

# Green chemistry from Mediterranean forests

The case of innovation from a biorefinery  
perspective producing value-added products  
(torrefied pellets and antioxidants)

Roots to riches  
Alghero, 26 September 2018



# Introduction

- To promote bioeconomy (sustainability/biodiversity, innovation/competitivity, socioeconomic rural development) and to add value to the forest value chain
  - Boosting the forest management
  - To obtain added-value products from Mediterranean forests
- Collaboration agreement in 2015:



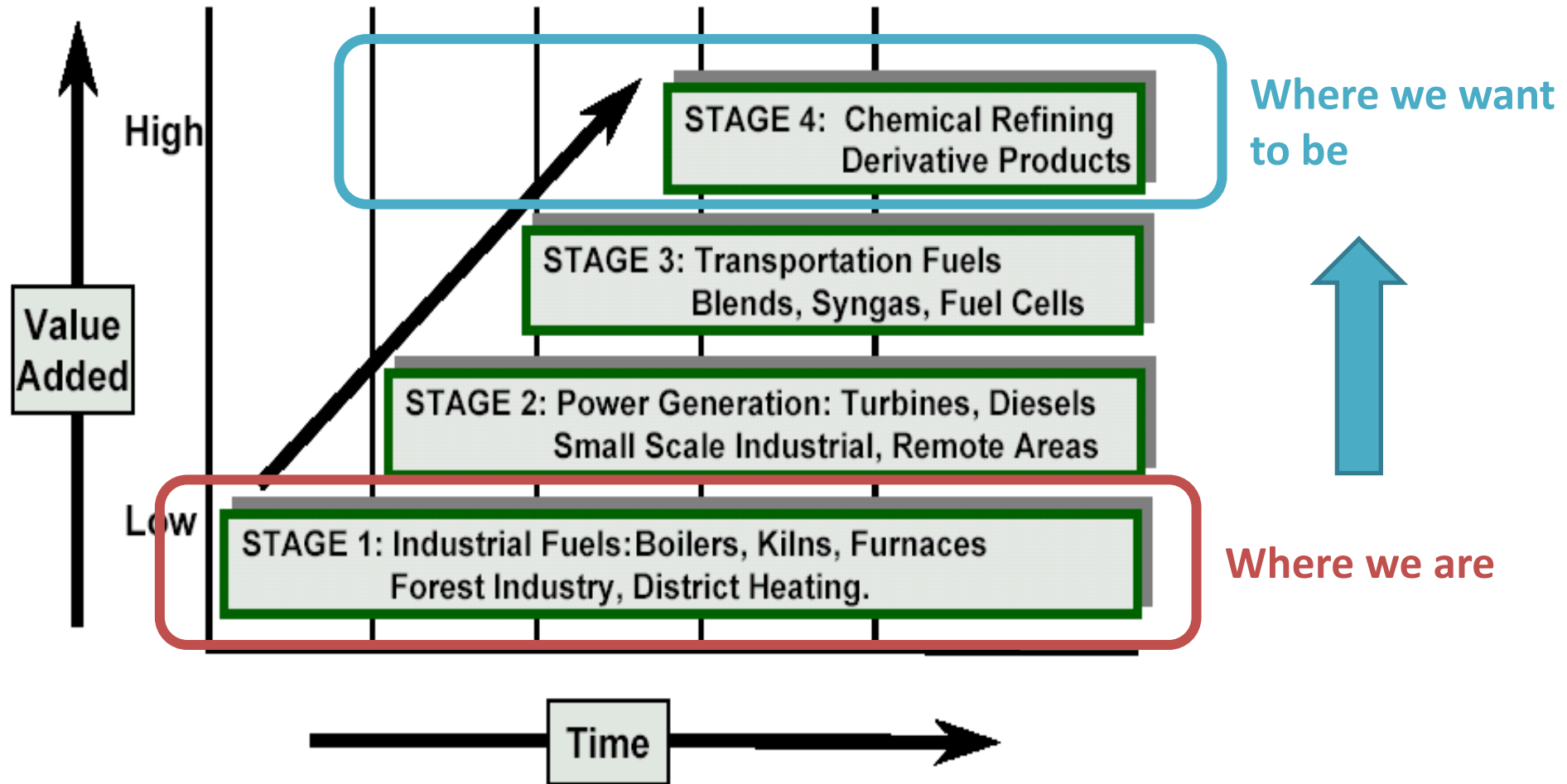
Generalitat de Catalunya  
Departament d'Agricultura, Ramaderia,  
Pesca, Alimentació i Medi Natural



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# Biomass uses scenario

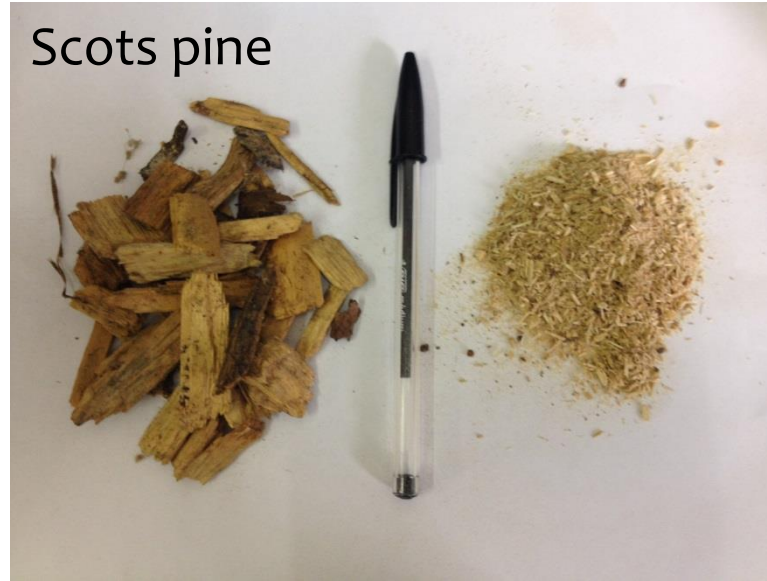


# Mediterranean forest biomass

Aleppo pine



Scots pine



Oak

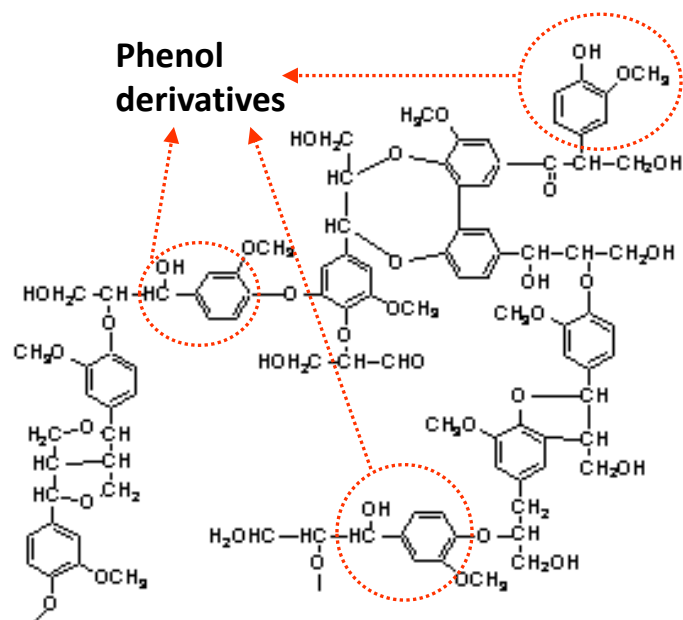


Cork oak



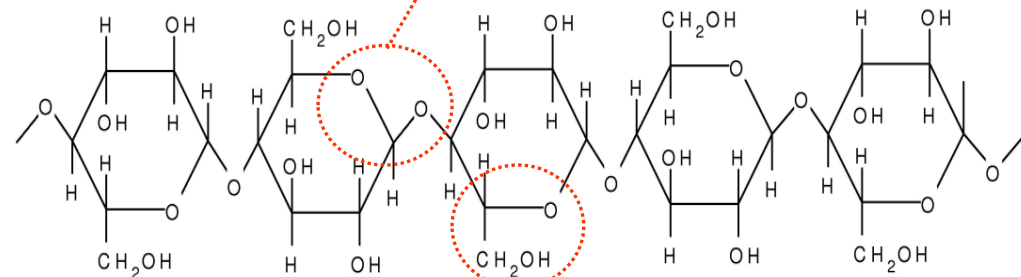
# Chemical structure of biomass

## Lignin



## Cellulose

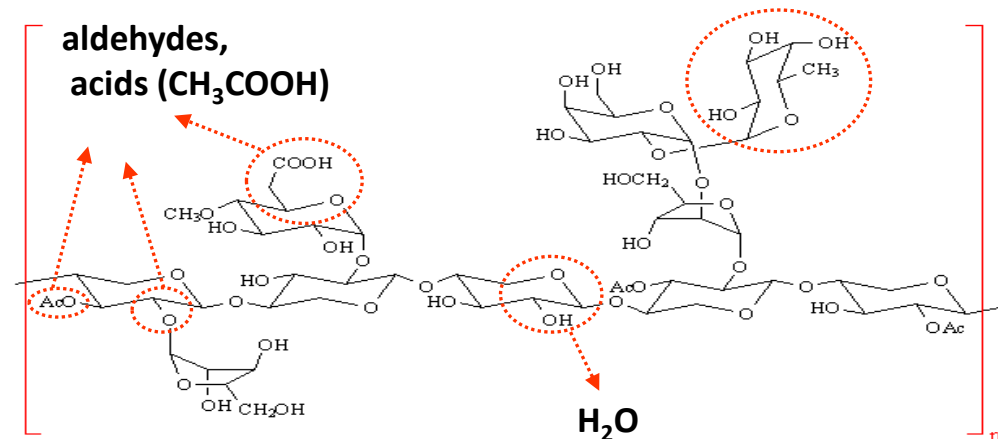
Ketones, aldehydes, acids



Furan derivatives

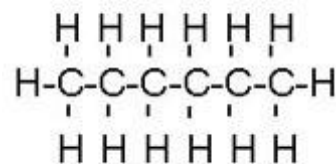
## Hemicellulose

aldehydes,  
acids (CH<sub>3</sub>COOH)



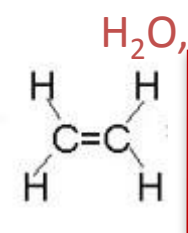
# Old and new chemistry

## Petrorefinery



Long hydrocarbon (alkane)

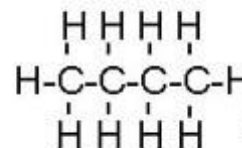
P; T ↑  
Cracking



H<sub>2</sub>O, P; T ↑

→ Acetic acid

→ Formaldehyde

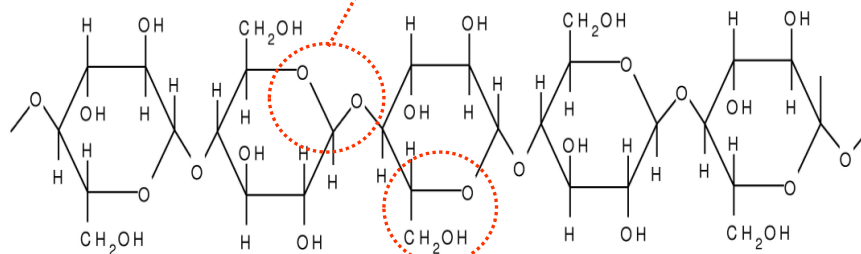


## Biorefinery



### Cellulose

Ketones, aldehydes, acids



Furan derivatives

→ Acetic acid

→ Formaldehyde

INITIAL  
COMPLEX  
RESOURCES



FINAL  
COMPLEX  
PRODUCTS

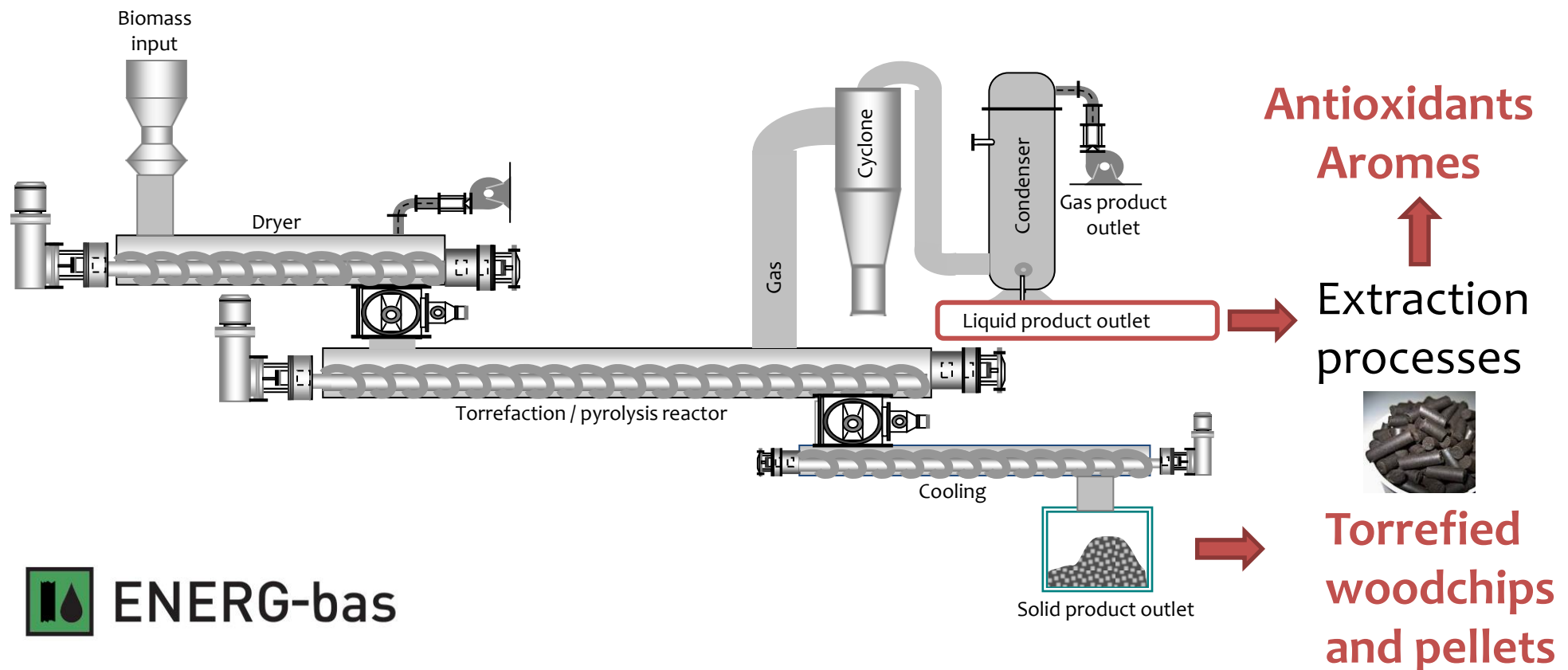
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# Local Mediterranean biorefinery

Thermochemical process: obtention of value-added products for **food industry** (**aromes**), **pharmaceutical**, **nutraceutical** and **cosmetic industry** (**antioxidants**) and **solid biofuels** (**torrefied woodchips and pellets**).



# Local Mediterranean biorefinery

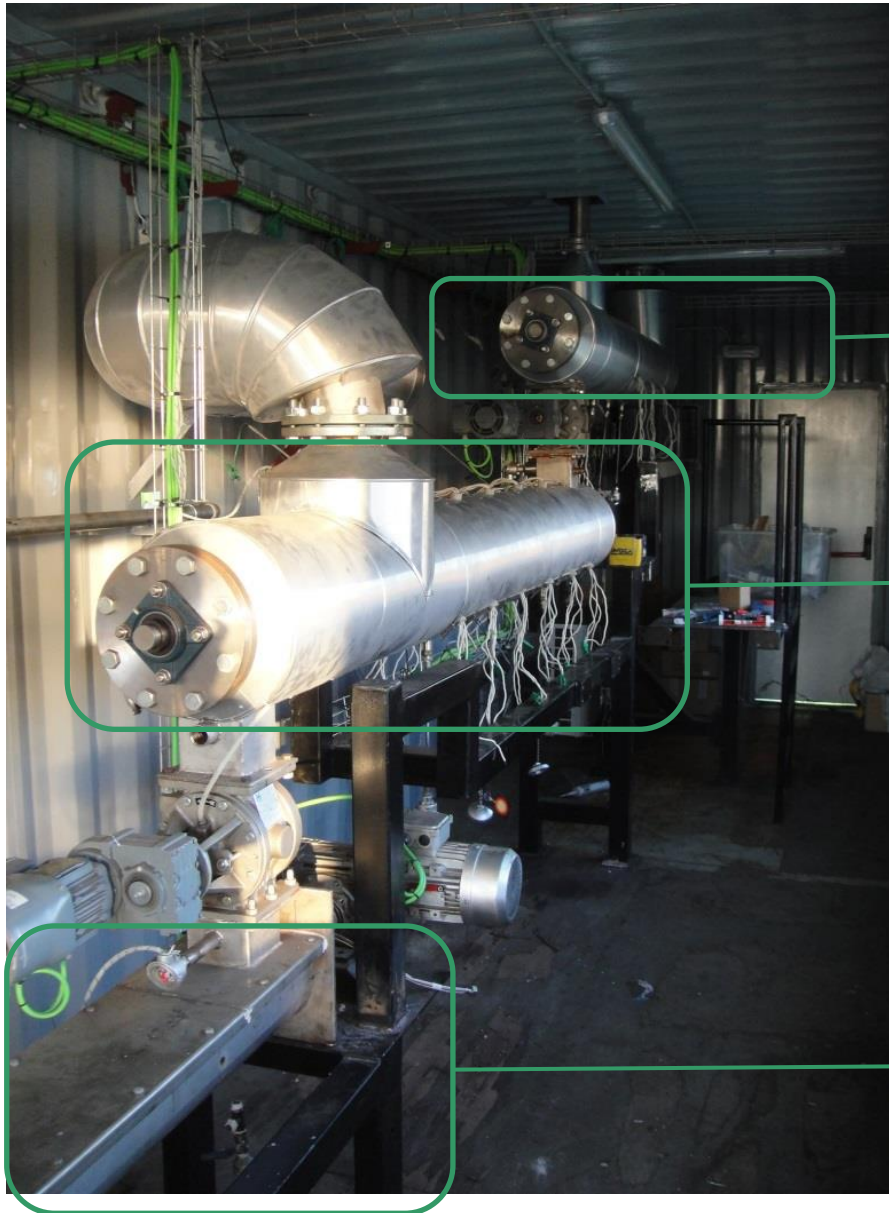
Thermochemical plant:

**Biomass torrefaction and pyrolysis**





# Local Mediterranean biorefinery



→ Dryer

→ Thermochemical reactor  
(torrefaction / pyrolysis)

→ Cooler

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# Torrefaction and pyrolysis

Aleppo pine



Stone pine



Oak



Cork oak



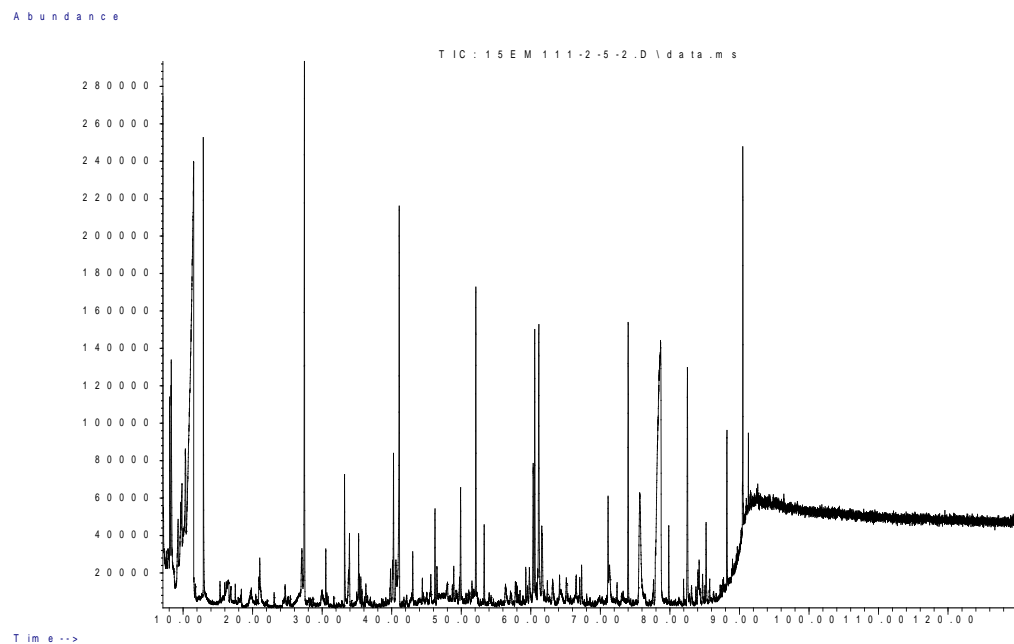
# Torrefied pellets



- higher energy density, hydrophobic, compact, can be grinded and has a lower ratio of oxygen- carbon (O / C).
- HHV of torrefied woodchips: increases 9 - 24% compared to untreated biomass.
- HHV of pellets: increases 14 - 41% compared to untreated biomass.
- Cork oak: not possible to pelletise



# Torrefied bio-oil



Aleppo pine 290 °C

- 52 identified compounds
- 8 added-value majority compounds:
  - Acetic acid
  - Furfural
  - 2(5H)-furanone
  - 2,5-dimethoxytetrahydrofuran
  - 1-acetoxy-2-butanone
  - Phenol
  - 2-furanone
  - Vanilline

- Quantification:

| Compound                     | Conc (mg/L) |
|------------------------------|-------------|
| Acetic acid                  | 4550,7      |
| Furfural                     | 2011,4      |
| 2,3-dimethoxytetrahydrofuran | 1215,3      |

# Pyrolysis bio-oil

More than 200 compounds:

## Alcohols and Phenols

|                           |
|---------------------------|
| 2-propen-1-ol             |
| 2-methoxy-4-methyl-phenol |
| Guaiacol                  |
| 4-ethyl-2-methoxy-phenol  |
| 2-methoxy-4-propyl-phenol |
| Eugenol                   |

## Aldehydes

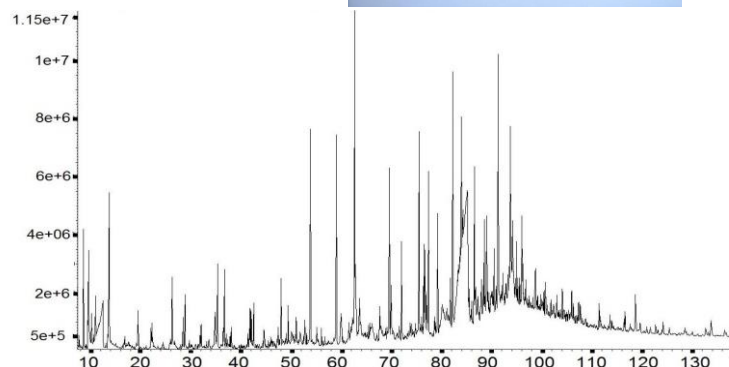
|   |
|---|
| hydroxy-acetaldehyde                    |
| Furfural                                |
| Vanillin                                |
| 5-(hydroxymethyl)-2-furancarboxaldehyde |
| 2,3-dihydroxybenzaldehyde               |

## Acids and esters

|                |
|----------------|
| Acetic acid    |
| Formic acid    |
| Methyl acetate |

## Others

|                               |
|-------------------------------|
| 2-methoxy-1,3-dioxolane       |
| 2,5-dimethoxy-tetrahydrofuran |



Aleppo pine  
500 °C

## Ketones

|   |
|---|
| 1-hydroxy-2-propanone                     |
| 2(5H)furanone                             |
| Acetovanilline                            |
| 2-hydroxy-3-methyl-2-cyclopenten-1-one    |
| 1-hydroxy-2-butanone                      |
| 1-(4-hydroxy-3-methoxyphenyl)-2-propanone |
| 2-butanone                                |

## Sugar

|              |
|--------------|
| Levoglucosan |
|--------------|



# Pyrolysis bio-oil: antioxidants

- Conventional solvent extraction
- Supercritical CO<sub>2</sub> extraction



**Purification**



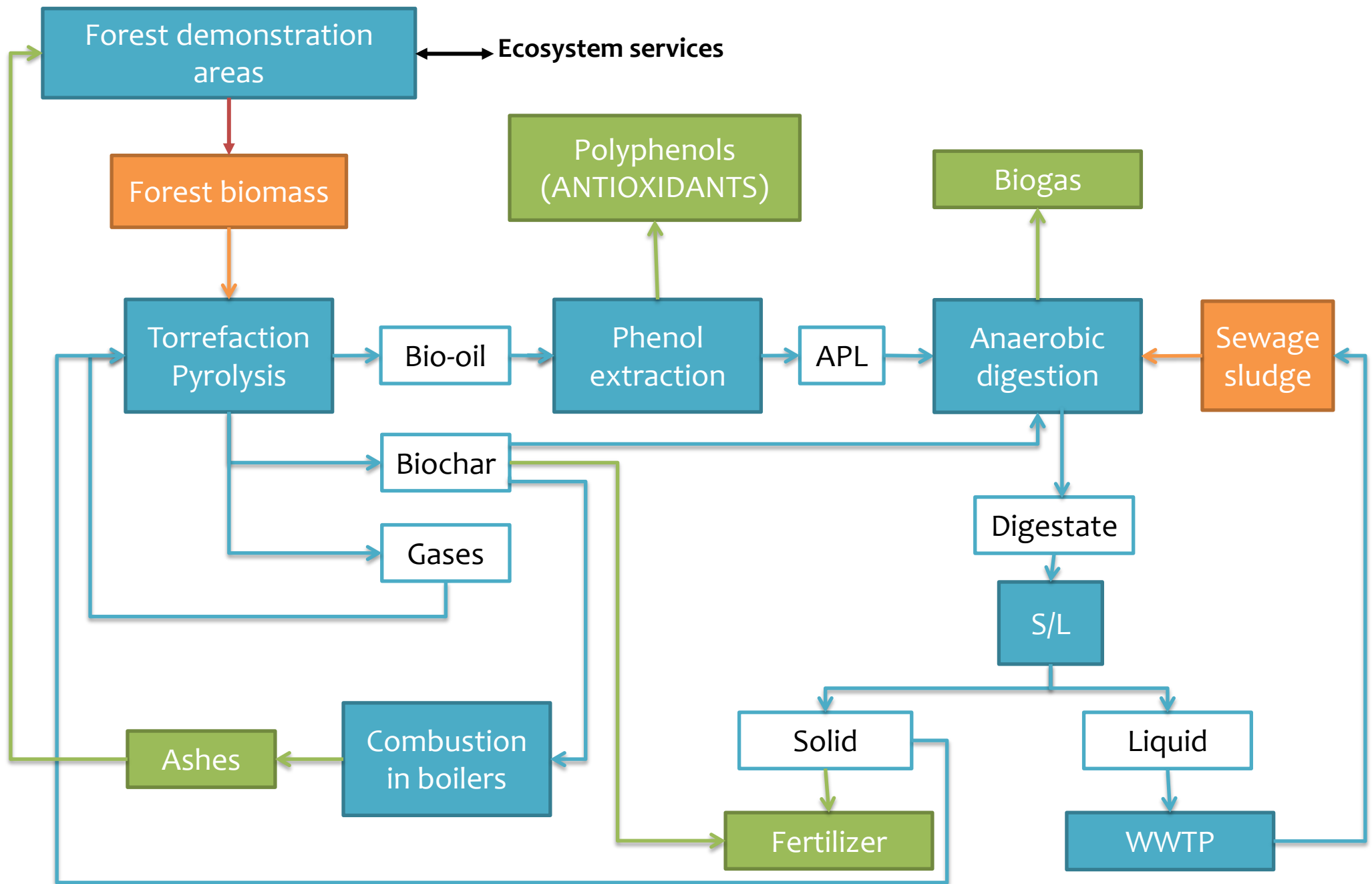
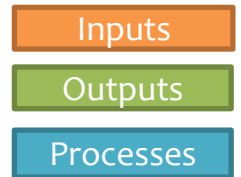
**Nutraceutical industry**  
**Pharmaceutical industry**  
**Cosmetic industry**



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# Innovative approaches



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