

This lecture is dedicated to
Husband, Friend, Soul mate



Riaan Marx



7 May 1968



26 January 2021

Isaiah 43:1-3 Do not fear, for I have redeemed you; **I have called you by name, you are mine.**

When you pass through the waters, I will be with you; and through the rivers, they shall not overwhelm you; **when you walk through fire you shall not be burned**, and the flame shall not consume you. For **I am the Lord your God, the Holy One of Israel, your Savior**



Turning waste into products: A circular economy concept

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2007 - present*



Electricity, PGMs, water,
coal, crude oil, biomass

Recovered
resources

RECYCLE

Products



Industrial processes

The circular economy concept

Products



New processes

Recycle and re-
processing



REDUCE

Industrial
waste

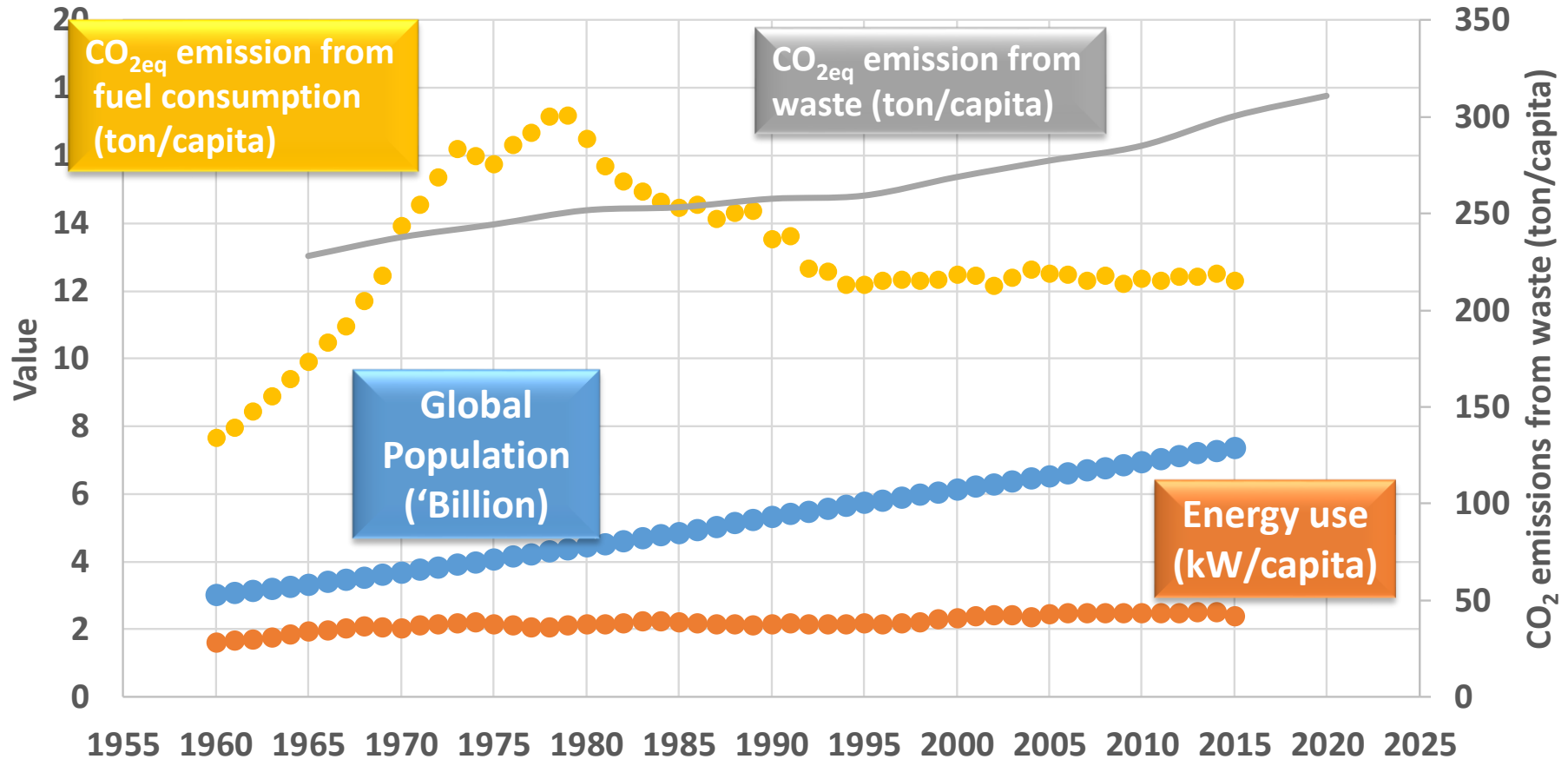


Domestic
waste



RE-USE

The problem with waste



The impact of increasing waste



Untreated wastewater in dams



Inadequate capacity



Raw sewage in rivers



Ocean dumping



Open landfill



Illegal Dumping

Current mitigating strategies

Composting



Sanitary landfill



Incineration



Landfill gas collection



33 % of waste still **dumped**

25.2 % on **open landfill**

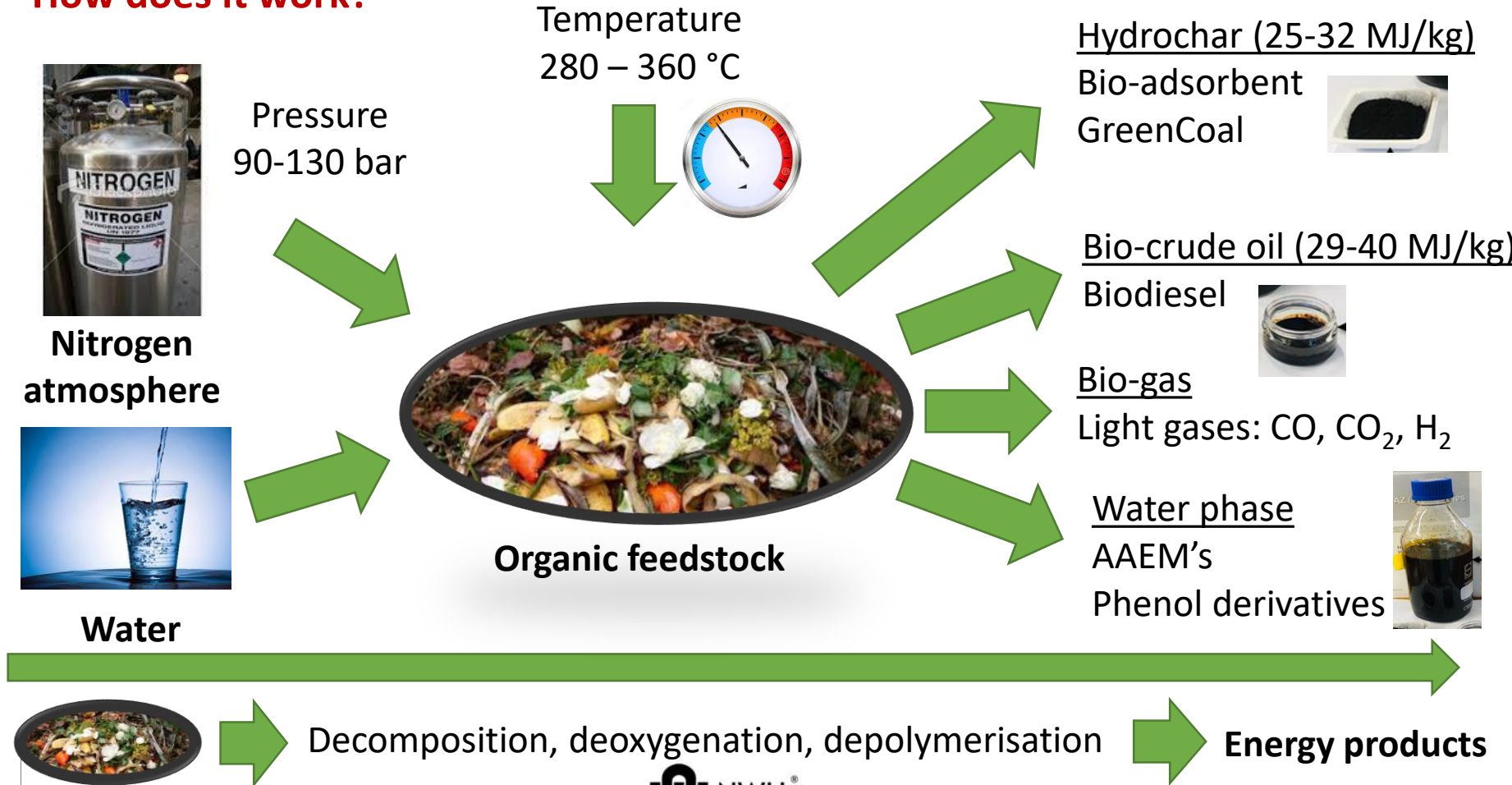
4 % unaccounted for

Waste recycle



Hydrothermal Liquefaction (HTL)

How does it work?



Research Question 1

**Effect of changing solvent from water
to primary sewage**

Hydrothermal Liquefaction (HTL)

MSW & Sewage feedstock properties

	Component	Mass %	Method
 ELSEVIER	Total Protein	12.2	ASM 078
	Total Fat	3.1	ASM 044
	Total Carbohydrates	79.9	ASM 075
	HHV (MJ/kg)	18.4±0.1	SANS 1928
Upgr Simu	Moisture	60.93 ± 4.19	NREL/TP-510-42621
wast	Ash	5.45 ± 0.2	NREL/TP-510-42622
Sanet	Volatile matter	32.74 ± 2.82	SANS 50
	Fixed carbon	2.05 ± 2.14	By Difference

Effect

		Water	Sewage	Fatty acid per gram of oil (g/g)
Bio-crude oil				
0.35	Atomic H/C	1.8 ± 0.3	1.5 ± 0.1	
0.30	Atomic O/C	0.4 ± 0.3	0.2 ± 0.03	
	N-content (mass %)	1.7 ± 0.2	2.2 ± 0.5	
0.25	HHV (MJ/kg)	32.1 ± 0.7	32.2 ± 0.4	
Hydrochar				
0.20	Atomic H/C	1.02 ± 0.04	1.06 ± 0.01	
0.15	Atomic O/C	0.13 ± 0.04	0.1 ± 0.05	
0.10	N-content (mass %)	3.4 ± 0.6	3.9 ± 0.3	
0.05	HHV (MJ/kg)	30.4 ± 1.6	29.2 ± 0.7	
Aq product				Total
	Total phenol (g/L)	2.87 ± 0.02	2.99 ± 0.04	
0.00	Carbon Balance (%)	87 ± 1.8	100 ± 6.5	
	Nitrogen Balance (%)	124 ± 8.5	113 ± 8.9	

Research Question 1 - answer

Sewage as solvent does not affect product yield
Sewage as solvent result in better carbon balance

Research Question 2

Upgrading of hydrochar to GreenCoal

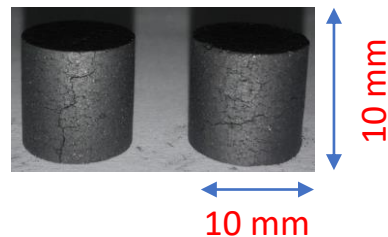
Upgrading of hydrochar to GreenCoal

Hydrochar and coal preparation

- Hydrochar **washed** with deionised **water** and **HCL**
HCL solution (1.96 mL of 32% HCl in 2 L of water)
- Filter cake **washed** with **water** until **neutral pH**
- Filter cake **dried at 60 °C** for 24 hours
- Hydrochar homogenised using the **cone and quartering** technique
- **Discard coal fines** filter cakes from Twistdraai coal mine,
Secunda, South Africa (12 μ m)
- Coal was homogenised using the **cone and quartering** technique

Upgrading of hydrochar to GreenCoal

GreenCoal pellet preparation



No binders added

No wax sealant added

No catalyst added

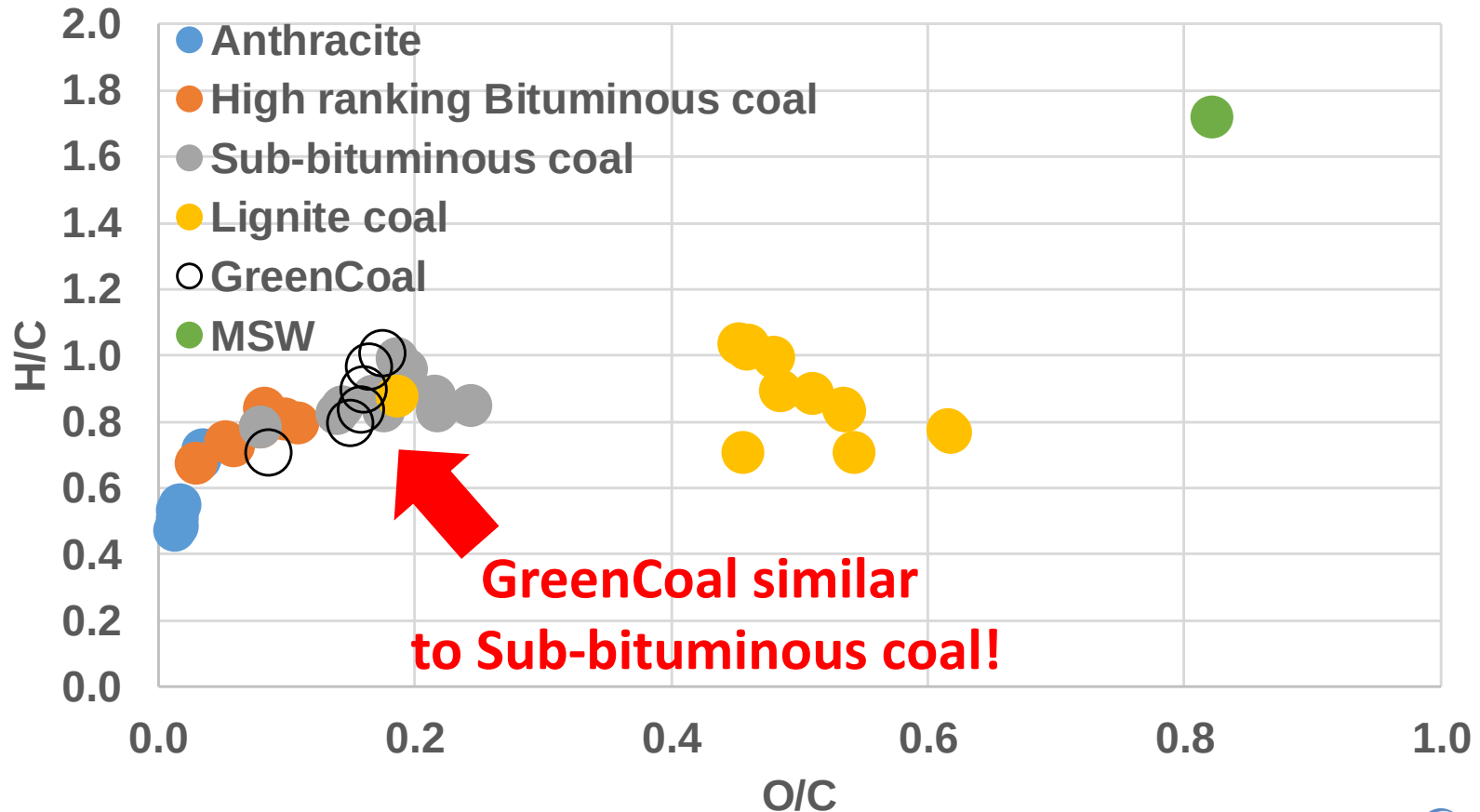
Pellet mixtures
cone and quartered
Hydrochar with coal
mixtures with
0-100 mass% hydrochar

Hand pressed pellets
 ± 0.75 g mixture
and 0.14 g water

Stored in air tight container
Cured at 100 °C for 15 hours
Before analysis

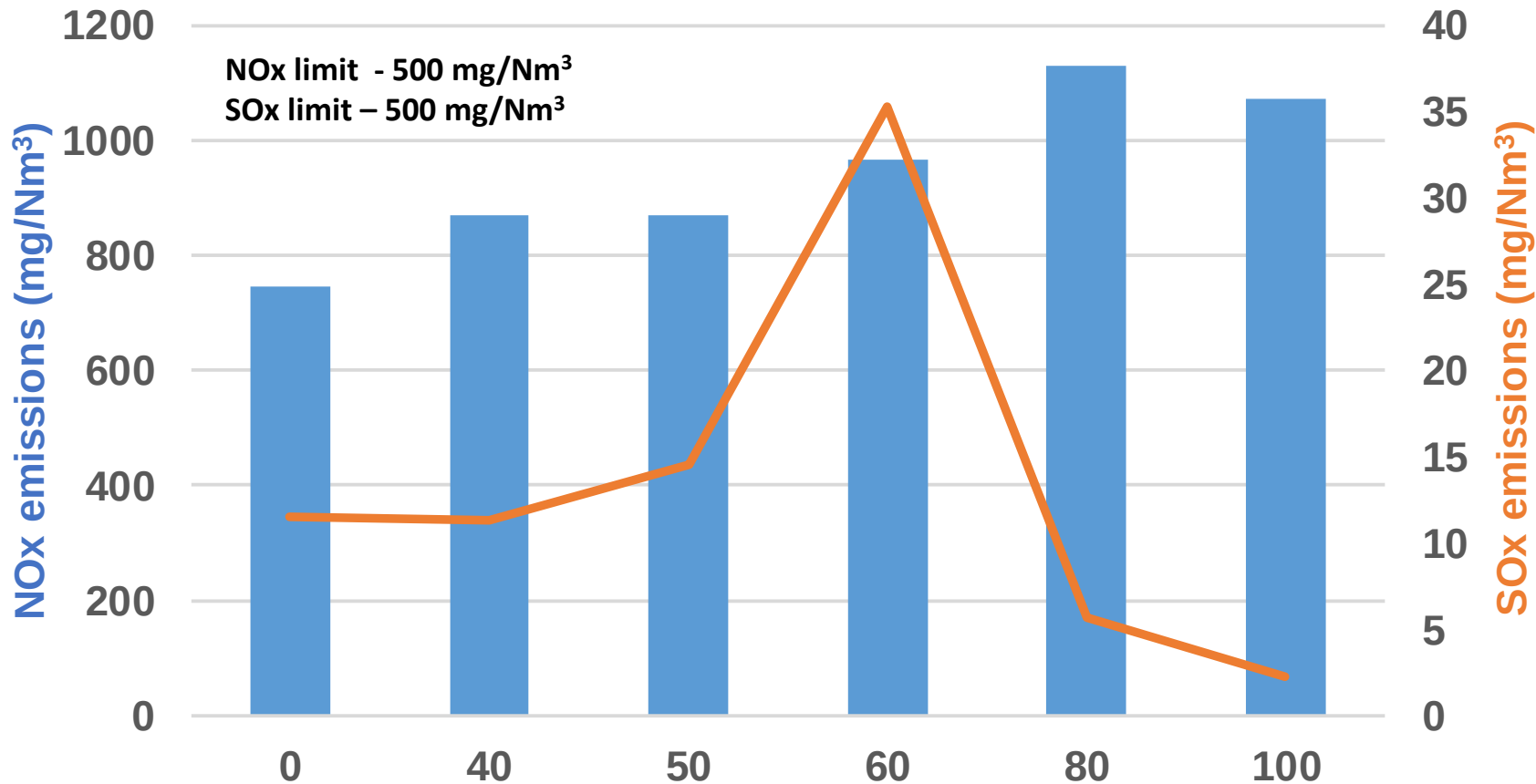
Upgrading of hydrochar to GreenCoal

GreenCoal pellet properties



Upgrading of hydrochar to GreenCoal

GreenCoal emissions performance



Research Question 2 - answer

A stable GreenCoal pellet can be produced
Hydrochar pellets reduce SO_x emissions

Research Question 3

Upgrading of hydrochar to a bio-waste adsorbent

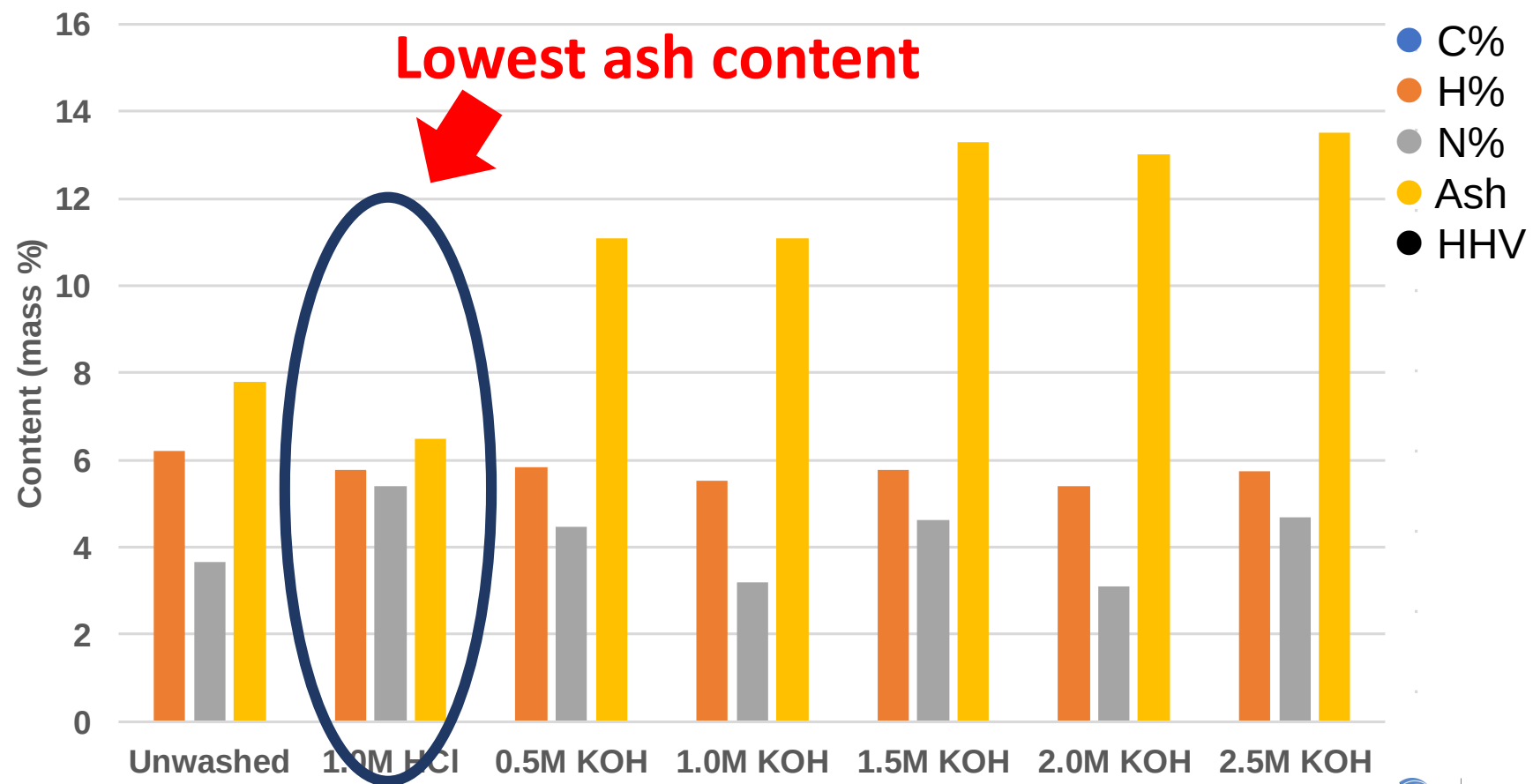
Upgrading of hydrochar to bio-waste adsorbents

Composition of aqueous product

Used to produce	Component	Concentration (g/L)
guaiacol	Vanillyl alcohol	0.06±0.02
Dental sedative	Guaiacol	0.08±0.05
Nylon	Phenol	0.22
Photography	Catechol	0.01
Beauty products	Resorcinol	0.28
Vanilla extract	Vanillin	0.04
Leather dyes	4-Nitrophenol	0.01
	Ca ²⁺	2.7
	K ⁺	3.7
	Mg ²⁺	0.2
	Na ⁺	0.5

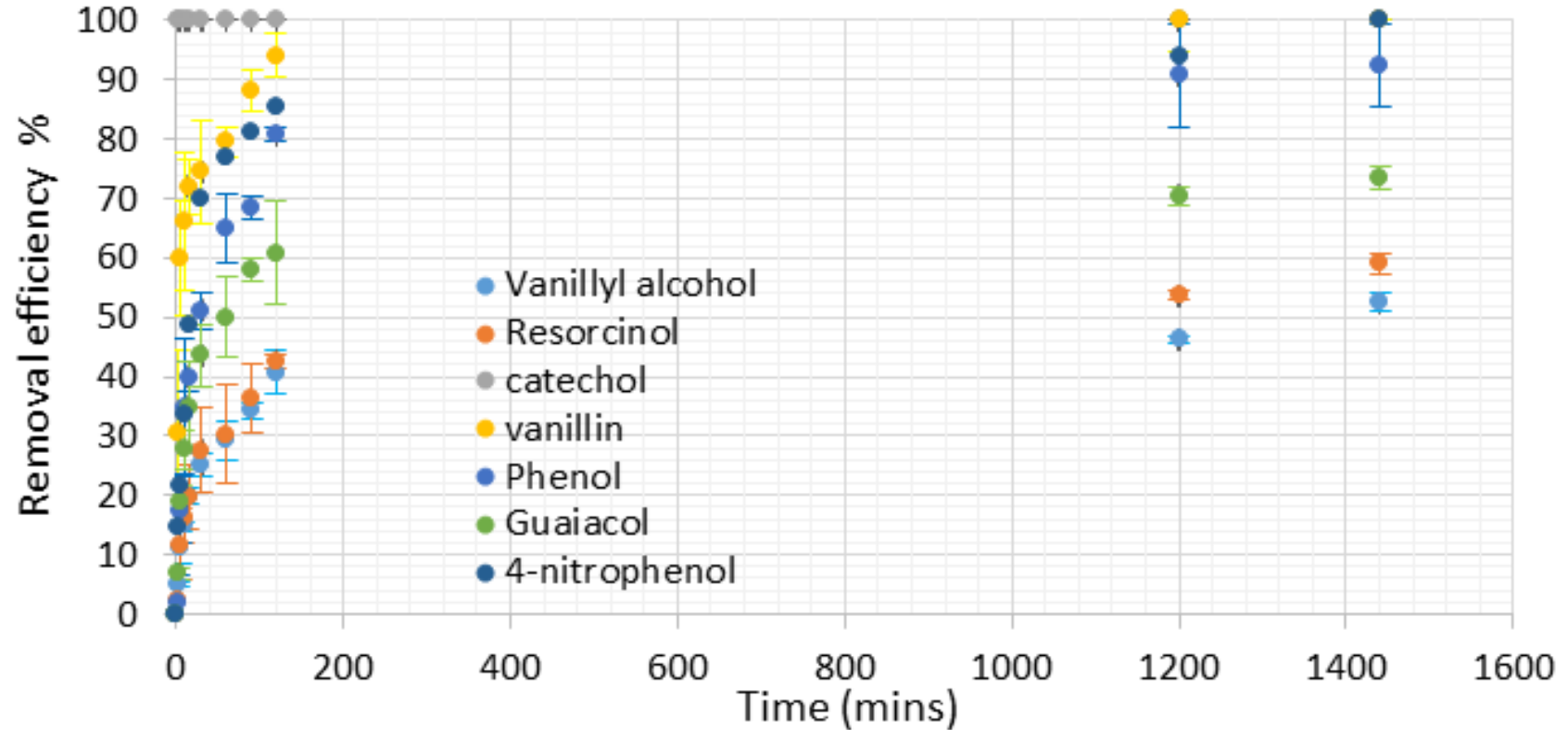
Upgrading of hydrochar to bio-waste adsorbents

Effect of chemical activation



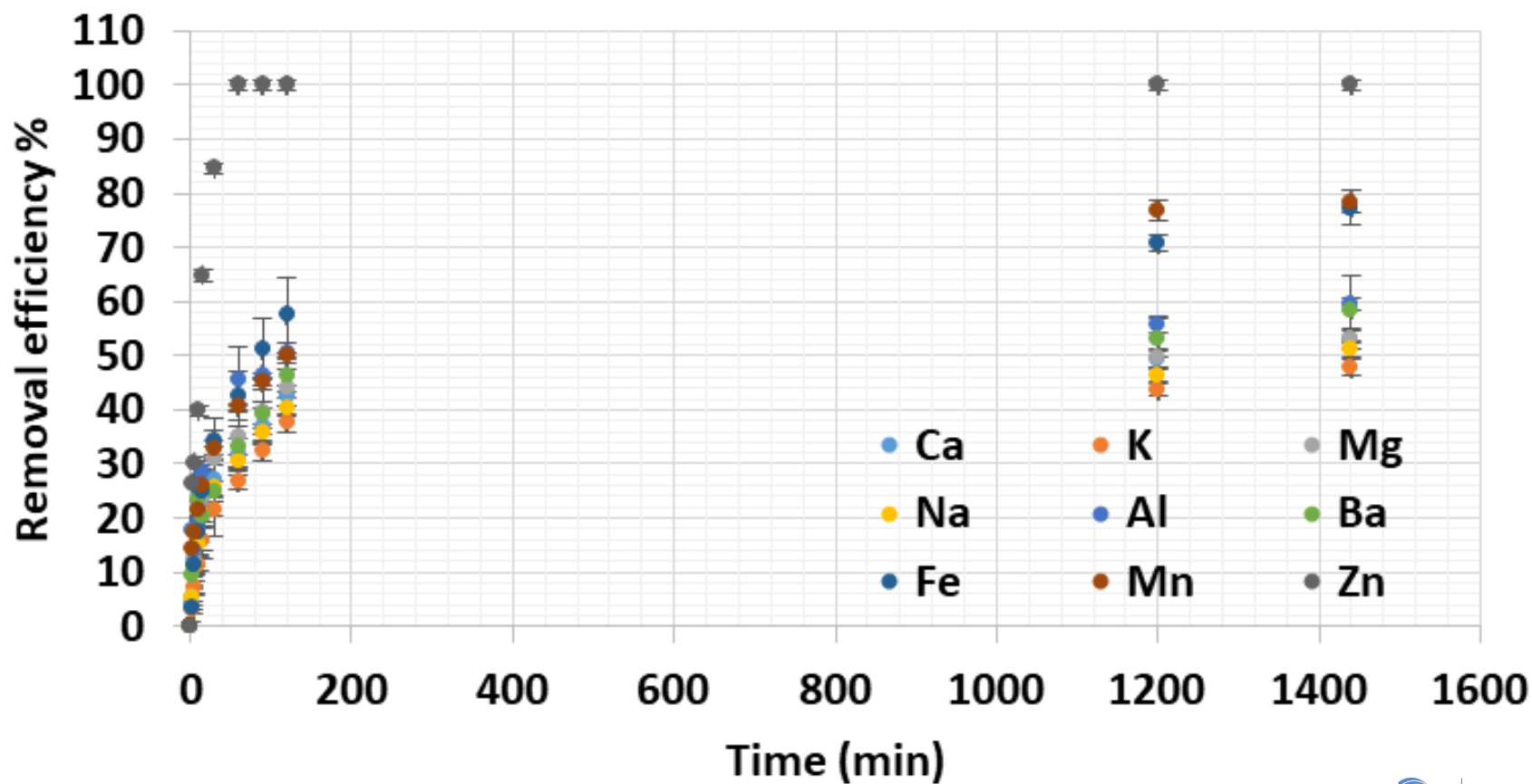
Upgrading of hydrochar to bio-waste adsorbents

Effect of initial concentration - Phenolics



Upgrading of hydrochar to bio-waste adsorbents

Effect of initial concentration - AAEM



Upgrading of hydrochar to bio-waste adsorbents

Component	Concentration Before adsorption	Concentration After adsorption	%Recovered
Vanillyl alcohol	0.06±0.02	0.03	50%
Catechol	0.01	0	100%
Phenol	0.22	0.02	92%
Guaiacol	0.08±0.05	0.03	74%
Resorcinol	0.28	0.1	59%
Vanillin	0.04	0	100%
4-Nitrophenol	0.01	0	100%
Ca ²⁺	2.7	1.3	36%
K ⁺	3.7	1.9	48%
Mg ²⁺	0.2	0.1	23%
Na ⁺	0.5	0.2	13%

Research Question 3 - answer

**Effective bio-waste adsorbent for
removal and recovery of phenolic
components**

Research Question 4

Upgrading of bio-crude oil to biodiesel

Upgrading of bio-crude oil to biodiesel



**Dried
Bio-crude oil**

+



**Novozymes 435
Lipase, 10 mass%**

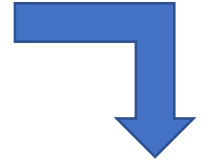
+



**FA:Methanol
1:3 to 1:28**



**Methanolysis
Temperature
27 °C – 60 °C
Residence time
6 – 24 hours**



**Drying at 80 °C
for 30 min**



**Crude biodiesel
recovered with
Diethyl ether**



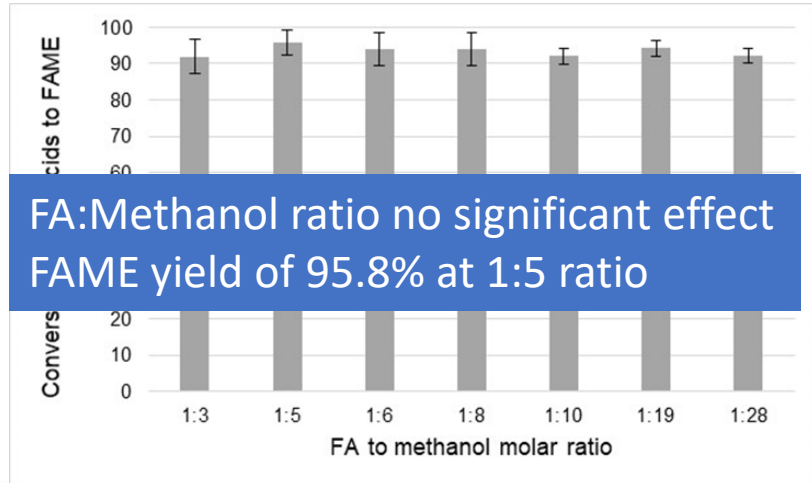
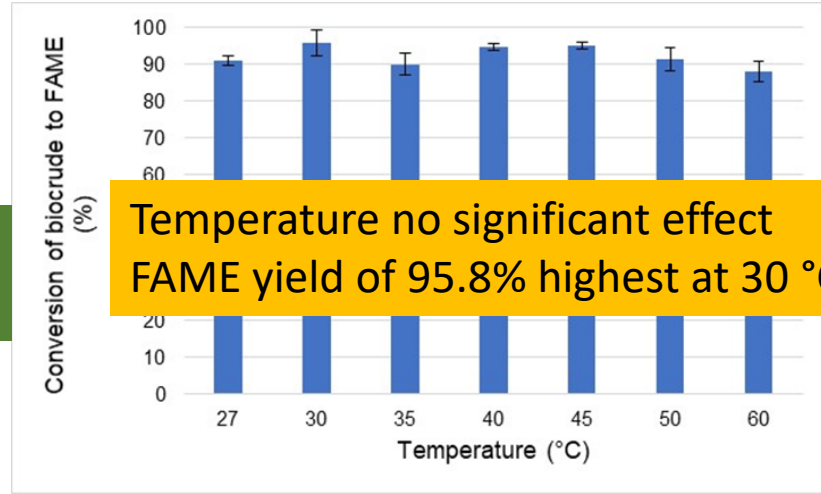
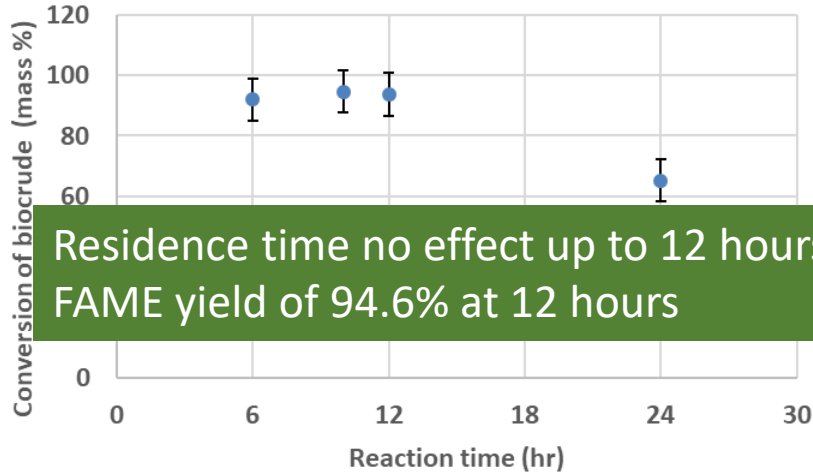
**Remove lipase
by filtration**



Dried biodiesel



Upgrading of bio-crude oil to biodiesel

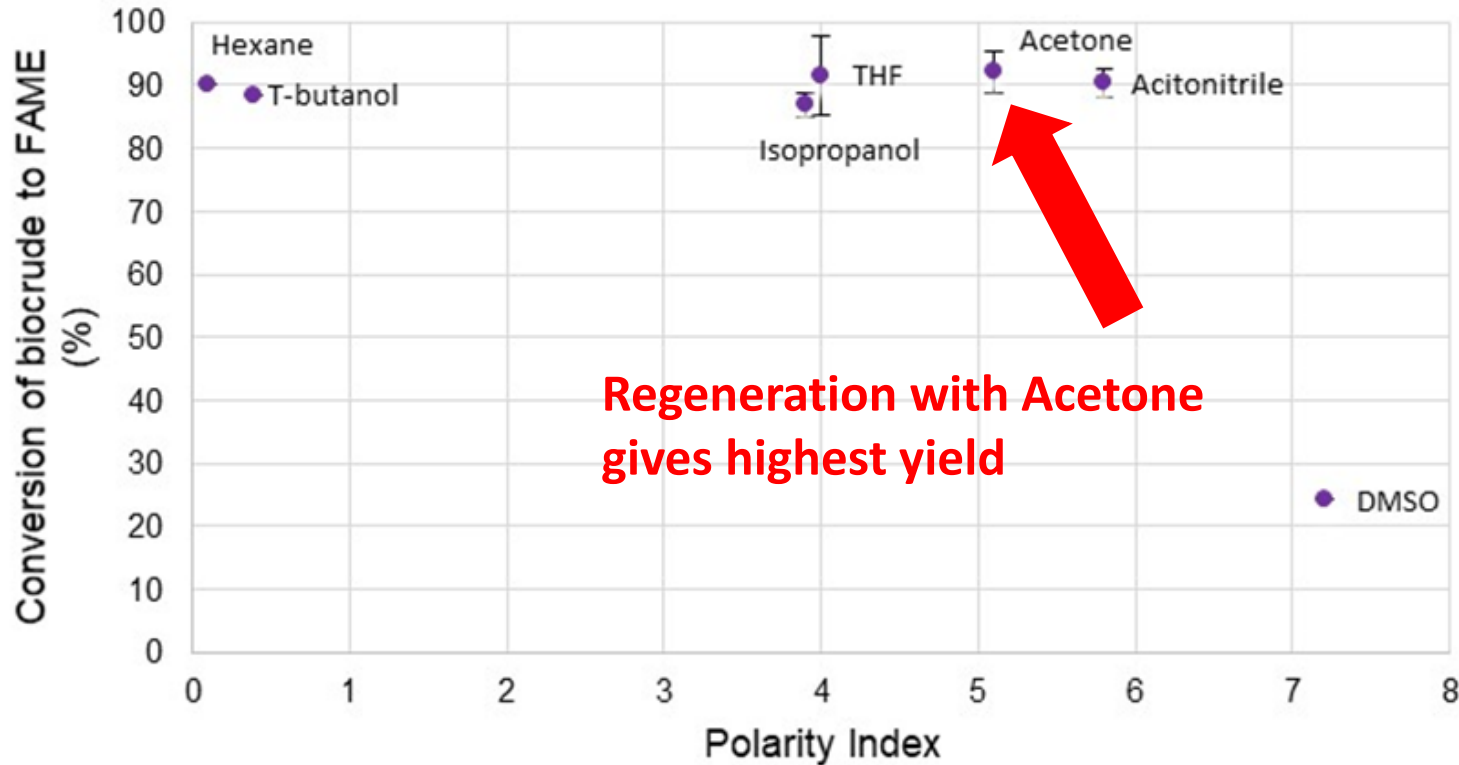


Bio-crude oil to Biodiesel



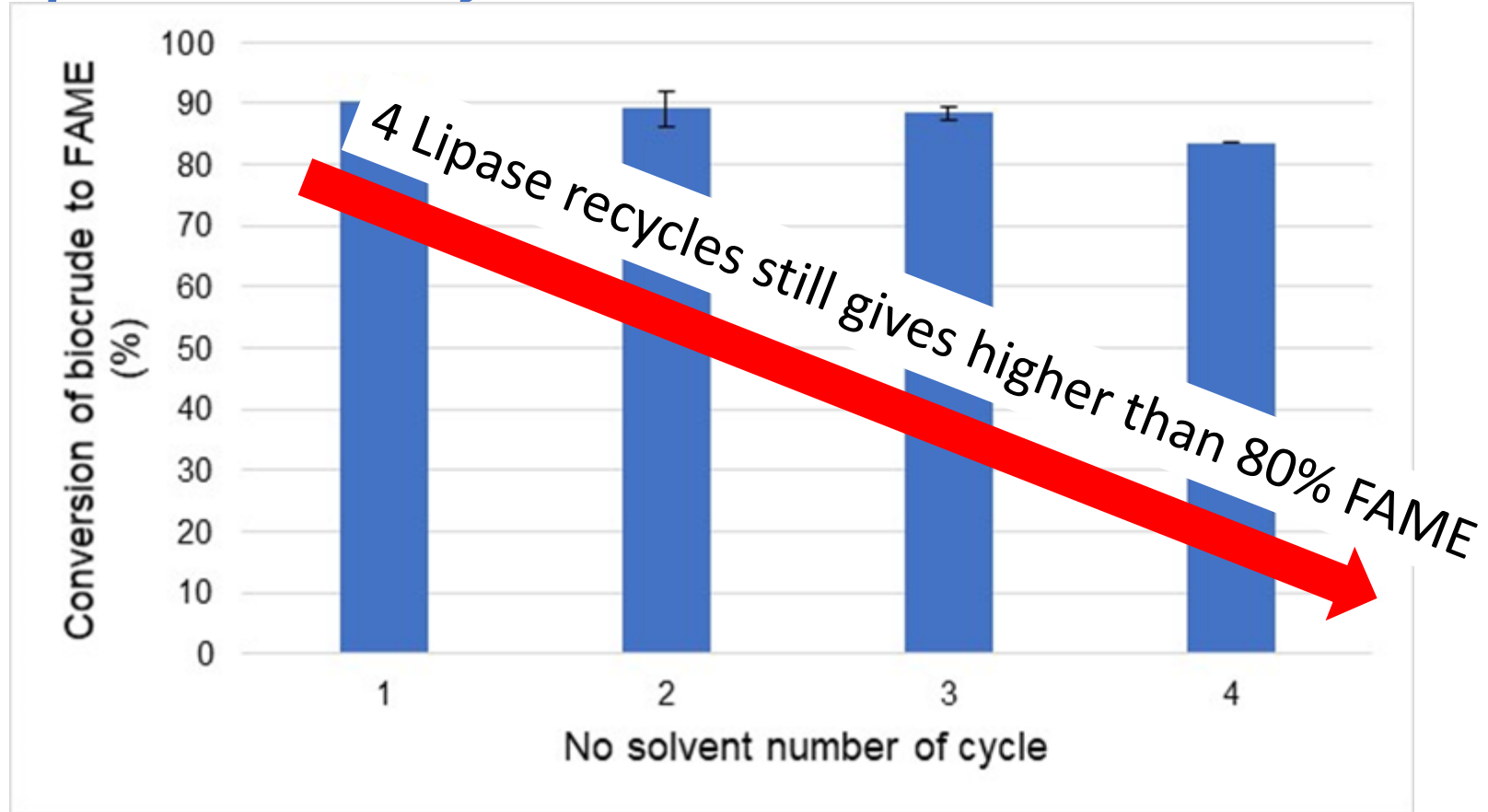
Upgrading of bio-crude oil to biodiesel

Lipase reusability



Upgrading of bio-crude oil to biodiesel

Lipase reusability



Research Question 4 - answer

**A high quality biodiesel can be produced
from HTL biocrude-oil using lipase
transesterification**

Research Question 5

**Upgrading of glycerine product from
biodiesel production to lignin-based
polyurethane foam**

Upgrading of biodiesel glycerine to polyurethane foam (PUF)

Lignin	Organosolv	Kraft	Lignosulphonate
Ash	2.6±0.2 ^a	20.2±0.0	16.7±0.4
C	57.7±0.7	51.7±0.7	42.8±0.1
H	5.2±0.0	3.7±0.2	4.0±0.1
N	0.8±0.1	0.2±0.0	0.2±0.0
O	34.1	32.1	40.2
S	0	4.1	4.5
Na	0.1	6.3	0
Ca	0.4	0	6.6
C ₉ formula ^b	C ₉ H _{9.1} O _{3.8} (OCH ₃) _{0.3}	C ₉ H _{5.9} O _{3.7} S _{0.3} (OCH ₃) _{0.9}	C ₉ H ₉ O _{6.2} S _{0.4} (OCH ₃) _{0.6}
MW C ₉ unit (g mol ⁻¹)	187.7	210.3	246.4

^a 95% Confidence interval based on triplicate analysis. ^b The methoxyl content is an estimate based only on the ³¹P NMR RII results for syringyl and guaiacyl content

Upgrading of biodiesel glycerine to polyurethane foam (PUF)

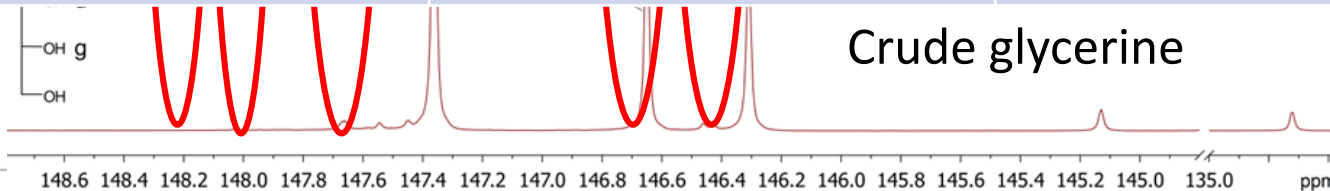
Polyol preparation

1. **Adjust pH** of glycerine to 8 using 98% H_2SO_4
2. Heat glycerine to **160 °C and add lignin (9:1 ratio)**
3. Reaction time of **90 min**
4. **Centrifuge at 66.7 Hz for 10 min** to separate liquid and solid products
5. **Recover supernatant** from ethanol through **vacuum evaporation** at 30 °C

Upgrading of glycerine to PUF



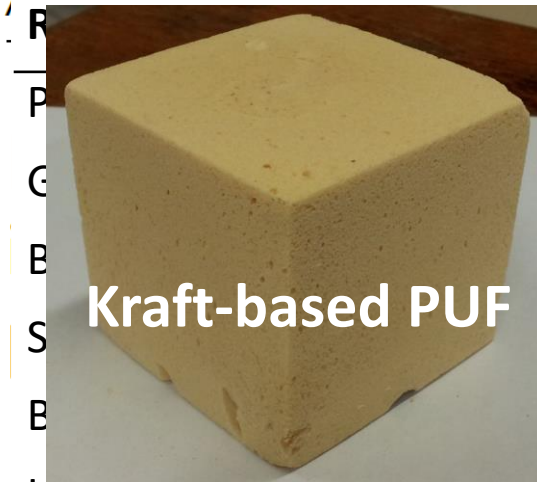
	ASTM D4272-11 Total hydroxyl content mg KOH/g	Ratio Primary OH/Secondary OH
Lignosulphonate polyol	555 ± 54	2.4
Kraft polyol	491 ± 15	1.7
Organosolv polyol	436	2.1
Crude glycerine polyol	466 ± 15	1.2
Crude glycerine	758 ± 13	2.4



Upgrading of glycerine to PUF

PUF Formulation

Polymers from
Renewable Resources



Isocyanate index

105^c

105

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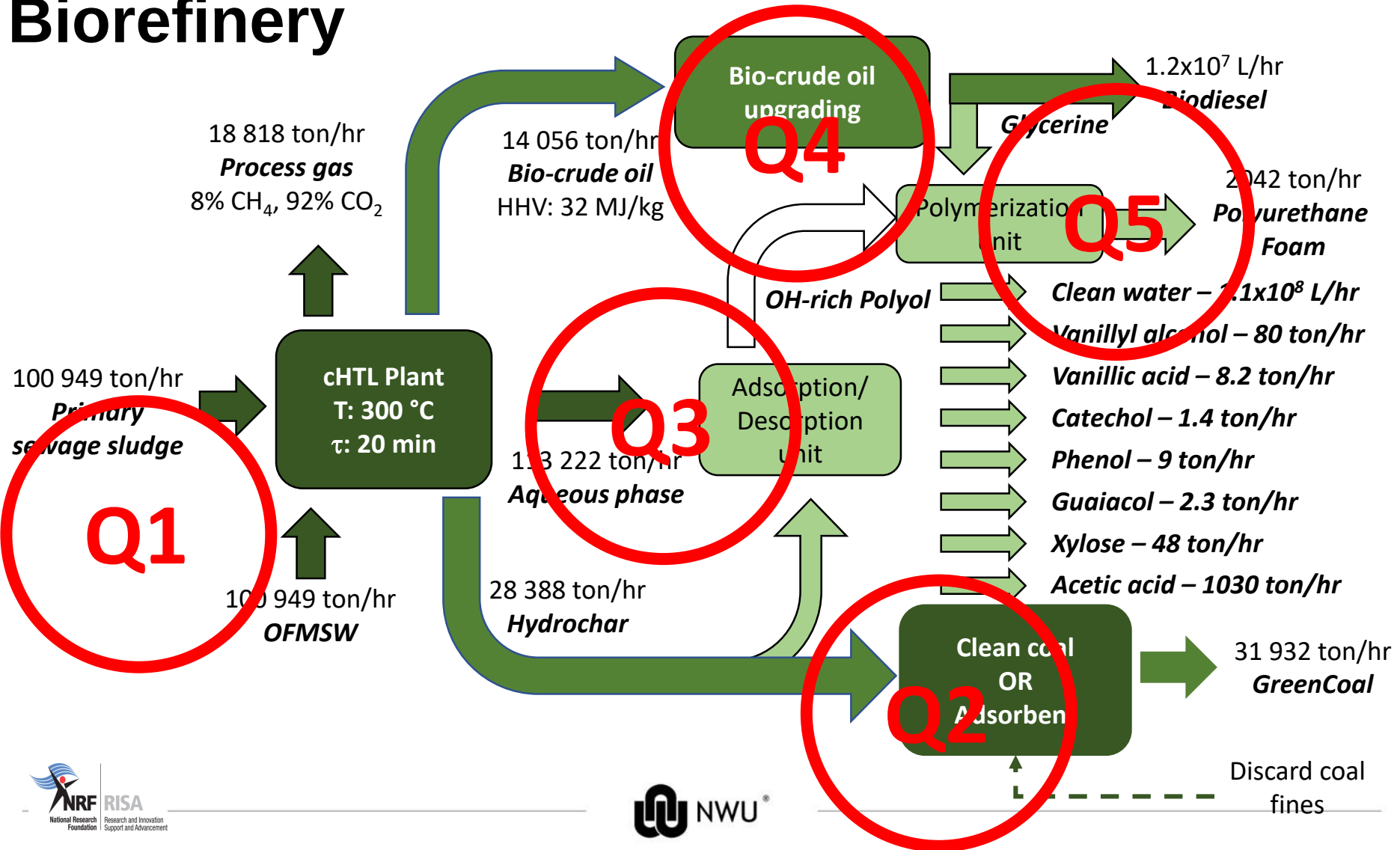
Research Question 5 - answered

Polyurethane foam insulation material can be produced from the biodiesel glycerine product using waste lignin as a an additional source of hydroxyl groups

SUSTAINABLE DEVELOPMENT GOALS



Biorefinery



Biorefinery

Product	Annual Production	Annual bulk market value Million \$
Biodiesel	1.1×10^{11} L	57
GreenCoal	2.8×10^8 ton	24
Platform chemicals	1.1×10^7 ton	262
Polyurethane foam	1.8×10^7 ton	22
Pure CO ₂ gas	7.751×10^{10} m ³	192
Electricity from biogas	3.6 TWh	9.2
Clean water	975 GL	-
TOTAL		\$ 365 million

Some references

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DSI/NRF Research Chair in Biofuels

Centre of Excellence in Carbon-based Fuels

Faculty of Engineering

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SOLI DEO GLORIA

