Thermochemical valorization of spent apple seeds: preliminary assessment by thermogravimetric analysis coupled with evolved gas characterization

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Abstract

Considering the whole process from cradle to grave, food production is one of the most energy intensive and polluting activities. In Europe, food waste is expected to rise to about 126 million tons a year by 2020, unless actions are taken to halt this trend [1]. A polygenerative concept could eventually alleviate part of its environmental issues as part of a circular food system. This study aims to evaluate the chance to further valorize exhausted apple seeds, after supercritical CO_2 ($ScCO_2$) extraction, and ultimately assess the suitability of thermochemical conversion routes based on pyrolysis and gasification. Apple seeds before and after extraction were characterized for their moisture and ash content, elemental composition (carbon, hydrogen, nitrogen and sulfur content), higher heating value (HHV). Thermal analysis was performed using a Simultaneous Thermogravimetric Analyzer coupled with a Fourier Transform Infrared Spectrometer for the analysis of evolved gases. The results showed that the main compound extracted was the lipid fraction. However, exhausted biomass still contained cellulosic and non-cellulosic polysaccharides as well as proteins still holding value and energetic content. HHV of spent apple seeds was 18 % less than untreated apple seeds. Thermogravimetry showed characteristic temperatures that can be attributed to the degradation of different biological compounds thank to the coupling with the analysis of evolved gases. In conclusion, the methodology presented here provided an insight into possible valorization routes of apples seed after $ScCO_2$ treatment by means of thermochemical conversion processes, underling the impact of $ScCO_2$ extraction on the subsequent exploitation of this substrate.

Keywords: Biorefinery, Food-processing, Extraction, Energy.

Introduction

Food value chain is one of the major contributors to environmental degradation and greenhouse gases (GHGs) emissions in all its stages: production, processing, storage, transportation, consumption and waste. Indeed, each year approximately 22 % of the total GHGs emitted on Earth comes from the agri-food sector [2].

In Europe, food production is a vital manufacturing sector with a turnover of circa € 1 trillion and the highest level of employment (4.2 million people in 2017) [3]. 40 % of European land is occupied by the food system. The system is the backbone of rural economies and its productivity has been boosted in the last 70 years thanks to industrialization, intensification and specialization [4] .

As clearly evidenced by Macarthur *et al.* [4], "a circular food system would be regenerative, non-wasteful, and healthy" reducing the actual food cost per person by 30 %. This wholesome cycle will restore fertility in degraded lands and minimize the use of fertilizers and pesticides, providing healthier food and energy to consumers and companies [4].

Modern biorefineries will evidently be part of such a system. As the International Energy Agency (IEA) [5] has defined, biorefining is "the sustainable processing of biomass into a spectrum of marketable products and energy", supporting an efficient and flexible conversion of biomass using a combination of processes. As final aim, a wide range of different products can be obtained. Conceptually, such a definition is similar to oil refineries, but broads the product limits from purely biomass-to-energy to the extraction of various compounds for several markets. Although different technologies (e.g. extraction, biochemical and thermochemical methodologies) should be integrated in a biorefinery, nowadays they are independently studied, impeding a real development through possible integrations. Integrated technologies with high potential can implement the biomass conversion into food and feed ingredients, fine chemicals, materials and bioenergy. As a result, an improved use of biomass is implicitly achieved, producing valuable compounds from the whole biological feedstock and consequently, reducing waste to dispose of.

A first process in this perspective was suggested by Budarin *et al.* [6] to obtain a wide range of possible products using wheat straw as single starting material. They integrated the extraction of waxes using supercritical CO_2 ($ScCO_2$) with low temperature microwave pyrolysis (< 200 °C). As a result of this integrated biorefinery, products could be

internally recycled for energy and supply purposes, increasing the overall final value. For example, authors proposed to use the liquid fraction as possible disinfectant or antifungal agent, and internally recycle the gases obtained from the combustion of char (mainly CO_2) to supply the requirements for the extraction process. Also, organic bio-oil could be exploited and refined to produce transportation fuels.

In this framework, the current study is intended to evaluate the possibility to blend waste-to-energy processes with the upstream extraction of bioactive compounds from food waste, in particular focusing on the effect of their extraction on the subsequent thermochemical valorization of apple (*Malus spp.*) residues. As stated by Ferrentino *et al.* [7], apple residues after juice-making process are still holding valuable compounds with several applications, for instance in bakery, cosmetic and oil-based products.

Apple seed [8] is a by-product of juice production and also abundantly available in the Italian region of South Tyrol. The region accounts for 19 000 hectares of dedicated area for apple production, supplying up to 50 % of the national Italian apple market, 15 % of the European and 2 % of the global apple market [9]. Approximately 70 million tons of apples are produced yearly worldwide. Moreover, noticeable amounts of apples are required for juice production, generating residues that account for 25 - 35 % of the weight of the raw material. For instance, in Germany, 200 to 250 ktons of wet apple pomace are produced per year, while pomace production from Japanese, Iranian, US-American, Spanish, and New Zealand apple processing was reported to amount respectively 160, 97, 27, and 20 ktons per year. The overall global apple pomace production was expected to exceed 3600 ktons per year in 2010 [10].

CO_2 is the most widely used fluid for extraction because it is safe, food grade and widely available. In its supercritical state (temperature of 31.1 °C and pressure of 7.4 MPa), compounds can be selectively extracted changing CO_2 properties. In fact, fluids at temperatures and pressures beyond the critical point can change the solvating properties, acting as solvent. Using this technology, the extracted compounds from apple seeds are mainly fatty acids, waxes and liposoluble compounds (i.e. tocopherols and Vitamin E), while other valuable compounds, remains in the defatted residue. For example antioxidants in form of polyphenols can be further recovered if another extraction step would be performed [11]. Apple seeds also contains cyanogenic glycosides (e.g. amygdalin and prunasin), highly toxic compounds for humans. These nitrogen glycosides remain into post extracted apple seeds, raising some health concerns if they are valorized as food and feed supplement. Indeed, when ingested, cyanogens release hydrogen cyanide as output of metabolic conversion, a poisonous molecule with a long history. Recently, Gunes *et al.* [12] has proposed an innovative method to further exploit defatted apple seed residues valorizing the antioxidants contained in the chewing gum production.

The aim of this work is to evaluate the chance to use apple seeds, after $ScCO_2$ extraction, as a raw material for downstream thermochemical conversion processes, such as pyrolysis and gasification. For this reason, samples before and after $ScCO_2$ extraction have been investigated by physicochemical and thermogravimetric analyses to define strategies for their further valorization.

Materials and Methods

Freeze-dried apple seeds samples before and after $ScCO_2$ extraction were used in this study, as received from the Food Quality Laboratory (e-Sense Lab) of the Free University of Bolzano. The extraction process will be discussed elsewhere.

Ultimate analysis

Ultimate analysis has been determined according to International standard protocols UNI EN ISO 18134-2:2015 and UNI EN 14775:2010 for moisture content and ashes respectively. A Vario MACRO cube, Elementar©, was used for determining the carbon, hydrogen, nitrogen, sulfur content. In short, the principle of such instrument is that during combustion at high temperatures (1000 °C) in excess of oxygen, carbon is converted into CO_2; H_2 into water; nitrogen into its oxides in form of gases and sulphur into SO_2. Other elements that compose the sample are removed by an absorption trap after combustion. Gases pass through a copper (Cu^{2+}) column by an inert carrier gas. This step has the function to remove the free O_2 in excess and to convert NO_x into N_2 gas. Then gases pass through a Thermal Conductivity Detector (TCD) and the quantity assessed [13].

Calorimetric bomb

Higher Heating Value (HHV) was measured using an isoperibolic calorimeter (IKA C200). Essentially, a colorimetry consists of a closed cylinder in pressure (30 bar O_2) into a vessel filled of deionized water. A thermocouple

has the function to indicate water temperature and a magnetic stirrer allows temperature to be as homogeneous as possible inside the vessel. Sample is burnt by a high voltage ignition and, the rise of water temperature is recorded. By knowing the heat capacity of the instrument material, the water and the fuse; it is possible to calculate the amount of heat released by a defined amount of the sample [14].

Fourier Transformed Infrared Spectroscopy with Attenuated Total Reflection (FT-IR ATR)

FT-IR is a technique to identify the molecular composition of a complex mixture that can be solid, liquid or gas. Essentially, when molecules are exposed to an electromagnetic beam with enough energy to excite electrons, bond that composes the sample can dissipate the energy by movements along them (i.e. vibrational, rotational, stretching, bending, rocking). Since each bond constituting the sample can have different but characteristic behaviour to dissipate this excitement, it is possible to identify complex molecules like those that compose biological matters. Furthermore, using a mathematical transformation (Fourier transformation) it is possible to relate the wavelength at which a bond is excited and the quantity of the absorbed energy by such bond, in function of the time. As a result, a plot called infrared spectrum is collected. Attenuated total reflection is a new approach that uses properties of evanescent waves formed when infrared (IR) light is introduced with an angle exceeding the critical angle for internal reflection [15]. When passing through a highly refractive crystal, an IR beam creates an evanescent wave that is proportionally attenuated according to sample chemical characteristics. The remaining, not absorbed electromagnetic wave exits the crystal and a detector measures the difference from the source.

A FT-IR, Tensor 27, Bruker© equipped with Platinum© ATR has been used to analyse apple seed biomass before and after $ScCO_2$ extraction using the associated Opus© 7.5 software. A resolution of 4 cm^{-1} and 16 scans has been chosen as trade-off among scanning time, absence of artefacts and fair signal to noise ratio. For each analysed substrate, the analysis has been repeated at least 3 times on different sub-samples.

TG/FT-IR (Evolved Gases Analysis)

In each test, 10 mg of sample have been analysed using a Netzsch Simultaneous Thermal analyser (Jupiter STA 449F3, Netzsch©) to obtain mass loss profiles in relation to the sample temperature during heating. Samples were heated from 40 °C to 900 °C at a heating rate of 10 °C min^{-1}, using both dried air as well as nitrogen at 20 mL min^{-1}. An additional flow of 20 mL min^{-1} of nitrogen, used a protective gas, was set in all the tests. Such analytical instrument was also coupled with the FT-IR spectrometer previously described through a transfer line at 220 °C. So, it was possible to monitor the evolution of gases as temperature rises. Evolution gas analysis (EGA) is becoming an important instrument to investigate thermal mass loss into gas phase [16]. A liquid Nitrogen cooled MCT (mercury-cadmium-telluride) has been adopted as detector, IR spectra were recorded with a resolution of 4 cm^{-1} every 15 seconds, with 32 scans every sample measurement in the range of spectrum between 4000 to 650 cm^{-1}. All the spectra have been baseline corrected using a concave rubber band correction algorithm with 10 iterations computed over 64 points. Each coupled TG/FT-IR test was repeated 3 times for each sample on different sub-samples.

Results

Ultimate and Calorimetric Analyses

Elemental analysis of apple seeds before and after the extraction gave some confirmations about the main compound that has been extracted. Although the extracted compound was already known to be the lipid fraction, it was interesting to notice a clear difference in the two samples.

Results obtained from samples analysed in triplicate showed a decrease in the carbon content after the extraction (from 53.5 to 46.9 %), indicating that the component extracted was entirely organic (see Table 1). Moreover, the ash content in samples after the extraction (4.21 %) was higher than those before (3.50 %) due to the decrease of the organic matter and the correspondent increase of the mineral matter. In addition, elemental analysis demonstrated that the extracted compound was mainly composed by C, H, O, but without N, with a relatively high HHV, which

accounted for about 20 % of the whole seed calorific value. As evidence of that composition, the C/N ratio between samples was 40 % lower in samples after the extraction in comparison with those before.

Table 1.Ultimate and calorimetric analyses of apple seeds found in the literature in comparison to results obtained in this study [8,17,18]

Literature (as received)	Measure	Value	
Ash	$\%wt_{db}$	4.1 ± 0.3	
Moisture	%	5.00 ± 0.46	
Carbon	$\%wt_{db}$	14.97	
Hydrogen	$\%wt_{db}$	2.93	
Nitrogen	$\%wt_{db}$	7.95	
		Experimental	
	Measure	**Before Extraction**	**After Extraction**
Ash	$\%wt_{db}$	3.50 ± 0.10	4.21 ± 0.05
Moisture	%	5.42 ± 0.13	5.47 ± 0.16
Carbon	$\%wt_{db}$	53.50 ± 0.17	46.90 ± 0.23
Hydrogen	$\%wt_{db}$	7.30 ± 0.01	6.30 ± 0.04
Nitrogen	$\%wt_{db}$	6.71 ± 0.15	9.30 ± 0.10
Oxygen	$\%wt_{db}$	31. 80 ± 0.26	36. 90 ± 0.30
Sulphur	$\%wt_{db}$	0.66 ± 0.12	0.60 ± 0.03
HHV	J/g	22572 ± 84	18241 ± 35

*db: dry basis

FT-IR

Samples have been firstly analyzed using FT-IR ATR to have more information about what chemicals were missing after the extraction. Characteristic spectra obtained from samples before and after have been overlapped to visually identify the missing peaks and then characterize each of them. Lee *et al.* [19] have recently used FT-IR measurement to identify the origin of soybeans by multivariate statistical analysis and, surprisingly, the spectrum was quite similar to the ones presented in this study. Thanks to this, it was much easier to define molecular bonds associated with the peaks represented in Fig. 1.

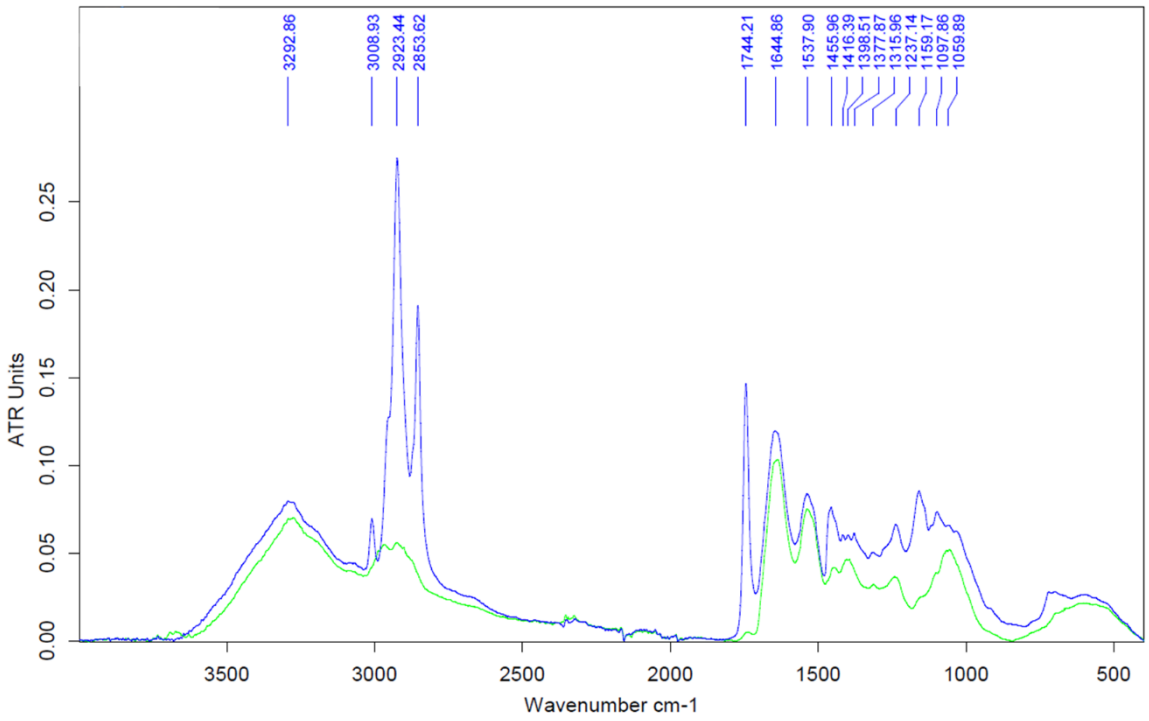

Fig. 1 FT-IR ATR spectra of apple seeds before (blue) and after (light green) $ScCO_2$ extraction

The region with a broad peak at about 3300 cm^{-1}, corresponds to the presence of free and intramolecular hydroxyl groups (-OH) and amine group (-NH) that might be related to the presence of polysaccharides and proteins. As evidence of this, the same band can be identified in samples before and after extraction, blue and green spectra in Fig. 1, respectively. On the contrary, the 3 intense peaks at around 3000 cm^{-1} are clearly distinguishable in the sample before but not after extraction. This was somewhat expected; these three peaks at around 3000 cm^{-1} are typical C–H stretching bonds representing mainly lipids. In particular, the band at about 3009 cm^{-1} corresponds to the C=H stretch, characteristic of unsaturated lipids. Furthermore, the next intense peak at 1744 cm^{-1} in the before extraction sample might be related to a C=O stretching, another band suggesting the presence of lipids. The fact that the bands previously described are strongly present in samples before the extraction and not in those after gave further evidence of the correct interpretation [19].

Conversely to the bands described so far, in the region between 1400 - 1000 cm^{-1} there are some similarities between the samples. This region seems to be mainly related to bonds stretches associated with proteins, carbohydrates and nucleic acids. For example, the unchanged bands at 1645 and 1538 cm^{-1} are typical bonds stretches of amides (I and II, respectively).

To sum up, identified bands and suggested biomolecular assignment are enlisted in Table 2 according to Lee *et al.* [19]. A spectrum similar to the one of the sample before extraction was broadly described by Scholz *et al.* [20] as medium to long aliphatic chains, precisely 1-Decanol ($C_{10}H_{22}O$) and 1-Phenyldodecane ($C_{18}H_{30}$). While, even if not clearly representative as in the previous sample, the most similar compound spectrum associated with post extracted samples was Polyamide-6. The most characteristic functional group of this molecule is a secondary amine (- NH -) group covalently bonded to a carbonyl group (C=O). Therefore, the results have been interpreted as proteins being the most present biomolecule in samples after the extraction of lipids using $ScCO_2$ treatment.

Table 2 FT-IR ATR band assignments of apple seeds before and after $ScCO_2$ extraction (adapted from [19])

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) [21]
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

Thermogravimetric Analysis coupled with FT-IR for Evolved Gas Evolution (TGA / FT-IR / EGA)

Thermal decomposition of samples was evaluated by thermogravimetric analysis. The resulting diagrams show the mass loss of samples and its derivatives curves (i.e. TG and DTG) at increasing temperatures. Fig. 2 shows TG and DTG curves of apple seeds before and after extraction, analyzed both under oxidative (air and nitrogen) and inert (pure nitrogen) atmosphere. Data obtained from the coupling with the FT-IR were computed to obtain the Gram Schmidt (GS) curve. The curve is of paramount importance to relate the amount of evolved gases measured by FT-IR spectrophotometer with mass loss. The GS curve can be defined as the sum of all IR absorbance for all wavelengths as a function of time (which in this case is linearly correlated with the temperature) [16].

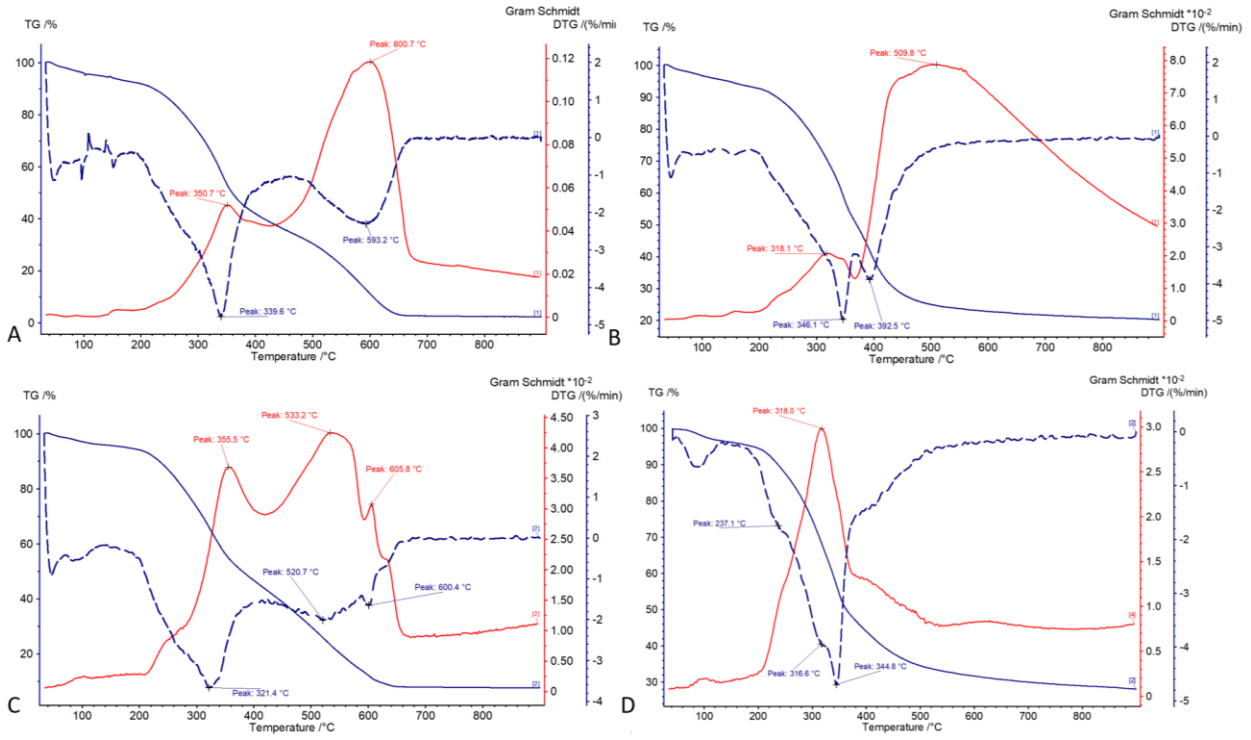

Fig. 2 TG, DTG and Gram Schmidt (GS) curves of A) Apple seed before extraction analyzed by TG in air, B) Apple seed before extraction analyzed by TG in nitrogen, C) Apple seed after extraction analyzed by TG in air, D) Apple seed after extraction analyzed by TG in nitrogen. DTG curves correspond to the dashed lines while GS curves to the solid ones.

For all curves, the initial mass loss below 120 °C is due to water evaporation. Therefore, samples lose on average 5.6 % of weight during the first step, according to the ultimate analysis section. Onset temperatures are ranging from 282 °C to 250 °C; analyses in air showed the major difference among samples. The onset temperature difference between samples before and after extraction analyzed in air is on average 278 °C for samples before and 251 °C after. This 10 % decrease in the onset temperature could be explained by the upstream extraction process of lipids. Lipids are long aliphatic chains made of 16 to 22 carbons. With respect to other biological compounds, such as polysaccharides or proteins, these long chains can absorb more heat before starting the first proper thermal degradation step.

All samples show a first degradation peak at around 340 °C, the sample with some differences in this respect was just post-extracted apple seeds analyzed in air. Again, for the same reason as before, this suggests that less energy is needed to begin the degradation in samples after extraction, therefore occurring at lower temperature. The peak shape resembles the typical curve of lignocellulosic biomass thermal degradation. Wu *et al.* [22] have recently studied this material using bamboo as feedstock, concluding that the different components of cellulosic material (i.e. lignin, cellulose and hemicellulose) have different thermal characteristics and different mechanisms of reaction at high temperatures. Such different degradation mechanisms can be seen by the deconvolution of this peak. Regarding samples analyzed in air, assuming 10 % of mass made of the sum of water and ashes, cellulosic degradation peak accounts for about 25 % of mass. While in nitrogen, both pre and post extraction samples have this peak at the same temperature, which is below 350 °C. Since no large difference can be seen among samples, it can be concluded that at this temperature non lipidic components are degraded. So other bio compounds, accounting for about 25 % of apple seed mass have the maximum degradation at this temperature. This percentage is in line with the carbohydrates content found by Yu *et al.* [8] in apple seeds.

The second peak formation seems to be more related to the presence of fatty acids. This was clear in samples analyzed before extraction in air and, somewhat differently in nitrogen. Samples before extraction analyzed in air present a second degradation peak with maximum at 591 °C on average. Although also in samples after extraction a small peak can be identified at around 600 °C, this can be explained by the efficiency of the extraction process. A perfect extraction process does not exist, residues and small parts of extractable compounds will remain into the matrix. So, this peak in post extracted samples could be explained by the degradation of lipids, even if in small amounts but enough to record a mass change at this specific temperature. Furthermore, samples after extraction analyzed by thermogravimetry in air showed a third large peak at about 525 °C. This peak is between the first peak, identified as characteristic of cellulose degradation, and the peak identified as the degradation of lipids and accounts for a mass change of about 33 % from 400 °C to 586 °C. According to the proximate analysis of apple seeds reported by Yu *et al.* [8], 37 % of this biomass is made of proteins.

By coupling the thermogravimetric analysis so far explained with the FT-IR technique, it is possible to monitor the evolution of gases during the thermal degradation. Fig. 3 represents such evolution at selected temperatures based on the GS curve peaks. At first sights the difference in the process atmosphere has a clear influence in the evolution of gases.

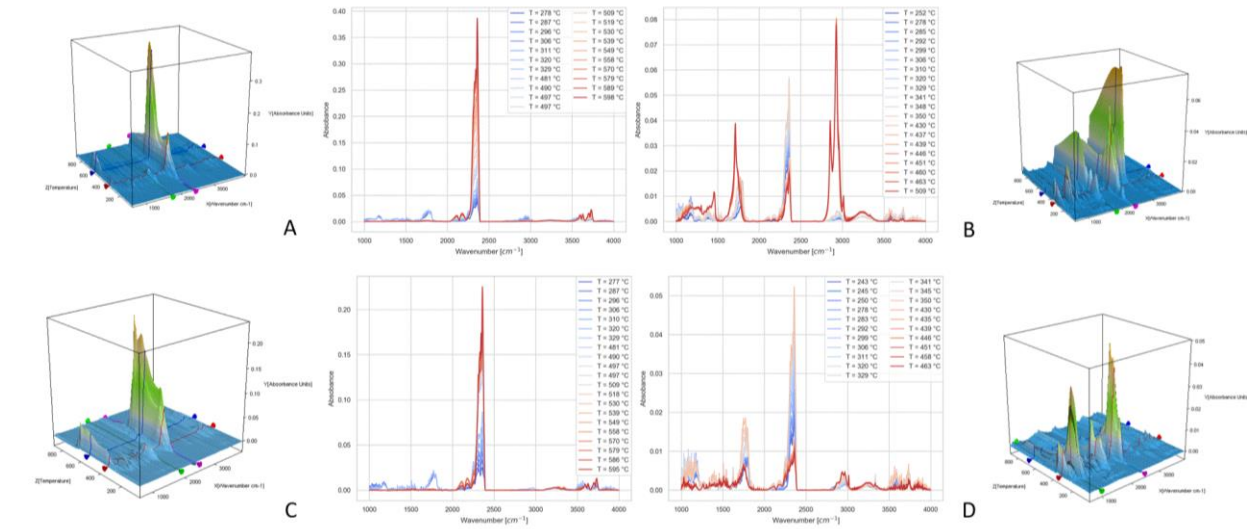

Fig. 3 IR spectra at increasing temperatures obtained from the different samples and under different purge gases A) Apple seed before extraction analyzed by TG in air, B) Apple seed before extraction analyzed by TG in nitrogen, C) Apple seed after extraction analyzed by TG in air, D) Apple seed after extraction analyzed by TG in nitrogen.

Gas evolution during thermochemical assessment in air (Fig. 3.A and 3.C) has the typical oxidative combustion gas peak, with the most characteristic absorbance at 2400 - 2200 cm^{-1} identified as CO_2. Next to this region, at 2200 - 2100 cm^{-1}, there are the two CO gas absorbance bands with almost the same trend in temperature as the latter compound. A closer view of this region (Fig. 5), especially in post extracted samples in air (Fig. 5.C), highlights the presence of a small peak at about 2250 cm^{-1} which can be attributed to C-N compounds. Specifically, it can be speculated that this small band can be a resulting combination of the degradation of cyanidins and proteins, since it was clear that those compounds are not extracted during $ScCO_2$ treatment. Then, at relatively low temperatures (less than 300 °C) a slight peak at about 1700 cm^{-1} can be seen and was attributed to C=O bonds absorbance (Fig. 4). Such band intensity is remarkable, supporting the analysis made by Yang *et al.* [23] attributing this band to hemiacetal cleavage as the main source of C=O groups in cellulose pyrolysis at temperature lower than 350 °C.

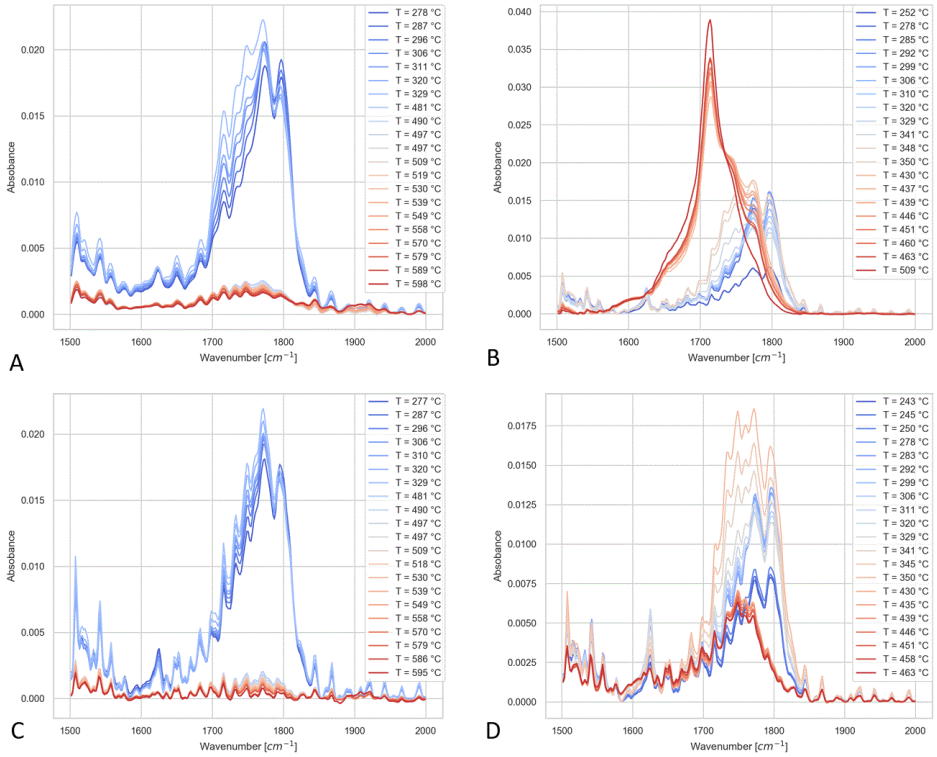

Fig. 4 Particular of the carboxyl peak in the 1500 – 2000 cm^{-1} IR region at increasing temperatures obtained for different samples and under different process atmospheres A) Apple seed before extraction analyzed by TG in air, B) Apple seed before extraction analyzed by TG in nitrogen, C) Apple seed after extraction analyzed by TG in air, D) Apple seed after extraction analyzed by TG in nitrogen.

Another small, low temperature peak appears at 1170 cm^{-1}, in the region where C-C and C-O bonds vibrations occur. This is more clearly distinguishable in samples before extraction than after. To conclude this analysis of evolved gases during thermogravimetric analysis in air of apple seeds before and after $ScCO_2$ of lipids, typical water vapor bands can be seen in the IR region from 3500 to 3770 cm^{-1}. This band was present in all temperature ranges analyzed, corroborating the fact that water is generated during the whole thermochemical process [24].

As it can be seen by Fig. 3 (3.B and 3.D), evolved gas diagrams of samples thermogravimetrically analyzed in nitrogen are more complicated than their equivalents in air. Apart from the water absorbance band at wavelength up to 3500 cm^{-1}, both spectra are quite different. The huge CO_2 peak distinguishable in air, it is different among samples and conditions (Fig. 5).

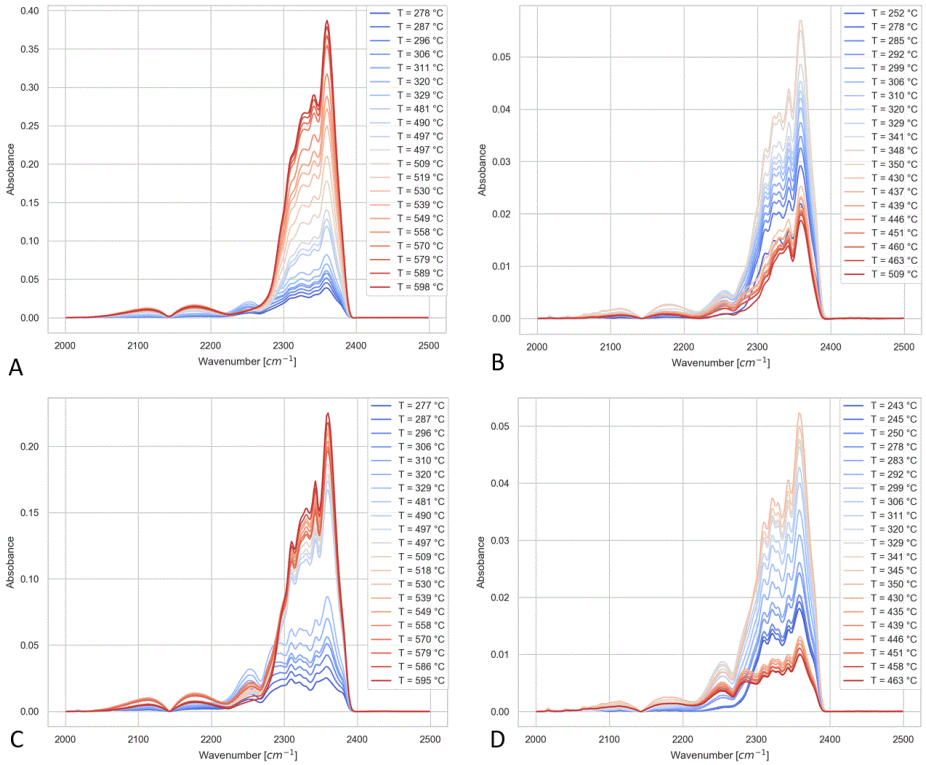

Fig. 5 Particular of the CO – CO_2 peak in the 2000 – 2500 cm^{-1} IR region at increasing temperatures from different samples and under different process atmospheres A) Apple seed before extraction analyzed by TG in air, B) Apple seed before extraction analyzed by TG in nitrogen, C) Apple seed after extraction analyzed by TG in air, D) Apple seed after extraction analyzed by TG in nitrogen.

Samples before extraction show two definite peaks at around 3000 cm^{-1} and 1750 cm^{-1} circa (Fig. 4). The first can be attributed to methane (CH_4) formation in absence of air. According to Xang *et al.* [23] the cleavage of aliphatic side chains and the secondary cracking of volatiles can explain the such release in methane. From the samples under investigation, the evidence of this theory is that lipidic aliphatic chains are cleaved in samples before extraction, while in post extracted biomass the peak in this region is markedly smaller. This can also be regarded as a confirmation of the correct identification of such region. The second peak at 1750 cm^{-1} can be attributed to C=O bonding vibrations characteristic of carbonyl compounds (e.g. ketones, aldehydes, acids and esters) [23]. The interesting feature of this band is that it seems to shift at lower wavelengths at increasing temperatures. This phenomenon has been encountered in both samples when using nitrogen as purge gas (Fig. 4.B and 4.D). A possible answer is that different biological compounds with increasing complexity degrades at increasing temperatures. The resulting peak formation is mainly temperature dependent, but the different origin lead to different gas outputs than can be distinguished by FT-IR analysis. As evidence of this speculation, Aburto *et al.* [25] analyzed thermal degradation of pectin from oranges. They identified signals in the 1730 – 1755 cm^{-1} region as free and esterified carboxyl groups respectively. It is also worth noting that both seed samples analyzed in this study have in these two regions, an apparent proportional intensity with the peak at around 3000 cm^{-1}, attributed in the previous part to methane formation due to aliphatic chains degradation.

Conclusion

This study can be considered as a framework to assess spent biomass using coupled TG / FT-IR instruments for EGA, with the final aim of studying the chance to further valorize such exhausted biomass and evaluate the most viable option. Particularly, the methodology presented here provided an insight into possible valorization routes of apples seeds after $ScCO_2$ treatment by thermochemical conversion processes, underling the impact of $ScCO_2$

extraction on the subsequent exploitation of this substrate. According to Yu *et al.* [8], 35 % of apple seeds composition is made of proteins, 24 % of carbohydrates, ≈ 28% of lipids and the remaining part is a combination of ashes (3.5 – 4 %) and moisture (≈ 5.5 %). It is most likely that the first peak in both TG and FT-IR at around 350 °C corresponds to the thermal degradation of both cellulosic and non-cellulosic carbohydrates. Since this peak is made of a series of smaller overlapping peaks, a mathematical deconvolution of peaks might be a viable approach. Proteins degradation might be related to the peak at 540 °C in post extracted samples analyzed in air. So far, it is not quite clear at which temperature proteins degradation occurs. This phenomenon may happen simultaneously with cyanidins degradation and the consequent cyanide formation (peak at 2250 cm^{-1} wavelength), or silently occur along the whole process, also because proteins are chemically non-homogeneous. What is clear is that more research is needed in this field. Moreover, according to this study, it can be concluded that spent apple seeds degrade at lower temperatures and have a lower HHV than unextracted samples. However, before the thermo-chemical conversion of spent apple seeds also other valuable compounds (i.e. carbohydrates and proteins) should be further extracted and fractionated in order to get the most out of this biomass.

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