Hydrothermal Liquefaction of Biorefinery Lignin-rich Streams: Carbon Recovery from Residual Aqueous Phase

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Summary

- Introduction
- Hydrothermal liquefaction of Lignin-rich streams
- Residual aqueous phase collection and characterization
- Aqueous phase valorization: Liquid-Liquid Extraction
- Conclusion and further developments

Ethanol biorefinery: Lignin-rich streams

Lignocellulosic biomass

Pretreatment (e.g. steam explosion)

Cellulose/ Hemicellulose

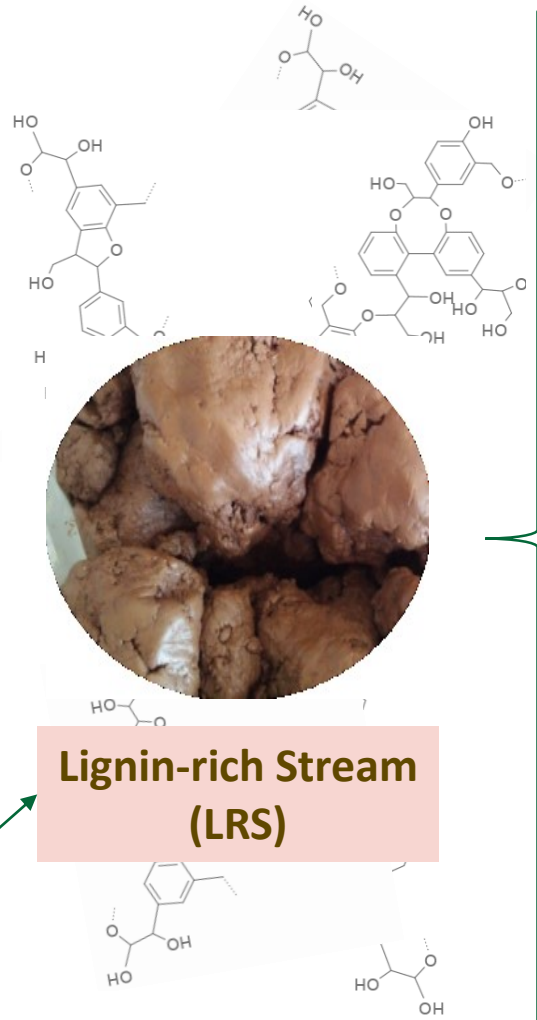
Lignin

Enzymatic hydrolysis

Fermentation

Ethanol distillation and separation

Ethanol



Lignin-rich Stream (LRS)

Parameter	Value	Unit
Total lignin	57.8	wt.% daf
Structural sugars	35.5	wt.% daf
Moisture	69.7	wt.% wb
Volatile matter	71.0	wt.% db
Ash	2.6	wt.% db
Fixed carbon	26.4	wt.% db
C	54.2	wt.% db
H	5.9	wt.% db
N	1.0	wt.% db
S	0.2	wt.% db
O*	36.1	wt.% db
Slurry pH	5	-

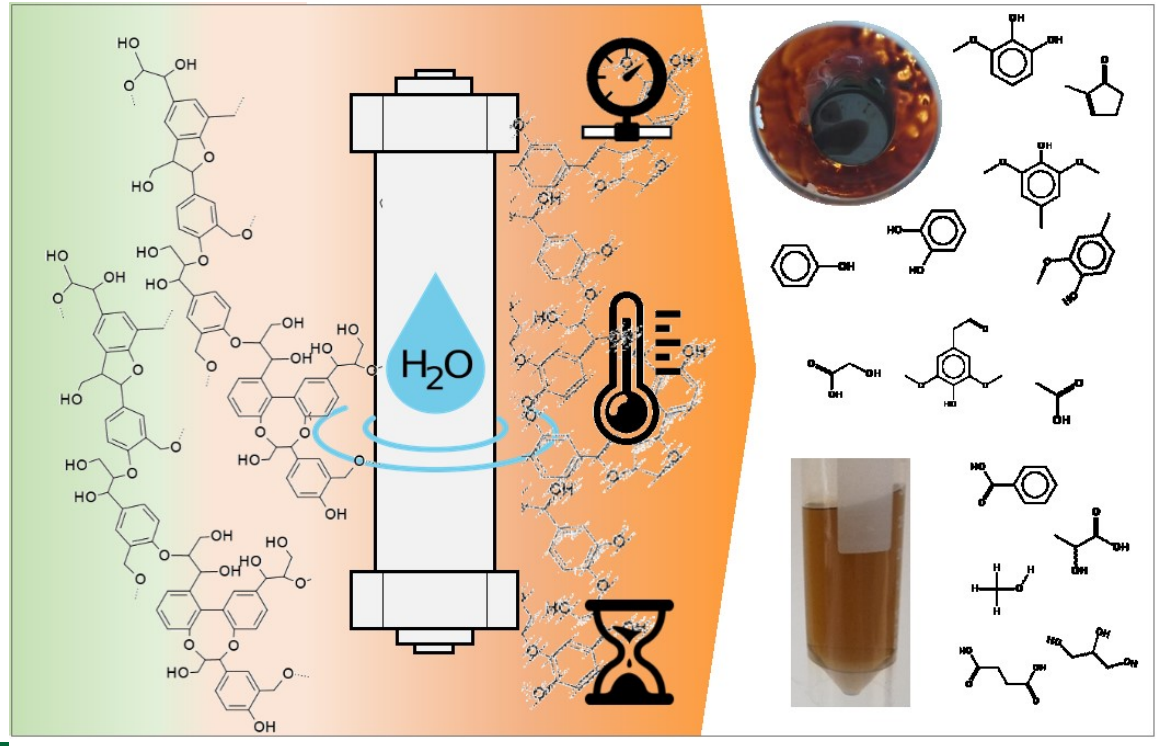
Hydrothermal Liquefaction of LRS

Micro-reactors test bench:

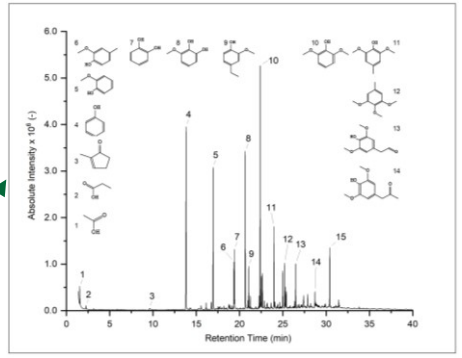
- Tubular batch reactor, OD 3/4”
- Fluidized sand bath
- Fast water bath cooling

HTL reaction conditions:

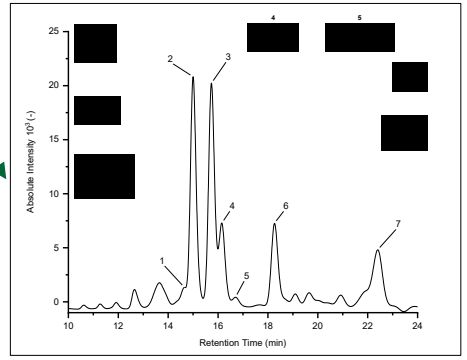
- Temperature = 350° C
- Residence time = 10 min
- Lignin to water ratio = 10 wt.%



GC-MS



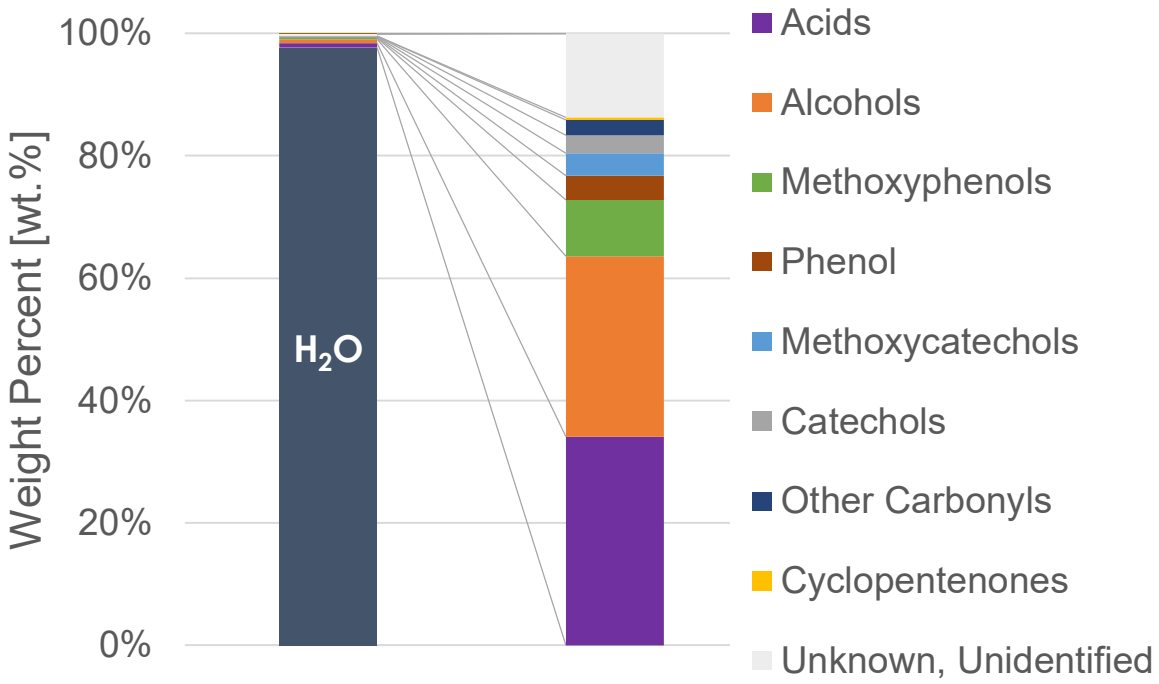
HPLC



LRS-HTL aqueous phase characterization

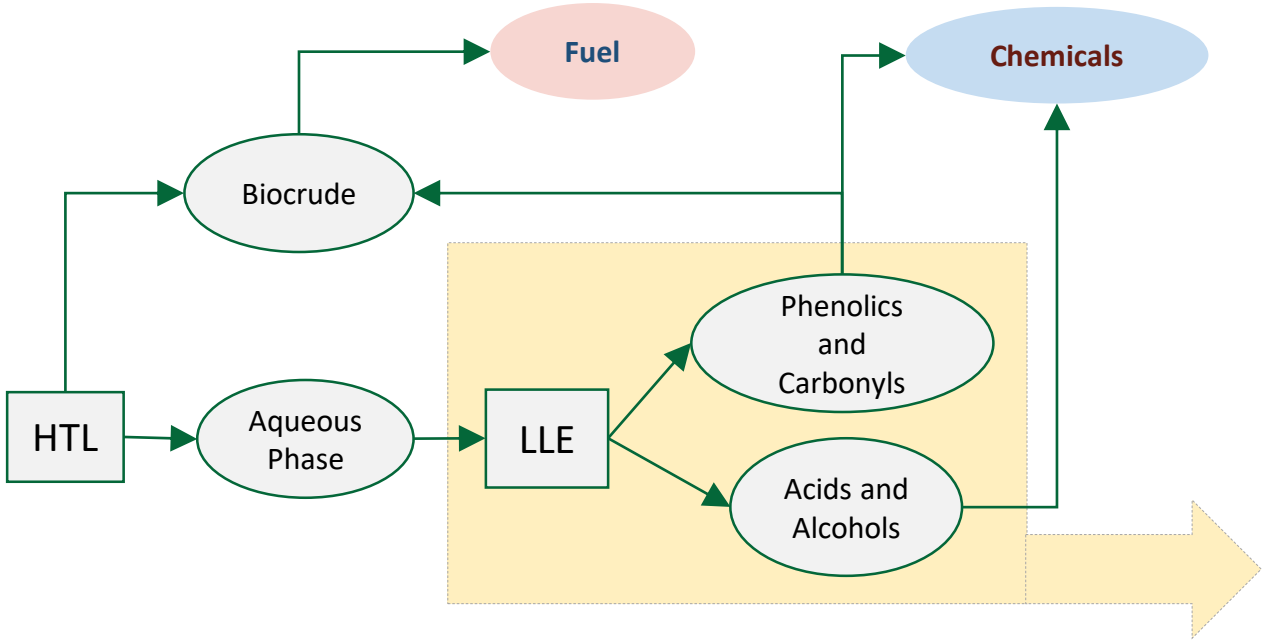
Analysis	Value	Units
TOC	9.73 ± 0.780	g/l
Water content KF Titration	97.7 ± 1.09	wt.%
ICP – Inorganic elements*	0.114	wt.%
pH	4.27	-

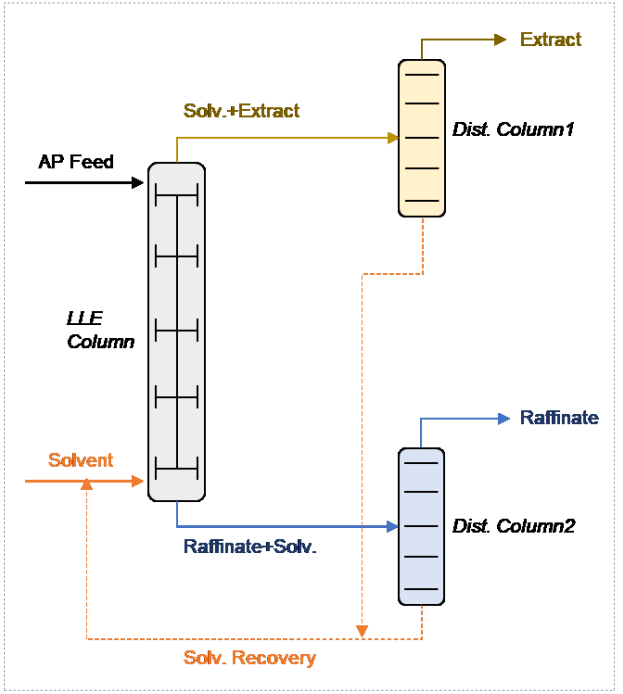
*Na, K, Ca, Fe, Al, Mg, Zn



- Total detected organics → **1.93 wt.%** → *GC-MS, HPLC*
- Organic mass balance closure → **83-86 %** → *KF, TOC*
  - Acids (34 wt.%) and Alcohols (30 wt.%)→ HPLC
  - Phenolics (20 wt.%) and Carbonyls (3.0 wt.%)→ GC-MS

Liquid-Liquid Extraction HTL integration





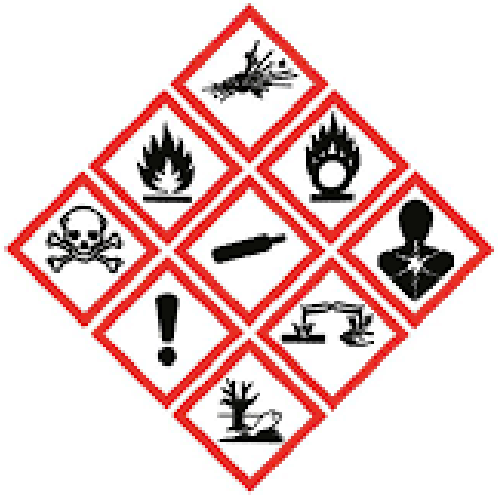
- Liquid-Liquid Extraction (LLE) → Selective separation of phenolics compounds
- Potential valorization pathways:
  - Biocrude yield enhancement for **Fuel** production
  - Precursors for **Chemicals and Bioproducts**

Solvent selection

ID	Name	DH_vap [kJ mol-1]	T_boil [°C]	Flash Point [°C]	Solubility in H2O [g/l]	Price* [$ kg-1]
DEE	Diethyl ether	28	34.5	-45	60.5	2.0
EtAc	Ethyl Acetate	33	77	-4	83	0.8
BuAc	Butyl Acetate	41	126	22	6.8	1.7
MIBK	Methyl Isobutyl ketone	40.5	117	13	19.1	1.4

*Updated using producer price index to adjust values

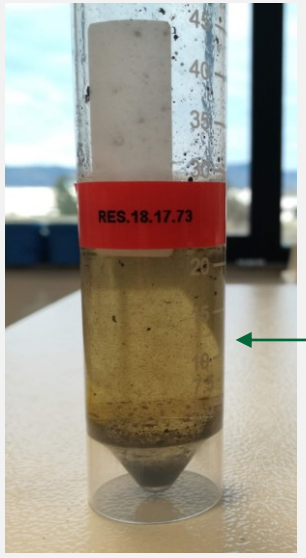
ID	Safety score	Healthy score	Env. Score	Ranking
DEE	10	3	7	Highly Hazardous
EtAc	5	3	3	Recommended
BuAc	4	2	3	Recommended
MIBK	4	2	3	Recommended

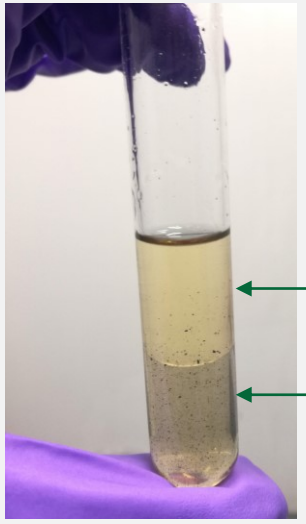


D. Prat, A. Wells, J. Hayler, H. Sneddon, C.R. McElroy, S. Abou-Shehada, P.J. Dunn, CHEM21 selection guide of classical- and less classical-solvents, Green Chem. 18 (2015)

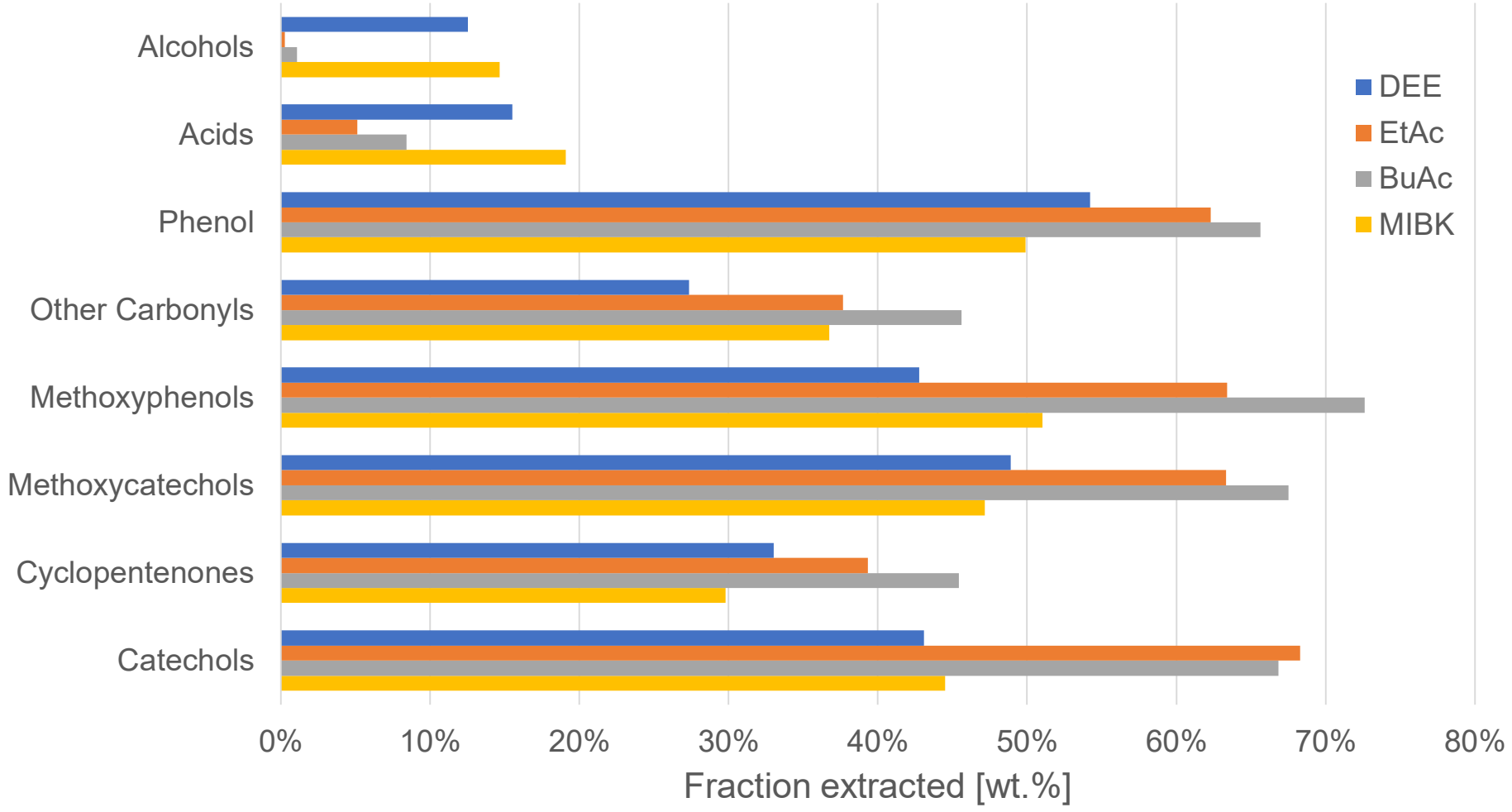
Liquid-Liquid Extraction tests

- **Lab scale solvents screening tests**
- **Experimental conditions**
  - Constant AP feed pH
  - Temperature 25°C
  - Extraction time 5 min
  - Phase separation after 5 min of centrifugation
  - Solvent to AP ratio = 1
- **Analytical methods**
  - AP feed: GC-MS and HPLC
  - Extract: GC-MS
  - Raffinate: HPLC



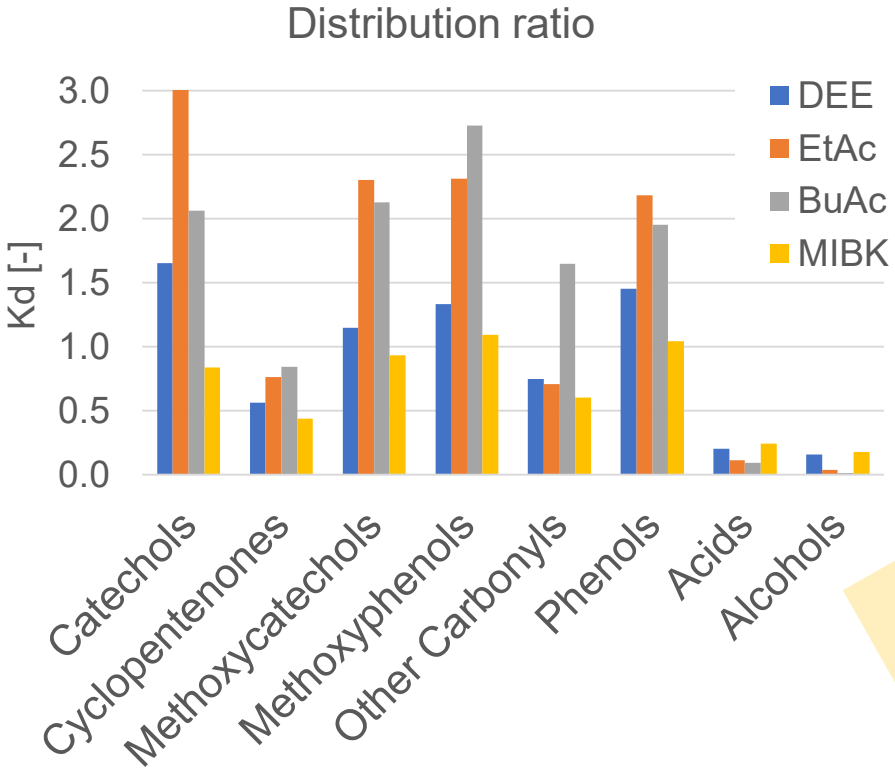


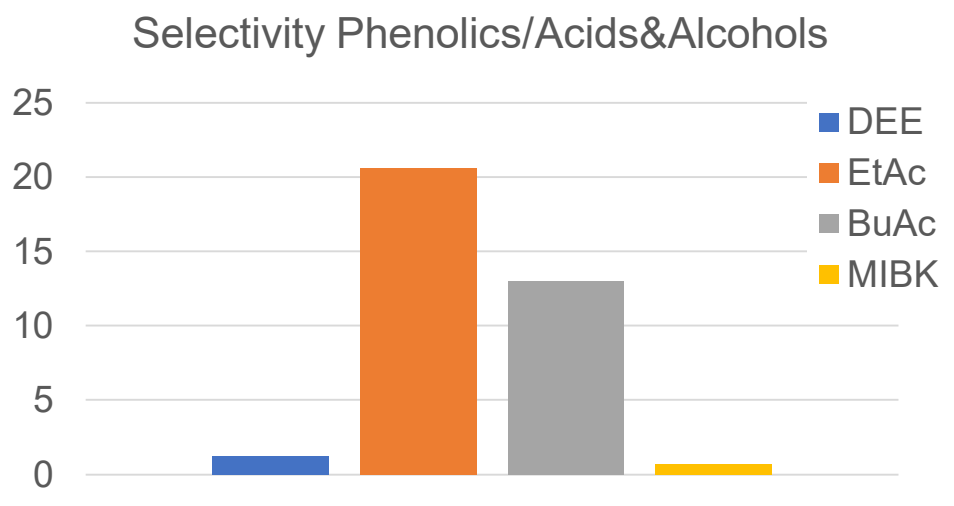
Liquid-Liquid Extraction: Extract recovery



- Fraction Extracted → $F_i = {}^{m_{i,org}}/_{m_{i,feed}}$

Liquid-Liquid Extraction: K_d and Selectivity





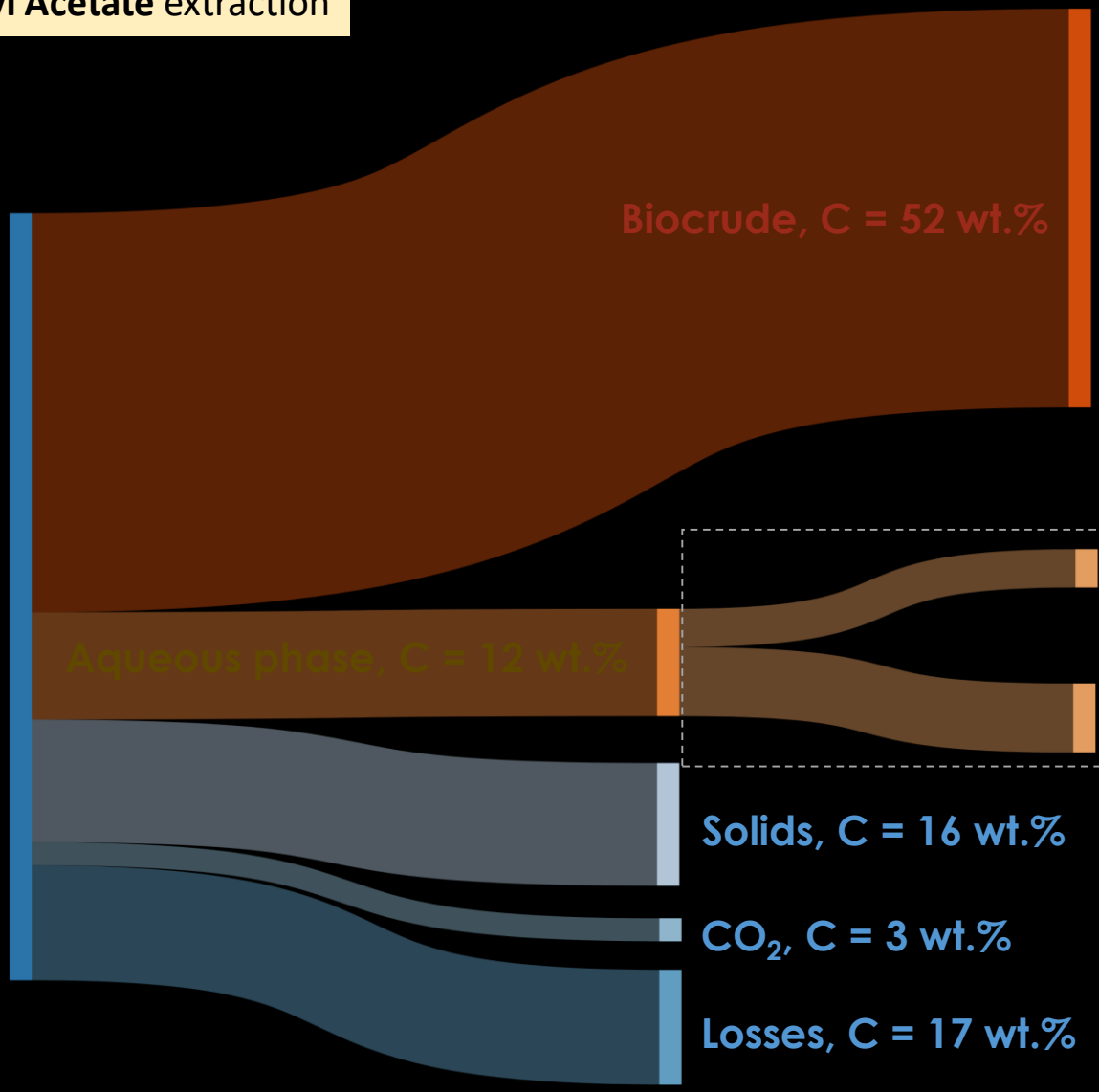
- Distribution ratio → $K_{d,i} = {}^{C_{extr,i}}/_{C_{raff,i}}$
- Selectivity → $\alpha_{P,A} = {}^{K_{d,P}}/_{K_{d,A}}$

Highest phenolics K_d and selectivity compared to acids and alcohols with **Ethyl acetate** and **Butyl acetate**

Li

Butyl Acetate extraction

HTL of LRS



LLE

- 83% phenolics
- 16% acids

- 13% phenolics
- 46% acids
- 41% alcohols

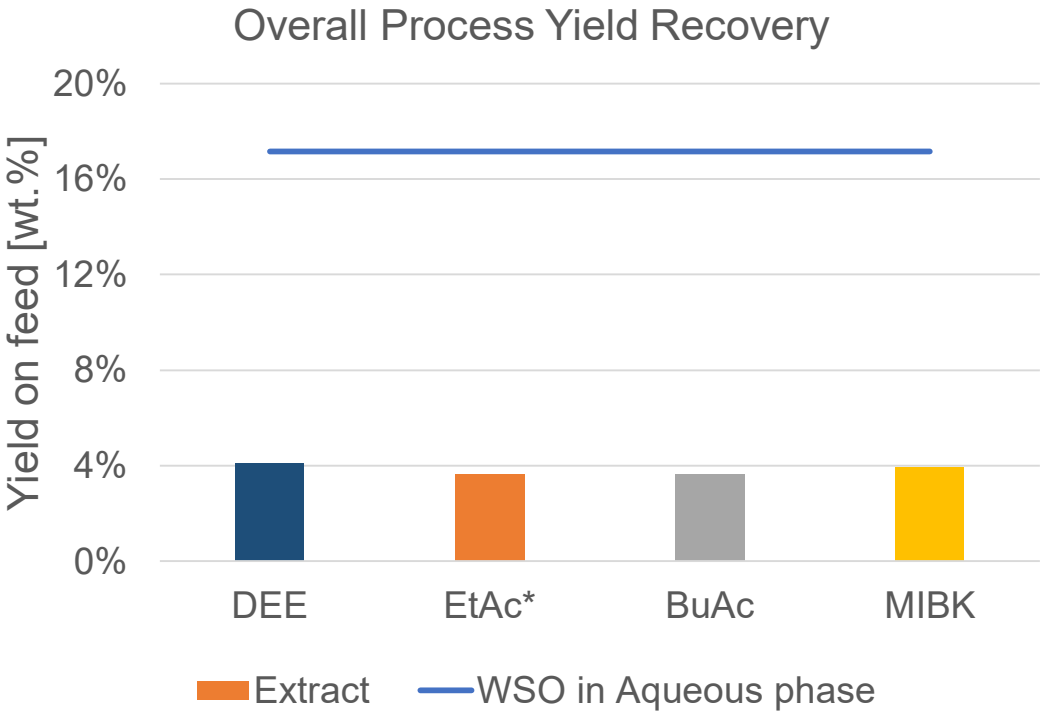
LLE integration for biocrude enhancement

HTL → AP → LLE

Extract

Biocrude

Fuel



- About **8 %** of increment in **Biocrude yield**
- No differences in extract yields changing the solvent
- DEE and MIBK extracts higher fractions of acids

*estimated acetic, propionic acids and methanol content from BuAc data

LLE integration for chemicals precursors

HTL → AP → LLE

Extract

Separation
Purification

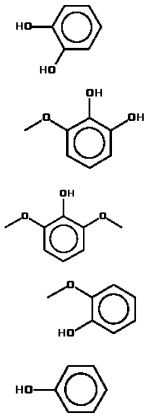
Chemical precursors

Chemicals

- Lignocellulosic Ethanol Biorefinery
  - Estimated lignin amount produced in EU: from **49 kTA (2017)** to **4340 kTA (2030)***

* Data estimated from ethanol data: C. Chudziak, G. Alberts, A. Bauen, Ramp up of lignocellulosic ethanol in Europe to 2030 Final Report, 2017, **E4tech**

Compound *extracted with EtAc*	Kd	Fraction extracted [wt.%]	Yield on feed * [wt.%]	Production 2017 [kTA]	Production 2030 [kTA]	Market size [kTA]	Price [$ kg-1]
1,2-Benzenediol	2.5	71%	0.02%	0.01	0.9	44[a]	4.0[b]
1,2-Benzenediol, 3-methoxy-	2.3	64%	0.05%	0.02	2.2	-	-
Phenol, 2,6-dimethoxy-	3.6	78%	0.06%	0.03	2.4	40[c]	2.0[c]
Phenol, 2-methoxy-	1.5	61%	0.03%	0.01	1.2		
Phenol	2.2	69%	0.05%	0.03	2.4	11400[b]	1.1[b]



* Estimation of compound purification efficiency of 10 %

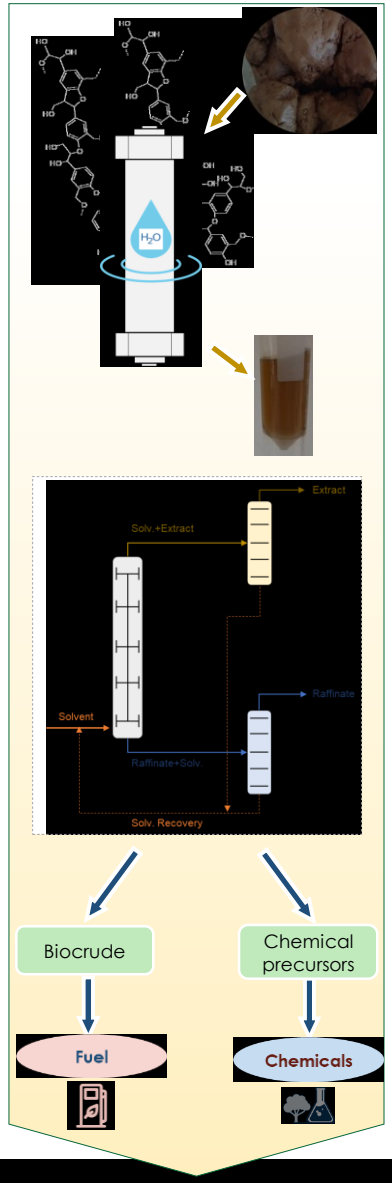
[a] https://www.gep.com/mind/blog/catechol-faces-supply-crunch-while-prices-rise

[b] A.N. Wilson, A. Dutta, B.A. Black, C. Mukarakate, J.A. Schaidle, W.E. Michener, G.T. Beckham, M.R. Nimlos, Valorization of Aqueous Waste Streams from Thermochemical Biorefineries, Green Chem. (2019) Accepted. doi:10.1039/c9gc00902g.

[c] P. Varanasi, P. Singh, M. Auer, P.D. Adams, B.A. Simmons, S. Singh, Survey of renewable chemicals produced from lignocellulosic biomass during ionic liquid pretreatment, Biotechnol. Biofuels. 6 (2013) 1. doi:10.1186/1754-6834-6-14.

Conclusions

- AP from LRS-HTL still contains **2-3 wt.% of organic matters**
  - 12 wt.% of C trapped in AP
- Liquid-liquid extraction (LLE) was evaluated as possible pathway for **selective organics recovery**
- **DEE**, **EtAc**, **BuAc** and **MIBK** were tested as extraction solvent
  - EtAc and BuAc → highest selectivity for phenolics extraction
  - 3 wt.% of C recovered in extract
- **LLE-Integration for biocrude yield enhancement**
  - Potential biocrude yield increment of 8 %
- **LLE-Integration for bio-based chemicals precursors**
  - Targeted molecules: *1,2 benzenediol*, *1,4-Benzenediol, 2-methoxy-*, *Phenol, 2,6-dimethoxy-*, *Phenol, 2-methoxy-*.



Thanks for the attention!

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