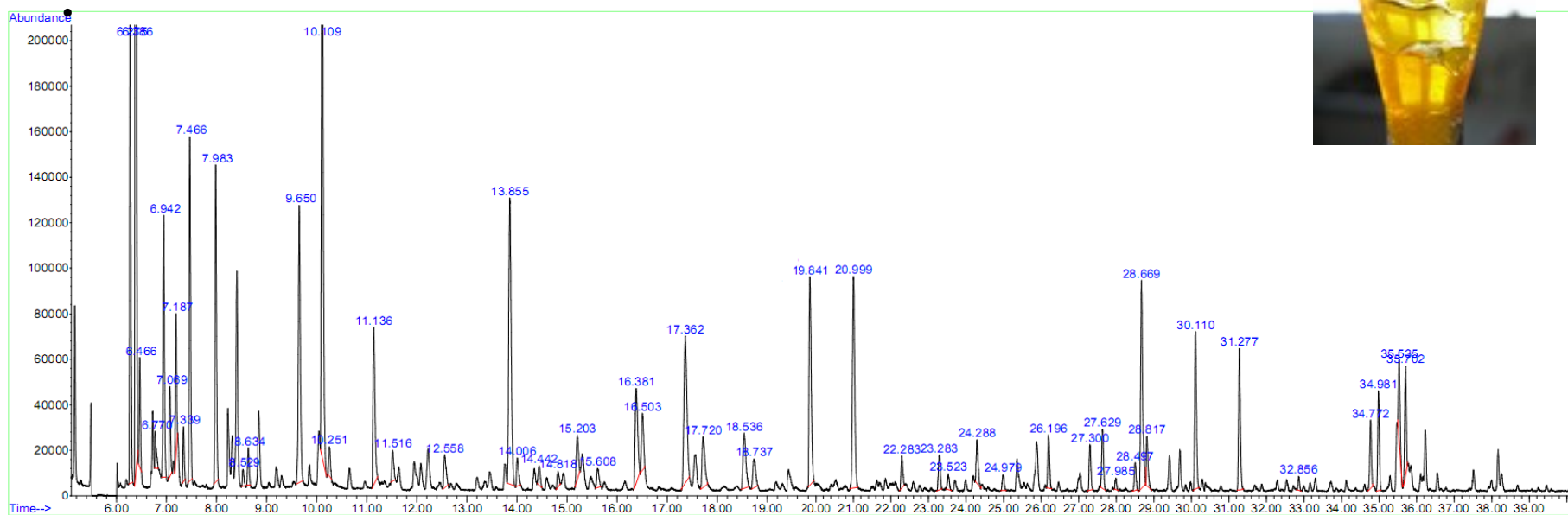


Fig. 5 GC-MS chromatogram of distillate (organic phase of distillate) (L15)

3. Bio-oil fractionation: liquid-liquid extraction

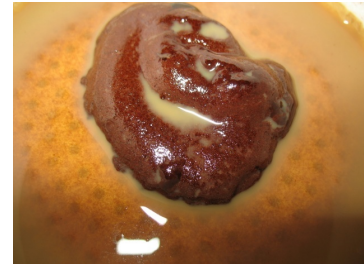
Solvent for pyrolytic lignin separation

1. Solvent precipitates pyrolytic lignin
(water, ethanol- water)

1:1



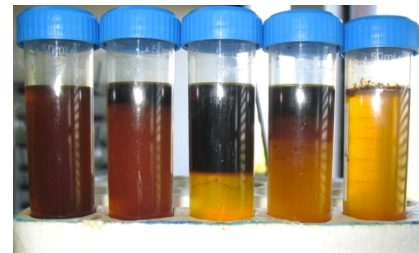
1:10 + turrax



2. Solvent does not dissolve pyrolytic lignin
(hexane, benzene, MTBE (methyl tert-butyl ether))



3. Hydrophobic solvent that dissolves pyrolytic lignin
(higher alcohols, esters, methylene chloride, MIBK
(methyl isobutyl ketone))



3. Bio-oil fractionation: liquid-liquid extraction

Best separation of (pyrolytic lignin + phenolic compounds) and (carbonyls + anhydrosugars + acids)

Table 4. Extraction of bio-oil J and bio-oil J dissolved in organic solvents with water (volume ratio (bio-oil : water : solvent)= (2:1:1))



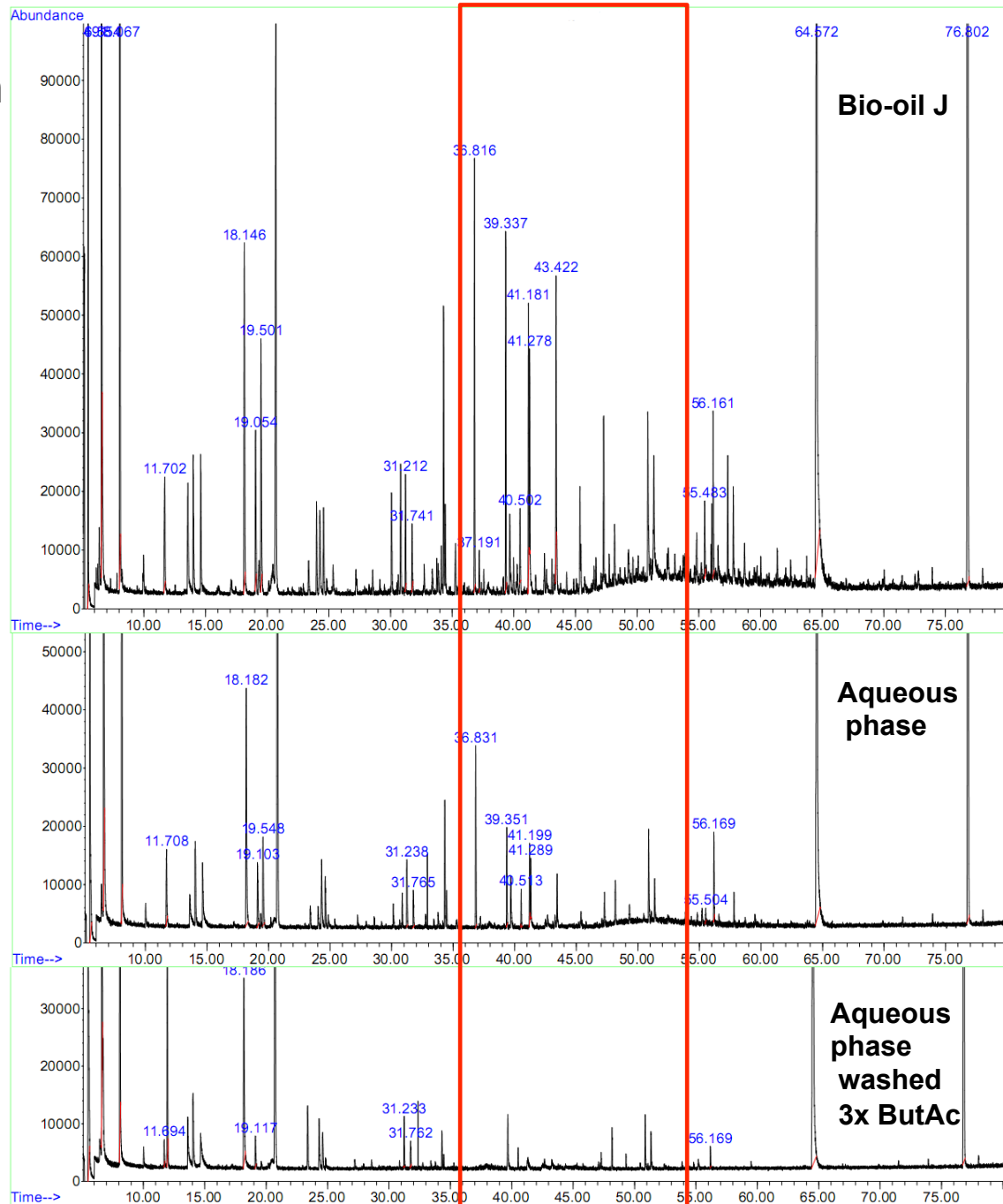
Water +solvent	organic phase	concentration		recovery	
	wt % ¹	carbonyls	acids	carbonyls	acids
		mol/kg	g KOH/kg	mol %	mol %
(no solvent)	30	2.6	32	19	17
Butyl acetate	72	1.6	29	22 (15)	31 (18)
Ethyl acetate	75	2.1	36	33 (20)	40 (26)
n-Pentanol	89	2.1	36	53	55
Isopentanol	87	2.6	39	50	53
n-Butanol	94	2.5	38	55	58

¹ fraction expressed as percentage of initial bio-oil mass; () in parenthesis separation after washing organic phase with water

4. Bio-oil fractionation

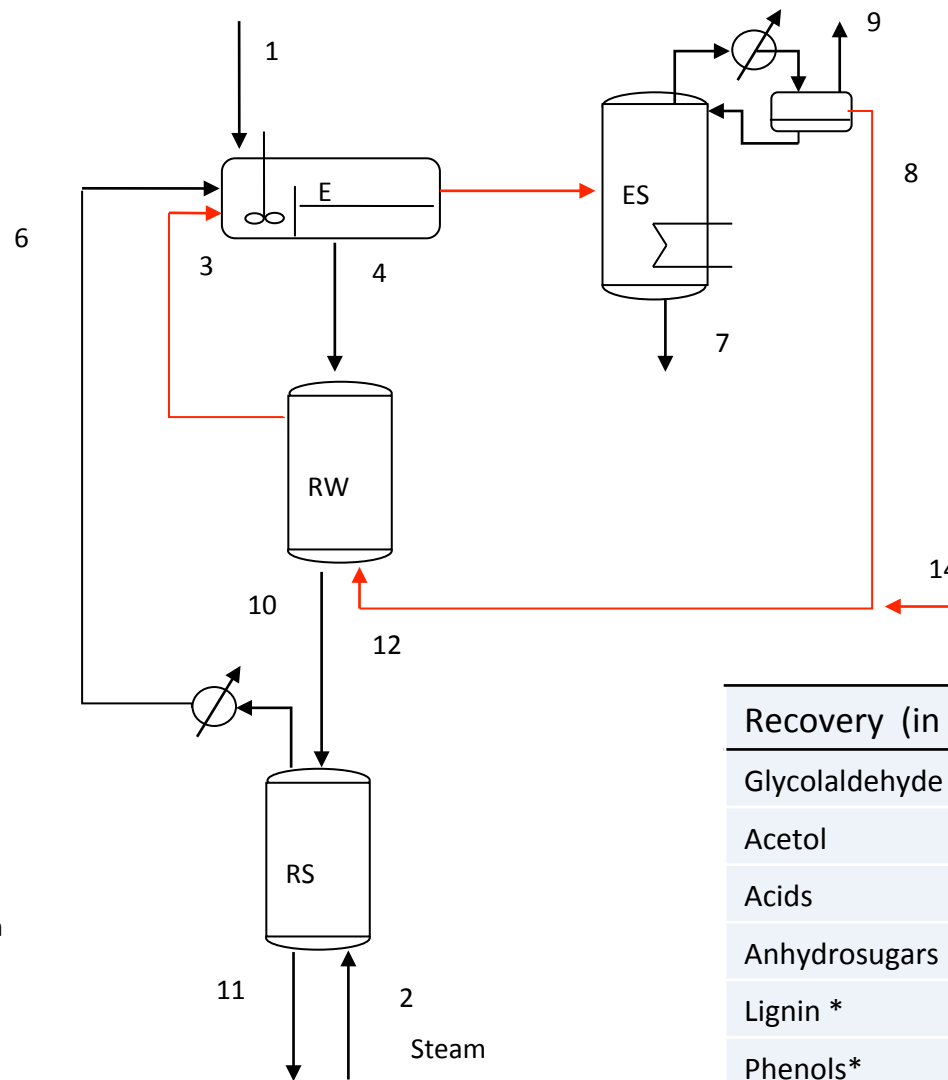
Fig. 7 Removal of phenolic compounds from aqueous phase

time	GC-MS chromatogram
5,498	Glycolaldehyde
6,58	Acetic acid
8,084	Acetol
11,708	Propionic Acid
18,182	Butanedial
19,103	2-Cyclopenten-1-one
19,548	2-Furaldehyde
31,238	Butirolactone
31,765	2(5H)-Furanone
34,312	2-hidroxy-3-metil-2-cyclopenten-1-one
36,831	Phenol
37,224	2-Metoxiphenol
39,351	2-Metilphenol
40,513	4-metil-5H-furan-2-one
41,199	4-metilphenol
41,289	3-metilphenol
43,435	2,4-dimetilphenol
55,504	Vanilin
56,169	Hidroquinone
64,553	Levoglucozano



4. Bio-oil fractionation: liquid-liquid extraction

(1) Bio-Oil 100 kg/h
 31.8% H₂O
 24% Lignin
 14% Glycolaldehyde
 6% Acetol
 6.5 % Acids
 6% Anhydrosugars
 5% Sugars
 3% phenols



(7) Pyrolytic lignin
 28 kg/h
 6.5 % H₂O
 76 % Lignin
 8% Phenols
 1,7% Acids

Solvent (butyl acetate)

(11) Aqueous fraction
 77 kg/h
 16.7 % Glycolaldehyde
 7.45 % Acetol
 7.6 % Acids
 7.8 % Anhydrosugars

Recovery (in aqueous fraction)	%
Glycolaldehyde	92
Acetol	95
Acids	90
Anhydrosugars	100
Lignin *	<10
Phenols*	<2

* estimated

Fig. 6 Separation process

4. Bio-oil fractionation – oxidation of aqueous phase

Table 5 . Oxidation of aqueous bio-oil phase with hydrogen peroxide and addition of NaOH to maintain pH 6,5-7,5

Compound	Initial wt. %	Final wt. %	Initial mol	Final mol
Glycolaldehyde	9,7	ND	2,57	0
Acetol	4,6	1,2	1,0	0,58
(a) Formic acid	2,5	6,5	0,87	5,48
(b) Acetic acid	4,4	2,2	1,18	1,34
(c) Propi3nic acid	3,4	1,2	0,72	0,62
Levogluconan	3,5	0,83	0,34	0,18
Total (g)	1591	3602		

- Yield of sodium formate 28 % (HCOONa/bio-oil).
- After acidification /distillation 19% (HCOOH/bio-oil)
- Sum of volatile acids (C₁-C₃) 39%

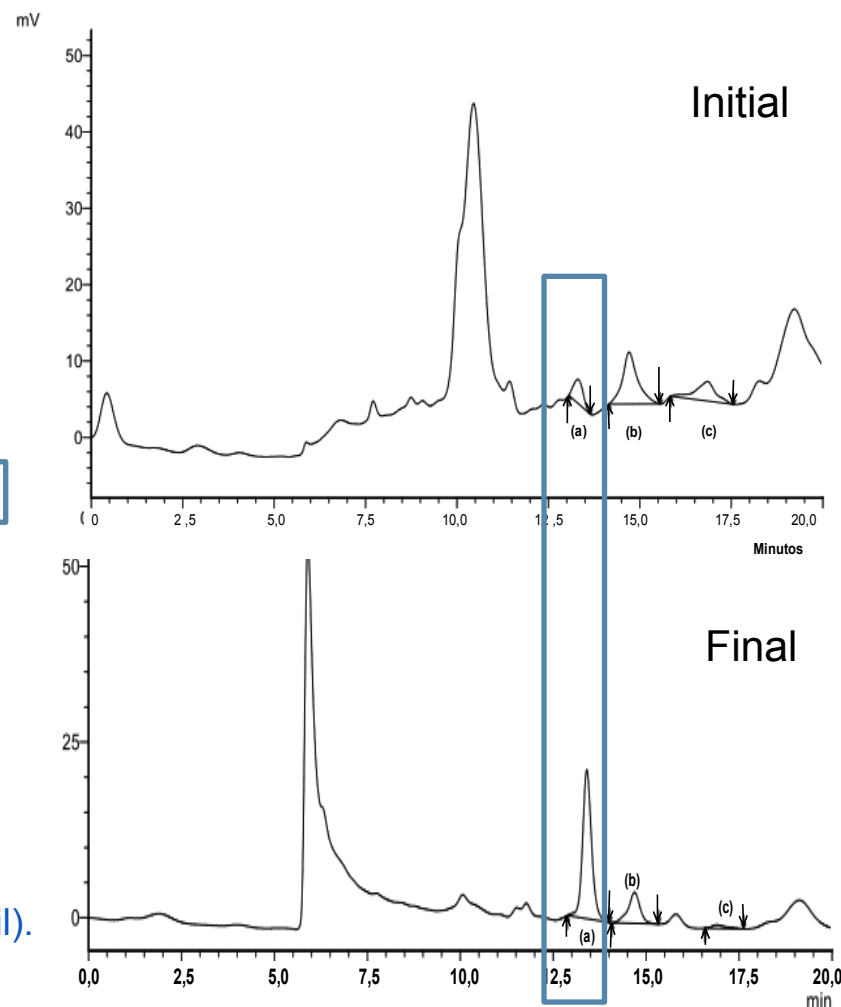


Fig. 8 HPLC- Chromatogram

5. Evaluation of potential applications of bio-oil fractions

Aqueous fraction as component of an acid additive for silage

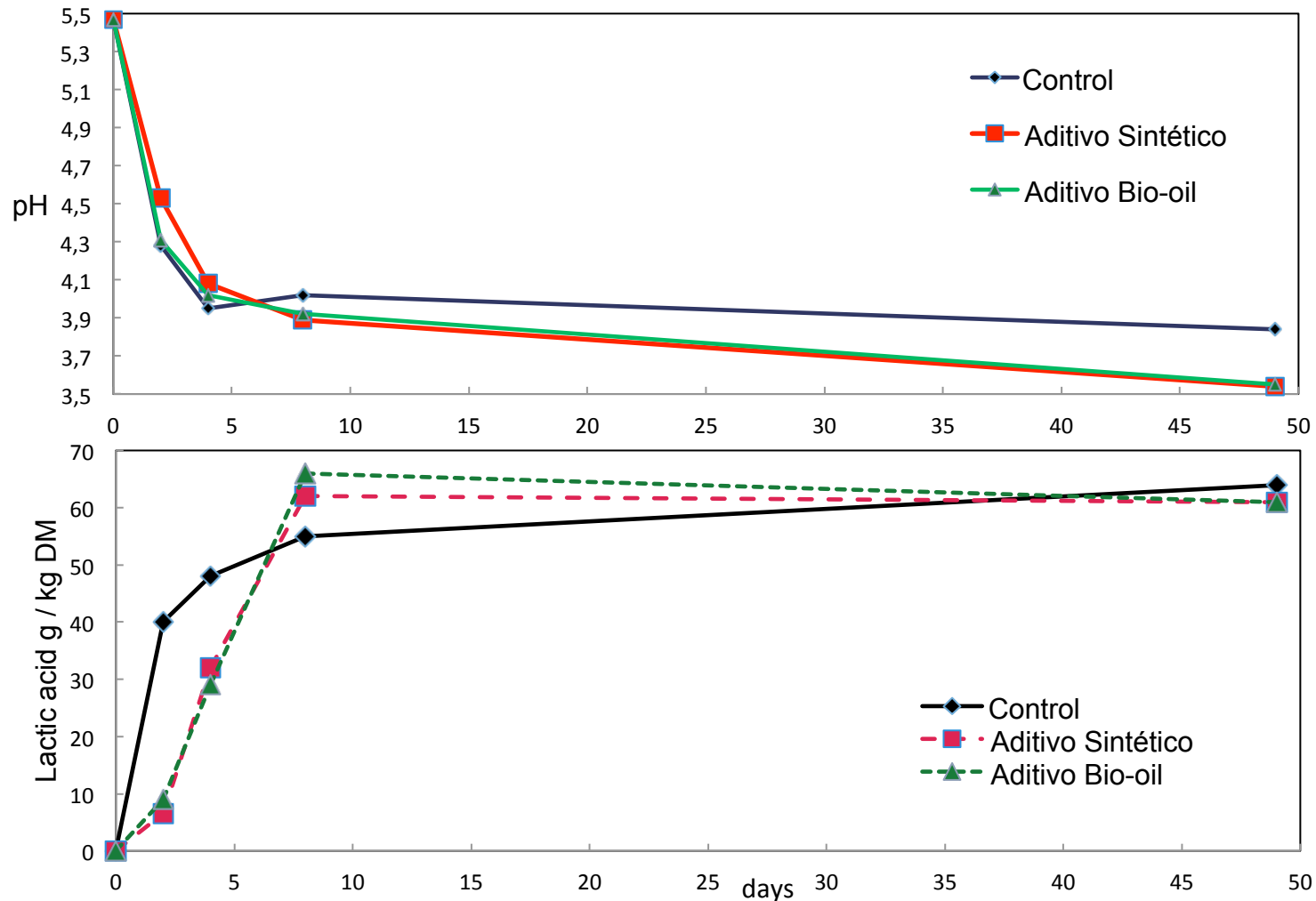


Fig. 9 Grass silage stabilization

5. Aqueous fraction as component for an acid silage additive

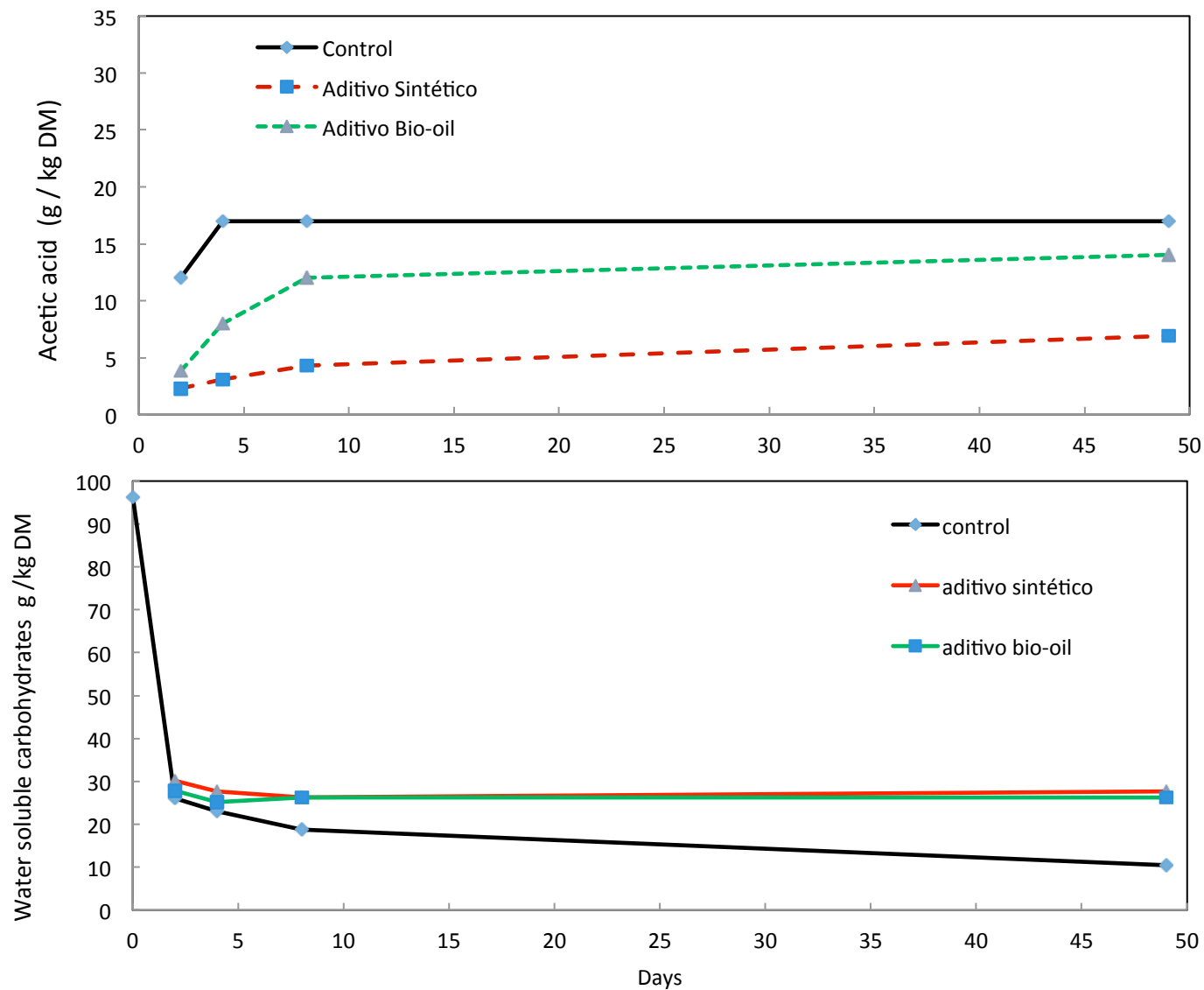
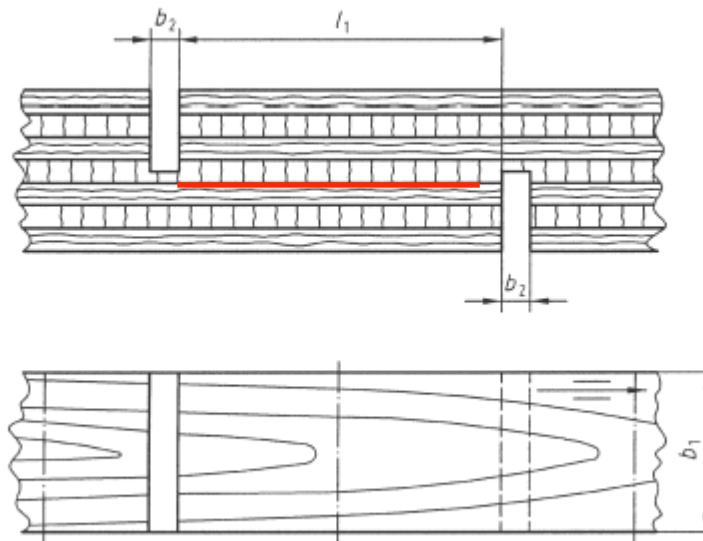


Fig. 10 Silage properties

5. Evaluation of potential applications of bio-oil fractions

Fraction of “pyrolytic lignin” as partial phenol replacement in phenol-formaldehyde resins for wood panels

Evaluation of bonding quality of plywood (EN-314)



5 Pre-treatments

5.1 Sequence of pre-treatment

5.1.1 Immersion for 24 h in water at $(20 \pm 3) ^\circ\text{C}$.

5.1.2 Immersion for 6 h in boiling water followed by cooling in water at $(20 \pm 3) ^\circ\text{C}$, for at least 1 h.

5.1.3 Immersion for 4 h in boiling water, then drying in the ventilated drying oven for 16 h to 20 h at $(60 \pm 3) ^\circ\text{C}$, then immersion in boiling water for 4 h, followed by cooling in water at $(20 \pm 3) ^\circ\text{C}$ for at least 1 h.

5.1.4 Immersion for (72 ± 1) h in boiling water, followed by cooling in water at $(20 \pm 3) ^\circ\text{C}$ for at least 1 h.

Table 1 — Pretreatments for the three bonding classes

	Pretreatments (according to EN 314-1)			
	5.1.1	5.1.2	5.1.3 ^a	5.1.4
Class 1: dry interior	X			
Class 2: covered exterior	X	X		
Class 3: non covered exterior	X		X	X

^a When full phenolic glues are used, pretreatment 5.1.3 can be used provided pretreatment 5.1.4 is occasionally used as a test of confirmation.

Table 2 — Requirements

Mean shear strength f_v N/mm ²	Mean apparent cohesive wood failure w %
$0,2 \leq f_v < 0,4$	≥ 80
$0,4 \leq f_v < 0,6$	≥ 60
$0,6 \leq f_v < 1,0$	≥ 40
$1,0 \leq f_v$	no requirement

Table 6. Evaluation of bonding quality of plywood (EN-314)

	Pre-treatment for dry interior use			Pre-treatment for non covered exterior use		
Resin	Shear strength (N/mm²) (% wood cohesive failure)			Shear strength (N/mm²) (% wood cohesive failure)		
Control (no substitution)	1,90 (70%)			1,72 (60%)		
	% phenol substitution with pyrolytic lignin					
	30 %	40%	50%	30%	40%	50%
Resin A	0,85 (10%)	0,68 (0%)	0,50(0%)	0,83 (10%)	-	-
Resin A*	1,07(0%)	-	-	0,66 (10%)	0,65 (22%)	0,63 (00%)
Resin B*	1,22 (20%)	-	-	1,01 (10%)	-	-

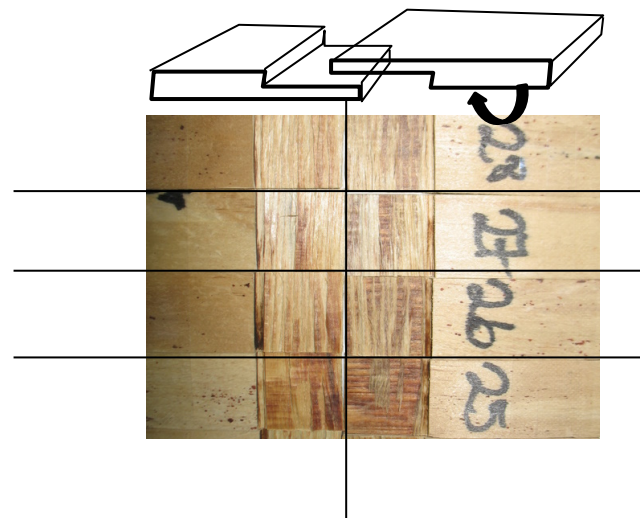
* Resin prepared with filler and extender ; (%) wood cohesive failure

Wood panel assembly

Temperature of press 150° C;

Press factor 1 min/mm;

Application rate 250 g resin / m²



Conclusions

1. Bio-oil produced by fast pyrolysis from sawdust of *pinus radiata* displayed high content of glycolaldehyde and low content of organic acids.
2. Determination of carbonyls by oximation (using triethanolamine) is a fast and simple method to assess content of reactive aldehydes and “aging” of bio-oil.
3. Three reactive aldehydes (glycolaldehyde, formaldehyde, butandial) have been identified corresponding to 66 % of total carbonyls.
4. Reactivity of bio-oil is an important issue that must be taken into account for the proper design of a process for bio-oil fractionation.
5. A separation process of bio-oil has been proposed that splits bio-oil in an organic phase, rich in lignin derived phenolic compounds and low in acids, and an aqueous phase, low in phenols and rich in carbonyl compounds and anhydrosugars.
6. Oxidation of aqueous fraction of bio-oil (glycolaldehyde) at slightly basic pH produced mainly formic acid in high yield.
7. Bio-oil fractions showed potential for applications in fenol-formaldehyde resins for wood panels and as silage additive.

Future work

- Separation process scale-up (FONDEF D11-I-1190)
 - Improving yield of glycolaldehyde by (catalytic) fast pyrolysis of biomass
 - Oxidation of aqueous bio-oil phase with air, catalysts.
- Improving resin formulations with pyrolytic lignin
- Other applications of organic acids from aqueous bio-oil fraction (fish silage, feed acidifiers)





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Thank you for your attention!

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