# APPLICATION OF BIO-OIL OTHER THAN FUEL WITH FOCUS ON CONTAMINATED Naples, Nov '23

**RUI GALHANO DOS SANTOS** 



Waste biorefinery technologies for accelerating sustainable energy processes





#### HIDDEN CLIMATE SCIENCE PIONEER



"An atmosphere of that gas would give to our earth a high temperature"

### August 1856

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.

#### **Eunice Foote**

#### **EVOLUTION OF CO<sub>2</sub> EMISSIONS**



#### CARBON DEPENDENCY ON THE CHEMICAL INDUSTRY



#### **Global Carbon Demand for Chemicals and Derived Materials**

in 2020 and Scenario for 2050 (in million tonnes of embedded carbon)





#### **ENERGY DEMAND**



Share of Renewable Energy in Power, 2011 and 2021





#### THE GENERATIONS TO COME







Humanity's past	*****	All the people who ever lived, $\sim$ 117 billion, ratio of 14:1 compared to the current population
Humanity's present	*	All the people who are alive today, ~8 billion, about 6.8% of all people who ever lived
Humanity's future		All the people who could ever live, about 100 trillion, assuming the Earth remains habitable

# WHAT CAN WE DO?

### KEY POINTS WHEN DEVELOPING NEW PROCESSES





### Holistic vision of the processes



Prioritize energy efficiency, recyclability, durability, social responsibility



Promote environmentally friendly and socially responsible systems



Promote a more sustainable and circular economy

#### WHY BIOMASS AND ITS DERIVATIVES?



### VERSATILITY FOR BIOPRODUCTS **AND BIOREFINERIES** Can be used to produce a wide range of bioproducts, including biofuels, bioplastics, and biochemicals matter) **ENERGY DIVERSITY AND SECURITY** CO<sup>2</sup> 4 Contributes to diversifying the

#### **RENEWABLE, SUSTAINABLE** AND ABUNDANT

Renewable and abundant resource, providing a sustainable alternative for energy and various industrial applications (e.g., >82% of the world's biomass is plant-based

energy mix, reducing dependence on a single energy source

#### **REDUCED GREENHOUSE GAS EMISSIONS**

Offers the potential to be a carbonneutral or even carbon-negative energy source



#### **URBAN WASTES – AN OPPORTUNITY?**







#### **BIOMASS CONVERSION TECHNOLOGIES/PROCESSES**



#### **BIOMASS PYROLYSIS - MECHANISMS**



#### **BIO-OILS – POTENTIAL REFINING TECHNIQUES**







#### **BIOMASS CONVERSION TECHNOLOGIES/PROCESSES**

Tashaiswas	Onerating Conditions	<b>D</b>	Technique Feasibility					
Techniques	Operating Conditions	Keaction	Advantages	Challenges				
	Physical processes to chemical productions							
	(Atmospheric) 80–250 °C		Production of alcohols, aldehydes, and acids	Avoid the polymerization reactions				
Distillation	(Vacuum) Low temperatures	_	Avoid polymerization reaction and degradation of thermally sensitive compounds	More expensive, energy intensive, and hard operation				
	(Molecular) High vacuum (<10 <sup>-6</sup> atmospheric pressure)	No reaction	Low distillation temperature and heating rates and high efficiency of fractionation					
Supercritical fluids	Mild conditions $(T > 32 \degree C P > 100 \text{ bar})$	_	Clean solvents and bio-oil with low viscosity and oxygen content	Energy intensive and hard operation system				
Liquid–liquid extraction	(Water extraction) Normal conditions (T and P)	_	Simple technique, increases the heating value and stability of bio-oil, and decreases the viscosity	Increases water/solvent content and decreases pH				
Emulsification	Warn conditions, surfactant, and co-surfactants	Emulsified with petroleum-based fuels	Classic and cost-effective route	High energy for production is the most important challenge of these processes				





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#### **GCxGC-TOFMS**



Ind. Eng. Chem. Res. 2022, 61, 27, 9567-9574

### PHYTOREMEDIATION - BIO-OIL PRODUCTION USING LEAD CONTAMINATED SWITCHGRASS FEEDSTOCK



According to US Agency for Toxic Substances and Disease Registry (ATSDR) superfund sites can have lead concentrations of above 10,000 mg/kg.

Commonly used methods for the cleaning of lands

- on-site stabilization
- ex-situ washing.

Lengthy Expensive modifies soil's nutritional and microbial balance





### PHYTOREMEDIATION - BIO-OIL PRODUCTION USING LEAD CONTAMINATED SWITCHGRASS FEEDSTOCK



#### Phytoextraction

absorb the metal contaminants in the soil by drawing the soluble metal ions into the shoots or aerial parts of the plant in the top 1–2 m of soil.

- more cost-effective method for metal extraction,
- environmental friendly because
- avoids the loss of topsoil experienced in excavation processes

The phytoremediation effectiveness depends on the site as well as the plant used, but most phytoremediation plants have shown a potential to reduce the organic pollutants by more than 50 %



### PHYTOREMEDIATION - BIO-OIL PRODUCTION USING LEAD CONTAMINATED SWITCHGRASS FEEDSTOCK





#### PHYTOREMEDIATION - BIO-OIL PRODUCTION USING LEAD CONTAMINATED SWITCHGRASS FEEDSTOCK

Mass balance for the four process routes. a Route 1, fast pyrolysis at 500 °C. b Route 2, acid hydrolysis with 4 % H3PO4 and fast pyrolysis at 500 °C. c Route 3, enzymatic hydrolysis with a combination of A. Niger, T. Reesei and H. Grisea and fast pyrolysis at 500 °C. d Route 4, acid hydrolysis with 4 % H3PO4, enzymatic hydrolysis with a combination of the three enzymes and fast pyrolysis at 500 °C



	Torrefied MFW at 275 °C			
Compositions	Organic compounds in the aqueous phase	Organic phase		
Maltol	4.7	19.94		
2-Furanmethanol	5.09	17.55		
2-Hydroxy-3-ethyl-2-cyclopenten-1-one	3.41	11.68		
Acetic acid	9.54	10.29		
1-(2-Furanyl)-Ethanone		4.09		
2-Hydroxy-3-methyl-2-cyclopenten-1- one		3.45		
Phenol		3.35		
1,5-Dimethyl piperidine-3-ol		3.26		
4(2-Propenyl)- phenol	2.1	2.99		
2-Methoxy phenol		2.83		
Propanoic acid		2.65		
Trimethyl pyrazine		2.3		
Methyl pyridine		1.81		
Methyl-2-hydroxy propanoate	4.3	1.69		
3-Ethyl-2,5-dimethyl pyrazine		1.59		
2-Furanmethanol acetate		1.48		
Pyridine				
1-Hydroxy-2-pentanone	1.24			
4-Hydroxy-4-methyl-2-pentanone	2.06			
2,6-Dimethyl pyrazine	1			
D-Manitol	1.76			
Dianhydromanitol	26.05			
Methyl tetradecanoate	2.6			
Methyl hexadecanoate	26.61			
Methyl 9-Octadecanoate	3.91			

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#### BIO-OIL FROM FOOD WASTE PYROLYSIS AFTER TORREFACTION

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#### **REFUSED DERIVED FUELS - PYROLYSIS**





Sample	ΡϹΟ	FOR	RDF
Density (g/cm <sup>3</sup> )	0.94	0.93	1.30
Dynamic viscosity (cP)	7.0	1.5	110.6
рН	3.0	2.1	3.1
C (%)	59.0	52.4	43.5
H (%)	8.9	7.9	5.0
N (%)	1.2	0.1	3.9
S (%)	-	-	-
O (%)	30.9	39.6	47.6
HHV (MJ/kg)	27.1	21.9	13.4

FOR – Forest residues

PCO – Pine Cones

RDF – Refuse derived fuels

#### **REFUSED DERIVED FUELS - SOLVOLYSIS**



<b>Reaction Time</b>	Temperature	Catalyst concentration	Yield
90 min	160°C	3%	11,66 %
205 min	160°C	3%	7,60 %
90 min	175°C	3%	7,29 %
90 min	160°C	10%	27,44 %
205 min	175°C	10%	33,28 %
205 min	175°C	10%	33,0 %
	Reaction Time   90 min   205 min   90 min   90 min   205 min   205 min	Reaction Time   Temperature     90 min   160°C     205 min   160°C     90 min   175°C     90 min   160°C     205 min   175°C     205 min   175°C	Reaction Time   Temperature   Catalyst concentration     90 min   160°C   3%     205 min   160°C   3%     90 min   175°C   3%     90 min   160°C   10%     90 min   175°C   10%     205 min   175°C   10%     205 min   175°C   10%



\*dried



#### **BIO-OIL FROM ALTERNATIVE CONTAMINATED FEEDSTOCKS**

Entry	Sample	Chemical anal	Chemical analysis (%)				HHV (MJ/kg)	
		Moisture	С	Н	0	Ν	S	
1	Pinewood	14.9	50.90	6.22	41.48	1.13	0.27	20.10
2	LPW	1.00	69.80	12.65	15.49	1.58	0.48	37.41
3	Paper sludge	76.1	33.90	4.93	58.64	2.00	0.53	nd
4	LPS	0.4	74.86	14.30	10.64	0.00	0.20	40.26
5	Swine manure	75	38.30	6.13	52.63	1.95	0.99	15.90
6	LSM	1.5	63.20	11.70	22.89	1.51	0.70	33.38

#### AQUEOUS EXTRACTION OF BIO-OILS

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



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#### **BIO-PLASTICS - POLYHYDROXYALKANOATES**

**"Polyhydroxyalkanoates (PHA)** are polyesters produced by several groups of bacteria as a carbon and energy reserve"



PHA



Paracoccus sp.







#### **PRODUCTION OF SUSTAINABLE ADHESIVES FOR BIO-OIL** DERIVATIVES



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PCT/PT2014/000058

WO/2015/034383

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EP3041886 A1

US9688806 B2

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>96% BIO-BASED COMPONENTS



#### under the law.

#### Therefore, this United States Patent

United

States

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America Grants to the person(s) having title to this patent the right to exclude others from mak-ing, using, offering for sale, or selling the evention throughout the United States of Imerica or importing the invention into the United States of America, and if the Invention is a process, of the right to exclude oth ers from using, offering for sale or selling throughout the United States of America, or porting into the United States of America, products made by that process, for the term set forth in 35 U.S.C. 154(a)(2) or (c)(1), subject to the payment of maintenance fees as provided by 35 U.S.C. 41(b) See the Maintenance Fee Notice on the inside of the cover.

Joseph Matat





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#### VALOR5



#### PU FOAMS FROM LIQUIFIED BIOMASS



### SUSTAINABLE BIO-BINDER FOR ROAD PAVEMENT PRODUCTION OF BITUMEN FROM BIO-OILS



Portucal



FÁTIMA-BATALHA

ALCÁCER DO SAL

Bio-oil bitumen with properties similar to those of 35/50 bitumen















#### RESEARCH

Bring together the valorization of biomass and the concept of biorefinery in an integrated platform for the upcycling of biomass, but above all of waste



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#### BIO2VALUE – AN INTEGRATED PLATFORM FOR THE RECOVERY OF BIOMASS AND WASTE



## ZERO WASTES | CO2 NEUTRAL | CIRCULAR

CAN BIO-OILS BE A SOLUTION IN THE TRANSITION TO A MORE SUSTAINABLE ECONOMY?





DEQ DEPARTAMENTO DE ENGENHARIA QUÍMICA TÉCNICO LISBOA

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## CHEMICAL ENGINEERING DEPARTMENT

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PREMIADA COM MEDALHA DE OURO NA EXPOSIÇÃO INTERNACIONA DO BIO DE JANEIRO DE 1928 E MACAU DE 1926 <sup>BARCELON 1920</sup> SELEMA 1930-11580A 1932 CEANCE DIPLEMA DE HONRA



