



Waste biorefinery technologies for accelerating sustainable energy processes

# Biomass as a source of renewable raw materials for bio-based products *via* acid-catalyzed liquefaction

RUI GALHANO DOS SANTOS  
APRIL 11<sup>th</sup> 2022



# Greenhouse effect

Eunice Foote  
1<sup>st</sup> Study  
acknowledging  
Greenhouse effect

Jonh Tyndall  
Full paper

1856

1859

1861

Jonh Tyndall  
Preliminary  
Fundings (letter)

382

*On the Heat in the Sun's Rays.*

ART. XXXI.—*Circumstances affecting the Heat of the Sun's Rays ;*  
by EUNICE FOOTE.

(Read before the American Association, August 23d, 1856.)

MY investigations have had for their object to determine the different circumstances that affect the thermal action of the rays of light that proceed from the sun.

Several results have been obtained.

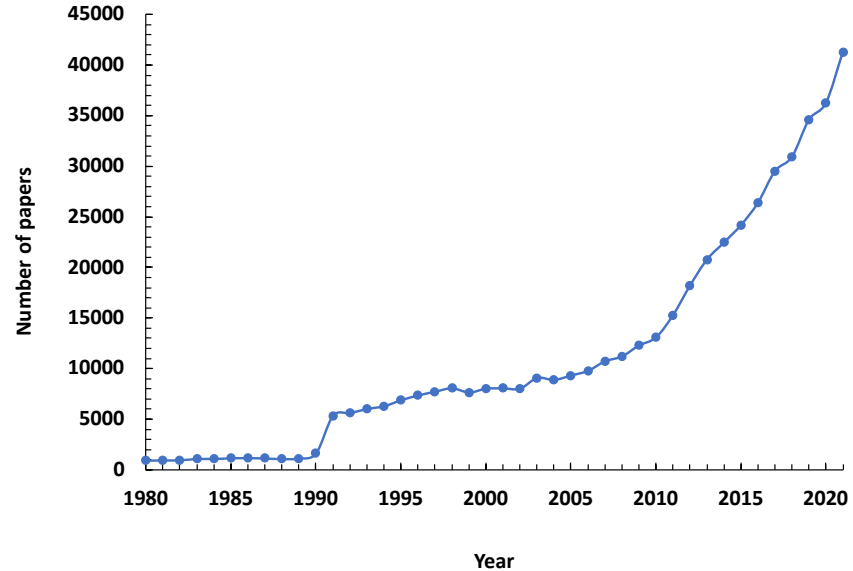
First. The action increases with the density of the air, and is diminished as it becomes more rarified.

The experiments were made with an air-pump and two cylindrical receivers of the same size, about four inches in diameter and thirty in length. In each

and the air was exhausted from ( After both had acquired the same in the sun, side by side, and which rose to 110° in the condensed to other. I had no means at hand of densation or rarefaction.

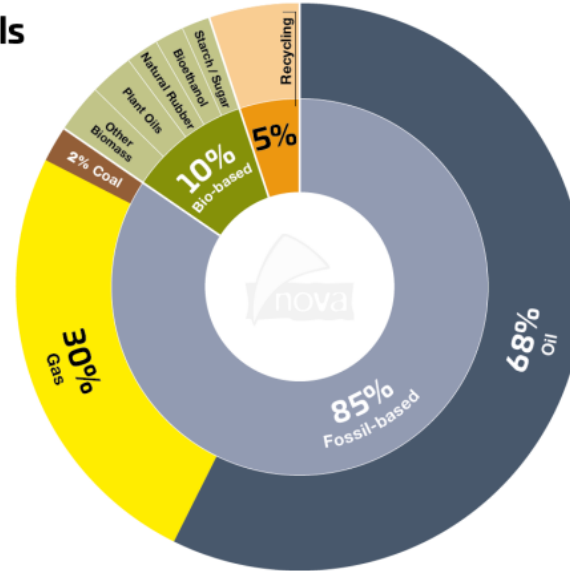


**Eunice Foote**  
1819-1888



## Global Carbon Demand for Organic Chemicals and Derived Materials by Type of Feedstock

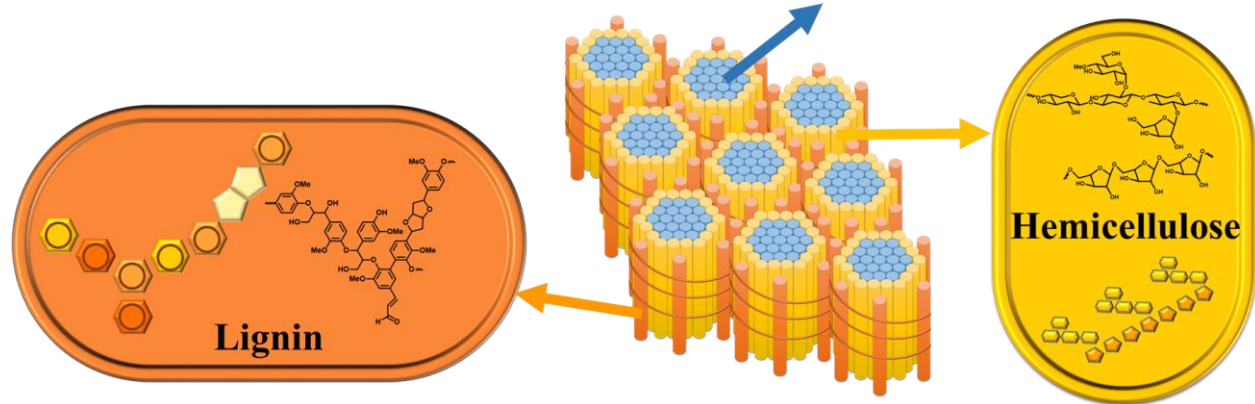
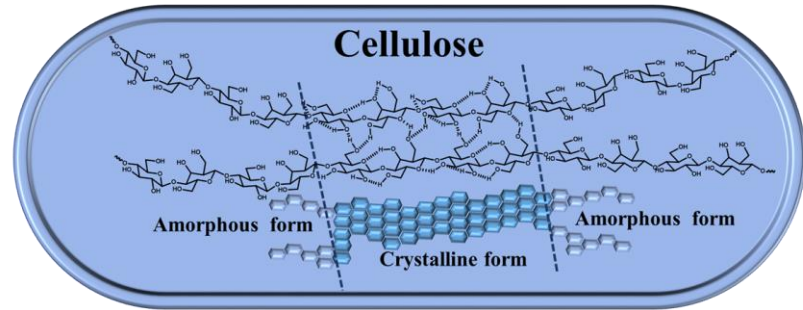
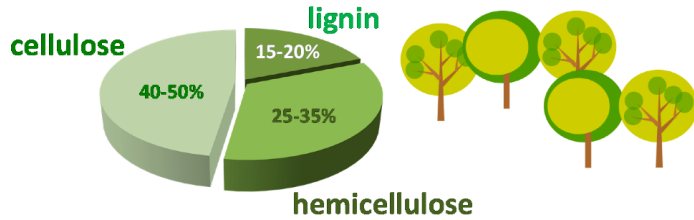
Total: **450 Mt embedded C/yr**



Reference Years: **2015 – 2020**

Main Sources: Plotrowski et al. (2015), Hundertmark et al. (2018),  
Levi and Cullen (2018), Skoczinski et al. (2021)  
available at [www.renewable-carbon.eu/graphics](http://www.renewable-carbon.eu/graphics)

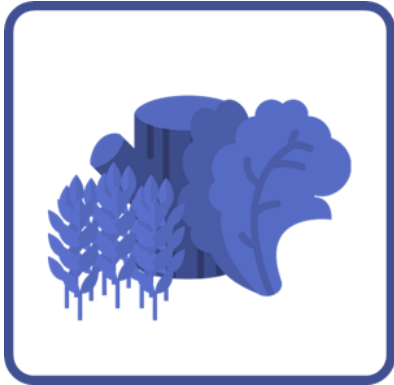
# BIOMASS AS RAW MATERIAL



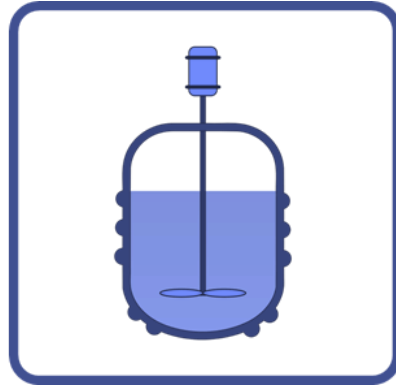
# FROM FOREST RESIDUES TO BIO-OIL

AN ADVANCED CHEMICAL AND ENERGY CARRIERS PLATFORM

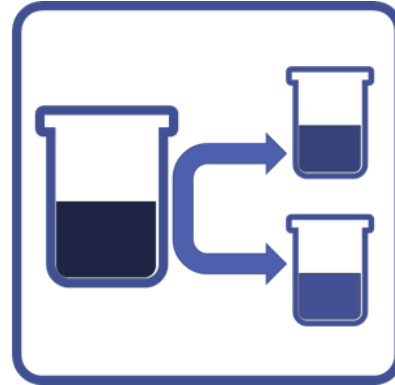
## THE OVERALL PROCESS



GATHERING RESIDUES



LIQUEFACTION



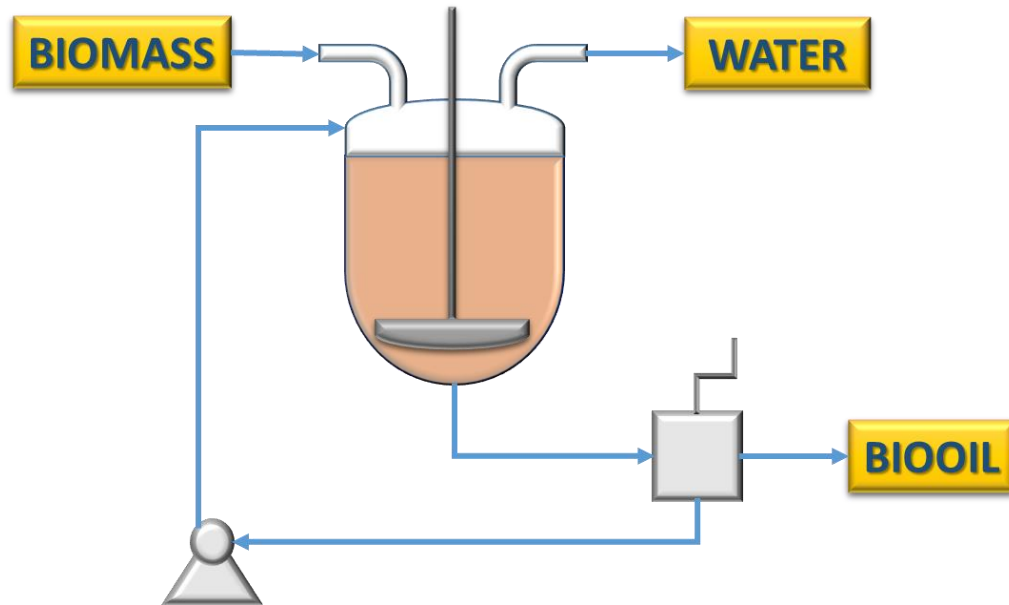
SEPARATION



USE

# BIOMASS LIQUEFACTION

## SIMULTANEOUS DEPOLYMERIZATION OF CELLULOSES AND LIGNIN



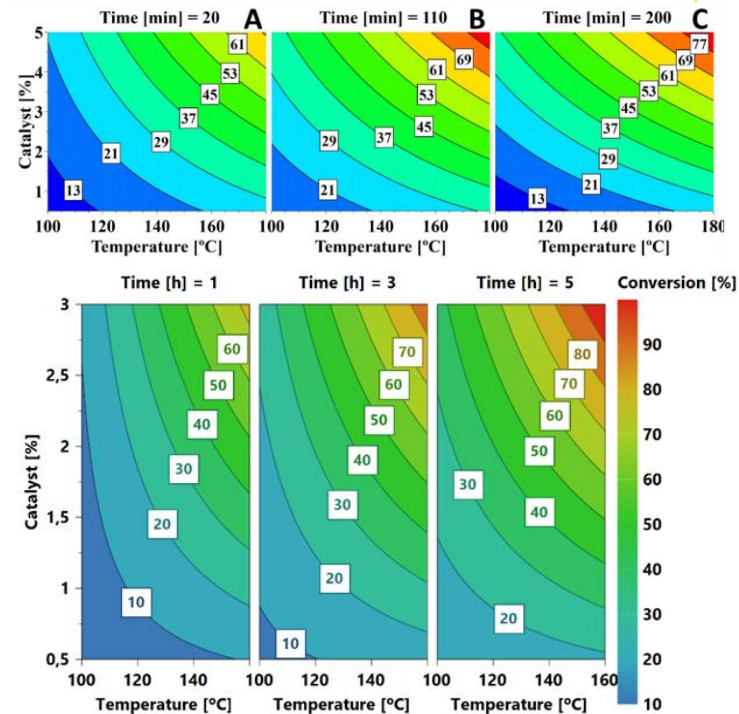
- SWELLING AGENT
- CATALYST
- SOLVENT

# BIOMASS LIQUEFACTION

## SIMULTANEOUS DEPOLYMERIZATION OF CELLULOSES AND LIGNIN

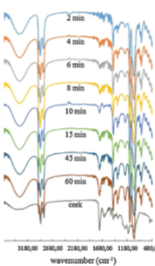
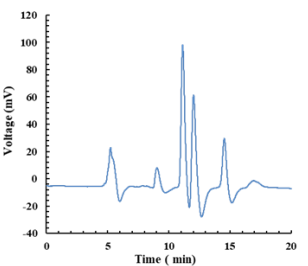
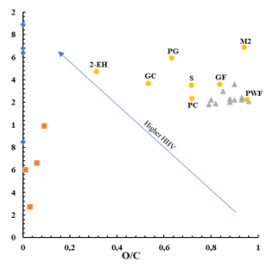
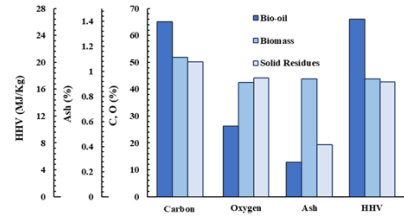
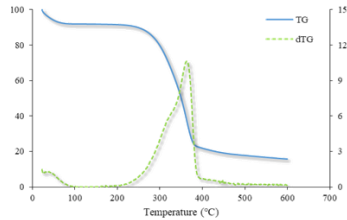
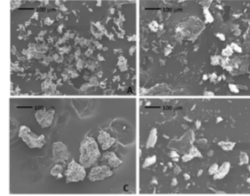
- Pinewood shaves
- Cork Powder and granules
- Potato peel
- Carob pod
- Eucalyptus sawdust
- Eucalyptus bark
- Burnt Pinewood
- Poplar
- RDFs
- Swine manure
- Pine nuts husk
- Pine cones
- Almond Husk
- Forest residues
- Cellulose paste
- *Stipa tenacissima*
- Straws
- Acacia
- Tomato Pomace
- *Stipa tenassissima*
- Margine
- Olive stones
- Wheat straws
- Acacia
- Pallete residues
- Sludges

- PTSA
- Sulfuric acid
- $AlCl_3$
- Triflates
- Others
- 2EH
- DEG
- Glycerin
- Solketal
- Organic Carbonates
- Glycerol formal
- Conventional heating
- Microwave-assisted
- Ultrasounds-assisted



# CHARACTERIZATION TECHNIQUES

Liquefaction Method	Reaction time (min)	Liquefaction Yields (%)	Acid number (mg KOH/g)	Hydroxyl number (mg KOH/g)
Conventional	135	94	6	725
Ultrasound-assisted	60	99	10.7	532
Microwave-assisted	5	96	9	180

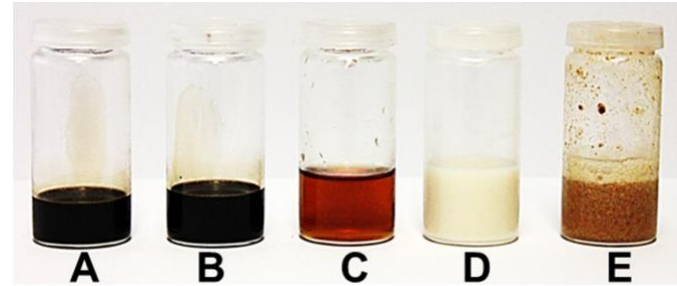


RT (min)	Composto	Area (%)
1	5.76 2-Ethylhexyl formate	0.22
2	6.09 2-Ethylhexyl acetate	0.14
3	7.46 1,3,4,6-Di-anhydro-α-D-glucopyranose	0.02
4	8.32 2-Ethylhexyl butanoate	0.32
5	8.66 2-Ethylhexyl methoxyacetate	0.12
6	10.72 Di-(2-ethylhexyl) malonate	0.44
7	11.87 3-allyl-5-t-butylhydroquinone	0.91
8	12.6 3-methylamino-1,2,4-triazole	0.32
9	13.26 2-ethylhexyl pentanoate	11.8
10	15.45 Di-(2-ethylhexyl) ether	3.96
11	16.44 5-Methylfurfural	2.02
12	16.67 Di-(2-ethylhexyl) glutarate	0.97
13	17.75 Melibiose	0.22
14	18.88 Di-(2-ethylhexyl) maleate	0.52
15	19.8 1-O-(2-ethylhexyl)-glucitol <sup>b</sup>	0.65
16	20.78 6-O-(2-ethylhexyl)-glucitol <sup>b</sup>	0.76
17	21.26 Di-(2-ethylhexyl) oxalate	2.27
18	22.46 Di-(2-ethylhexyl) adipate	2.55
19	24.29 1-O-(2-ethylhexyl)-α-D-glucoside <sup>b</sup>	19.6
20	24.84 Trealose	2
21	25.89 Quinic Acid	1.51
22	27.7 1-O-(2-ethylhexyl)-β-D-glucoside <sup>b</sup>	2.07
23	28.21 β-Lactose	0.52
24	28.82 α-Lactose	0.72
25	29.17 D-Mannose	1.25
26	32.29 2,5-Di-O-methyl-D-Ribitol triacetate	0.58
27	32.72 1-O-(2-ethylhexyl)-α-D-mannofuranoside <sup>b</sup>	5.84
Total da Área Identificada		68.2

- Infrared Spectroscopy (FTIR-ATR)
  - Thermogravimetric analysis (TGA)
  - Electron microscopy (SEM)
  - Mono- and bi-dimensional NMR
  - Karl-Fischer
  - Molecular Weight (GPC)
  - Calorific value (HHV|LHV)
  - Ultimate analysis (CHNS/O)
  - Gas chromatography (GC-MS)
  - Liquid Chromatography (HPLC)
  - Acid and hydroxyl value (OH|H)
- and more...

# CORK LIQUEFACTION

## PRODUCTION OF SUSTAINABLE ADHESIVES FOR CORK



VALOR5

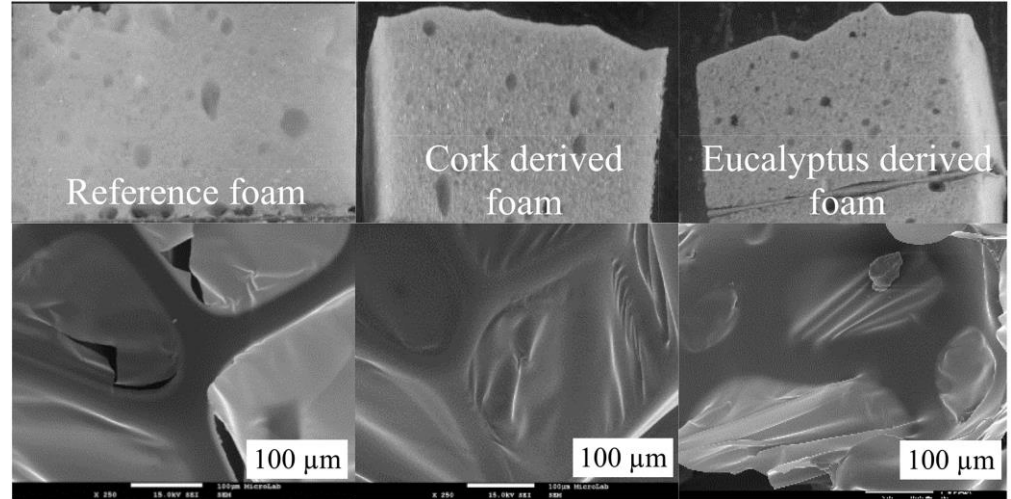
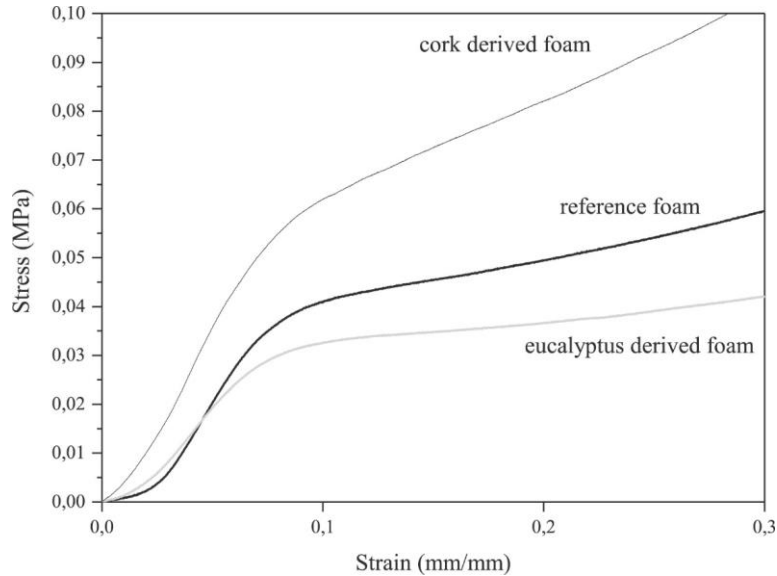
Samples	$\theta$ (mm)	Torsion angle (°)	Torque (N m)	Shear strength (MPa)	Breakage point
CP50		63.00	6.56	0.93	Cork
Epoxy	33	66.33	8.37	1.19	Cork
Wood		62.33	6.44	0.91	Cork

- PT107143
- PCT/PT2014/000058
- WO/2015/034383
- CN 105745256 A
- EP3041886 A1
- US9688806 B2



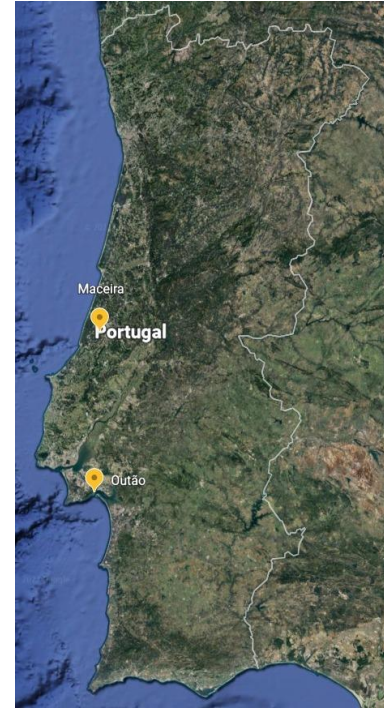
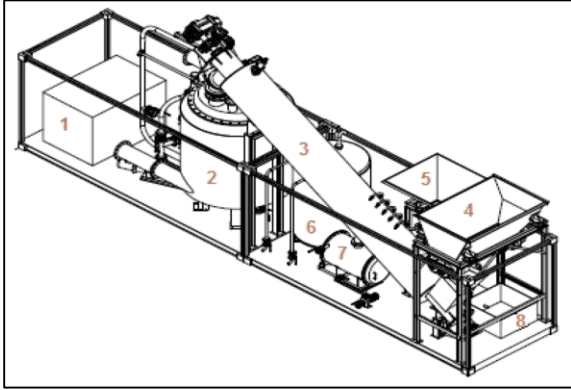
>96% BIO-BASED COMPONENTS

# PU FOAMS FROM LIQUIFIED BIOMASS



# BIOMASS LIQUEFACTION

## PILOT PLANT DESIGN AND CONSTRUCTION



## BITUMEN PRODUCTION FROM BIO-OILS

**Objective:** Development of a bio-binder for road pavement



Parameter	
Penetration (0.1mm)	47
Softening Point (°C)	90.6



Bitumen from bio-oil with properties similar to those from 35/50 bitumen

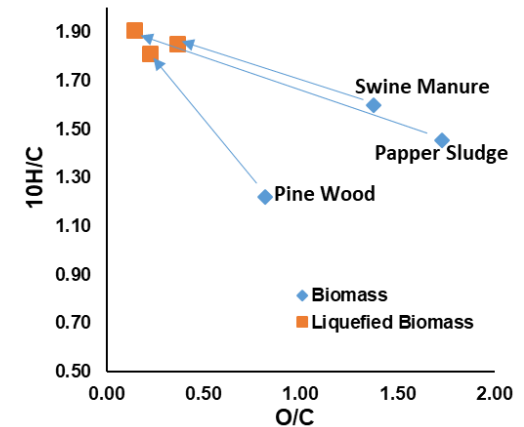
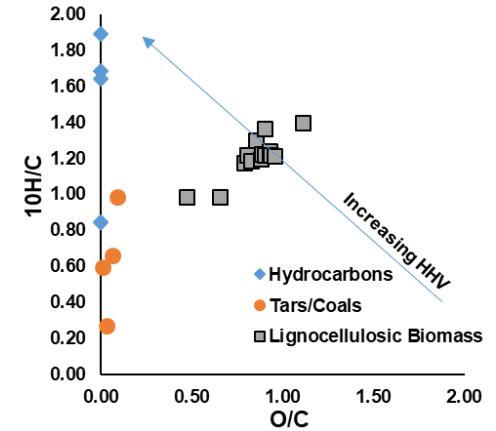


# BIO-OILS AND ORGANIC EXTRACT AS BIO-FUELS

Entry	Sample	Moisture (%)	HHV (MJ/kg)
1	Cork wastes [18]	20	21.6
2	Liquefied cork	0.7	34.14
3	Aqueous extract	9.7	20.29
4	Organic extract	1.0	37.91

Sample	Water content (%)	High heat value (MJ/Kg)
Poplar Chips	29.1	13.9
Liquefied Poplar biomass (organic extract) <sup>a</sup>	0.5	35.2
Poplar Pellets [46]	n.a.	≈ 20.0
Torrefied wood [47]	2–3	20–25
Coal [47]	6–15	18–30
Natural gas [48]	n.a.	37.3

<sup>a</sup> After extraction.



## DEVELOPMENT OF FUEL MAPS FOR FOREST MANAGEMENT AND VALORIZATION



Parameter	Bio-oil	FPBO	HTLBO
$T_i$ (°C)	213	251	
$T_h$ (°C)	624	667	
$T_{max}$ (°C)	244	369	
$DTG_{max}$ (%min <sup>-1</sup> )	18.21	7.89	
$DTG_{mean}$ (%min <sup>-1</sup> )	4.53	4.20	
$S$ (% <sup>2</sup> °K <sup>-3</sup> min <sup>-2</sup> ) x 10 <sup>-7</sup>	3.89	1.28	

[1] <https://doi.org/10.1007/s10973-011-1604-8>.

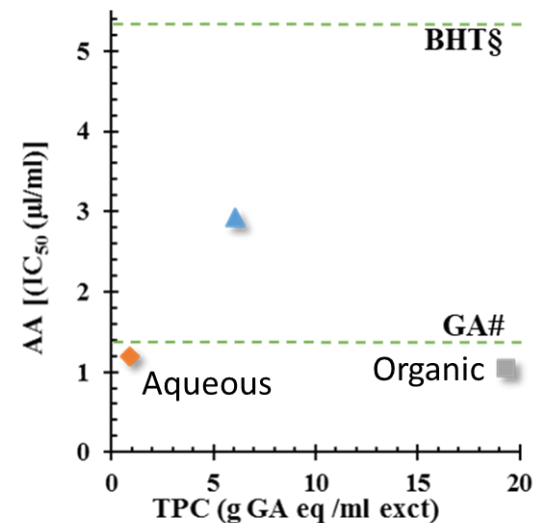
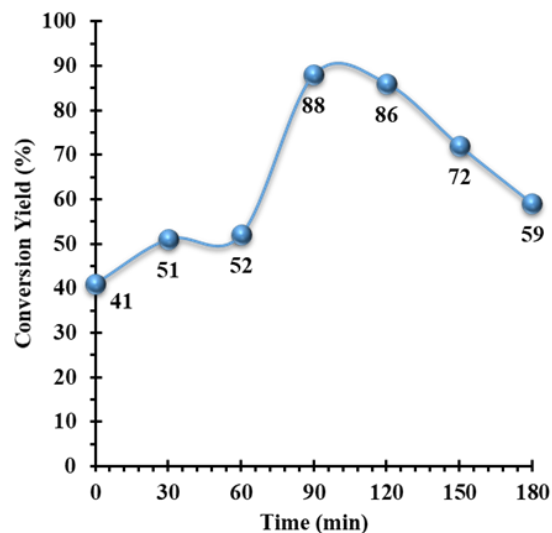


Diesel/Bio-oil emulsions



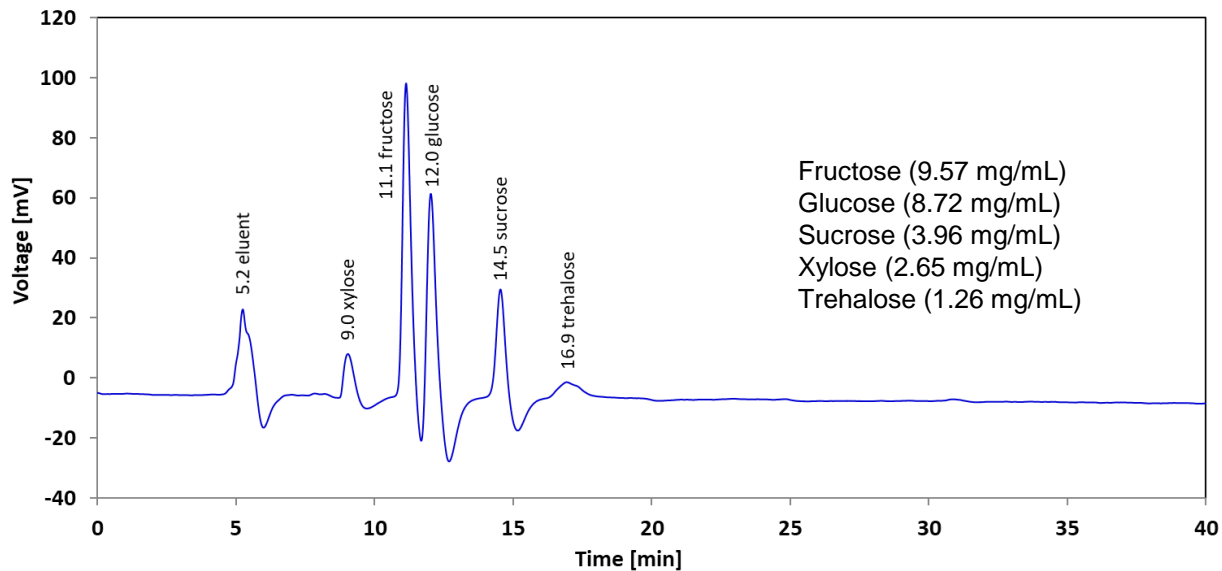


# CAROB POD WAST



Sample	Sugar Content (g/L)			AA (µl/ml)	TPC (g GA eq/ml extr)
	Glucose	Sucrose	Maltose		
Bio-oil	--	--	--	2.92	6.05
Aqueous	21.70±1.11	42.70±2.47	43.21±0.89	1.19	0.92
Organic	--	--	--	1.05	19.3

BHT – butylated hydroxytoluene  
 GA – Gallic acid  
 AA – Antioxidant activity  
 TPC – Total phenolic content



Fructose (9.57 mg/mL)  
Glucose (8.72 mg/mL)  
Sucrose (3.96 mg/mL)  
Xylose (2.65 mg/mL)  
Trehalose (1.26 mg/mL)

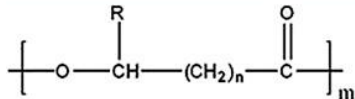
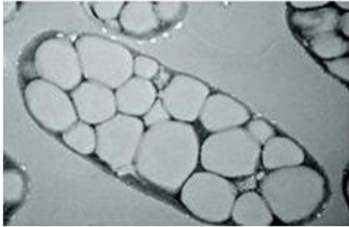


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## BIO-POLYMERS PRODUCTION AND SUSTAINABLE ADDITIVES

PHA



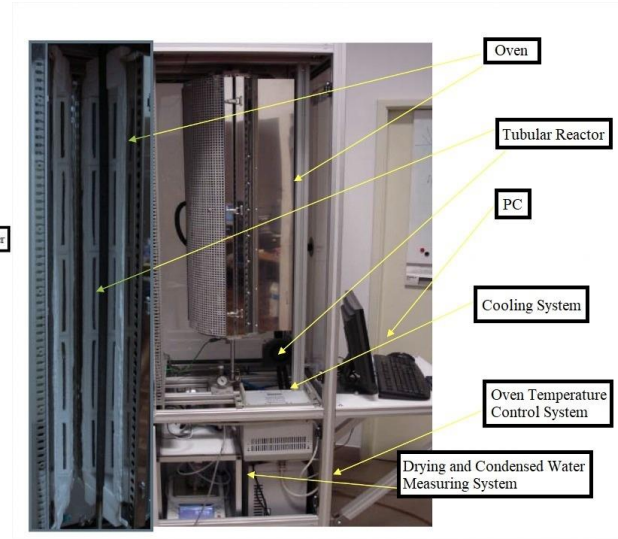
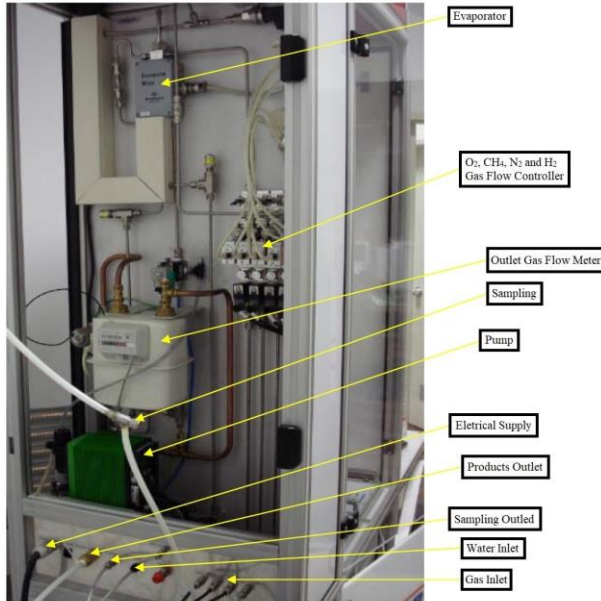
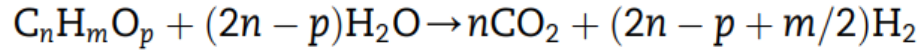
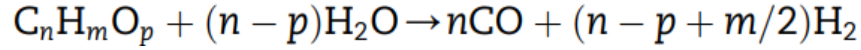
Cell dry weight

Bacteria	Carbon source	CDW (g/L)
<i>Pseudomonas chlororaphis</i> DSM 19603	Sugar mixture	3.58
	Aqueous extract	3.52
<i>Pseudomonas resinovorans</i> NRRL B-2649	Sugar mixture	2.21
	Aqueous extract	4.20
<i>Pseudomonas putida</i> DSMZ 6125	Sugar mixture	1.78
	Aqueous extract	3.19



# STEAM REFORMING OF BIO-OILS

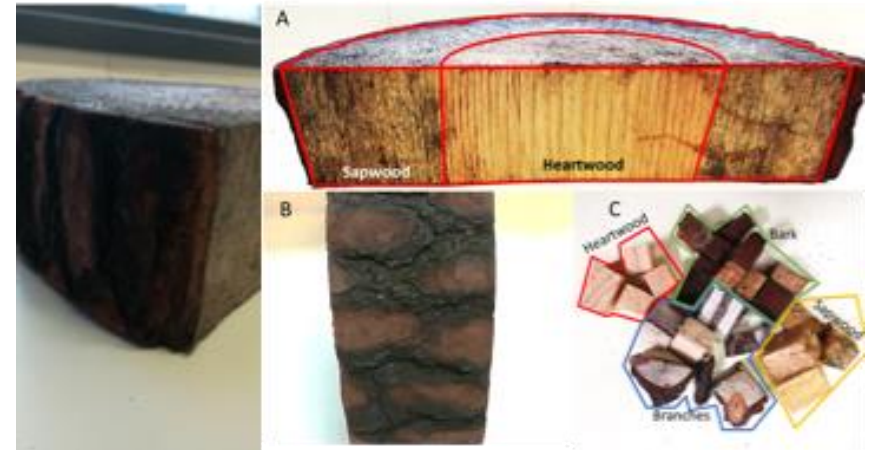
## PRODUCTION OF HYDROGEN-ENRICHED GASEOUS STREAMS



	Weight (%)		
	C	H	O
<b>Pyrolytic Heavy oil</b>	46.3	5.48	48.19
<b>Pyrolytic Light oil</b>	39.59	7.09	53.32
<b>HTL Heavy oil</b>	60.03	5.55	34.42
<b>HTL Light oil</b>	45.92	6.31	47.76
<b>Bio-oil</b>	<b>69.8</b>	<b>12.65</b>	<b>17.55</b>

# Burnt wood liquefaction

Sample ID	Biomass	Time (min)	Conversion (%)
1	Bark	0	14
2		45	35
3		60	55
4		90	49
5		120	51
6		180	42
7		300	45
8	Sapwood	0	29
9		45	62
10		60	79
11		90	67
12		120	73
13		180	80
14		300	82
15	Heartwood	0	40
16		45	63
17		60	84
18		90	73
19		120	76
20		180	83
21		300	82
22	Branches	0	40
23		45	54
24		60	62
25		90	63
26		120	70
27		180	64
28		300	68
29	Pinewood	0	43
30		45	71
31		60	74
32		90	71
33		120	72
34		180	76
35		300	80



## Alternative solvents

	2-EH (%w/w)	PG (%w/w)	S (%w/w)	GF (%w/w)	PC (%w/w)	GC (%w/w)	Biomass Conversion (%)
1	100	-	-	-	-	-	71.2
2	-	100	-	-	-	-	79.4
3	20	80	-	-	-	-	93.7
4	80	20	-	-	-	-	83.9
5	-	-	100	-	-	-	96.4
6	20	-	80	-	-	-	89.0
7	80	-	20	-	-	-	81.9
8	-	-	-	100	-	-	95.5
9	20	-	-	80	-	-	83.6
10	80	-	-	20	-	-	69.7
11	-	-	-	-	100	-	96.5
12	20	-	-	-	80	-	96.6
13	80	-	-	-	20	-	86.4
14	-	-	-	-	-	100	98.7
15	20	-	-	-	-	80	92.3
16	80	-	-	-	-	20	77.3

90 min, 3% w/w cat, 160°C

# Research team and collaborators

W I R E

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**Thank you!**