




Pyrolysis: a technological platform for Bioenergy, Biofuels and Bio-products

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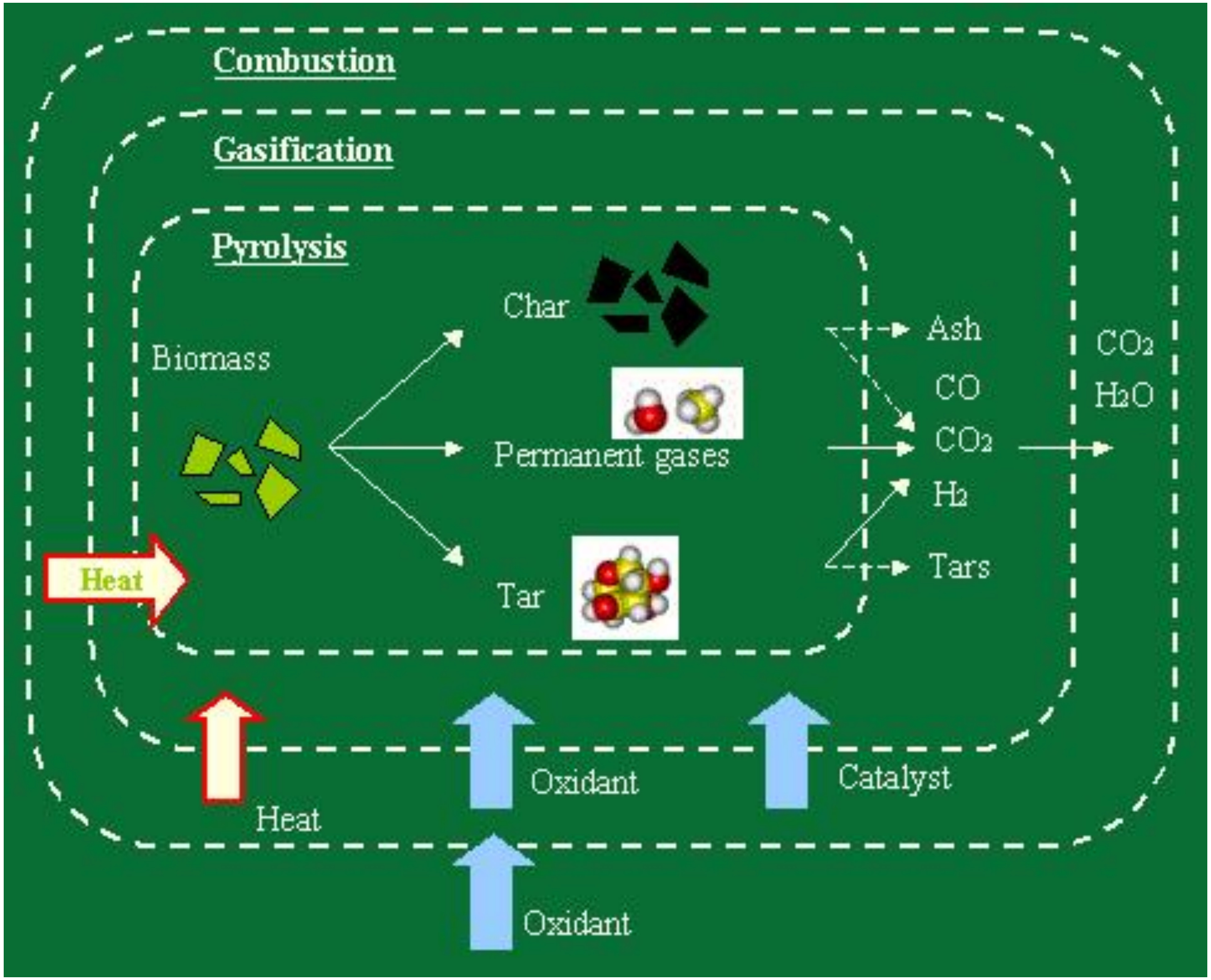
18 de Maio de 2022

18th May 2022

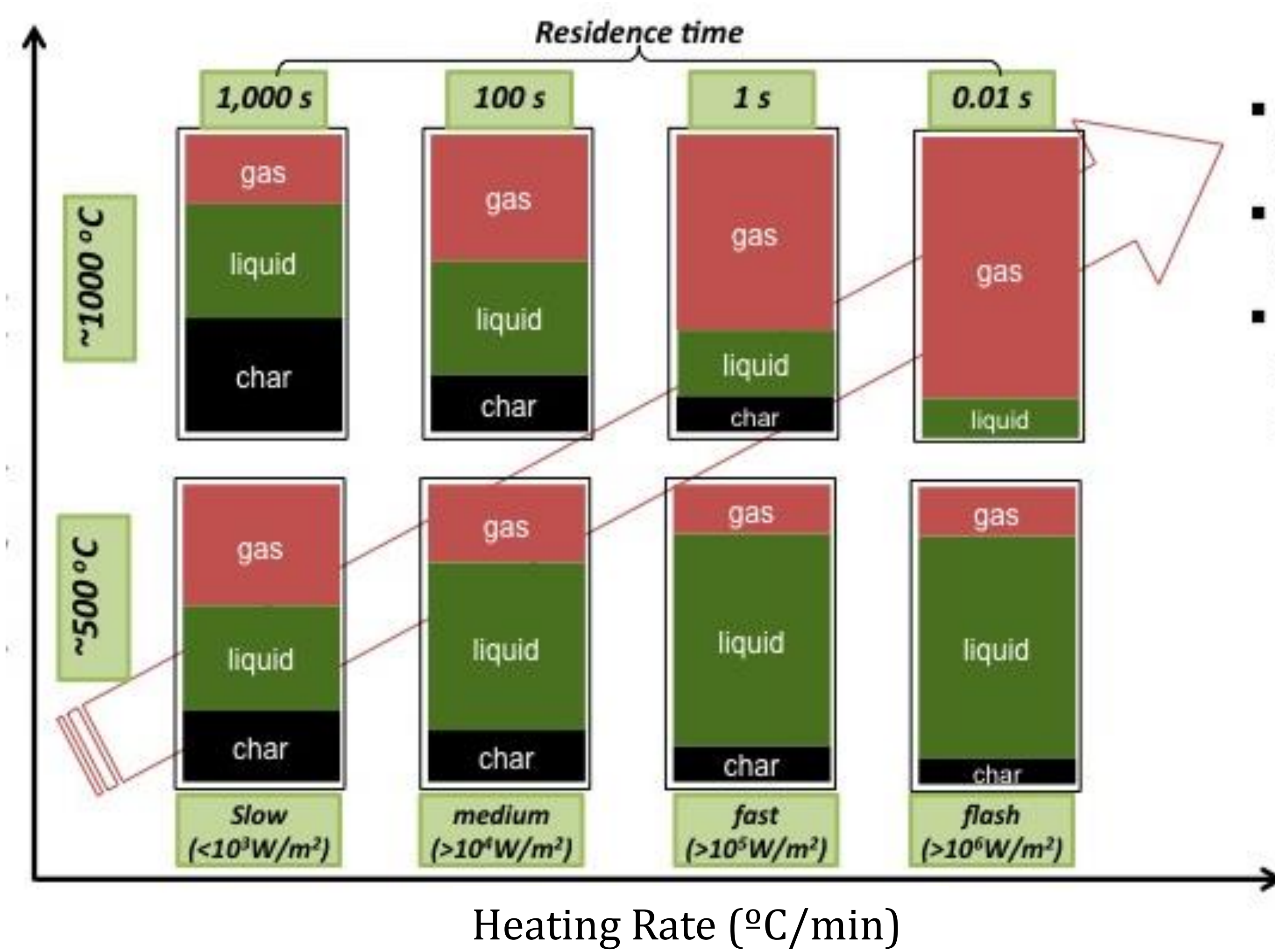
Pyrolysis is the <u>direct thermal decomposition</u> of the organic matrix in the absence of oxygen to produce solid, liquid and gas products.



Biomass Conversion Processes

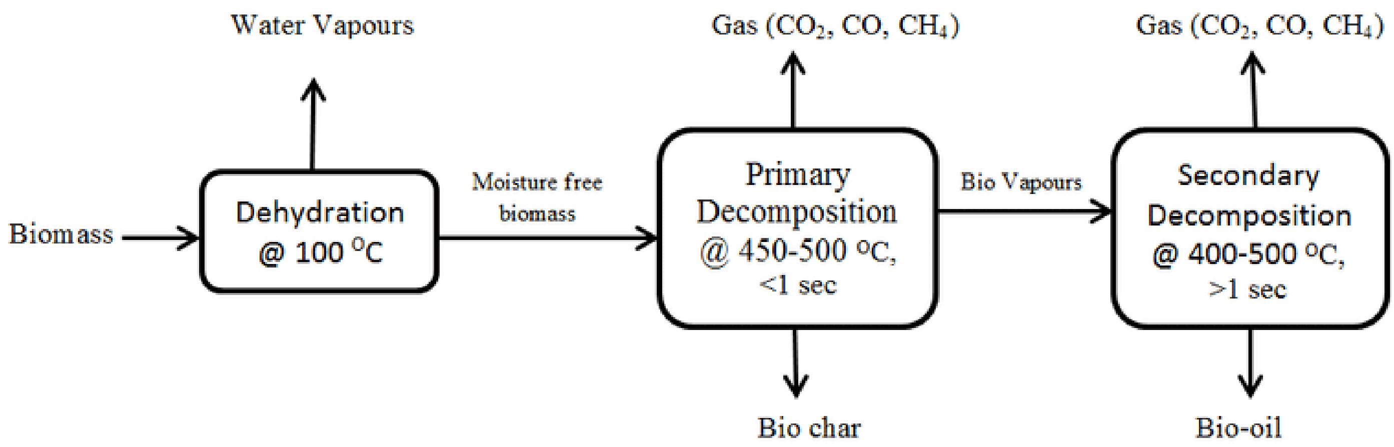
	Liquid	Solid	Gas
Fast Pyrolysis Moderate temperature Short reaction time	75%	12%	13%
Carbonisation Low temperature Long reaction time	30%	35%	35%
Gasification High temperature Long reaction time	5%	10%	85%

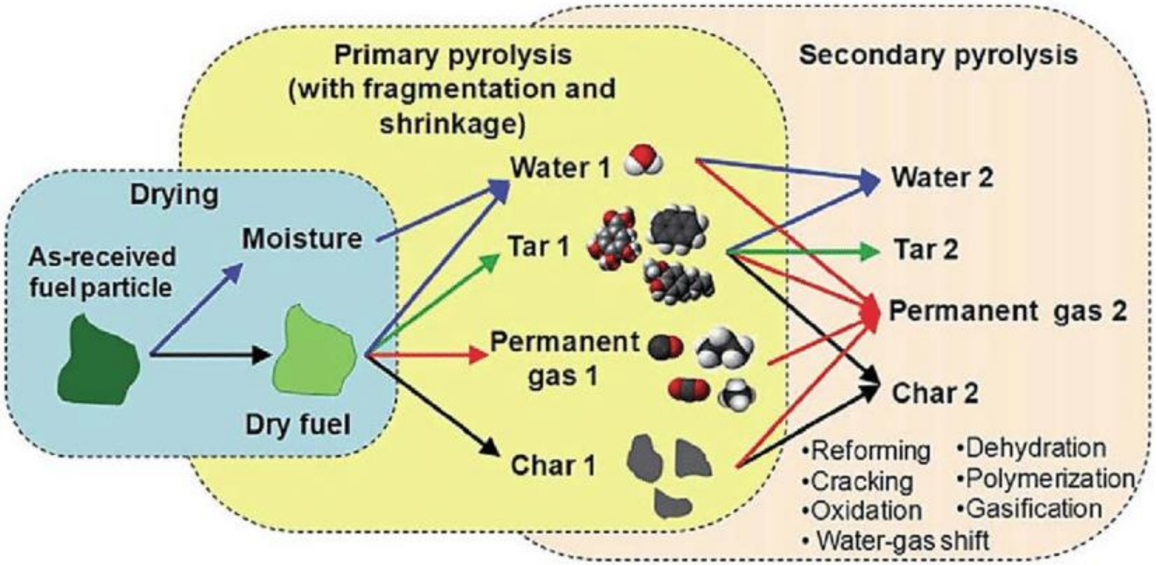
Critical parameters: Heating/cooling rate and residence time



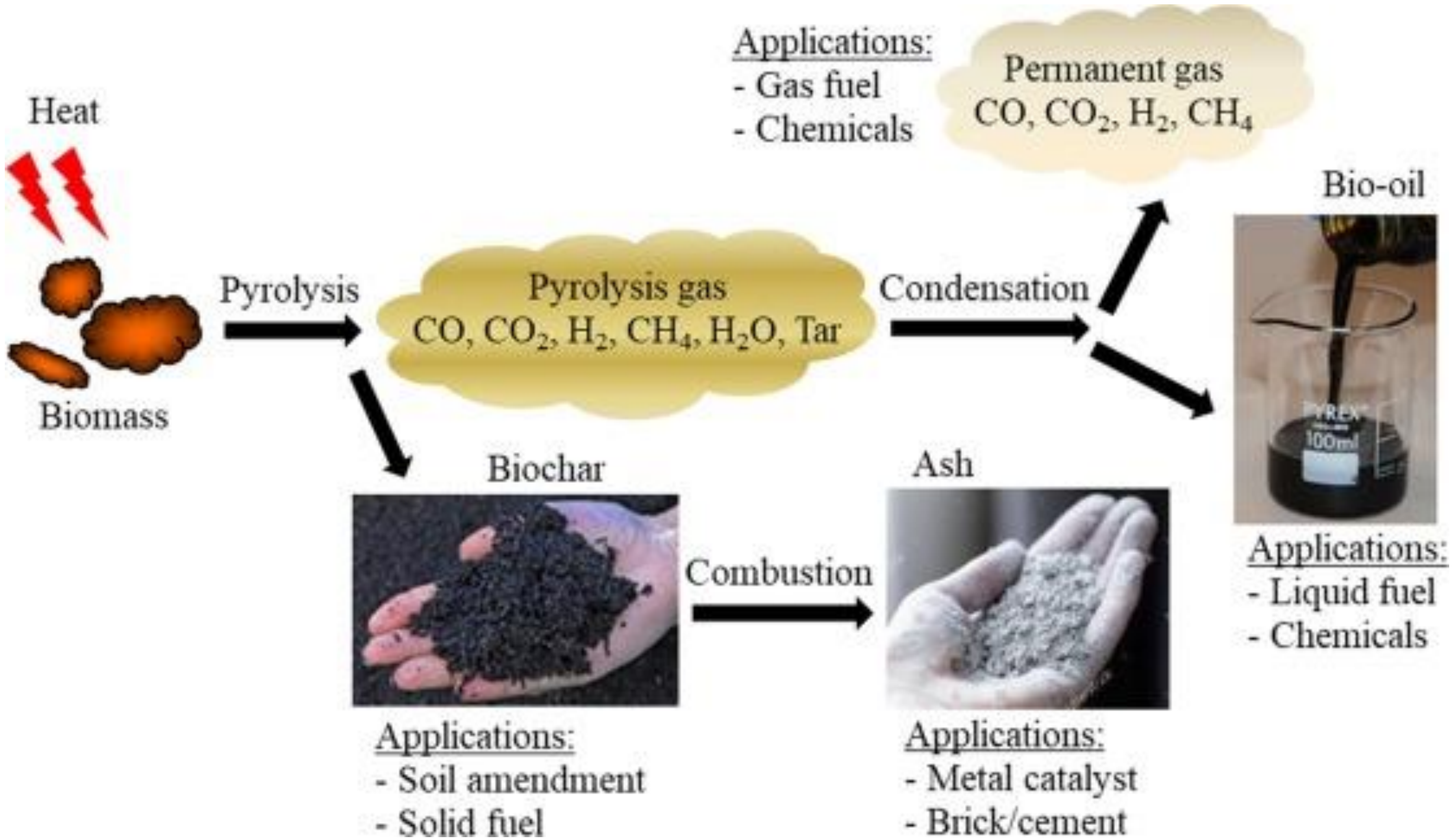
- decrease time
- increase temp.
- Increase heating rate

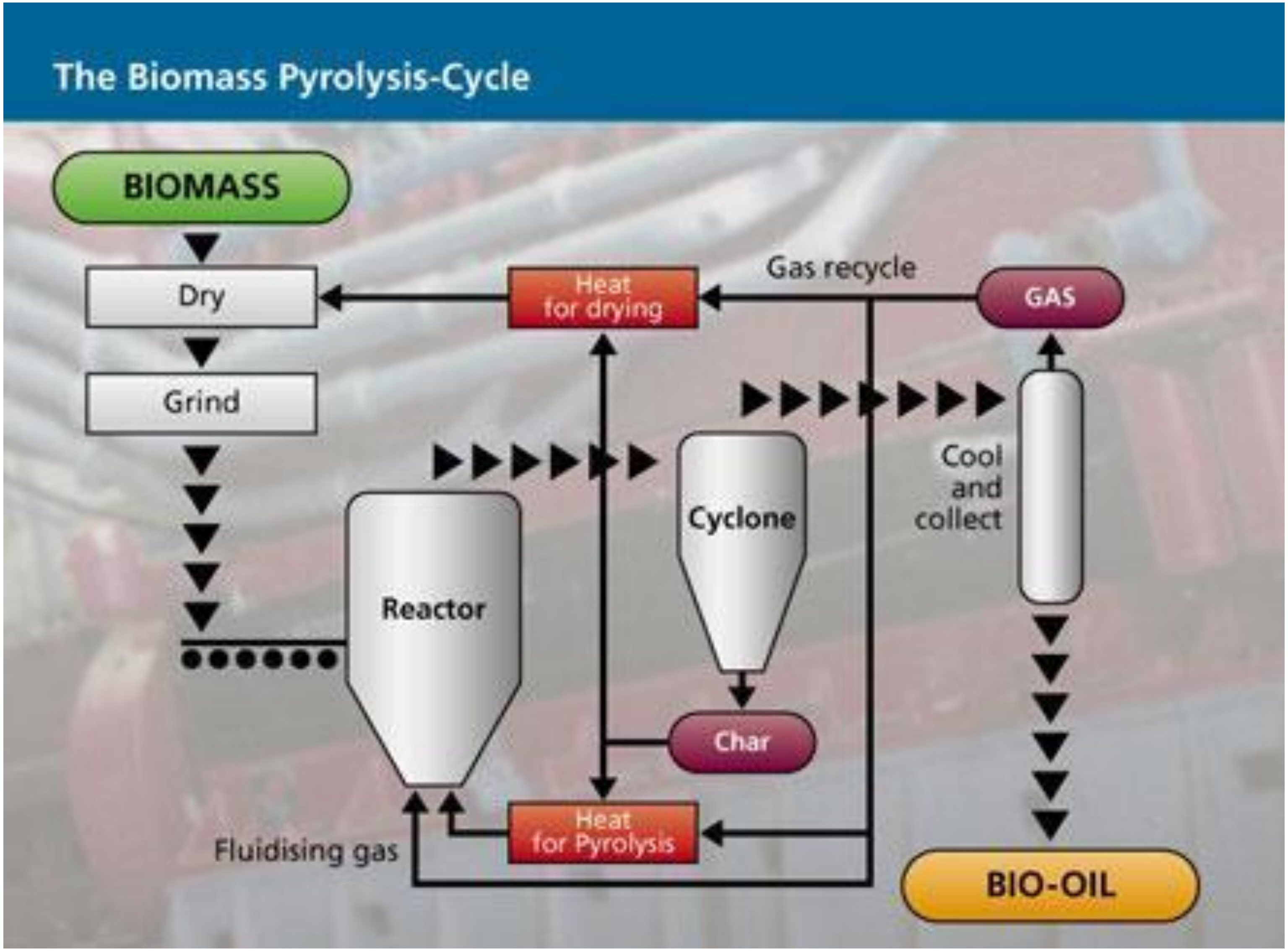
Pyrolysis Reactions



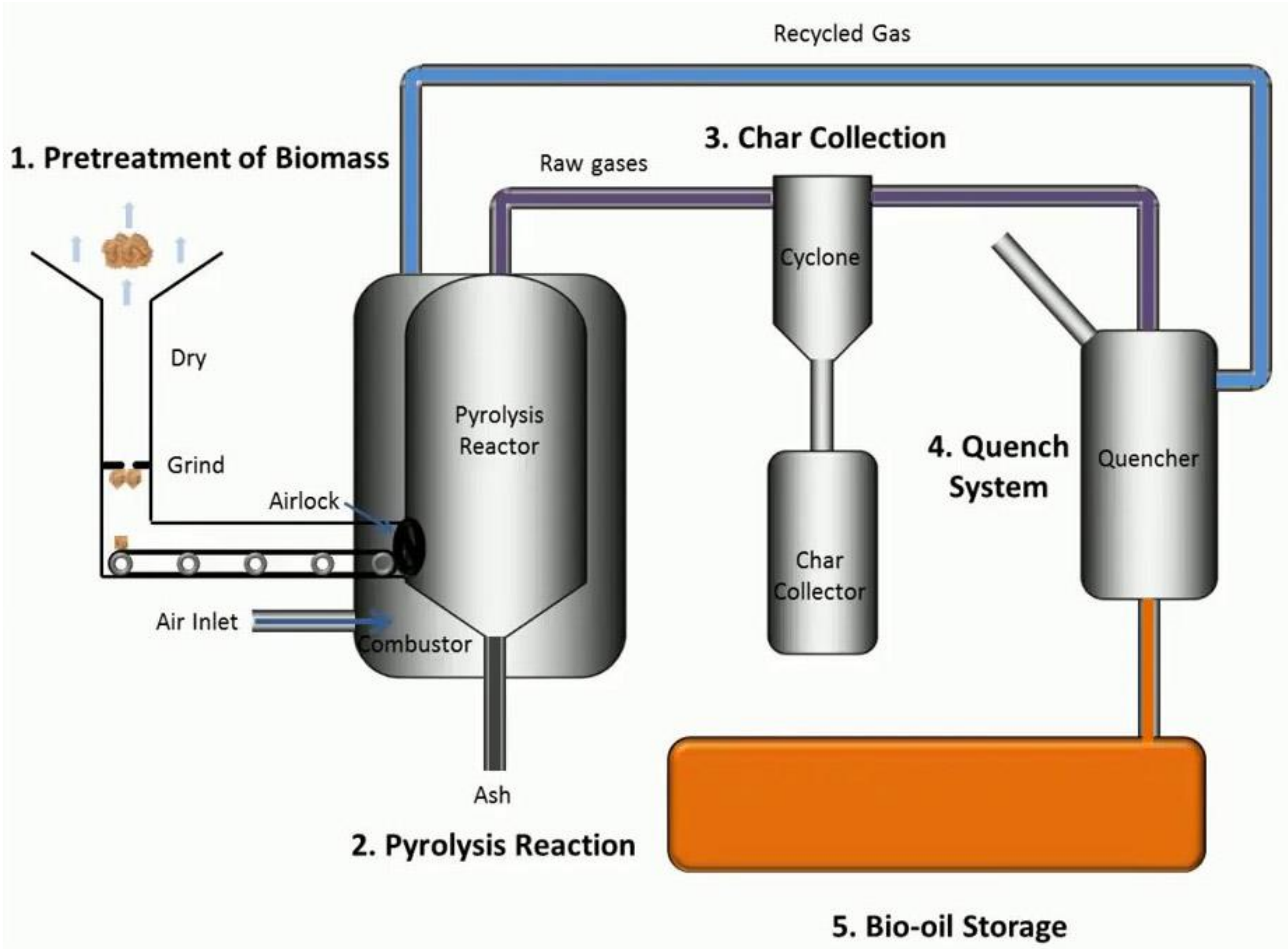


Pyrolysis Products

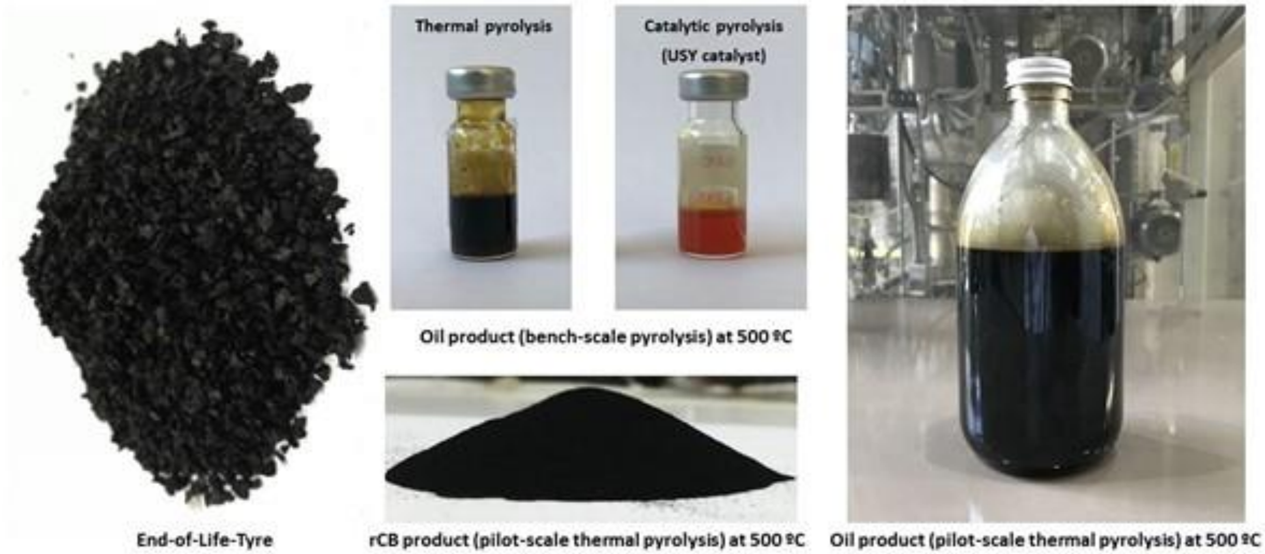


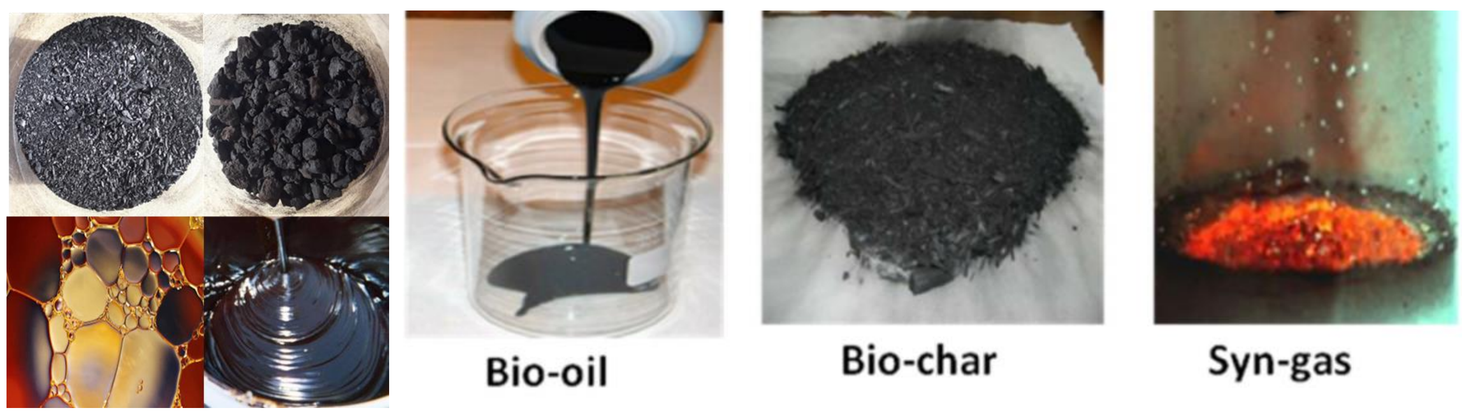

The Biomass Pyrolysis-Cycle
BIOMASS
Dry
Grind
Heat for drying
Gas recycle
GAS
Reactor
Cyclone
Cool and collect
Char
Heat for Pyrolysis
Fluidising gas
BIO-OIL

Pyrolysis Process

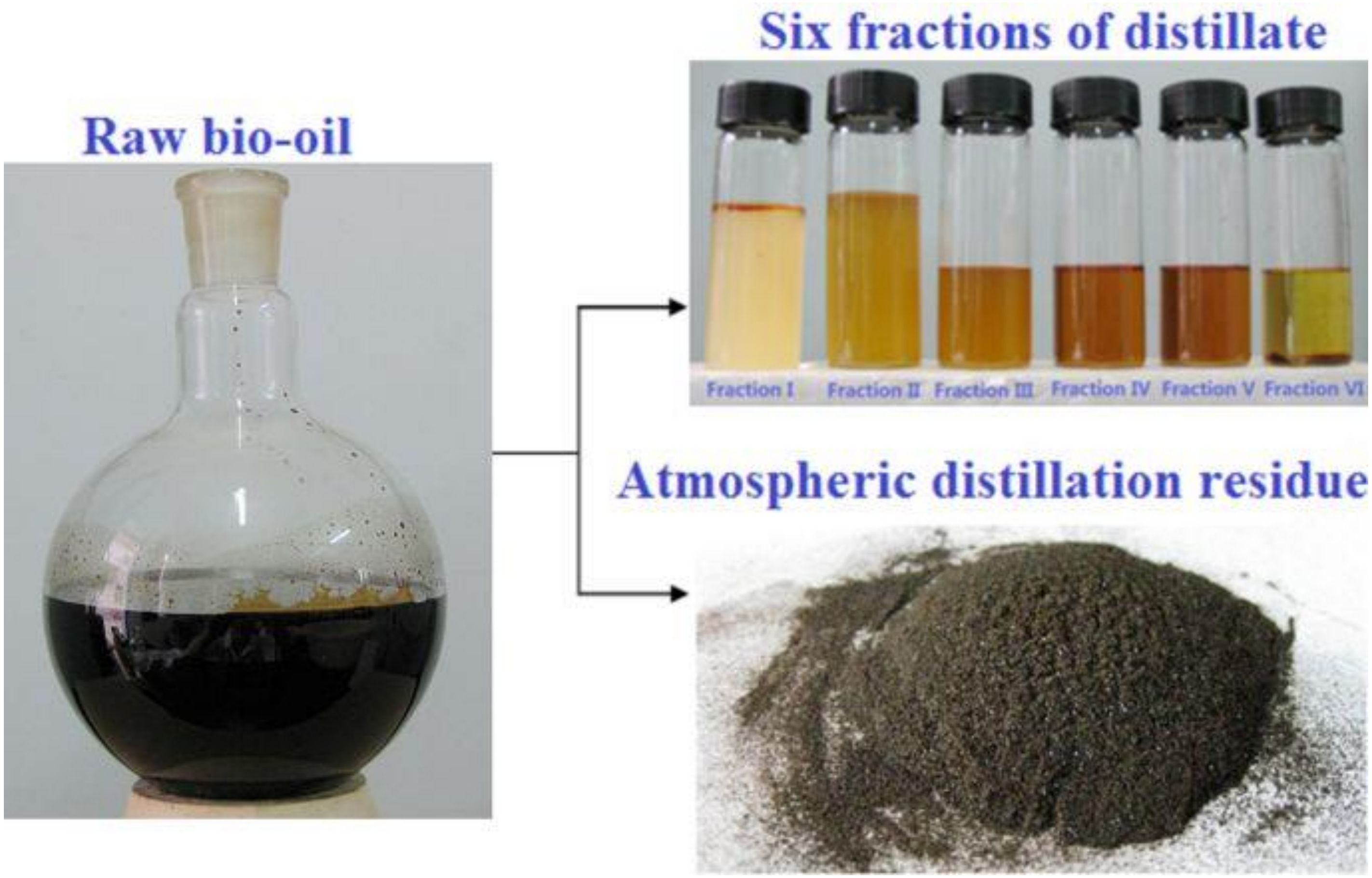


Pyrolysis Products

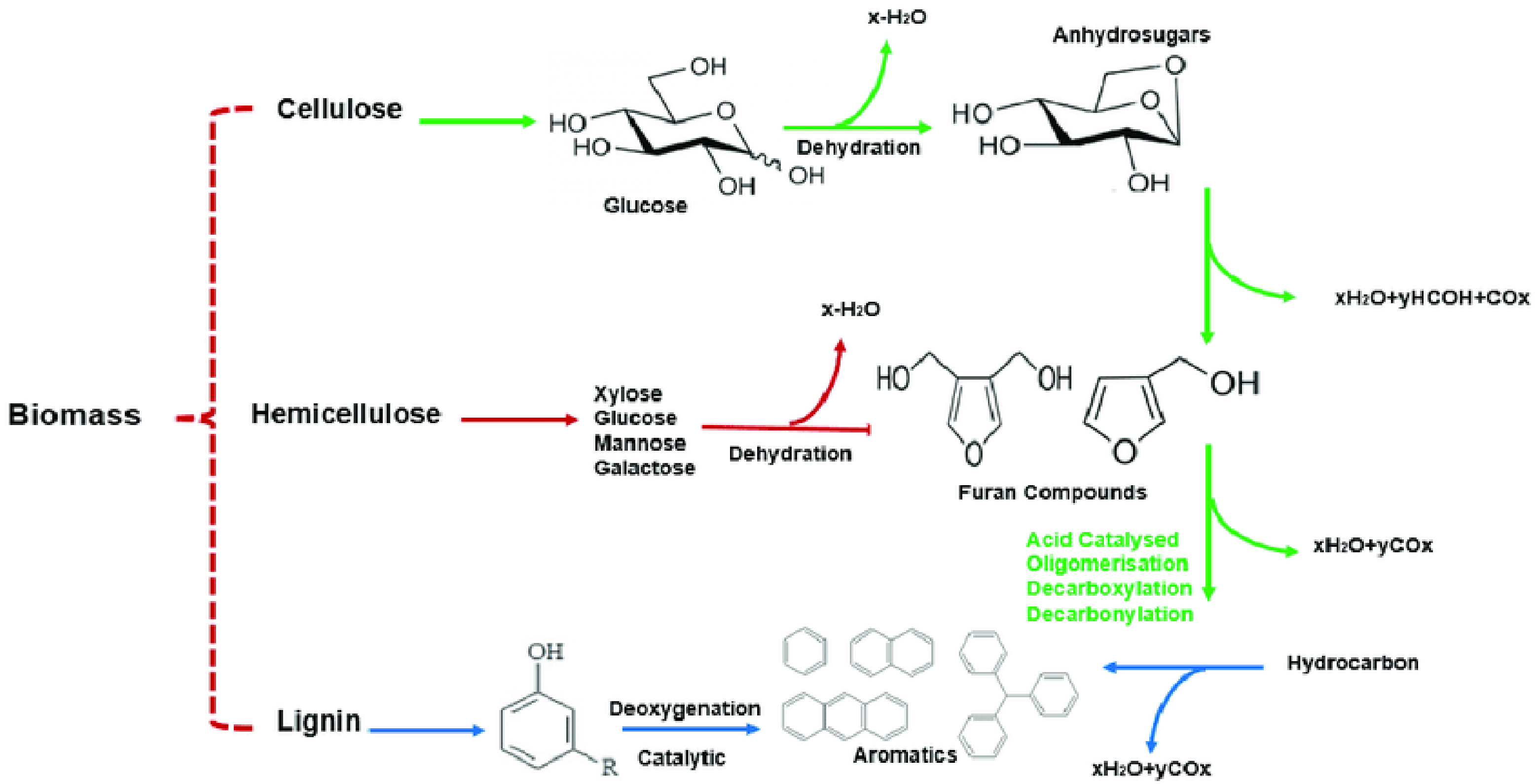




Pyrolysis Products



Pyrolysis of lignocellulosic biomass



Pyrolysis of biomass wastes

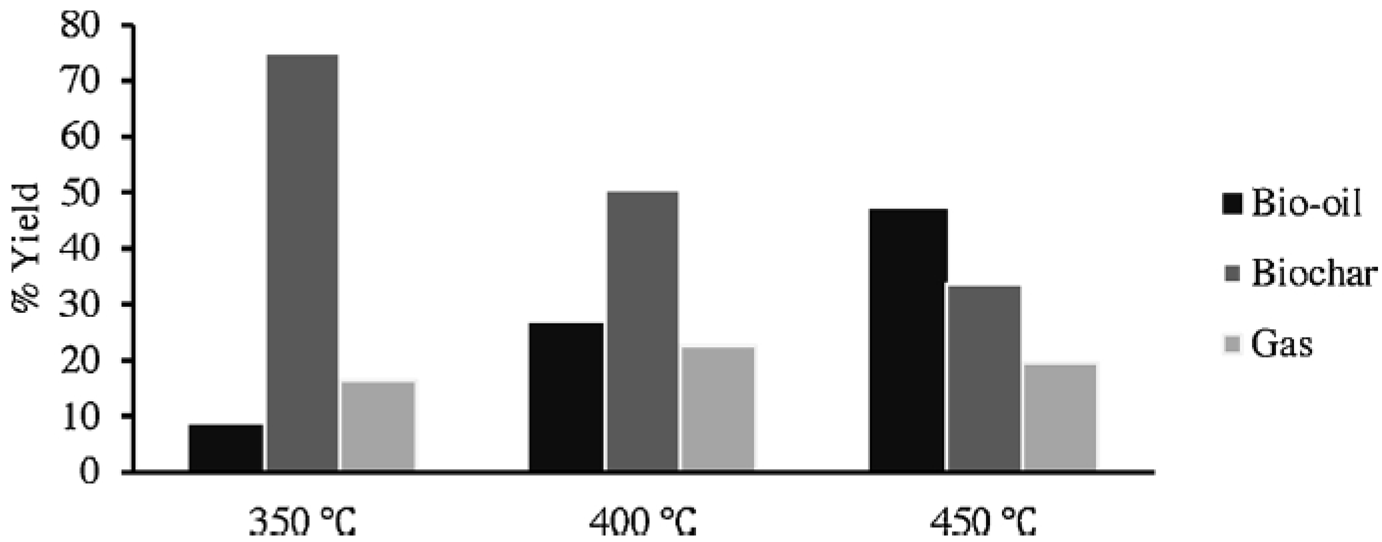


Fig. 4. Corrugated cardboard (CCB) pyrolysis product (oil, char, and gas) yields.

Sotoudehnia et al., Characterization of bio-oil and biochar from pyrolysis of waste corrugated cardboard *Journal of Analytical and Applied Pyrolysis* 145 (**2020**) 104722

Pyrolysis of biomass wastes

Composição do Bio-óleo

Compostos
Cíclicos
Aromáticos
Oxigenados

350 ºC

400 ºC

450 ºC

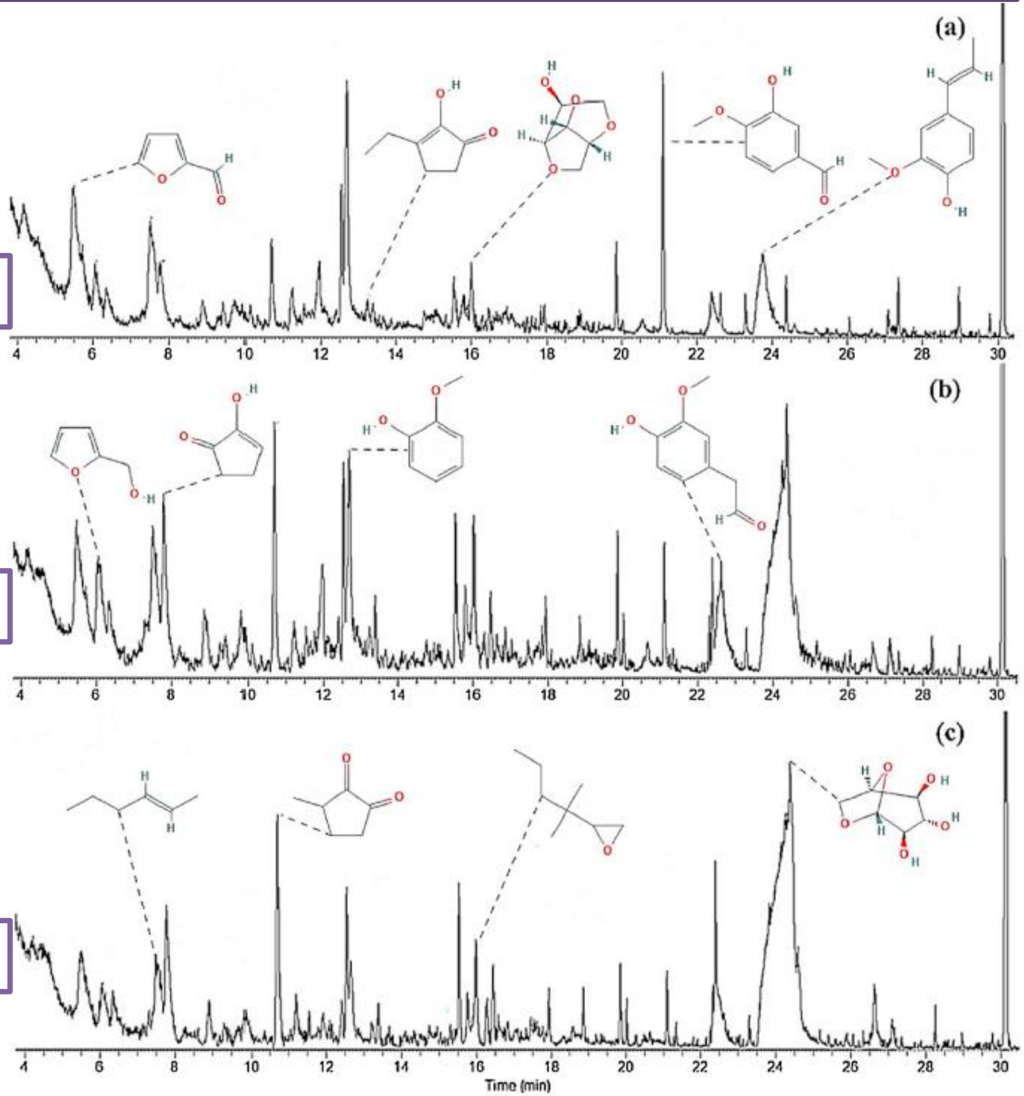


Fig. 10. GC-MS Chromatograms of corrugated cardboard (CCB) fresh bio-oil at (a) 350 °C, (b) 400 °C, and (c) 450 °C.

Compound	Formula	M+
Furfural	$C_5H_4O_2$	96
2-Furfuryl alcohol	$C_5H_6O_2$	98
Butanedial	$C_4H_6O_2$	86
2-Hexene, (E)-	C_6H_{12}	84
2-Hydroxycyclopent-2-en-1-one	$C_5H_6O_2$	98
2-Propylfuran	$C_7H_{10}O$	110
Phenol	C_6H_6O	94
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	$C_6H_8O_2$	112
Heptanal	$C_7H_{14}O$	114
Styrene	C_8H_8	104
2H-Pyran-2,6(3H)-dione	$C_5H_4O_3$	112
1,2-Cyclopentanedione, 3-methyl	$C_6H_8O_2$	112
1-Acetyloxypropane-2-one	$C_5H_8O_3$	116
Butanoic acid, 2-propenyl ester	$C_7H_{12}O_2$	128
Furaneol	$C_6H_8O_3$	128
Phenol, 2-methoxy-	$C_7H_8O_2$	124
2-Furancarboxaldehyde, 5-(hydroxymethyl)-	$C_6H_6O_3$	126
2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-	$C_7H_{10}O_2$	126
Pentane, 3-ethyl-3-methyl-	C_8H_{18}	114
Octane, 2-methyl-	C_9H_{20}	128
Guauacol,3-methyl-	$C_8H_{10}O_2$	138
3,4-Dimethylcyclohexanol	$C_8H_{16}O$	128






Pyrolysis of biomass wastes

Properties of bio-oil obtained from corrugated cardboard (CCB) pyrolyzed at various temperatures.

Sample ID	Water content (%)	Calorific Value (MJ kg^{-1})	pH
CCB350 Bio-oil	58.3	21.2	3.17
CCB400 Bio-oil	52.0	21.5	3.25
CCB450 Bio-oil	50.0	21.7	4.13

Proximate and ultimate analysis and calorific value of corrugated cardboard (CCB) and pyrolysis biochars.

	CCB	CCB 350 °C Biochar	CCB 400 °C Biochar	CCB 450 °C Biochar
% N	0.12 ± 0.01	0.11 ± 0.01	0.16 ± 0.01	0.18 ± 0.01
% C	43.24 ± 0.00	46.84 ± 0.01	51.33 ± 0.47	54.17 ± 0.32
% H	5.80 ± 0.03	5.70 ± 0.01	4.80 ± 0.06	3.70 ± 0.03
% Ash	4.0 ± 0.2	5.0 ± 0.3	5.2 ± 0.3	12.3 ± 0.6
% Fixed carbon	13.1 ± 0.7	17.2 ± 0.9	27.8 ± 1.4	41.8 ± 2.1
Calorific value (MJ kg^{-1})	18 ± 0.9	18.4 ± 0.9	19.7 ± 1.0	20.4 ± 1.0

ASTM quality standards for pyrolysis bio-oil used for combustion in boilers

Table 6.1. ASTM burner fuel standard D 7544 for fast pyrolysis bio-oil.

Property	**Grade G**	**Grade D**
Gross heat of combustion, MJ/kg, min	15	15
Water content, % mass, max	30	30
Pyrolysis solids content, % mass, max	2.5	0.25
Kinematic viscosity at 40 °C, mm^2/s, max	125	125
Density at 20 °C, kg/dm^3	1.1–1.3	1.1–1.3
Sulphur content, % mass, max	0.05	0.05
Ash content, % mass, max	0.25	0.15
pH	Report	Report
Flash point, °C, min	45	45
Pour point, °C, max	-9	-9

Table 1
Comparison of selected properties of bio-oils derived from pyrolysis of rice husk and bio-oils derived from pyrolysis of wood and heavy petroleum fuel oil.

Properties		Bio-oils derived from pyrolysis of rice husk [9]	Bio-oils derived from pyrolysis of wood [10]	Heavy petroleum fuel oil [11]
Water content (wt%)		25.2	15–30	0.1
pH		2.8	2.5	–
Elemental composition (wt%)	C	41.7	54–58	85
	H	7.7	5.5–7.0	11
	O	50.3	35–40	1.0
	N	0.3	0–0.2	0.3
Ash		–	0–0.2	0.1
HHV (MJ/kg)		17.42	16–19	40
Viscosity (at 50 °C) (mPa s)		128	40–100	180
Solids (wt%)		–	0.2–1	1
Distillation residue (wt%)		–	Upto 50	1






Catalytic upgrading of pyrolysis oil or vapors

The major drawbacks of the bio-oil is that it is:

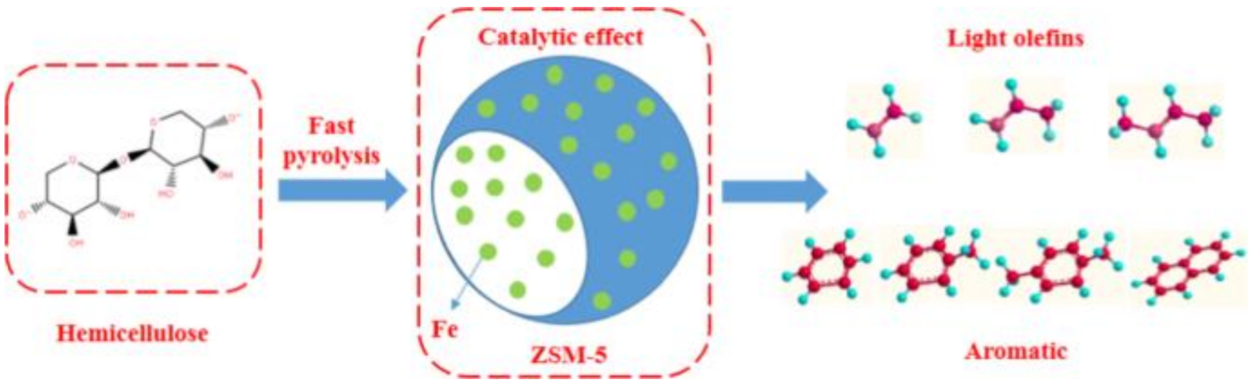
- highly oxygenated,
- viscous,
- corrosive and
- thermally unstable

Presence of water and oxygenated compounds reduces its calorific value and change significantly the combustion characteristics.

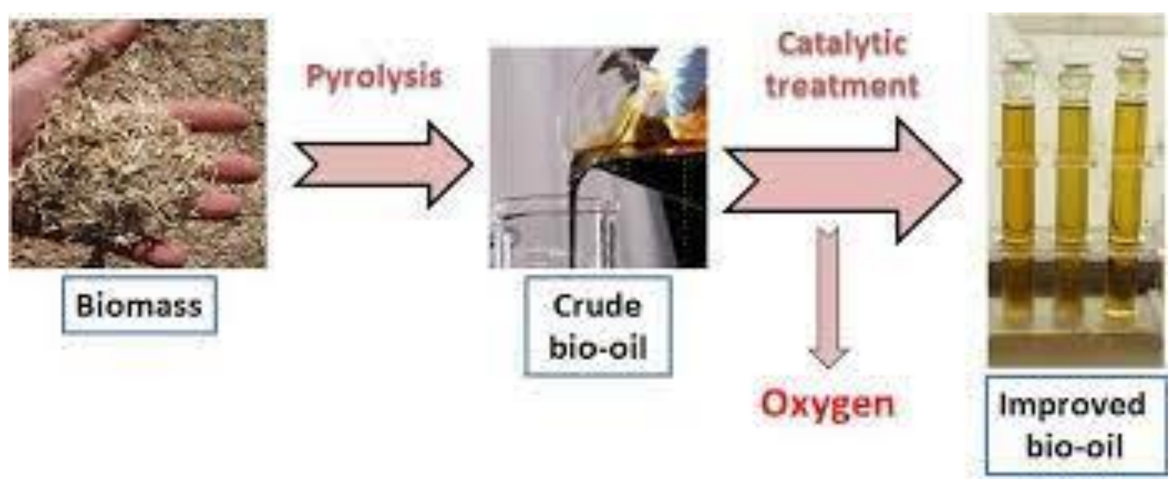
Presence of particles and water limits its potential for direct use in engines or turbines.

Catalytic upgrading of pyrolysis oil or vapors

Direct use of the catalyst during pyrolysis



Pyrolysis + Catalytic upgrading of the bio-oil



Catalytic upgrading of pyrolysis oil or vapors

Type of catalytic treatments:

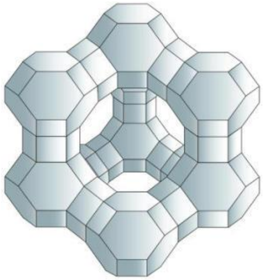
(1) CoMo or NiMo + H_2 - hydrodeoxygenation or hydrotreating catalysts

Remove sulphur from fossil fuels

Remove oxygen or nitrogen from fossil fuels

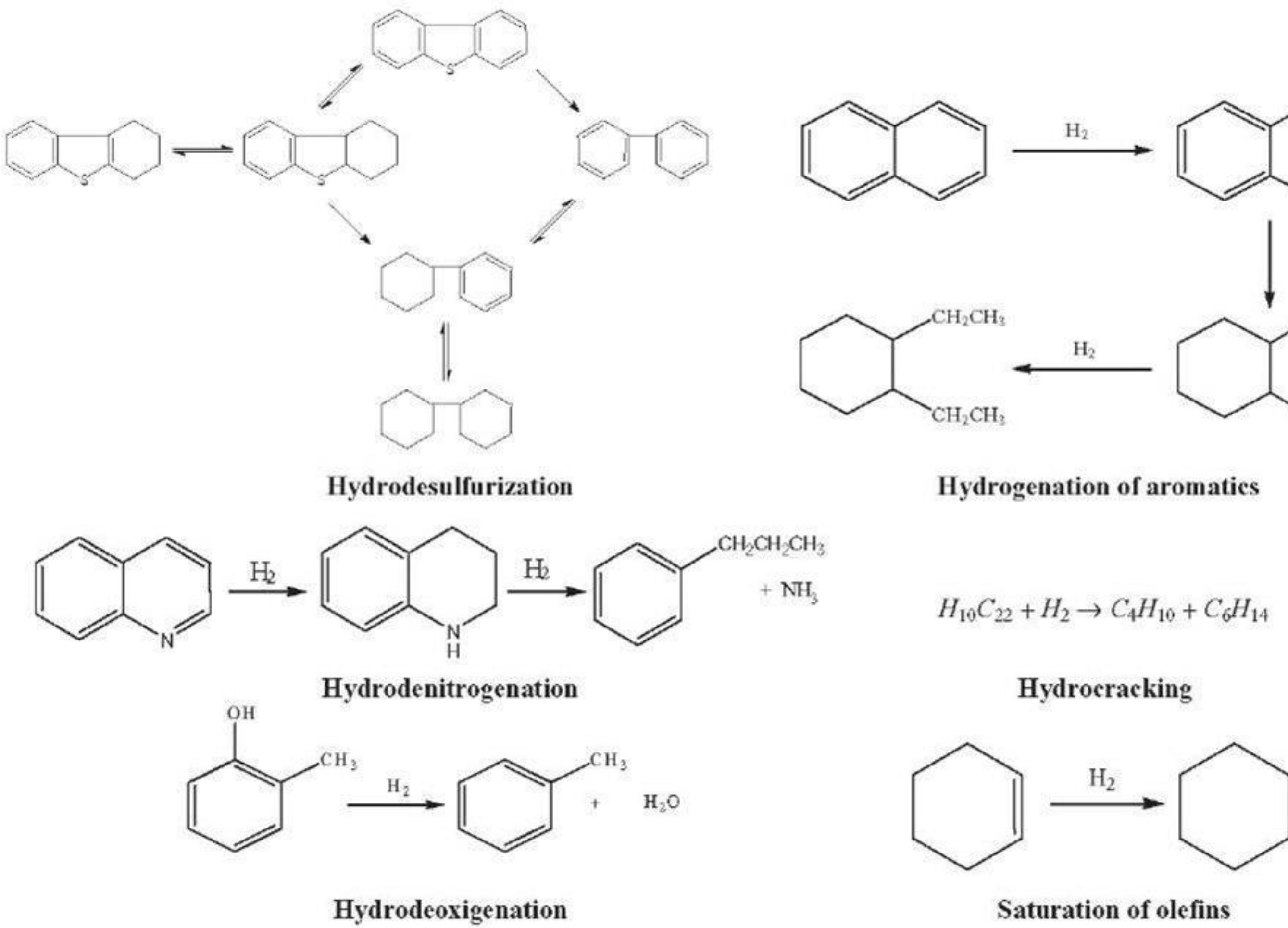
Convert double bond to single bonds

(2) zeolite upgrading

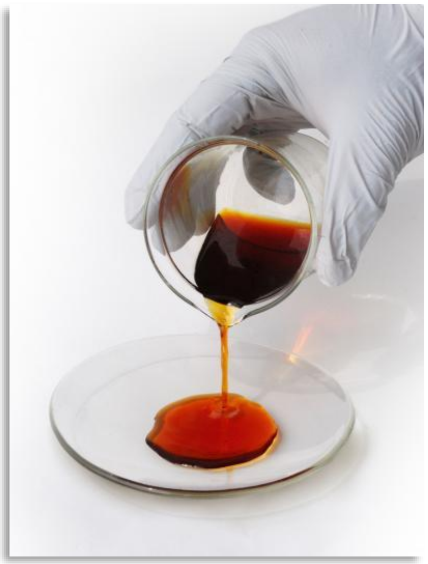


Catalytic cracking - break large hydrocarbon molecules into gasoline, diesel, kerosene, waxes and all kinds of other by-products of petroleum.

Catalytic upgrading of pyrolysis oil or vapors

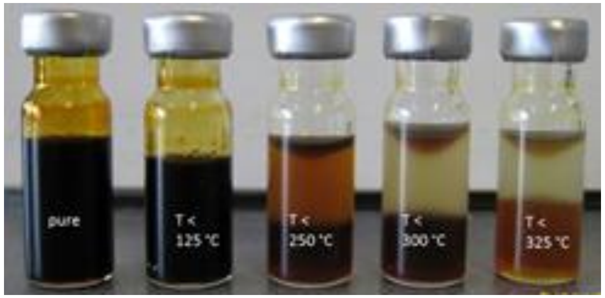


Pyrolysis Bio-oils



Upgrading/Hydrodeoxygenation

- Biofuels
- Bioliquids



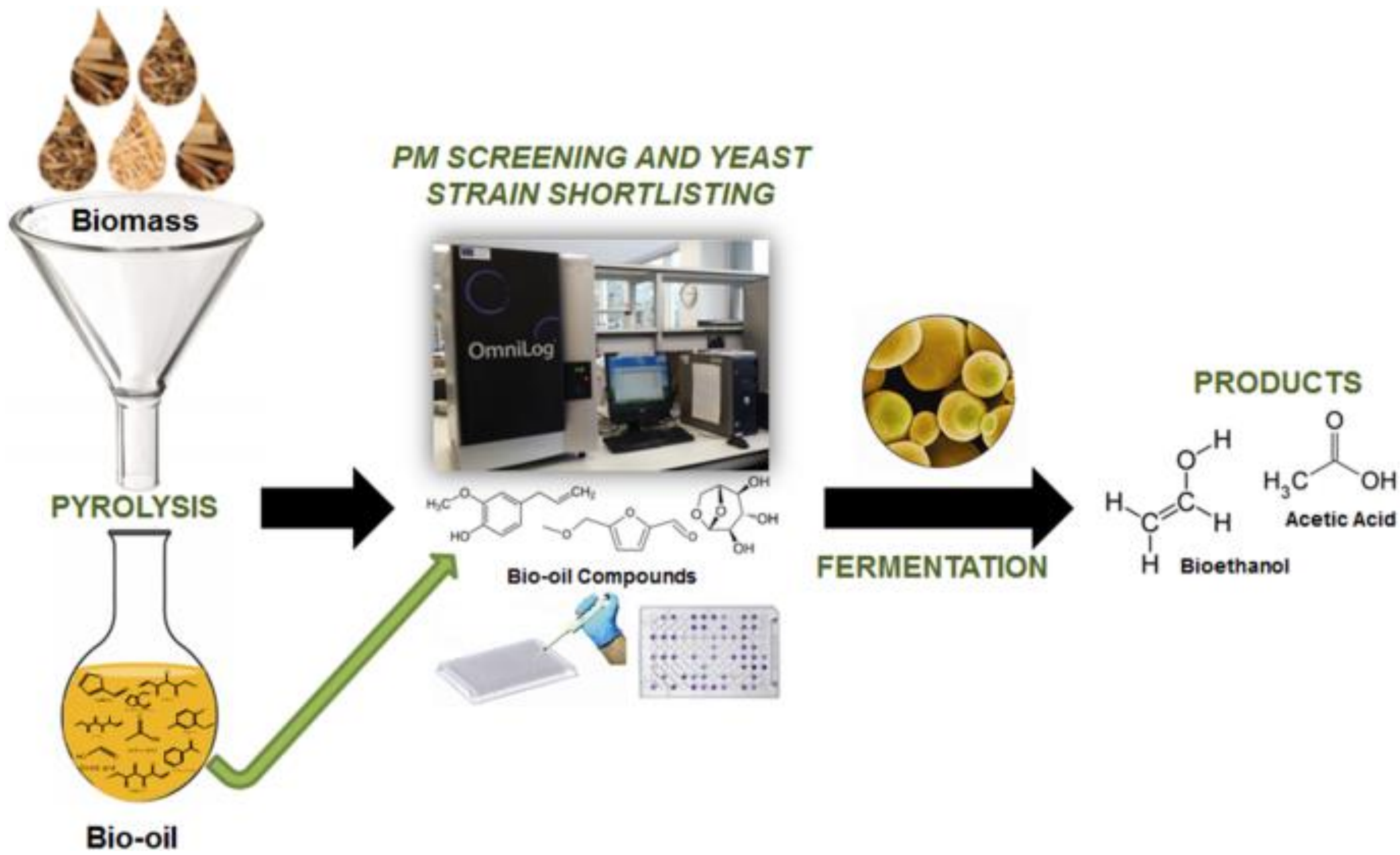
Adapted from: http://www.btg-btl.com

Biological Fermentation

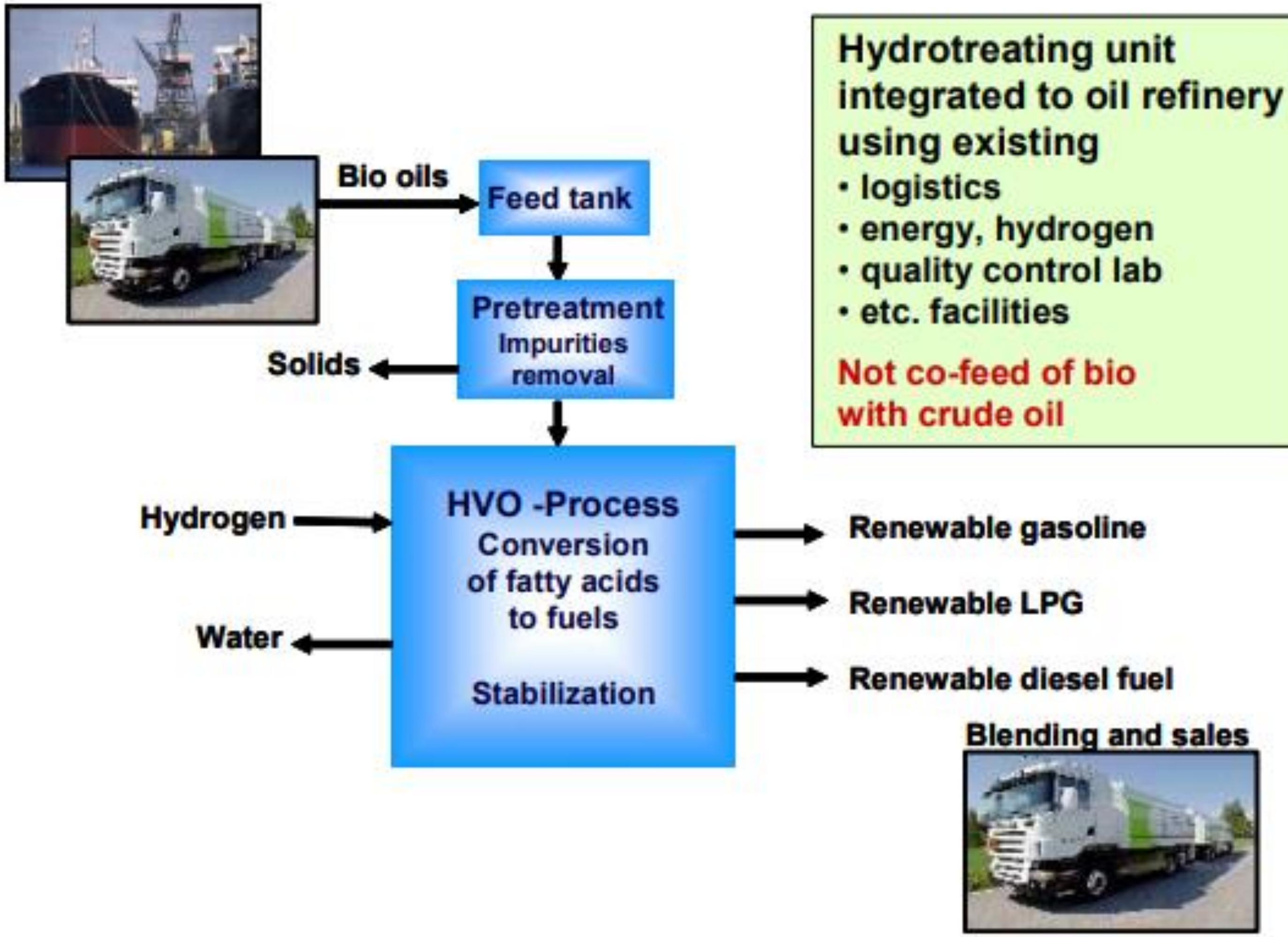
- Bulk Chemicals
- Specialty Chemicals
- Biopolymers

Production of Rhamnolipids - Biosurfactants

Production of Bioethanol and Acetic acid

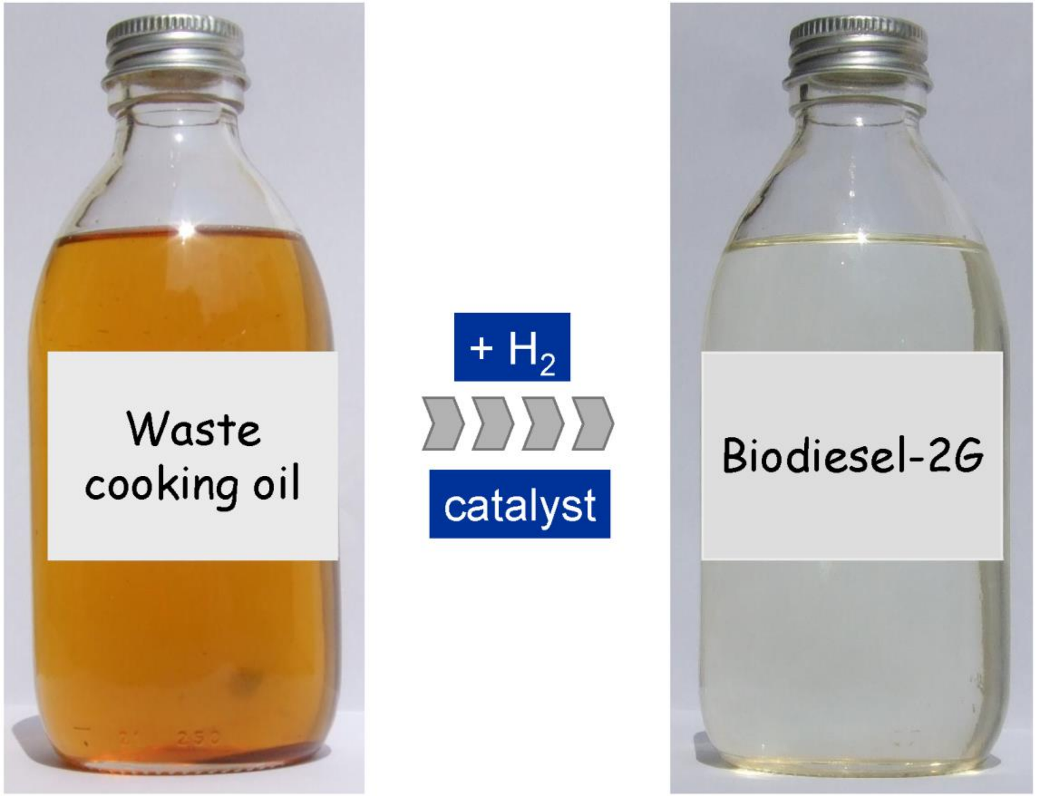


Pyrolysis of oils and fats



Pyrolysis of oils and fats

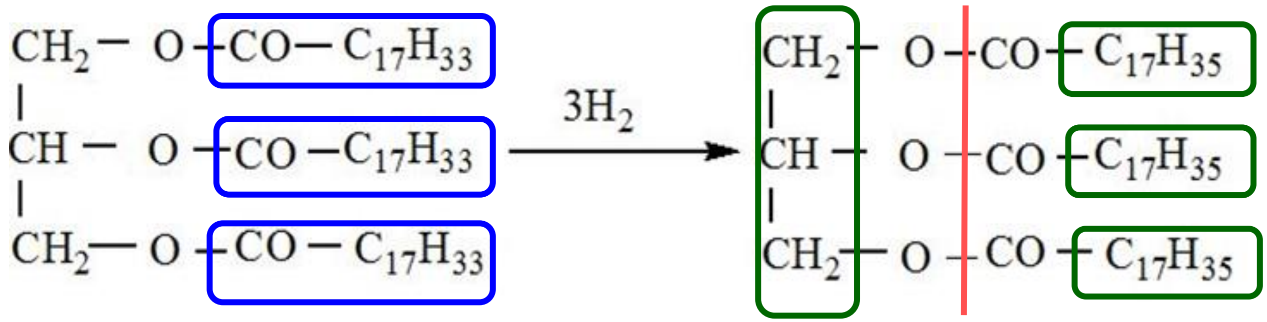
HVOs - Hydrogenated vegetable oils - Second generation biodiesel



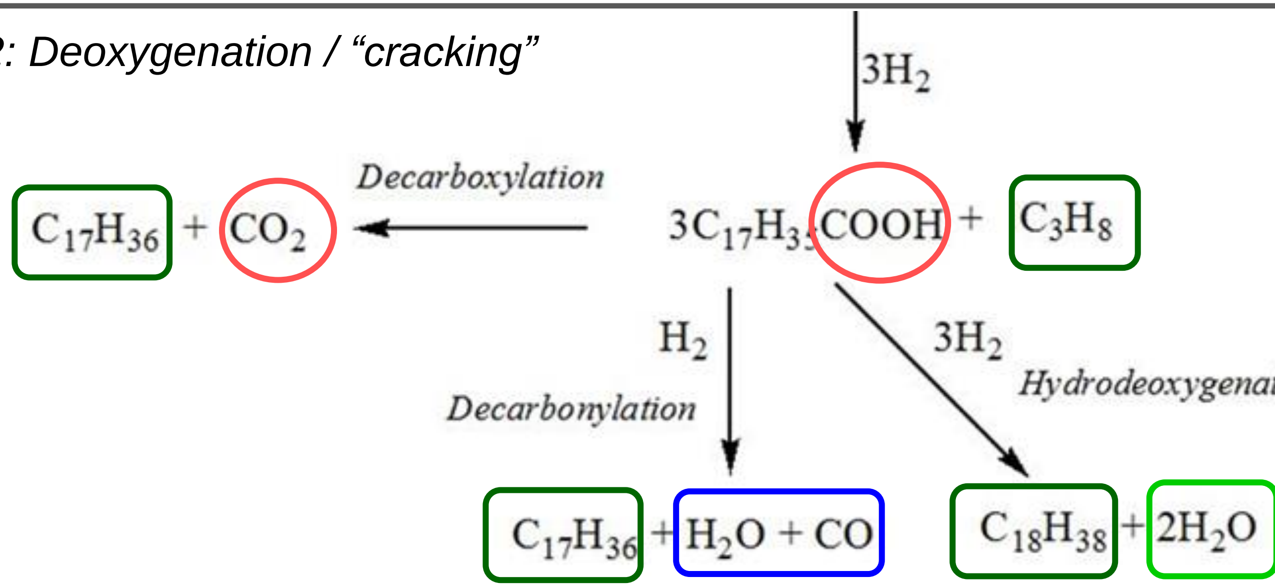
Diretiva (UE) 2018/2001 do Parlamento Europeu e do Conselho de 11 de dezembro de 2018 relativa à promoção da utilização de energia de fontes renováveis

Hydrogenation of oils and fats

Step 1: Hydrogenation of double bonds C=C



Step 2: Deoxygenation / "cracking"



Triglyceride pyrolysis

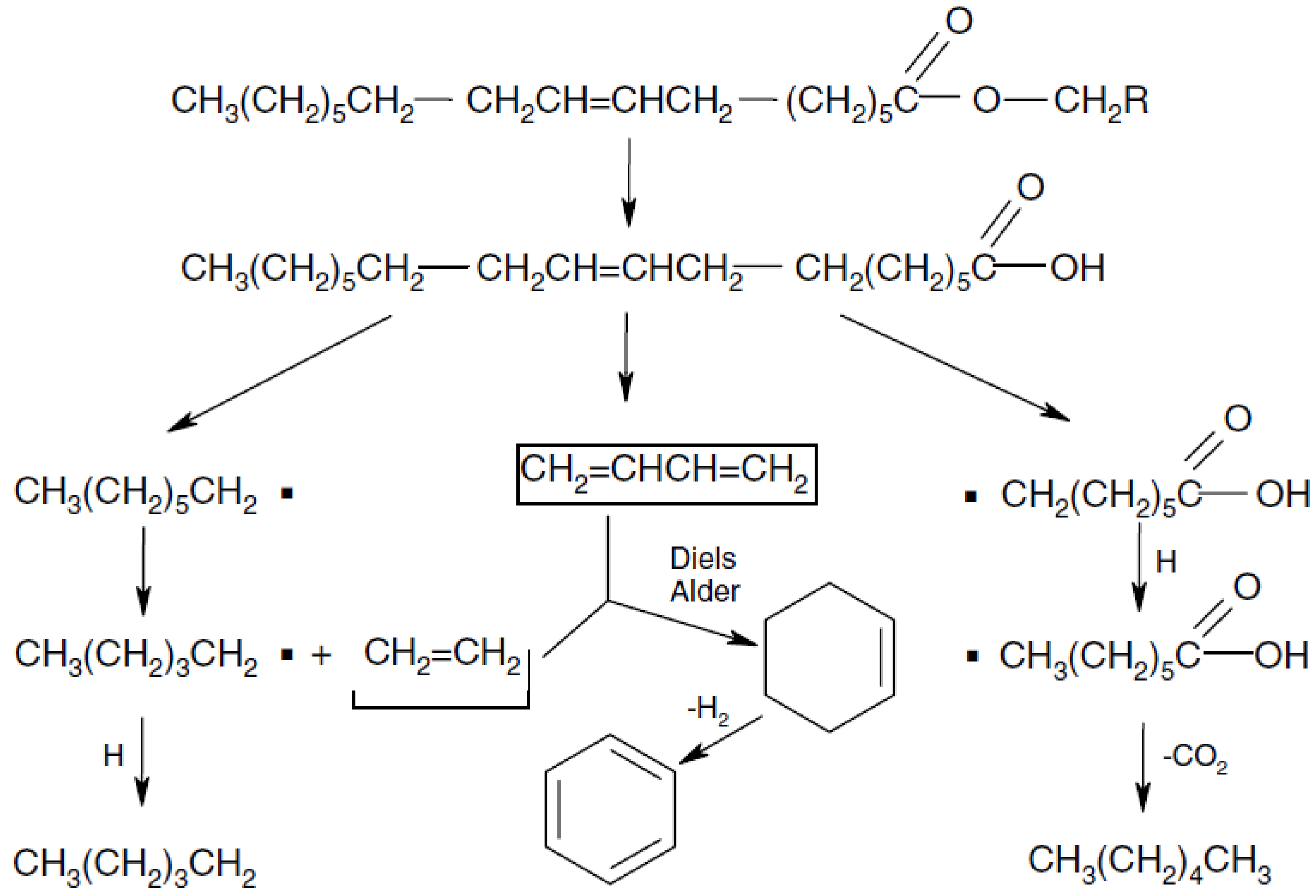
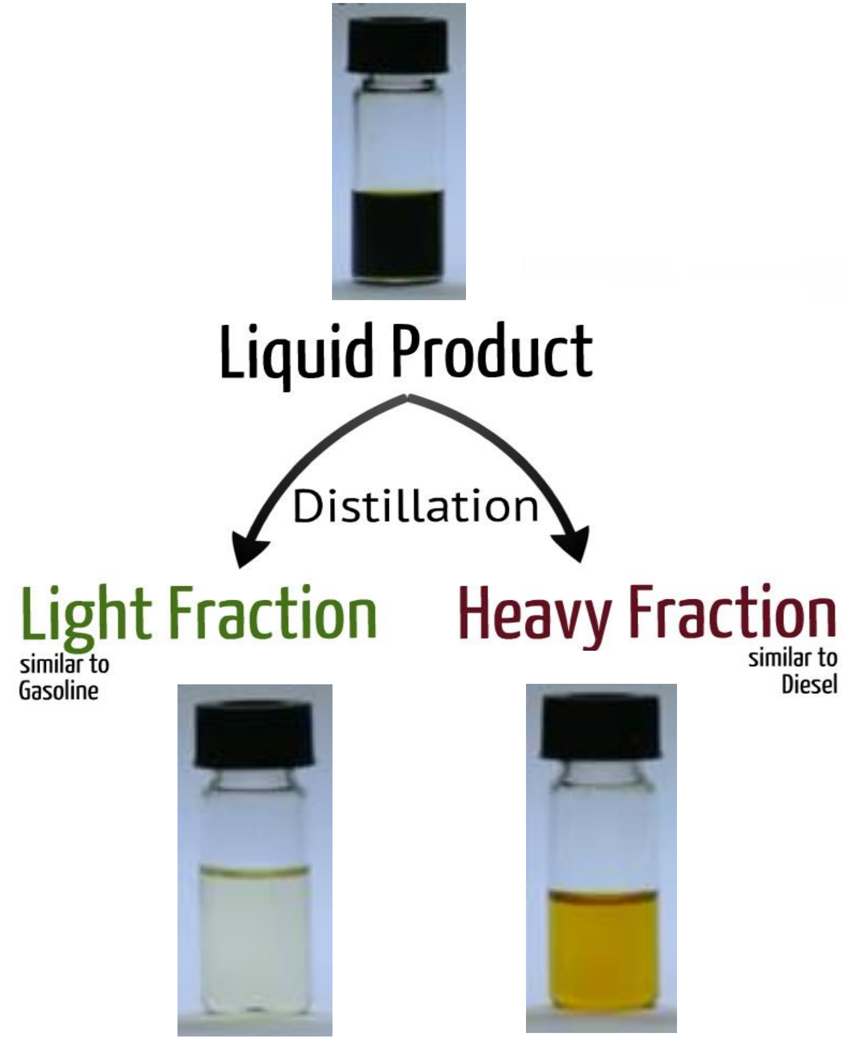
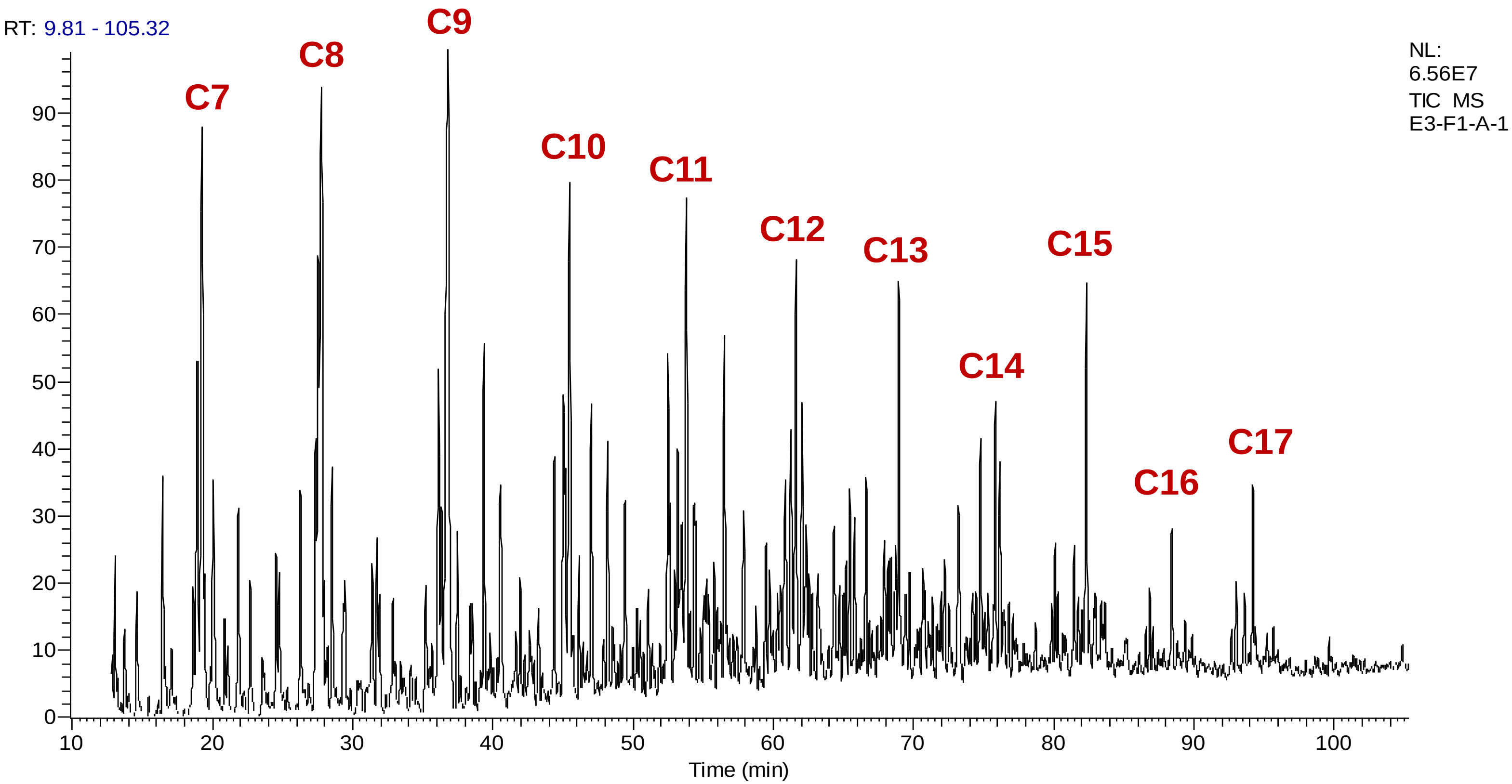


Fig. 3. Reaction mechanism for the pyrolysis of triglycerides (Schwab et al., 1988).

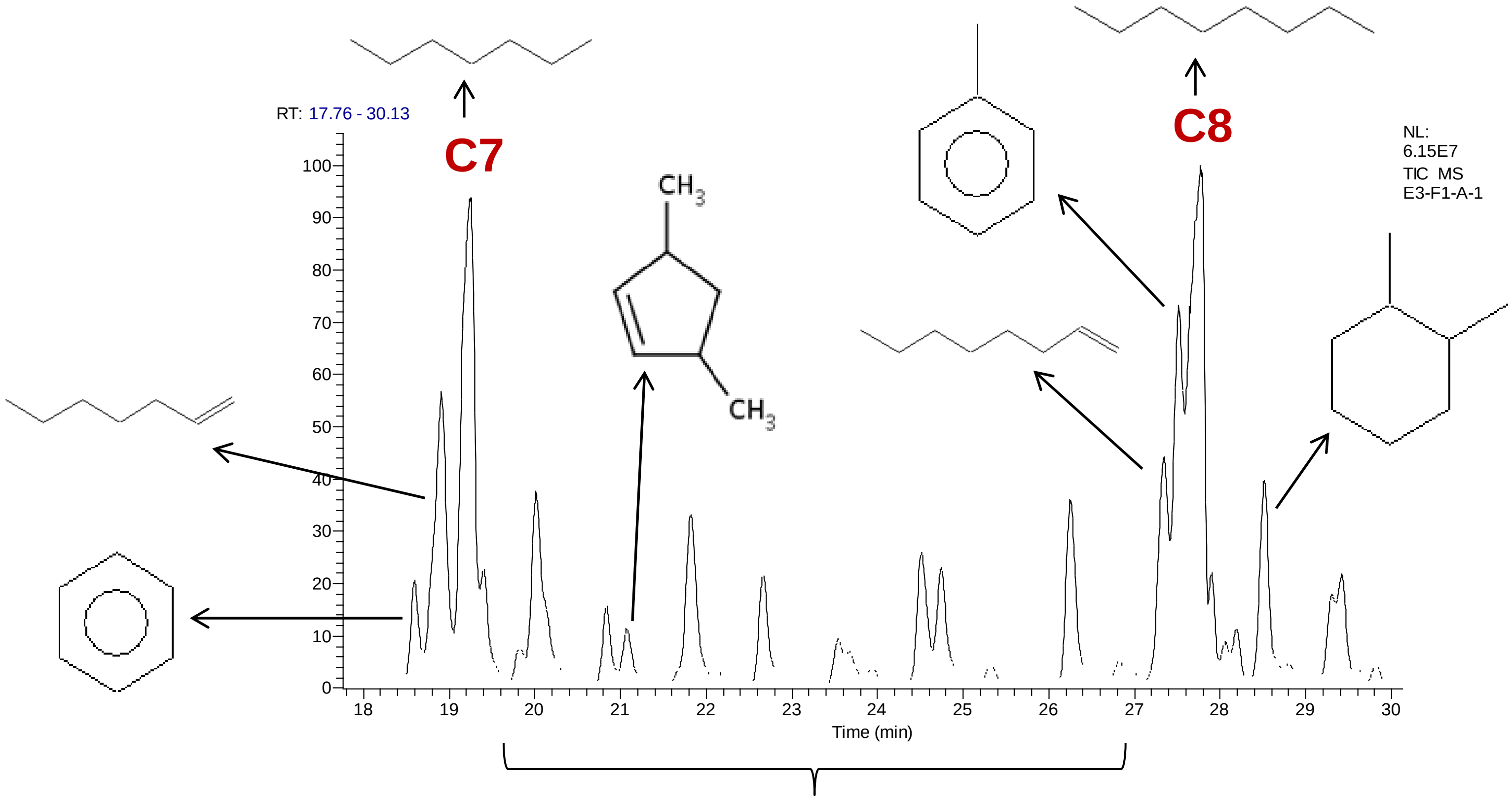
Pyrolysis of olive husk oil



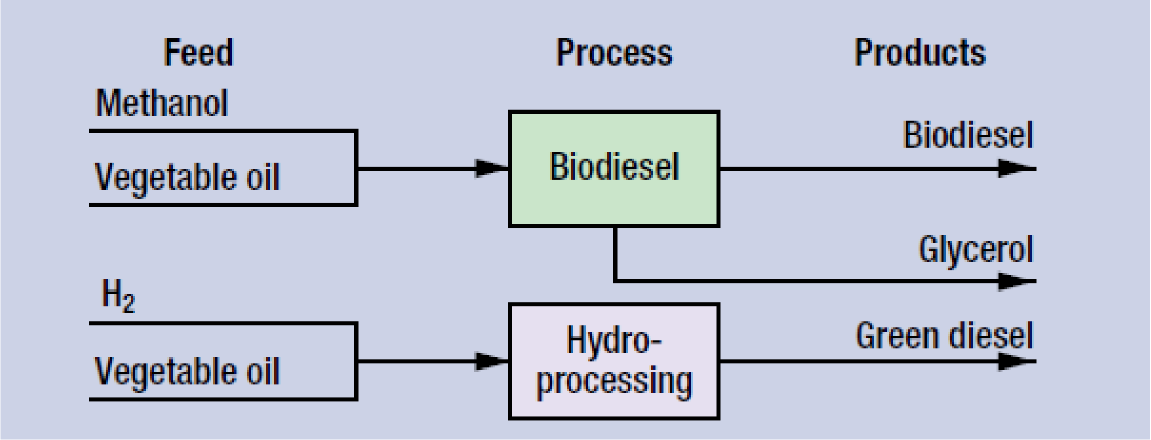
GC-MS profile – Light Fraction



GC-MS profile – Light Fraction



Heptene or Cyclopentene isomers



Honeywell UOP

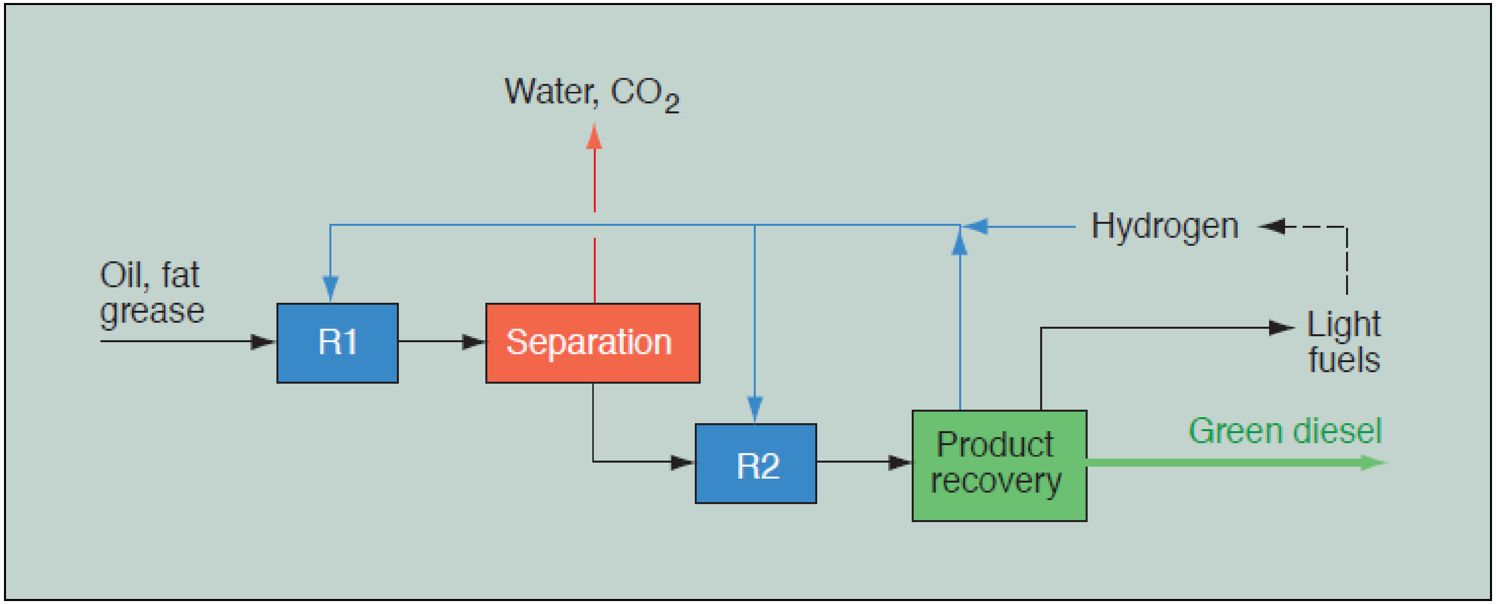
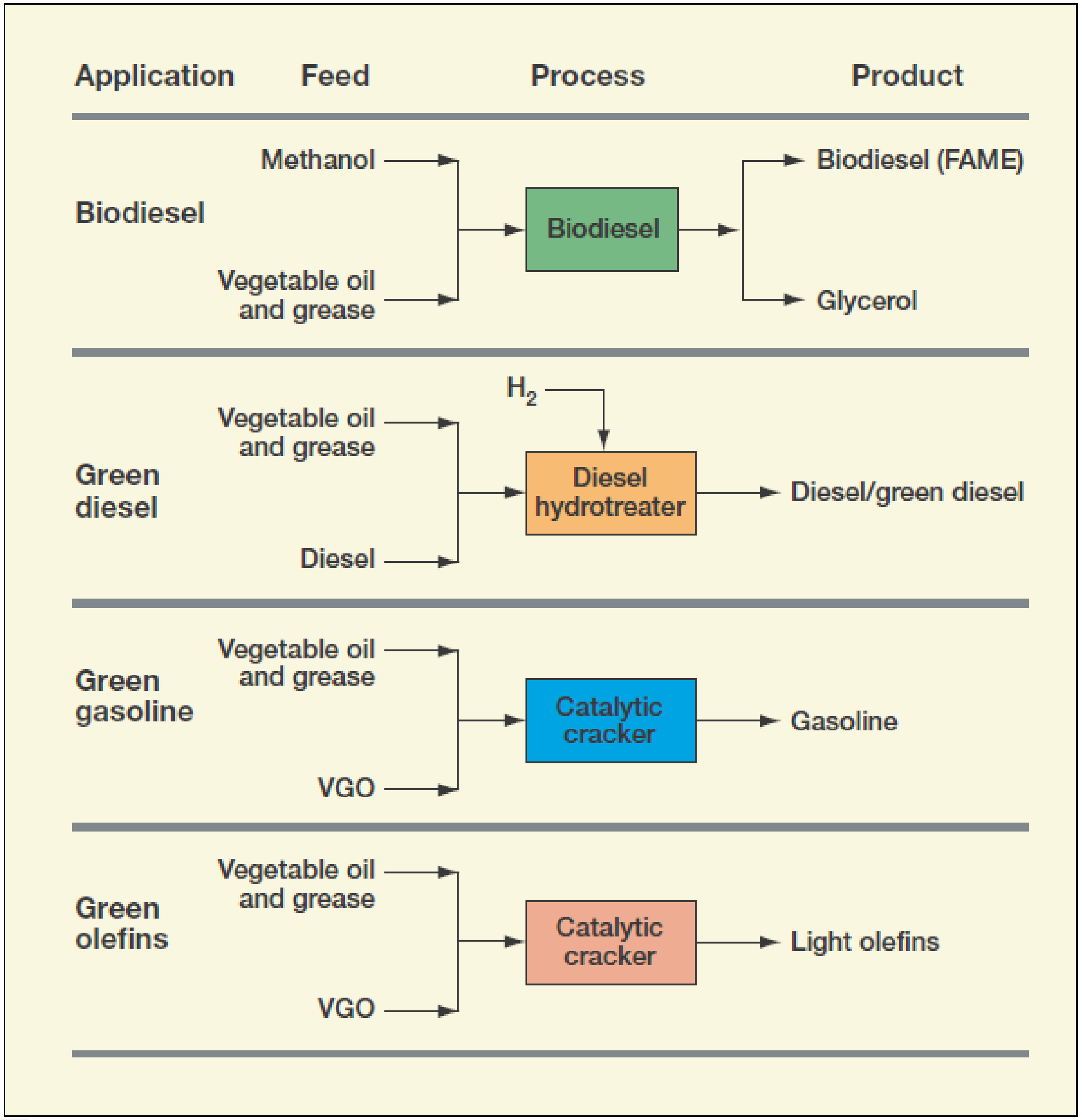
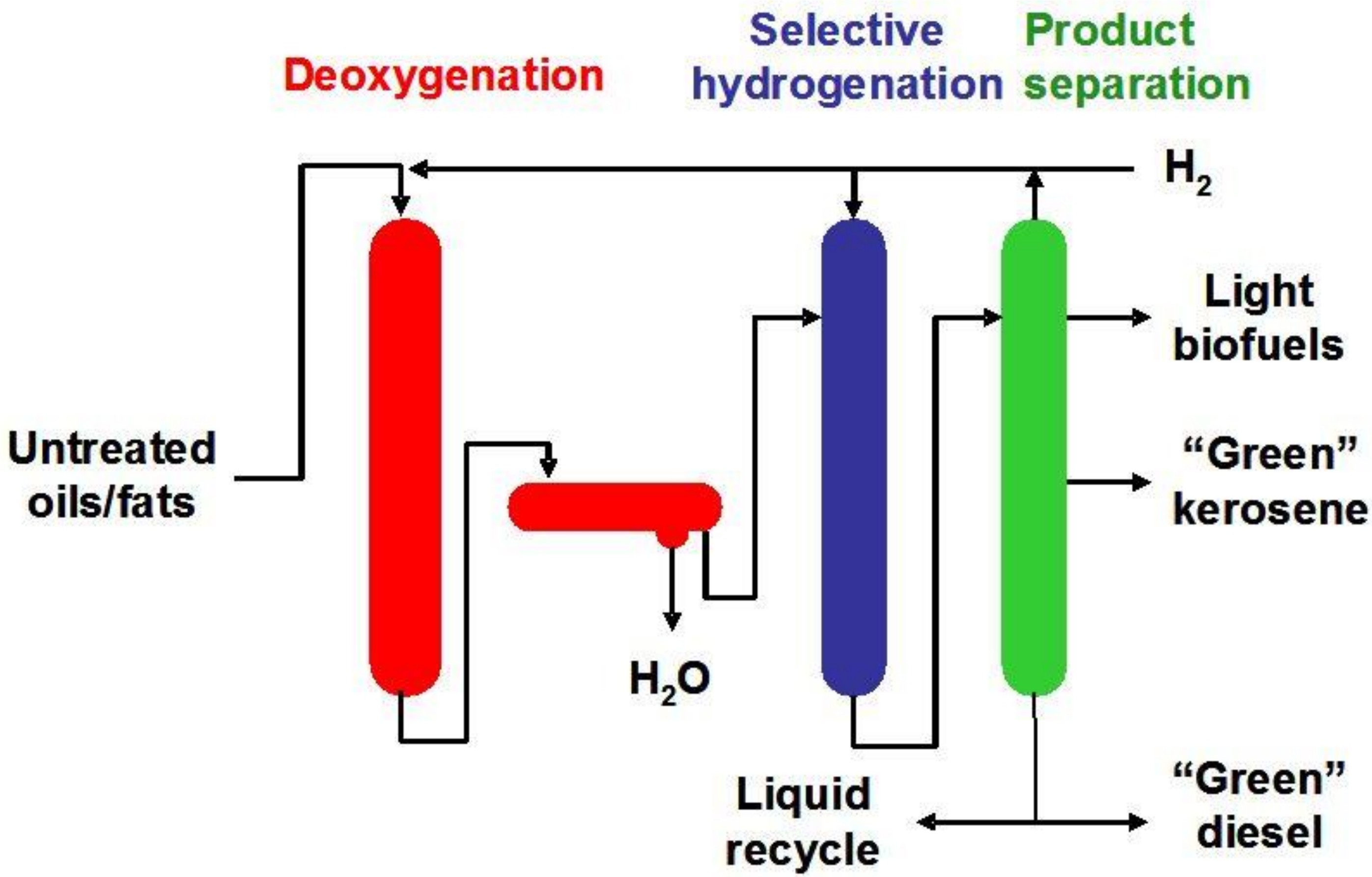


Figure 1 Simplified Ecofining process diagram


Application
Feed
Process
Product
Methanol
Biodiesel
Vegetable oil and grease
Biodiesel
Biodiesel (FAME)
Glycerol
H_2
Vegetable oil and grease
Green diesel
Diesel hydrotreater
Diesel/green diesel
Diesel
Vegetable oil and grease
Green gasoline
Catalytic cracker
Gasoline
VGO
Vegetable oil and grease
Green olefins
Catalytic cracker
Light olefins
VGO

Honeywell UOP Ecofining™ process



https://uop.honeywell.com/en/industry-solutions/renewable-fuels

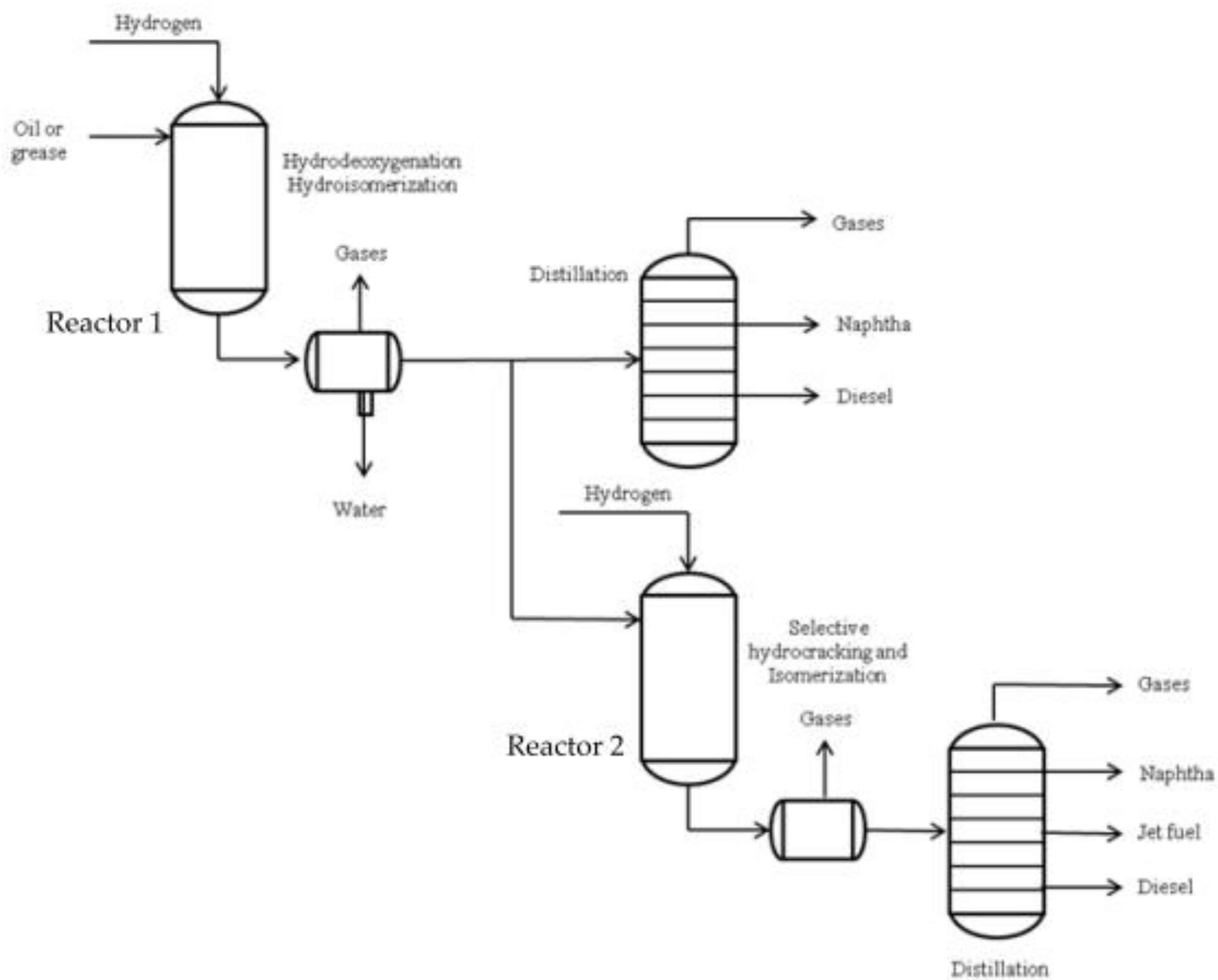


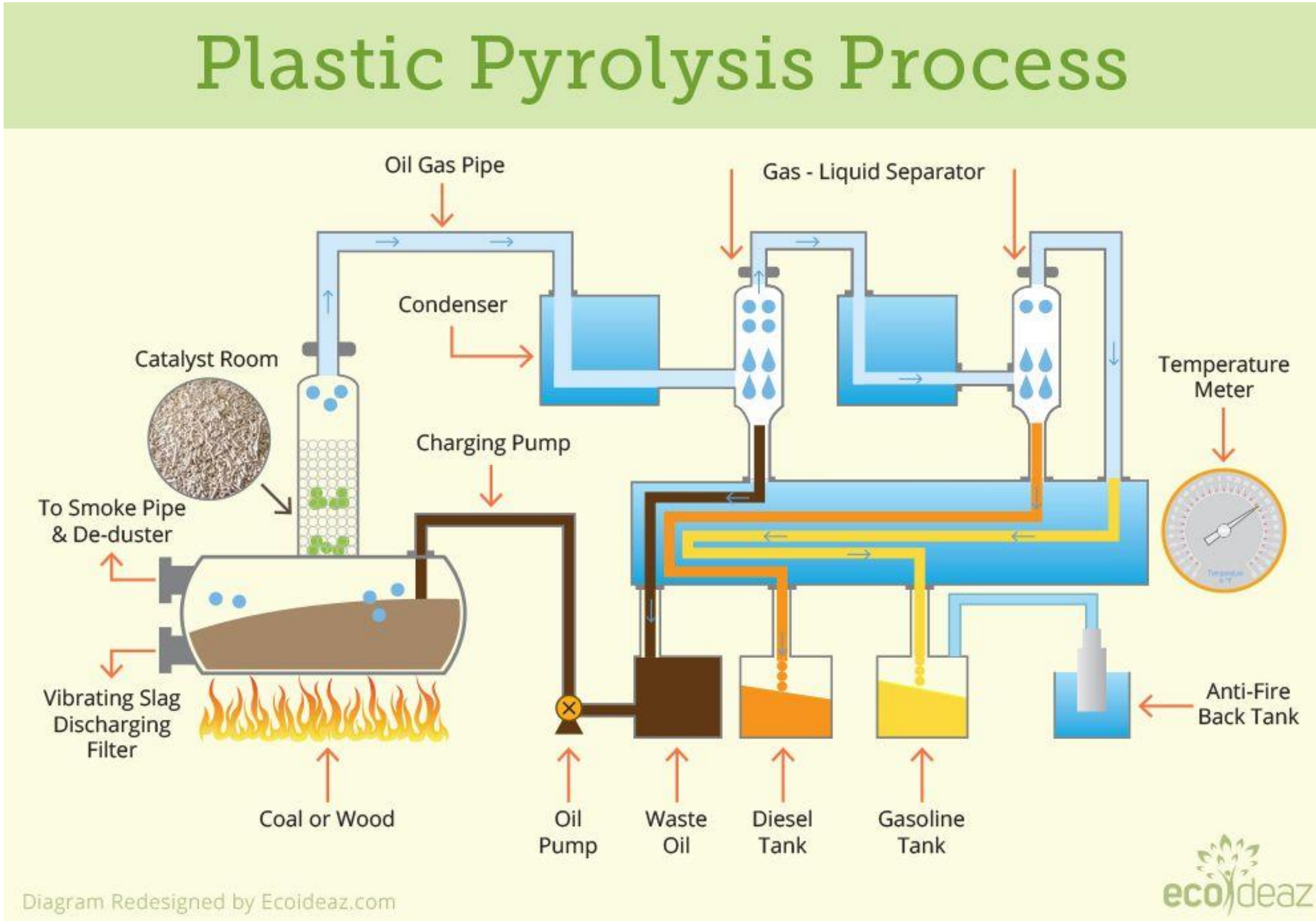
Figure 3. Schematic representation of a two-step process for obtaining green naphtha, jet fuel, and diesel coupling hydrodeoxygenation and selective hydrocracking.

Pyrolysis: a technological platform for Bioenergy, Biofuels and Bio-products

Paraguay

Galp Energia Licenses UOP/Eni Ecofining Hydroprocessing Technology for Renewable Diesel Production

Pyrolysis: a technological platform for Bioenergy, Biofuels and Bio-products



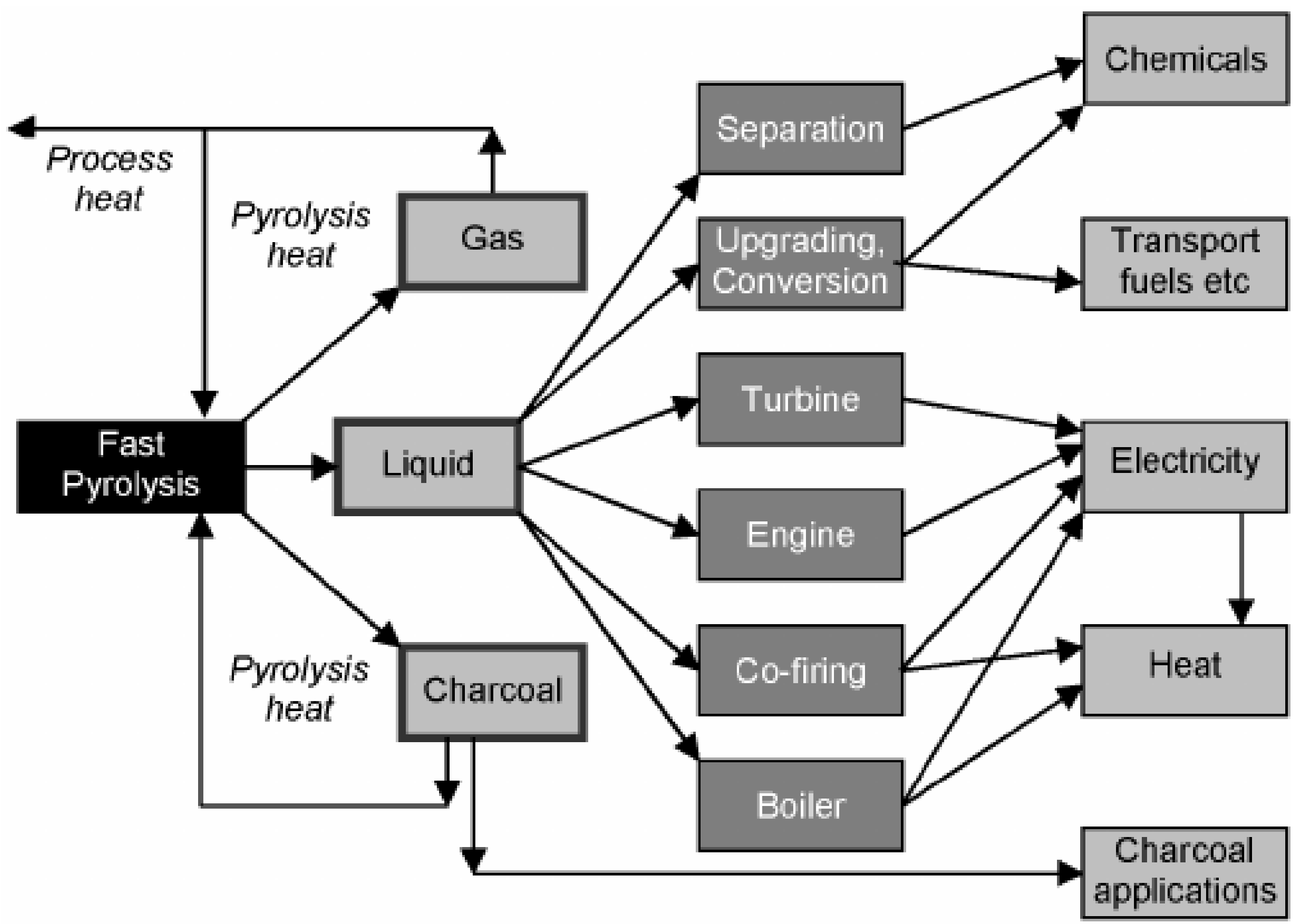
Pyrolysis: a technological platform for Bioenergy, Biofuels and Bio-products

https://www.idtechex.com/en/research-article/could-pyrolysis-help-the-world-overcome-its-plastic-waste-problem/21261






Pyrolysis as a plattform for production of bioenergy and biofuels



Pyrolysis of waste oils for the production of biofuels: A critical review
Guangcan Su, Hwai Chyuan Ong, M. Mofijur, T.M. Indra Mahlia, Yong Sik Ok
https://doi.org/10.1016/j.jhazmat.2021.127396

Hydrocarbons recovery through catalytic pyrolysis of compostable and recyclable waste plastics using a novel desk-top staged reactor
Prakashbhai R. Bhoi, Md Hafizur Rahman
https://doi.org/10.1016/j.eti.2022.102453

Thank you for your attention

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Any questions?