PYROLYSIS OF MIXTURES OF PULPING LIQUOR AND SODIUM FORMATE TO PRODUCE A PHENOLIC BIO-OIL

Jamie St. Pierre and Adriaan van Heiningen
University of Maine, Orono, ME, USA

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Outline

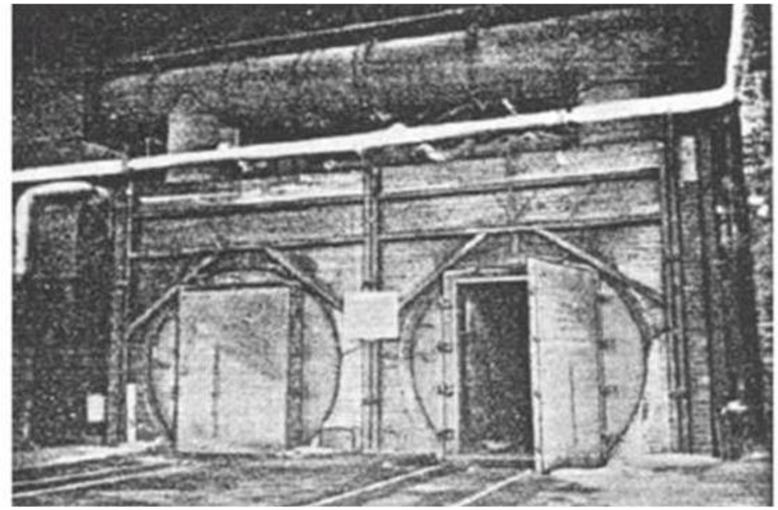
- Black Liquor as a Feedstock for Fuels and Chemicals
- Commercial Implementation in the Past: Rinman Process
- Background for pyrolysis with added formate salts
- Scheme for implementation in a mill
- Experimental set-up for pyrolysis of Soda-AQ black liquor
- Results and discussion
- Conclusions
- Future work

Black Liquor as a Feedstock

- World annual production: 200 Million Tonne/year
- Currently utilized as low-value fuel (13 – 15 MJ/kg)[1]
- 1.2 – 1.8 tons spent liquor solids per tonne of pulp[1]
- Organic-to-inorganic ratio: 1.4 – 1.6 kg/kg
- Modern Kraft mill uses 1/3 of black liquor energy for excess electricity generation
- Carbon-containing product of higher value than electricity could be produced instead
- **OBJECTIVE**: Production of significantly deoxygenated bio-oil from black liquor using pyrolysis

[1] Tran and Vakkilainnen, 2008

The Rinman Process



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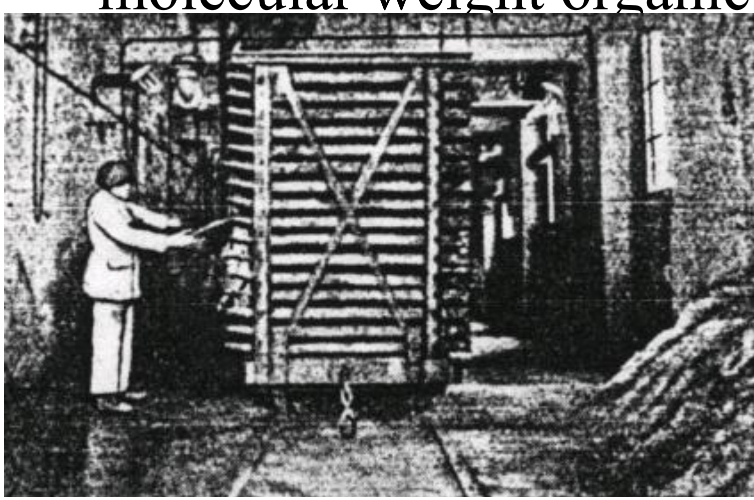
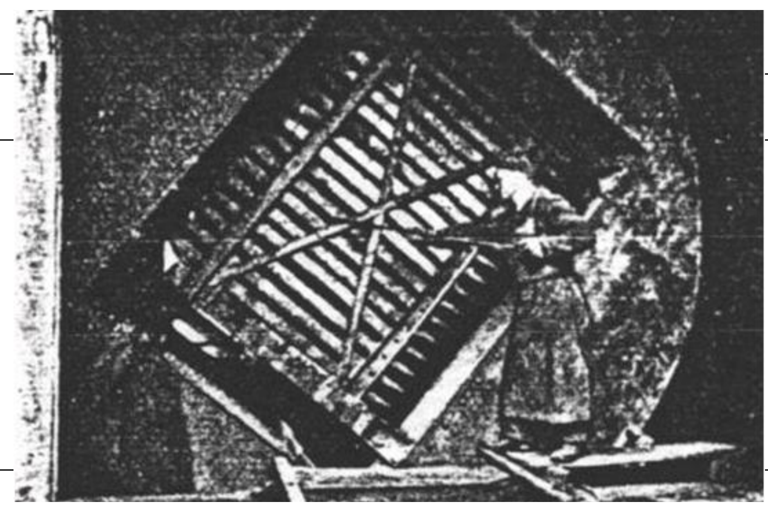
molecular weight organics





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[1]Rydholm, 1985; Rinman, 1916; Rinman, 1920; Niemelä, 2012

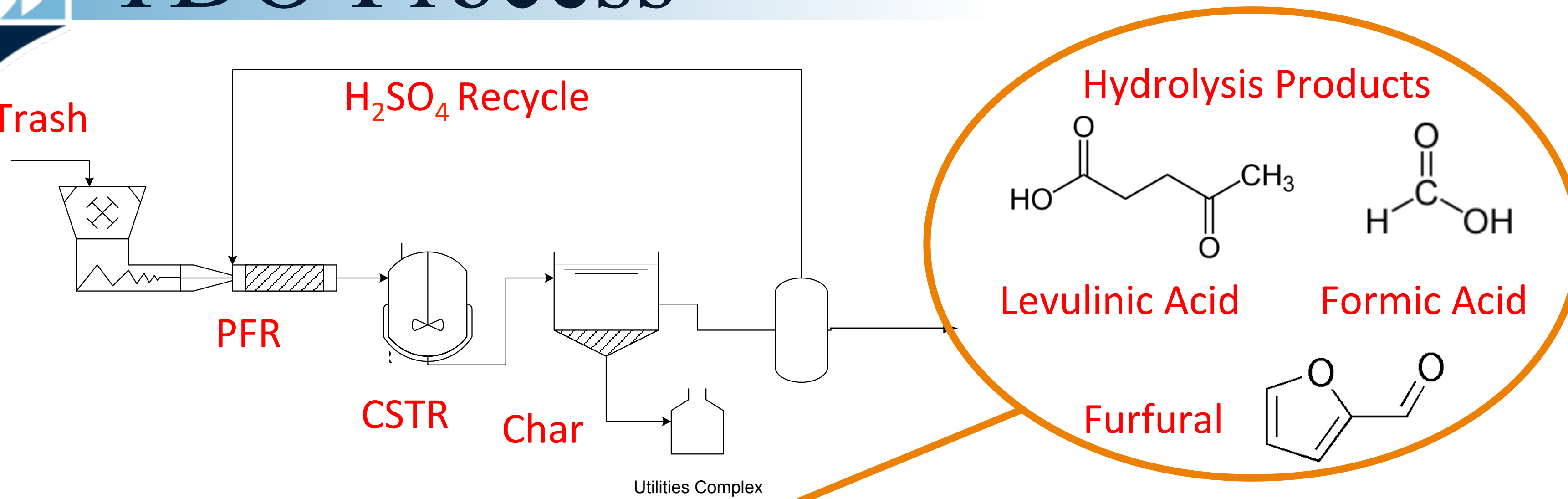
Pyrolysis with Formate Salts

- Formic acid is known to donate hydrogen
- Formate salts can decompose into H_2 and CO at pyrolysis temperatures

$$Ca(HCOO)_2 \xrightarrow[\Delta]{} CaCO_3 + CO + H_2$$

- Two innovative processes at the University of Maine
  - **Thermal Deoxygenation (TDO) of hydrolyzed biomass**
  - **Formate-Assisted Pyrolysis (FASP) of biomass**

TDO Process

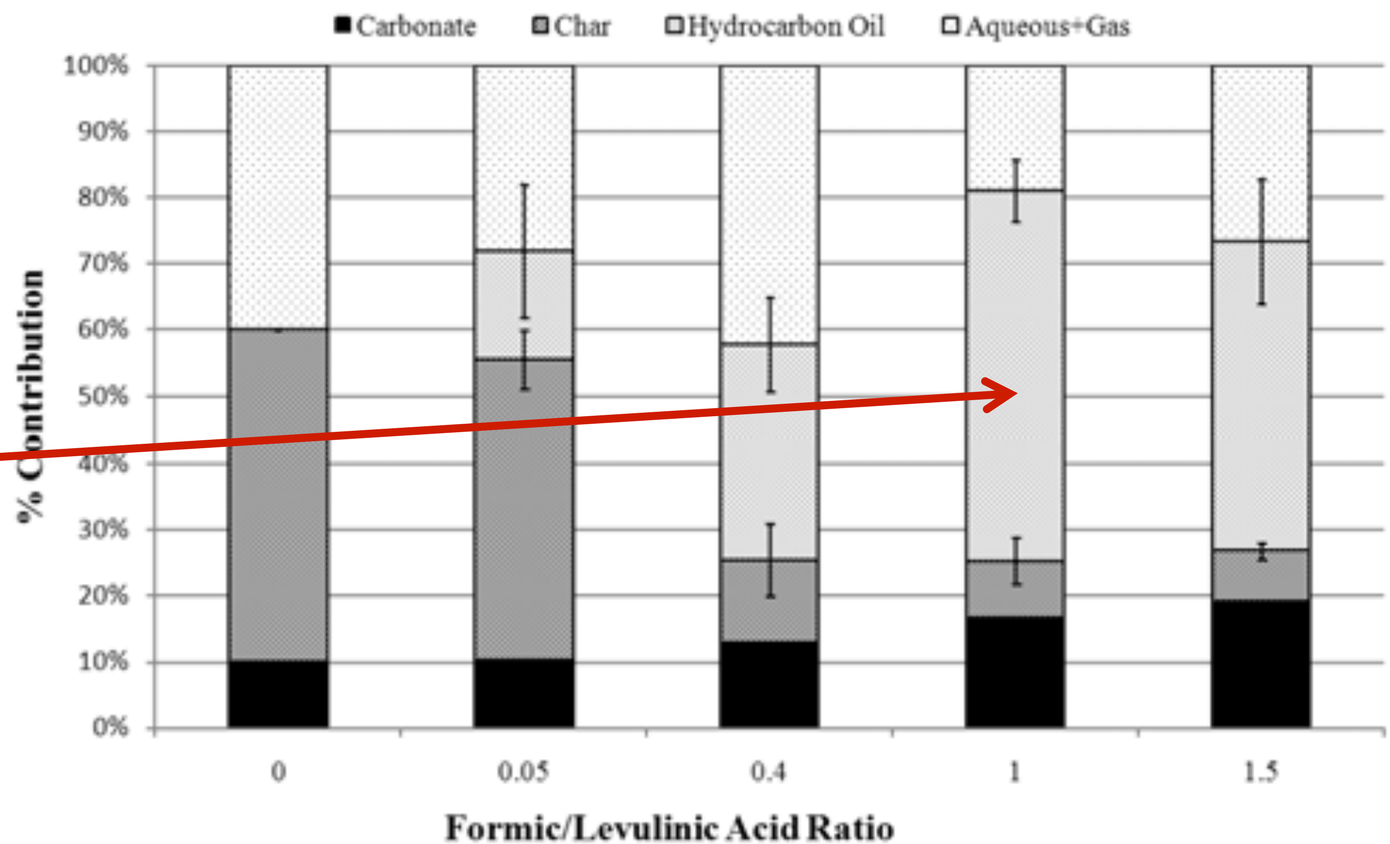


Levulinic Acid + Formic Acid

$+ \ Ca(OH)_2 + \Delta$

P.A. Case et al., Green Chem. 2011

Thermal Deoxygenation (TDO)



Carbon distribution in TDO products versus FA/LA molar ratio

P. Case et al., Green Chemistry, 14 (1), 85 – 89 (2012)

Formate-Assisted Pyrolysis (FAsP)

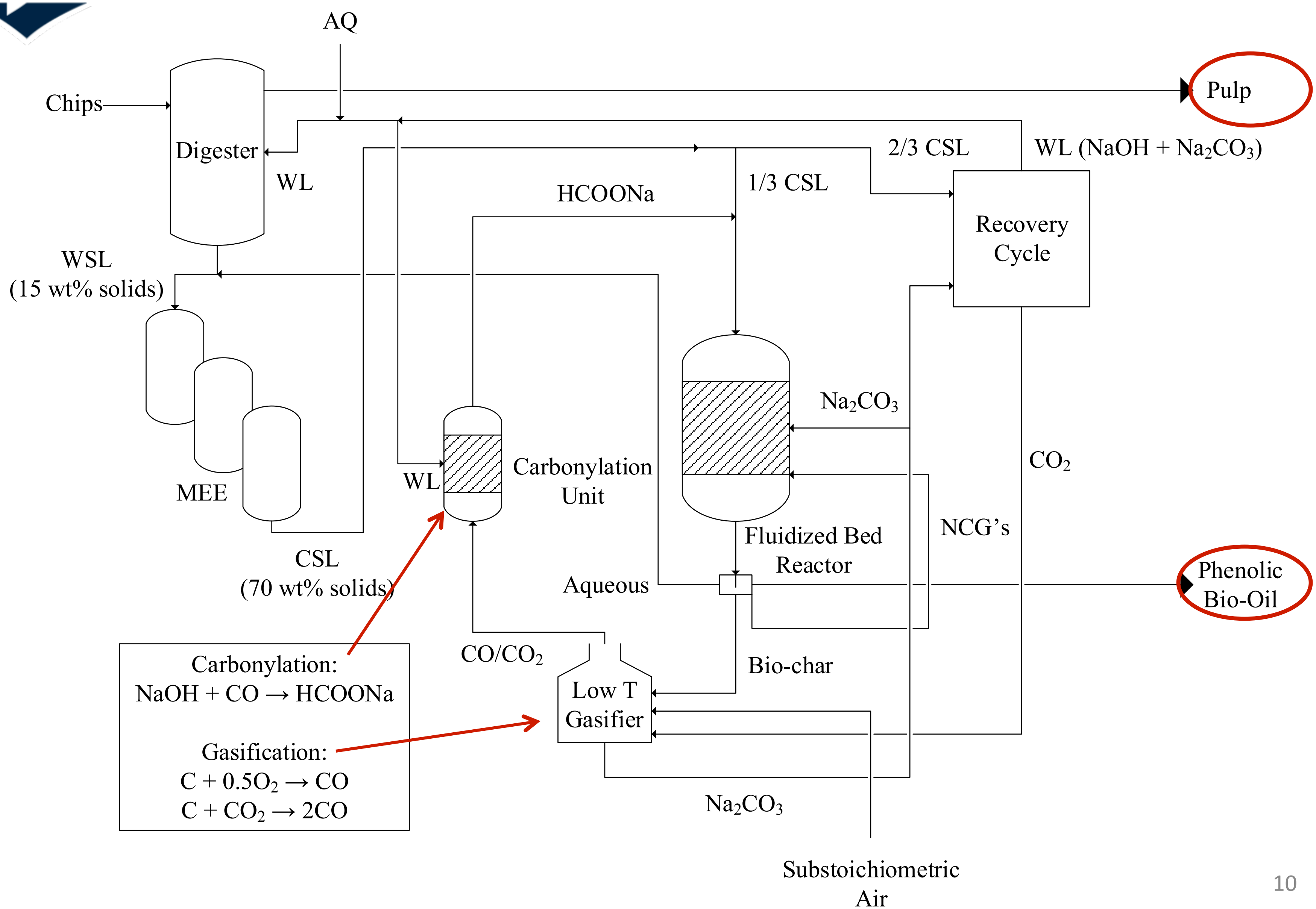
Bio-oil from lignin (Indulin AT) with calcium formate (1g FA + 0.5 g $Ca(OH)_2$/g Indulin AT)[1]

- Yield increase yield from 23.3 to 32.5 wt%
- O/C molar ratio decreases from 0.19 to 0.067
- HHV increases from 30.7 → 41.7 MJ/kg
- Char yield decreases from 41.0 → 34.8 wt%
- Bio-oil quality increases with formate charge

[1]Mukkamala et al., 2012

TDO of Soda-AQ Black Liquor

Black Liquor TDO in Pulp Mill



Characterization of Pulping Products

NE Hardwoods, Soda-AQ, L/W 3.5 L/kg, 16% EA. 0.1 % AQ

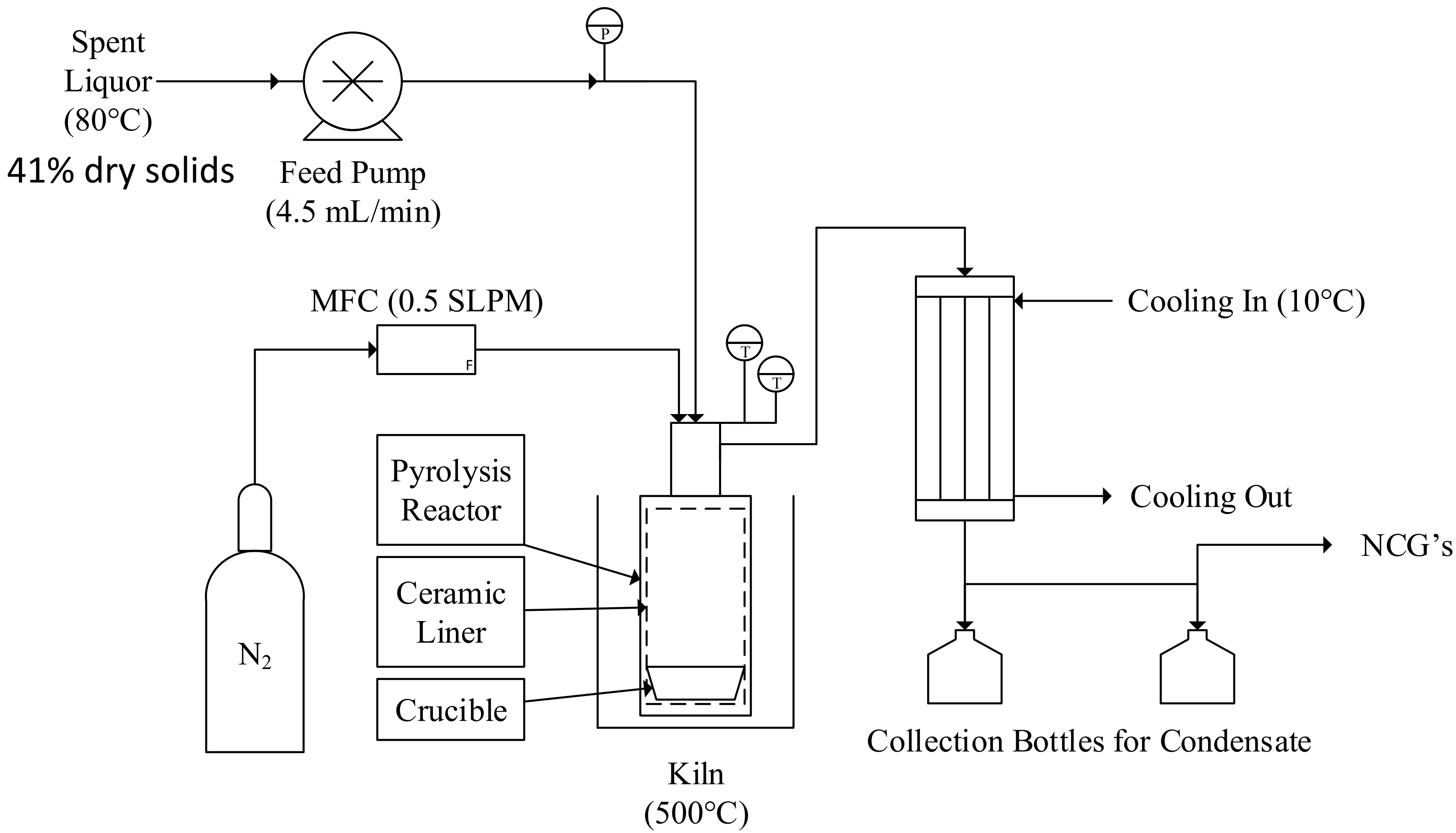
- Liquor Properties

Dry Solids (wt%)	REA (g/L as Na_2O)	Lignin (wt% on d.s.)	Sugars/Acids (wt% on d.s.)	Ash (wt% on d.s.)	Org:Inorg (w:w)
18.6 ± 0.9	6.4 ± 2.1	33.4 ± 5.4	15.9 ± 3.1	40.7 ± 2.2	1.2 ± 0.2

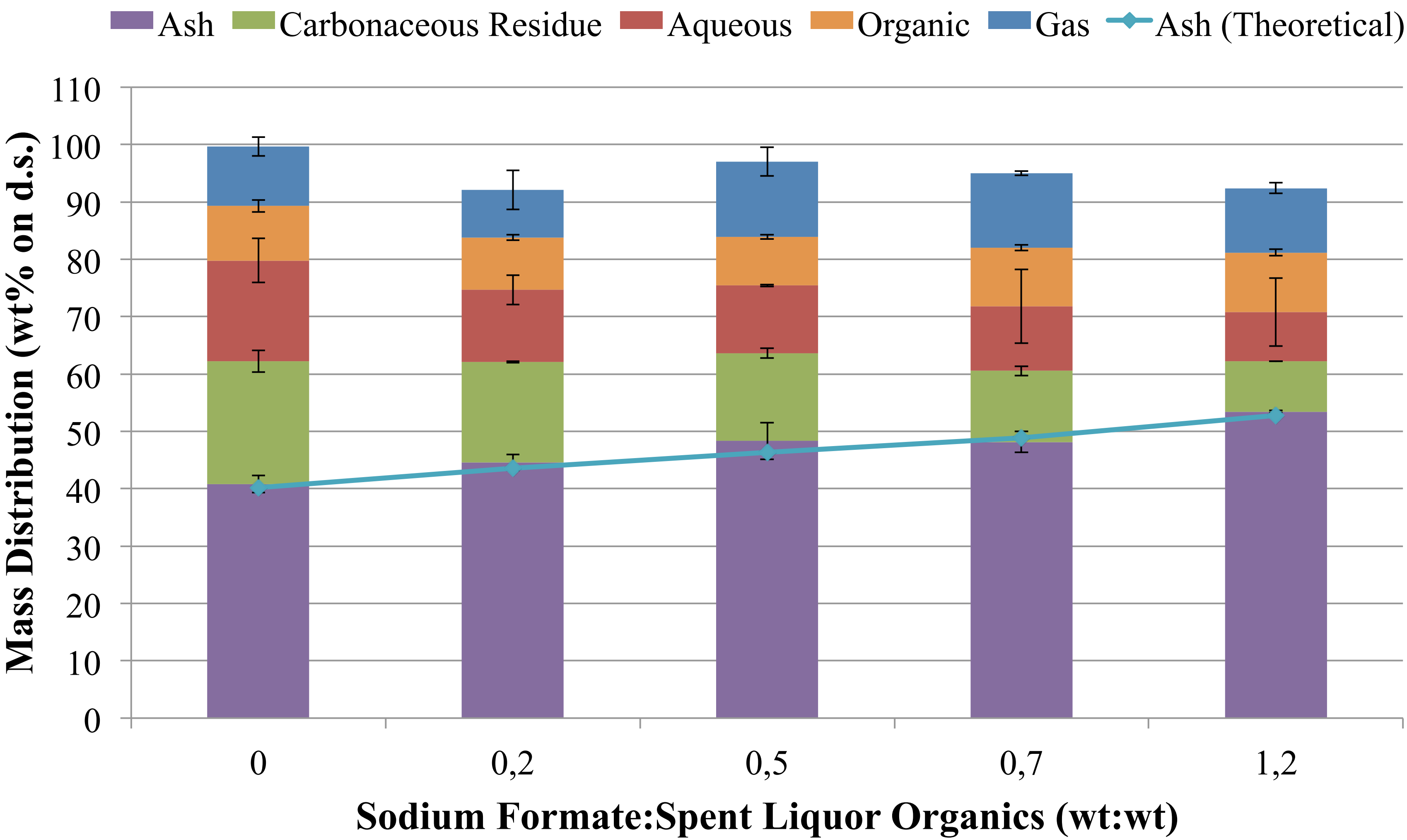
- Pulp Properties

Pulp Yield (%)	Rejects (%)	Kappa No.
50.0 ± 2.1	0.8 ± 0.4	18.3 ± 5.6

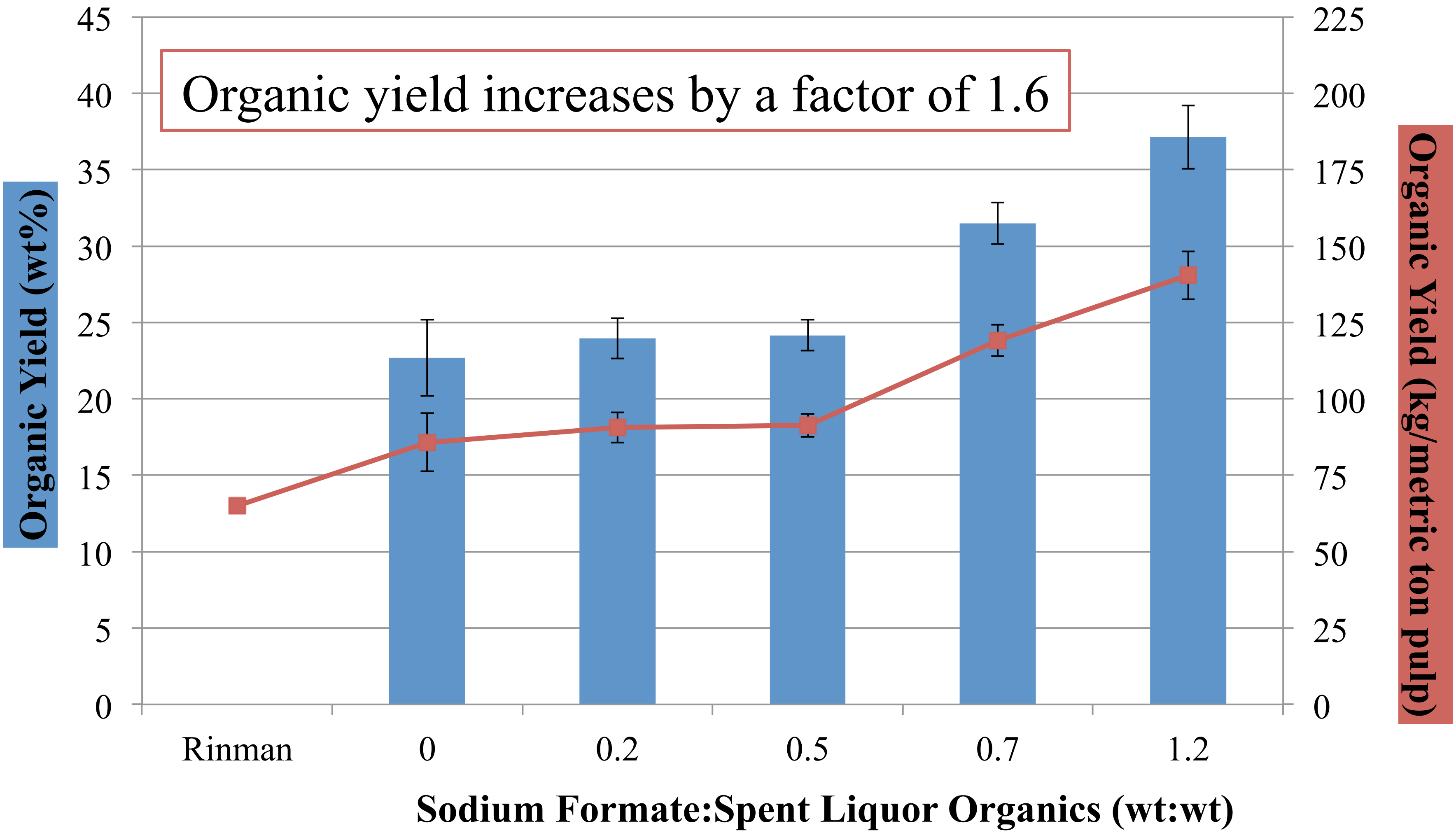
Reactor Schematic



Pyrolysis Mass Balances



Organic Yields after Pyrolysis



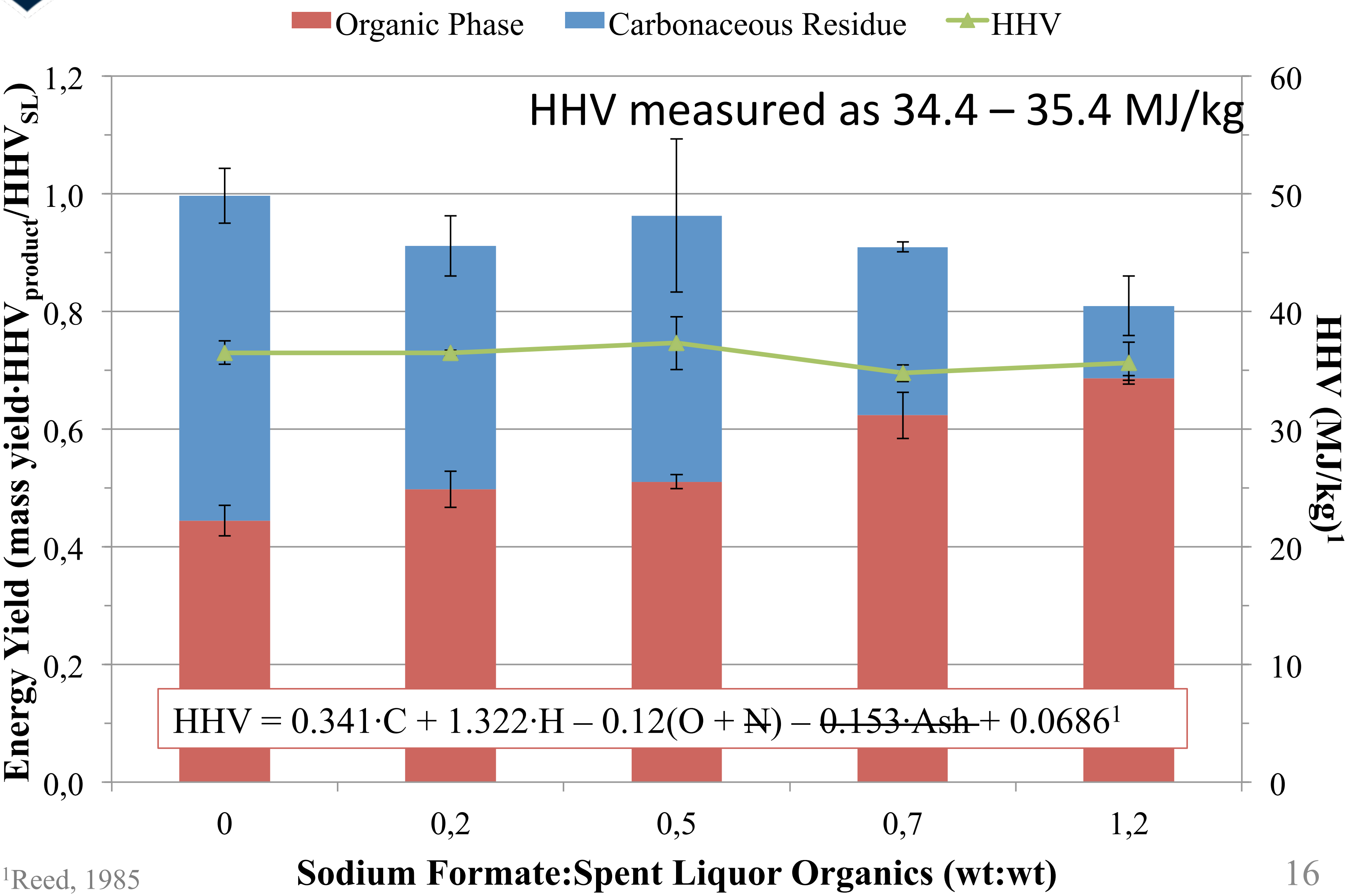
Ultimate Analysis

		Sodium Formate/Spent Liquor Organics (wt/wt)				
	Feedstock	**0**	**0.2**	**0.5**	**0.7**	**1.2**
O:C*,† (mol/mol)	0.36	0.08	0.09	0.12	0.11	0.09
H:C† (mol/mol)	1.62	1.28	1.35	1.26	1.30	1.35

*Based on organic material in feed; †dry.

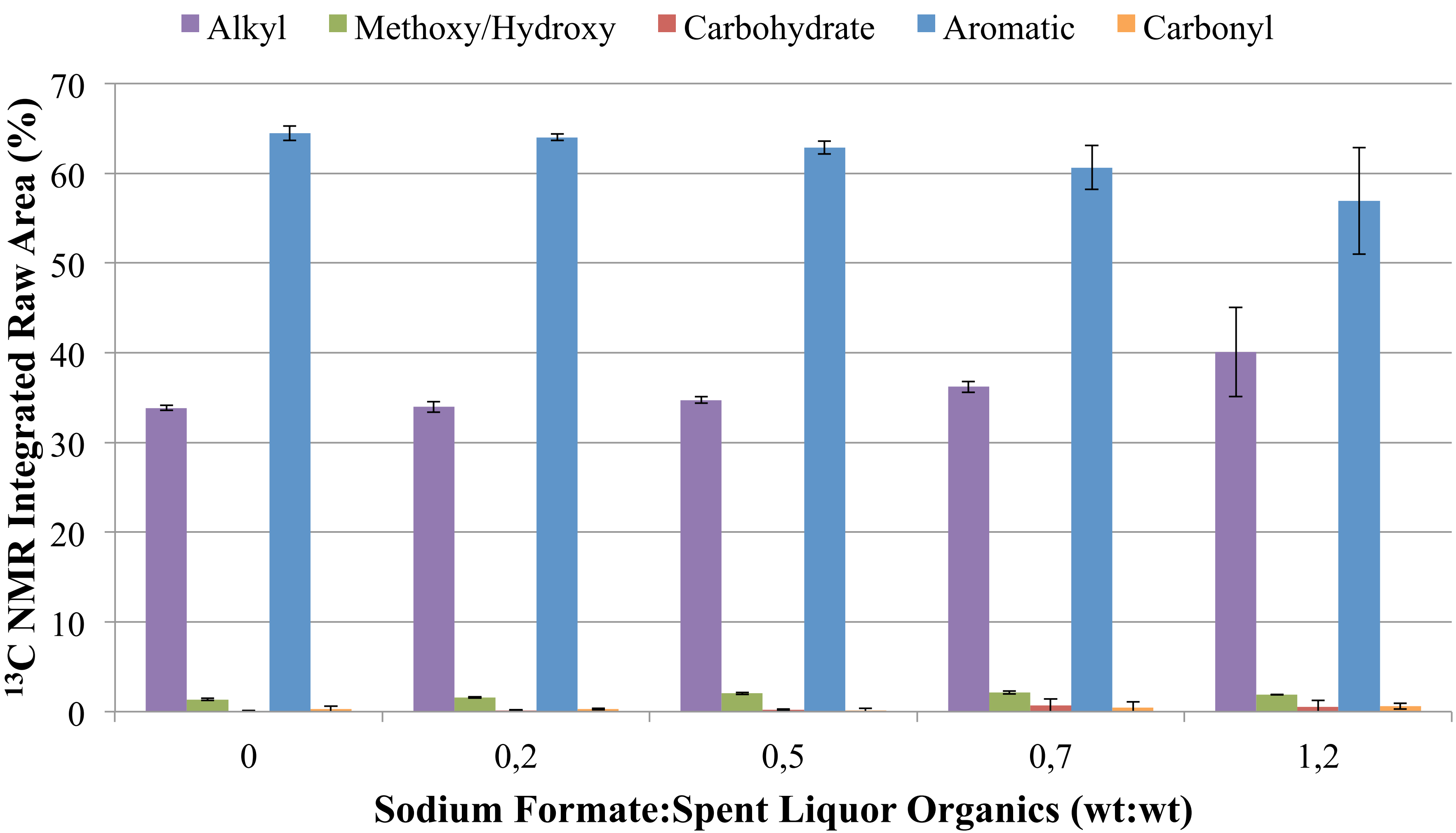
- Significant deoxygenation occurring (~ 70 % reduction)
- ~ 20% reduction in hydrogen content

Energy Yields



[1]Reed, 1985

^{13}C NMR of Bio-Oil



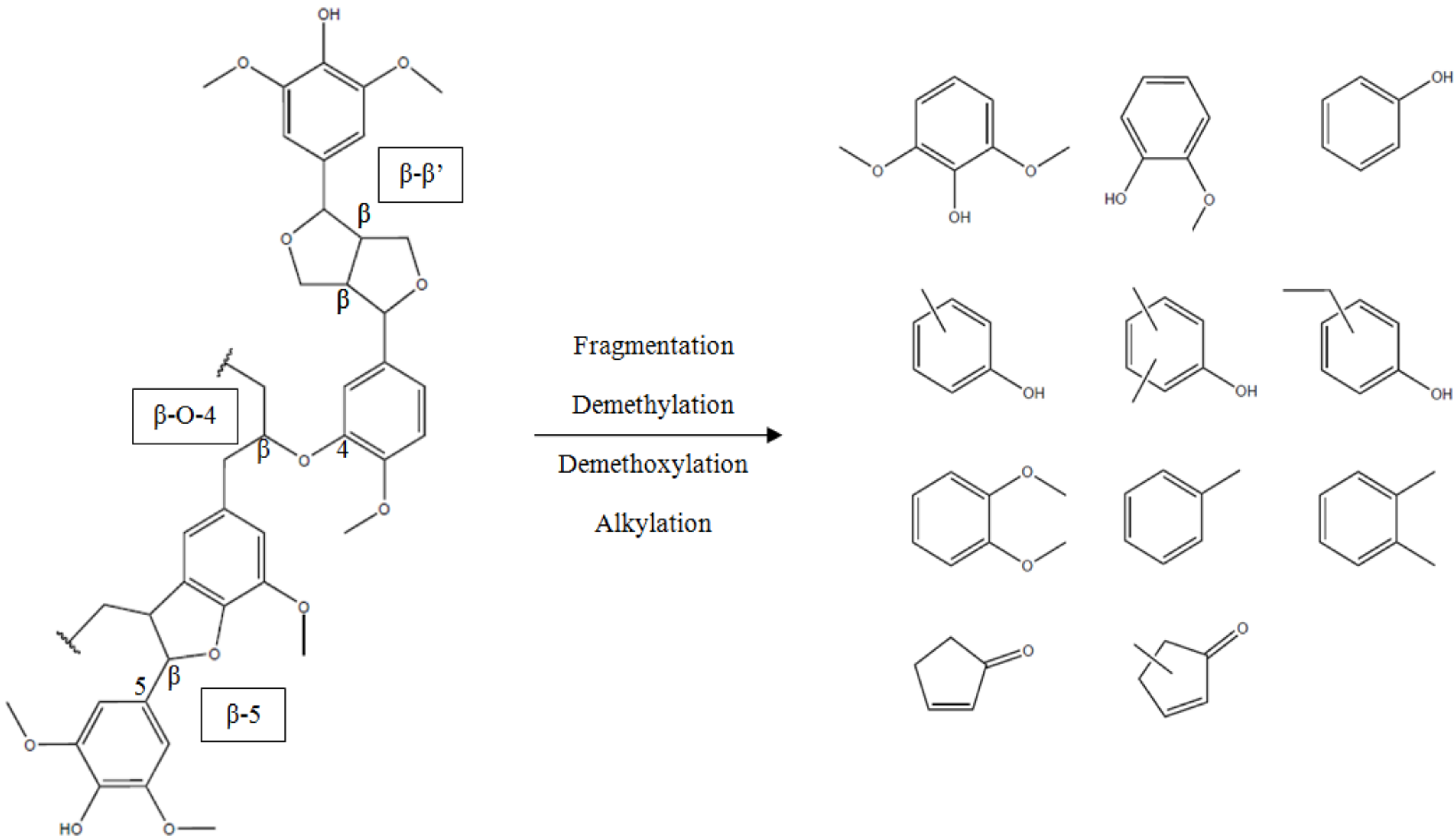
Bio-Oil Molecular Weight Distribution

	0	0.2	0.5	0.7	1.2
M_w (g/mol)	303	--*	314	--	315
M_n (g/mol)	195	--	201	--	200
PDI (M_w/M_n)	1.57	--	1.56	--	1.57

*not determined.

- Oligomers dominate
  - Bio-oil density greater than that of water
- Hypotheses
  - C – C linkages remain intact
  - CH_3OH from demethoxylation causing condensation via decomposition to formaldehyde which crosslinks with phenolics to form methylene bridges

GC/MS of Bio-Oil

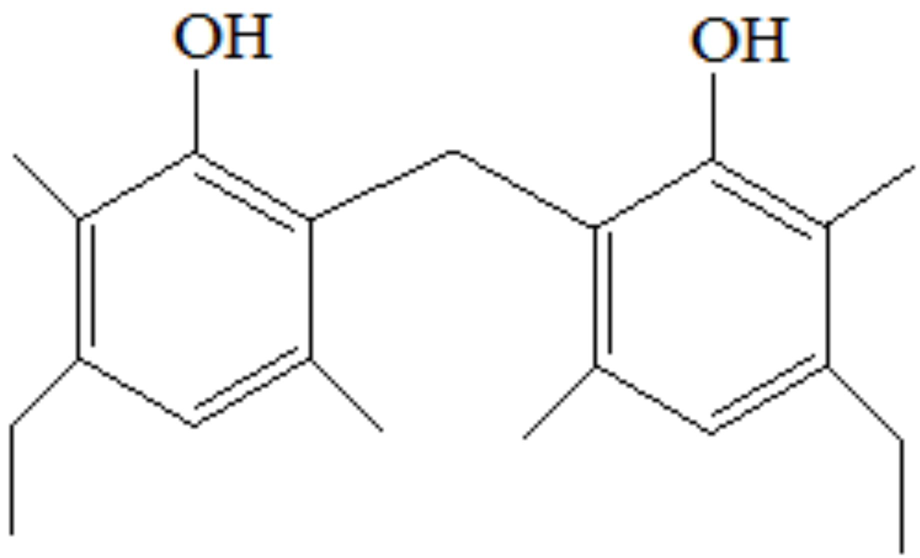


Only 4-8 % of compounds identified!

Image: St. Pierre et al., 2015

Representative Global Structure

Structure accounting for NMR, GPC, and Elemental analysis



$C_{21}H_{28}O_2$
$M_w = 313$ g/mol
O:C = 0.10
H:C = 1.33

No anhydrosugars or acids observed; Most likely converted to cyclic ketones by the presence of sodium compounds

Conclusion

- Formate increases bio-oil yield by a factor of 1.6
- But, similar product distributions for all bio-oils
  - Phenolics dominant compound type
  - Ethyl substituted phenolics most prominent
  - Substituent position on methyl substituted phenolics: m > o > p
  - Demethoxylation observed
  - Cyclic ketones increase as formate loading is increased

Future Work

- Recommendations for Future Work
  - Fast pyrolysis using Na_2CO_3 pellets as fluidizing and heat transfer media
  - Pyrolysis of softwood Kraft spent liquor

Thank You!

Questions?

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^{13}C NMR of Bio-Oil

^{13}C Assignment	Shift (ppm)[1]	Integrated Area (%)*
Carbonyl	165 — 215	0.5 ± 0.3
Aromatic	110 — 165	64.7 ± 3.0
Carbohydrate	70 — 110	0.2 ± 0.2
Methoxy/Hydroxy	54 — 70	1.7 ± 0.3
Alkyl	1 — 54	32.9 ± 2.5
Aromatic + Alkyl	—	97.6

*Corrected to account for incomplete longitudinal relaxation[1].

[1]Joseph et al., 2010