Biorefining of waste for energy, fuel and chemicals

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Northumbria, 19th November 2018

School of Engineering

5 academic disciplines

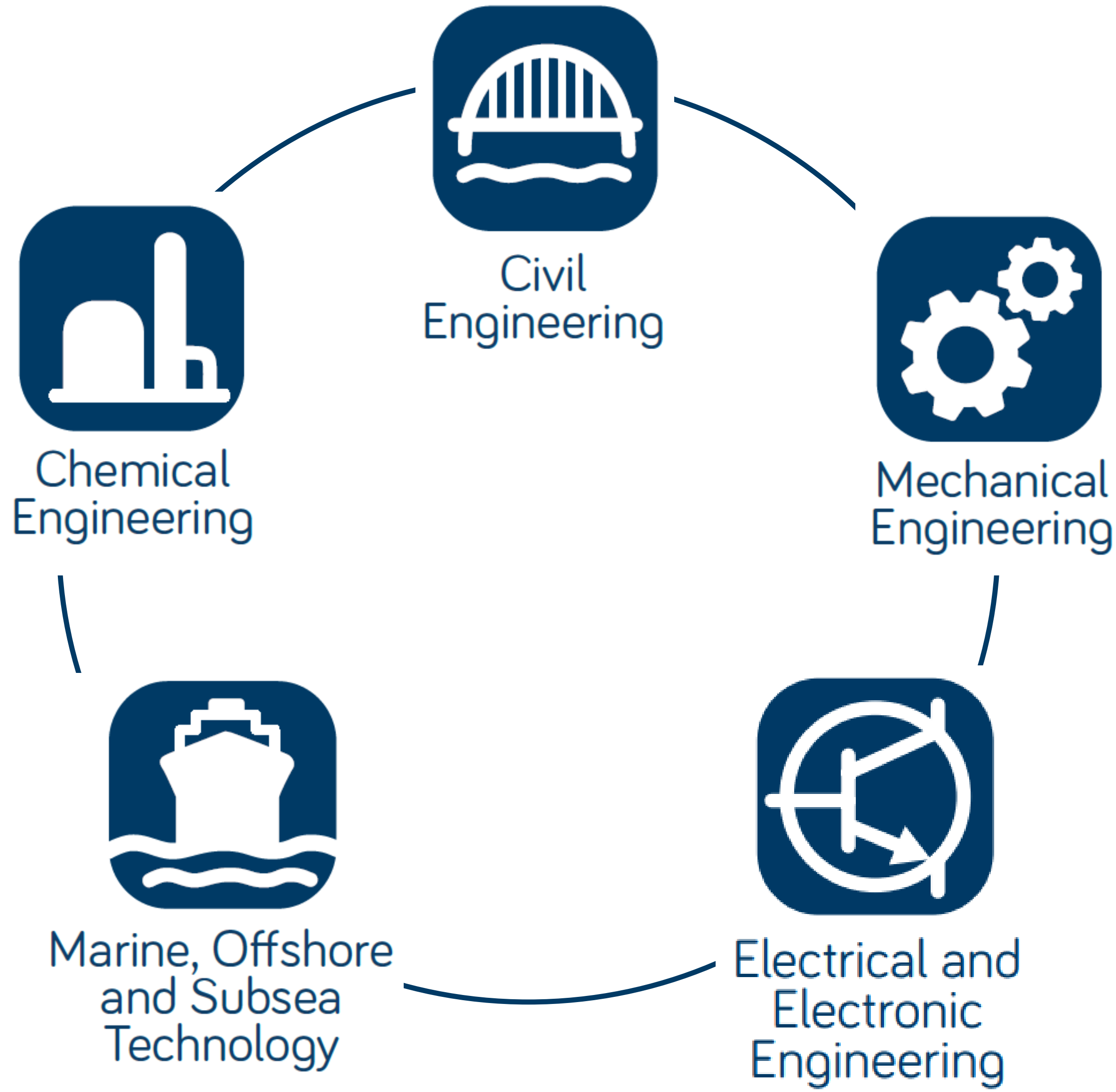
500 staff, 3200 students (21% female students)

Integrated Engineering

Bio and Environmental

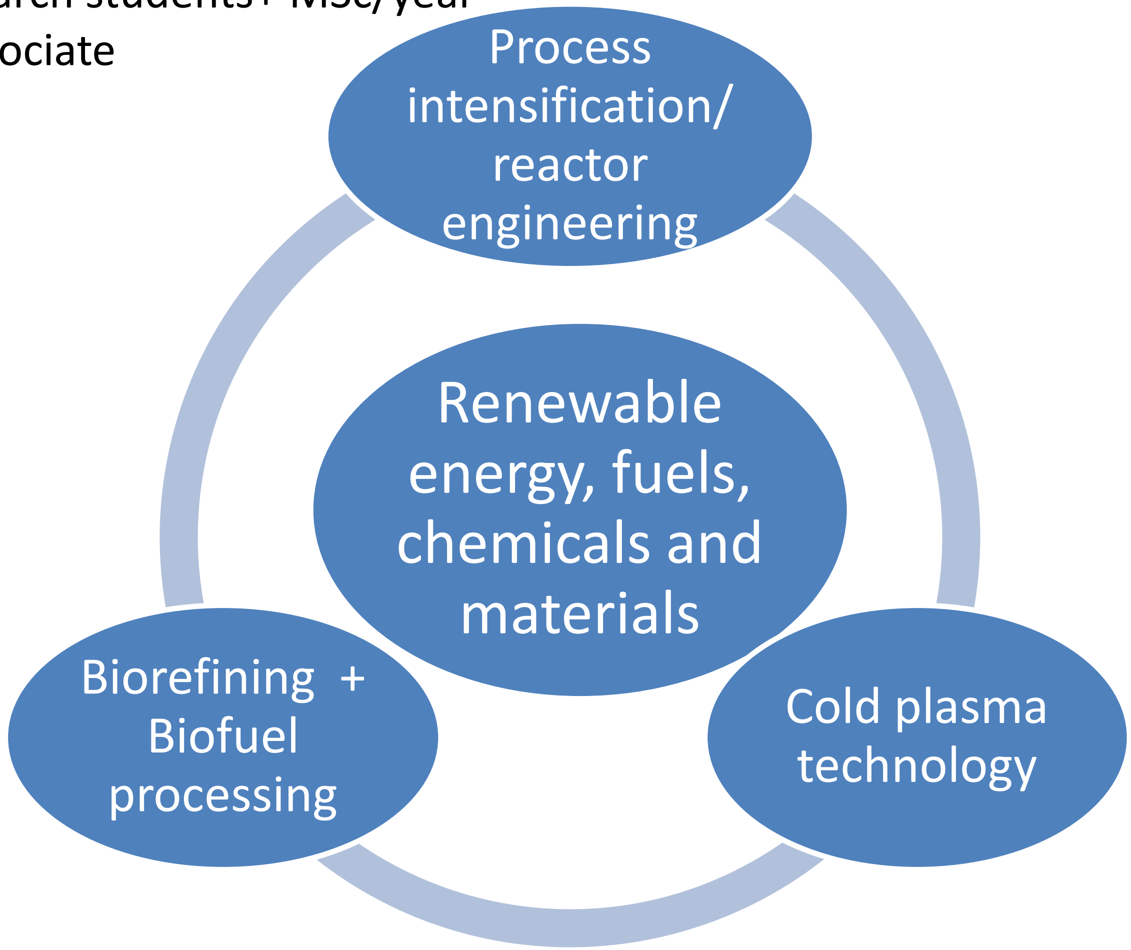
Infrastructure

Materials and Manufacturing



Dr Phan's Research Group

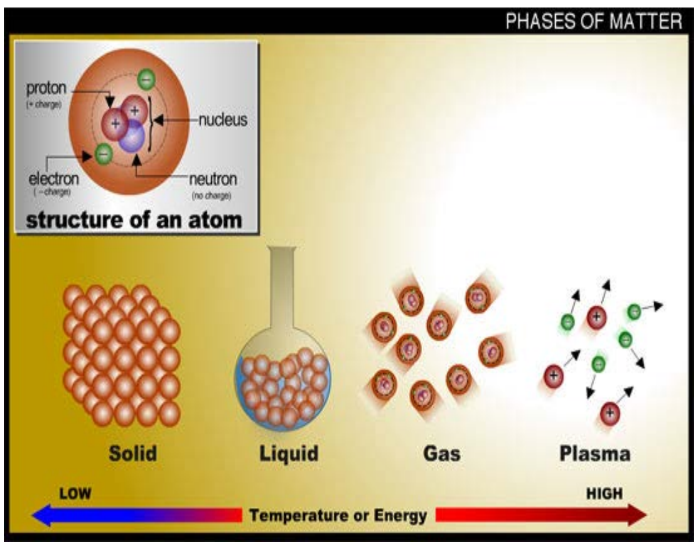
- 10 PhD students
- 4-6 MEng research students+ MSc/year
- 2 Research Associate
- 1 Anh Phan

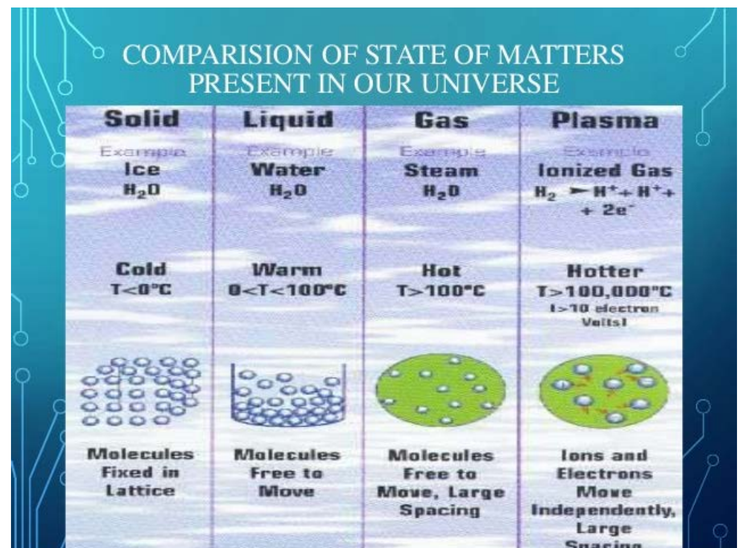


What is plasma?

- In **physics** and **chemistry**, **plasma** is a <u>gas</u>, in which a certain proportion of its particles are **<u>ionized</u>**. The presence of a number of charge carriers makes the plasma **<u>electrically conductive</u>** so that it responds strongly to **<u>electromagnetic fields</u>**.

- The fourth state of matter



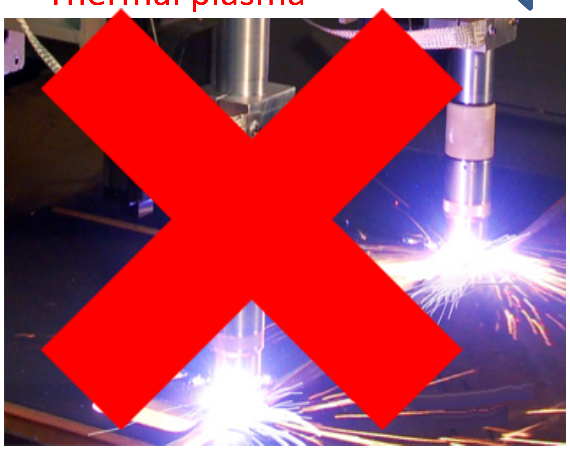


Plasma

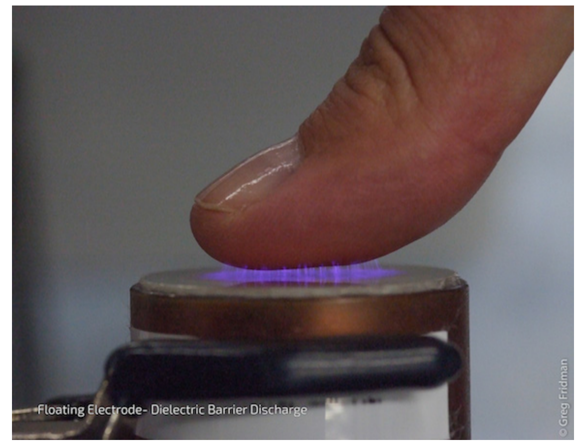
Not being used in chemical processes due to complex cooling process and energy intensive

- Catalyst preparation/regeneration/activation
- Catalytic chemical processes
- Thermodynamically unfavourable reactions etc.

Thermal plasma



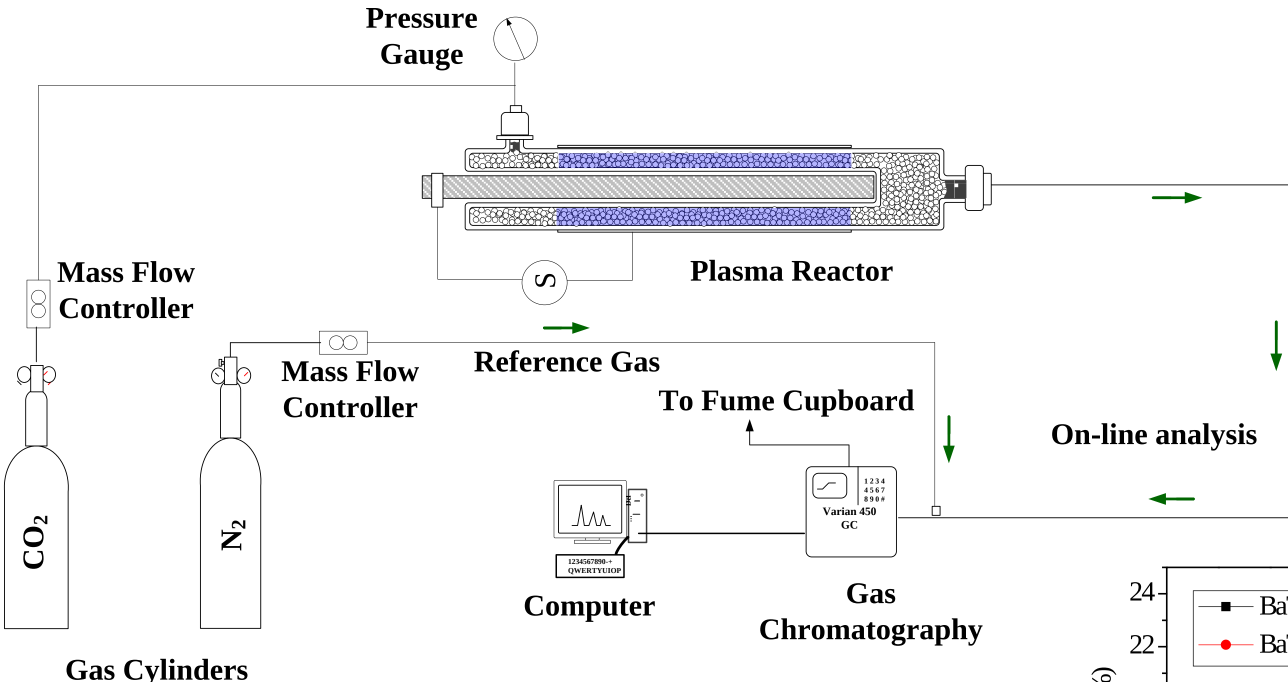
Cold (non-thermal) plasma

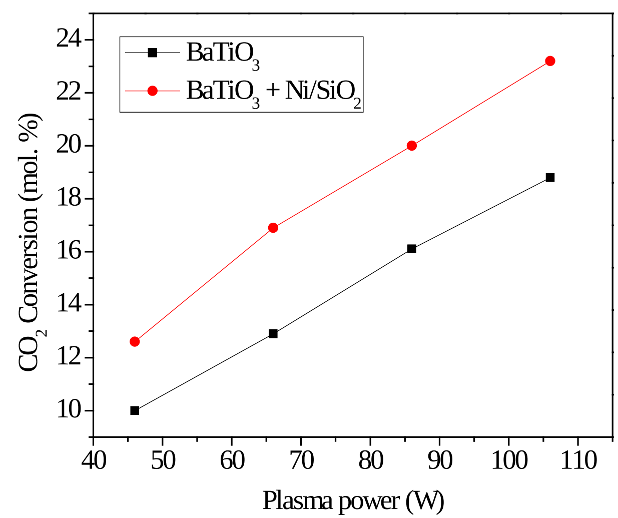


- Thermal plasmas are hot (10,000 to 20,000K)
- $T_e = T_N = T_{ion} = 10{,}000\text{-}20{,}000K$
- Ionization: electron collisions with preliminary excited hot atoms and molecules
- Not chemically selective.

- They operate close to ambient temperature
- T_e (10,000 to 100,000K) $>> T_N = T_{ion}$ (ambient temperature)
- Ionization: electron collisions with "cold" excited atoms and molecules
- Chemically selective

Cold plasma for CO_2 dissociation





Kui, Z. et al. (2017), Ind. Eng. Chem. Res, 56(12)3204-3216

Cold plasma for liquid waste treatment

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Waste glycerol

Waste cooking oil

Waste lubricant

Cold plasma

Atmospheric temperature

- Hydrogen
- Hydrocarbon
- Alcohol
- Acetol (Hydroxyacetone)

Harris J. et al. (2018), Green Chemistry, 20, 2578-2587

Waste glycerol conversion

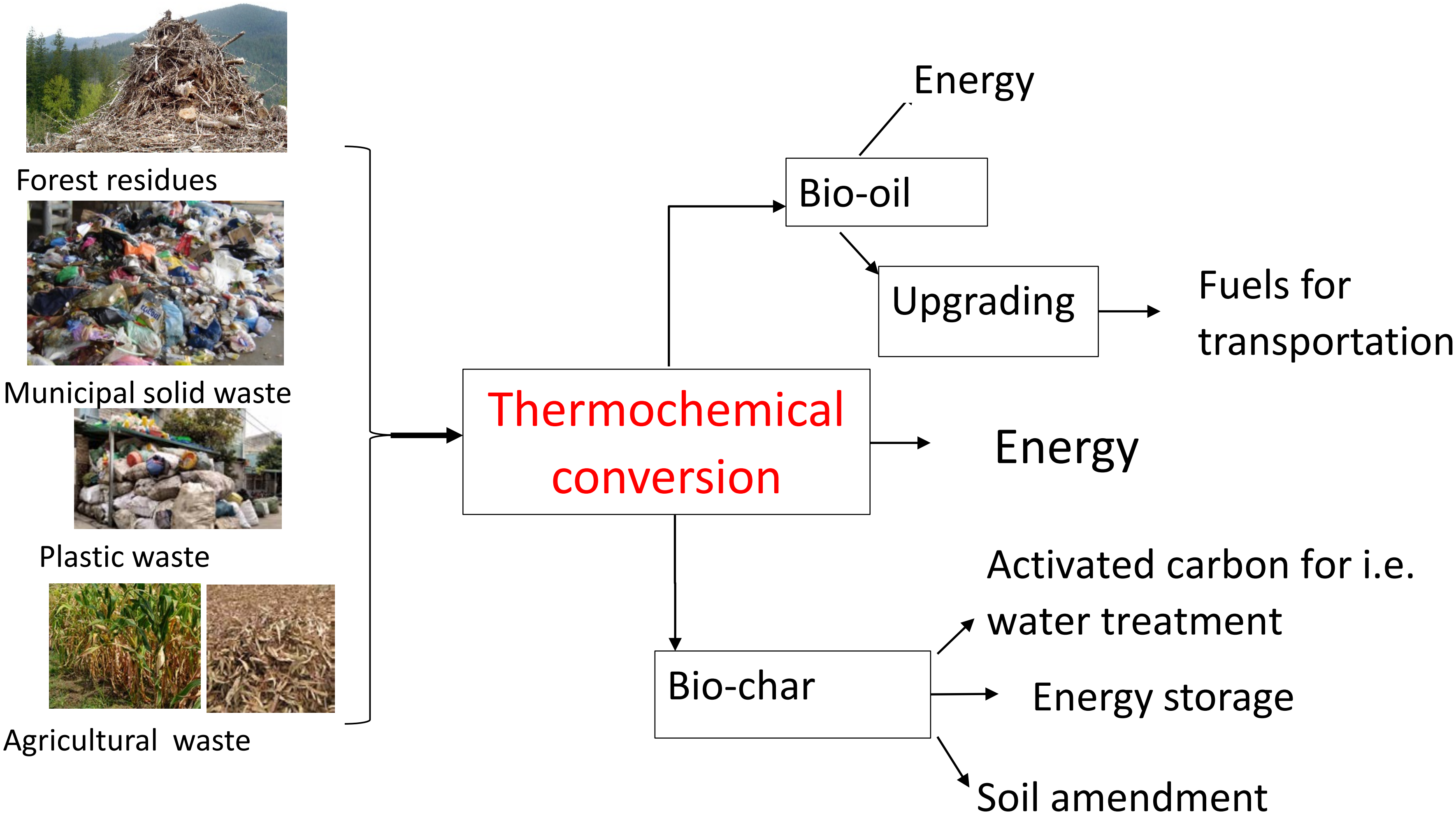
	Yield (%wt)					
	H_2	CO_2	CO	CH_4	$C_{2\text{-}4}$	Acetol
Conventional method @300-350°C)	0.17	5.9	3.78	9.36	2.87	11.25
Cold plasma (no catalyst)[1]	1.01	3.46	8.56	3.25	9.26	34.92
Cold plasma (no catalyst)	2.72	10.79	9.90	4.44	10.34	58.20
Cold plasma (no catalyst)*	0	0	17.32	2.75	18.13	12.16
Cold plasma (packing materials)	2.45	13.80	12.21	0.87	31.37	0.22
Cold plasma & catalyst (Ni/Al_2O_3)	7.02	44.98	34.81	3.46	8.85	0.19

* *Change carrier gas from N_2 to He*
[1] *Low plasma power*

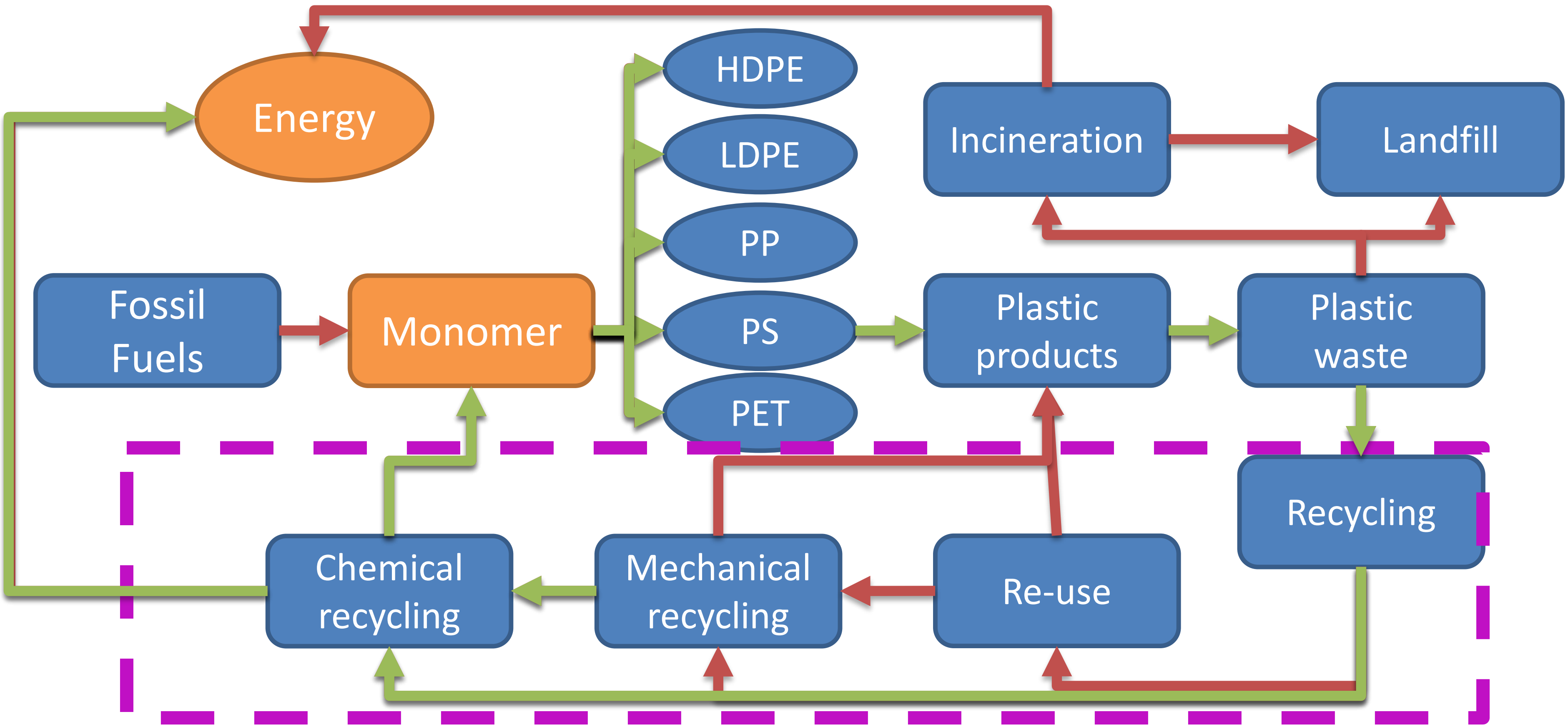
Compared to theoretical yield: 8.7%wt

Harris J., Phan A.N. and Zhang K.. Green Chemistry, 20, 2578-2587

Waste-to-energy, fuel and chemicals



Sustainability and plastics



Plastic waste pyrolysis

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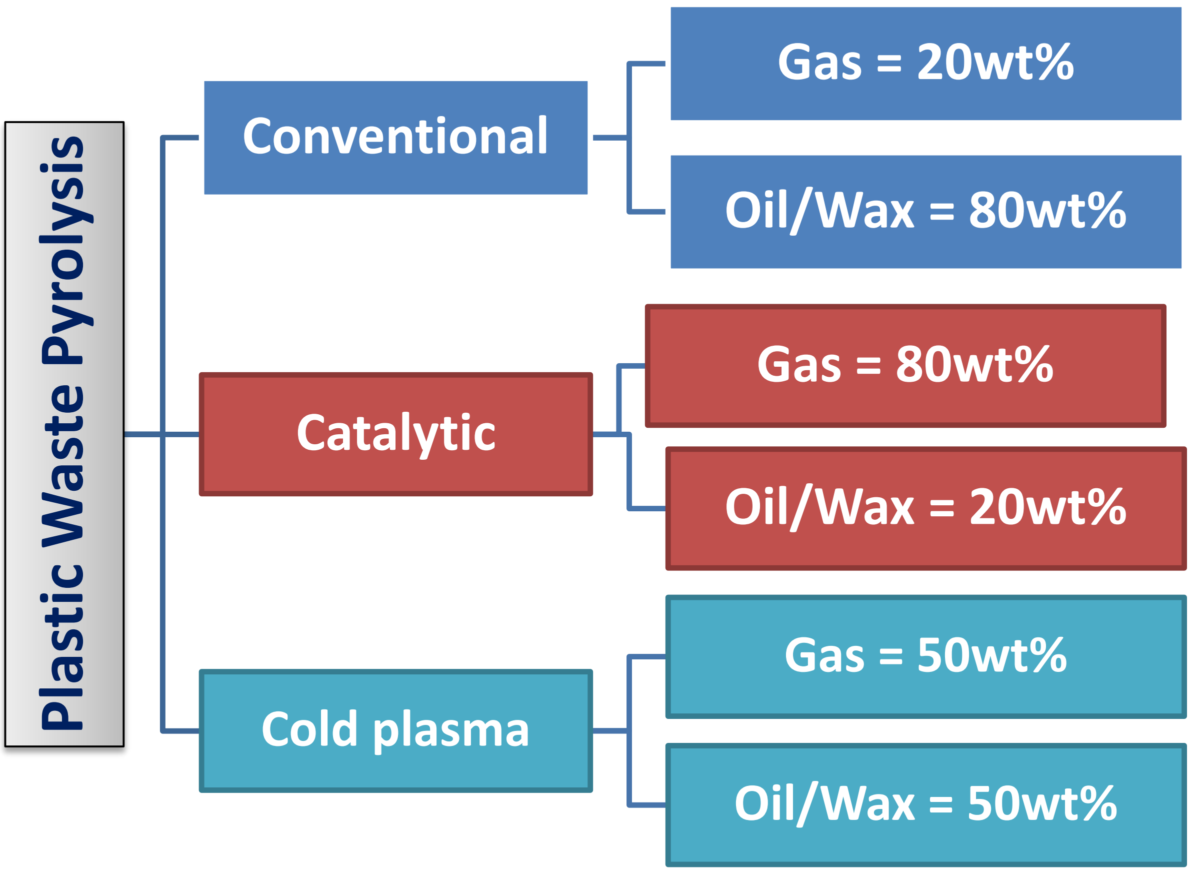
The Independent :
https://ind.pn/2P6xfjJ
Government Europa:
https://www.governmenteuropa.eu/cold-plasma-pyrolysis/90589/



- Kinetic studies
- Study the synergetic effect of plasma and catalytic pyrolysis
- Targets: Chemical recovery and hydrogen production

LS Diaz-Silvarrey at al. Green Chemistry 20 (8), 1813-1823

Pyrolysis of biomass waste

Q =10-15% of biomass energy

Biomass/waste
$C_6H_{10-11}O_{3.5-5.0}N_{0...}$

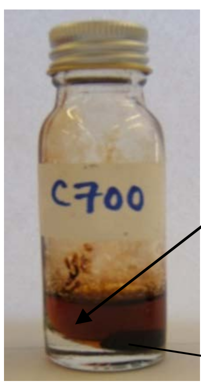
Moisture <15%

- *Inert Environment*
- *T=450-800^oC*
- *Atmospheric pressure*
- *Heating rate: 0.1K/s-100K/s*

Gas [10-20%wt]
- Majority: CO, CO_2 (50-80%vol)
- Small fractions: H_2, CH_4 and C_{2-4}

Liquid [45-80%wt: 30-70% energy]
- Acidic pH=2-4
- High water content (15-30%wt)
- High oxygen content (40-45%wt)
- Complex mixture
- Oil phase: [$CH_{1.44-1.48}O_{0.43-0.70}$]

Char (solid residue): 5-40%wt- 17-60% energy



Aqueous phase [85-90%]

Heavy oil phase [10-15%]

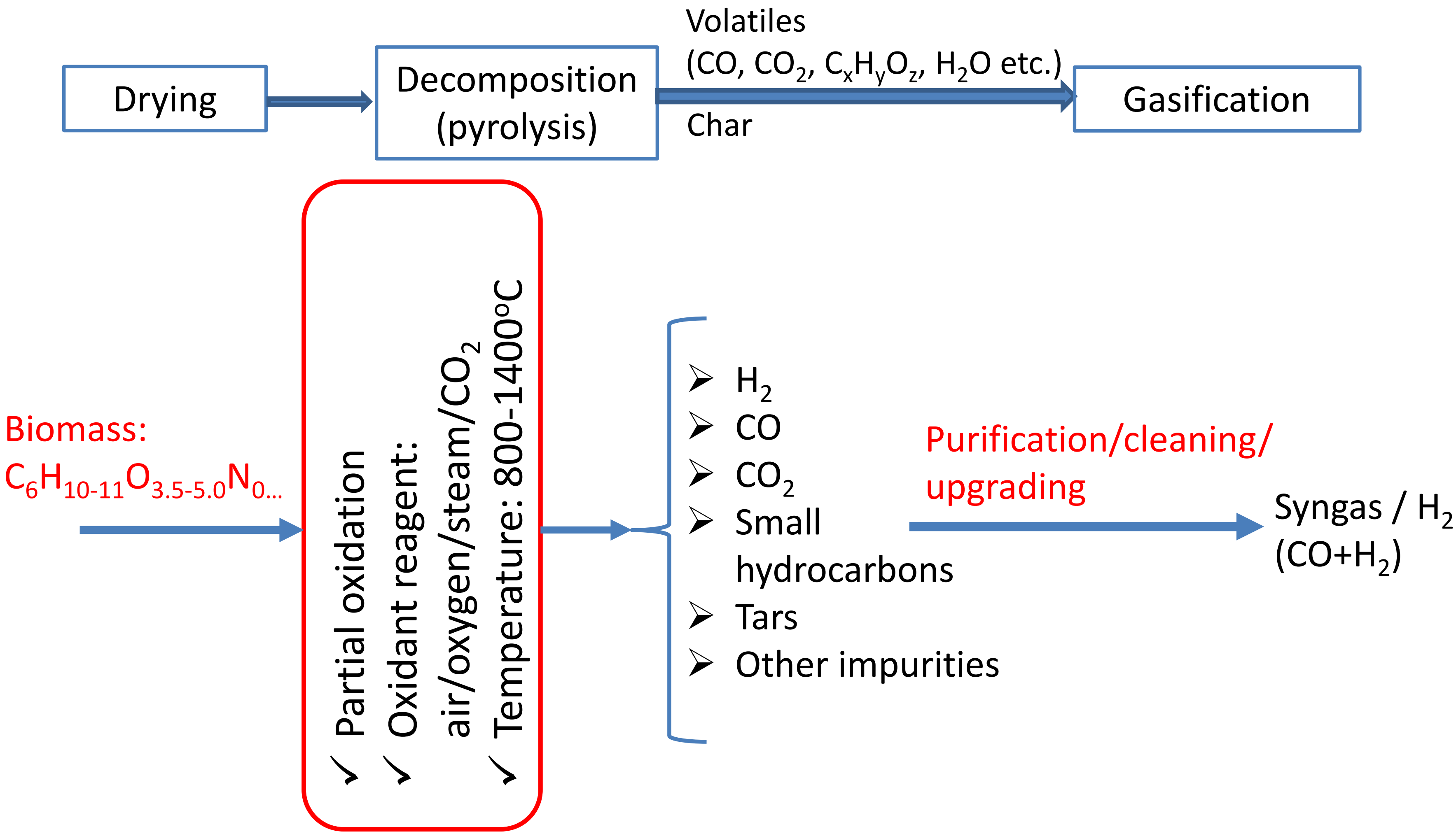
Upgrading pyrolysis liquid-bio-oil

- Catalytic Cracking:
  - Oxygen removed in the forms of CO and CO_2
  - Conditions: T=380°C, atmospheric pressure
  - Catalysts: Zeolite i.e. HZSM-5
  - **Challenges**: coke formation; ~ 30% oxygen removed
- Hydro-deoxygenation:
  - Oxygen removed in the forms of H_2O, CO_2 and/or CO
  - Conditions: ~500L H_2/1L of bio-oil; T=350°C, pressure >100 bar
  - Catalysts: transition metals (palladium, platinum etc.), hydrodesulphonation catalysts (Co-MoS_2/Al_2O_3), zero valent metals (Fe, Zn, Al and Mg)
  - **Challenges**: rapid catalyst deactivation; large amount of hydrogen required

PLASMA???

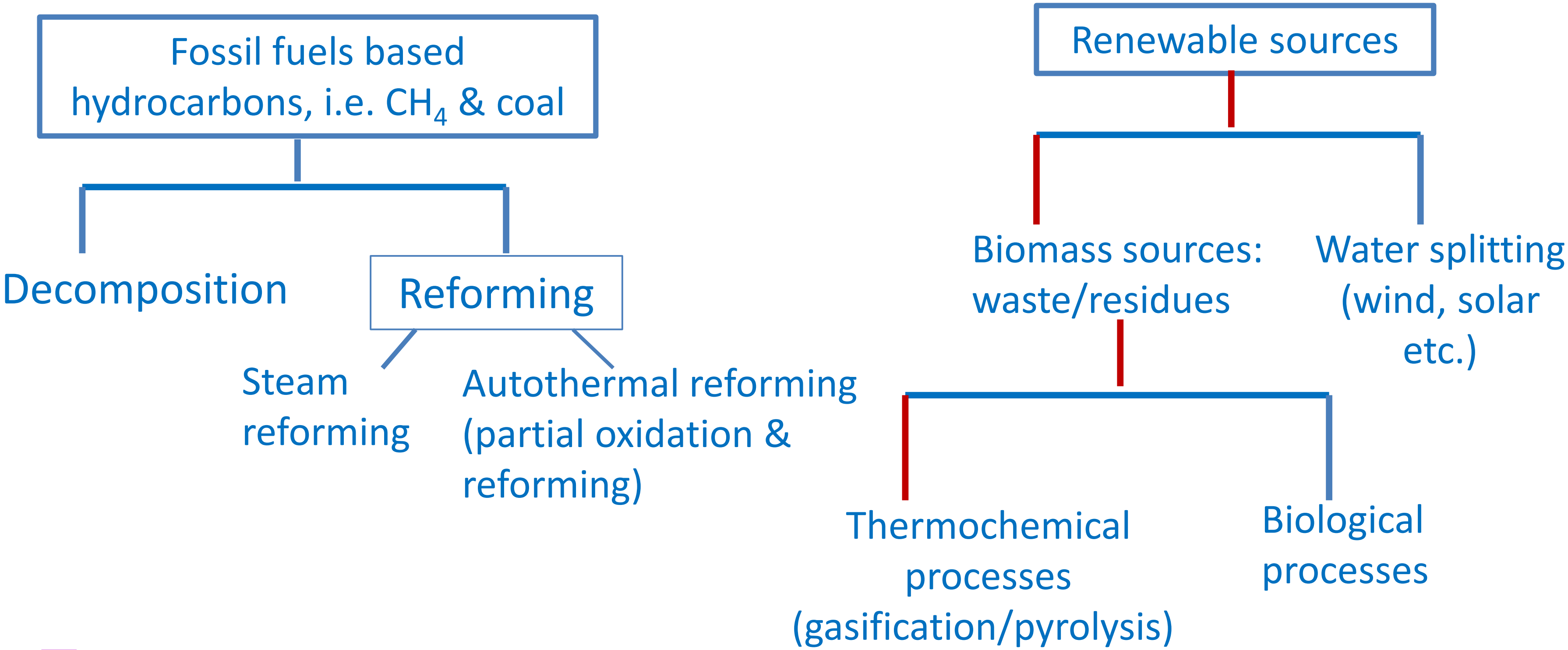
- Esterification:
  - Oxygen compounds converted into ester forms
  - Conditions: T>100°C; atmospheric pressure
  - Catalyst: homogeneous or solid form
  - **Challenges**: deactivation of solid catalysts; small percentage of oxygen removed

Biomass gasification



Hydrogen: a versatile and clean energy carrier

❑ Production



❑ Applications:

- Transportation
- Industry: refineries, chemical etc.
- Energy storage

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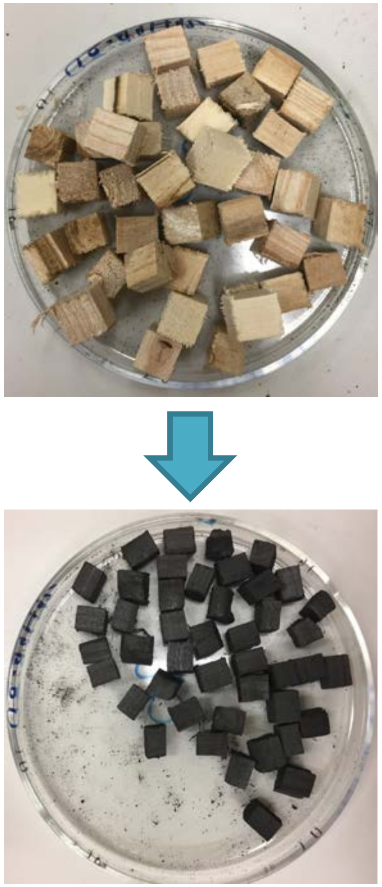
Char derived from pyrolysis step [22-25%wt]

Temperature (ºC)	Feedstock	600	700	800	900
Proximate analysis (%wt, dry basis)					
Volatile matter	84.12	10.09	7.17	4.62	3.64
Ash content	0.51	2.44	2.60	2.72	2.76
Fixed carbon	15.37	87.47	90.23	92.66	93.60
Ultimate analysis (%wt, dry basis)					
C	41.80	85.81	87.04	87.26	87.57
H	6.39	2.36	1.90	1.71	1.50
O	51.50	11.44	10.61	10.52	10.32
N	0.32	0.39	0.45	0.51	0.61
HHV (MJ/kg)	17.69	32.48	33.00	33.46	33.64
Surface area (m^2/g)	-	38	78	82	98



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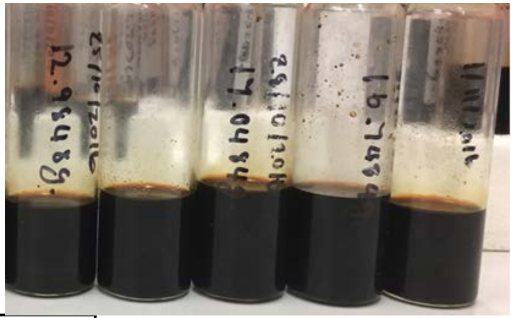
Condensable fraction in volatiles derived from pyrolysis step [48-52%wt]



Temperature (^{o}C)	600	700	800	900	Heavy fuel oil (Zhang et al., 2013)
C (%wt)	44.65	43.67	44.54	44.71	85.10
H (%wt)	7.53	7.61	7.65	7.41	10.90
O (%wt)	47.82	51.28	47.81	47.88	1.00
Water content (%wt)	43.85	44.11	44.58	43.68	0.10
pH	2.28	2.31	2.43	2.38	-
HHV (MJ/kg)	17.34	16.50	17.48	17.18	41.83

Non-condensable fraction in volatiles derived from pyrolysis step [25-30%wt]

Gas composition (%mol)	Pyrolysis temperature (^oC)			
	600	700	800	900
H_2	4.54 ± 0.13	7.31 ± 0.28	9.27 ± 0.19	10.26 ± 0.26
CO	38.50 ± 0.16	42.71 ± 0.05	45.39 ± 0.12	47.58 ± 0.17
CO_2	32.81 ± 0.11	27.48 ± 0.18	23.11 ± 0.14	20.08 ± 0.04
CH_4	14.62 ± 0.32	16.28 ± 0.10	16.73 ± 0.06	18.45 ± 0.20
C_2-C_5	10.53 ± 0.35	6.22 ± 0.22	5.50 ± 0.17	3.63 ± 0.18
H_2/CO	0.12	0.17	0.20	0.22

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Effect of particle size

Particle size (cm^3)	**0.5**	**1**	**2**
Char properties			
C	87.88	87.57	87.35
H	1.42	1.50	1.65
O	10.09	10.32	10.36
N	0.61	0.61	0.64
HHV (MJ/kg)	34.00 ± 0.37	33.64 ± 0.36	33.31 ± 0.52
Surface area (m^2/g)	124	98	82
Condensable fraction in volatiles			
C	46.43	44.71	41.48
H	7.37	7.41	7.05
O	46.20	47.88	51.47
Water content (%wt)	43.59 ± 0.35	43.68 ± 0.81	46.17 ± 0.41
HHV (MJ/kg)	18.00 ± 0.43	17.18 ± 0.21	14.92 ± 0.68

Effect of particle size

Gas composition (%mol)	Particle size (cm^3 cube)		
	0.5	1	2
H_2	11.37 ± 0.21	10.26 ± 0.26	8.18 ± 0.23
CO	48.43 ± 0.32	47.58 ± 0.17	47.09 ± 0.28
CO_2	18.99 ± 0.13	20.08 ± 0.04	23.47 ± 0.17
CH_4	18.43 ± 0.25	18.45 ± 0.20	16.40 ± 0.22
C_2-C_5	2.78 ± 0.09	3.63 ± 0.18	4.86 ± 0.12
H_2/CO	0.23	0.22	0.17

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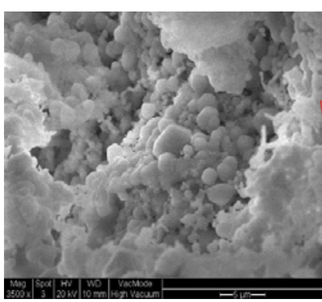
Thermal decomposition

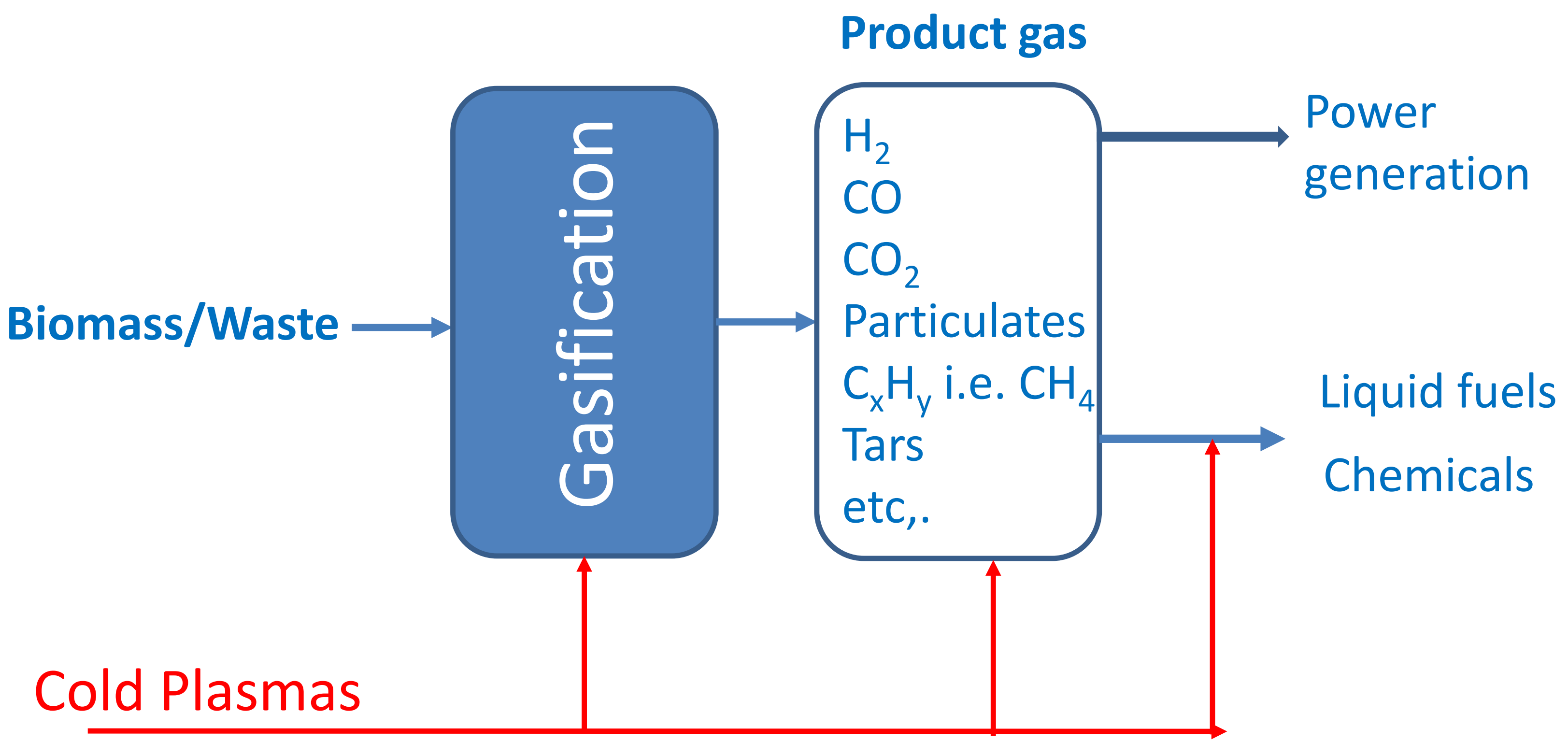
	Temperature only	Temperature & steam
CO_2 (%mol)	1.20 ± 0.18	12.21 ± 0.25
H_2 (%mol)	56.04 ± 0.39	60.98 ± 0.43
CH_4 (%mol)	0.95 ± 0.11	0.35 ± 0.14
CO (%mol)	41.81 ± 0.18	26.46 ± 0.46
Solid residue (%wt)	12.33 ± 0.3	0.20 ± 0.17
Tar yield (%wt)	4.21 ± 0.34	2.85 ± 0.70
Gas yield (%wt)	83.46 ± 0.24	96.75 ± 0.35
Water (g)	5.42 ± 0.37	11.11 ± 0.15

Theory: 68%

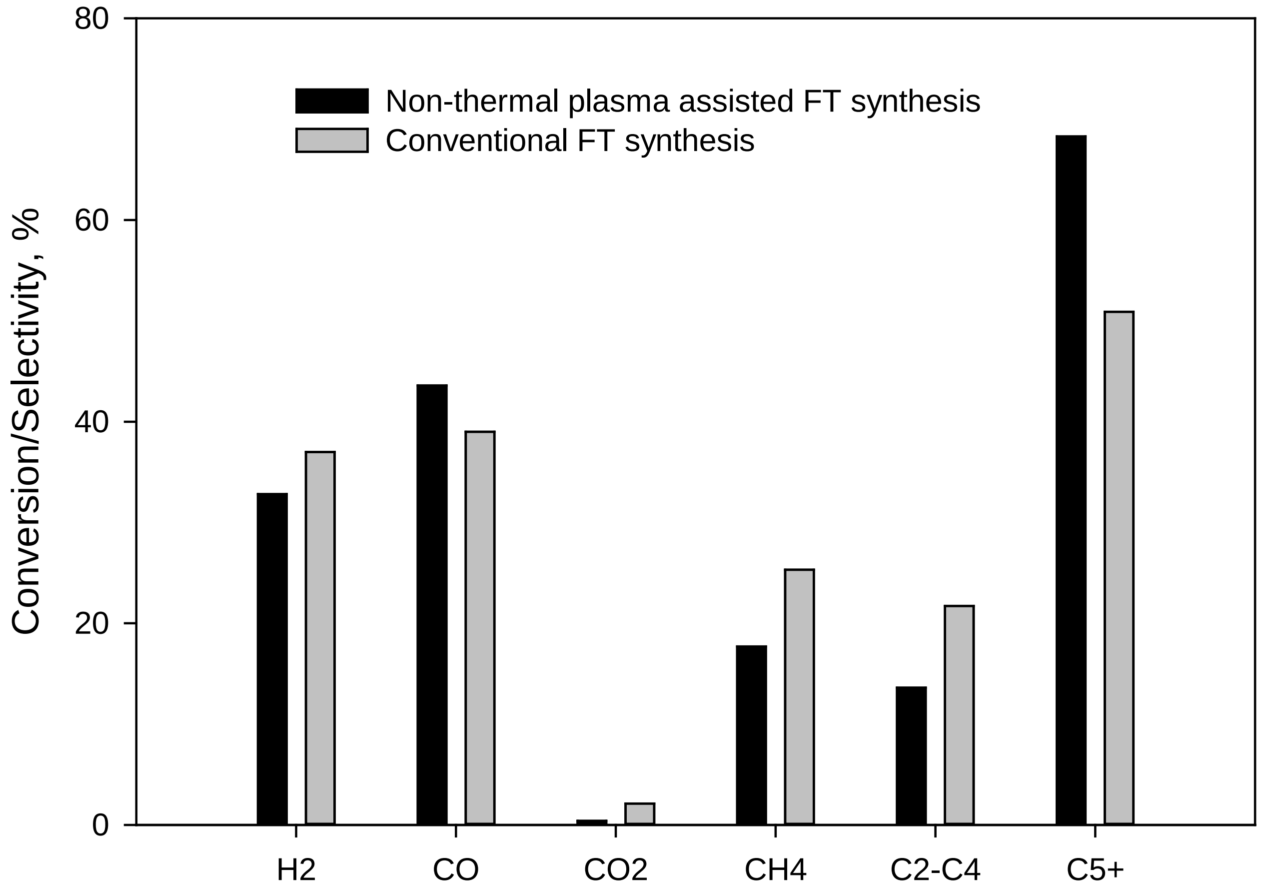


Carbon content: 0.03%wt

Next step: Biomass gasification



Fischer-Trospch (FT) synthesis at atmospheric conditions



Opportunities for collaborations

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Main research areas/what I can offer:

- **Thermochemical processes: pyrolysis and gasification of waste for energy, fuel and chemicals**
- **Cold plasma technologies for bio-refining and chemical processes**
- **Process intensification/reactor engineering/flow reactors for green chemistry and catalyst screening etc.**
- **Kinetic modelling**
- **Biofuel/biodiesel processing**
- **CO_2 utilisation**

Acknowledgments

- **Funders**

www.ibd-project.eu

H2020 – SPIRE-08-2015

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- **Process Intensification Group (PIG)**
- **PhD students**

Thank you for your attention

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