Valorization of pyrolysis by-products from sugar cane bagasse for the protection of biomaterials

Febrina Dellarose Boer[1,2], Marie France Thevenon[1,2],
Jean-Michel Commandré[1,2], Mériem Fournier[3]

[1]CIRAD, UR BIOWooEB, Montpellier, France
[2]BIOWooEB, Univ. Montpellier, CIRAD, Montpellier, France.
[3]LERFOB, AgroParisTech, INRA, Nancy, France

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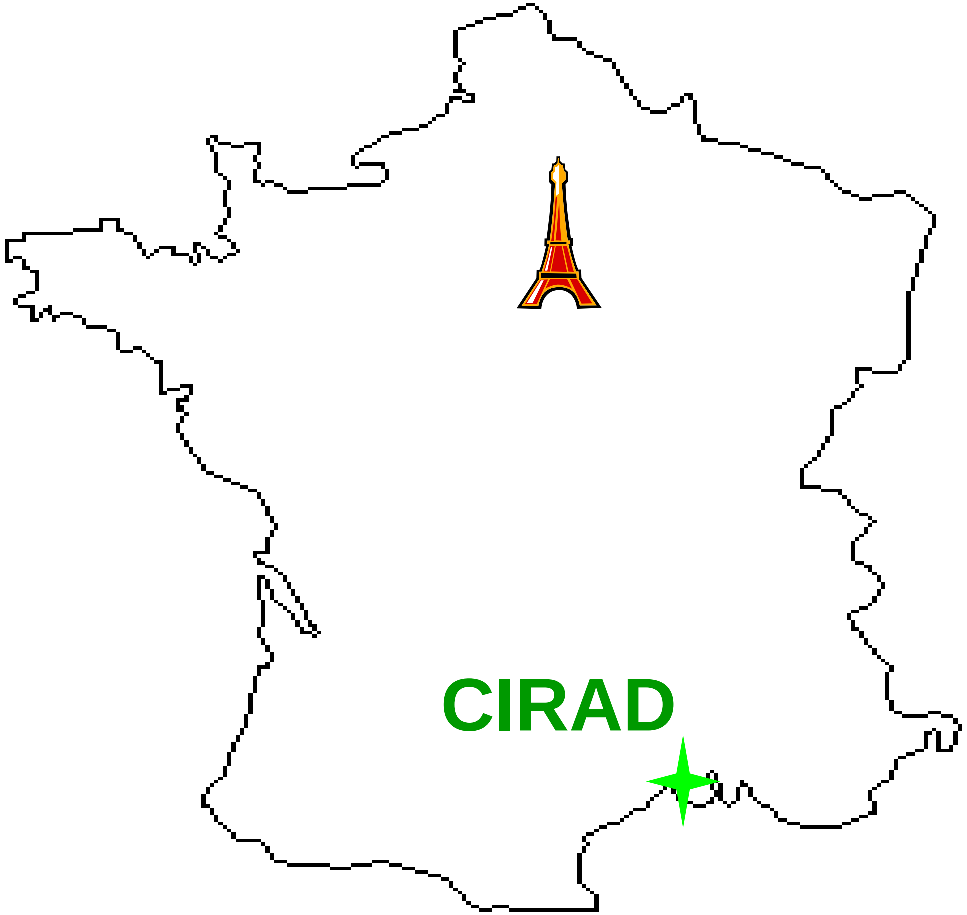

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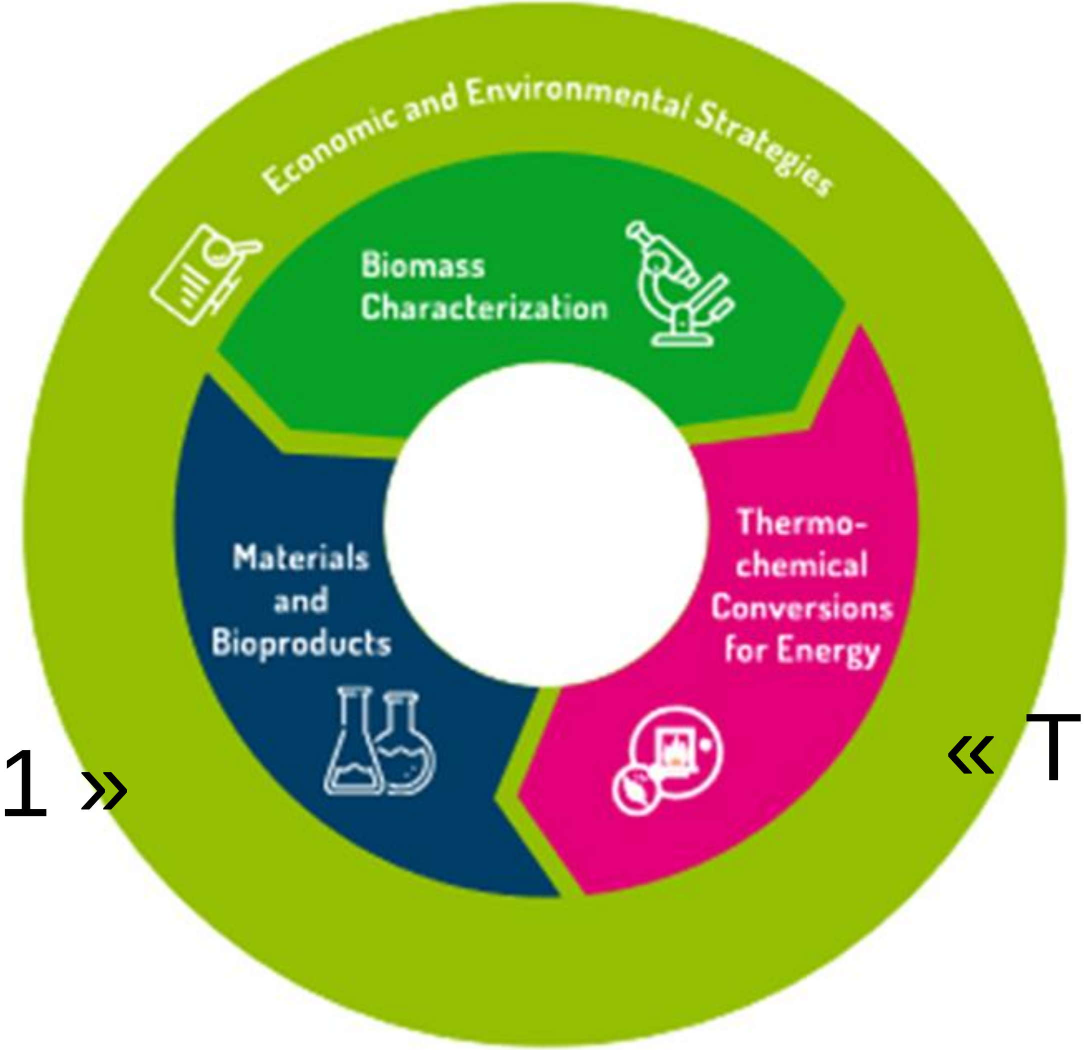


« Team 1 »

« Team 2 »

Febrina

....
or
Work together
....

Introduction

Biomass as an energy source

- Low density
- Low calorific value
- Susceptible to moisture and microbial degradation

Source: CIRAD (in Lecaille 2012)

VALORIZATION

Source: Helen Soteriou (2016)

Energy: Slow pyrolysis

Wood protection

wood is susceptible to threats from biological agents such as fungi and insects

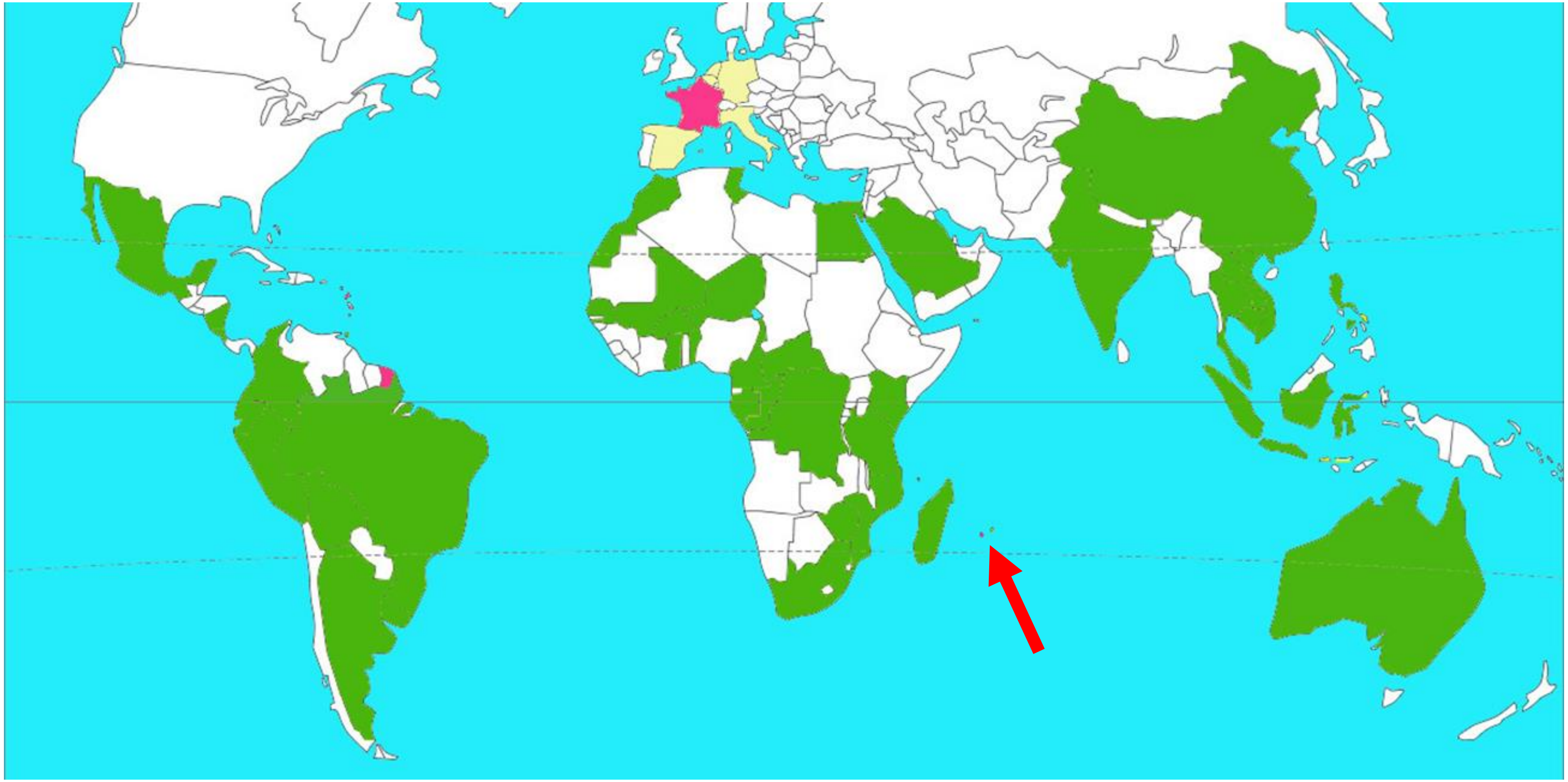
By-product:

Bio-oil

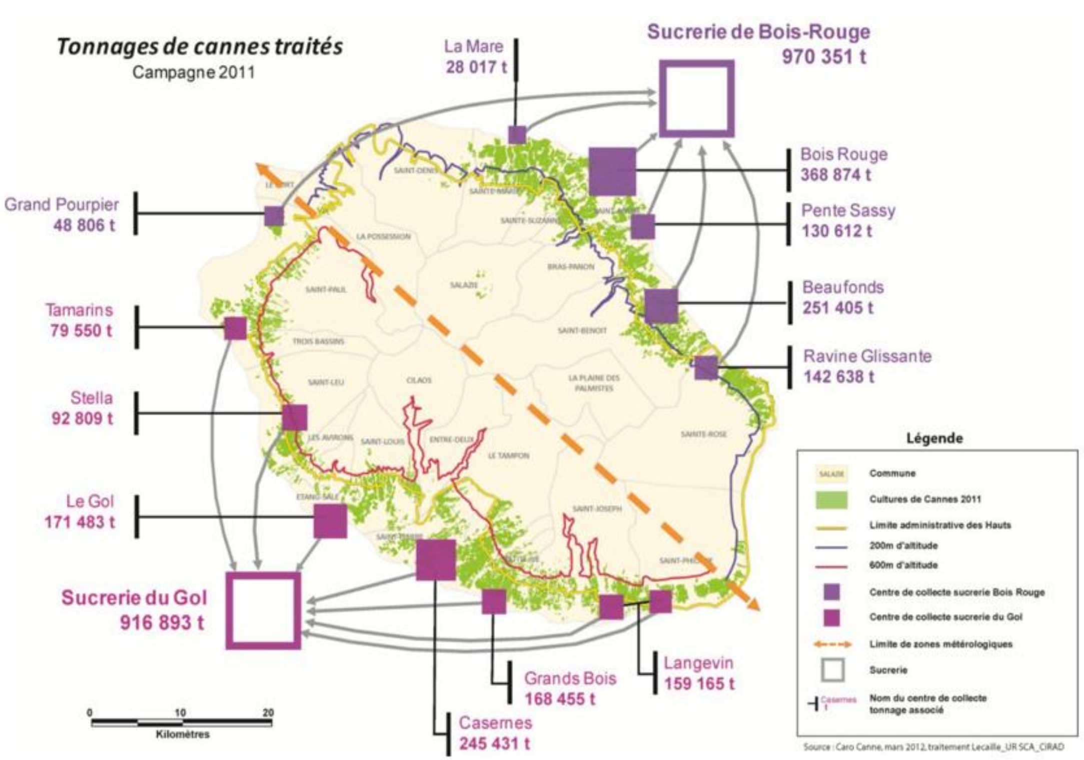
VALORIZATION

Alternative to creosote
+ No or less PAHs

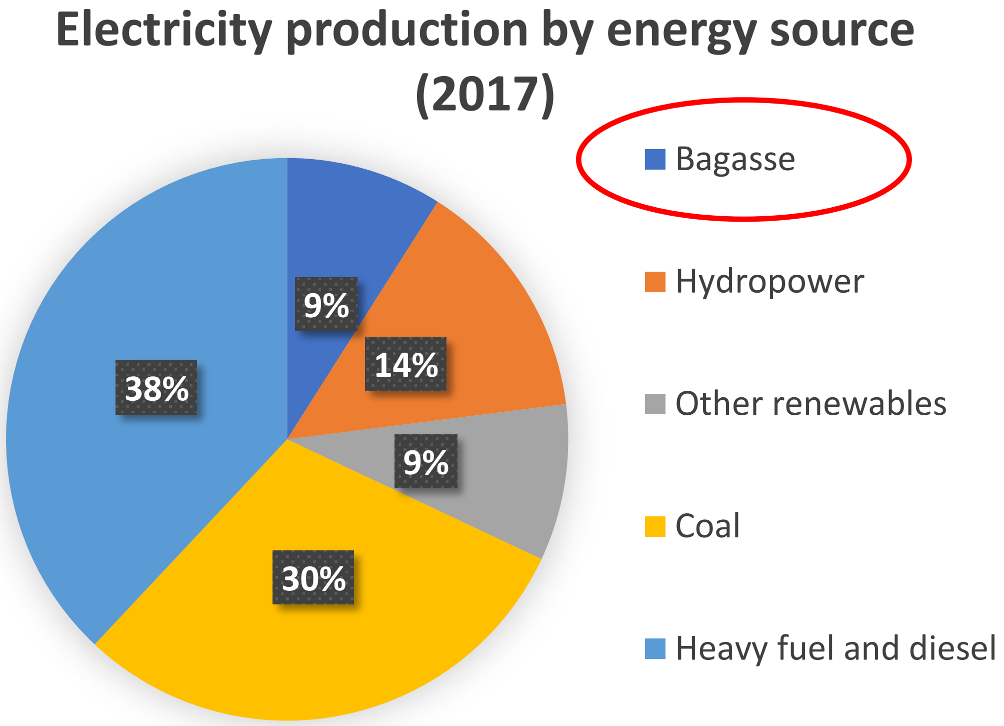
Sugarcane in Reunion island



Sugarcane in Reunion island



Source: Caro canne (in Lecaille 2012)



Source: Energy Balance, Reunion Island 2017 (2018)

- Sugarcane industry plays an important role in agricultural sector
- 550,000 tons of bagasse were produced and recovered per year as it becomes an important source for renewable energy source (Selosse *et al.* 2018).

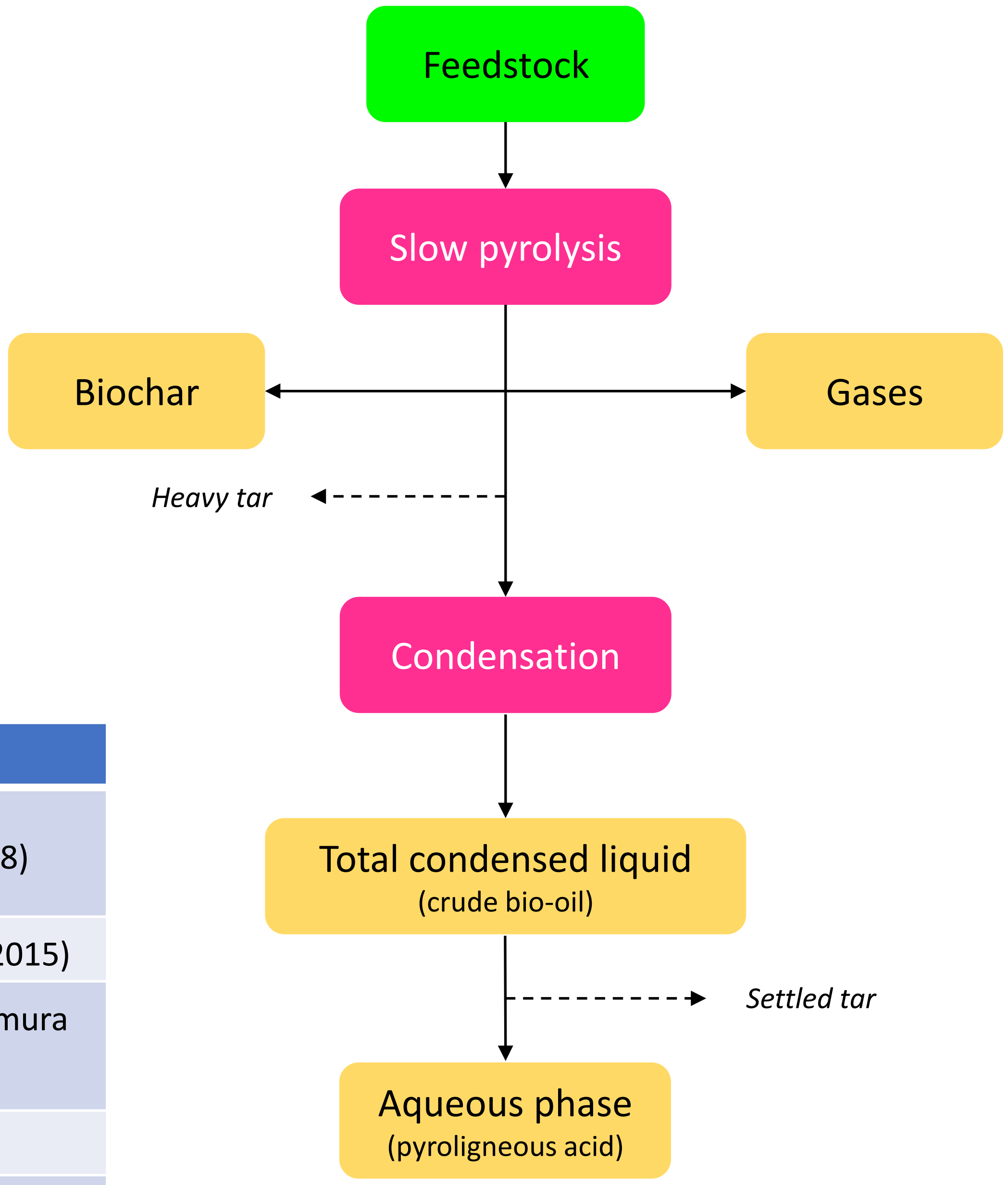
Biocidal application of bio-oil

Study of bio-oil for wood treatment

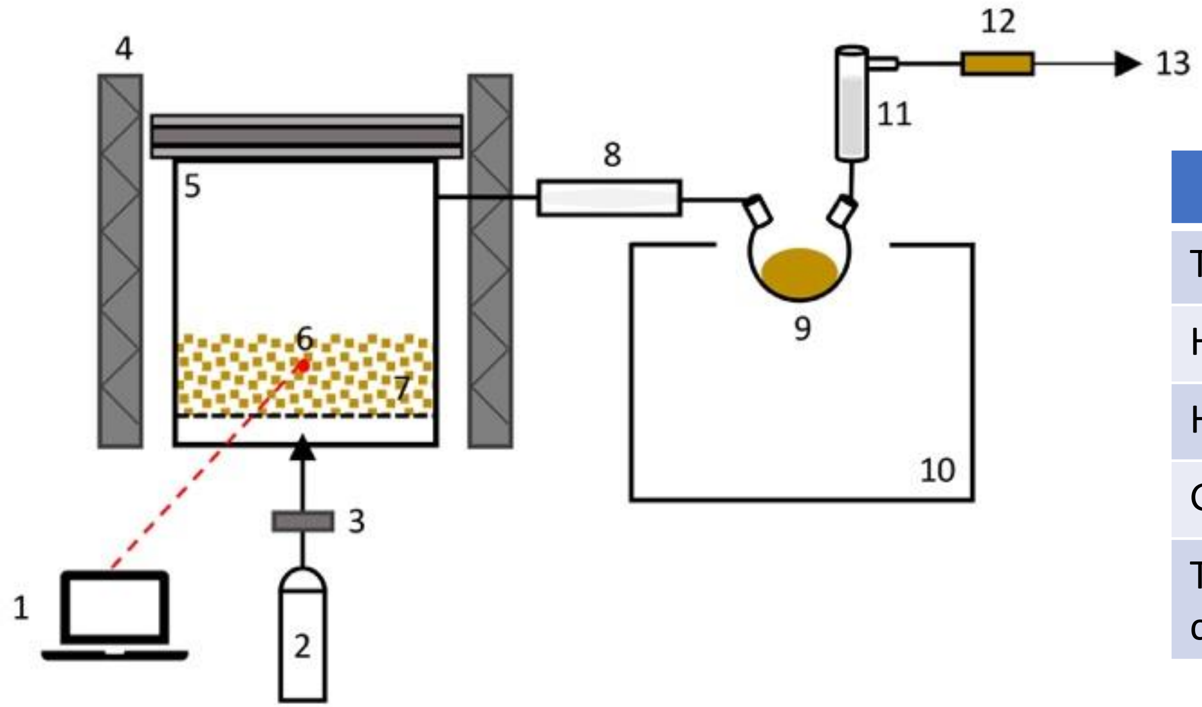
Biomass	Temperature	Reference
Giant cane	450—525 °C	Temiz *et al.* 2013
Macadamia nut shell	NA	Kartal *et al.* 2011
Scots pine	450; 550; 600 °C	Temiz *et al.* 2010
Oil palm trunk	300; 400; 500 °C	Lee *et al.* 2010

Study of pyroligneous acid / wood vinegar

Biomass	Temperature	Target	Reference
Oil palm trunk	350, 400, 450 °C	Antifungal and antitermic activity	Oramahi *et al.* (2018)
Wood and bamboo*	400	Antifungal activity	Theapparat et al. (2015)
Laban wood (Vitex pubescens)	300, 400, 450	Antifungal and antitermic activity	Oramahi and Yoshimura (2013)
Coconut shell	300—400	Termiticidal activity	Wititsiri (2011)
Wood**	NA	Termiticidal activity	Yatagai *et al.* (2002)



Methods: slow pyrolysis process



Parameter	Value
Temperature	400, 500 °C
Heating rate	1, 10°C/min
Holding time	30 and 60 min
Gaseous atmosphere	N2 1L/min
Temperature of condenser	-20 °C

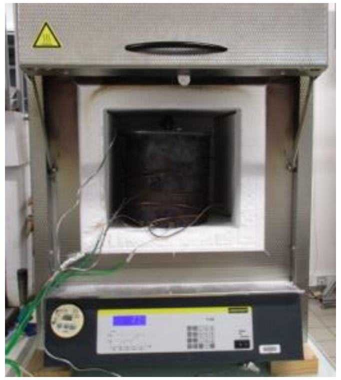


Figure 1. Experimental set-up of the pyrolysis reactor: (1) temperature control, (2) nitrogen gas supply, (3) flow control, (4) muffle furnace, (5) pyrolysis reactor, (6) thermocouple, (7) bagasse/char, (8) condenser, (9) condensed liquid, (10) cooling bath, (11) electrostatic precipitator, (12) light products, and (13) gas vent.

Methods: bio-char and bio-oil analysis

Bagasse

Biochar

- **Proximate analysis**: ash content, volatile matter content, fixed carbon
- **Ultimate analysis**: C H N analysis using an elemental analyzer VariMACROcube referred to the ASTM D5373 and NF EN ISO 16948
- **Calorific value** (a bomb calorimetric PAAR 6200 (NF EN ISO 18125))

Muffle furnace for proximate analysis

elemental analyzer VariMACROcube

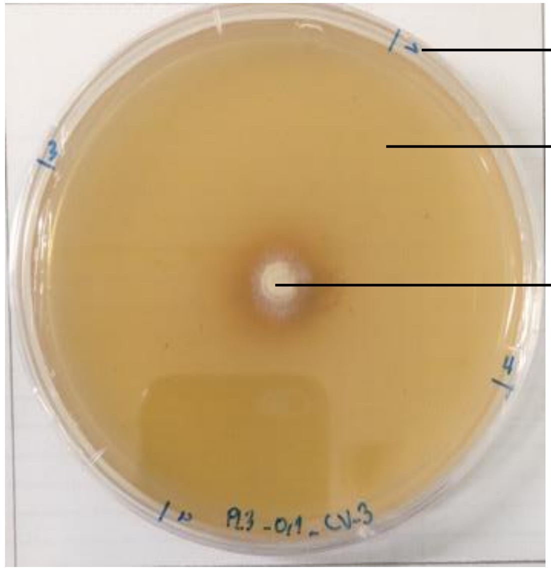
- **Water content**: Karl Fisher titration Mettler Toledo (ASTM E 203).
- **Chemical composition**: GC-MS (Agilent 6890N equipped with a DB1701 capillary column)

Karl Fisher

Bio-oil

Methods: fungal test

- Type of test: Inhibition test using two type of fungi: *Coniophora puteana* and *Trametes versicolor*
- Treatment: crude bio-oil 0.01; 0.05; 0.10; 0.15; 0.20; 0.25 % in malt-agar medium (v/v)
- Control: Sterile malt-agar medium (40 g malt, 20 g agar, 1 L distilled water)
- Measured parameters: Radial growth (Kartal *et al.* 2011)



A 9 cm-diameter petri-dish

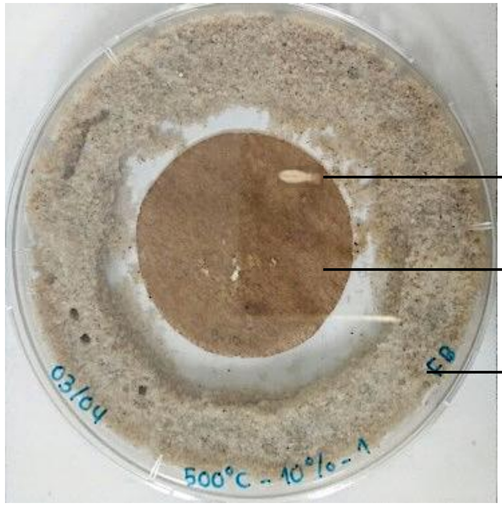
30 mL of sterile malt and agar medium + bio-oil (v/v)

A fungus with 0.5 cm of diameter was placed centrally

The inhibition rate was determined by comparing the fungal growth of the treated medium with the control (petri-dishes contained only malt-agar medium).

Methods: termite test

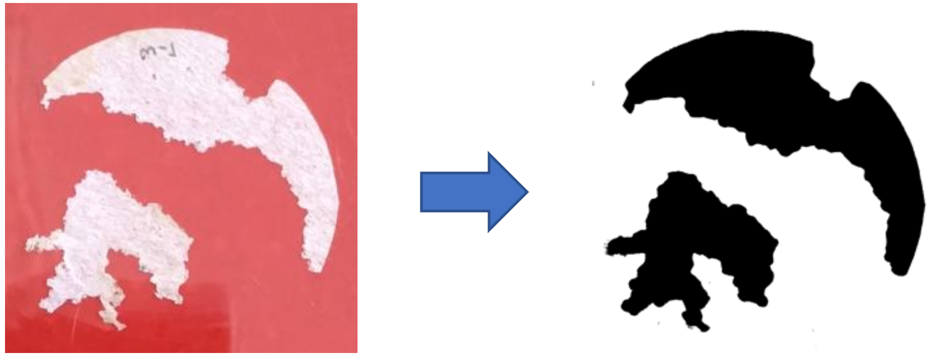
- Type of test: Screening test (*Reticulitermes flavipes*)
- Treatment: joseph paper treated with crude bio-oil 1, 3, 5, 10% in ethanol (v/v)
- Control: joseph paper treated with distilled water and ethanol
- Measured parameters: Paper loss area and mortality
- Duration of test: 4 weeks



Workers termites (20/medium)

Joseph paper diameter of 42.5 mm

Sand + water (4:1 v/v)

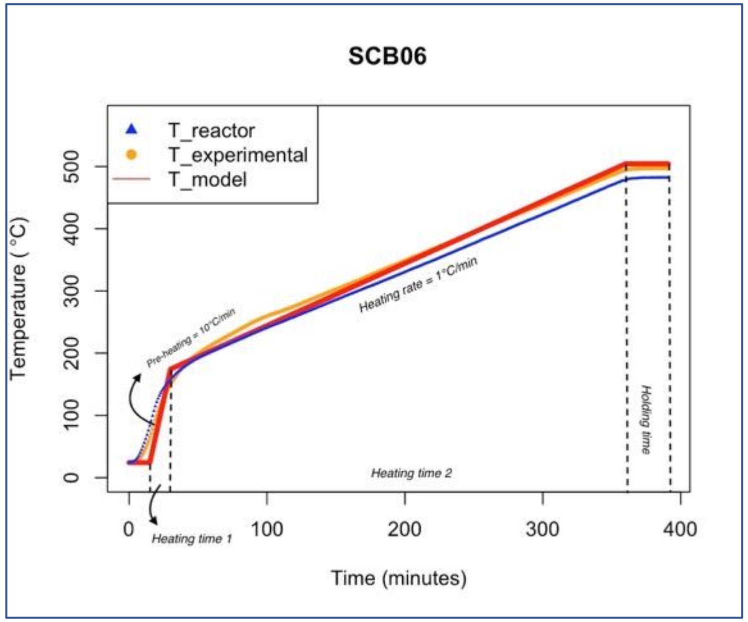


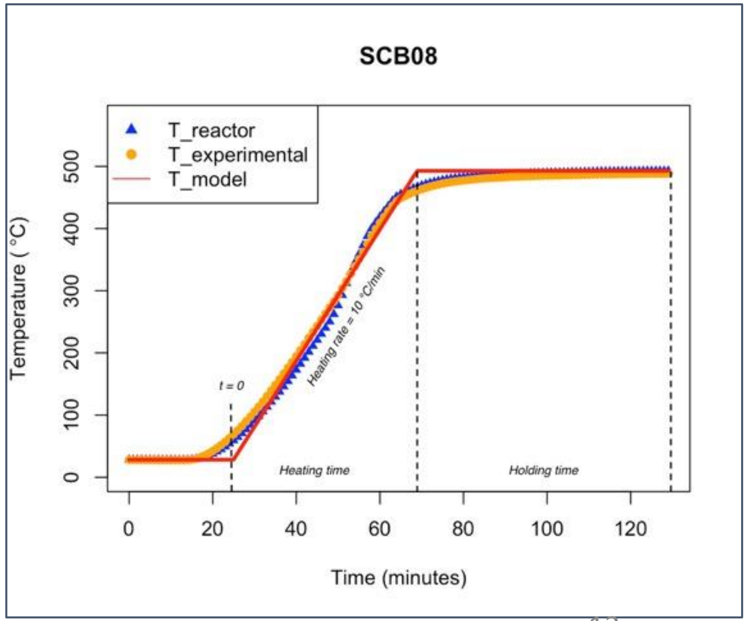
Paper loss area

Results

Pyrolysis (°C; °C/min; min)	Treatment	Yield (%)	
		Biochar	Bio-oil
400; 1; 30	SB01	35.12 ± 0.96	49.67 ± 0.28
400; 1; 60	SB02	34.63 ± 0.20	49.18 ± 1.33
400; 10; 30	SB03	33.87 ± 0.26	51.33 ± 1.26
400; 10; 60	SB04	33.58 ± 0.70	51.26 ± 1.54
500; 1; 30	SB05	31.32 ± 0.25	51.24 ± 0.71
500; 1; 60	SB06	30.42 ± 0.31	52.61 ± 0.95
500; 10; 30	SB07	29.13 ± 0.09	54.98 ± 0.72
500; 10; 60	SB08	28.84 ± 0.37	53.89 ± 2.10

- Among the parameters observed, **temperature is the most important parameter** which influence the pyrolysis yield while heating rate and holding time have no significant effect to the yield of biochar.
- However, the heating rate was observed to affect the bio-oil yield.





Results: Biochar

Process conditions	Proximate analysis				Elemental analysis					
	Volatile matter (wt%)	Fixed carbon (wt%)	Ash content (wt%)	Fixed carbon yield (wt%)	Carbon (wt%)	Hydrogen (wt%)	Nitrogen (wt%)	Oxygen (wt%)	H/C-ratio	O/C-ratio
Bagasse	82.39	13.37	4.24	-	47.31	5.62	0.38	46.69	1.43	0.74
400 °C; 1 °C/min; 30 min	25.67	63.54	10.79	25,01	69.50	3.81	0.55	26.14	0.66	0.28
400 °C; 1 °C/min; 60 min	24.31	63.97	11.72	25,09	70.23	3.66	0.58	25.53	0.63	0.27
400 °C; 10 °C/min; 30 min	25.80	61.39	12.81	23,45	70,35	3.32	0.65	25.68	0.57	0.27
400 °C; 10 °C/min; 60 min	24.56	62.29	13.15	24,08	69.40	3.46	0.62	26.52	0.60	0.29
500 °C; 1 °C/min; 30 min	14.33	72.67	13.00	26,16	73.53	3.07	0.53	22.87	0.50	0.23
500 °C; 1 °C/min; 60 min	13.01	73.01	13.99	25,82	75.70	3.08	0.61	20.61	0.49	0.20
500 °C; 10 °C/min; 30 min	16.01	68.50	15.50	23,40	72.90	2.74	0.62	23.74	0.45	0.24
500 °C; 10 °C/min; 60 min	16.43	70.50	13.07	24,30	71.95	2.85	0.57	24.63	0.48	0.26

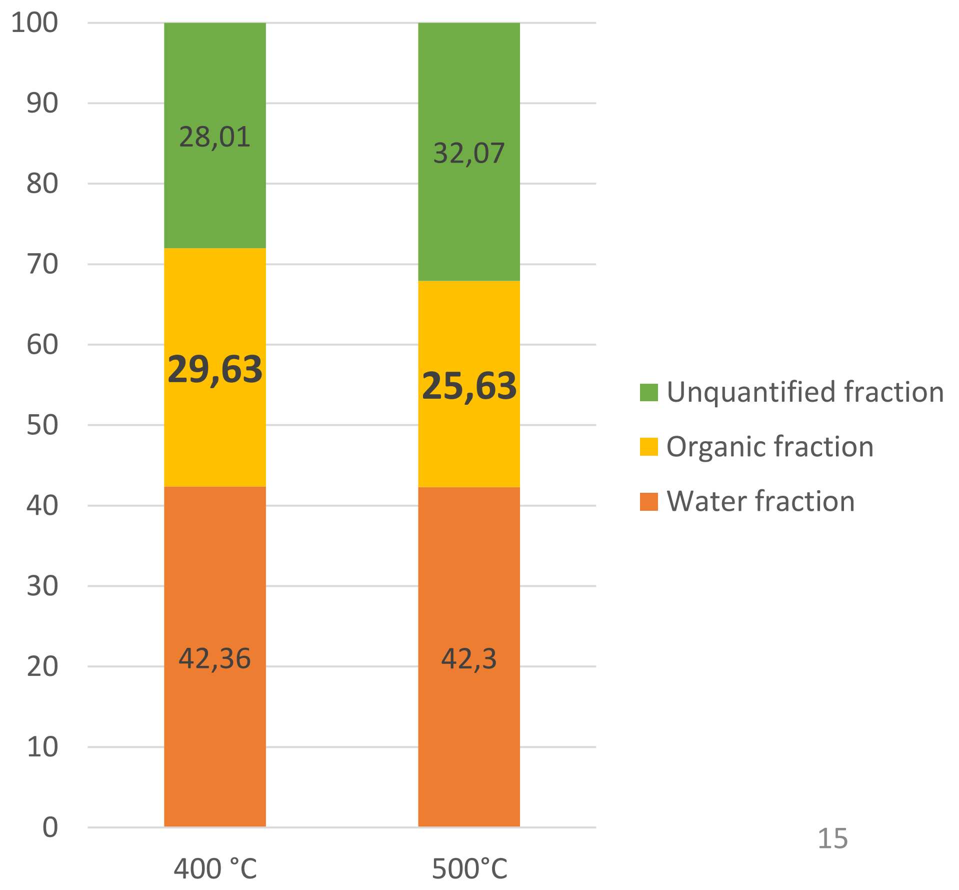
Process condition	Biochar yield (wt%)	HHV (MJ/kg)	Energy yield (%)	Energy density
400 °C; 1 °C/min; 30 min	35.12	27.44	53.12	1.51
400 °C; 1 °C/min; 60 min	34.63	27.41	52.33	1.51
400 °C; 10 °C/min; 30 min	33.87	27.20	50.78	1.50
400 °C; 10 °C/min; 60 min	33.58	26.86	49.73	1.48
500 °C; 1 °C/min; 30 min	31.32	28.52	49.25	1.57
500 °C; 1 °C/min; 60 min	30.42	28.67	48.08	1.58
500 °C; 10 °C/min; 30 min	29.13	27.81	44.65	1.53
500 °C; 10 °C/min; 60 min	28.84	27.85	44.27	1.54

(HHV of sugarcane bagasse = 18.14 MJ/kg)

Results: Bio-oil

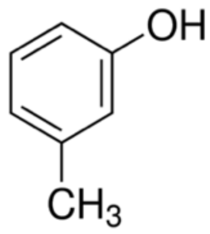
Compound of bio-oil (%)	400 °C; 10°C/min; 60 min	500 °C; 10°C/min; 60 min
Water fraction	42.36	42.30
Glycolaldehyde	3,35	3,18
2-Propanone,1-hydroxy-	3,32	2,91
Acetic acid	8,48	7,22
Formic acid	1,70	1,60
Propionic acid	0,37	0,31
Methanol	2,28	1,90
Furfural	1,19	0,45
2-furanmethanol	0,20	0,18
Levoglucosan	1,79	1,75
DGP (1,4:3,6-dianhydro-α-D-glucopyranose)	0,63	0,52
Phenol	0,21	0,22
Phenol-2-methyl	0,04	0,04
Phenol-3-methyl+Phenol-4-methyl	0,11	0,11
Phenol-2-methoxy	0,22	0,20
Phenol-2-methoxy-4-methyl	0,16	0,14
2,6-dimethoxyphenol	0,30	0,27
Phenol-4-ethyl-2-methoxy	0,15	0,12
Isoeugenol	0,14	0,13
2-methoxy-4-vinylphenol	0,24	0,18
Polycyclic aromatic hydrocarbon	0.00	0.00
Non identified compounds	28.01	32.07

- Carboxylic acids, alcohols, aldehydes , ketones, furans, and anhydrosugars were the main compound of the organic fraction of the bio-oil
- Acetic acid is the largest component in the bio-oil

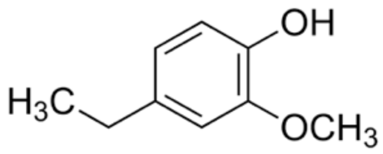


Important compounds

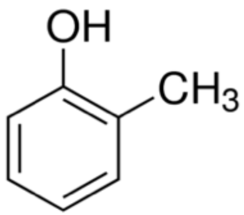
Bagasse bio-oil	Reference
Acetic acid (7.22—8.48 %)	Mohan *et al.* 2008
Formic acid (1.60—1.70 %)	Yatagai *et al.* 2002
Propionic acid (0.31—0.37 %)	Barbero-Lopez *et al.* 2019
Formaldehyde (0.24—0.36%)	Wititsiri 2011
Furfural (0.45—1.19%)	Fagernas *et al.* 2013
Phenol (0.21—0.22)	Oramahi and Yoshimura (2012)
Guaiacol derivatives	Mohan et al 2008; Mourant 2005



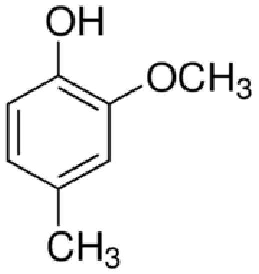
Phenol-3-methyl



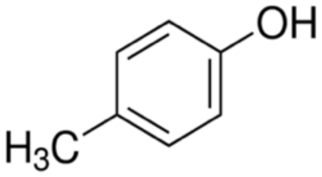
Phenol-4-ethyl-2-methoxy



Phenol-4-methyl



Phenol-2-methoxy-4-methyl

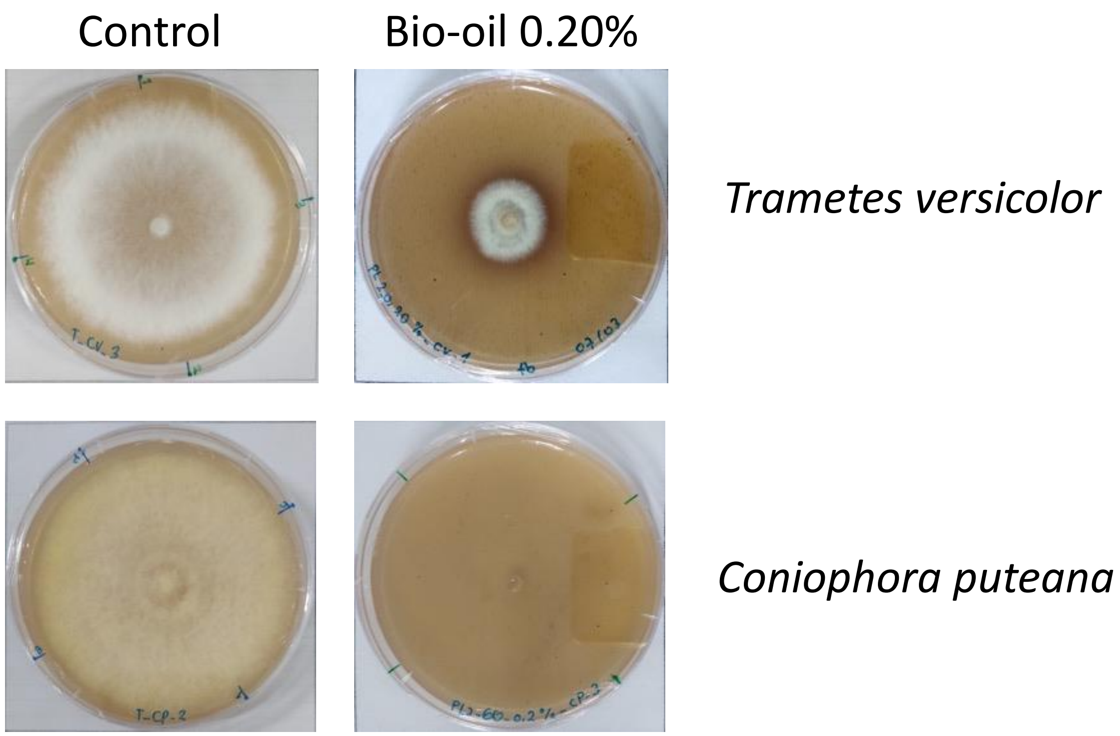


Phenol-2-methyl

Antifungal activity

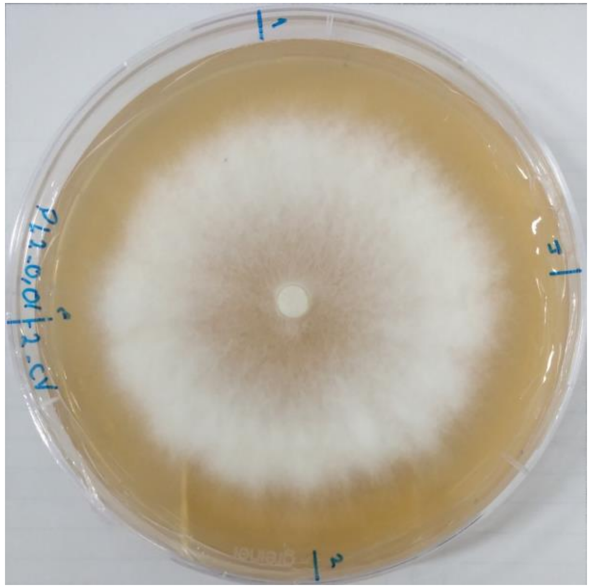
Bio-oil	Concentration (%)	Inhibition (%)	
		C. puteana	T. versicolor
400°C	0.05	20.71 ± 5.70 (B)	21.24 ± 3.15 (A)
	0.10	47.34 ± 2.70 (CD)	44.06 ± 1.64 (C)
	0.15	**100 ± 0.00** (E)	64.23 ± 12.14 (D)
	0.20	100 ± 0.00 (E)	93.30 ± 13.39 (E)
	0.25	100 ± 0.00 (E)	**100 ± 0.00** (E)
500°C	0.05	10.47 ± 4.14 (A)	21.80 ± 5.31 (A)
	0.10	37.70 ± 9.69 (C)	36.79 ± 1.51 (B)
	0.15	58.09 ± 7.41 (D)	57.52 ± 7.79 (D)
	0.20	**100 ± 0.00** (E)	84.87 ± 17.55 (E)
	0.25	100 ± 0.00 (E)	**100 ± 0.00** (E)

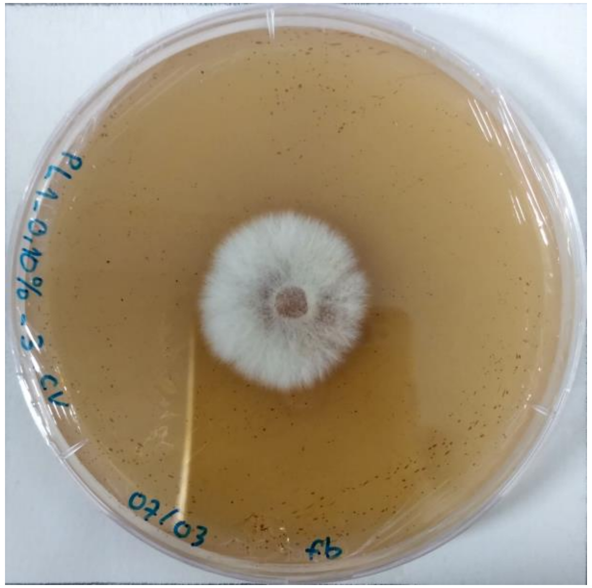
Means (n=5) within each column and factor followed by the same letter are not significantly different

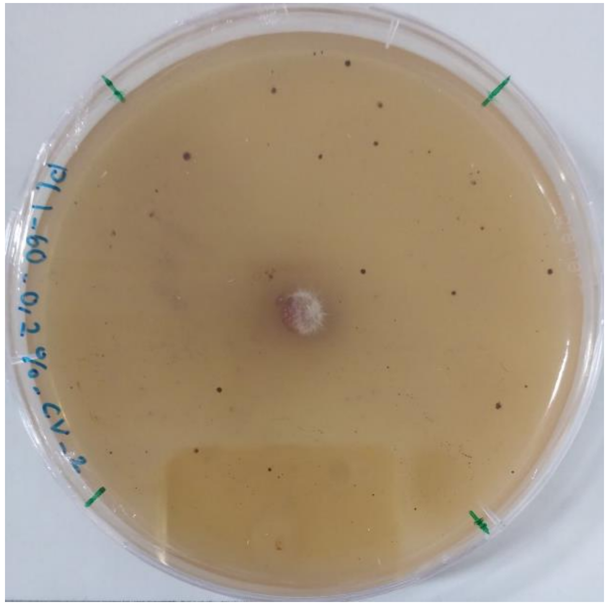


- Propionic acid, acetic acid and furfural exhibited an antifungal activity.
- Guaiacols derivatives such as phenol-2-methyl, phenol-3-methyl, phenol-4-methyl, phenol-2-methoxy-4-methyl, and phenol- 4-ethyl-2-methoxy were also responsible for the ability of bio-oil to inhibit fungi (Mohan et al 2008; Mourant 2005).

Trametes versicolor







Bio-Oil *0,01%* *0,1%* *0,2%*

Anti-termite activity

Percentage of the bio-oil treated paper and control consumed by termites (T = 400 °C)

Treatment	Paper area loss (%)	Mortality (%)	Day of contact with paper
Control (distilled water)	71.77 ± 1.66 (A)	0.58 ± 1.67 (A)	1
Control (ethanol)	54.63 ± 2.90 (B)	0.58 ± 1.67 (A)	1
Bio-oil 1%	56.67 ± 2.87 (B)	10.00 ± 8.66 (B)	2
Bio-oil 3%	47.19 ± 4.55 (C)	20.00 ± 10.00 (B)	3
Bio-oil 5%	31.54 ± 16.13 (D)	35.00 ± 21.79 (B)	4
Termites only	-	98.33 ± 2.89	-

Means within each column and factor followed by the same letter are not significantly different
Means (n = 3) ± SD

- The bio-oil had **a toxic (repellent ?)** effect on the termites
- Presence of formic acid, formaldehyde and phenols exhibited the termiticidal activity
- Result of the bio-oil produced at the temperature of 500°C are similar

Ethanol

CONTROLS

Water

Bio-Oil *1%* *5%* *10%*

CONCLUSION & Perspectives

Selection of Pyrolysis parameters for Energy Producing

Production of Bio-Oils

Interesting chemical composition of bio-oils

The bio-oil had Biological activity against both fungi and termites

The next steps…

Bio-oil polymerization outside and inside wood, Leaching

Wood impregnation

Treated wood - biological tests (screening tests)

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