Freie Universität Bozen
Libera Università di Bolzano
Free University of Bolzano

Thermochemical valorization of spent apple seeds

Preliminary assessment by thermogravimetric analysis coupled with evolved gas characterization

J. Paini, V. Benedetti, M. Scampicchio, M. Baratieri, F. Patuzzi

Structural Waste in the Food System

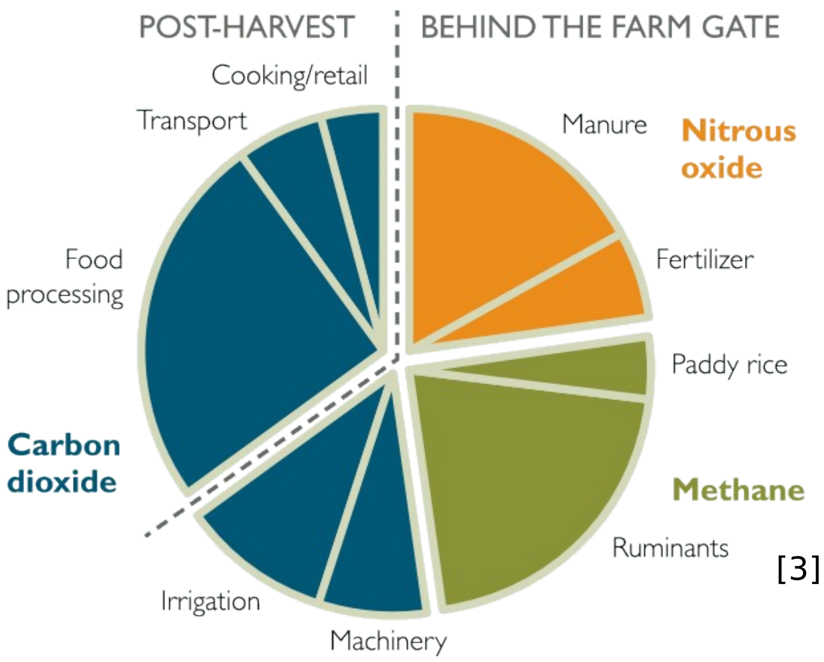
- One of the major contributors to environmental degradation and GHG emissions [1]

FIGURE ES.1. Indicative shares of the approximately 10 $GtCO_2$-eq of total greenhouse gases emitted by the global agri-food sector in 2010.

Sources: IPCC, 2014. 5th Assessment Report- Mitigation: Chapter 11, Agriculture forestry and other land use; Chapter 10, Industry; Chapter 8, Transport. FAO, 2011a.

Some Numbers:

- Almost 22% of total greenhouse gases emitted 2010 [2]



[3]

[1] *FAO "Energy - Smart" Food for People and Climate: Issue Paper 66 (2011)*

[2] *Sims et al. Opportunities For Agri-Food Chains To Become Energy-Smart (2015)*

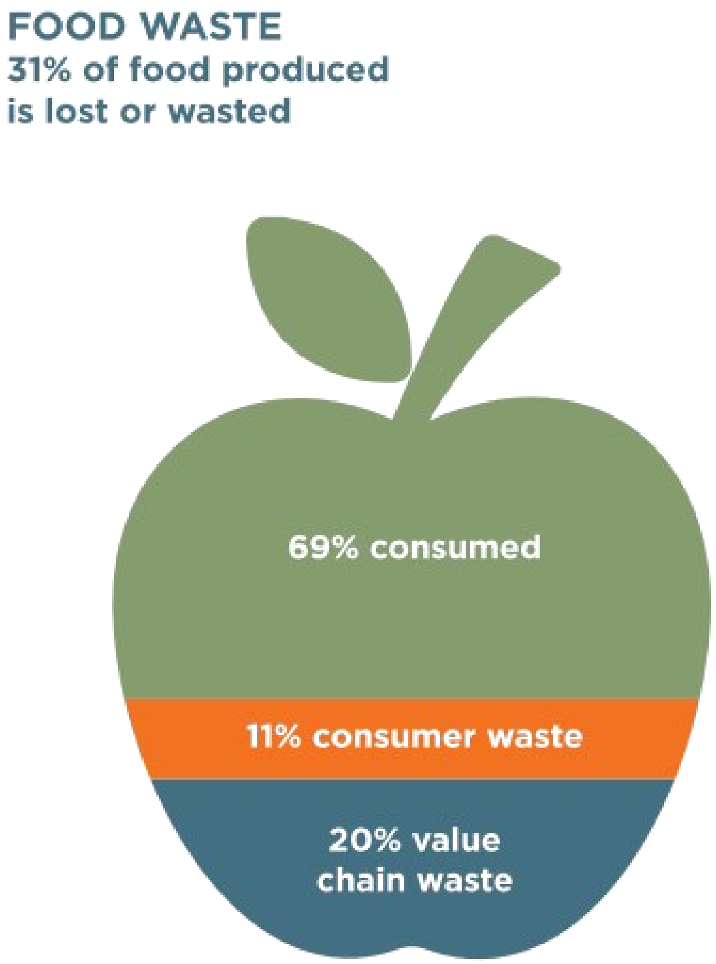
Introduction

Structural Waste in the Food System

- One of the major contributors to environmental degradation and GHG emissions [1]

Some Numbers:

- **31%** of the food edible mass is left along the chain [3]



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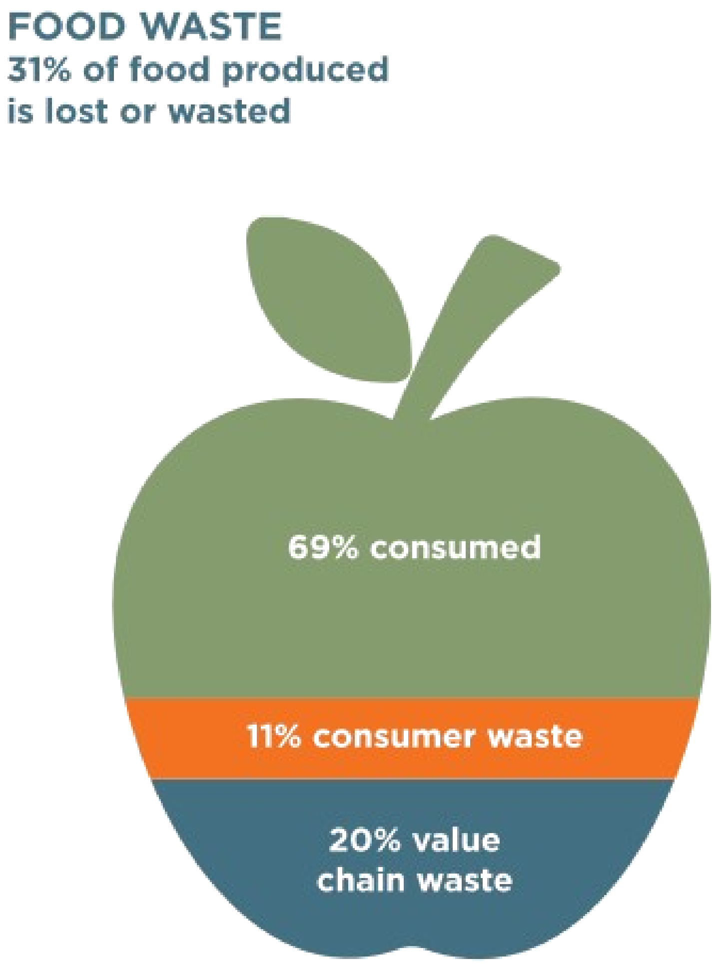
→ **Biorefinery Concept**



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Background

Apple seeds: a hidden resource

- Apple seed is a by-product of juice production [4]
- Abundant in the Italian region of South Tyrol [5]
  - 19 000 hectares of dedicated area
  - 50 % of the national
  - 15 % of the European
  - 2 % of the global apple market
- 70 million tons produced yearly worldwide [6]
- 25 - 35 % of the raw material weight is residue

[4] X. Yu et al., Proximate composition of the apple seed and

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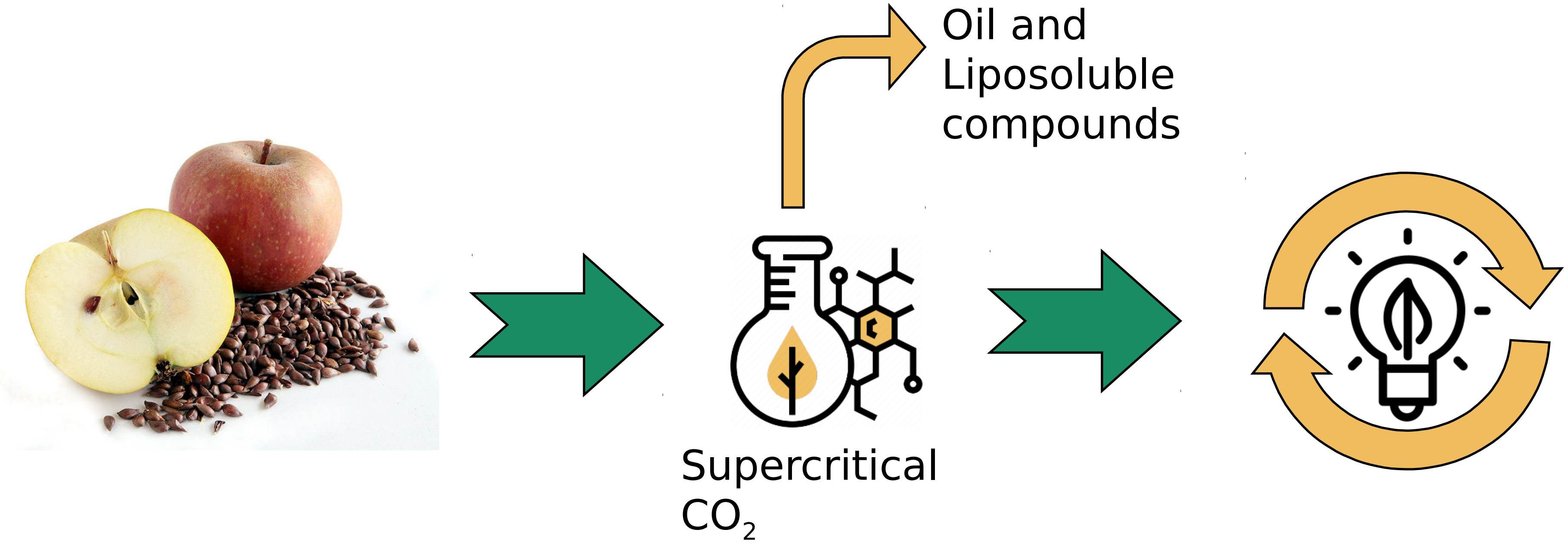
Extraction of valuable compounds by $ScCO_2$

[4] *X. Yu et al., Proximate composition of the apple seed and*

Background

Research questions

- What are the characteristics of residues after both treatments ?
- How the extraction affects sample thermal properties ?
- Can spent biomass after the extraction be further valorized thermochemically ?



Materials and methods

Samples before and after extraction:

- Proximate Analysis
  - Ashes
  - Moisture content
- Ultimate Analysis
  - Elemental Analyzer (CHNS)
- Fourier-Transformed Infrared analysis with Attenuated Total Reflectance (FT-IR / ATR)
- Thermal Analyses
  - Calorimetric Bomb
  - Thermogravimetric coupled with Fourier-Transformed Infrared for Evolved Gases Analysis (TG / FT-IR / EGA)

Results

Elemental analysis

		Before Extr.	After Extr.
Moisture	%	5.42 ± 0.13	5.47 ± 0.16
C	$\%wt_{db}$	53.50 ± 0.17	46.90 ± 0.23
H	$\%wt_{db}$	7.30 ± 0.01	6.30 ± 0.04
N	$\%wt_{db}$	6.71 ± 0.15	9.30 ± 0.10
S	$\%wt_{db}$	0.66 ± 0.12	0.60 ± 0.03
O	$\%wt_{db}$	31. 80	36. 90
Ash	$\%wt_{db}$	3.50 ± 0.10	4.21 ± 0.05

*db: dry basis

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Carbon

Hydrogen

Sulphur

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Higher Heating Value

		Before Extr.	After Extr.
HHV	J/g	22572 ± 84	18241 ± 35

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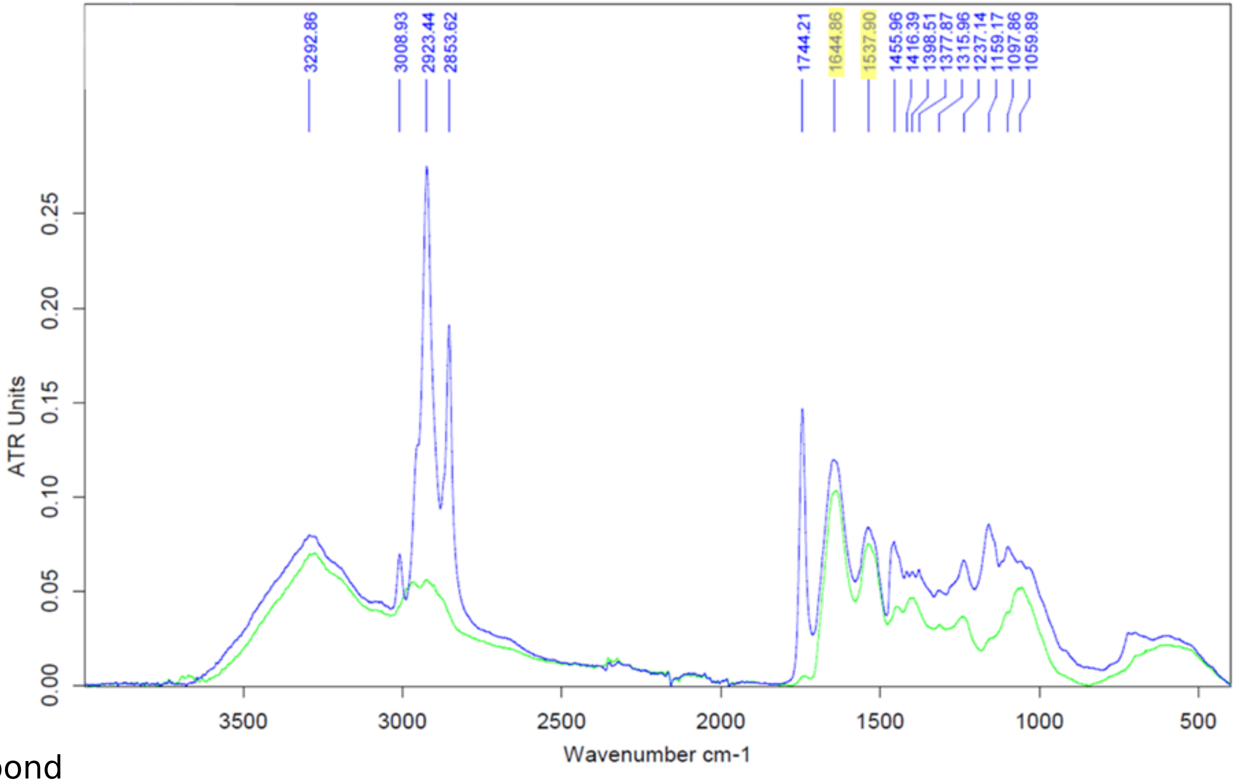
- 19% HHV difference Before Vs After Extr.

Preliminary assessment by FT-IR / ATR

Wavenumber (cm^{-1})	Vibration	Suggested molecular assignment
3293	N-H and O-H stretching	Polysaccharides and proteins
3009	C=H stretching	Unsaturated lipids
2923	C-H stretching (asym. *)	Mainly lipids, proteins and carbohydrates
2854	C-H stretching (sym.°)	Mainly lipids, proteins and carbohydrates
1744	C=O stretching	Lipids
1645	C-O, C-N stretching	Amide I (protein)
1538	C-N stretching N-H bending	Amide II (protein)
1456	CH_2 bending	Lipids
1398	CH_3 bending COO^- stretching (sym.°)	Proteins and fatty acids
1237	PO^{2-} stretching (asym. *)	Phospholipids (mainly phosphatidylcholine)
1159	CO-O-C stretching (asym. *) CO stretching	Esters, oligosaccharides, triacyclglycerols
1060	PO^{2-} stretching (sym.°) CO stretching	Nucleic acids Starch
≈600	O-C-O bending	CO_2

asym. * = asymmetrical bond stretch sym.° = symmetrical bond stretch



Before Extraction in Blue After Extraction in Green

Table Taken from [7] *B.J. Lee et al. Discrimination and prediction of the origin of Chinese and Korean soybeans using Fourier transform infrared spectrometry (FT-IR) with multivariate statistical analysis, PLoS One. 13 (2018)*

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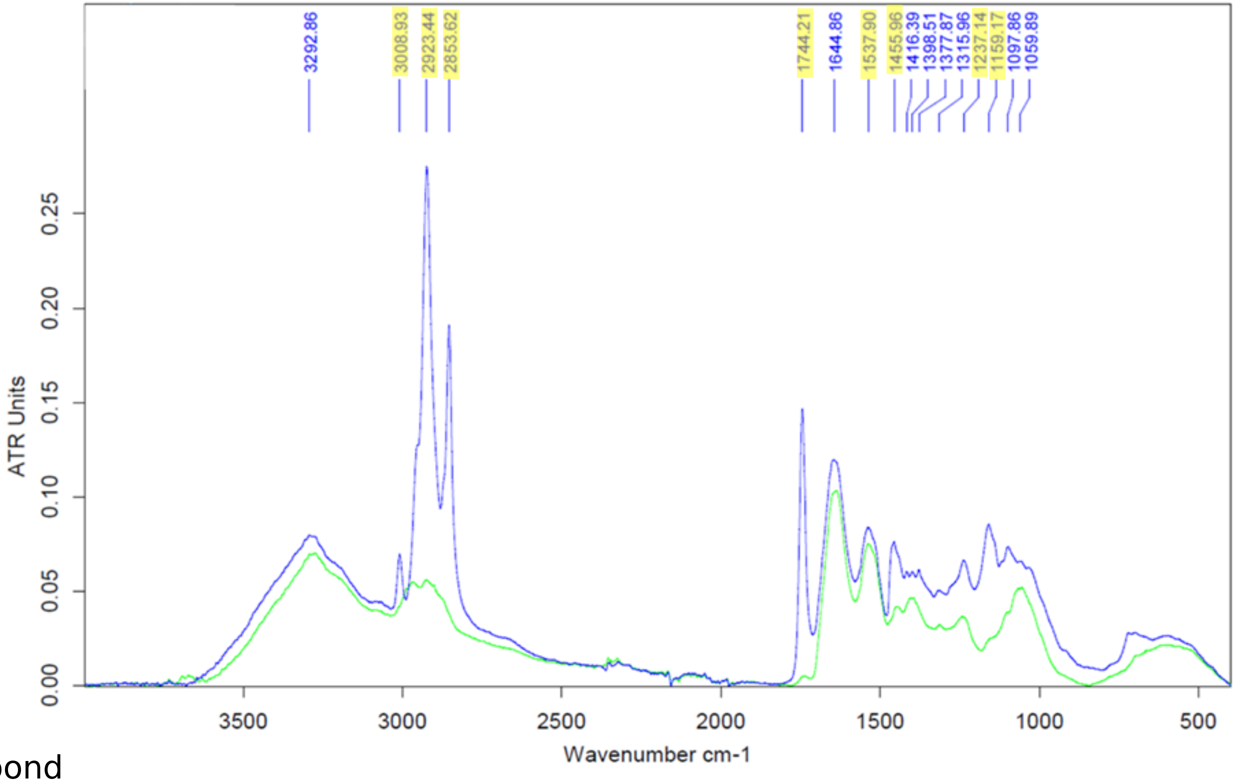

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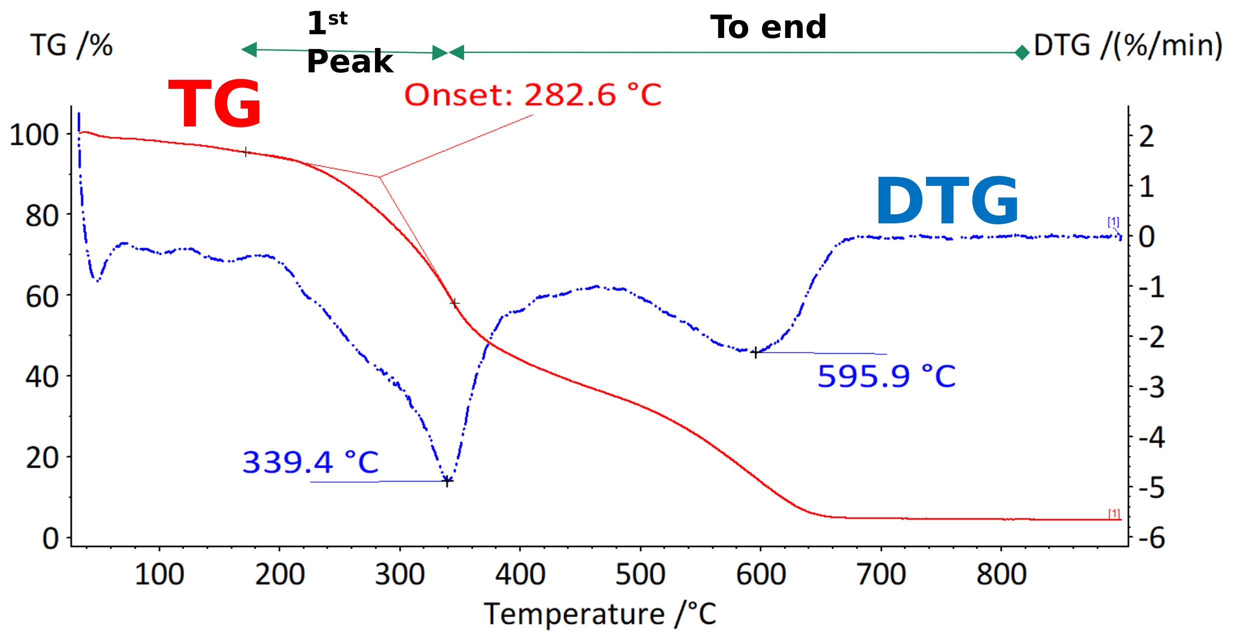
Results

Thermogravimetric analysis

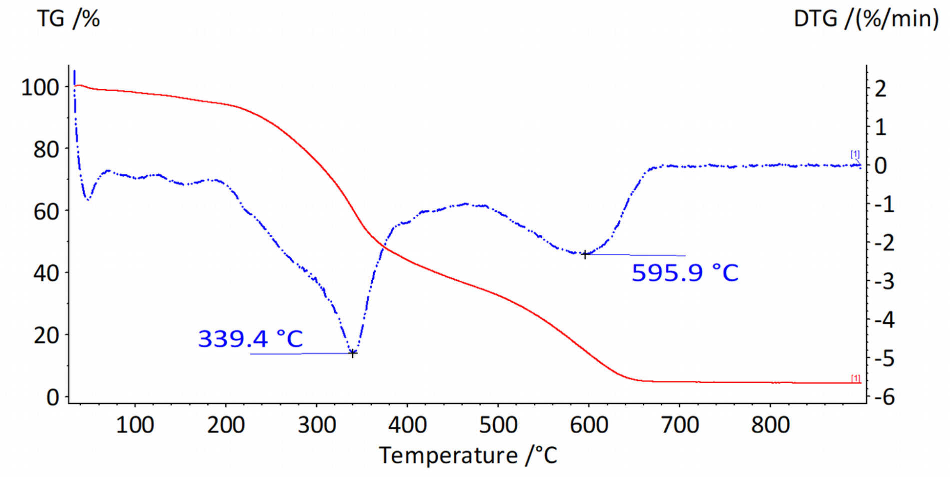
- Weight difference in relation to the Temperature
- Useful to physically characterize how a material reacts with temperature
- Using N_2 is possible to replicate pyrolytic reactions
- Samples before and after extraction have been analyzed in air and N_2
- A FT-IR spectroscopy can be coupled to TGA to obtain real-time information about the evolved gases during thermochemical reactions

Apple seeds before extraction analysed by TG in Air
(ID: Pre-Air)

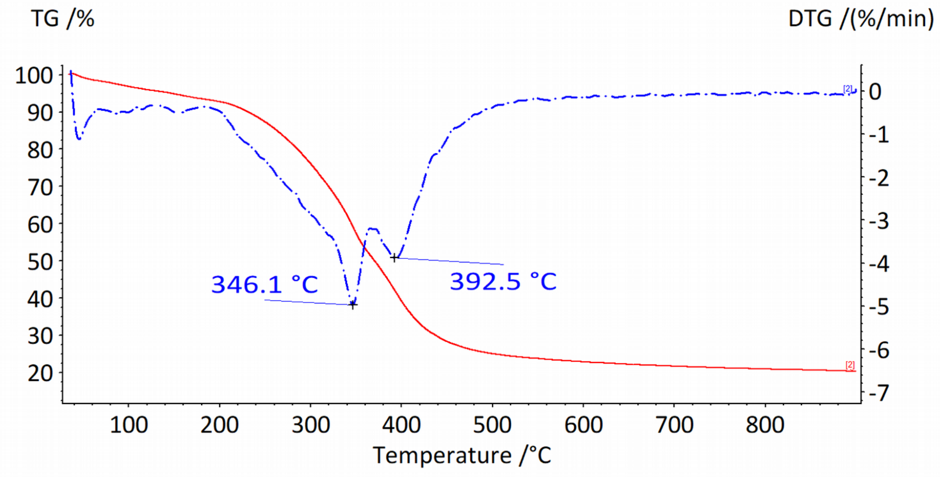


Results

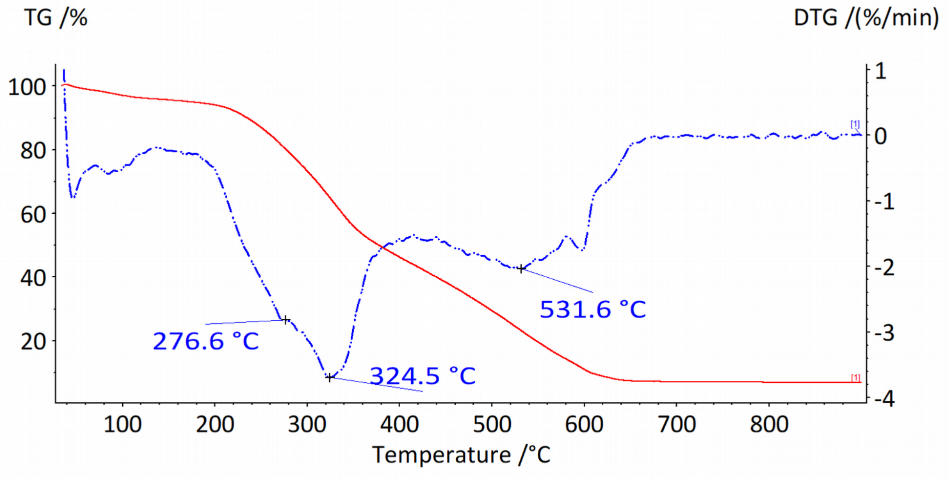
- Pre-Air



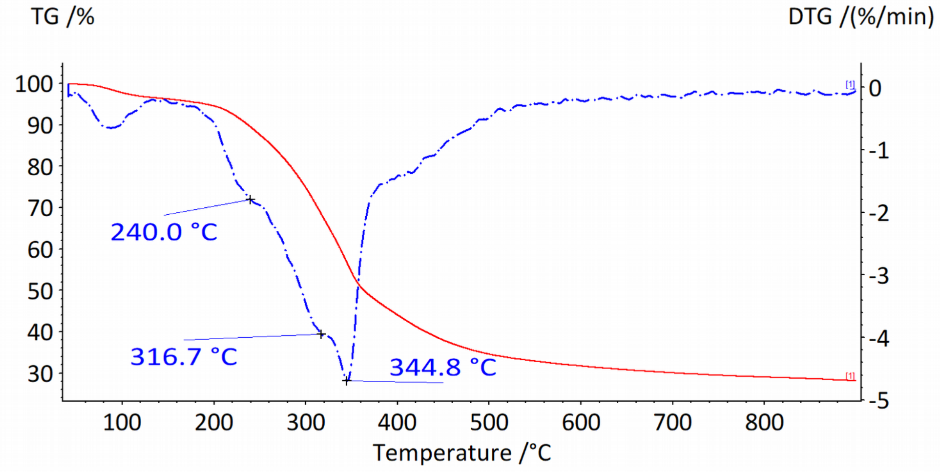
- Pre-N_2



- Post-Air



- Post-N_2



Thermogravimetric analysis

- Peak Temperatures

T°C	Onset		1st peak		2nd peak	
Pre-Air	277.6	±3.5	340.3	±0.7	591.3	±7.9
Post-Air	250.8	±2.6	323.3	±1.6	526.0	±5.8
Pre-N_2	282.1	±2.6	346.0	±0.6	393.4	±1.3
Post-N_2	270.9	±0.7	326.3	±0.1	345.3	±0.6

Differences Air Pre Vs Post	°C
T° Onset	- 26.8
T° First DTG Peak	- 17.0
T° Second DTG Peak	- 65.3

Differences N_2 Pre Vs Post	°C
T° Onset	- 11.2
T° First DTG Peak	- 19.7
T° Second DTG Peak	- 48.2

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Thermogravimetric analysis

- Mass Changes from total mass

%	Mass change 1st peak	Mass change to end	Residual Mass	Unburnt (residual - ashes)
Pre-Air	33.46	55.68	10.66	7.16
Post-Air	28.72	58.19	13.09	8.88
Pre-N_2	34.01	39.67	26.33	22.82
Post-N_2	37.91	28.26	33.84	29.62

Differences Air Pre Vs Post	%
First Peak	- 4.74
To end	2.51
Residual mass	2.43
Unburnt	1.71

Differences N_2 Pre Vs Post	%
First Peak	3.90
To end	- 11.41
Residual mass	7.51
Unburnt	6.80

Thermogravimetric analysis

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%	Mass change 1st peak	Mass change to end	Residual Mass	Unburnt (residual - ashes)
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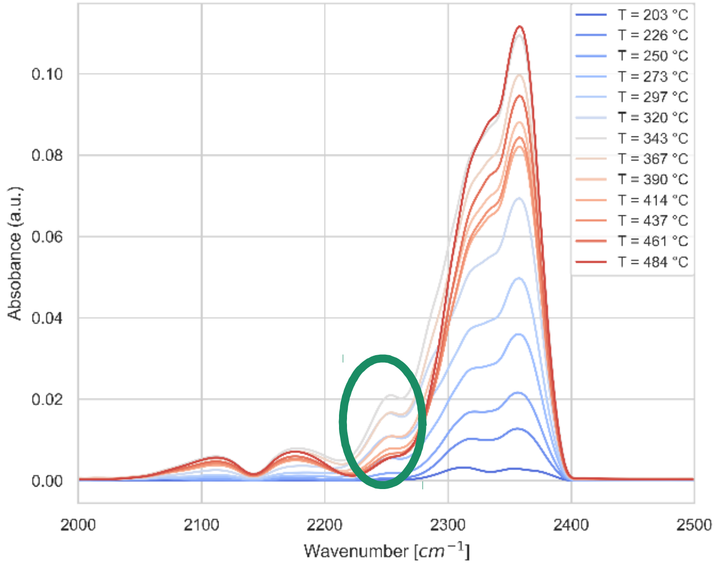
First Peak	- 4.74
To end	2.51
Residual mass	2.43
Unburnt	1.71

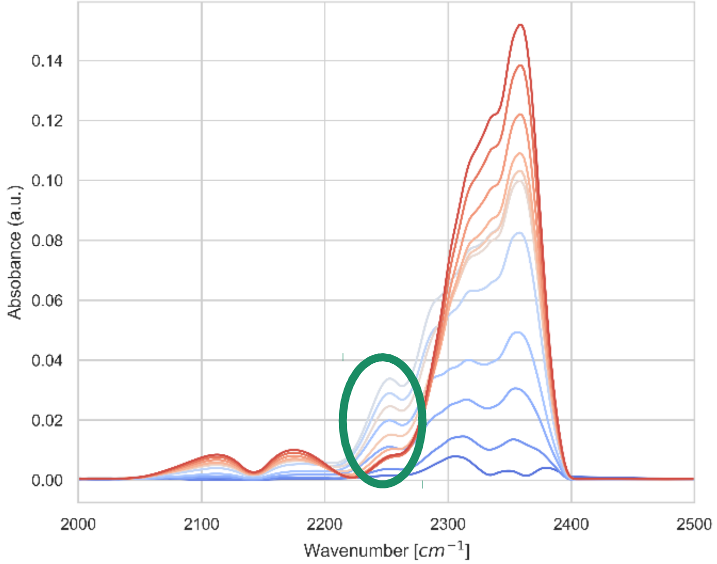
Differences N_2 Pre Vs Post	%
First Peak	3.90
To end	- 11.41
Residual mass	7.51
Unburnt	6.80

Results

TG/FT-IR/EGA in air

- Band at 3295 cm-1 corresponds to O–H stretching vibrations [9]
- Peaks at around 3000 cm-1 are due to the aliphatic saturated C–H stretching vibration [9]
- Bands between 1600 and 1800 cm-1 are indicative of free and esterified C=O groups [9]
- The peaks at about 1000 cm-1 are assigned to C–O–C linkage of lignocellulosics [9]
- Peaks at 877 cm-1 characterize β-glycosidic linkage of cellulose [9]
- Isocyanic acid peak (CHNO) at around 2250 cm-1 [8]



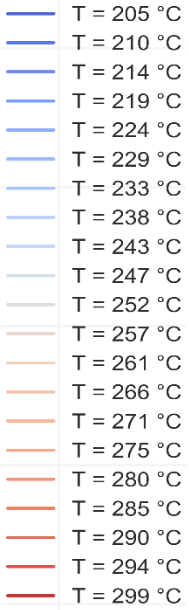


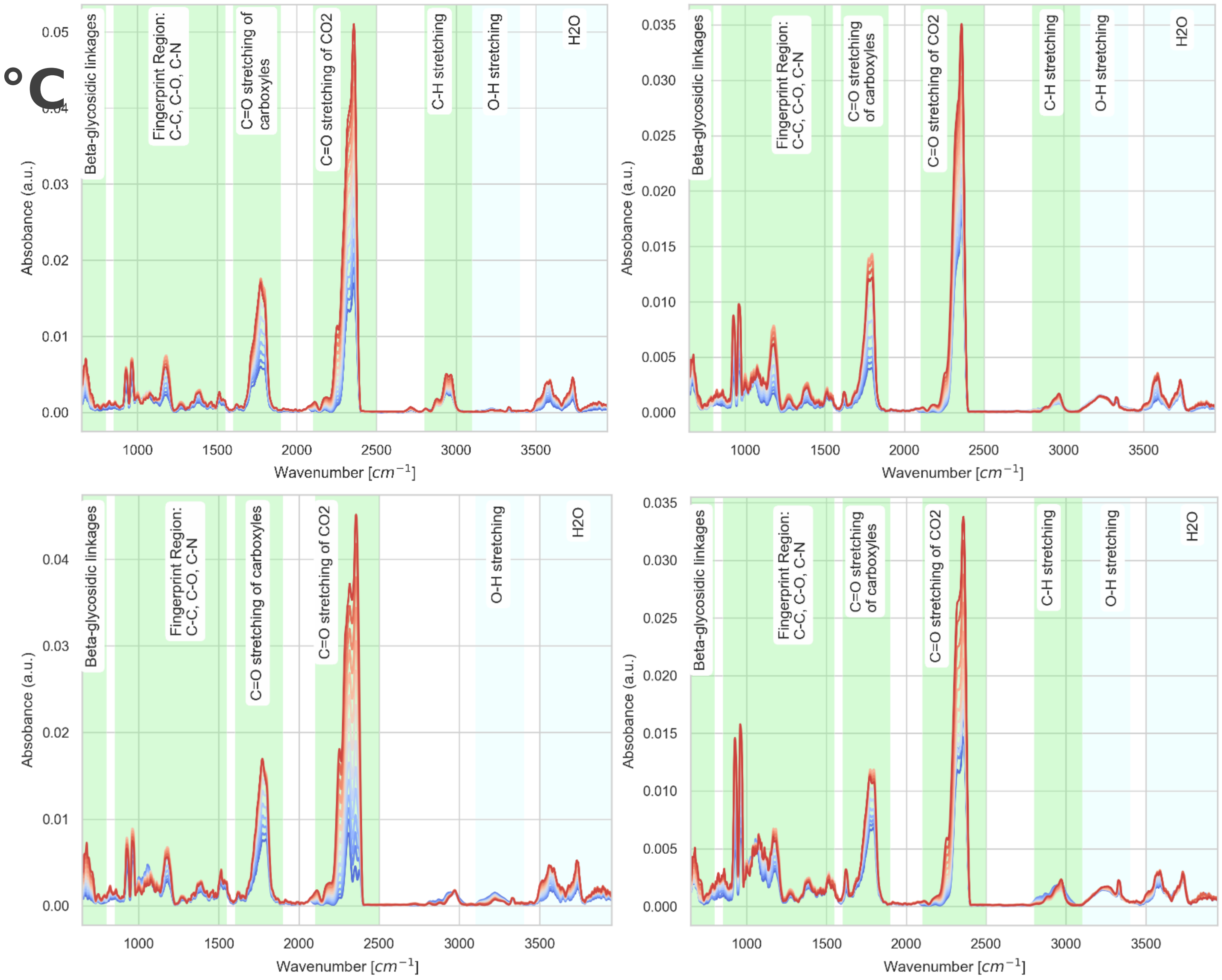
[8] NIST Standard Reference Database 69: NIST Chemistry WebBook
[9] Sidi-Yacoub et al. Characterization of lignocellulosic components in exhausted sugar beet pulp waste by TG/FTIR analysis. J. of Thermal Analysis and Calorimetry (2019)

Results

200°C – 300°C

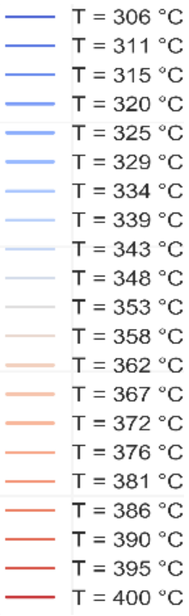
- Pre-Air
- Post-Air
- Pre-N_2
- Post-N_2



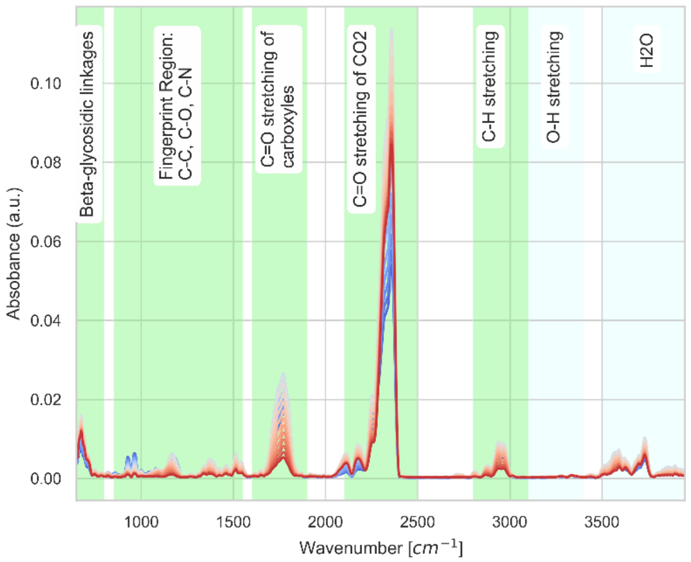


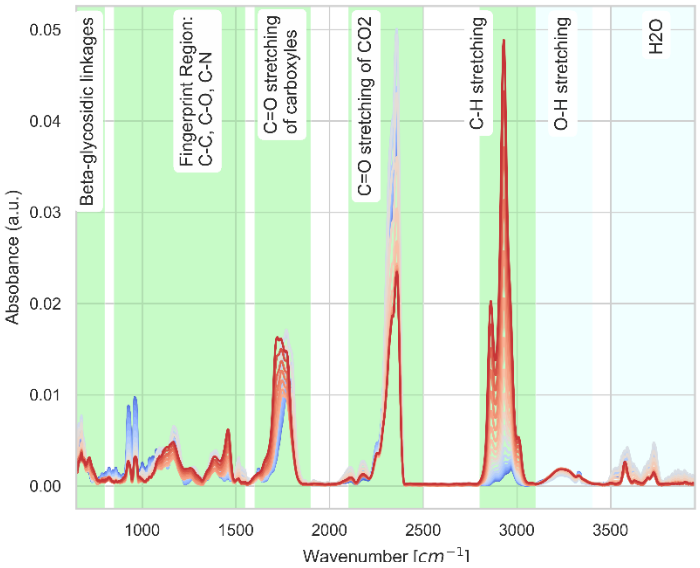
Results

300°C – 400°



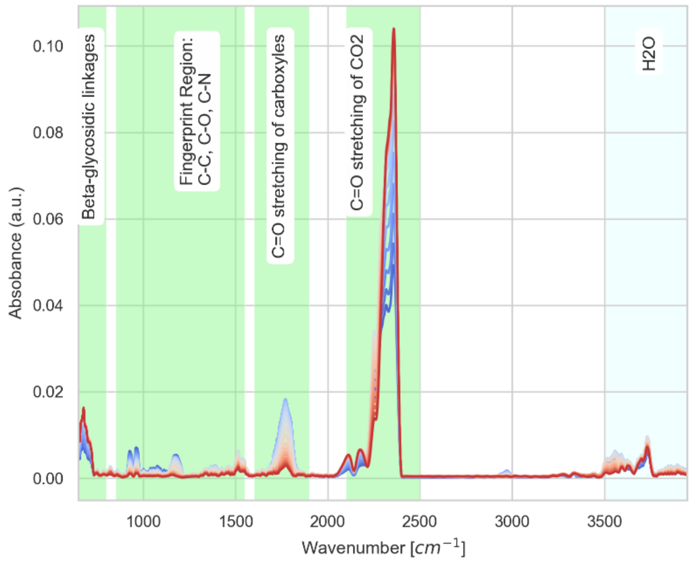
- Pre-Air

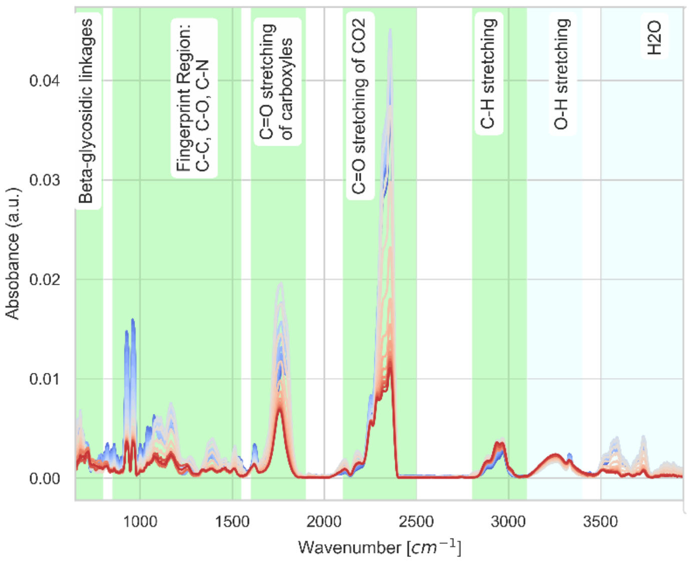




- Pre-N_2

- Post-Air





- Post-N_2

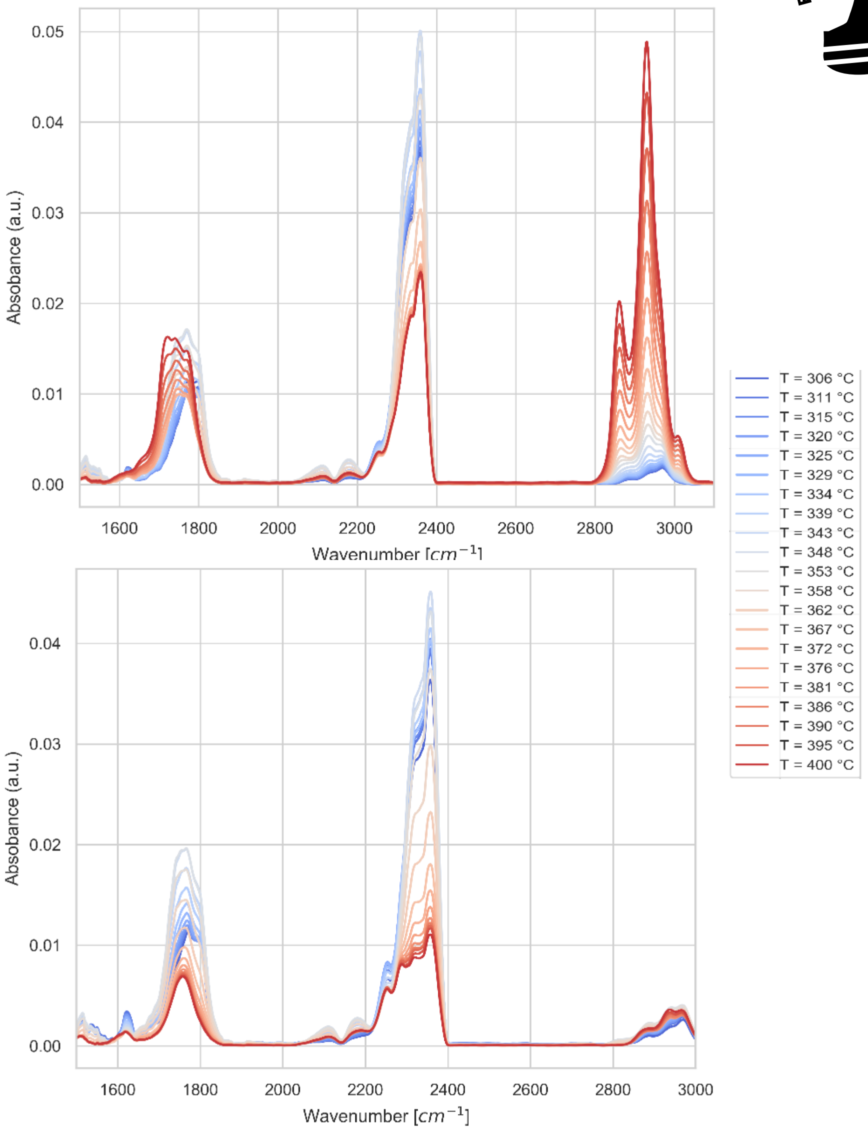
Results

TG/FT-IR/EGA in N_2

- C-H stretch below 3000 cm^{-1} in samples before extraction: Possible fatty acids in gas phase [8]
- In samples after extraction, peaks overlap at around 2300 cm^{-1} [8]
- Evolution of gases at different temperatures in the C=O region (1600- 1800 cm^{-1}) in post extracted samples
- Derivatives of Furan from carbohydrates

[8] NIST Standard Reference Database 69: NIST Chemistry WebBook

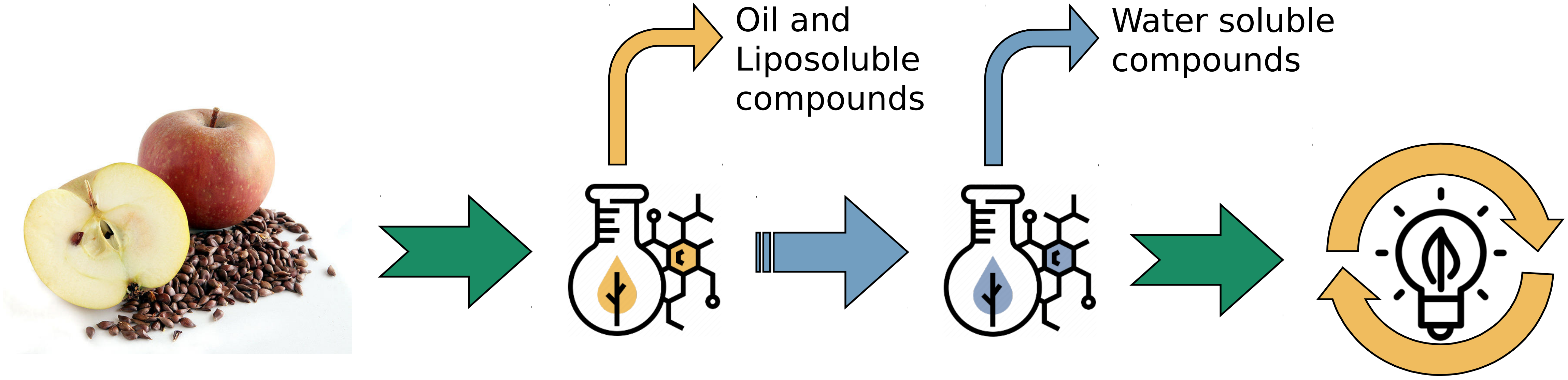
- Befor e Extr.
- Post Extr.



Conclusion

To recap:

- Apple seed as interesting resource for valued compounds
- Effect of extraction on thermochemical properties by means of TG/FT-IR/EGA
  - Lipid extraction affects thermal properties, reducing HHV
  - Increase in char yield in samples after extraction
  - Lipids volatilizes into gaseous fatty acids
- Future research: Thermal consequences of further extracting water soluble compounds (e.g. polysaccharides,…)



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Thank you for your attention

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