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ASSESSING THE PRODUCTS AND THERMODYNAMIC TRANSITIONS OF HYDROTHERMAL TREATMENT OF ANAEROBIC SLUDGE

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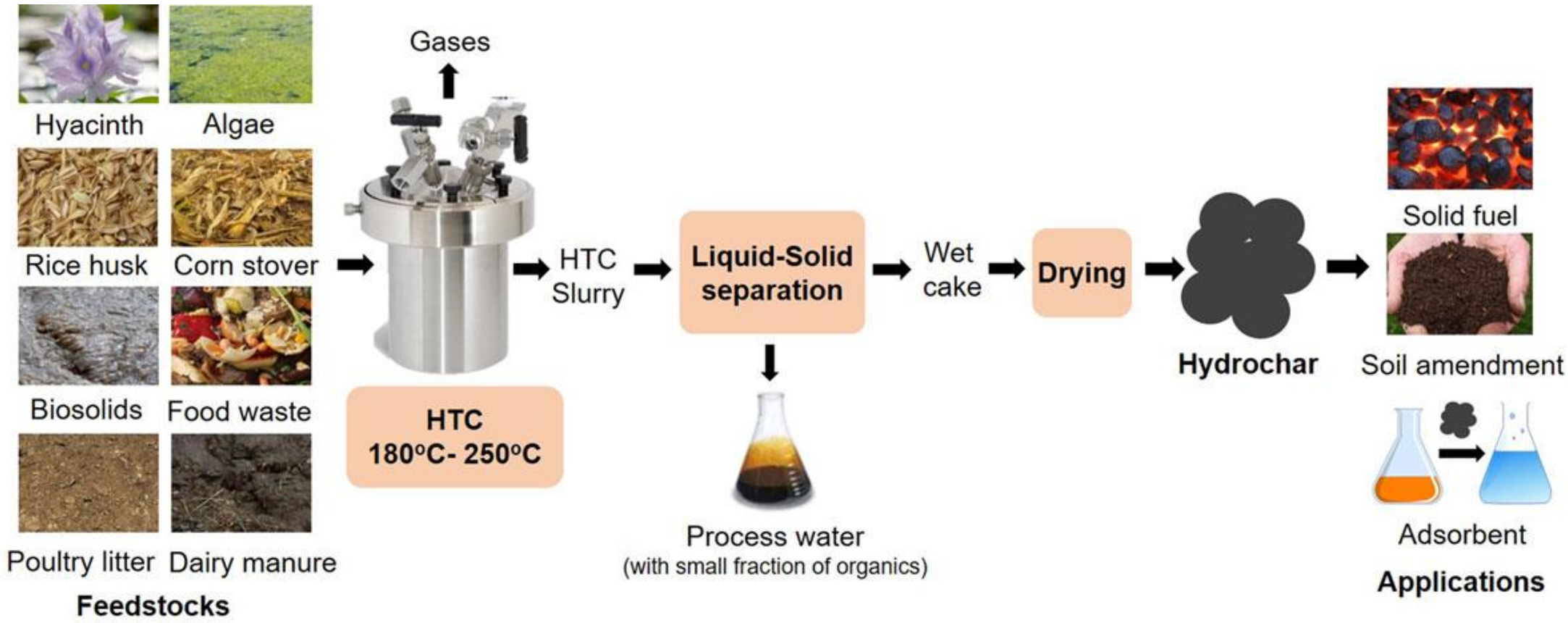
Available liquid biowaste in Lesvos

- 45 three-phase olive presses with ~ 100 t of OMWW per hour of operation. (Vakalis et al., 2021)
- 18 dairy production facilities and it is calculated that 26.387 cubic meters of whey from dairy farm are available per year. (Chatzimaliakas et al., 2021)
- Residues from the alcoholic beverage industry with smaller quantities; 6t of Anise from ouzo production (Altiparmaki et al., 2022); Winesludge from the processing of 20.746 kg of grapes (Vasileiadou et al., 2022)
- A sludge AD plant has been projected to be developed with a capacity of 17.500 tons per year.

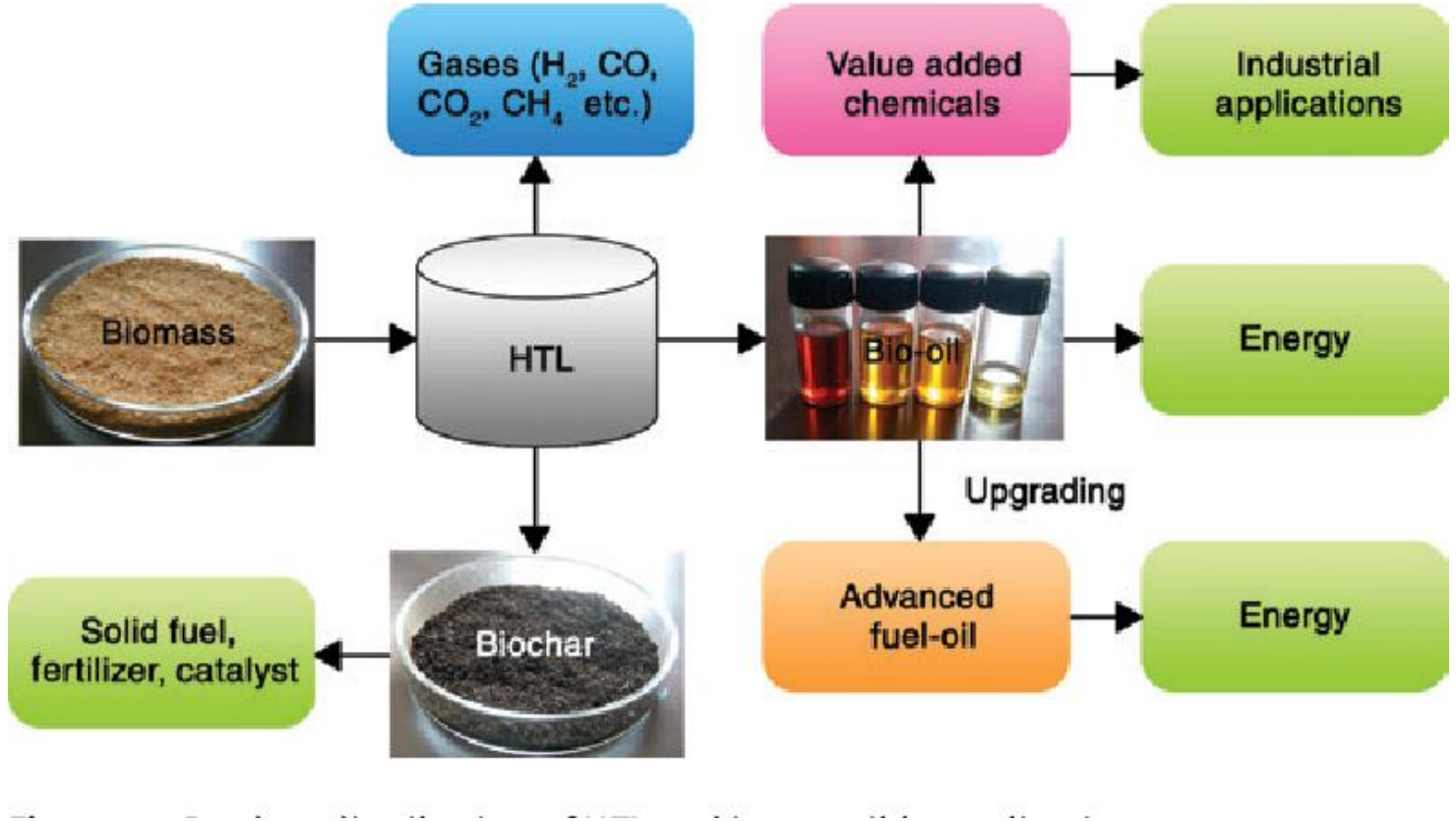
Hydrothermal carbonization process



Source: Sivaprasad, Manandhar and Shah, The Ohio State University (2021)

From HTC to HtL

- Higher T ranges: (usually) 300 – 350
- Higher quality of liquids and gases
- Hydrochar improves



Background and scope of the study

- Wastewater and digestate management is a timely and interesting challenge due to the variable existing valorisation technologies. Also, there is a local interest in island communities.
- Anaerobic digestion is a common and successful practice for sludge treatment and the management of digestate is a challenge.
- Several projects are developed or will be developed on the island of Lesvos in relation to HT; @ WWTP and @ an olive oil production facility.
- This study focuses on the effect of temperature of hydrothermal treatment on the quality of products with a focus on VFAs.
- A secondary focus I the investigation of underlying mechanisms that can be assessed in future studies.

Utilized sludge – existing AD plant on Lesvos

- 2 rectangular UASB reactors (2.4 x 2.4 m)
- V_{total} = 41 m^3 (100 m^3/d treatment capacity)
- GLS separator connected to a gasholder and biogas purification unit (chemical upgrade with MEA solution)
- Ambient reactor temperature

Period	Winter	Summer
Q_{in} (m^3 d^{-1})	25.2 ± 1.8	82.0 ± 7.9
Temperature (°C)	13.5 ± 0.7	22.7 ± 3.8
HRT (h)	39.4 ± 3.2	12.2 ± 1.8
OLR_{UASB} (kgCOD m^{-3} d^{-1})	0.19 ± 0.07	1.32 ± 0.31

Thank you Dr. Seintos!

Materials and Methods – HT experiments

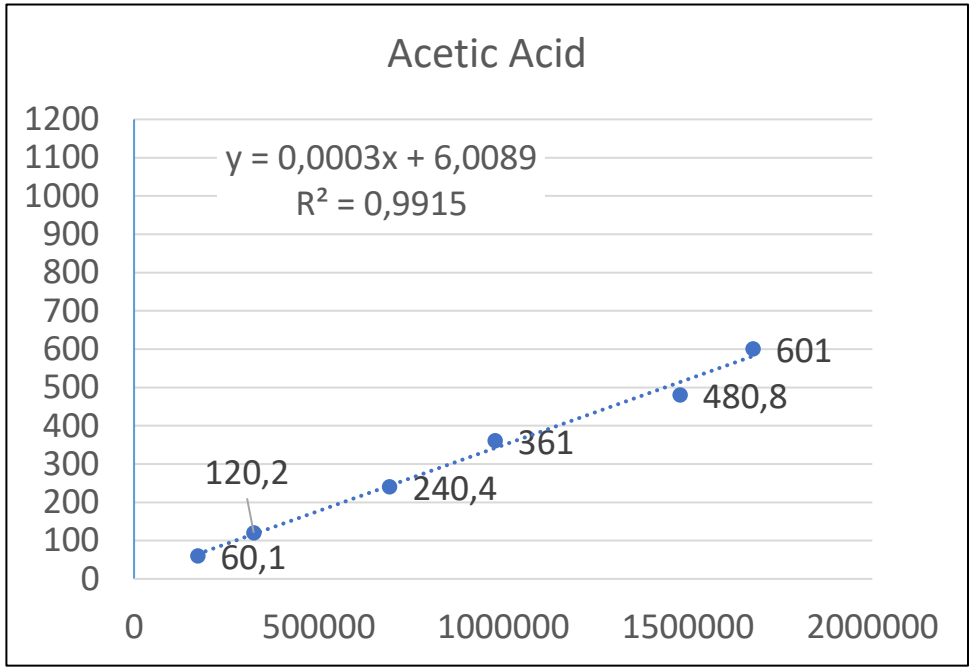
- Anaerobic digestate of 6% TS and 2% VS underwent hydrothermal liquefaction between 280 – 340 °C for 1 h.
- The HT Liquor was separated from the hydrochar via centrifugation & filtration.
- Soxhlet extraction was used to separate the liquids that were trapped on the surface of hydrochar (extraction with isopropanol).
- The liquids were assessed for their COD, TPC & pH
- Plasma gas chromatography was used for the measurement for the concentration of VFAs in the liquids
- A modified tar protocol was used for cleaning the HtL gases, that were stored downstream in Tedlar bags for offline measurement in a GC – BID.

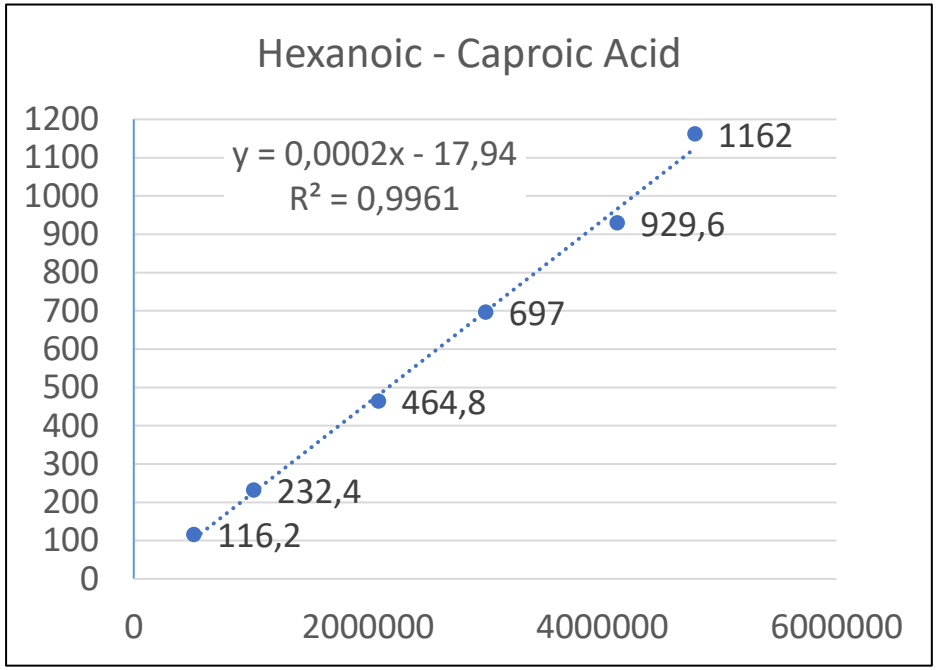
HTC reactor & GC-BID @ EML (UAEGEAN)

- Parr hydrothermal reactor 4570A
- 1 L/ CSTR, max: 550 °C/ 350 bar
- Modified for continuous operation with the connection of gas burettes, a liquid pipette and a HP condenser.
- Continuous connection with a GC-BID for gas measurements

- Shimadzu Nexis GC-2030
- GC – BID (plasma) detector
- Gas column: **Restec ShinCarbon 80/100**
- Liquid columns: MEGA – 5, MEGA – 10, **MEGA – FFAP** (ACID), MEGA – 624

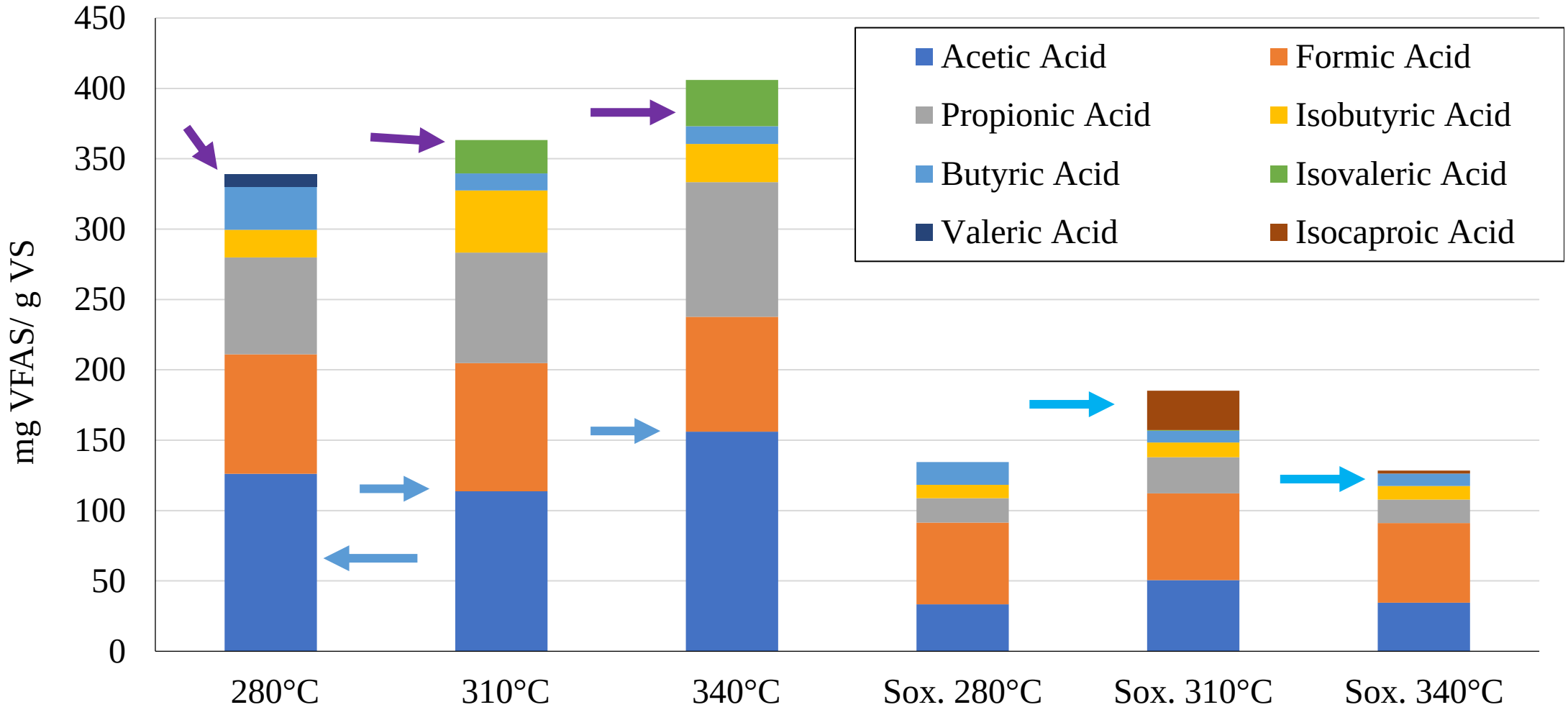
Materials and Methods – VFA method/ GC - BID

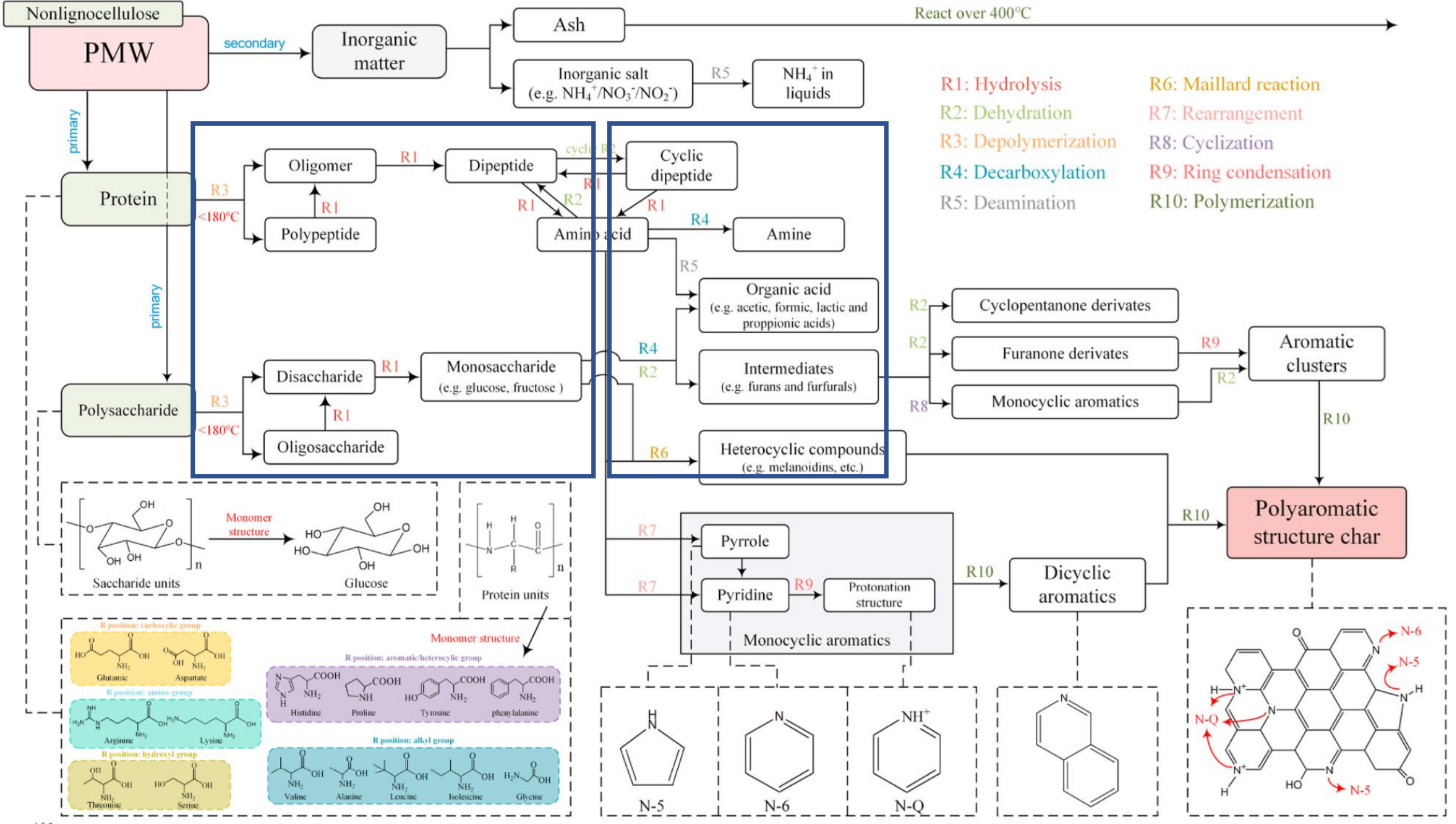




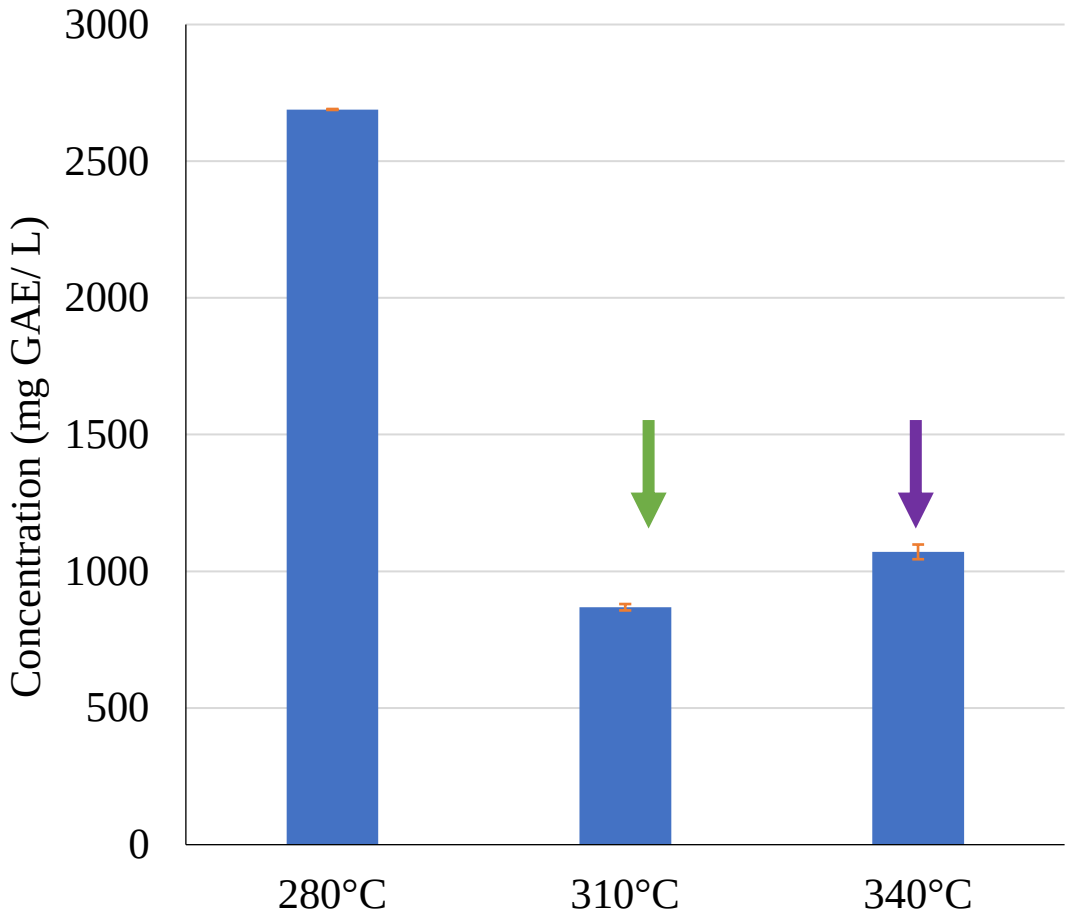
	Agilent HP – FFAP
Injection Vol	1 µl
Injection Temp	160 °C
Oven Temp. Program	80 °C to 230°C
Flow Rate	59 mL/min
BID Temperature	280 °C

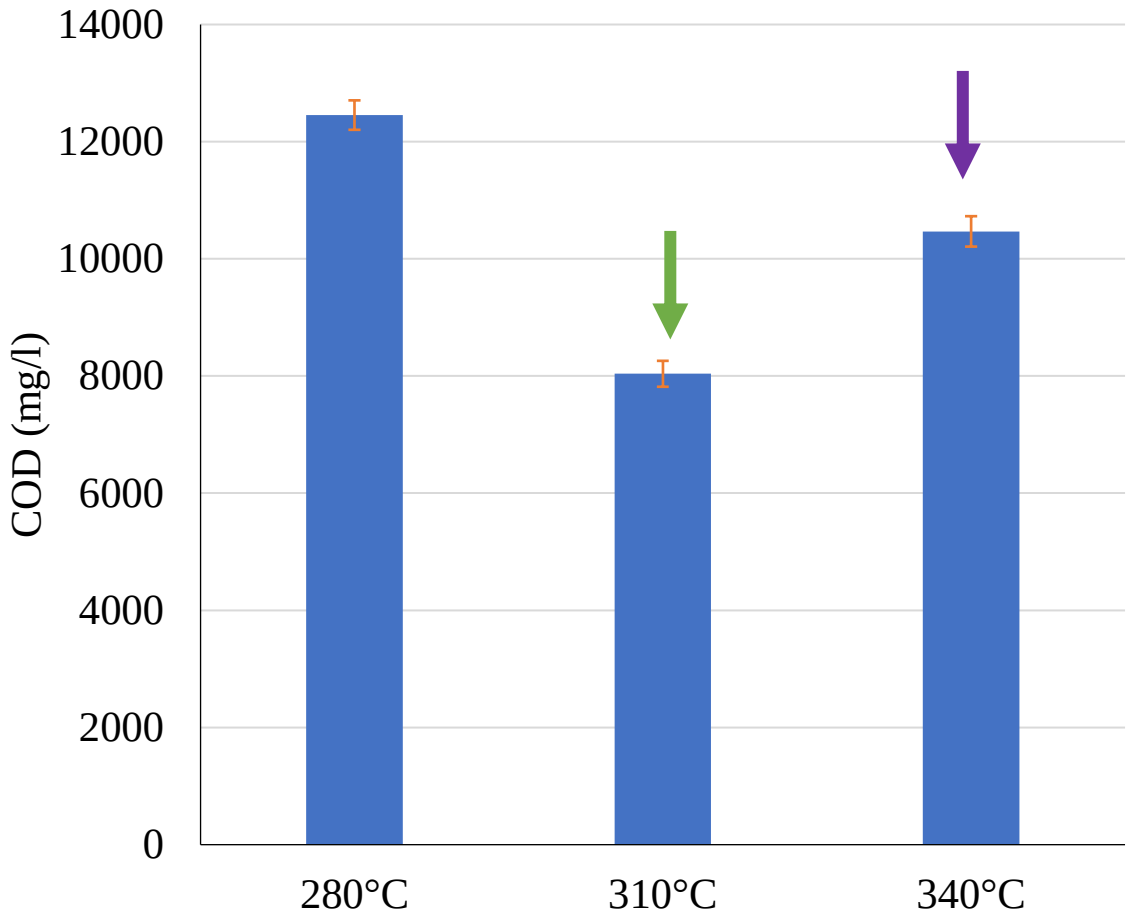
Production of VFAs via HT – Results




Nonlignocellulose
PMW
secondary
Inorganic matter
Ash
React over 400°C
Inorganic salt (e.g. $NH_4^+/NO_3^-/NO_2^-$)
R5
NH_4^+ in liquids
R1: Hydrolysis
R2: Dehydration
R3: Depolymerization
R4: Decarboxylation
R5: Deamination
R6: Maillard reaction
R7: Rearrangement
R8: Cyclization
R9: Ring condensation
R10: Polymerization
primary
Protein
R3
<180°C
Oligomer
R1
Dipeptide
cyclic R2
Cyclic dipeptide
Polypeptide
R1
R2
Amino acid
R4
Amine
R5
Organic acid (e.g. acetic, formic, lactic and proppionic acids)
primary
Polysaccharide
R3
<180°C
Disaccharide
R1
Monosaccharide (e.g. glucose, fructose)
R4
R2
Intermediates (e.g. furans and furfurals)
Oligosaccharide
R1
R6
Heterocyclic compounds (e.g. melanoidins, etc.)
R2
Cyclopentanone derivates
R2
Furanone derivates
R9
Aromatic clusters
R8
Monocyclic aromatics
R2
R10
Polyaromatic structure char
Saccharide units
Monomer structure
Glucose
Protein units
Monomer structure
R7
Pyrrole
R7
Pyridine
R9
Protonation structure
Monocyclic aromatics
R10
Dicyclic aromatics
R position: carboxylic group
Glutamic
Aspartate
R position: aromatic/heterocyclic group
Histidine
Proline
Tyrosine
phenylalanine
R position: amino group
Arginine
Lysine
R position: hydroxyl group
Threonine
Serine
R position: alkyl group
Valine
Alanine
Leucine
Isoleucine
Glycine
N-5
N-6
N-Q
N-6
N-5
N-Q
N-5

TPC (left) and COD (right) analysis

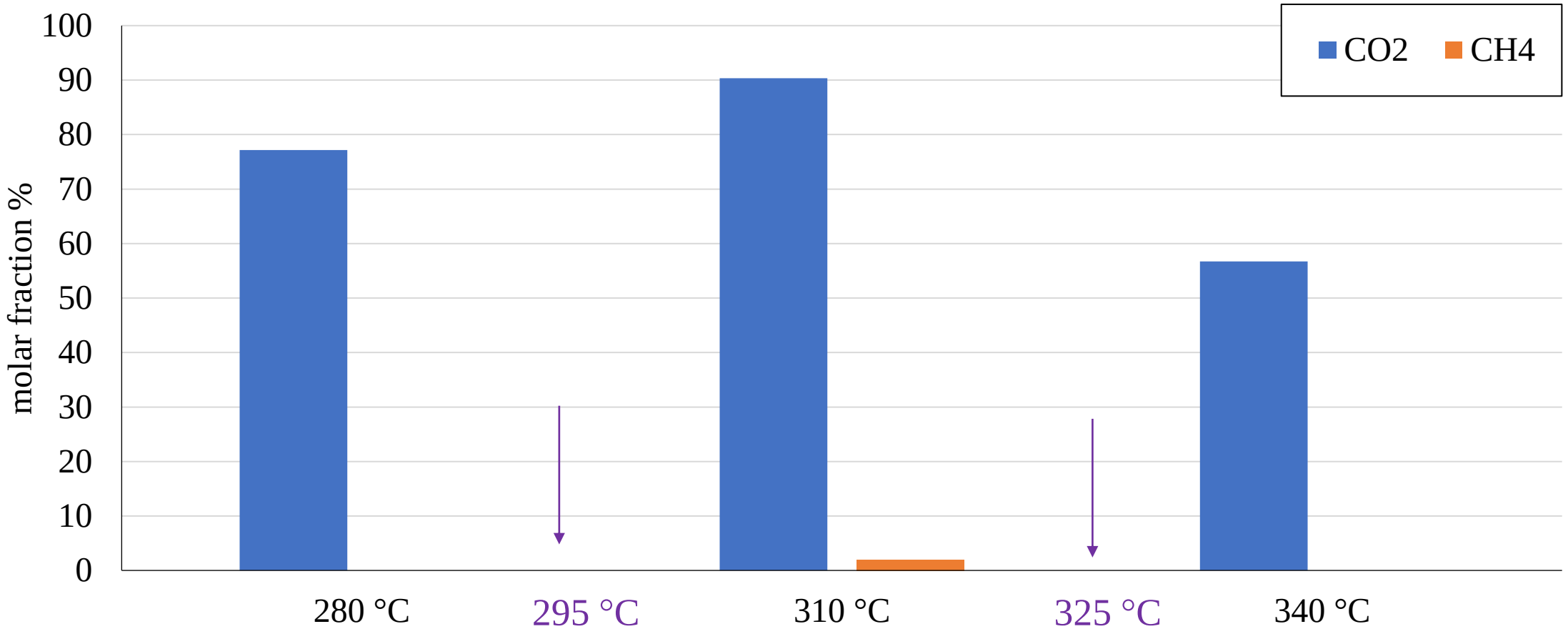




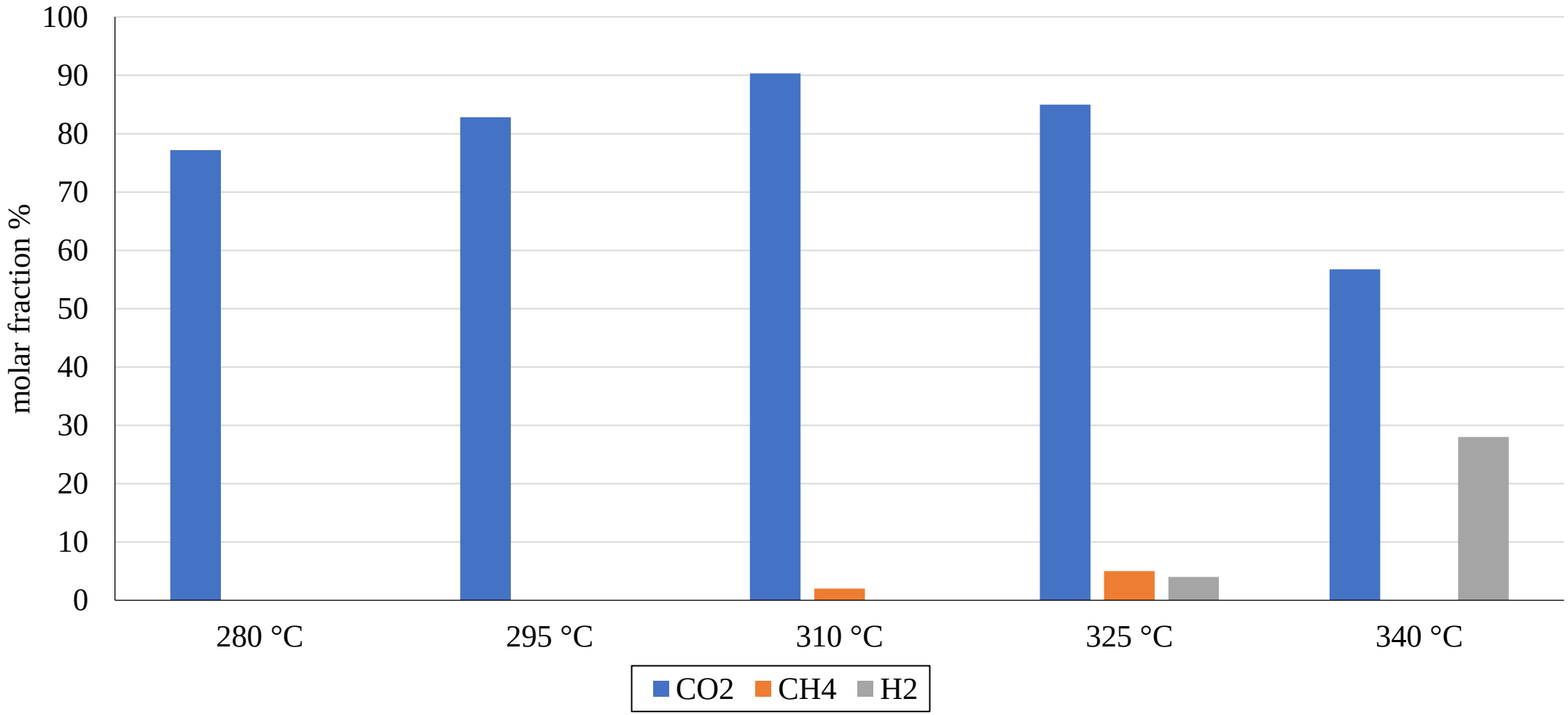
What could explain the previous results?

- The role of the gases as intermediates for the production of high-quality liquid (and solid) products should be investigated.
- The one hypothesis is that carbon is reintroduced by the reaction of carbon dioxide with other intermediates.
- The other hypothesis is that methane is an intermediate gaseous product before the final production of hydrogen and carbon dioxide or carbon
  - $CO_2 + 4H_2 <-> CH_4 + 2H_2O$ (Sabatier)
  - $2H_2 + C <-> CH_4$ (hydrogasification)

CO_2 and CH_4 analysis (3 Temperatures)



Gas analysis (5 Temperatures)



Discussion points

- Autocatalytic Reduction of CO2 into Formic Acid during HT
  - (Jin et al., 2021); Andérez-Fernández et al., (2022)
- Fatty acids have a high presence on biocrude and are increasing the calorific value of the bio-oil (Yang et al., 2019).
  - Nonetheless, their production mechanism is not clear (deoxygenation vs secondary production)
  - The presence of carboxylic acids can indicate the possibility of carboxylation processes.
- Type I aqueous phase reforming in moderate HT temperatures favors the presence of methane (Kruse, 2009).
  - Fast reaction times may prevent the proper identification → continuous measurement may be necessary.

Discussion and Conclusions

- HTL can produce significant amounts of VFAs and this can be an interesting valorisation pathway.
- The use of GC-BID and of an HP-FFAP column usefully identified a wider range of short-chain fatty acids.
  - Extension of the methods will target heavier fatty acids of interest. Also, utilization of the column MEGA-10.
  - Different concentrations of proteins/ lipds etc. usually result to different types of produced fatty acids, e.g. lip./ prot. →Linoleic acid; pol./ prot. 6-Octadecenoic acid
- The fluctuation of short VFAs along with the values of COD and TPC indicates the propagation of underlying thermodynamic mechanisms, i.e. char-gas reactions.
- Methane appears to be an intermediate product for HTL upgrade of gases and liquids, but more experiments are necessary.
  - Upcoming use of a semi- continuously operating gas sampling probe, tar trap and gas analysis via GC-BID/ Restek

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THANK YOU FOR YOUR ATTENTION!

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