2^{nd} GENERATION BIO-CRUDE OIL VIA HYDROTHERMAL LIQUEFACTION OF AGRICULTURAL WASTES

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BIO-BASED FUELS IN FOCUS

Increased energy demands – New government regulations

Residual biomass is largely available – potential feedstock for fuels

Two main thermo-chemical processed can be applied

PYROLYSIS

HYDROTHERMAL LIQUEFACTION

HYDROTHERMAL LIQUEFACTION (HTL)

Thermochemical conversion of biomass into liquid fuels

Processing in hot, pressurized water environment for sufficient time

Break down solid biopolymeric structure to mainly liquid components

HTL benefits over classic pyrolysis:

- No need for drying step – No restrictions in feedstocks
- Solvents act as catalysts due to their properties at high temperatures
- HTL bio-crude oil is better in terms of yield and properties

STUDY OBJECTIVES

2nd Generation biofuels production from agricultural wastes via HTL

Utilization of crude glycerol (biodiesel by-product) as co-feed in HTL

Study of HTL main parameters in quantitative and qualitative terms

Temperature

Residence time

Biomass / glycerol ratio

MATERIALS

BIOMASS MILLING

SIEVING → 180 – 1000 μm

	Olive tree Branches	Wheat Straw
Moisture (wt.%)	9.2	8.6
Ash (wt.%)	3.01	3.04
Cellulose (wt.%)	48.45	33.08
Hemicellulose (wt.%)	14.9	25.73
Lignin (wt.%)	31.45	35.22
Total extractives (wt.%)	11.1	19.4
Carbon (wt.%)	48.75	44.78
Hydrogen (wt.%)	5.9	5.54
Nitrogen (wt.%)	1.35	0.88
Oxygen (wt.%)	44.0	48.8

MATERIALS

CRUDE GLYCEROL

Property	Value
Density (15 °C) (kg/m^3)	1.14
Viscosity (40 °C) (mm^2/s)	48.34
Soap content (wt.%)	21.00
Acid value (wt.%)	0.00
Moisture (wt.%)	0.17
Carbon (wt.%)	38.72
Hydrogen (wt.%)	9.41

HYDROTHERMAL LIQUEFACTION PARAMETERS

VARIABLE PARAMETERS

1. Temperature (280° - 350 °C)
2. Residence Time (10 – 60 min)
3. Biomass / Glycerol Ratio (1:0 – 1:1)

FIXED PARAMETERS

1. Solvent used (Deionized water)
2. Solid to liquid ratio (1:10)
3. Initial vessel compression (30 bar)

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METHODOLOGY

BIOMASS

+

GLYCEROL

DEIONIZED WATER

→

PARR REACTOR

- **Batch autoclave reactor**
- **Vessel volume 250 mL**
- **Operation up to 500°C – 300 bar**
- **Heating – Cooling regulation**

HTL PRODUCTS

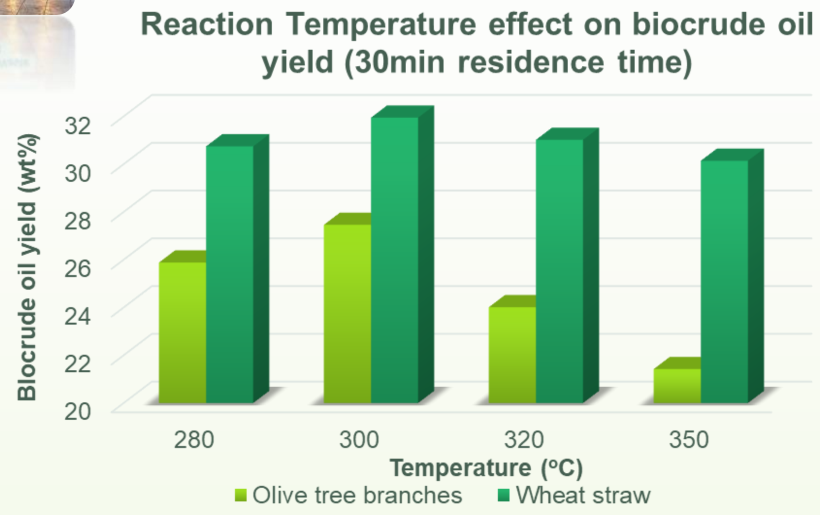
Gas Product

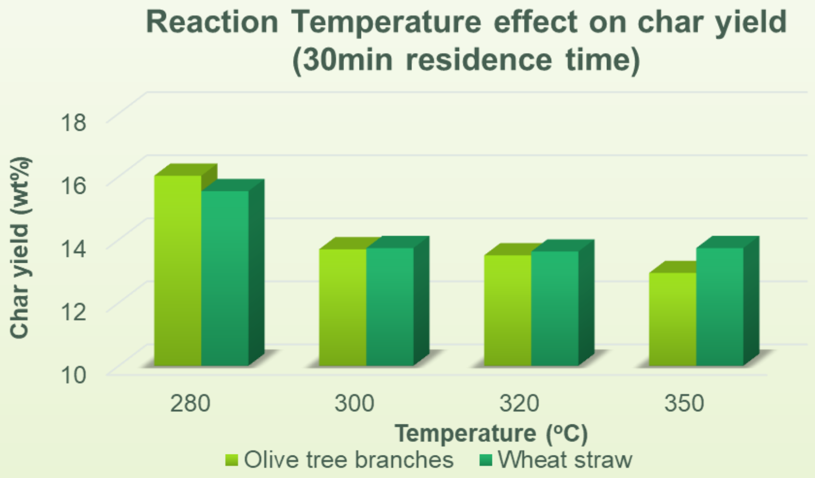
Solid Residue (Hydrochar)

Aqueous Phase

Bio-crude oil

TEMPERATURE EFFECT ON HTL





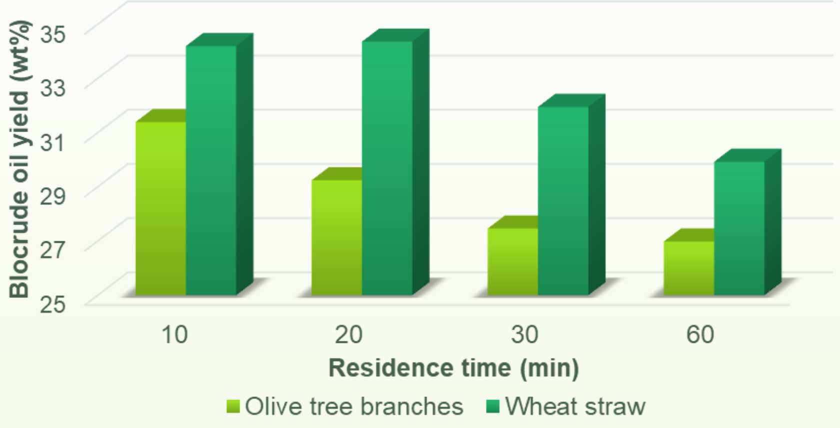
280ᵒC: Partial biomass liquefaction (especially lignin)

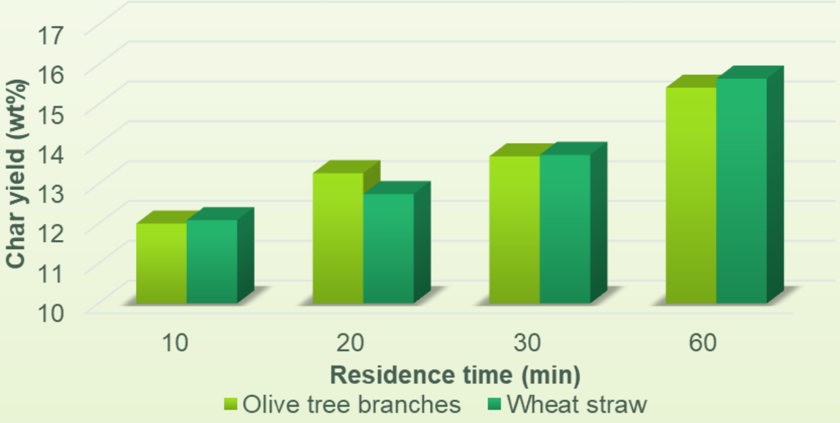
300ᵒC: OPTIMAL liquefaction temperature

>300ᵒC: Conversion of liquid → gas products

>300ᵒC: Partial reduction of solids → gas products

RESIDENCE TIME EFFECT ON HTL





- **Residence time correlation with biomass structure**
- **Optimal residence time:**

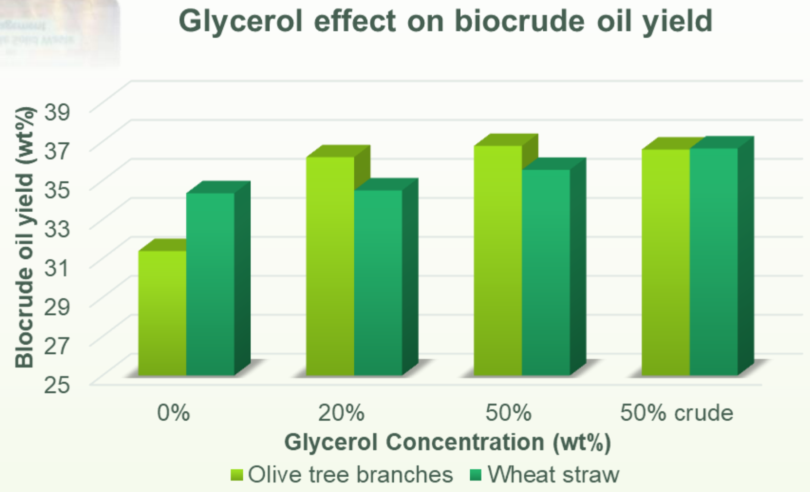
Olive Tree Branches	**10 min**	Lignin 31.5 wt%
Wheat Straw	**20 min**	Lignin 35.2 wt%

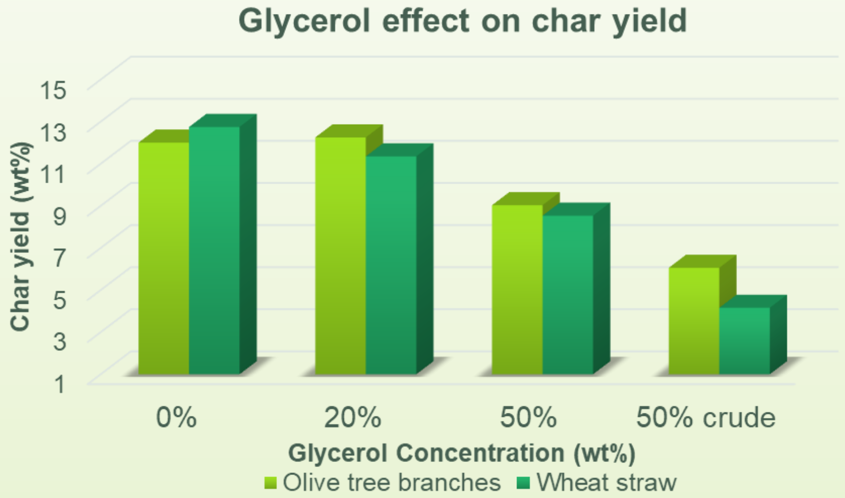
- **High residence time →**

1) **Secondary cracking reactions**
2) **Free radicals reactions**

Conversion of liquid to solid / gas products

GLYCEROL EFFECT AS CO-FEED IN HTL





Glycerol quantity (wt%)	0%	25%	50%	50% crude
Olive aqueous phase (mL)	95	95	98	100
Straw aqueous phase (mL)	95	96	98	100

- **Slight increase of bio-crude oil yield**
- **Increasing glycerol ratio → no significant effect in yield**
- **Increase of glycerol addition → Decrease in solid yield**

LIQUEFACTION OF LIGNIN IN AQUEOUS PHASE

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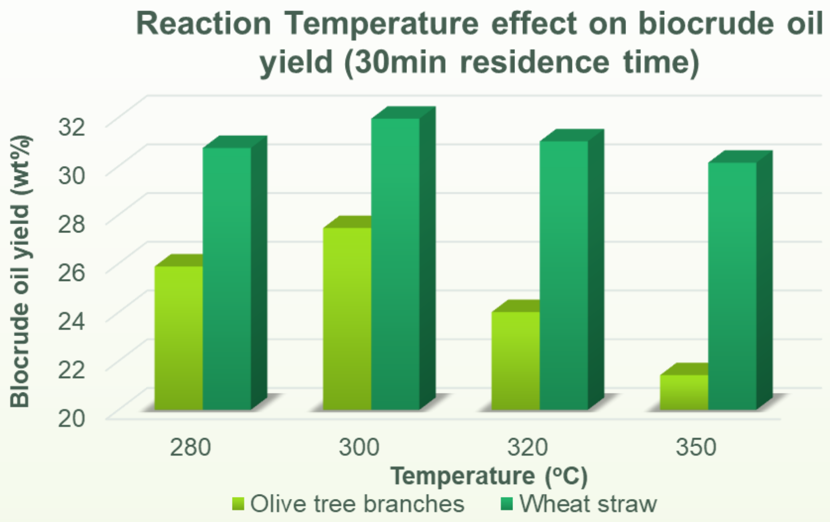
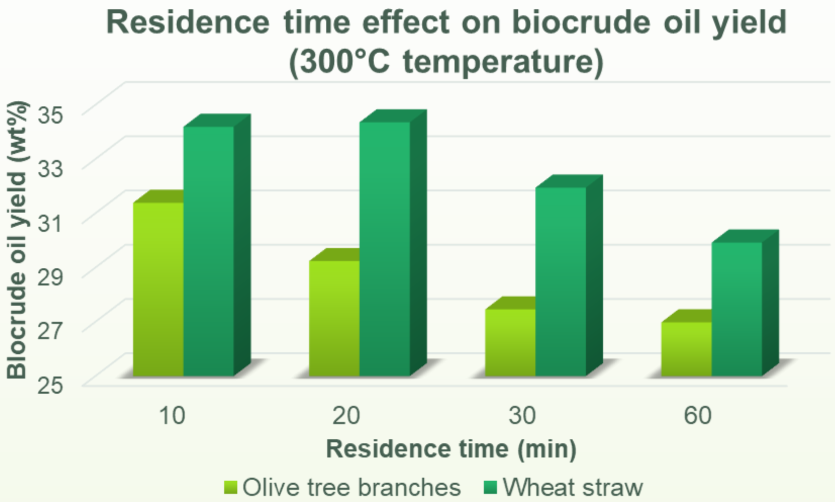
COMPARATIVE HTL STUDY IN BIOMASS

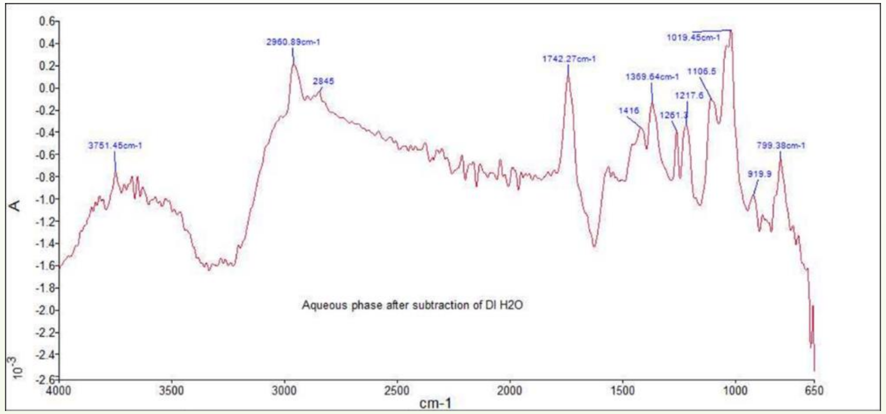




- **Bio-crude oil main component → liquefied lignin**
- **Cellulose- Hemicellulose → Liquefaction in aqueous phase**
- **Olive tree branches → High cellulose content → max oil yield in low residence time**
- **Wheat Straw → Higher Lignin content → higher res. Time – higher maximum oil yield**

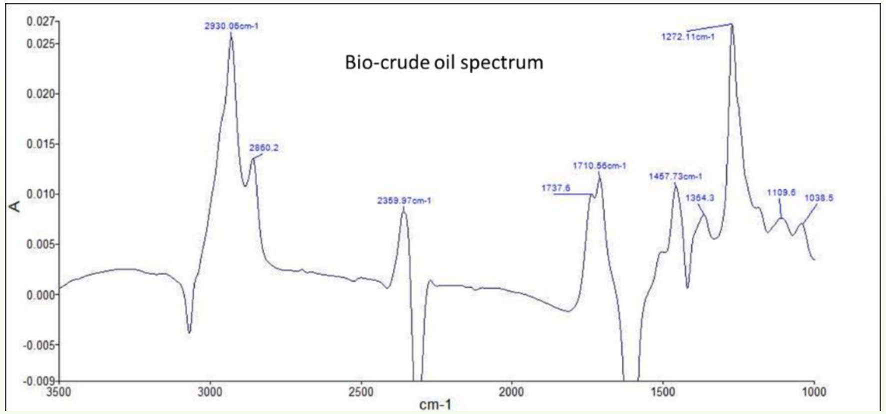
LIQUID PRODUCTS COMPOSITION (FT-IR)

AQUEOUS PHASE



- Alkanes
- Aromatics
- Alcohols
- Phenols
- Carbonyl group compounds

BIO-CRUDE OIL



- Alkenes - Alkynes
- Esters
- Ethers
- Alcohols
- Phenols
- Carboxylic acids

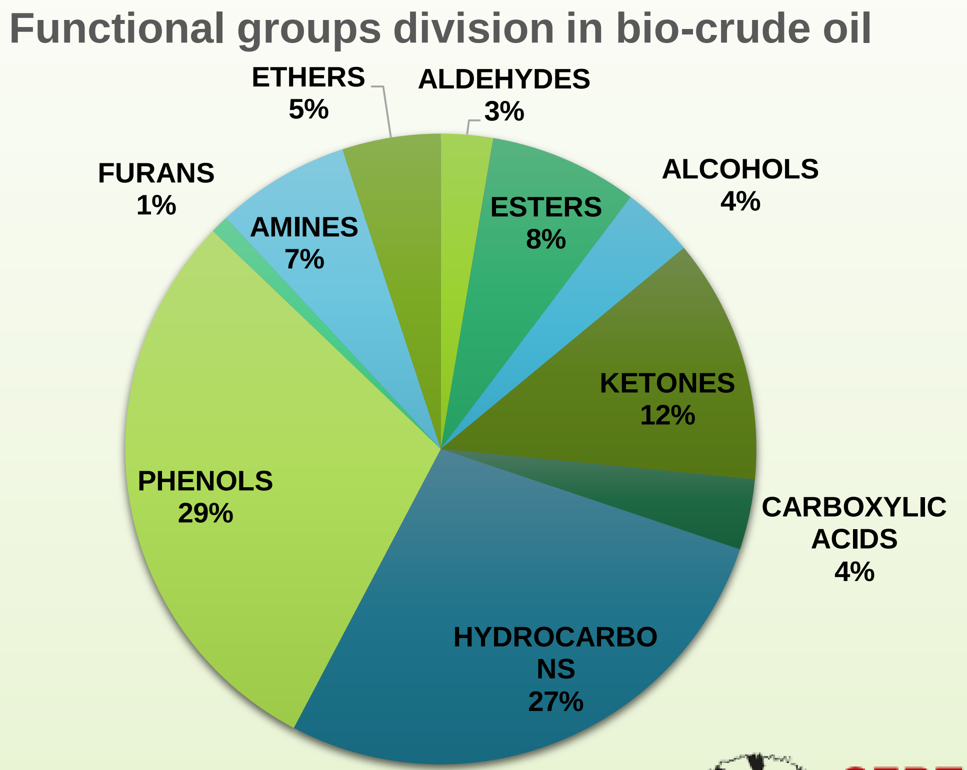
GC-MS ANALYSIS IN OIL AND GAS PRODUCTS

GAS PRODUCTS

Chemical Compound	Concentration %v/v
Hydrogen	0.7 – 1.8
Ethane	0 – 0.08
Propane	0 – 0.16
Hydrocarbons C_6^+	0.2 – 0.35
Carbon Dioxide	97.8 - 99

- **Mainly CO_2 + Light Hydrocarbons**

BIO-CRUDE OIL



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CONCLUSIONS

1. HTL of agricultural biomass → potential process for biofuels production

2. Lignin is the main factor in hydrothermal liquefaction oil yield

3. Successful recycling of waste crude glycerol via HTL – yield increase

4. Maximum oil yield obtained from wheat straw HTL at 300°C – 10 min – 1:1 crude glycerol

Thank you very much for your attention

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