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ARISTOTLE UNIVERSITY OF THESSALONIKI

Biomass Group
LABORATORY OF CHEMICAL PROCESS AND PLANT DESIGN

Microwave pretreatment of residual biomass blends with crude glycerol prior to pyrolysis by means of the GlyCo Bio-Diesel Project concept

P. Manara, M. Ganesapillai, A. Zabaniotou

ΕΥΡΩΠΑΪΚΗ ΕΝΩΣΗ
ΕΥΡΩΠΑΪΚΟ ΤΑΜΕΙΟ ΠΕΡΙΦΕΡΕΙΑΚΗΣ ΑΝΑΠΤΥΞΗΣ

ΑΝΤΑΓΩΝΙΣΤΙΚΟΤΗΤΑ ΕΠΙΧΕΙΡΗΜΑΤΙΚΟΤΗΤΑ
ΕΠΙΧΕΙΡΗΣΙΑΚΟ ΠΡΟΓΡΑΜΜΑ
ΕΠΑΝ ΙΙ
ΕΣΠΑ 2007-2013
η περιφέρεια στο επίκεντρο της ανάπτυξης

ΕΣΠΑ 2007-2013
πρόγραμμα για την ανάπτυξη

Υπουργείο Παιδείας και Θρησκευμάτων, Πολιτισμού και Αθλητισμού
ΓΓΕΤ – ΕΥΔΕ-ΕΤΑΚ

Ε. Π. Ανταγωνιστικότητα και Επιχειρηματικότητα (ΕΠΑΝ ΙΙ), ΠΕΠ Μακεδονίας – Θράκης, ΠΕΠ Κρήτης και Νήσων Αιγαίου, ΠΕΠ Θεσσαλίας – Στερεάς Ελλάδας – Ηπείρου, ΠΕΠ Αττικής

LABORATORY OF CHEMICAL PROCESS AND PLANT DESIGN

Biomass & Waste Group

Main Research Activities

- **Applied & basic research** concerning **the thermochemical conversion** of **biomass** and **waste** into **energy** and **high added value materials.**
- **Thermochemical Valorization of Biomass and Waste both by pyrolysis and gasification: Lab and Pilot scale Experiments & Modeling and simulation of such processes using commercial software.**
- **Assessment of bio-energy plants** and renewable energy sources units **through detailed techno-economic studies**
- **Design of integrated energy systems of conjunct thermochemical processes with ICEs and fuel cells.**

Goal of Biomass Group

Development of new processes & products for valorisation of biomass and waste

Thermochemical Conversion of recyclable and renewable materials → Research & Development

- ENERGY
- BIOFUELS
- MATERIALS
- H2

INNOVATION

GREEN TECHNOLOGY ⟷ GREEN PRODUCTS

CONTENTS

- BIODIESEL & GLYCEROL PRODUCTION
- CASE STUDY: Olive kernels + Glycerol blends
- SYMBIOTIC SCHEME
- EXPERIMENTATION
- RESULTS AND DISCUSSION
- CONCLUSIONS

GLYCEROL: a biodiesel by-product

- Transesterification of vegetable oils and animal fats
- Biodiesel production generates about 10 wt% of crude glycerol.

- *As biodiesel production increases, so does production of the primary by-product.*

GLYCEROL valorisation

- Waste glycerol valorization on-site for energy, fuels and materials production is a key management strategy related to sustainability and environmental performance of the biodiesel production system
- Among other options, co-valorization of crude glycerol with biomass via thermochemical conversion appears to be of great perspective.

GLYCEROL Co-valorisation

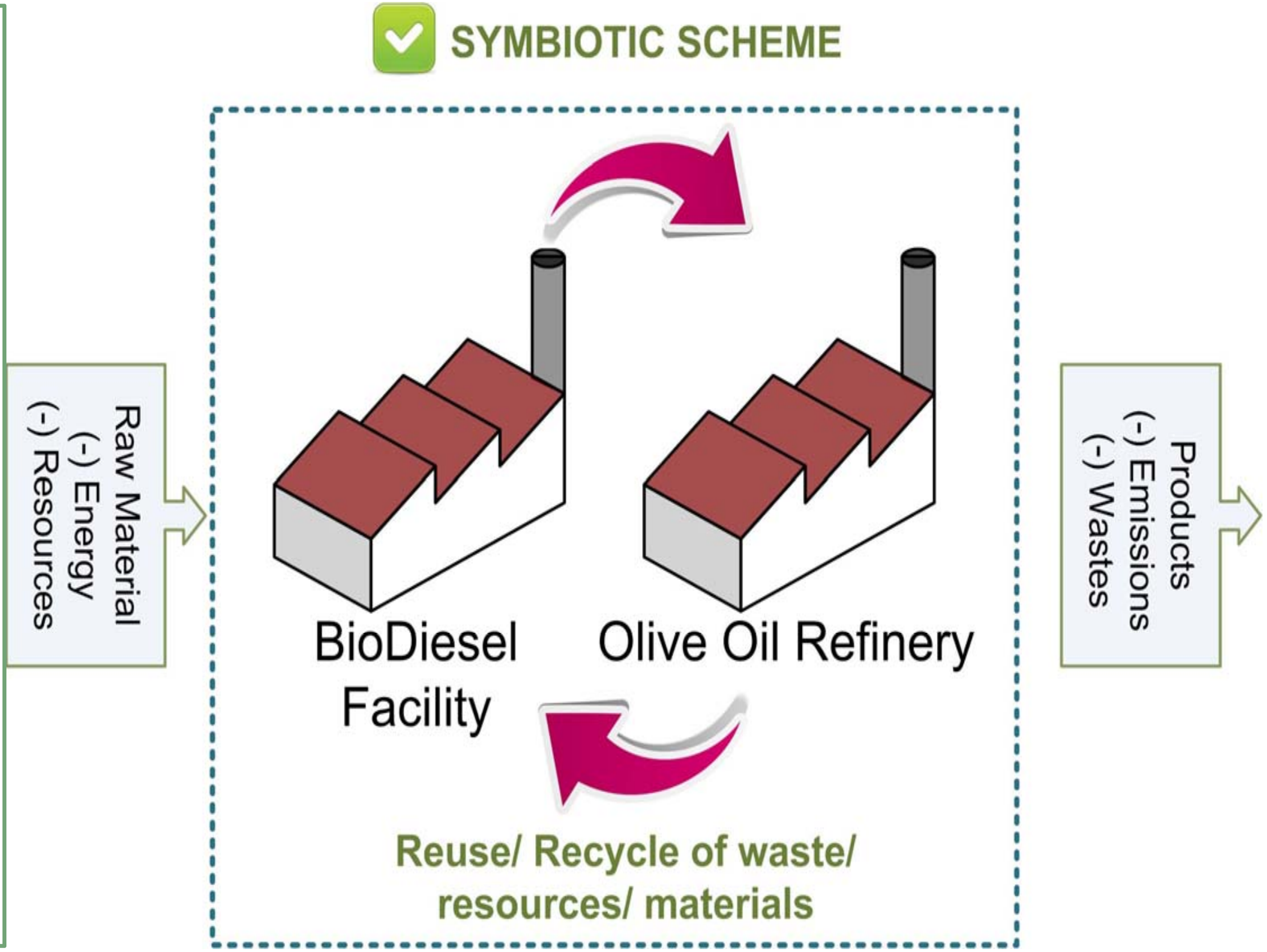
A key task is to indicate the potential link between biodiesel production units and agricultural industries

EXAMPLE

- Crude glycerol &olive kernels co-valorization
- Symbiotic scheme between biodiesel production units and olive oil refineries

CONCEPT

Symbiosis concept seeks to improve biodiesel production plant's energy balance, resource efficiency and to offer a solution for waste materials (crude glycerol, agro-wastes) recovery.



EXPERIMENTAL WORK

- Glycerol-based fuels preparation
- Microwave pretreatment
- Characteristics
- Pyrolysis experimental setup and procedure
- Co-pyrolysis
- Pyrolysis products

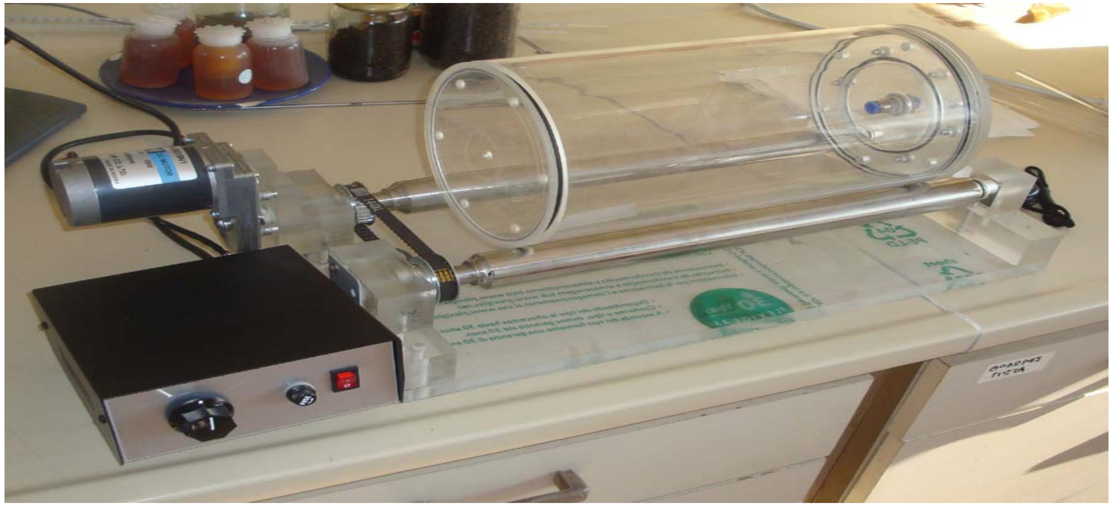
Conventional Mixing

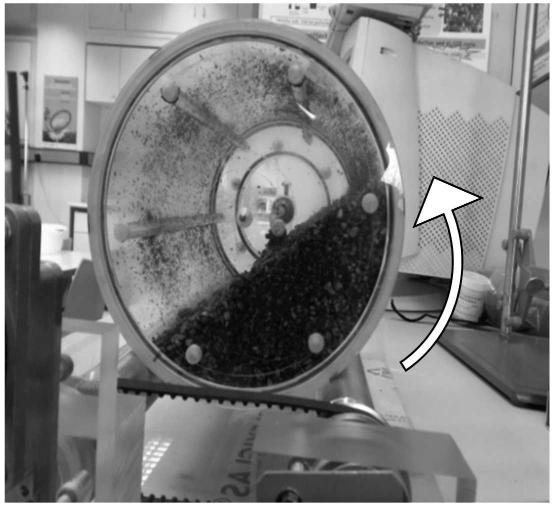
AIM: Development of "drop in" fuel to be used in existing installations

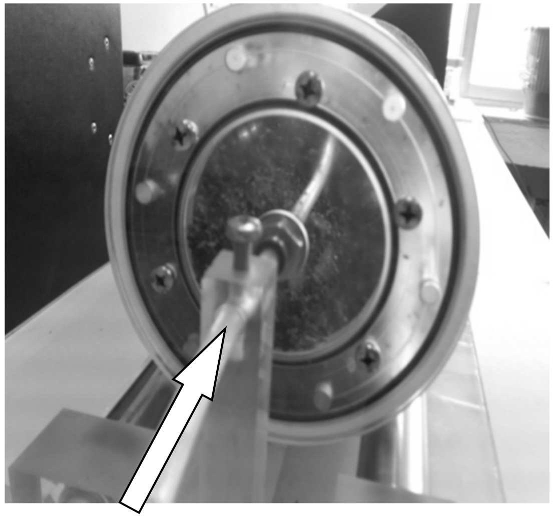
- Homogenation of the mixture without agglomerations: Mixing procedure
- Maintainance of similar physicochemical characteristics with biomass feedstock (operational problems avoidance).

➢ **Apparatus Design**
➢ **Testing Protocol Development**
➢ **Definition of operating parameters**

MIXING







Glycerol-based fuel characteristics

- ❑ Crude glycerol in olive kernel <25 wt%
  - → delivered a non-homogenous mixture
- ❑ crude glycerol in olive kernel >49 wt %
  - → produced slurries

⇨ 25 wt% crude glycerol in olive kernel

→ to maintain the rheological characteristics

→ feasible (technically) to be fed in the reactors (scale-up)

Ultimate and proximate analysis

- Feedstock: ***Crude Glycerol & Olive Kernels Mixture***

Ultimate analysis of the Crude Glycerol/ Olive Kernel (CG-OK) mixture

	Proximate Analysis (% d.w.)				Ultimate Analysis (% d.w.)					HHV
	Moisture	Volatile Solids	Ash	Fixed Carbon	C	H	N	S	O	(MJ kg^{-1})
Crude Glycerol	27.22	92.25	6.98	0.780	57.40	9.59	0.02	0.03	25.98[a]	28.50
Olive Kernel	4.20	74.70	2.70	18.50	48.59	5.73	1.57	0.05	41.36	20.46
25wt% Crude Glycerol-Olive Kernel Mixture	9.81	81.80	5.55	12.65	49.90	7.33	0.84	0.04	36.34[a]	**22.19**

[a] Calculated by difference, O (%) = 100-C-H-N-S-Ash

Elemental analysis

ICP-OES analysis

Elemental Analysis (ppm)	Crude Glycerol	Olive Kernel	25wt% Crude Glycerol-Olive Kernel mixture
Al	2.56	168.57	127.14
As	0.48	0.19	0.29
Ba	-	0,86	0.57
Ca	5.14	7490.67	5619.36
Cd	-	-	-
Co	-	-	-
Cr	-	85.57	64.10
Cu	-	10.87	8.13
Fe	2.46	727.58	546.15
K	47680.30	5678.29	**16178.94**
Mg	3.53	3127.40	2346.36
Mn	-	20.98	15.66
Na	173.45	138.76	147.51
Ni	0.00	51.79	38.77
P	22.85	756.30	572.97
Pb	-	-	-
Si	5.17	373.42	281.43
Sr	-	7.32	5.51
V	-	-	-
Zn	-	11.69	8.69

Enhanced potassium concentration as a result of the catalyst used in the transesterification process

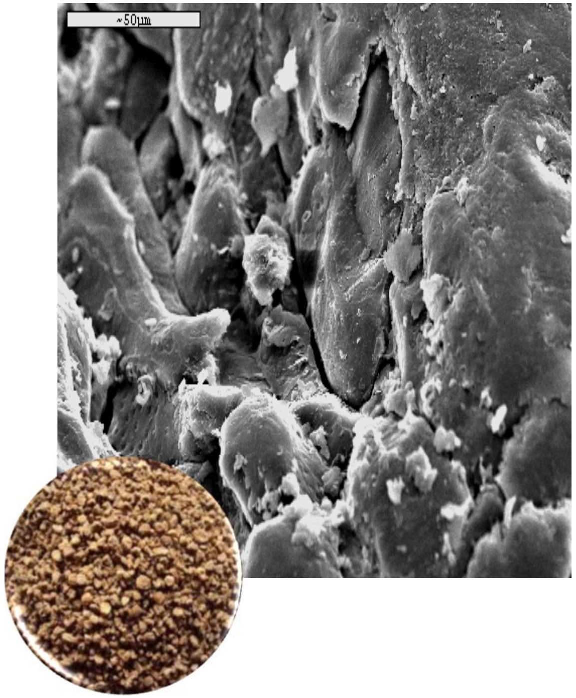
MICROWAVE PRETREATMENT (a)

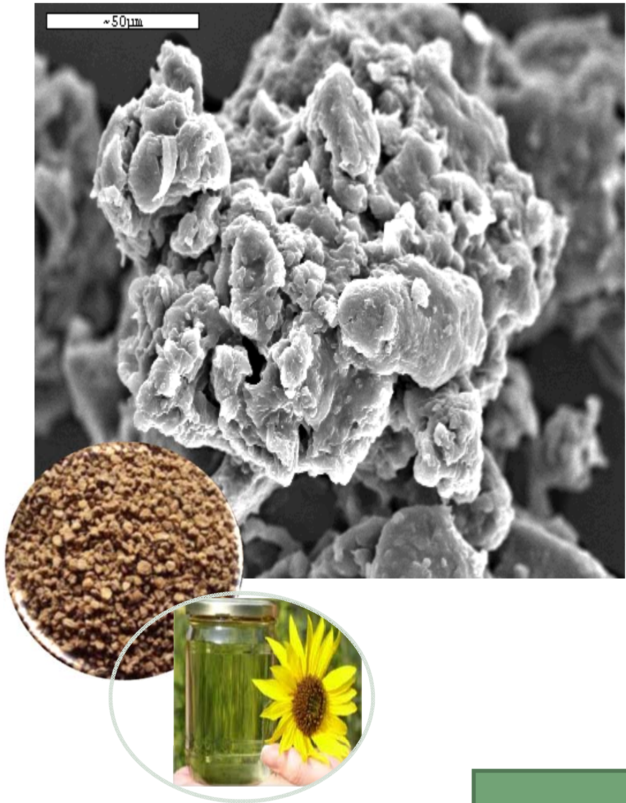
- Microwave activation (preprocessing)
- Experiments performed in batch laboratory scale with a commercial microwave oven operated at a frequency of 2.45 GHz.
- Olive kernel-crude glycerol mixtures were exposed to microwave irradiation:
  - at several different microwave output power (100 to 600 W),
  - for varied exposure time (60-300 sec),
  - in a wide proportion of crude glycerol to olive kernels (15-50 wt%).

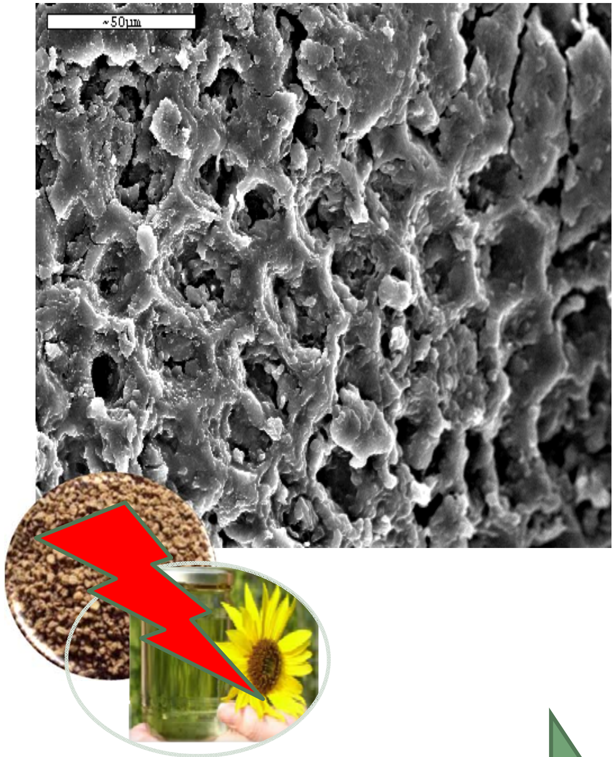
MICROWAVE PRETRETMENT (b)

- Microwave output power <300W, irradiation time <180 s and crude glycerol addition in olive kernels less than 25wt% →made any significant change in the mixture,
- further raise in content (25wt%), resulted in the formation of hot spots and therefore to char/ash formation, attributed to the friction during the dipole-dipole interaction, evolving in large volume of heat.
- **<u>Optimum behavior, in the preprocessing stages: </u>**A crude glycerol content of 25wt%, in the prepared crude glycerol-olive kernel mixture, irradiated at a low microwave output power of 300 W for 180 seconds.

SEM analysis







Pyrolysis

SEM, with a 15 kV accelerating electron voltage

Impact of microwave pretreatment

- The microstructure of the olive kernels revealed the formation of inter-lamellar amorphous structure

- The addition of crude glycerol created a flake-like morphology, indicating the adsorption of crude glycerol onto the surface of the olive kernels

- Pre-treating with microwave (at 360 W for 180 sec), created enormous pores of uniform sizes on the surface (Honeycomb structure).

MW assisted PYROLYSIS

- Two sets of pyrolysis experiments were performed, using two types of fuels:

- ❖ Conventional mixture of 25wt% crude glycerol in olive kernel,
  and
- ❖ Microwave activated mixture of 25wt% crude glycerol content in olive kernel, irradiated at a low microwave output power of 300 W for 180 seconds.

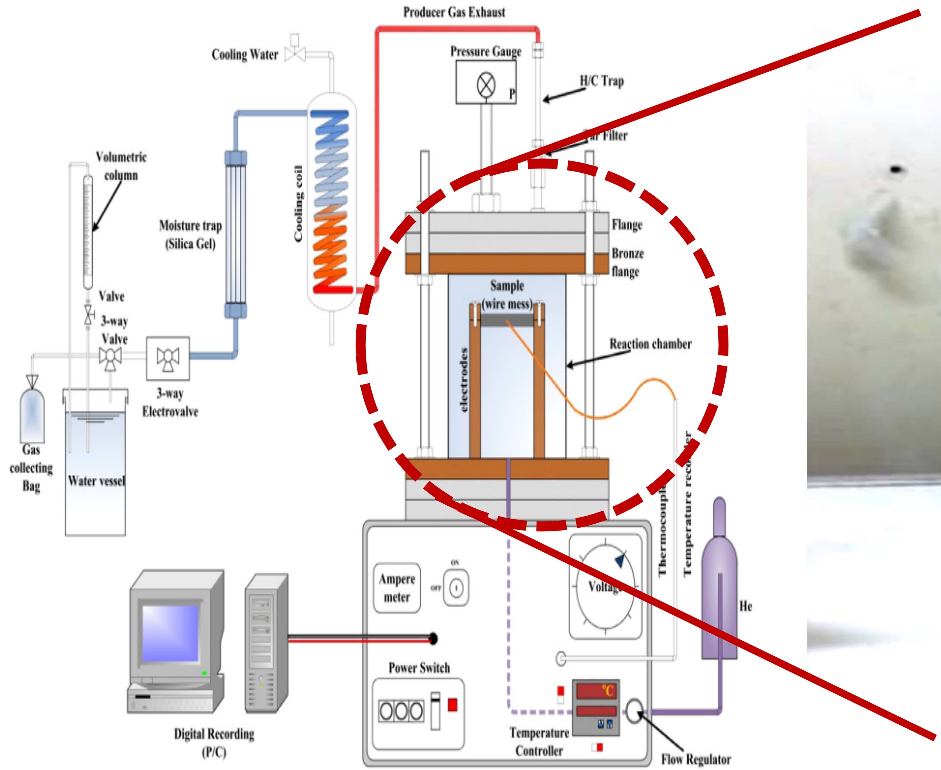
Why Pyrolysis: a method of waste valorization

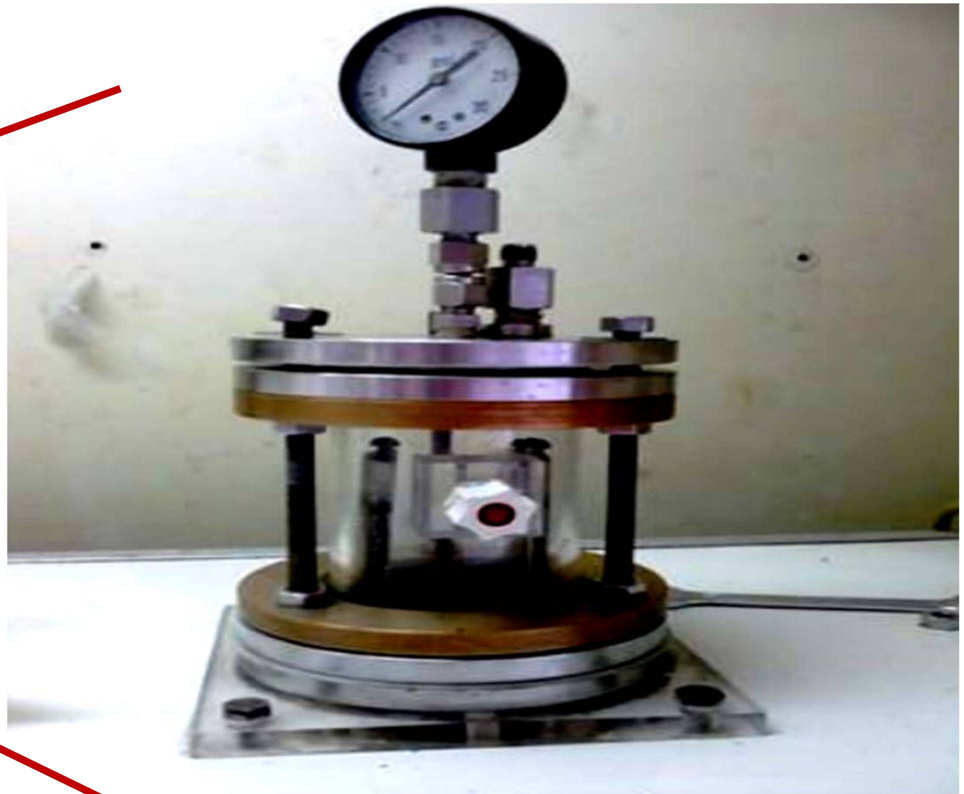
- Biomass pyrolysis is considered to be a sustainable energy technology, practiced widely in waste management.

- Particularly in pyrolysis, advances in heat transfer technology are essential
- Microwave that propagates through the material, resulting in dissipation of electric energy into heat (internal and volumetric) may assist towards this direction.

The Pyrolysis Reactor Layout

The Pyrolysis Reactor





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Procedure

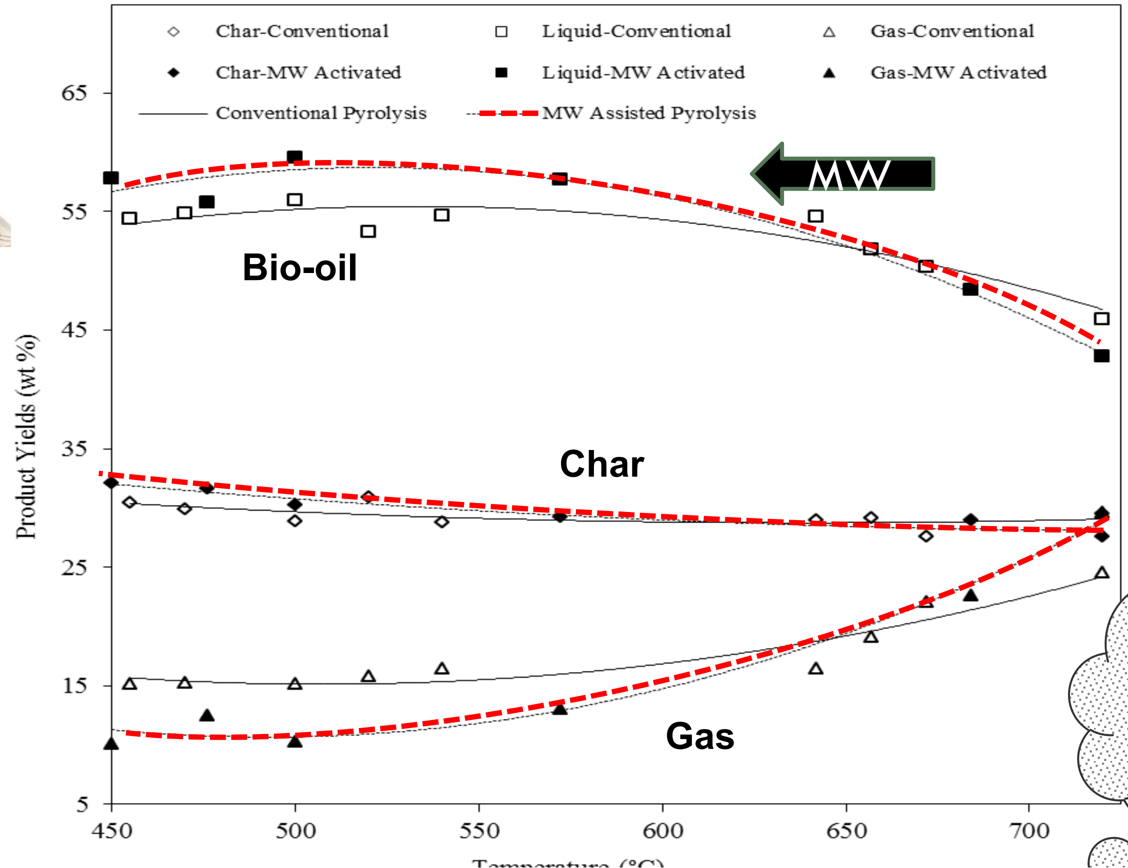
The carrier gas used in the experiment was Helium(99.99%).

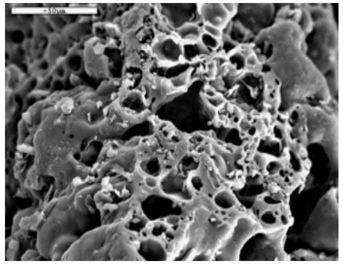
Temperature range of 450°C to 750°C,

Heating rate of approximately 50°C s^{-1}

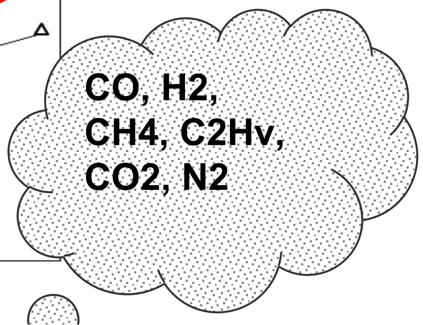
Experimental Procedure

RESULTS I





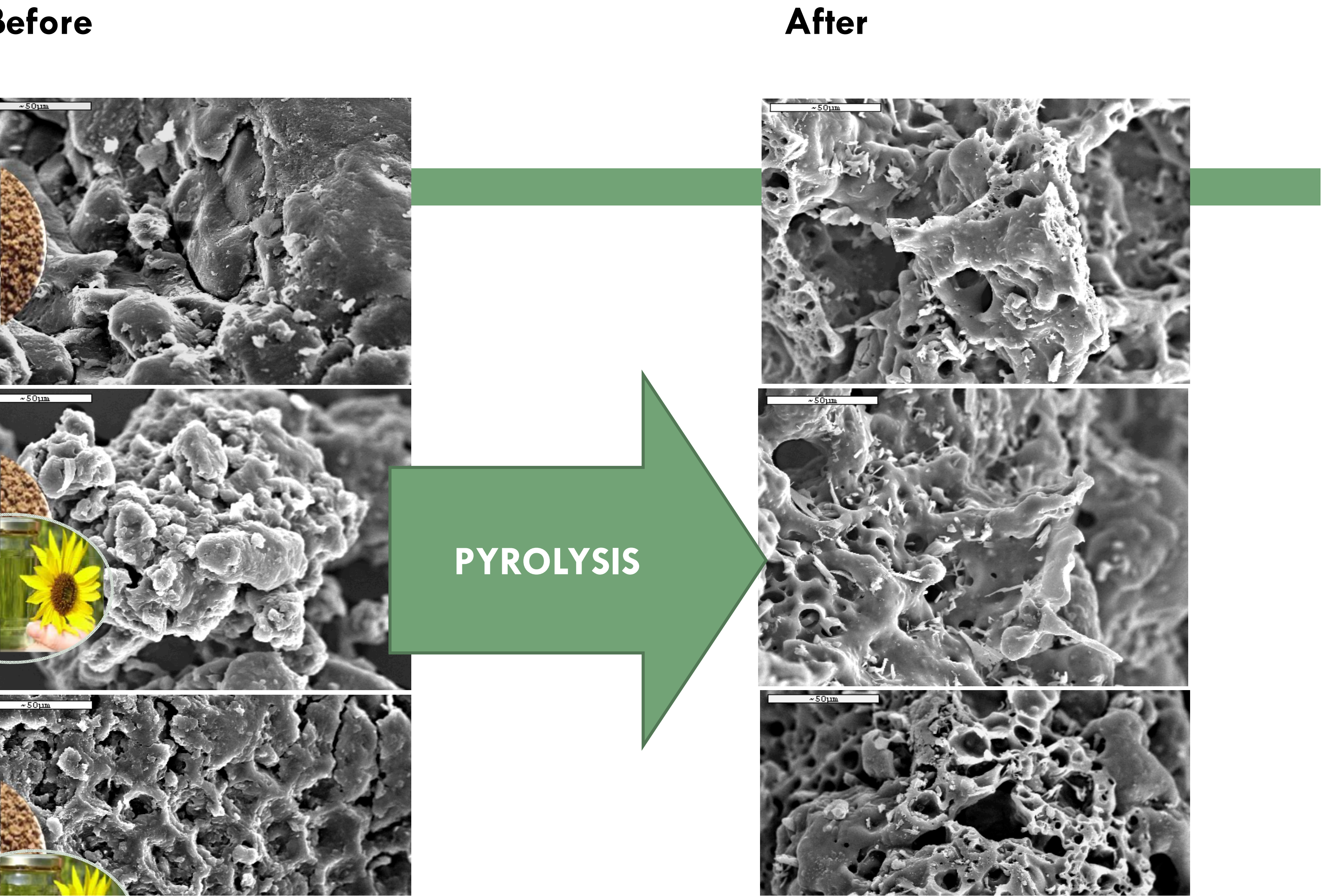
MW -Char



RESULTS II

icrowave activated samples post pyrolysis :

- **Higher yield in bio-oil production at lower temperature**, in comparison with the non-activated sample.
- A maximum liquid yield (59.53wt%) was obtained, at 500°C.
- At higher temperatures (> 500°C): enhanced gas production, in comparison with the non-microwave activated sample.
- At higher temperature, the gas yield was higher, comparing with the non-microwave activated material.



Before
After
PYROLYSIS
~50µm
~50µm
~50µm
~50µm
~50µm
~50µm

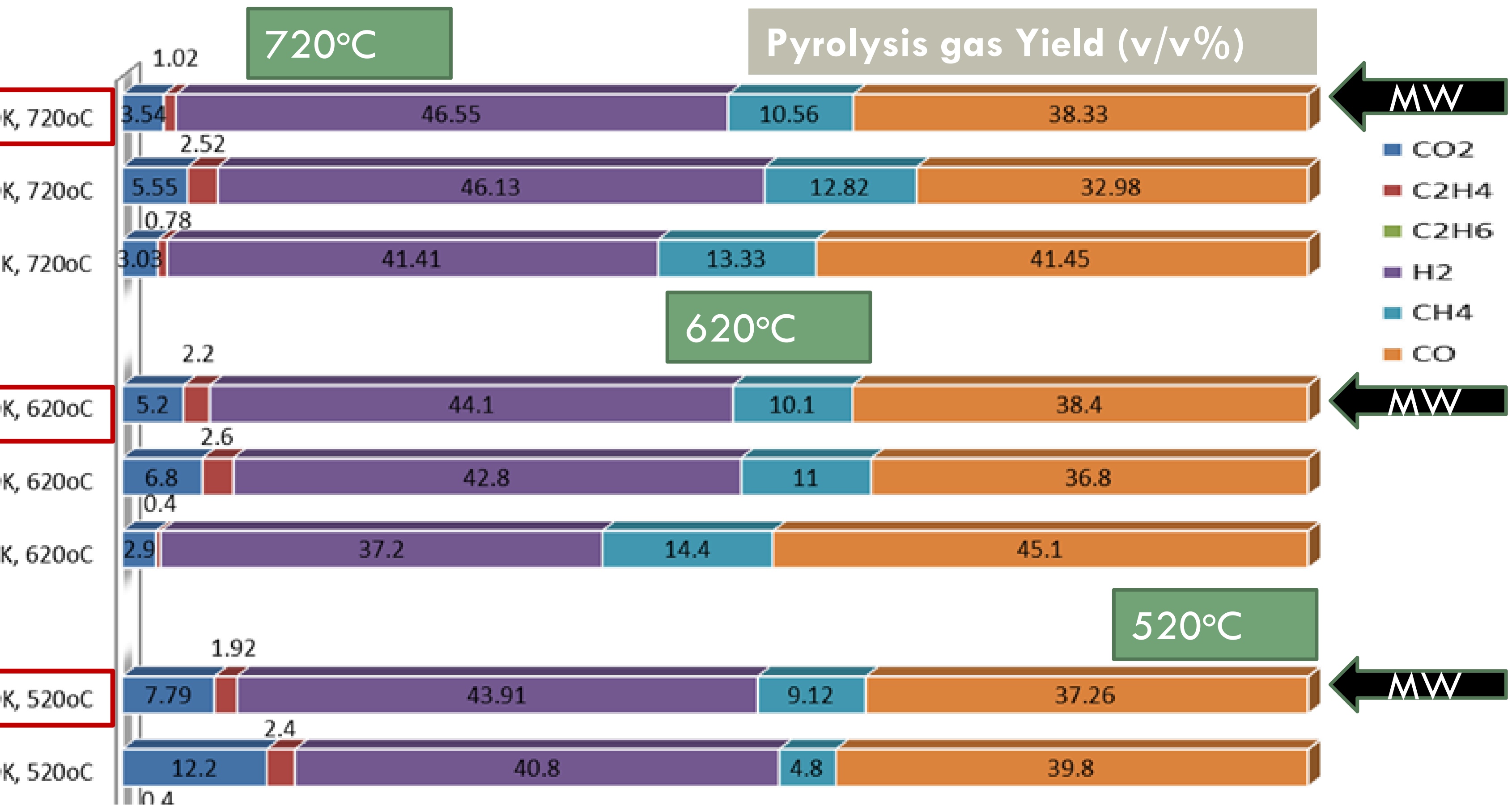
RESULTS III

The surface morphology of the particles drastically differed after both, the microwave pretreatment and the pyrolysis process

Comparison of char before and after microwave activation and pyrolysis revealed that the lateral surface before pyrolysis ruptured internally forming cracks in the inner structure, while the pyrolysis char still maintained large network of irregular, deep macro-pores ($5\ \mu m$ < pore size < $30\ \mu m$).

Biochar produced: the developed macro-pores, could either induce, oxygen diffusion during combustion application or hold

RESULTS IV



720°C
Pyrolysis gas Yield (v/v%)
1.02
K, 720oC
3.54
46.55
10.56
38.33
MW
2.52
K, 720oC
5.55
46.13
12.82
32.98
0.78
K, 720oC
3.03
41.41
13.33
41.45
CO2
C2H4
C2H6
H2
CH4
CO
620°C
2.2
K, 620oC
5.2
44.1
10.1
38.4
MW
2.6
K, 620oC
6.8
42.8
11
36.8
0.4
K, 620oC
2.9
37.2
14.4
45.1
520°C
1.92
K, 520oC
7.79
43.91
9.12
37.26
MW
2.4
K, 520oC
12.2
40.8
4.8
39.8
0.4

RESULTS V

rolysis gas from microwave activated feedstock:

Enhanced syngas (H_2+CO) production (84.9vv%),
compared to
the non-microwave activated samples (79.1vv%),
at 720°C.

CONCLUSIONS

icrowave activation: A potential pretreatment for enhanced oduction of value added fuels via post-pyrolysis.

e targeted yield (bio-char, bio-oil, and syngas) obtained epend on the preprocessing procedures.

fuel with higher amount of uniform pores (honey comb structure) as delivered .

us, at lower temperatures, the recombination reactions and uid production were dominant, whereas at higher temperature, e gas yield was higher, comparing with the non-microwave tivated material.

SCALE -UP

ilot Pyrolysis unit (DEPOTEC)

lot Gasification System (SMARt CHP)

AKNOWLEDGEMENTS

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Thank You for your Attention

Contact Details: Prof. Anastasia A. Zabaniotou

azampani@auth.gr; azampani@gmail.com

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