Torrefaction at low temperature as a promising pretreatment of lignocellulosic biomass in anaerobic digestion

Dolores Hidalgo, PhD (dolhid@cartif.es)

Introduction

Lignocellulosic biomass is very abundant throughout the world and is the focus of many investigations that seek the best method to value this raw material as a source of renewable energy.

biogas

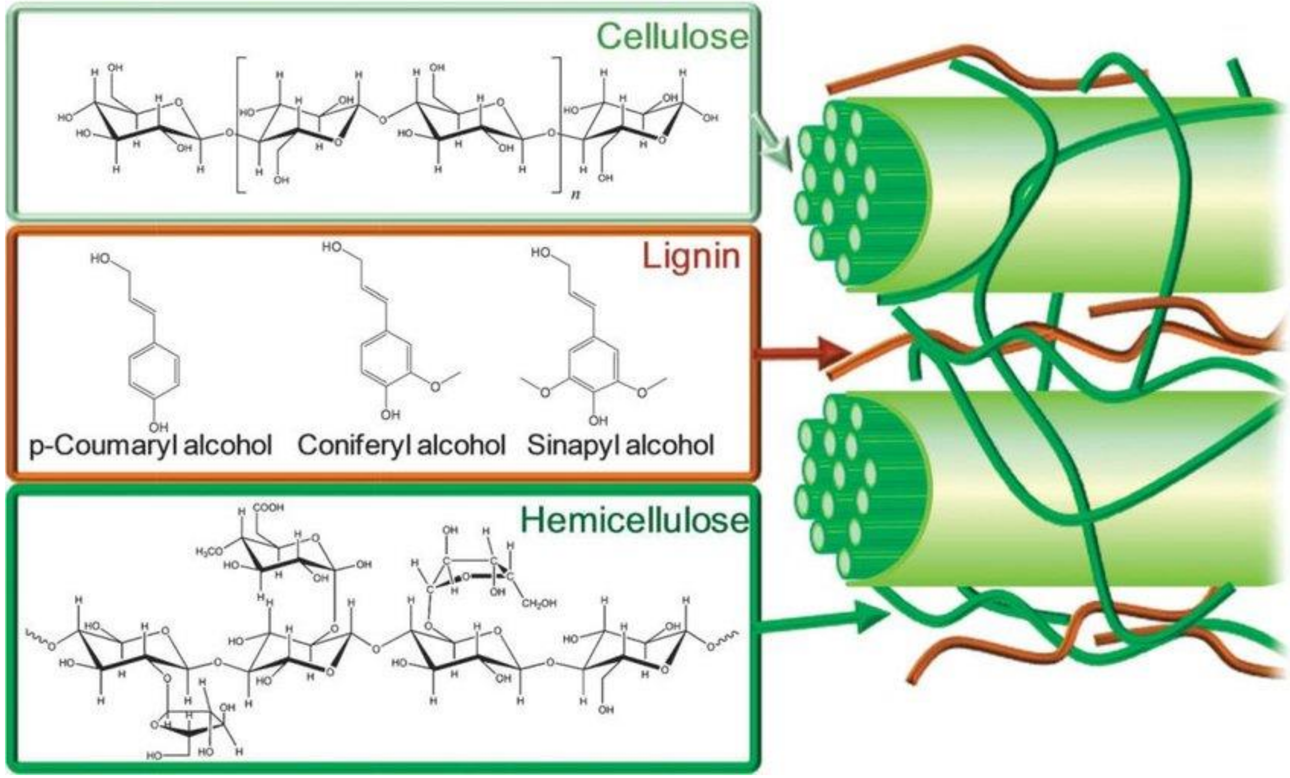
Among these methods, the **anaerobic digestion** of lignocellulosic residues is an option that is gaining interest for the production of methane.

However, and although lignocellulosic biomass presents multiple positive characteristics for bioenergy production, is also associated with several **deficiencies**:

- non-uniform physical properties,
- structural heterogeneity,
- low energy density,
- and low bulk density,
- apart from its recalcitrant nature to microbial attack.

Introduction

The intrinsic structure of this material, composed mainly of cellulose, hemicellulose and lignin, makes its **digestibility difficult** and with it, its degradation and conversion into biogas.



It is proved that the **connected structure** of lignin and hemicellulose provides a **physical barrier** to cellulose breakdown and thus limits its rate of biodegradation.

Introduction

To recover the monomeric sugars present in the carbohydrate fractions for later use in bioprocesses, a **pretreatment stage** is required to open the structure of the material, facilitating its degradation by enzymes and microbes. Numerous methods have been developed to pretreat lignocellulosic biomass:

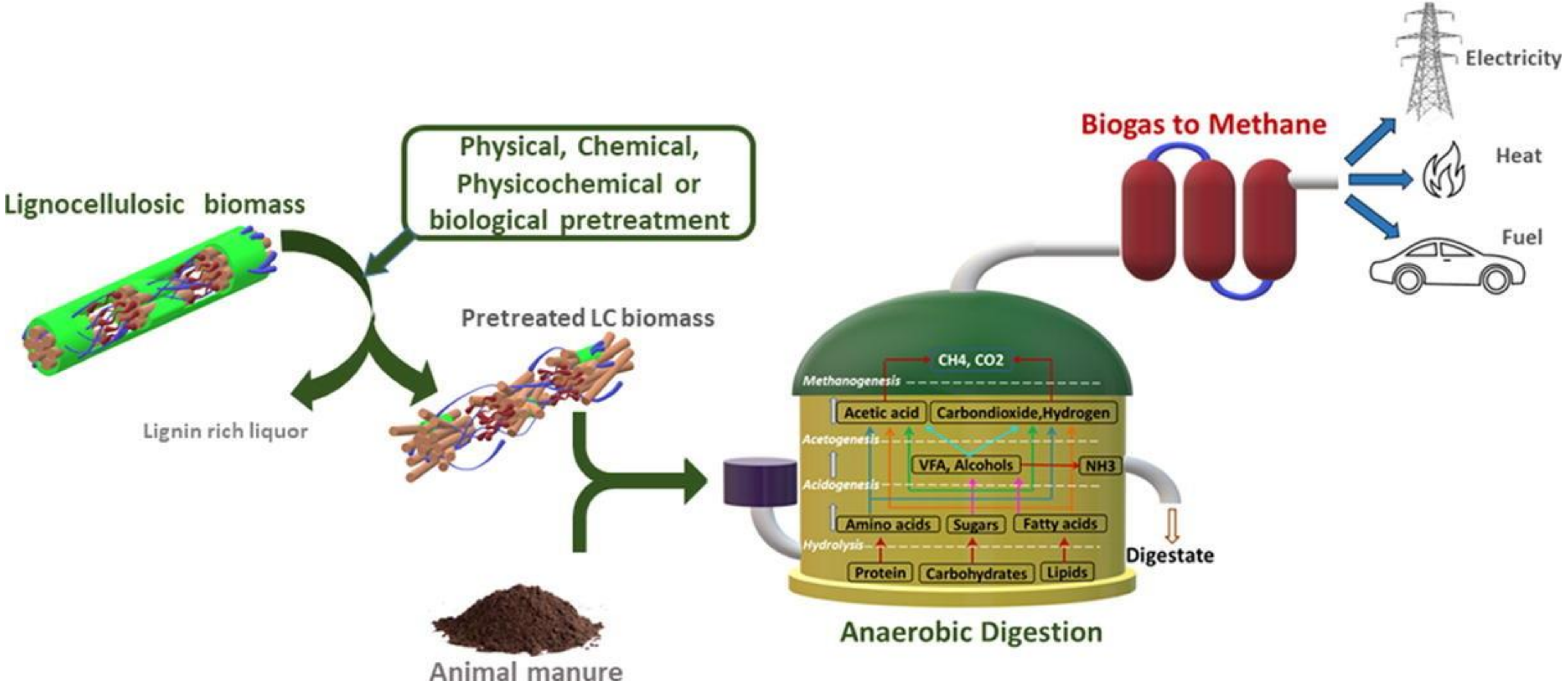


Figure source: Abraham et al. (2020). DOI: 10.1016/j.biortech.2019.122725

Previous work

Four methods to pretreat lignocellulosic biomass have been evaluated:

Cavitation

Pelleting

Extrusion

Torrefaction

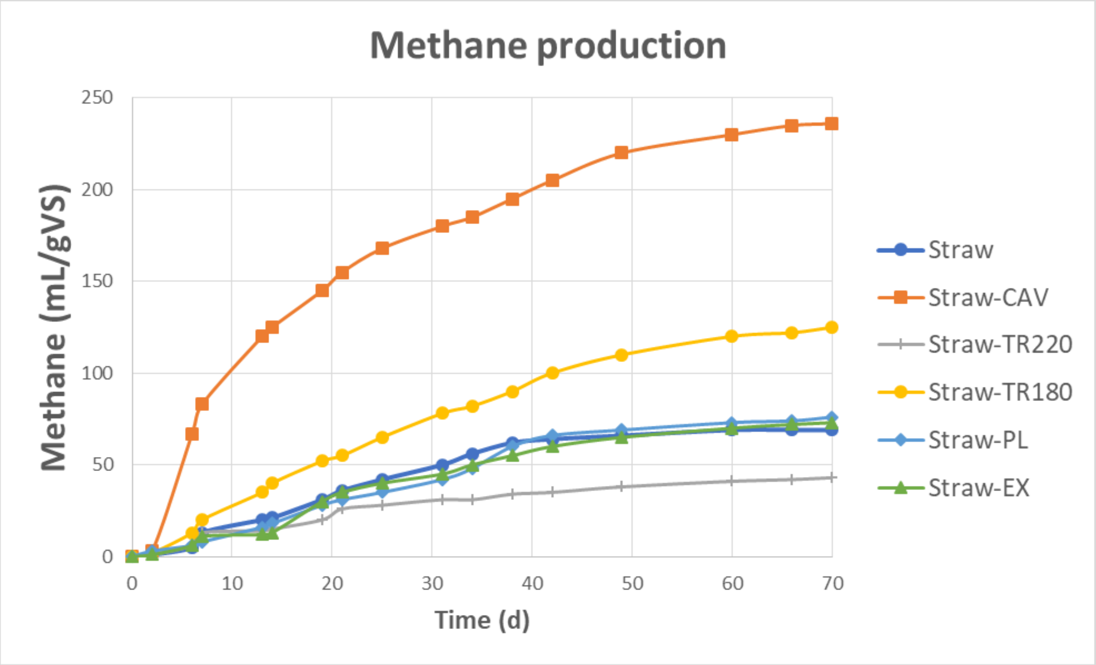
With the aim to improve the production of methane by anaerobic digestion of:

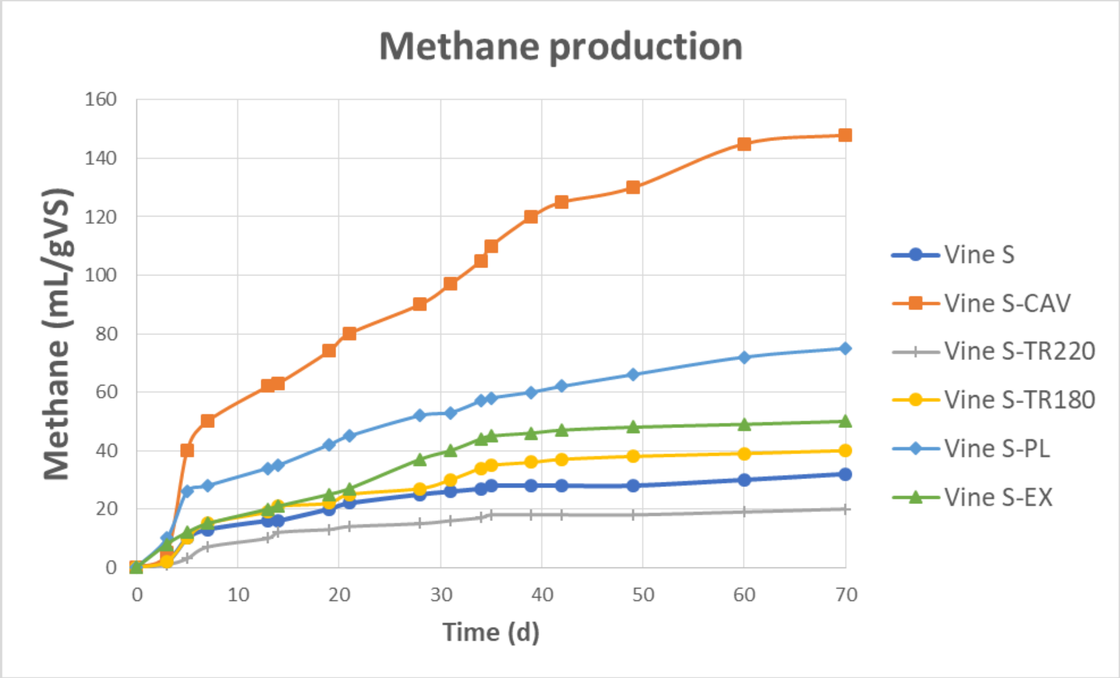
- Barley straw
- Vine shoot

Previous work

Digestion of milled cereal straw and vine shoots

Pretreatments: Cavitation (CAV), Torrefaction at 220ºC (TR220), Torrefaction at 180ºC (TR180), Pelleting (PL) and Extrusion (EX)





Ref. *Hidalgo, D., Martín-Marroquín, J. M., Castro, J., Gómez, M., & Garrote, L. (2022). Influence of cavitation, pelleting, extrusion and torrefaction petreatments on anaerobic biodegradability of barley straw and vine shoots. Chemosphere, 289, 133165.*

Previous work: Lessons learnt

- The effect of torrefaction pretreatment temperature on the AD behavior is very remarkable. Torrefaction carried out at 180 °C increased methane production, 81% for straw and 25% for vine shoots, while the process at higher temperatures (220 °C) negatively affected biogas production from both feedstocks.

  - **Torrefaction temperature is a key parameter** that must be carefully selected for optimal results in a subsequent anaerobic digestion and for the whole economy of the process.

  - The **composition of the lignocellulosic biomass** to be digested is also a factor to take into account when selecting the conditions for the torrefaction stage.

- Torrefaction can reduce biomass volume and, in this way, **facilitate logistic** in biomass management activities.

- Torrefaction is a **mature technology** widely used on an industrial scale, so it is a good candidate to be installed as a complement to an anaerobic digestion facility.

Previous work

- The main drawback of this technology is its **high energy consumption**:

  - Heat recovery and the use of renewable energies are necessary for these processes to be economically viable.

  - The use of air instead of an inert gas could be an interesting option to reduce the operating costs involved in this pretreatment process.

New work aims

- To **assess the effect of biomass torrefaction pretreatment**, at moderate temperature and under air atmosphere conditions, on the efficiency of the anaerobic digestion process, in terms of biogas and methane production.

- **Two feedstocks**, barley straw and vine shoot, with different content of lignin, cellulose and hemicellulose will be subjected to these processes consecutively, evaluating the influence of the biomass composition and pretreatment temperature on methane efficiency.

- In addition, **chemical and structural changes** in the feedstocks due to thermal pretreatment and the volatile fatty acids profile during the digestion process will be also studied.

Materials and methods

Inoculum and substrates

- **Digestate** from an anaerobic reactor operating in a municipal wastewater treatment plant, was used as inoculum.

- **Barley straw and vine shoot** were used as substrates and collected from local farms.

Biomass pretreatment process

- Vine shoot and barley straw were first **dried** at room temperature and then **mechanically milled**, using a hammer mill and a blade mill respectively.

- The torrefaction process was applied to the milled feedstocks through a muffle furnace under an air atmosphere.

- Samples of both biomasses were consecutively placed in porcelain capsules and **torrefacted** in batch mode at **100, 130, 180 and 210°C for 24 h**.

Materials and methods

Milling (first step)

Materials and methods

Torrefaction

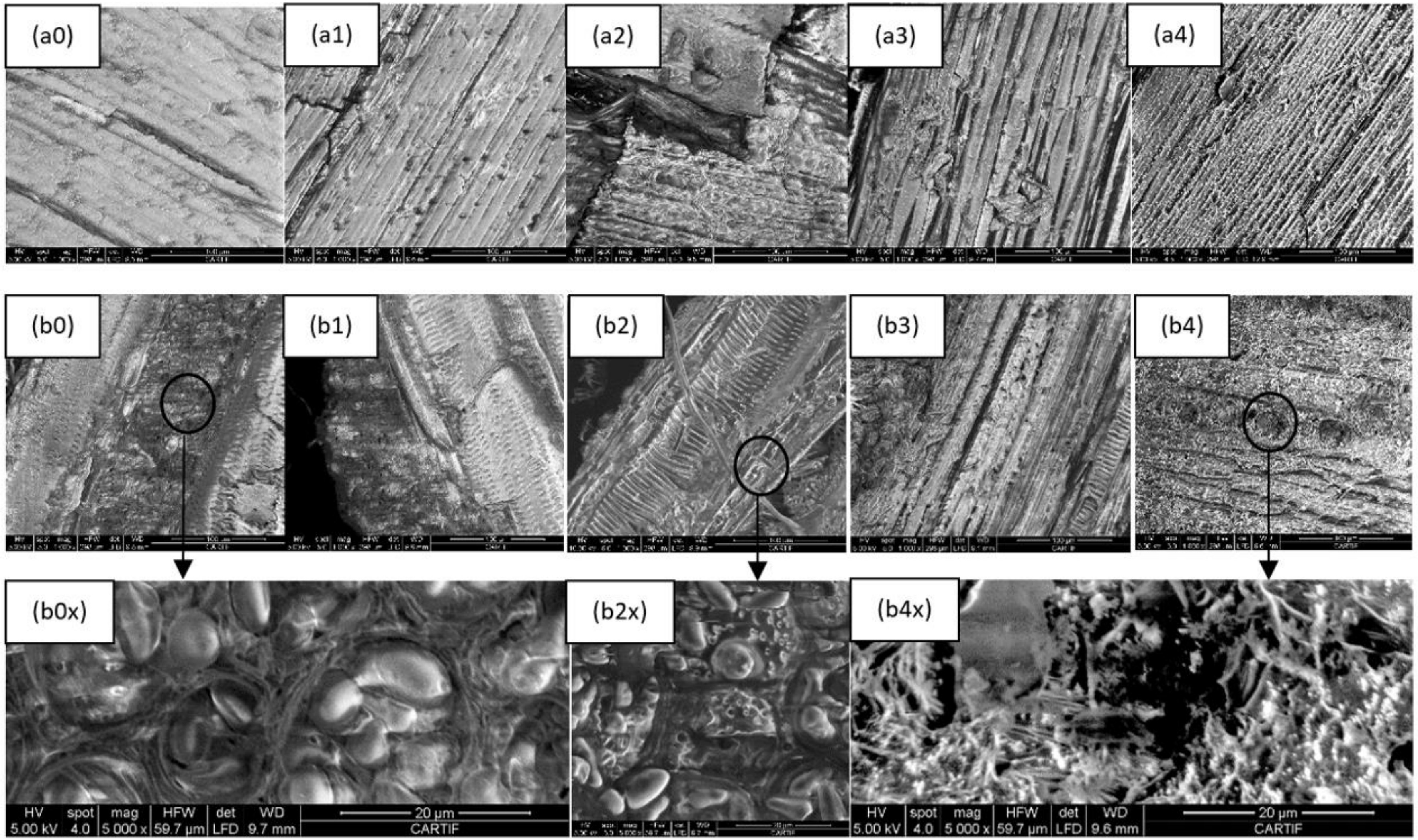
100, 130, 180 and 210°C for 24 h

Materials and methods

BMP Analysis

In order to study the effect of the pretreatment on the biodegradability of the biomass, **batch experiments** were run in glass serum bottles with a liquid volume of 1,000 mL.

Results: SEM Analysis



SEM images of biomass surface: (x 1000) barley straw (a) and vine shoot (b), particles untreated (0) and pretreated by torrefaction at 100 ºC (1), 130ºC (2) 180 ºC (3) and 210 ºC (4); (x5000) detail of starch granules in (b0), (b2) that disappear in (b4).

Results: SEM Analysis

- The SEM images of the untreated biomass show the robust structure and relatively smooth surface in straw and vine shoot fibers.

- The ability of the pretreatment to create **structural damages** on the biomass morphology is observed. The structure became loose and disordered with pretreatment temperature.

- Higher temperatures damage the structure of plant cells, with the appearance of large cracks that increased the surface exposed to microbial attack during digestion and elimination of the outer layer.

- **Carbohydrate reserves** (mostly starch granules) are clearly observed in all the vine shoot samples with the exception of samples pretreated at 210 ºC (starch depolymerization and degradation).

Results: Biomass composition

- The **main lignocellulosic fractions** of the biomasses under study were **estimated** using the TGA-PKM* method (Díez et al., 2020).

	Torrefaction temperature (T)				
Barley straw	untreated	100ºC	130ºC	180ºC	210ºC
Cellulose (C)	48.7%	48.7%	48.7%	48.3%	49.1%
Hemicellulose (HC)	22.0%	23.7%	23.2%	21.6%	0.0%
Lignin (L)	29.3%	27.6%	28.1%	30.1%	50.9%
Weight loss	0%	2.7%	5.5%	7,0%	45,3%
Vine shoot	untreated	100ºC	130ºC	180ºC	210ºC
Cellulose (C)	27.0%	26.8%	27.3%	34.9%	44.9%
Hemicellulose (HC)	43.1%	43.8%	43.4%	33.1%	0.6%
Lignin (L)	29.9%	29.4%	29.3%	32.0%	54.5%
Weight loss	0%	0.1%	1.0%	5.8%	44.4%

*The method applies deconvolution techniques on the derived thermogravimetric (DTG) pyrolysis curves obtained by thermogravimetric analysis (TGA) implementing a pseudocomponent kinetic model (PKM)-based approach.

Results: Biomass composition

- The **main lignocellulosic fractions** of the biomasses under study were **estimated** using the TGA-PKM* method (Díez et al., 2020).

- It is first observed that the raw vine shoot (hard wood) has a higher hemicellulose content (43.1% vs 22.0%) and a lower cellulose content (27.0% vs 48.3%), compared to raw barley straw.

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- The **torrefaction temperature** has a clear influence on the resulting composition of the pretreated samples, mainly at T > 130ºC.

	Torrefaction temperature (T)				
Barley straw	untreated	100ºC	130ºC	180ºC	210ºC
Cellulose (C)	48.7%	48.7%	48.7%	48.3%	49.1%
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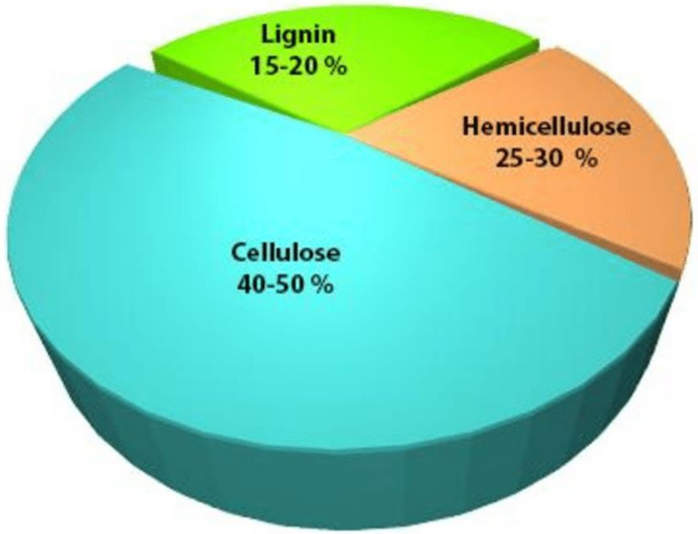
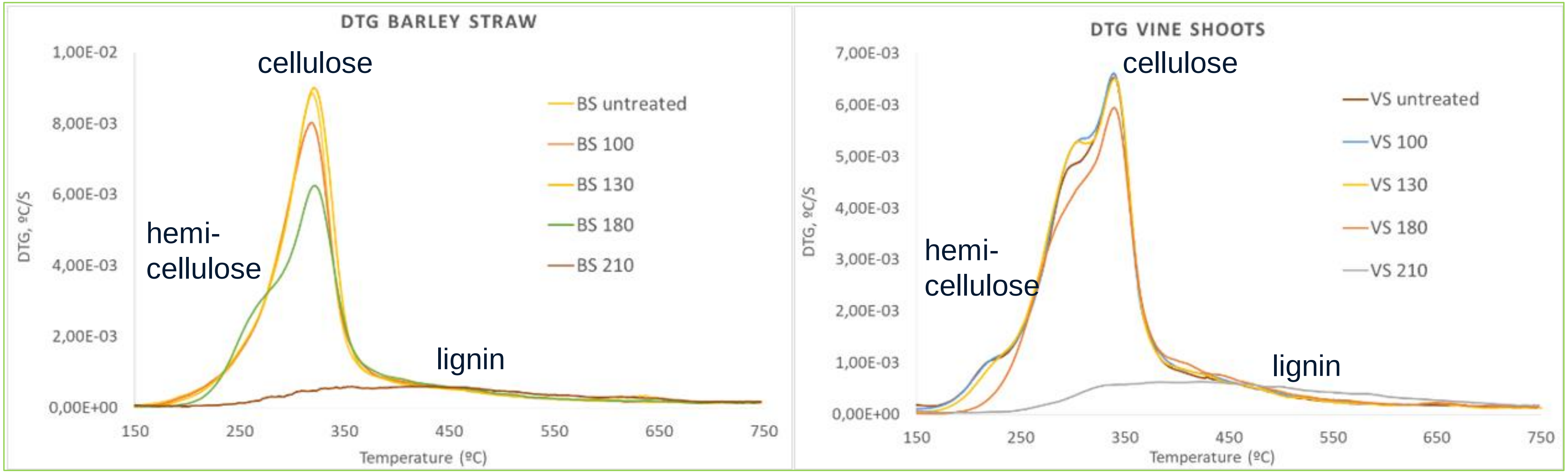
Results: Biomass composition

- From these results it can be concluded that **barley straw and vine shoot pretreated by torrefaction could have increased digestibility** due to the degradation of hemicellulose, given that in untreated biomass this component is digested more slowly and also make it difficult for microorganisms to access the cellulose.

- It is observed that even starting from biomasses with very different **composition** in terms of cellulose, hemicellulose and lignin content, these **become similar** when the samples are subjected to more than 200ºC.



Results: Devolatization behavior (DTG curves)

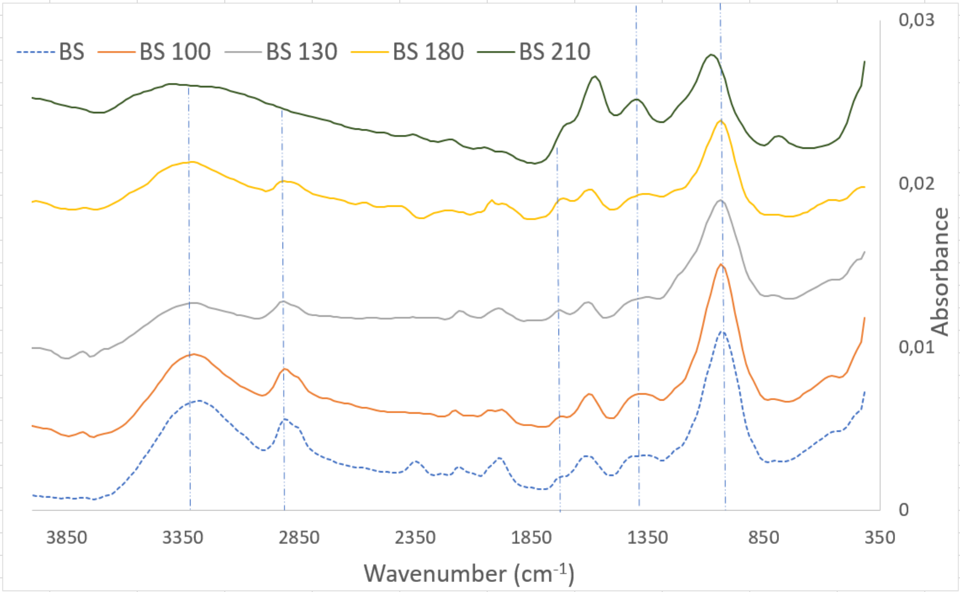


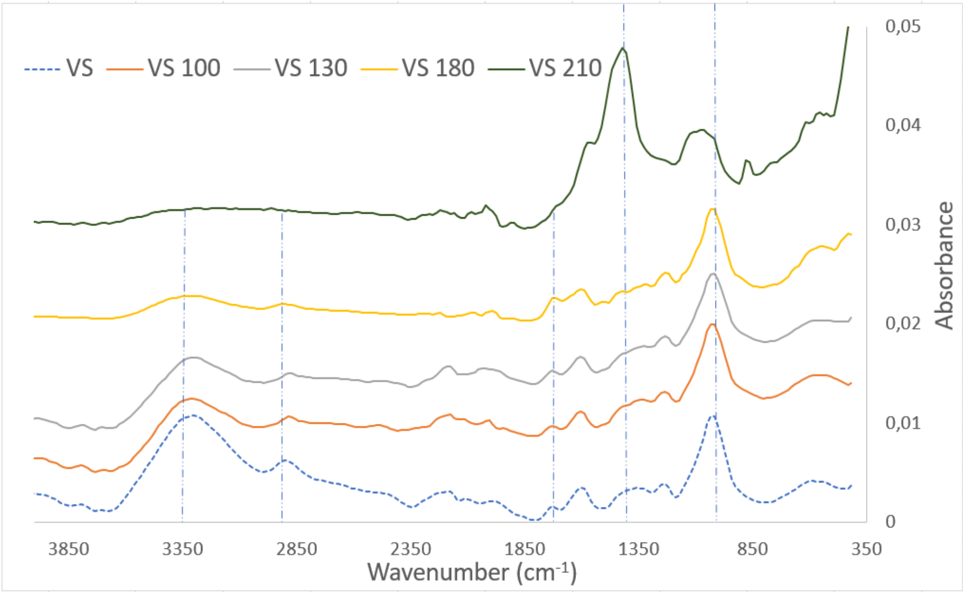
- The DTG curves show a **similar behavior**, in terms of peaks observed, for barley straw and vine shoot, although the shape of the peaks is different.

- At temperatures above 150°C, the **degradation of lignocellulosic compounds** begins to be evident.

- Lower peaks are observed as a trend in the cellulose zone and hemicellulose zone when pretreatment T increases, which corroborates the effect of temperature on modifying the composition of the biomass.

Results: Functional groups (FTIR spectra)





- The FTIR spectra show that the **absorption peaks** in all the regions were reduced with the temperature, which implies that the **lignocellulosic structure** of both biomasses was **interrupted** with the increase in the temperature of the torrefaction pretreatment.

- Therefore, it can be assumed that the **protective layer** (hemicellulose-lignin) that surrounds the cellulose **was broken** by the effect of temperature, producing a change in the chemical structure of the barley straw and the vine shoot compared to the untreated raw material, and more pronounced as the heat treatment gained in intensity.

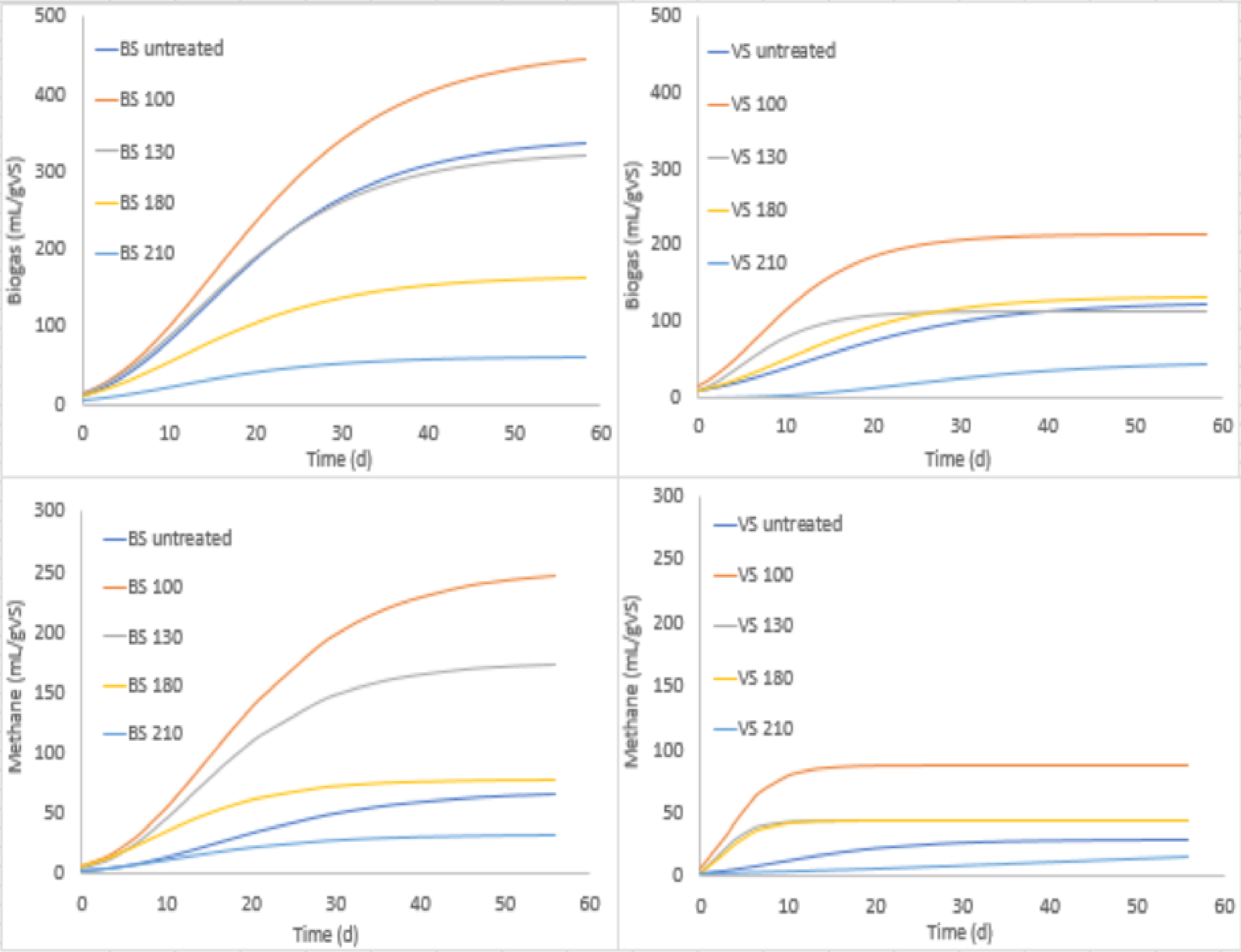
Results: Methane production (BMP Analysis)

- The pretreatment assayed showed a different degree of effectiveness on biogas production according the test temperature when applied to barley straw or vine shoot.

- In both cases, the application of the pretreatment revealed to affect positively or negatively the biogas yield depending on the specific pretreatment temperature.

- All the tests showed methanogenic activity from the first moment, indicating a rapid start up by the anaerobic microbiota of the inoculum.

Results: Methane production (BMP Analysis)



Modified Gompertz model fitting

Results: Methane production (BMP Analysis)

- The **maximum rate of biogas** generation was obtained between days 10 and 20 for barley straw and between days 5 and 15 for the vine shoot, with torrefaction at 100ºC being the most efficient pretreatment with a production of around 11 and 9 mL biogas/gVS.d, respectively.

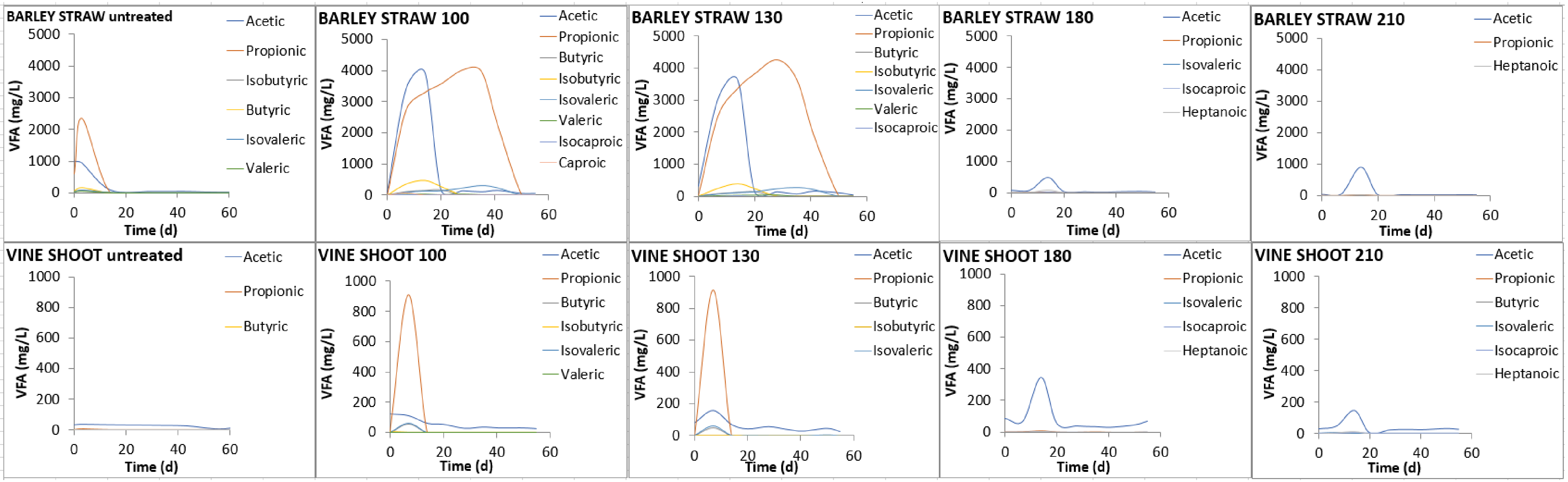
- Greater methane production is observed with all pretreatments except torrefaction at 210ºC, which negatively affects biomass biodegradation in all cases, both in terms of biogas and methane production.

- **Torrefaction at 100ºC pretreatment** was certainly **the most beneficial** for the digestion process, since a production confirming that maximum of, approx., 275 and 210% enhancement in the methane yield was obtain with this low-temperature pretreatment.

- **Torrefaction at 210°C was negative** for biogas and methane production from barley straw and vine shoot. In both cases, biogas production was reduced by 50%.

Results: VFA profiles

- The amount and type of volatile fatty acids (VFA) generated during the anaerobic digestion of barley straw or vine shoot depends, fundamentally, on the application or not of a pretreatment.



- **Propionic and acetic acids** dominate VFA profiles in all the experiments, however these profiles change drastically with the type of biomass digested and the pretreatment temperature. **No inhibition** due to VFA accumulation was observed.

Summary and Conclusions

The effects of torrefaction pretreatment of barley straw and vine shoot under different conditions were compared by analysing the components, the micro-structure, VFA profiles and the biogas and methane production kinetics.

- Considerable reduction in hemicellulose and changes in chemical bonds of the biomass were observed due to the **thermal pretreatment**, which contributes in different degree to biomass biodegradability according to the applied temperature.

- The **cumulative methane yields** of feedstocks under study pretreated at 100, 130 and 180ºC were higher than the untreated, and the maximum biogas production and highest digestion efficiency was obtained with the pretreatment at 100ºC.

- The process of **torrefaction pretreatment** at low temperature is fast and **easily deployed** using commercial equipment, so it is a promising technology to facilitate anaerobic digestion of lignocellulosic biomass.

Thank you for your attention

Dr. Dolores Hidalgo

Circular Economt Area Director
Fundación CARTIF
dolhid@cartif.es