Budapest University of Technology and Economics

CONVERSION OF BIOMASS TO FUELS AND BASIC CHEMICALS

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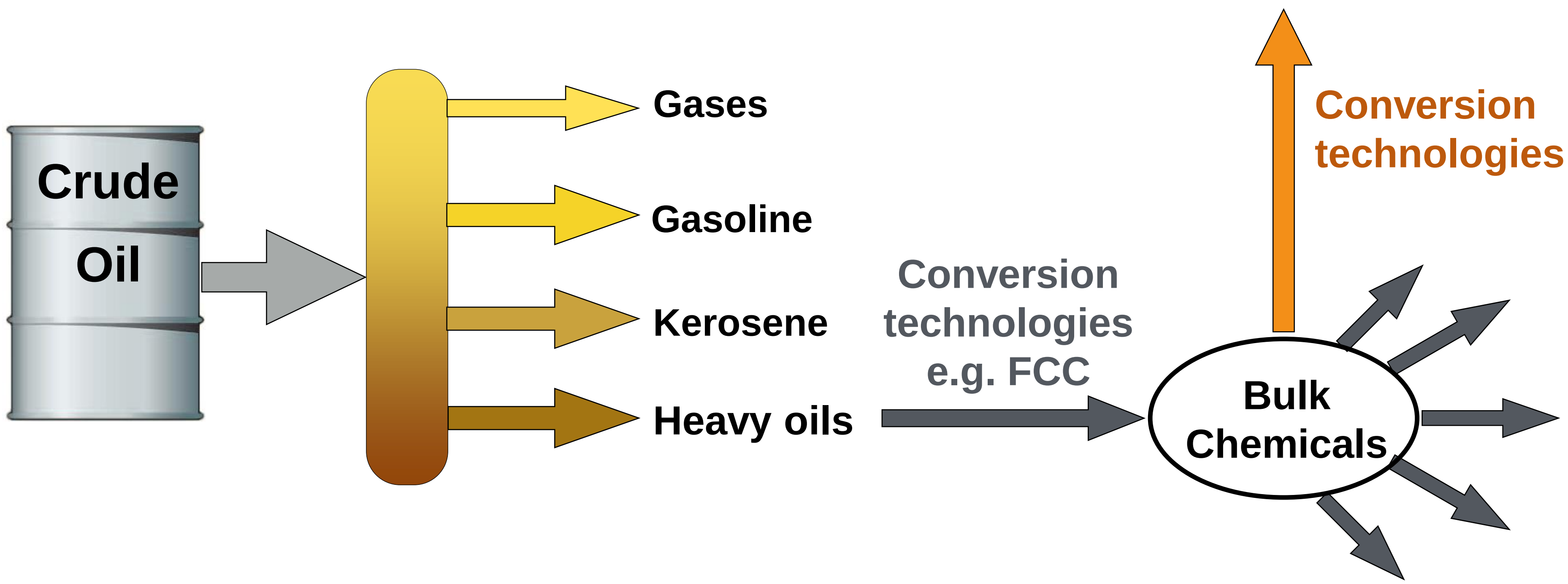
The global energy production and the carbon based products of the chemical industry are almost exclusively based on fossil carbon resources.

The processing of crude oil continuously provides transportation fuels, bulk chemicals for both petrochemical and fine chemical industries



The gradual replacement of fossil resources with renewable ones and identification of alternative synthetic routes are key challenges of future's energy and chemical industry.

Náray-Szabó, G.; Mika, L. T. *Green Chem.* **2018**, 20, 2171,

Biomass could be an ideal alternative as it is one of the most abundant carbon resources and globally available on the Earth.




However, the selection and consumption of appropriate resources have become a controversial issue due to the dramatically increased utilization of edible resources.

The utilization of biomass-based waste streams have to be preferred!

Mika, L. T.; Cséfalvay, E.; Németh, Á. *Chem. Rev.*, **2018,** *118***,** 505**.**
Mika, L. T.; Cséfalvay, E.; Horváth, I. T. *Catal. Today*, **2015**, *247*, 33.
Horváth, I. T.; Anastas, P. *Chem. Rev.*, **2007**,*107*, 2169.

Replacement of Fossil Resources

AND

HANGING RESOURCES, BUILDING BLOCKS, SOLVENTS, PRODUCTS AND ....

Fossil Resources

Coal

Natural Gas

Oil

Fossil Basic Chemicals

Methanol
Ethylene
Propylene
Butadiene
Benzene
Toluene
Xylene
$CO:H_2$

Renewable Basic Chemicals

Ethanol
Glycerol
Fructose
Xylose
Glucose
Fatty acids
Chitin
...

and natural gas

Renewable Resources

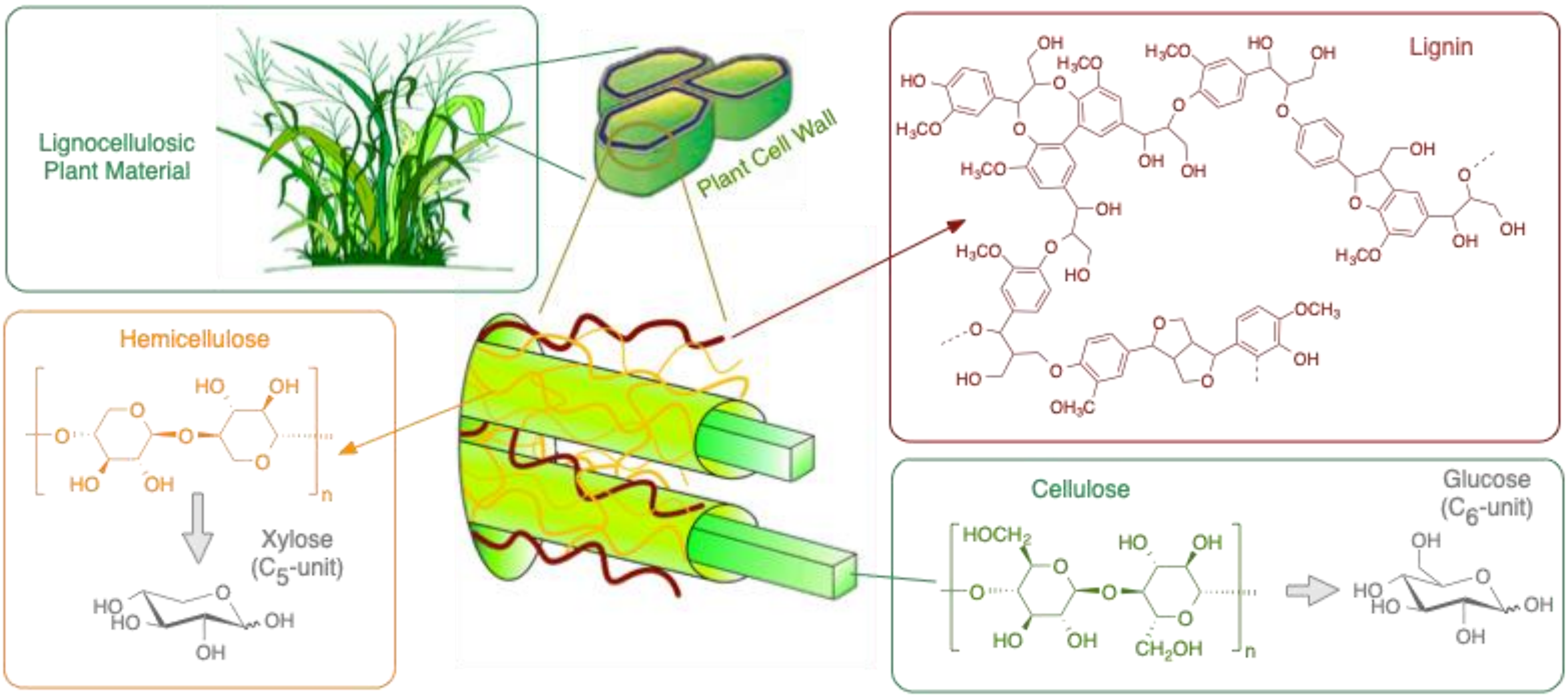
Carbon-dioxide

Water

Lignocellulose

Lipids and Oils

SCHEMATIC ILLUSTRATION OF LIGNOCELLULOSE



Other components: lipids, oils, inorganic salts etc.

Mika, L. T.; Cséfalvay, E.; Németh, Á. *Chem. Rev.*, **2018,** *118*, 505.

ELEMENTAL COMPOSITION OF FOSSIL AND SELECTED BIOMASS RESOURCES

Resources	Carbon (wt%)	Hydrogen (wt%)	Oxygen (wt%)	Nitrogen (wt%)	Sulfur (wt%)
Anthracite	91.0-94.0	2.0-4.0	2.0-5.0	0.6-1.2	0.6-1.2
Bituminous coal	83.0-89.0	4.0-6.0	3.0-8.0	1.4-1.6	1.4-1.7
Petroleum	**83.0-87.0**	**10.0-14.0**	**0.05-1.5**	**0.1-2.0**	**0.05-6.0**
Black coal	76.0-87.0	3.5-5.0	2.8-11.3	0.8-1.5	0.5-3.1
Peat	52.0-56.0	5.0-6.5	30.0-40.0	1.0-3.0	0.05-0.3
Miscanthus fresh	47.3-47.7	5.8-6.0	42.1-43.5	0.33-0.45	0.05-0.08
Switchgrass	43.5-47.5	5.8-6.2	37.6-44.8	0.36-0.77	0.04-0.19
Sorghum stalk	40.0-46.1	5.2-5.8	40.6-40.7	0.39-1.40	0.20-0.27
Straw (average)	45.0-47.0	5.8-6.0	40.0-46.0	0.4-0.6	0.05-0.2
Corn cob	49.0	5.4	44.6	0.4	-
Corn stover	42.6	5.1	36.5	0.83	0.09
Forest residues	48.0-52.0	6.0-6.2	40.0-44.0	0.3-0.5	< 0.05
Wood without bark	48.0-52.0	6.2-6.4	38.0-42.0	0.1-0.5	< 0.05
Sunflower husk	47.4	5.8	41.4	1.4	0.05

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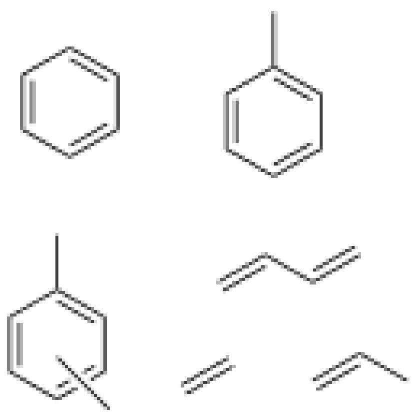
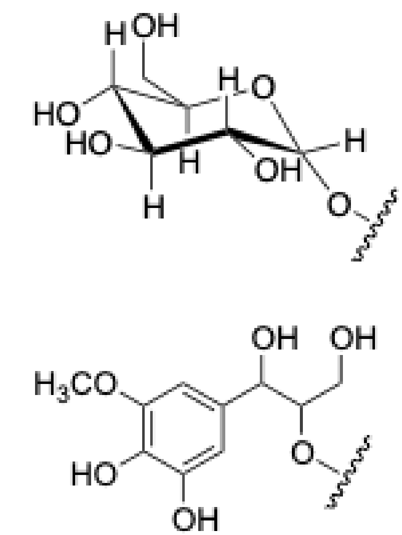
CONVERSION STRATEGIES OF PETROLEUM AND BIOMASS BASED FEEDSTOCKS

MŰEGYETEM 1782

Petroleum

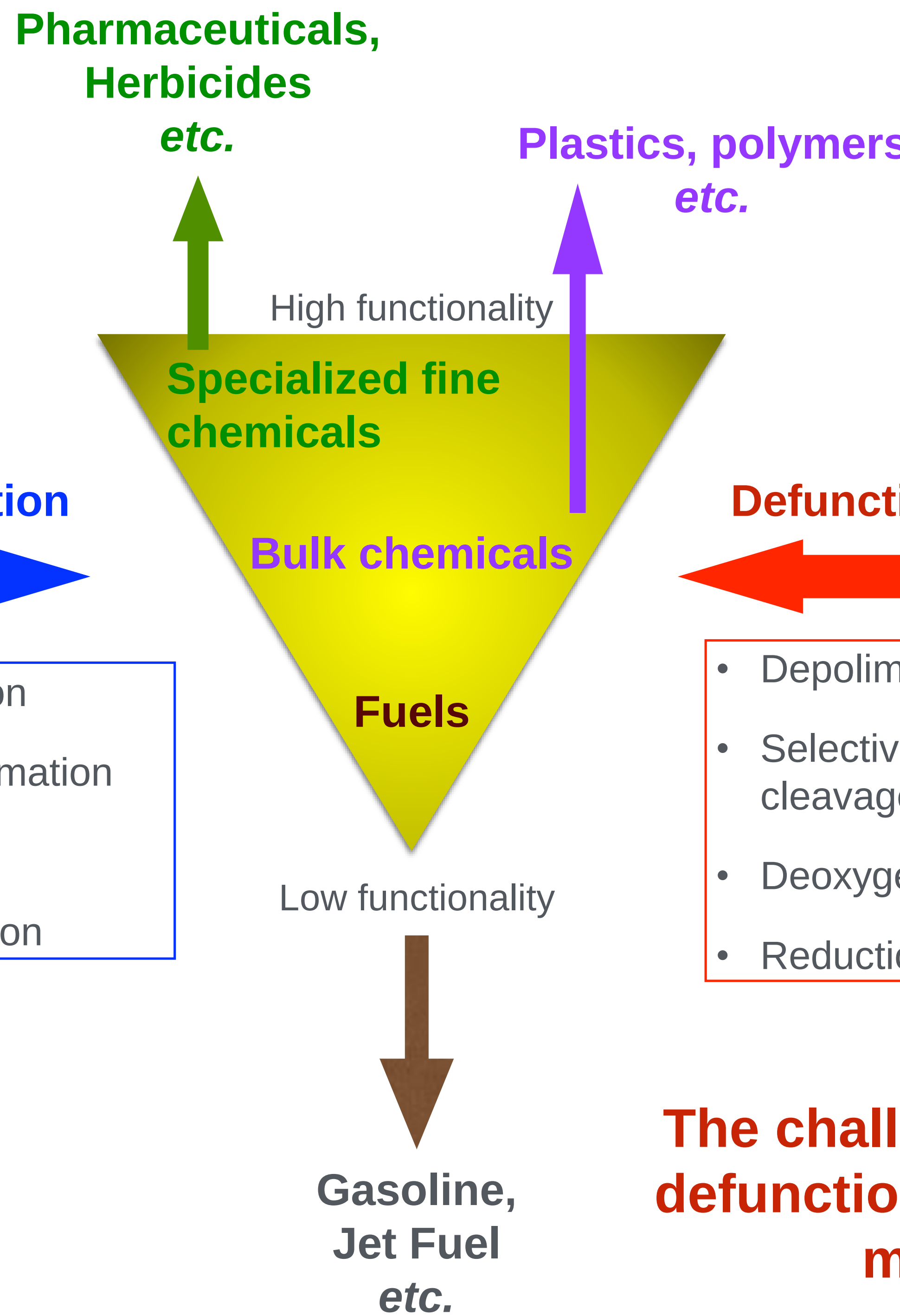


Renewable



Functionalization

- Polymerization
- C-C bond formation
- Oxidation
- Oligomerization



Defunctionalization

- Depolimerization
- Selective bond cleavage
- Deoxygenation
- Reduction

The challenge is selective addition of functionality

The challenge is selective defunctionalization/depolymerization

Mika, L. T.; Cséfalvay, E.; Németh, Á. *Chem. Rev.*, **2018,** *118*, 505.
Deuss, P. J.; Barta, K.; de Vries, J. G. *Catal. Sci. Technol.* **2014**, *4*, 1174–24.

BIOMASS WASTE VALORIZATION PROCESSES

Wastes

Pretreatment and/or Preprocessing

Drying, grinding, organosolv separation etc.

Chemo- and/or bio**catalytic conversion** of selected fraction

to produce

Initial Platform Chemicals as building blocks

Pyrolysis and Gasification

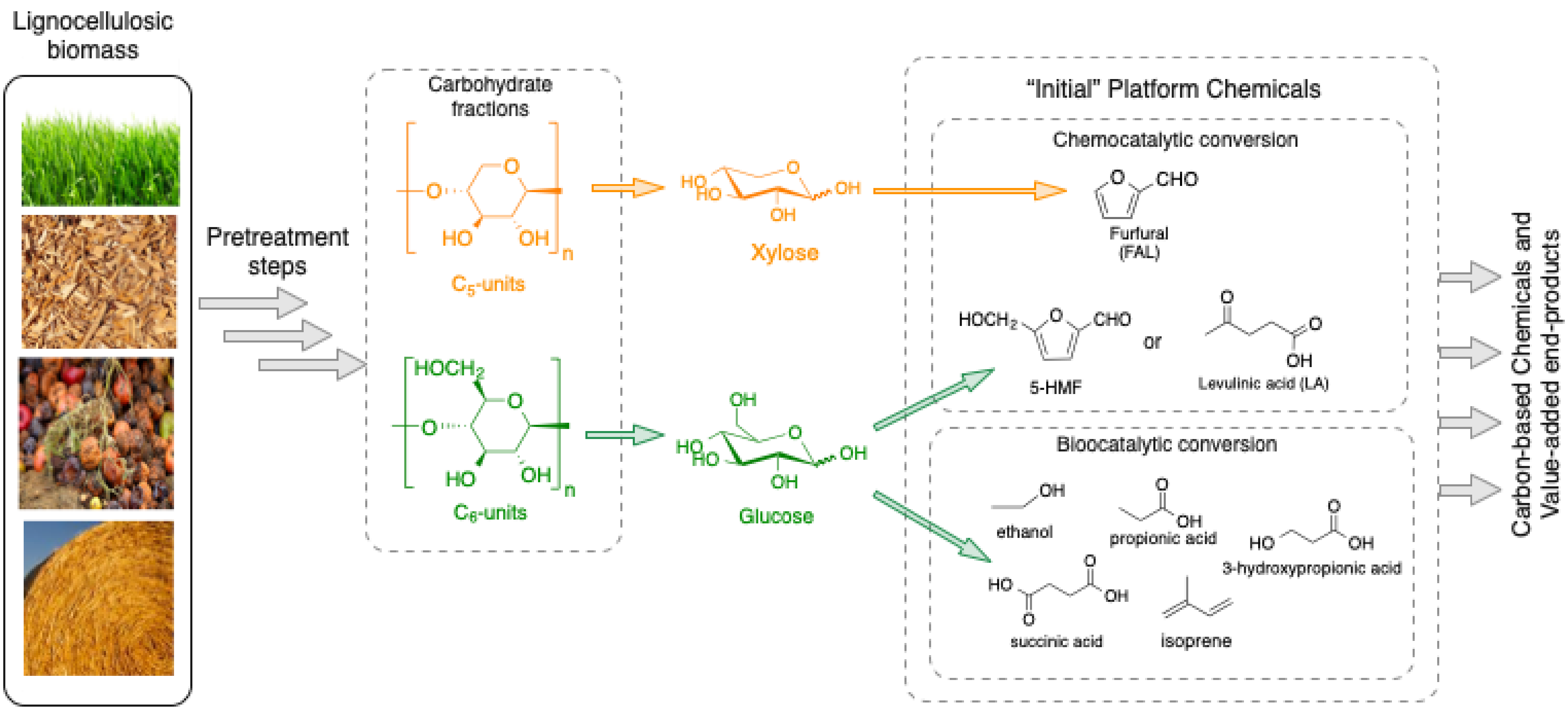
to produce

gaseous energy carriers, C_1 building blocks, and hydrogen

Hydrothermal liquefaction

to produce bio-oil(s) that can be utilized as a feedstock of existing refinery structure

The destruction of lignocellulosic feedstocks followed by oxygen removal from its cellulose and hemi-cellulose content by catalytic processes results in the formation of **Initial Platform Chemicals (IPCs)**



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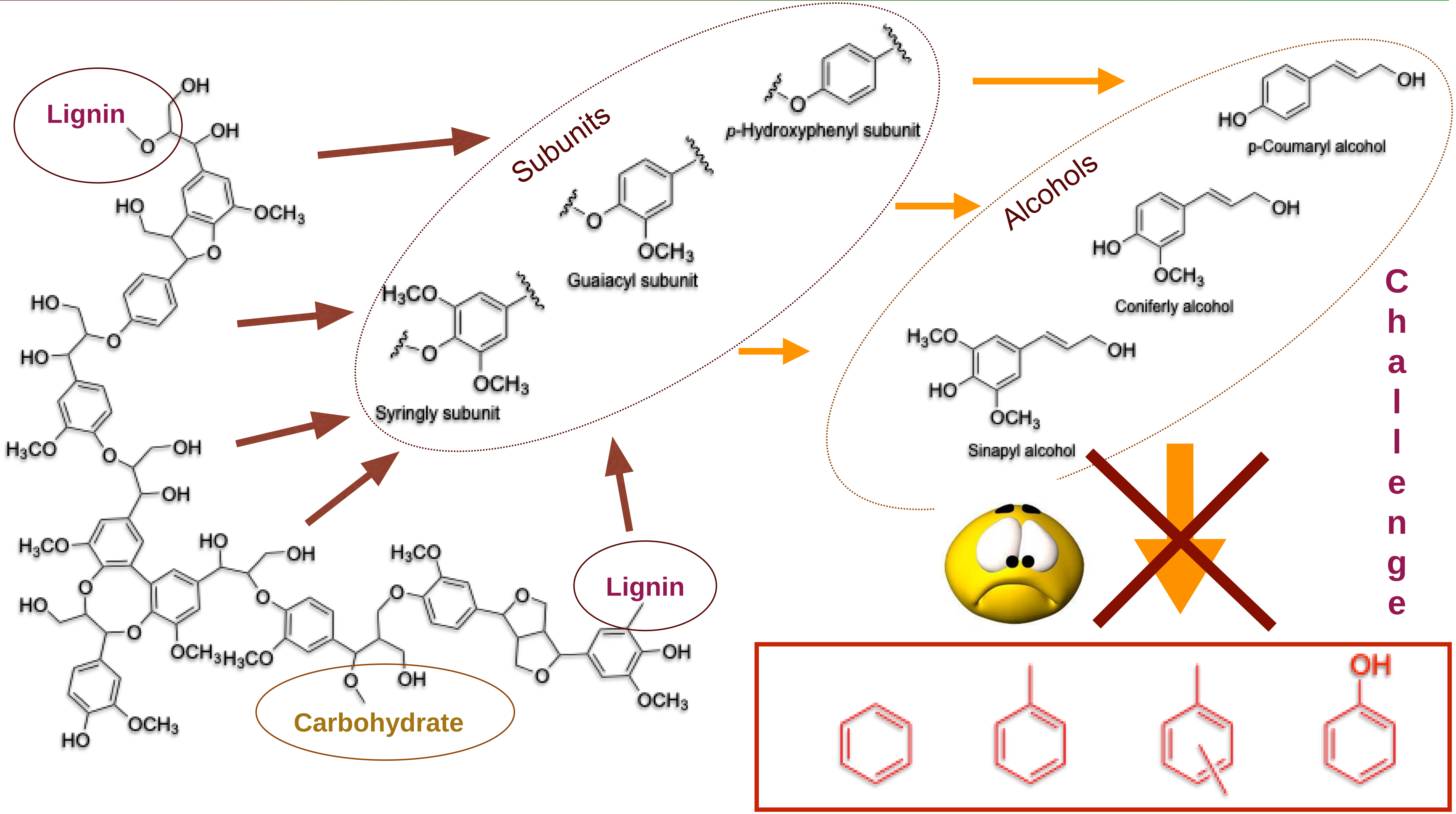
CONVERSION OF LIGNIN FRAGMENT TO MONOLIGNOLS AND TO ???



Although several functionalized aromatics were successfully synthesized from lignin, no data have been reported on its conversion to phenol, toluene, benzene, and other simple aromatic building blocks.

Deuss, P. J.; Barta, K.; de Vries J. G. *Catal. Sci. Technol.*, **2014**, *4*, 1174.

PROCESSES INVOLVED IN BIOMASS GASIFICATION

Biomass gasification process consists of many overlapping processes: drying, pyrolysis, partial oxidation, reforming, clean up etc..

Preprocessing of biomass → **Gasification** → **Gas clean-up and reforming** → **Gas utilization**

Preprocessing of biomass	Gasification	Gas clean-up and reforming	Gas utilization
Size reduction, Drying Preparation of gasifying agents	Heating Chemical reactions Catalysis	Separation of tar from syngas Gas reforming Catalysis	Gas turbine Gas burner Fuel cell Power generation

Upstream process

Gasification process

Downstream processes

PRE-PROCESSING OF BIOMASS RESIDUES

- Biomass collected from farm, agricultural - and forest lands may contain high moisture.
- Drying is needed to obtain a desired range of water content for the gasification processes.
- Drying is an energy intensive process which may decrease the overall energy efficiency of the process.
- In the case of gasification, waste heat can be utilized to decrease the moisture content of the biomass which will increase the overall efficiency of the process.
- Perforated bin dryers, band conveyor dryers and rotary cascade dryers have been used to dry biomass
- In the case of generating combined heat and power, biomass moisture should be as low as possible to increase the overall efficiency and decrease the net cost of electricity.
- Having low moisture content of raw biomass (typically less than 10%) drying stage may be eliminated from the process.

MOISTURE CONTENTS OF VARIOUS WASTE RESOURCES

Forestry residues

Agricultural residues

Food waste

Type	Moisture content (wt%)
Bark	45–65
Coniferous tree with needles	50–60
Fresh wood chips and sawdust	40–60
Dry wood chips and sawdust	10–20
Fresh wood chips	40–60
Wood chips stored and air-dried	30–40
Waste wood	10–30
Yard waste, mostly wood chips	38.07
Corn stover	5–6.06
Corn stalk	8.02
Rice hulls	10.94
Rice straw	9
Post-hydrolysis lignocellulose	13–20.6
Sunflower stalks sundried after harvesting in India	9.20
Wheat straw for gasification or energy	6.00–11
Mixed waste paper	8.75
Sugar cane bagasse in Hawaii	10.39
Average in the EU	70–80
Average in the USA	72
Dining halls in South-Korea	80

Mika, L. T.; Caéfalvay, E.; Horváth, I. T. *Catal. Today*, **2015**, *247*, 33.

GASIFICATION REACTIONS

Carbonation

$C + CO_2 \rightleftharpoons 2\,CO$
Boudouard reaction

$C + H_2O \rightleftharpoons CO + H_2$
Water-gas reaction

$C + 2H_2 \rightleftharpoons CH_4$
Hydrogasification

$C + 0.5O_2 \rightleftharpoons CO$

Oxidation

$C + O_2 \rightleftharpoons CO_2$

$CO + 0.5O_2 \rightleftharpoons CO_2$

$CH_4 + 2O_2 \rightleftharpoons CO_2 + H_2O$

$H_2 + 0.5O_2 \rightleftharpoons H_2O$

Water-Gas Shift

$CO + H_2O \rightleftharpoons CO_2 + H_2$

Methanation

$2CO + 2H_2 \rightleftharpoons CH_4 + CO_2$

$2CO + 3H_2 \rightleftharpoons CH_4 + H_2O$

$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$

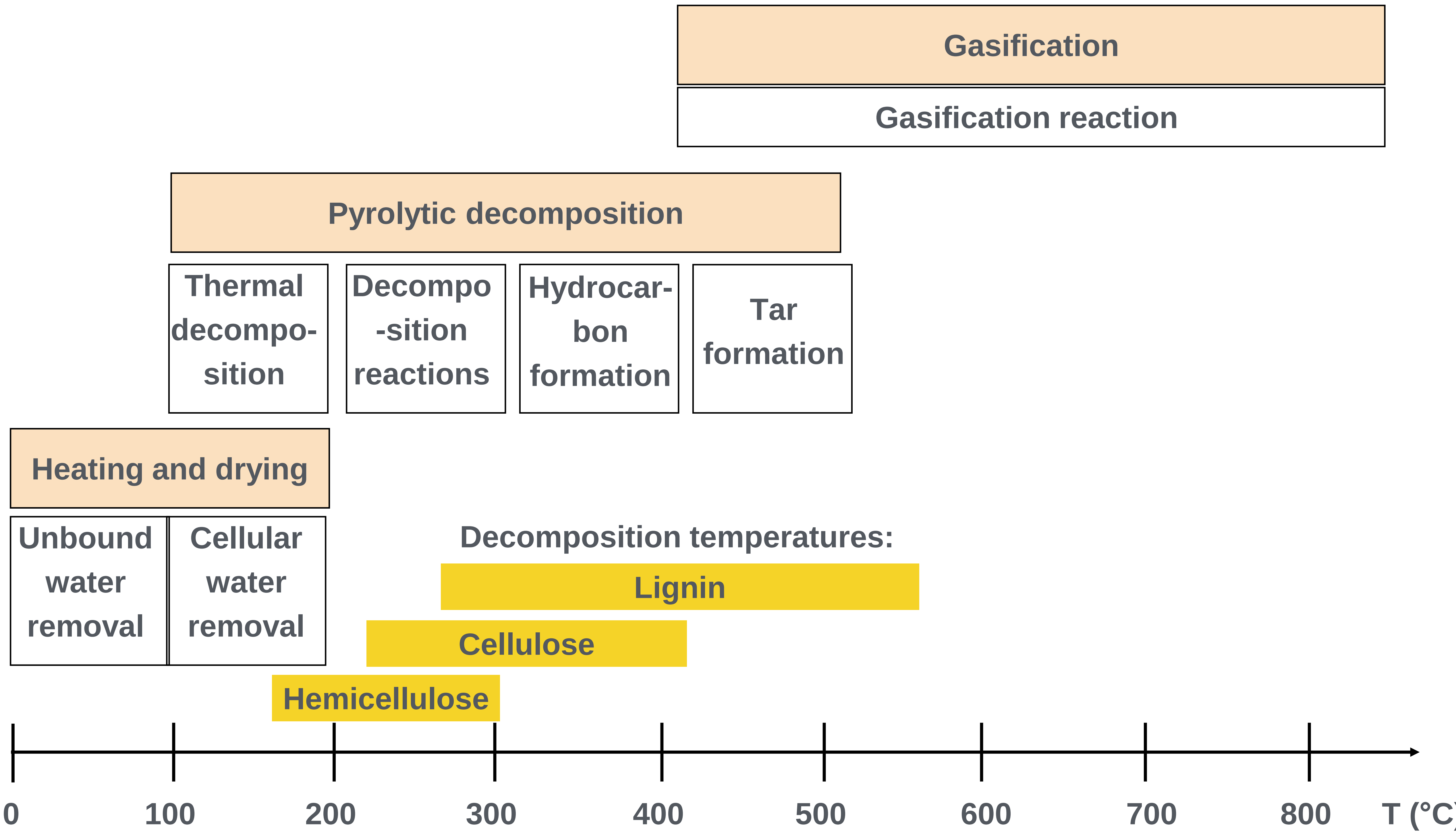
Steam reforming

$2CH_4 + H_2O \rightleftharpoons CO + 3H_2$

$2CH_4 + 0.5O_2 \rightleftharpoons CO + 2H_2$

Sikarwar, V. S.; Zhao, M.; Clough, P.; Yao, J.; Zhong, X.; Memon, M. Z.; Shah, N.; Anthony, E. J.; Fennell, P. S.
Energy Environ. Sci. **2016**, *9*, 2939–2977.

PROCESSES AT DIFFERENT TEMPERATURES



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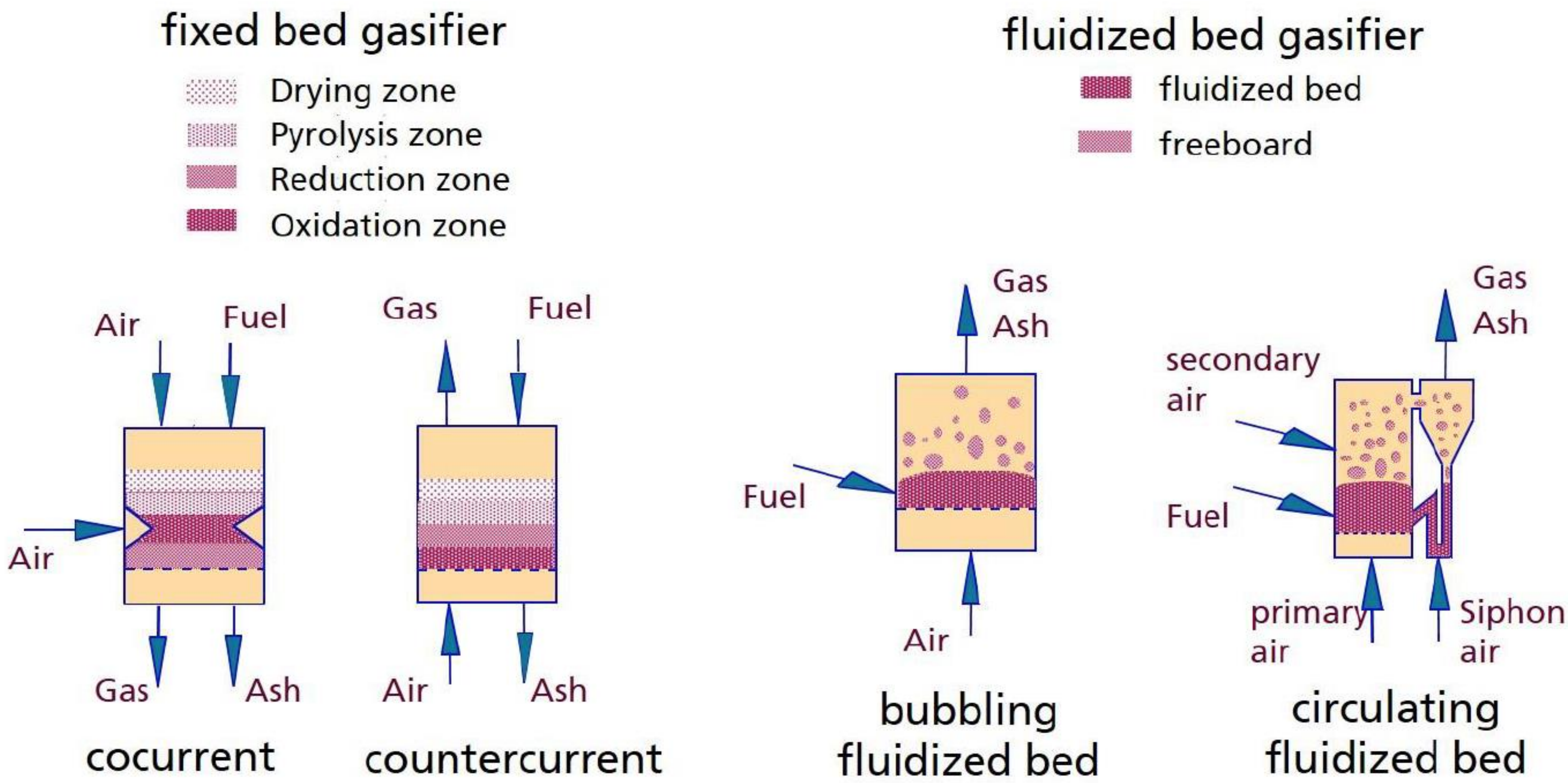
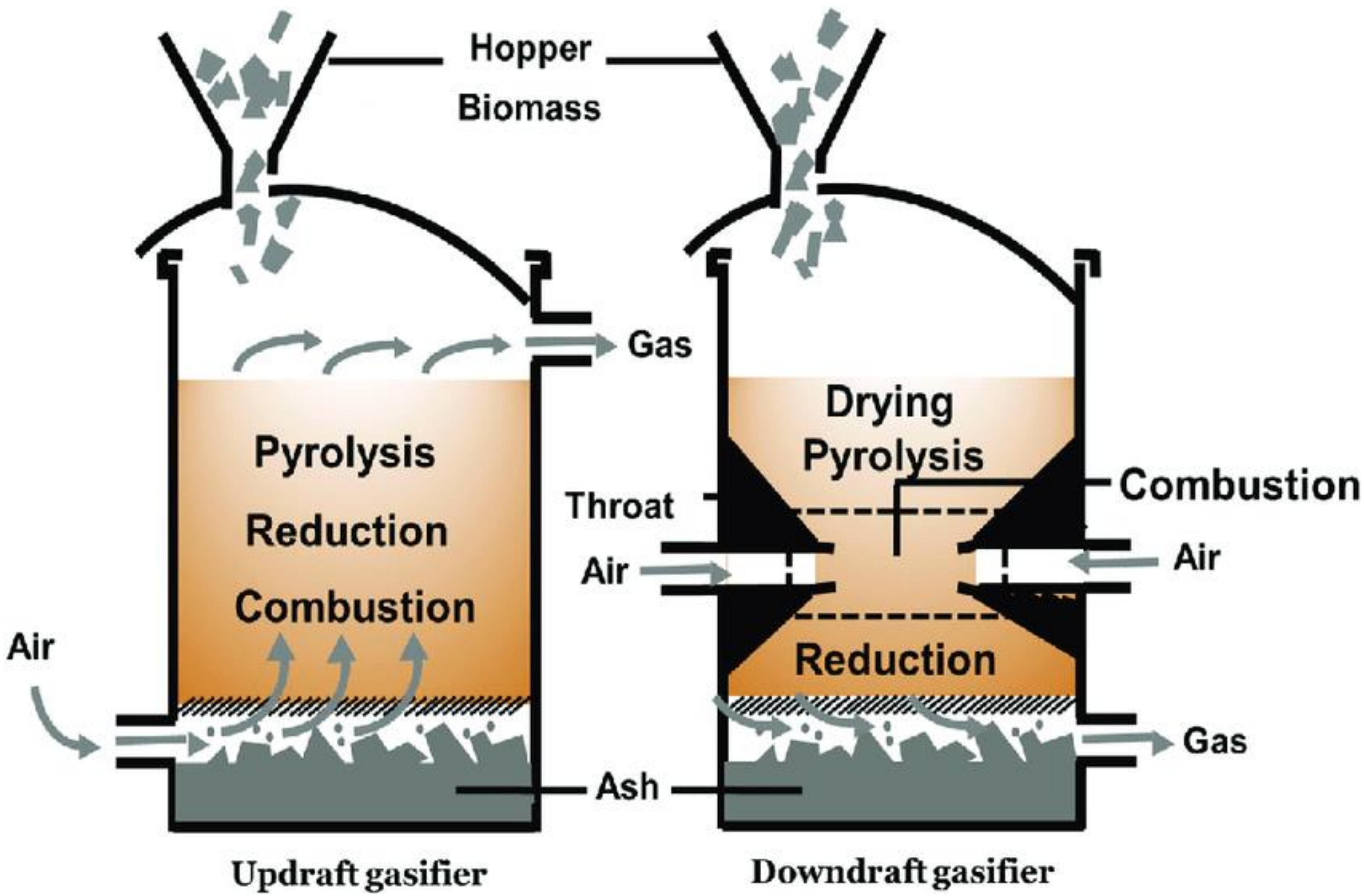
Gasifiers are categorized based on types of bed and flow. The gasifier bed can be a fixed-bed or a fluidized bed.



Kumar, A.; Jones, D.; Hanna, M. *Energies* **2009**, 2, 556–581.

Difference between updraft and downdraft fixed bed gasifiers



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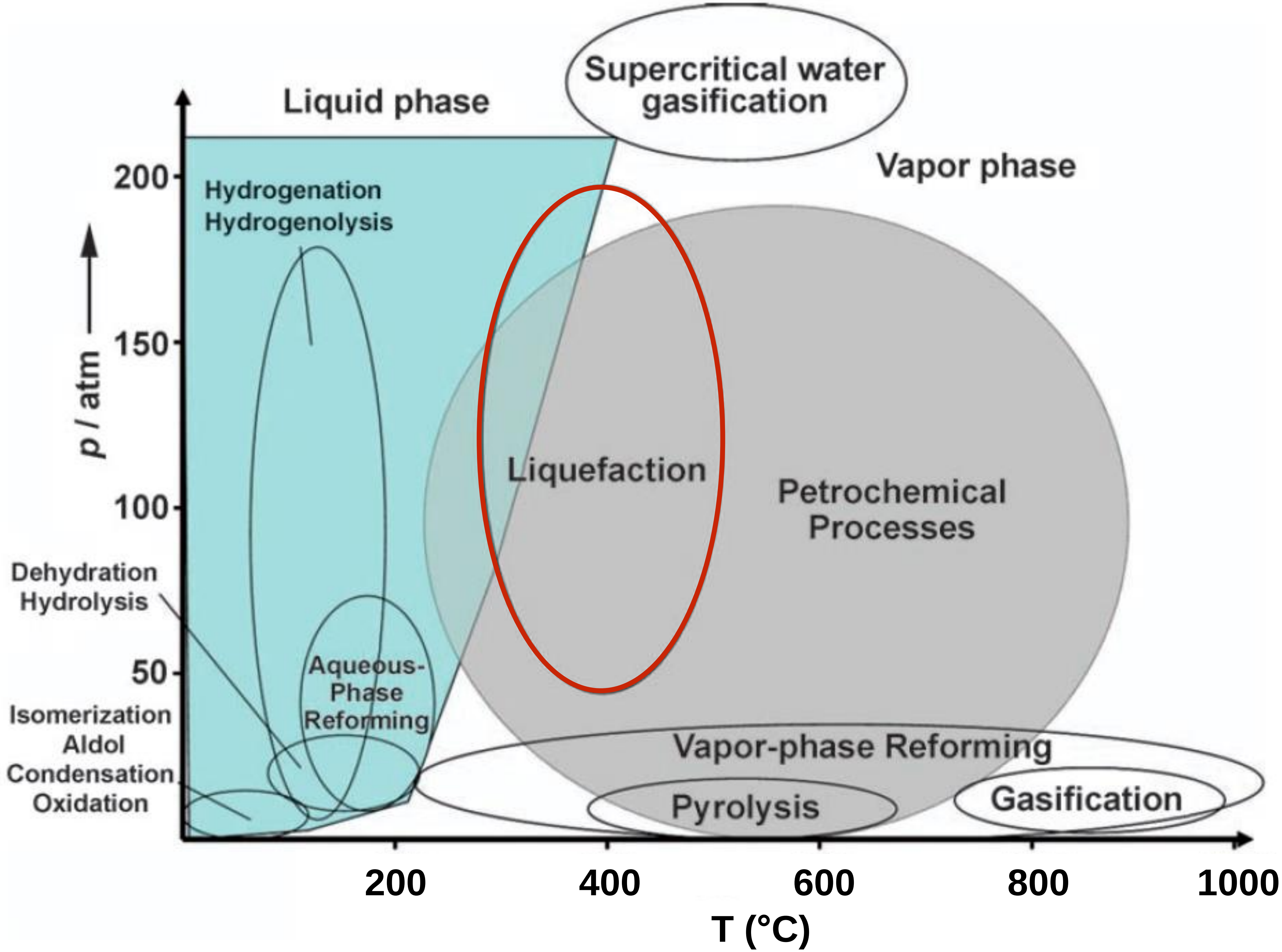
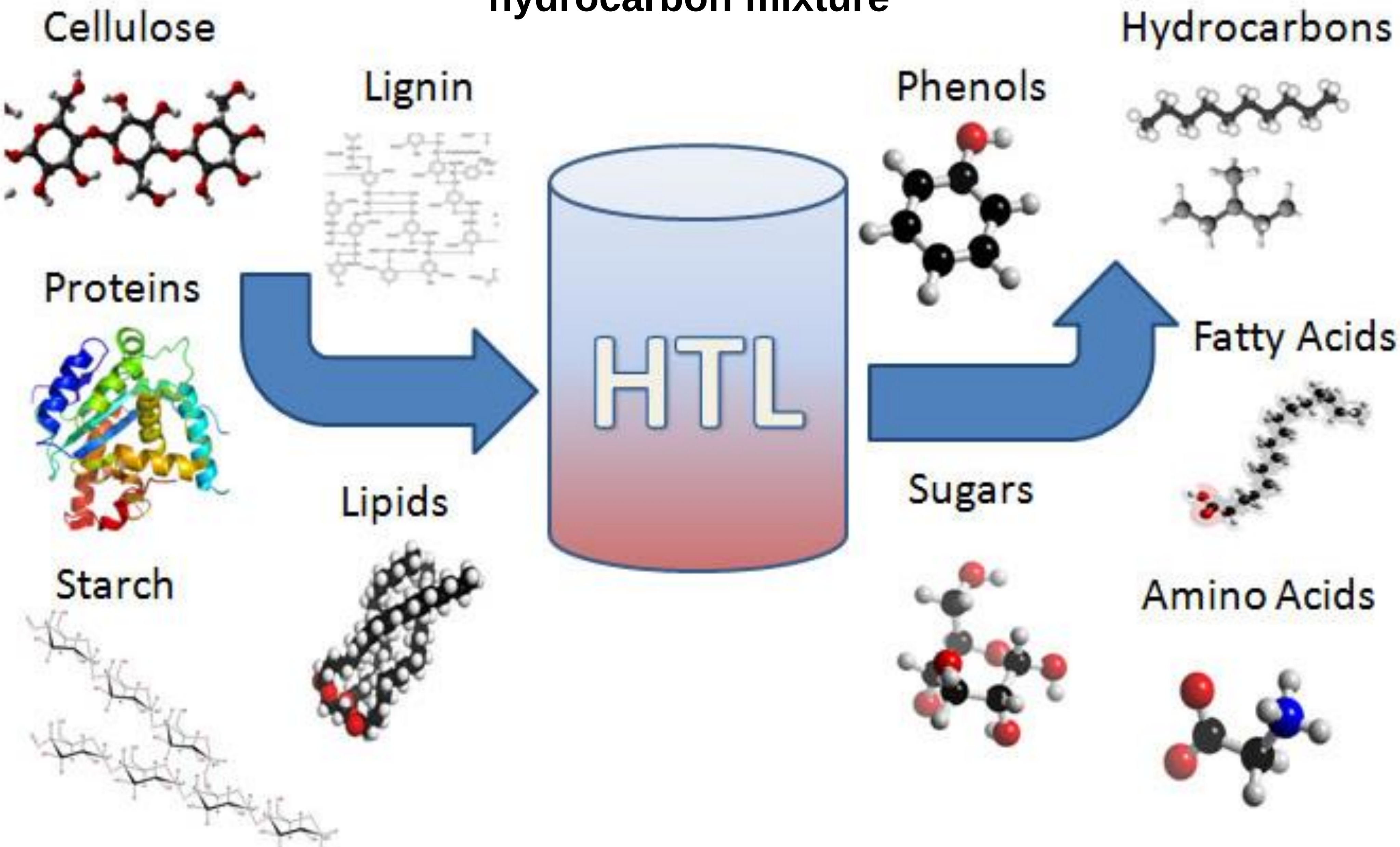


Chheda, J. N.; Huber, G. W.; Dumesic, J. A. *Angew. Chem. Int. Ed*. **2007**, *46*, 7164–7183.

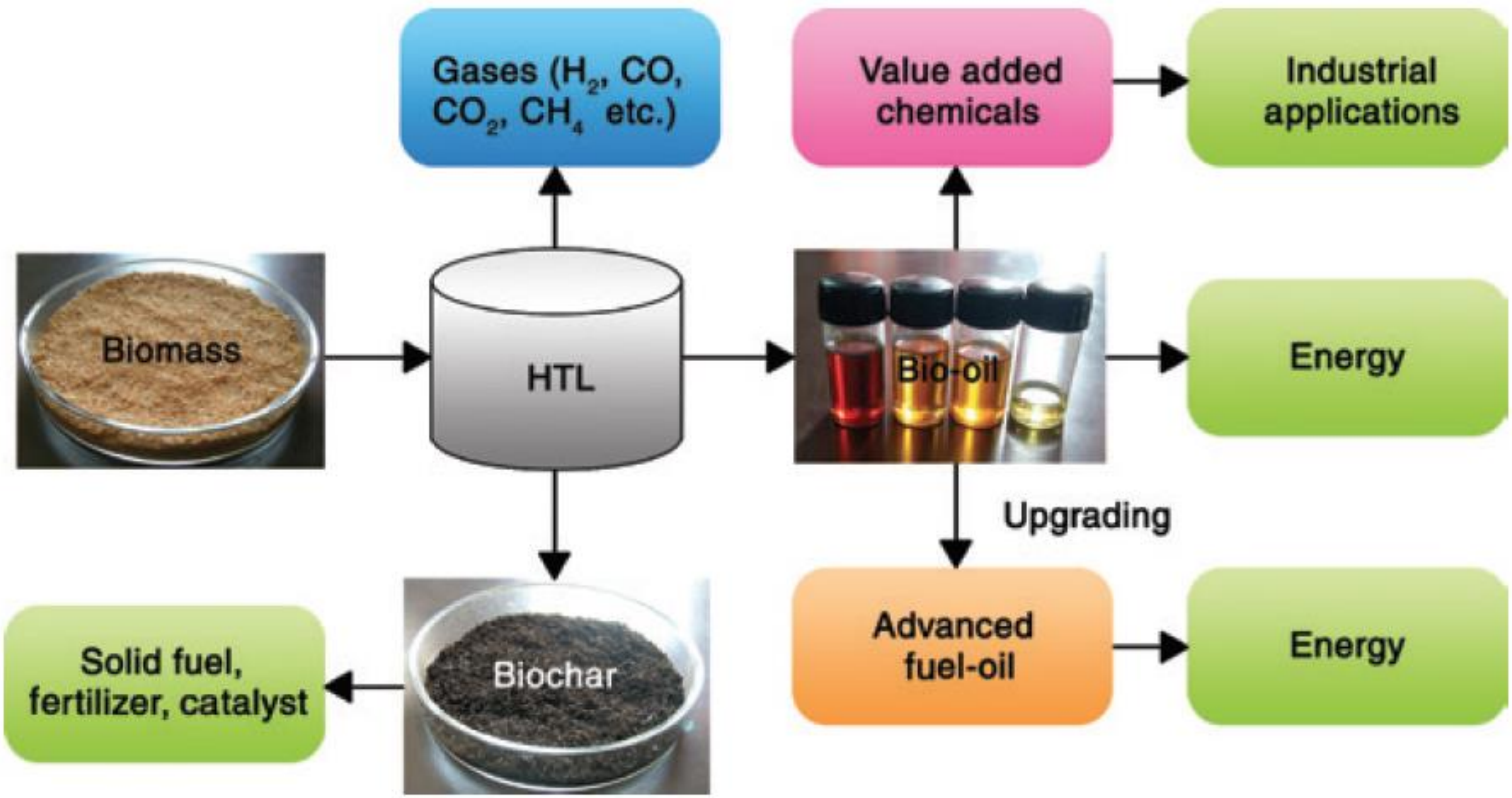
HYDROTHERMAL LIQUEFACTION (HTL) TECHNOLOGY

Hydrothermal liquefaction (HTL) is a thermal depolymerization process used to convert wet biomass into crude-like oil -sometimes referred to as bio-oil or biocrude- under moderate temperature and high pressure

Objective: Breakdown of macromolecules of biomass to produce liquified hydrocarbon mixture

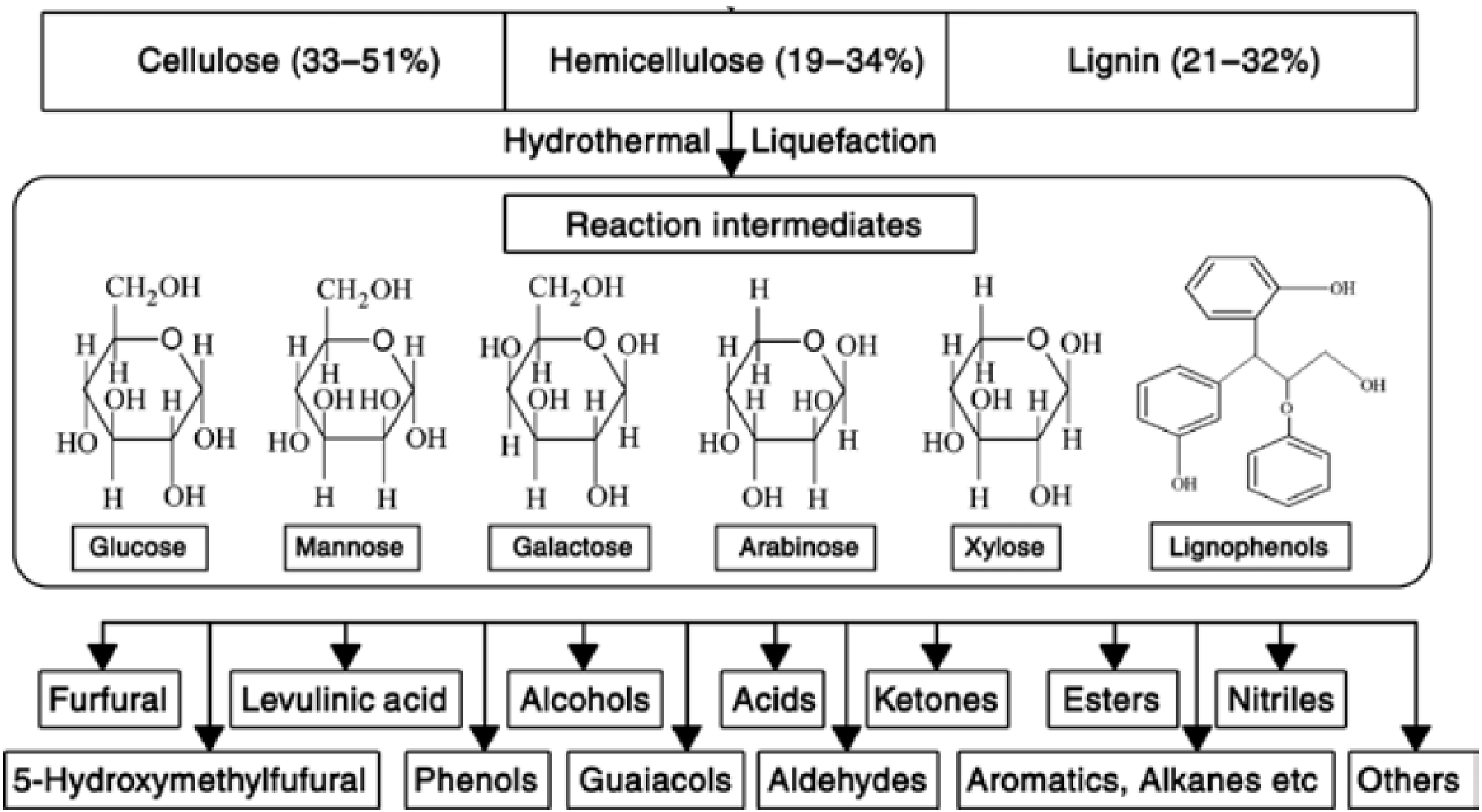


Objective: Breakdown of macromolecules of biomass to produce liquified hydrocarbon mixture



Jindal, M. K.; Jha, M. K. *Rev. Chem. Eng.* **2016**, 32, 2998.

SIMPLIFIED DECOMPOSITION PATHWAY OF BIOMASS FRACTIONS



Jindal, M. K.; Jha, M. K. *Rev. Chem. Eng.* **2016**, 32, 2998.

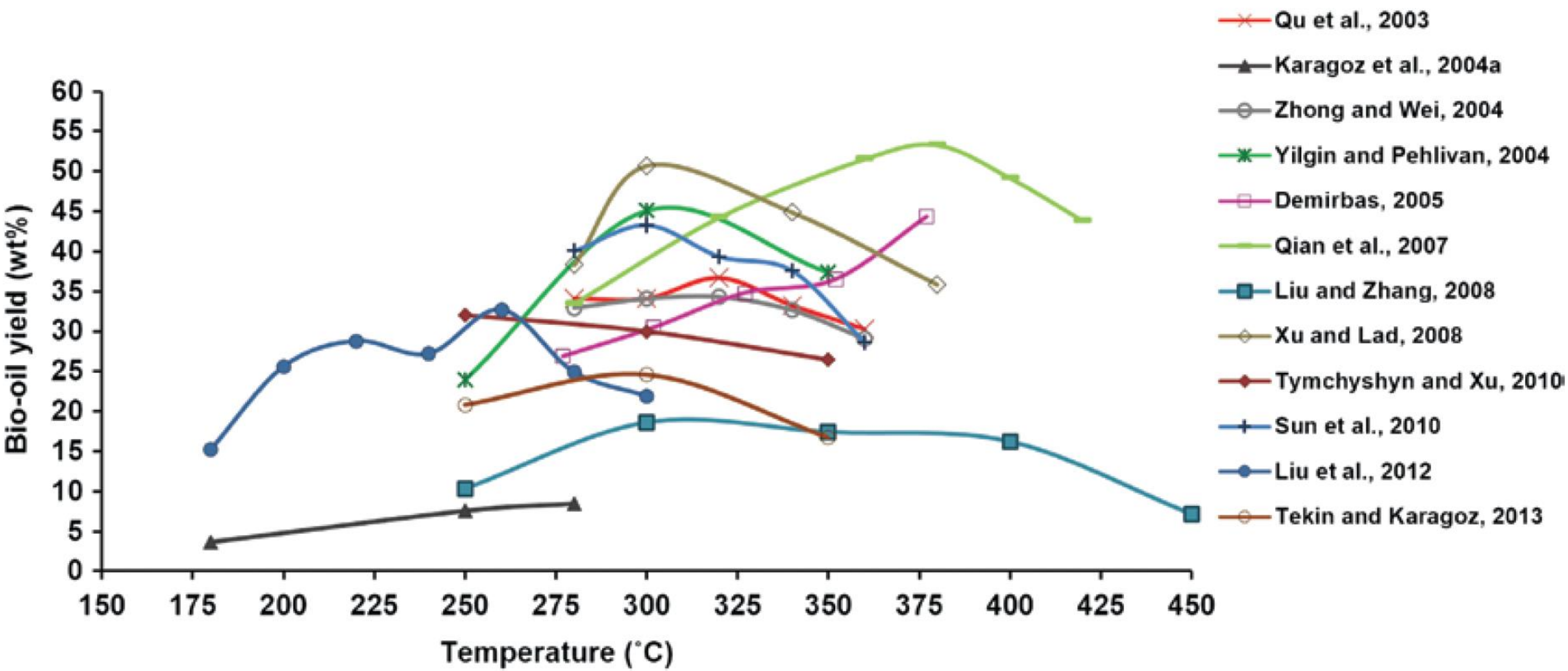
BIO-OIL YIELDS FROM DIFFERENT PROCESSES

M Ű E G Y E T E M 1 7 8 2

Main influencing factors

Temperature | Pressure | Catalyst | Solvent

Gas components | pH | Reaction time



Jindal, M. K.; Jha, M. K. *Rev. Chem. Eng.* **2016**, 32, 2998.

BIO-OIL YIELDS FROM DIFFERENT PROCESSES

Main influencing factors

Temperature

300-450 °C

Pressure

50-200 bar

Gas components

(reductive environment)

10-50 bar H_2

Solvent/co-solvent

Water

Alcohols (MeOH, EtOH)

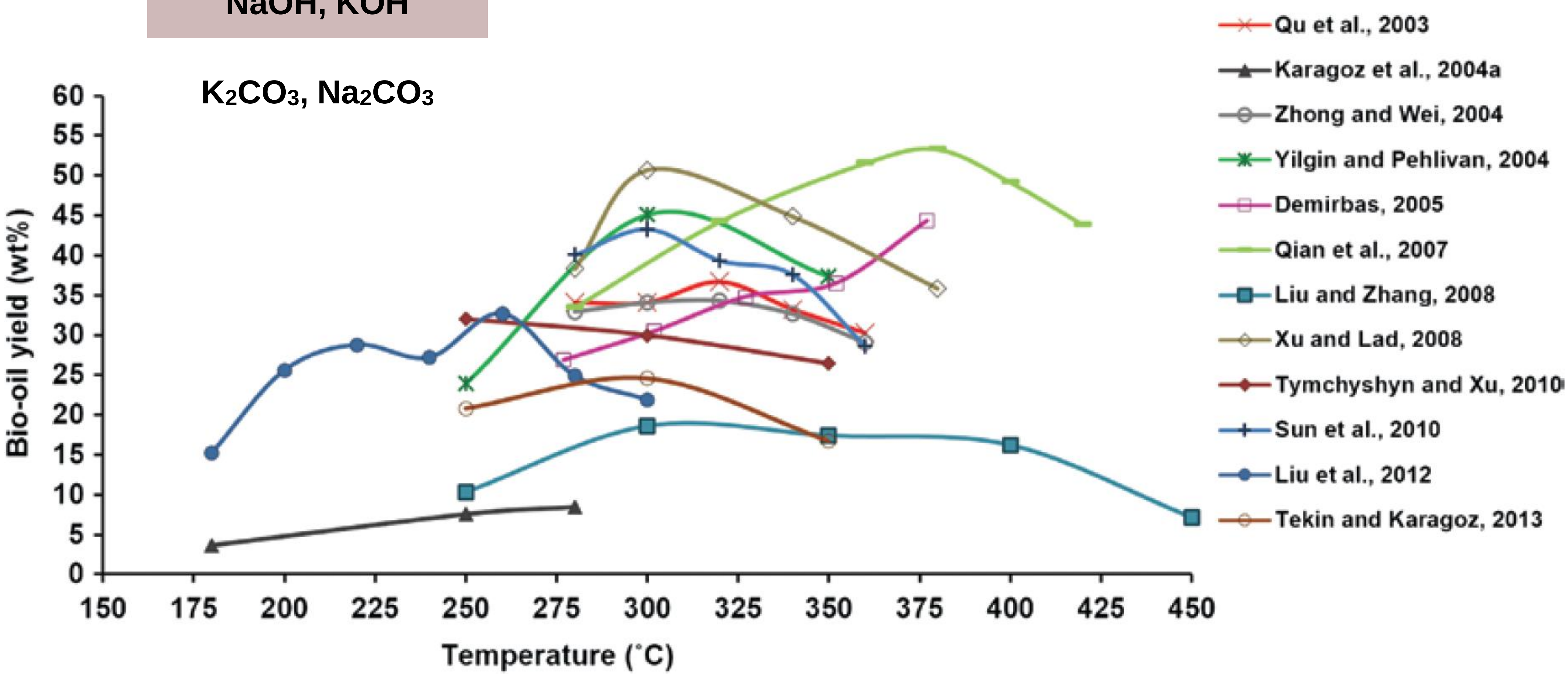
Catalyst

NaOH, KOH

K_2CO_3, Na_2CO_3

Residence time

Feedstock



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