BAUXITE RESIDUE VALORISATION AND BEST PRACTICES CONFERENCE

Leuven 5-7 October 2015

UNIVERSITY of GUELPH

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Synergistic Co-Processing of Red Mud with Pyrolysis Bio-Oil: From Neutralization to Catalysis

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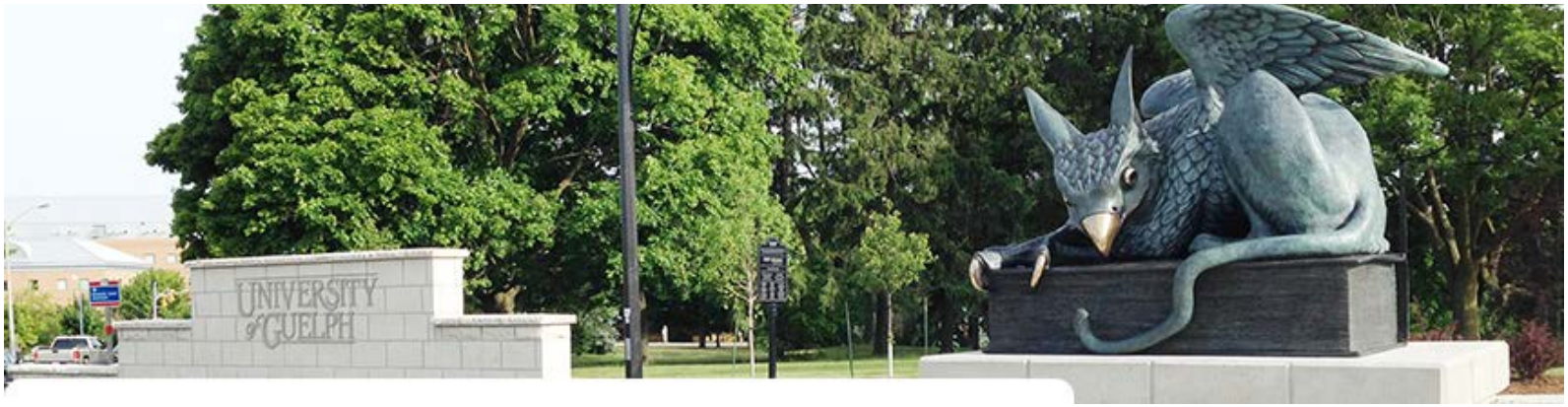
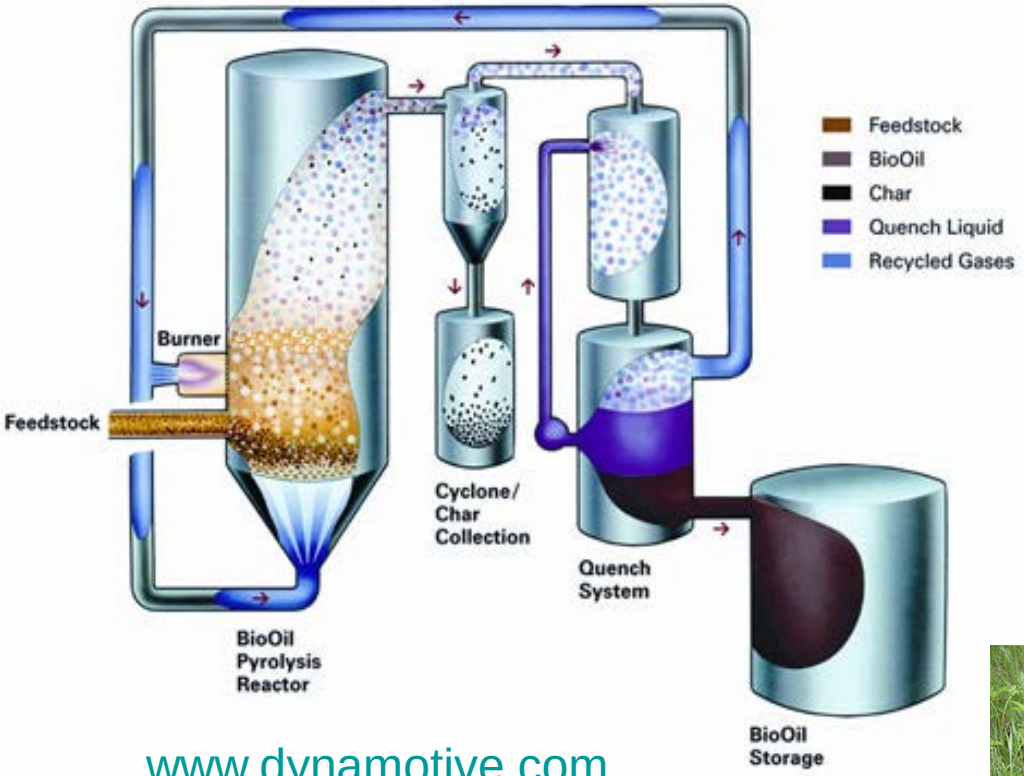
(GWC)^2:The Guelph-Waterloo-Centre for Graduate Work in Chemistry



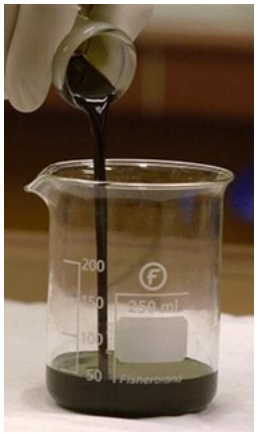
Pyrolysis of Biomass to Bio-Oil



www.dynamotive.com

(500 °C, 1-2 seconds)

CO, CO_2, H_2, CH_4



Gas

(10-20 %)

→ Heat

Bio-oil

(60-75%)

→ Fuel

Bio-char

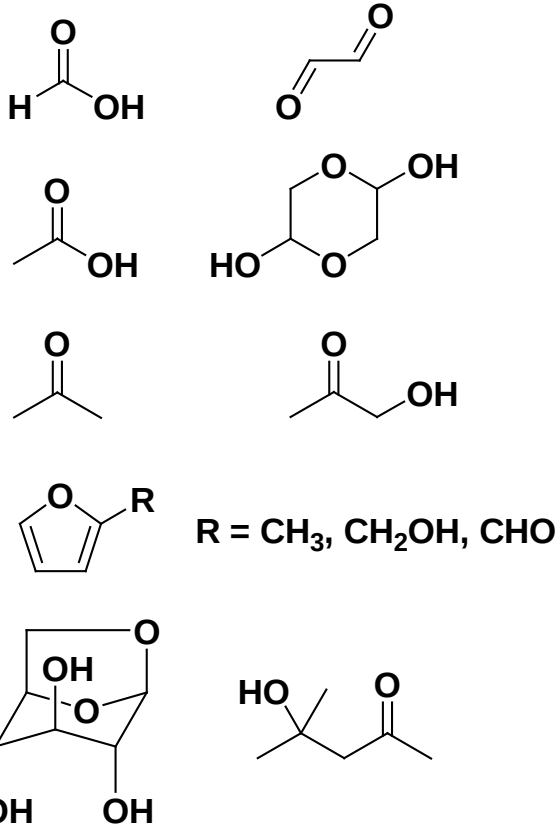
(15-20 %)

→ Soil

- **Actual composition is highly complex, reactive and dependent on feed-stock and actual process used.**
- **Once started the process is thermally self-sustaining.**

The Nature of Bio-Oil: The Black Death …

Reactive Compounds in bio-oil:



200 tons/day Guelph Plant (defunct)

Bio-oil obtained by DYNAMOTIVE

Acidity: pH ~ 2

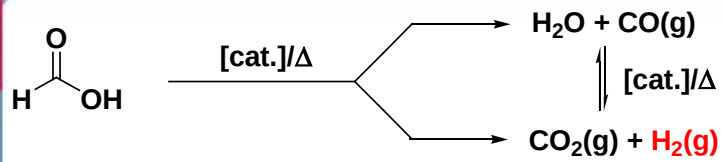
Oxygen content: ~ 50 % w/w

Water content: 20-50 % w/w

Not suitable as engine fuel "as is".

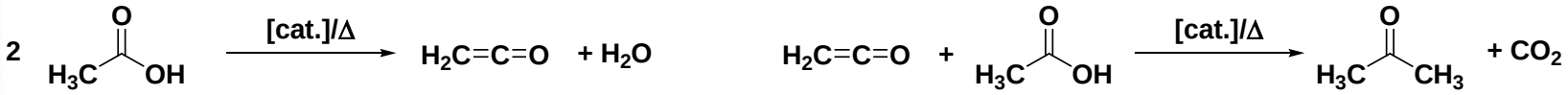
Rapidly "*kills*" typically used catalysts.

Bio-Oil Upgrading to Viable Low-Acid Fuel

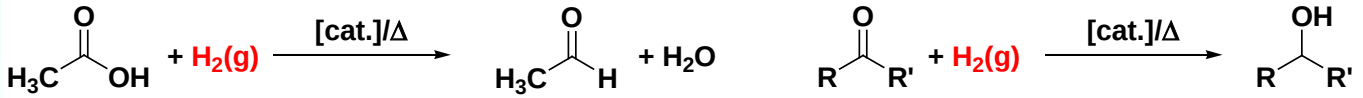


Thermal decomposition of formic acid
Watergas shift reaction
(in situ source of hydrogen)

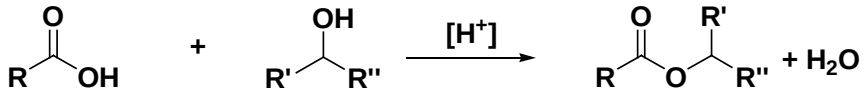
Ketonization of acetic acid



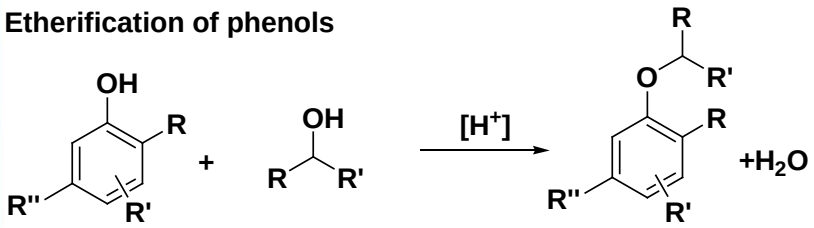
Hydrogenation carbonyls to alcohols



Esterification of carboxylic acids



Etherification of phenols



Wang, H., J. Male, et al. (2013). "Recent Advances in Hydrotreating of Pyrolysis Bio-Oil and Its Oxygen-Containing Model Compounds." ACS Catalysis 3(5): 1047-1070.

All reactions aim at reducing the overall acidity/reactivity (= oxygen content) of the bio-oil.

Catalysts and support must be acid, water and *coking* stable !

Cannot have leaching of Re, Rh, Ru, Ir, Ni, Pd, Pt or other heavy-toxic metal into the fuel.

Is there a universal & promiscuous catalyst for all reactions in the same pot ?

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Non-Toxic Catalytically Active Metals ?

IUPAC Periodic Table of the Elements

1																	18
1 H hydrogen 1.007 94(7)	2											13	14	15	16	17	2 He helium 4.002 602(2)
3 Li lithium 6.941(2)	4 Be beryllium 9.012 182(3)											5 B boron 10.811(7)	6 C carbon 12.0107(8)	7 N nitrogen 14.0067(2)	8 O oxygen 15.9994(3)	9 F fluorine 18.998 4032(5)	10 Ne neon 20.1797(6)
11 Na sodium 22.989 769 28(2)	12 Mg magnesium 24.3050(6)	3	4	5	6	7	8	9	10	11	12	13 Al aluminium 26.981 538 6(8)	14 Si silicon 28.0855(3)	15 P phosphorus 30.973 762(2)	16 S sulfur 32.065(5)	17 Cl chlorine 35.453(2)	18 Ar argon 39.948(1)
19 K potassium 39.0983(1)	20 Ca calcium 40.078(4)	21 Sc scandium 44.955 912(6)	22 Ti titanium 47.867(1)	23 V vanadium 50.9415(1)	24 Cr chromium 51.9961(6)	25 Mn manganese 54.938 045(5)	26 Fe iron 55.845(2)	27 Co cobalt 58.933 195(5)	28 Ni nickel 58.6934(2)	29 Cu copper 63.546(3)	30 Zn zinc 65.409(4)	31 Ga gallium 69.723(1)	32 Ge germanium 72.64(1)	33 As arsenic 74.921 60(2)	34 Se selenium 78.96(3)	35 Br bromine 79.904(1)	36 Kr krypton 83.798(2)
37 Rb rubidium 85.4678(3)	38 Sr strontium 87.62(1)	39 Y yttrium 88.905 85(2)	40 Zr zirconium 91.224(2)	41 Nb niobium 92.906 38(2)	42 Mo molybdenum 95.94(2)	43 Tc technetium [98]	44 Ru ruthenium 101.07(2)	45 Rh rhodium 102.905 50(2)	46 Pd palladium 106.42(1)	47 Ag silver 107.8682(2)	48 Cd cadmium 112.411(8)	49 In indium 114.818(3)	50 Sn tin 118.710(7)	51 Sb antimony 121.760(1)	52 Te tellurium 127.60(3)	53 I iodine 126.904 47(3)	54 Xe xenon 131.293(6)
55 Cs caesium 132.905 451 9(2)	56 Ba barium 137.327(7)	57-71 lanthanoids	72 Hf hafnium 178.49(2)	73 Ta tantalum 180.947 88(2)	74 W tungsten 183.84(1)	75 Re rhenium 186.207(1)	76 Os osmium 190.23(3)	77 Ir iridium 192.217(3)	78 Pt platinum 195.084(9)	79 Au gold 196.966 569(4)	80 Hg mercury 200.59(2)	81 Tl thallium 204.3833(2)	82 Pb lead 207.2(1)	83 Bi bismuth 208.980 40(1)	84 Po polonium [209]	85 At astatine [210]	86 Rn radon [222]
87 Fr francium [223]	88 Ra radium [226]	89-103 actinoids	104 Rf rutherfordium [261]	105 Db dubnium [262]	106 Sg seaborgium [266]	107 Bh bohrium [264]	108 Hs hassium [277]	109 Mt meitnerium [268]	110 Ds darmstadtium [271]	111 Rg roentgenium [272]							

Key: atomic number / Symbol / name / standard atomic weight

57 La lanthanum 138.905 47(7)	58 Ce cerium 140.116(1)	59 Pr praseodymium 140.907 65(2)	60 Nd neodymium 144.242(3)	61 Pm promethium [145]	62 Sm samarium 150.36(2)	63 Eu europium 151.964(1)	64 Gd gadolinium 157.25(3)	65 Tb terbium 158.925 35(2)	66 Dy dysprosium 162.500(1)	67 Ho holmium 164.930 32(2)	68 Er erbium 167.259(3)	69 Tm thulium 168.934 21(2)	70 Yb ytterbium 173.04(3)	71 Lu lutetium 174.967(1)
89 Ac actinium [227]	90 Th thorium 232.038 06(2)	91 Pa protactinium 231.035 88(2)	92 U uranium 238.028 91(3)	93 Np neptunium [237]	94 Pu plutonium [244]	95 Am americium [243]	96 Cm curium [247]	97 Bk berkelium [247]	98 Cf californium [251]	99 Es einsteinium [252]	100 Fm fermium [257]	101 Md mendelevium [258]	102 No nobelium [259]	103 Lr lawrencium [262]

Notes

- 'Aluminum' and 'cesium' are commonly used alternative spellings for 'aluminium' and 'caesium'.
- IUPAC 2005 standard atomic weights (mean relative atomic masses) are listed with uncertainties in the last figure in parentheses [M. E. Wieser, *Pure Appl. Chem.* **78**, 2051 (2006)]. These values correspond to current best knowledge of the elements in natural terrestrial sources. For elements that have no stable or long-lived nuclides, the mass number of the nuclide with the longest confirmed half-life is listed between square brackets.
- Elements with atomic numbers 112 and above have been reported but not fully authenticated .

- **Hydrogenating metals are all toxic and cannot be in product fuel.**
- **Hydrogenating metals are expensive and vulnerable to coking.**
- **Non-toxic metals in green: Na, K, Mg, Ca, Ti, Fe, Zn, Al, Si (occurring naturally as cation or oxide).**

Red Mud as a *Sacrificial* Catalyst

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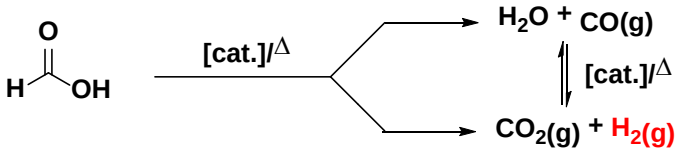
Fe_2O_3

$+ H_2$ | $- H_2O$

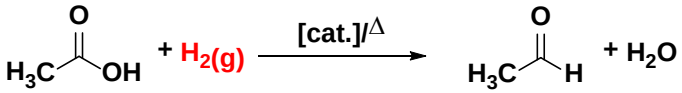
$+ CO$ | $- CO_2$

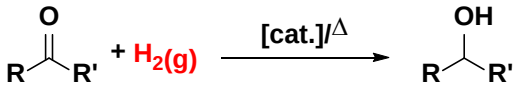
$Fe_3O_4/FeO/Fe$

Decomposition of formic acid (WGSR)



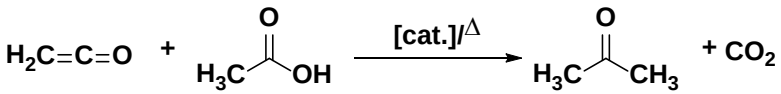
Hydrogenation carbonyls to alcohols





TiO_2

Ketonization of acetic acid (and other carboxylic acids)



SiO_2

Al_2O_3

Na^+/Ca^{2+}

Brønstedt/Lewis Acid/Base Catalysts:

hydration/dehydration/hydrolysis

C=C & C=O activation

Traces:

Cr^{3+}/U^{4+}

Promoters

???

In situ reduction of hematite to iron suboxides and carbides generates active WGSR and hydrogenation catalyst.

Red Mud is neutralized by RCOOH and H_2CO_3.

High Bio-Oil/Red Mud ratios: Upgrading

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Hard Wood Chips

Pyrolysis

450 +/- 10 ºC
@ 1000 ºC/s
steel shot carrier
residence time in
pyrolyzer < 2 s

Bio-Oil

H_2O [%]	pH	TAN [mg/g]
~ 40	2.8	124

ABRI-TECH Inc., Namur, QC.

Run	Yield [g/%]	H_2O [%]	pH	TAN [mg/g]
+ H_2O	5.9/24	0.7	5.2	19.6
No H_2O	3.9/16	0	5.7	2.8

bio-oil (25 g)
water (25g)
RM (7 g)
365 °C, no H_2(g)
4 hours @ T

Red Mud Catalyst

E. Karimi et al., *Applied Catalysis B: Environmental, Appl. Catal., B 2014, 145, 187.*

Oil: Elemental Analysis & Heating Value

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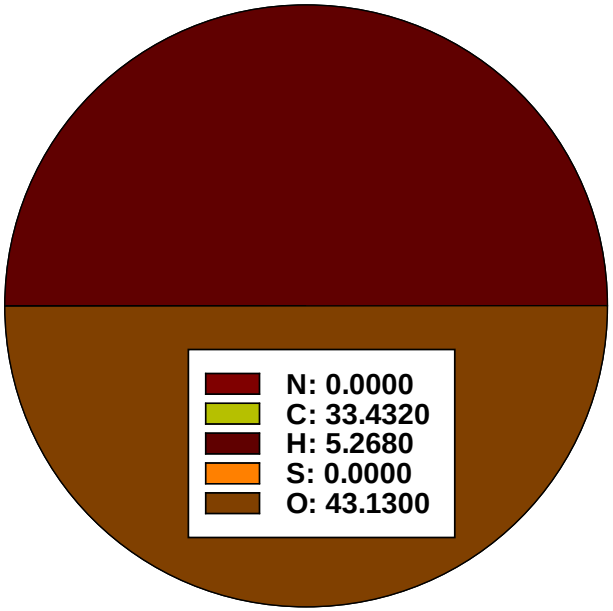
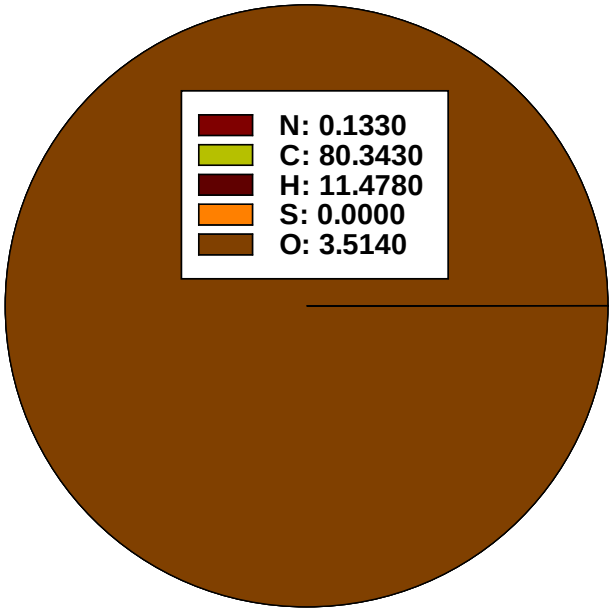
Before Upgrading



Heating	Value
12	kJ/g

After Upgrading



Heating	Value
34	kJ/g

EA: Marie Correia, Ben Scott; HV: Isabella Aigner, Cedric Briens (ICFAR)

RM before and after upgrading reaction:

Before (RM)

Non-Alkaline & Magnetic ⇒
33 % carbon content (EA)
Sodicity: 28.9 mg/g

$\chi \approx 500$ [m^3/Kg) (magnetic)

Sodicity by ICP-MS

Nick Schrier, UofG, Lab Services Division

⇐ Alkaline & Non-magnetic
… essentially no carbon
Sodicity: 51.4 mg/g

$\chi \approx 30$ [m^3/Kg] (non-magnetic)

After (RRM); XRD/Moessbauer
→ Magnetite & Maghemite

More typical results …

Reaction Conditions:

T = 375 °

Time = 2 h

BO : RRM = 7.5 :1

$p(H_2)$ = 4.3 MPa

(optimum from DOE study)

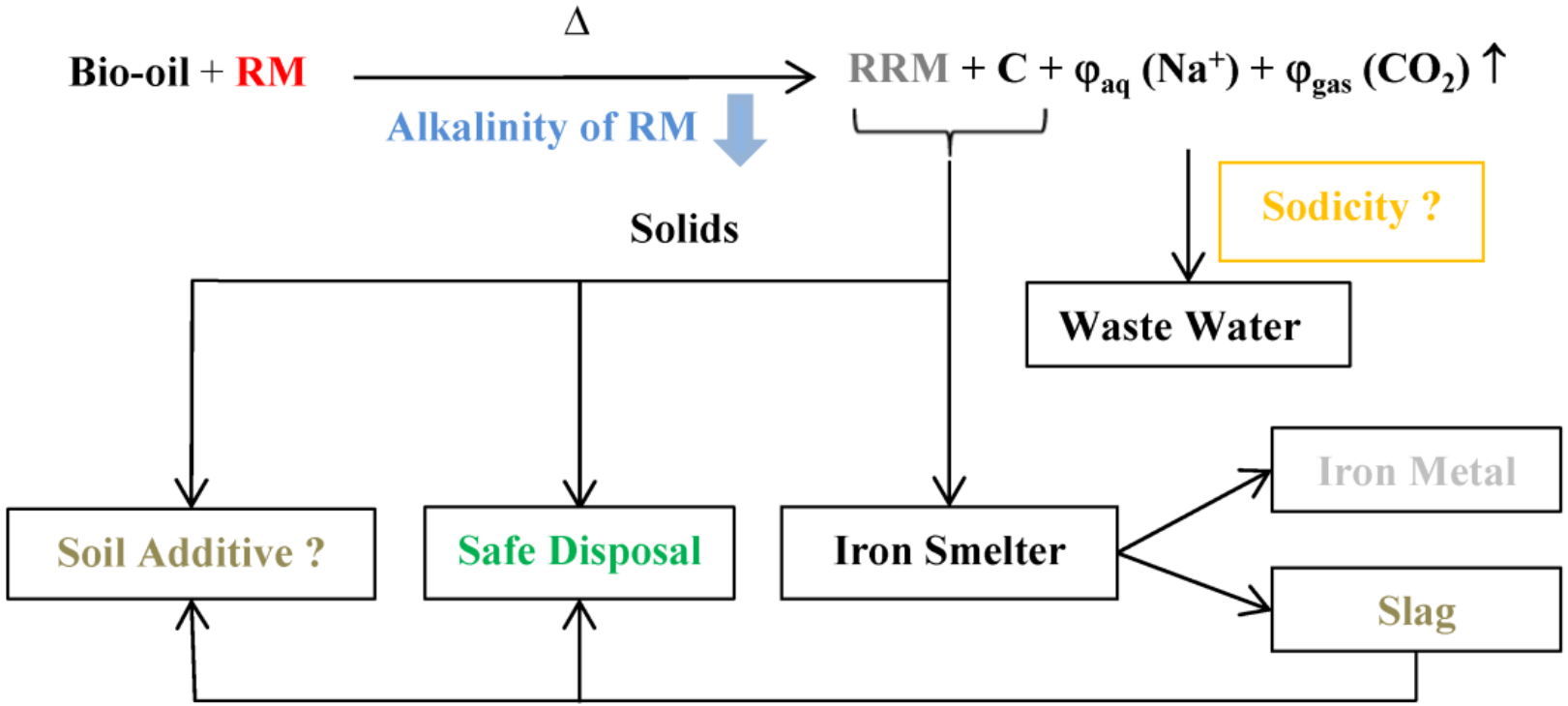
Bio-Oil (g)	RRM (g)	Solid Phase (g)	Organic Phase (g)	Organic Liquid Yield (%)	pH Aqu. Phase	Carbon Organic Phase (%)	Carbon Solid Phase (%)	HHV Organic Phase (MJ/kg)
20	3	2.84	1.45	7	4	73.7	15	36

a) S. Lee, M. Ahmed, M. Schlaf, **2015**, *unpublished results.*

b) Venderbosch, R. H. *ChemSusChem* **2015**, *8*, 1306.

Low Bio-Oil/Red Mud ratios: Neutralization

- … forget about making fuel, but rather use acidic bio-oil simply as the ***limiting reagent***:

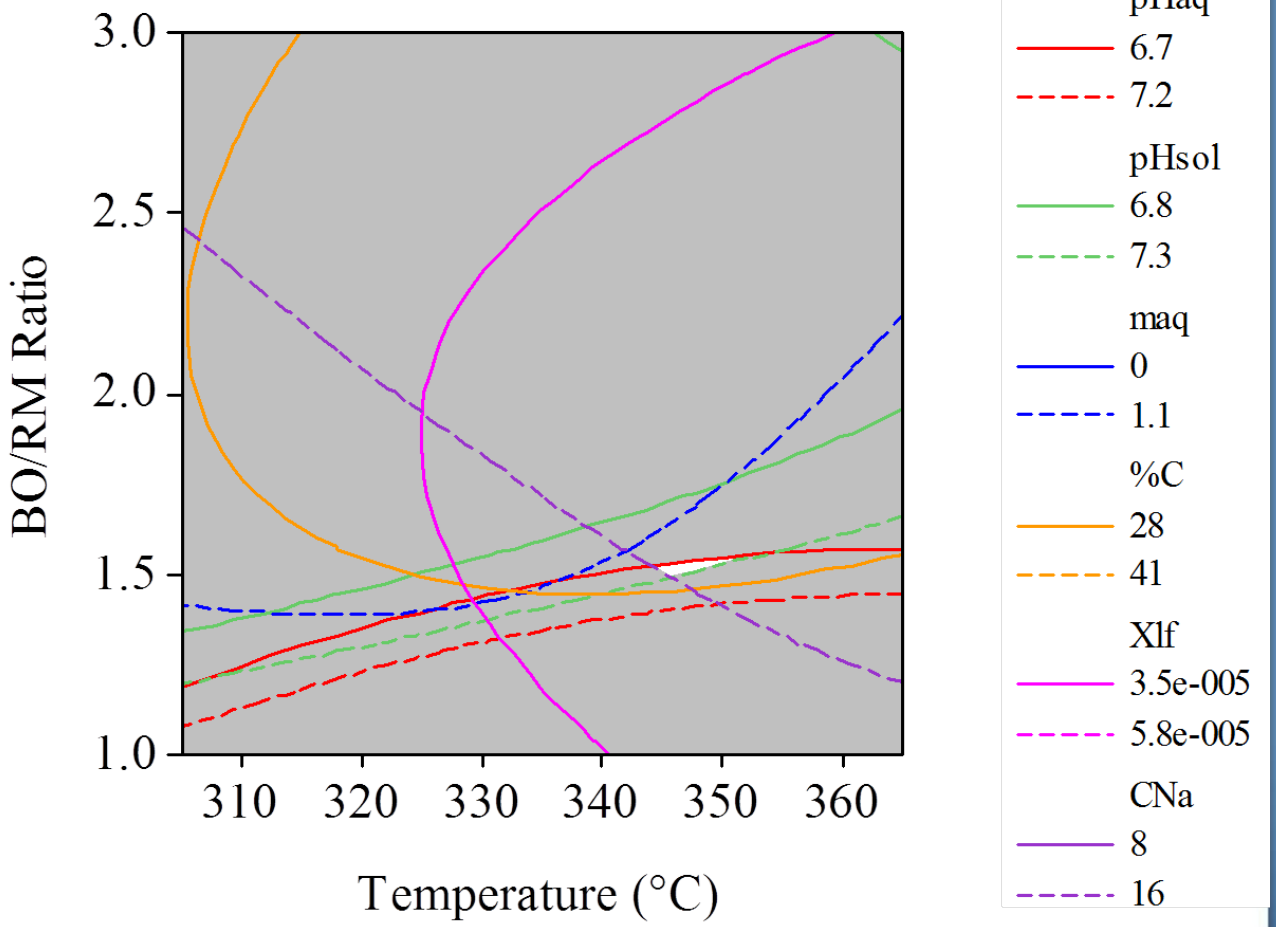


- **Always achieves RM neutralization/carbonization.**
- **Independent of bio-oil quality.**

Jollet, V.; Gissane, C.; Schlaf, M. Energy & Environmental Science **2014**, *7*, 1125.

Optimization of Neutralization Reaction

DOE study gives as optimum: Middle point of highlighted white area at a **Bio-Oil/Red Mud ratio of 1.5** (w/w) and a process temperature of **349 °C** at a fixed reaction time of **30 min.**



- **Minimizes $[Na]_{aq}$ and m_{aq}**
- **Maximizes of %C and χ_{lf}**
- **Stabilizes pH of solid/aqueous phases close to pH = 7**

Jollet, V.; Gissane, C.; Schlaf, M. Energy & Environmental Science **2014**, *7*, 1125.

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Challenges & Opportunities

1. **Sources of biomass ?**
2. **Cost of pyrolysis bio-oil: 50-100 $/ton**
   (… maybe cheaper in India/China/Brazil/Russia … ?).
3. **CAPEX/OPEX … ???**
4. **Can the neutralized/reduced/carbonized Red Mud be safely disposed of or used as**
   a. **… a soil additive (Fe/C fertilizer) … ?**
   b. **… an iron ore binder additive … ?**
   c. **… somewhere else … ?**

Your Thoughts ?

Thank You !!!

Acknowledgements

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Ben Scott (EA)
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Mohamed Ahmed (upgrading)

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(Bio-Oil)

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(TGA)

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Leandro Passos Ribeiro
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ABIN-RIBBA