

# Biomass Conversion and Biorefinery

## INTEGRAL VALORIZATION OF TAGASASTE (*Chamaecytisus proliferus*) UNDER THERMOCHEMICAL PROCESSES

--Manuscript Draft--

<b>Manuscript Number:</b>	BCAB-D-17-00017R1	
<b>Full Title:</b>	INTEGRAL VALORIZATION OF TAGASASTE ( <i>Chamaecytisus proliferus</i> ) UNDER THERMOCHEMICAL PROCESSES	
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<b>Funding Information:</b>	Secretaría de Estado de Investigación, Desarrollo e Innovación (CTQ2013-46804-C2-1-R)	Prof. Manuel J. Diaz-Blanco
	Agencia de Innovación y Desarrollo de Andalucía (RNM 2323)	Dr. López F.
<b>Abstract:</b>	<p>The generation of compounds derived from lignocellulosic biomass fractionation has a boost in recent years. An interesting plant could be Tagasaste (<i>Chamaecytisus proliferus</i>) due to its high biomass production and its leguminous nature. A sequence of acid hydrolysis, as pretreatment, and pyrolysis of the solid residue, as treatment, has been used in its valorization. An experimental design (H<sub>2</sub>SO<sub>4</sub> acid concentration 0.5%-2%, temperature 130-170°C and time 30-60 min) has been used to study the hydrolysis process. In the proposed acid hydrolysis process, under 170°C as operational temperature, 0.5% of H<sub>2</sub>SO<sub>4</sub> and 30 min for the operation time, 91.75% of the initial xylose have been extracted. The thermal behavior of both Tagasaste trunks-large branches and some solid residues after hydrolysis (furthest and center points in the experimental design) process and raw material have been studied by thermogravimetric analysis under nitrogen atmosphere at different heating rates (5, 10, 15 and 20 °C min<sup>-1</sup>). The thermal degradation of the studied materials is influenced by its initial composition. Then, the higher reactivity of hemicelluloses can accelerate the pyrolysis degradation reaction. However, higher cellulose content implies lower activation energy in pyrolysis process.</p>	
<b>Response to Reviewers:</b>	<p>INTEGRAL VALORIZATION OF TAGASASTE (<i>Chamaecytisus proliferus</i>) UNDER THERMOCHEMICAL PROCESSES</p> <p>Reviewer #1: General Comments:</p>	

In general, the TGA is only very short described and not discuss in detail.  
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This manuscript could be published after minor revisions as follows in the attached pdf.  
The revisions include contextual and formal aspects. Please check also again the formal aspects of your paper.

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It is clear that the optimum range, in which the extraction of hemicellulose maximum is observed, depends on each species. This range also depends on the age of the plant and the area that has been planted. In this regard, over 30 experiments were carried out (and made the corresponding analysis) to find a range that is able to cover most variables and in which the maximum extraction is sought.

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The figure has been obtained with higher resolution

## INTEGRAL VALORIZATION OF TAGASASTE (*Chamaecytisus proliferus*) UNDER THERMOCHEMICAL PROCESSES

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General Comments:

The abstract should be in a single paragraph.

Put the variables in italics (in the text) coinciding with the equations.

-The abstract has been shortened in a single paragraph.

-All variables have been changed to italics both in text and tables.

-

Some specific comments:

Section 2

Describe the TGA experiments. Why did the authors only carry out experiences at one heating rate? Generally, several heating rates are applied in order to analyze the influence of this parameter on the thermal treatment behavior.

According to the referee, to determine apparent activation energy using Flynn-Wall-Ozawa method, several TGA curves at different heating rates ( $\beta$ ) are essential. The thermogravimetric analysis of the raw material and solid residues were performed at various heating rates, namely 5, 10, 15 and 20 °C min<sup>-1</sup>. In fact, several heating speeds should be used. In fact 4 (as seen in the lines obtained in figure 7) have been used.

Included: Page 8. “Based on the described kinetic method, collection of multiple curves at multiple heating rates is required. For that reason, thermogravimetric analyses were performed at four different heating rates: 5, 10, 15 and 20 °C min<sup>-1</sup>. For this tests fine powder size (about 0.20 mm) of raw material and solid residues have been used.”

Section3.1.

In the last paragraph, the authors exposed that the second major fraction corresponds to the lignin (19.8%). However, the hemicellulose fraction is equal to 27.9%.

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Section 3.2.3

The authors applied FWO method at degree of conversion between 0.25 and 0.75.

Explain why this range is considered.

The non-isothermal method kinetic method (FWO) used in this study has become a common analytical technique. Therefore, Equation (B.1) is a fundamental relation that determines the kinetic parameters on the basis of thermogravimetric data is based on the degree of conversion and also the heating rates. The studied degrees of conversion (0.25, 0.50 and 0.75) are widely used to represent the evolution of  $E_a$  as a function of the major components in lignocellulosic materials (cellulose, hemicellulose and lignin). In addition, the raw material studied has hemicellulose fraction of 27.9% (near to =0.25), 38.9% as cellulose (near to =0.5) and 19.8% as Klason lignin (near to =0.75).

#### Conclusions

Expand the conclusions.

Conclusion section has been rewritten following the suggestions of the referee.

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Reviewer #4:

General Comments:

I have some recommendations for adjustments in language, style and content. They are shown below.

Some specific comments:

Page 1 Line 28: due to instead of because

Deleted: because

Included: due to

Page 2 Line 52 and so an: species instead of specie

Deleted: species  
Included: specie  
Page 5 Line 57: other materials instead of others materials  
Deleted: others materials  
Included: other materials

Page 7: Following the equation not all variables are explained in the text (two times X)  
Deleted: X  
Included:  $X_{av}$  in Eq. A.1  
Included:  $X_{av}$  is the average value of the variable  
Page 7 Line 35 : Eq.A.2 instead of Eq.A2  
Deleted: Eq. A2  
Included: Eq. A.2

Page 8 Line 6: Following the equation T is not explained (Temperature)  
Page 8 Line 10 Included: T is the reaction temperature (K) and...

Page 10 Line 35 following: glucoligomers or gluco-oligomers?  
Deleted: gluco-oligomers  
Included: glucooligomers (and in all of the text)

Page 11 Line 28-33: be more precise  
Deleted: "Furthermore, López et al. [29], shown the operational ranges suitable for xylose extraction, which it was quantitative at 170°C and a statistical low influence of operation time variable is observed. Therefore, the use of non isothermal conditions or short times must be advisable. This is quite important if low acid concentration is used."  
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Page 12 Line 40 following: Structure of the sentence is not clear  
Deleted: "Under this condition, the liquid phase obtained after autohydrolysis of the raw material under the optimum conditions contained 2.3% glucose, 9.8% xylose, 2.5% xylo-oligomers, 0.6% arabinose, 1.1% furfural and 0.1% 5-OH methyl furfural."  
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Page 13 Line 33-35: phrasing hard to understand  
Deleted: The higher temperature peak for the raw material was represents of 360°C and only 16.6%/min is found.  
Included:  
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Page 14 Line 25: spelling error: from instead of form  
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*In the last paragraph, the authors exposed that the second major fraction corresponds to the lignin (19.8%). However, the hemicellulose fraction is equal to 27.9%.*

*Deleted:* “The major fraction in raw material is cellulose (analyzed as glucan), to 38.9% (at TAPPI T 203-om-93), followed by the Klason lignin to 19.8 % (after quantitative acid hydrolysis) and the hemicelluloses fraction (calculated as the sum of xylan, araban, acetyl groups and others) to 27.9%.”

*Included:* “The major fraction in raw material is cellulose (analyzed as glucan), to 38.9% (at TAPPI T 203-om-93), followed by hemicelluloses fraction (calculated as the sum of xylan, araban, acetyl groups and others) to 27.9% and Klason lignin to 19.8 % (after quantitative acid hydrolysis).

#### *Section 3.2.3*

*The authors applied FWO method at degree of conversion between 0.25 and 0.75. Explain why this range is considered.*

The non-isothermal method kinetic method (FWO) used in this study has become a common analytical technique. Therefore, Equation (B.1) is a fundamental relation that determines the kinetic parameters on the basis of thermogravimetric data is based on the degree of conversion and also the heating rates. The studied degrees of conversion (0.25, 0.50 and 0.75) are widely used to represent the evolution of  $E_a$  as a function of the major components in lignocellulosic materials (cellulose, hemicellulose and lignin). In addition, the raw material studied has hemicellulose fraction of 27.9% (near to  $\alpha=0.25$ ), 38.9% as cellulose (near to  $\alpha=0.5$ ) and 19.8% as Klason lignin (near to  $\alpha=0.75$ ).

### *Conclusions*

*Expand the conclusions.*

Conclusion section has been rewritten following the suggestions of the referee.

*Deleted:* “In the proposed acid hydrolysis process, under 170°C as operational temperature, 0.5% of H<sub>2</sub>SO<sub>4</sub> and 30 min for the operation time, a quantitative xylose extraction is observed. The liquid phase obtained after autohydrolysis of the raw material under these conditions 91.75 % of hemicellulose could be extracted.

The thermal degradation of the studied materials is influenced by its composition. In this sense higher reactivity of hemicelluloses can accelerate the pyrolysis degradation reaction. However, higher cellulose content implies a lower  $E_a$  in the pyrolysis degradation process.”

*Included:* “In this work, a sequence of acid hydrolysis, as pretreatment, and pyrolysis of the solid residue, as treatment, have been used in its valorization. An experimental design (H<sub>2</sub>SO<sub>4</sub> acid concentration 0.5%-2%, temperature 130-170°C and time 30-60 min) has been used to study the hydrolysis process. Under 170°C as operational temperature, 0.5% of H<sub>2</sub>SO<sub>4</sub> and 30 min for the operation time, a quantitative xylose extraction is observed. The liquid phase obtained after autohydrolysis of the raw material under these conditions 91.75 % of hemicellulose could be extracted. Some solid residues after hydrolysis (furthest and center points in the experimental design) process and raw material have been studied by thermogravimetric analysis under nitrogen atmosphere at different heating rates (5, 10, 15 and 20 °C min<sup>-1</sup>).

The thermal degradation of the studied materials is influenced by its composition. In this sense higher reactivity of hemicelluloses can accelerate the pyrolysis degradation reaction. The maximum peak temperature for this major peak is 373°C, with a maximum weight loss rate of 22.3%/min for medium hydrolyzed material.

Effect of heating rate on TG and DTG curves was also presented. Activation energy has been obtained by the Flynn-Wall-Ozawa method. The values of activation energy obtained under three degree of conversion (0.25-0.75) ranged between 167.3-207.2 kJ mol<sup>-1</sup> for Tagasaste as raw material and 159.2-210.4 kJ mol<sup>-1</sup> for solid residues obtained after hydrolysis and are consistent with the range of values obtained by similar lignocellulosic materials. The higher reactivity of hemicelluloses can accelerate the pyrolysis degradation reaction. However, higher cellulose content implies lower activation energy in pyrolysis process.

## INTEGRAL VALORIZATION OF TAGASASTE (*Chamaecytisus proliferus*) UNDER THERMOCHEMICAL PROCESSES

### Reviewer #1:

### Reviewer #4:

#### General Comments:

*I have some recommendations for adjustments in language, style and content. They are shown below.*

#### Some specific comments:

*Page 1 Line 28: due to instead of because*

*Deleted: because*

*Included: due to*

*Page 2 Line 52 and so an: species instead of specie*

*Deleted: species*

*Included: specie*

*Page 5 Line 57: other materials instead of others materials*

*Deleted: others materials*

*Included: other materials*

*Page 7: Following the equation not all variables are explained in the text (two times X)*

*Deleted: X*

*Included:  $X_{av}$  in Eq. A.1*

*Included:  $X_{av}$  is the average value of the variable*

*Page 7 Line 35 : Eq.A.2 instead of Eq.A2*

*Deleted: Eq. A2*

*Included: Eq. A.2*

*Page 8 Line 6: Following the equation T is not explained (Temperature)*

*Page 8 Line 10 Included: T is the reaction temperature (K) and...*

*Page 10 Line 35 following: glucoligomers or gluco-oligomers?*

*Deleted: gluco-oligomers*

*Included: glucooligomers (and in all of the text)*

*Page 11 Line 28-33: be more precice*

*Deleted: "Furthermore, López et al. [29], shown the operational ranges suitable for xylose extraction, which it was quantitative at 170°C and a statistical low influence of operation time variable is observed. Therefore, the use of non isothermal conditions or short times must be advisable. This is quite important if low acid concentration is used."*

*Included:*

*"Furthermore, López et al. [29] shown that a suitable operational temperature to obtain quantitative xylose extraction is produced from 170°C. In addition, a statistical low influence of operation time variable was observed. Therefore, the use of non-isothermal conditions or short operation times, mainly if low acid concentration is used, must be advisable."*

*Page 12 Line 40 following: Structure of the sentence is not clear*

*Deleted:* “Under this condition, the liquid phase obtained after autohydrolysis of the raw material under the optimum conditions contained 2.3% glucose, 9.8% xylose, 2.5% xylo-oligomers, 0.6% arabinose, 1.1% furfural and 0.1% 5-OH methyl furfural.”

*Included:*

“Under this condition, 2.3% glucose, 9.8% xylose, 2.5% xylo-oligomers, 0.6% arabinose, 1.1% furfural and 0.1% 5-OH methyl furfural in the liquid phase obtained after autohydrolysis are found. These conditions could be proposed as optimum conditions for maximum hemicelluloses extraction.”

*Page 13 Line 33-35: phrasing hard to understand*

*Deleted:* The higher temperature peak for the raw material was represents of 360°C and only 16.6%/min is found.

*Included:*

For the raw material, the higher temperature peak, with only a maximum weight loss rate of 16.6%/min, was found at 360°C.

*Page 14 Line 25: spelling error: from instead of form*

*Deleted:* form

*Included:* from

## General List of changes

### Abstract

*Deleted:* “The generation of compounds derived from lignocellulosic biomass fractionation has a boost in recent years. An interesting plant could be Tagasaste (*Chamaecytisus proliferus*) due to its high biomass production and its leguminous nature. A sequence of acid hydrolysis, as pretreatment, and pyrolysis of the solid residue, as treatment, has been used in its valorization. The thermal behavior of both Tagasaste trunks-large branches and the solid residue after hemicellulosic extraction by acid hydrolysis of the same raw material were investigated using thermal analysis techniques (TGA). In the proposed acid hydrolysis process, under 170°C as operational temperature, 0.5% of H<sub>2</sub>SO<sub>4</sub> and 30 min for the operation time, 91.75% of the initial xylose have been extracted. The thermal degradation of the studied materials is influenced by its initial composition. Then, the higher reactivity of hemicelluloses can accelerate the pyrolysis degradation reaction. However, higher cellulose content implies lower activation energy in pyrolysis process.”

*Included:* “The generation of compounds derived from lignocellulosic biomass fractionation has a boost in recent years. An interesting plant could be Tagasaste (*Chamaecytisus proliferus*) due to its high biomass production and its leguminous nature. A sequence of acid hydrolysis, as pretreatment, and pyrolysis of the solid residue, as treatment, has been used in its valorization. An experimental design (H<sub>2</sub>SO<sub>4</sub> acid concentration 0.5%-2%, temperature 130-170°C and time 30-60 min) has been used to study the hydrolysis process. In the proposed acid hydrolysis process, under 170°C as operational temperature, 0.5% of H<sub>2</sub>SO<sub>4</sub> and 30 min for the operation time, 91.75% of the initial xylose have been extracted. The thermal behavior of both Tagasaste trunks-large branches and some solid residues after hydrolysis (furthest and center points in the experimental design) process and raw material have been studied by thermogravimetric analysis under nitrogen atmosphere at different heating rates (5, 10, 15 and 20 °C min<sup>-1</sup>). The thermal degradation of the studied materials is influenced by its initial composition. Then, the higher reactivity of hemicelluloses can accelerate the pyrolysis degradation reaction. However, higher cellulose content implies lower activation energy in pyrolysis process.”

*Page 1 Line 28: due to instead of because*

*Deleted:* because

*Included:* due to

*Page 2 Line 52 and so an: species instead of specie*

*Deleted:* species

*Included:* specie

*Page 5 Line 28:*

*Deleted:* the components in the raw material are decomposed by heating to a relatively low temperature

*Included:* the components in the raw material are decomposed by heating

*Page 5 Line 57: other materials instead of others materials*

*Deleted:* others materials

*Included:* other materials

*Page 6 Line 1:*



*Deleted:* The major fraction is cellulose (analyzed as glucan), to 38.9% (at TAPPI T 203-om-93), followed by the Klason lignin to 19,8 % (after quantitative acid hydrolysis) and hemicelluloses fraction (calculated as the sum of xylan, araban, acetyl groups and others) to 27.9%.

*Included (in Section 3):* The major fraction in raw material is cellulose (analyzed as glucan), to 38.9% (at TAPPI T 203-om-93), followed by hemicelluloses fraction (calculated as the sum of xylan, araban, acetyl groups and others) to 27.9% and Klason lignin to 19.8% (after quantitative acid hydrolysis).

*Page 6 Line 52:*

*Deleted:* Hemicellulose

*Included:* hemicellulose

*Page 7 Line 22:*

*Deleted:* X

*Included:*  $X_{av}$  in Eq. A.1

*Included:*  $X_{av}$  is the average value of the variable

*Page 7 Line 35 :*

*Deleted:* Eq. A2

*Included:* Eq. A.2

*Page 8 Line 10*

*Included:* T is the reaction temperature (K) and...

*Page 8 Line 21:*

*Included:* “Based on the described kinetic method, collection of multiple curves at multiple heating rates is required. For that reason, thermogravimetric analyses were performed at four different heating rates: 5, 10, 15 and 20 °C min<sup>-1</sup>. For this tests fine powder size (about 0.20 mm) of raw material and solid residues have been used.”

*Page 10 Line 35 following: glucoligomers or gluco-oligomers?*

*Deleted:* gluco-oligomers

*Included:* glucooligomers (and in all of the text)

*Page 11 Line 28-33:*

*Deleted:* “Furthermore, López *et al.* [29], shown the operational ranges suitable for xylose extraction, which it was quantitative at 170°C and a statistical low influence of operation time variable is observed. Therefore, the use of non isothermal conditions or short times must be advisable. This is quite important if low acid concentration is used.”

*Included:*

“Furthermore, López *et al.* [29] shown that a suitable operational temperature to obtain quantitative xylose extraction is produced from 170°C. In addition, a statistical low influence of operation time variable was observed. Therefore, the use of non-isothermal conditions or short operation times, mainly if low acid concentration is used, must be advisable.”

*Page 11 Line 52:*

*Deleted:* nonisothermal

*Included:* non-isothermal (this error has been corrected in the following pages)

*Page 12 Line 40:*

*Deleted:* “Under this condition, the liquid phase obtained after autohydrolysis of the raw material under the optimum conditions contained 2.3% glucose, 9.8% xylose, 2.5% xylo-oligomers, 0.6% arabinose, 1.1% furfural and 0.1% 5-OH methyl furfural.”

*Included:*

“Under this condition, 2.3% glucose, 9.8% xylose, 2.5% xylo-oligomers, 0.6% arabinose, 1.1% furfural and 0.1% 5-OH methyl furfural in the liquid phase obtained after autohydrolysis are found. These conditions could be proposed as optimum conditions for maximum hemicelluloses extraction.”

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*Page 14 Line 25:*

*Deleted:* form

*Included:* from

*Page 15 Line 16*

*Deleted:* “In the proposed acid hydrolysis process, under 170°C as operational temperature, 0.5% of H<sub>2</sub>SO<sub>4</sub> and 30 min for the operation time, a quantitative xylose extraction is observed. The liquid phase obtained after autohydrolysis of the raw material under these conditions 91.75 % of hemicellulose could be extracted.

The thermal degradation of the studied materials is influenced by its composition. In this sense higher reactivity of hemicelluloses can accelerate the pyrolysis degradation reaction. However, higher cellulose content implies a lower E<sub>a</sub> in the pyrolysis degradation process. ”

*Included:* “In this work, a sequence of acid hydrolysis, as pretreatment, and pyrolysis of the solid residue, as treatment, has been used in its valorization. An experimental design (H<sub>2</sub>SO<sub>4</sub> acid concentration 0.5%-2%, temperature 130-170°C and time 30-60 min) has been used to study the hydrolysis process. Under 170°C as operational temperature, 0.5% of H<sub>2</sub>SO<sub>4</sub> and 30 min for the operation time, a quantitative xylose extraction is observed. The liquid phase obtained after autohydrolysis of the raw material under these conditions 91.75 % of hemicellulose could be extracted. Some solid residues after hydrolysis (furthest and center points in the experimental design) process and raw material have been studied by thermogravimetric analysis under nitrogen atmosphere at different heating rates (5, 10, 15 and 20 °C min<sup>-1</sup>).

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Effect of heating rate on TG and DTG curves was also presented. Activation energy has been obtained by the Flynn-Wall-Ozawa method. The values of activation energy obtained under three degree of conversion (0.25-0.75) ranged between 167.3-207.2 kJ mol<sup>-1</sup> for Tagasaste as raw material and 159.2-210.4 kJ mol<sup>-1</sup> for solid residues obtained after hydrolysis and are consistent with the range of values obtained by similar lignocellulosic materials. The higher reactivity of hemicelluloses can accelerate the pyrolysis degradation reaction. However, higher cellulose content implies lower activation energy in pyrolysis process.

*Page 15 Line 42:*

*Deleted:* theAndalusian

*Included:* the Andalusian

*Page 16 Line 33:*

*Deleted:* (nd)

*Included:* pp.

*Page 21 Line 42:*

*Deleted:* Gašparovič L.,

*Included:* Gašparovič L,

*Table 5.* the degree of conversion have been changed.

[Click here to view linked References](#)

1           **INTEGRAL VALORIZATION OF TAGASASTE (*Chamaecytisus proliferus*)**  
2  
3           **UNDER THERMOCHEMICAL PROCESSES.**  
4

5  
6           J. M. Loaiza, F. López, M. T. García, J. C. García and M. J. Díaz\*

7  
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10           Chemical Engineering Department. Campus “El Carmen”. University of Huelva, Av. 3  
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15           \*Corresponding author: Díaz, M.J. (dblanc@uhu.es)  
16  
17

18  
19  
20           **Abstract**  
21

22  
23           The generation of compounds derived from lignocellulosic biomass fractionation has a  
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25           boost in recent years. An interesting plant could be Tagasaste (*Chamaecytisus*  
26  
27           *proliferus*) due to its high biomass production and its leguminous nature. A sequence of  
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29           acid hydrolysis, as pretreatment, and pyrolysis of the solid residue, as treatment, has  
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31           been used in its valorization. An experimental design ( $\text{H}_2\text{SO}_4$  acid concentration 0.5%-  
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33           2%, temperature 130-170°C and time 30-60 min) has been used to study the hydrolysis  
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35           process. In the proposed acid hydrolysis process, under 170°C as operational  
36  
37           temperature, 0.5% of  $\text{H}_2\text{SO}_4$  and 30 min for the operation time, 91.75% of the initial  
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39           xylose have been extracted. The thermal behavior of both Tagasaste trunks-large  
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41           branches and some solid residues after hydrolysis (furthest and center points in the  
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43           experimental design) process and raw material have been studied by thermogravimetric  
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45           analysis under nitrogen atmosphere at different heating rates (5, 10, 15 and 20 °C min<sup>-1</sup>).  
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47           The thermal degradation of the studied materials is influenced by its initial composition.  
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49           Then, the higher reactivity of hemicelluloses can accelerate the pyrolysis degradation  
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1 reaction. However, higher cellulose content implies lower activation energy in pyrolysis  
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3 process.  
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8 **Keywords:** Acid hydrolysis; Pyrolysis; Tagasaste; Biorefinery  
9

## 10 **1. Introduction**

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12  
13 To date, fossil sources have been the main resources to obtain energy or chemicals, but  
14  
15 these resources produce negative effects due to environmental pollutions [1].  
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18  
19 To remedy this situation, new primary fractionation methods of biomass, secondary  
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21 conversion pathways and processes have to be developed [2]. It's the forest biorefinery  
22  
23 concept: it's to integrate the overall biomass conversion processes to produce fuels,  
24  
25 power, heat, and value-added chemicals. It is analogous to today's petroleum refinery,  
26  
27 which produces multiple fuels and products from petroleum [3]. Biomass fuels or  
28  
29 biofuels are technogenic solid, liquid or gaseous fuels generated from natural biomass  
30  
31 resources via some processing [4]. Lignocellulose biorefinery will most probably be  
32  
33 pushed through with the greatest success, due to the optimal situation for the raw  
34  
35 material and conversion products have a good position in the traditional petrochemical  
36  
37 as well as in the future bio-based product market [5-7].  
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40  
41 In these biorefinery schemes, the hemicelluloses fraction, are not being isolated for  
42  
43 industrial use yet, however, they have a high potential and could be used in many  
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45 applications [8-9]. Generally, dilute acid pretreatment is effective in hydrolyzing  
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47 hemicellulose component that has been investigated and adopted by several cellulosic  
48  
49 ethanol pilot plants [10].  
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1 Moreover, the generation of lignocellulosic biomass fractionation derived compounds  
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3 (chemical and biofuels) has gained momentum in recent years and it is assumed that  
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5 could be a partial solution [11], first, because the decline in production from existing  
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7 sources (attached to the environmental damage that these traditional sources are  
8  
9 generating), and secondly, in order to achieve sustainable production of these  
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11 compounds.  
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14  
15 On the other hand, under biorefinery concept, almost all the types of biomass raw  
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17 materials can be converted to different classes of high value compounds through jointly  
18  
19 applied conversion technologies [12-13]. Many examples from bibliography can be  
20  
21 cited about different pretreatment methods to enhance the extraction of carbohydrates in  
22  
23 the process from lignocellulosic materials. Hot water or weak acid hydrolysis at an  
24  
25 elevated temperature are the first step that is typically used to hydrolyze carbohydrates  
26  
27 from lignocellulosic materials [14-16]. In this area, numerous investigations on dilute  
28  
29 acid hydrolysis of different lignocellulosics such as eucalyptus wood, corncobs,  
30  
31 sugarcane bagasse and sorghum straw have been performed by several research groups  
32  
33 [17-19] due to the ability to extract hemicelluloses and a valuable solid phase for the  
34  
35 acid hydrolysis. Moreover, this process can facilitate the hemicellulose polymers  
36  
37 dissolution, which can be used to obtain oligomers, xylose and arabinose for a variety of  
38  
39 novel applications in the chemical, pharmaceutical and food industries [20] and also as  
40  
41 fermentation media for the production of substances with a high added value such as  
42  
43 ethanol fuel and xylitol [21-22].  
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51 The current trend is the use of fast growing and environmentally sustainable specie [23].

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53 Moreover, on the selection of an optimum biomass source, to obtain the highest possible  
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55 amount of biomass given the climatic conditions, is a key factor when selecting the  
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1 crops. In this sense, Tagasaste (*Chamaecytisusproliferus L.F. ssp palmensis*) is a fast-  
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3 growing specie and it grows back repeatedly after being cut off close to the ground.  
4  
5 Moreover, is a legume and nitrogen fixer, and is well adapted to planting on degraded  
6  
7 soils. It will tolerate dry sites and soil pH ranging from 5.5 to 7.5 [24].  
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10 To obtain an optimal valuation for this specie the use of its biomass in energy  
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12 production could be an important breakthrough. In this process, to determine precise  
13  
14 operational process control is necessary. It is also important to determine the processes  
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16 occurring within the thermal behavior. For these reasons, the initial exploratory thermal  
17  
18 studies and kinetic modeling of the thermal behavior of biomass is, therefore, important  
19  
20 steps in assessing the contribution of raw materials, its pretreatments, and their  
21  
22 interactions during the devolatilization stage [25]. The understanding of kinetics of this  
23  
24 thermal behavior of the new raw material used in this study is important in the design  
25  
26 and operation of thermal processes. In this sense, pyrolysis plays an important role as  
27  
28 the first chemical step in gasification and combustion, in this process, the components in  
29  
30 the raw material are decomposed by heating (350-800°C) in the absence of oxygen.  
31  
32 During this process, the structure of the raw material is broken down into volatile  
33  
34 matter. The main pyrolysis gases are CO, H<sub>2</sub>, CH<sub>4</sub>, and H<sub>2</sub>O. However, tar, oil, naphtha,  
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36 and residual solid char are included [25].  
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44 Gravimetric techniques (isothermal and non-isothermal) have generally been used to  
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46 investigate the reactivity of the carbonaceous materials [26]. In this sense,  
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48 thermogravimetric analysis (TGA) can be used to investigate thermal events and  
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50 kinetics of pyrolysis and oxidation of the lignocellulosic raw materials. TGA analysis  
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52 provides a measurement of weight loss of the sample as a function of time and  
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54 temperature. The kinetics of the thermal events can then be determined by the  
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1 application of the Arrhenius equation corresponding to mass degradation in each  
2 thermal process.  
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5  
6 In this work, Tagasaste was characterized in chemical and energy terms, and assessed  
7 its potential as a lignocellulosic raw material and its integral fractionation. The first step  
8 in this valorization process is the separation of hemicelluloses by acid hydrolysis. The  
9 liquor from this pretreatment was evaluated as a source of oligomers and  
10 monosaccharides, and the solid phase assessed for the production of energy. The second  
11 step focuses on determining the kinetic degradation mechanism that describes the  
12 thermal degradation by the pyrolysis process of this specie.  
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## 25 **2. Materials and methods**

### 26 **2.1. Characterization and storage of raw material**

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28 Tagasaste branches and twigs with 0.5-5 cm in diameter were used. These pieces were  
29 obtained by trimming Tagasaste plants from which leaves and non-wood twigs were  
30 removed prior to grinding in a hammer mill. The material was collected from several  
31 experimental plots in the municipality of Trigueros (Huelva, Spain). This raw material  
32 used, which was prepared in accordance with Tappi T-257, was analyzed for the  
33 following parameters: ethanol-benzene extractives (TAPPI-204), ash (TAPPI T-211)  
34 and holocellulose [27].  
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47 To this end, portions of the homogenized wood lot were subjected to quantitative acid  
48 hydrolysis with 72% sulphuric acid (TAPPI T-249-em-85). The solid residue after  
49 hydrolysis was recovered by filtration and considered as Klason lignin. The  
50 monosaccharides and acetic acid contained in hydrolysates were determined by HPLC  
51 in order to estimate (after corrections for stoichiometry and sugar decomposition) the  
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1 contents of samples in cellulose (as glucan), hemicelluloses (as xylan), and acetyl  
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3 groups.  
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5  
6 The chemical characterization of Tagasaste used in this study and the characterization of  
7  
8 the other materials by various authors are shown in Table 1.  
9

## 10 11 12 13 **2.2. Acid hydrolysis processing of wood samples.** 14

15 Raw material and water were mixed in the desired proportions and treated in a 2 dm<sup>3</sup>  
16 stainless steel reactor (Parr Instruments Company, Moline, Illinois, USA) using a  
17 liquid/solid ratio (LSR) of 8 kg water/kg raw material, on dry basis (the moisture  
18 content of material was considered as water). The reactor was fitted with four-blade  
19 turbine impellers, heated by an external fabric mantle and cooled by cool water  
20 circulating through an internal loop. The reaction media stirred at 150 rpm and heated to  
21 reach the desired temperature. Time zero was considered to be the beginning of the  
22 isothermal stage. The operating conditions were 130, 150 and 170°C temperature; 30,  
23 45 and 60 min operating time and 0.5, 1.25 and 2% H<sub>2</sub>SO<sub>4</sub> content and a liquid/solid  
24 ratio of 8 kg water by kg raw material, on a dry basis. When the pretreatment was  
25 finished, the reactor was immediately cooled down by cooling water and then removed  
26 from heating jacket.  
27

28 After treatment, solid residues were recovered by filtration, washed with water, air-  
29 dried, weighted for yield determination. Aliquots of the solid phase were analyzed for  
30 moisture and composition (duplicate) using the same methods as for raw material  
31 analysis. An aliquot of the liquors was filtered through 0.45 mm membranes and used  
32 for direct HPLC determination of monosaccharides, oligomers and hemicelluloses  
33 extracted.  
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### 2.3. Experimental design for acid hydrolysis processes. Multiple regression models.

In order to relate the dependent (yield, glucose, xylose, hemicelluloses extracted) and independent variables (temperature, time and acid concentration) in process with the minimum possible number of experiment, a  $2n$  central composite factor experimental design was used, making it possible to construct a second-order polynomial in the independent variables and the identification of statistical significance in the variables was used. Independent variables were normalized by using the equation A.1.

$$X_n = \frac{X - X_{av}}{(X_{max} - X_{min})/2} \quad \text{Eq. A.1}$$

where  $X$  is the absolute value of the independent variable concern,  $X_{av}$  is the average value of the variable, and  $X_{max}$  and  $X_{min}$  are its maximum and minimum values respectively. The range of variation of independent variables was determinate according previous work (data not show). The number of tests required was calculated as  $N = 2^n + 2n + nc$ . Where  $2^n$  being the number of points constituting the factor design,  $2n$  that of axial points, and  $nc$  that of central points. Under our conditions,  $N = 16$ . The experimental results were fitted to the following second-order polynomial (Eq. A.2):

$$Y = a_o + \sum_{i=1}^n b_i X_{ni} + \sum_{i=1}^n c_i X_{ni}^2 + \sum_{i=1; j=1}^n d_i X_{ni} X_{nj} \quad (i < j) \quad \text{Eq. A.2}$$

The independent variables used in the equations relating to both types of variables were those having a statistical significant coefficient (viz. those not exceeding a significance level of 0.05 in the student's-test and having a 90% confidence interval excluding zero).

### 2.4. Pyrolysis kinetic analysis by Flynn-Wall-Ozawa method

Activation energy ( $Ea$ ) is considered to be the most important of the kinetic parameters because it describes how the reaction changes as a function of temperature. In this sense, the ability to follow the changes in activation energy as a function of conversion

1 is of great interest to the thermal analyst. For a single-reaction mechanism, activation  
2 energy should be a constant value throughout the weight loss region.  
3  
4

5 The activation energy values of the degradation process were determined by the  
6 isoconversional Flynn-Wall-Ozawa (FWO) method [32-33] defined by Eq. B.1.  
7  
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$$9 \ln(\beta) = \ln\left(\frac{A E_a}{R g(\alpha)}\right) - 2.315 - 0.4567 \frac{E_a}{RT} \text{ (Eq B.1)}$$

10 Where  $\beta$  is the heating rate,  $A$  is the pre-exponential factor,  $g(\alpha)$  is a function of the  
11 conversion,  $E_a$  is the activation energy,  $T$  is the reaction temperature (K) and  $R$  is the  
12 gas constant.  
13  
14

15 Therefore, for different heating rates ( $\beta$ ) and a given degree of conversion ( $\alpha$ ), a linear  
16 relationship is observed by plotting of natural logarithm of heating rates ( $\ln\beta$ ), versus  
17 ( $1/T$ ) obtained from thermal curves recorded at different heating rates will be a straight  
18 line whose slope ( $-0.4567 (E_a/RT)$ ) will calculate the activation energy.  
19  
20

21 The underlying assumption is that the reaction model,  $g(\alpha)$ , is identical at a given degree  
22 of conversion ( $\alpha$ ) for a given reaction under different thermal conditions [34].  
23 Moreover, this method can be used for determination of the  $E_a$  values without any  
24 knowledge of the reaction mechanisms [35]. Disadvantage of this method is the serie of  
25 measurements at different heating rate which must be made for the same sample mass  
26 and the same volume flow of inert gas and their fluctuation can cause of errors [36]. In  
27 this study four replicates of each material were tested to prevent these errors.  
28  
29

30 Based on the described kinetic method, collection of multiple curves at multiple heating  
31 rates is required. For that reason, thermogravimetric analyses were performed at four  
32 different heating rates: 5, 10, 15 and 20 °C min<sup>-1</sup>. For this tests fine powder size (about  
33 0.20 mm) of raw material and solid residues have been used.  
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### 3. Results and discussion

The major fraction in raw material is cellulose (analyzed as glucan), to 38.9% (at TAPPI T 203-om-93), followed by hemicelluloses fraction (calculated as the sum of xylan, araban, acetyl groups and others) to 27.9% and Klason lignin to 19.8% (after quantitative acid hydrolysis).

#### 3.1. Acid hydrolysis stage

The normalized values of independent variables (temperature, acid concentration and operation time), the solid yield, glucose and xylose and other hemicelluloses extracted contents in the liquid phase relative to the initial raw material are shown in Table 2. The time to reach the operating temperature in not isothermal process between 130°C and 170°C has not been taken into consideration due to the short time heating the reactor, between both temperatures, elapsed compared to both heating from ambient temperature. The influence of differences in non-isothermal operation time can be quite accurately approximated by that of temperature.

Data in Table 2 are shown as percentage composition of solid fraction with respect to initial raw material and solid yield. Among the obtained results the variations ranges in solid phase: 46.6-83.3% of solid yield; in liquor: glucose between 60.6% and 95.3 %; xylose between 10.3% and 74.8% and a total hemicellulose extracted between 40.2% and 91.8% have been observed. The error in mass balance was less than 5% in all components.

These results imply that glucose was extracted between 4.7% and 39.4% concerning the initial content of glucan in the raw material and xylose between 25.2% and 89.7%. It is assumed to be a considerable difference because the working hypothesis was to

1 maximize the extraction of hemicellulose derivatives while minimizing that of cellulose  
2  
3 derivatives to get the maximum power capacity.  
4

5  
6 According with Section 2.3, to assess the relative influence of the selected independent  
7  
8 variables (time, temperature and acid concentration) on each dependent variable (solid  
9  
10 yield, glucose content, xylose content and total hemicelluloses extracted), the  
11  
12 polynomial mathematical models were obtained (Table 3) by substituting the values of  
13  
14 the measured independent variables for each dependent variable, and applying a  
15  
16 polynomial model analysis. Each value used to obtain the equations is the average of  
17  
18 three measurements. The differences between the experimental values and those that  
19  
20 were estimated using the previous equations never exceeded 10% for glucose, solid  
21  
22 yield, xylooligomers, total hemicellulose extracted and 5% in the rest. Suitable fits with  
23  
24 values of  $R^2$  greater than 0.94 in all cases have been obtained.  
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30 In order to estimate the influence of operational variables on extracted liquor after raw  
31  
32 material hydrolysis, and to compare different conditions, the surface responses in Fig.1  
33  
34 were plotted. The space among three response surfaces represents the whole range of  
35  
36 values for each dependent variable that was used at three extreme values, +1, 0, -1, of  
37  
38 the most influential variable (operation temperature in the case of glucose, xylose  
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40 contents and total hemicellulose extracted). Solid yield decreases with increasing any  
41  
42 conditions, under high temperature and under low acid concentration can be observed.  
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46  
47 Only the xylose content (Fig. 2), under high temperature, shows a little increase. This is  
48  
49 probably due to the speed of the reaction and the relatively high temperature, which  
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51 increased the rate of xylose formation but also xylose degradation.  
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55 For glucose, (Fig.3), it can be seen that extraction rate increase with increasing acid  
56  
57 concentration or temperature. There was a decline of glucoligomers for increased  
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1 concentration of acid and temperature, and conversely an increase in glucoligomers with  
2  
3 increasing time is observed.  
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5  
6 The results in this work were compared than reported by Weiqi *et al.* [37] (xylose  
7  
8 between 0.6% and 4.1%, with a maximum temperature of 200°C and operation time 20  
9  
10 min) and with others results to that found for Gütsch *et al.* [38] and Feria *et al.* [39]  
11  
12 (with a extraction of 13.5 g/100 g with conditions of 2.5 wt% H<sub>3</sub>PO<sub>4</sub> at 175°C in 10 min  
13  
14 reaction time and 13.1% over dry wood with conditions of 0.1 mol/L H<sub>2</sub>SO<sub>4</sub> at 140°C in  
15  
16 35 min reaction time, respectively). The utilization of sulfuric acid reduces treatment  
17  
18 temperatures at a given wood yield as compared to autohydrolysis [37].  
19  
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22  
23 According to previous discussion, operating conditions of 170°C, 30 min, 2% H<sub>2</sub>SO<sub>4</sub>  
24  
25 were selected as optimum conditions for acid hydrolysis. Using a temperature of 170°C  
26  
27 (T +1) provided the highest concentrations of xylose (Fig. 2) and the lowest  
28  
29 concentrations of oligomers.  
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32  
33 The operation time and acid concentration used had little effect on the xylose  
34  
35 concentrations; however, using high acid concentrations reduced the contents in xylo-  
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37 oligomers and minimized the extraction of gluco-oligomers (Fig. 3).  
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41 If we combine xylose, xylo-oligomers and furfural; xylan in the raw material was  
42  
43 extracted by 10.3-74.8%. Moreover, if other oligomer fractions of the raw material are  
44  
45 excluded, hemicelluloses were extracted by 57-76% (Fig. 4). These results are similar to  
46  
47 that obtained by Feria *et al.* [39] in *E. globulus*.  
48

49  
50 Furthermore, López *et al.* [29] shown that a suitable operational temperature to obtain  
51  
52 quantitative xylose extraction is produced from 170°C. In addition, a statistical low  
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54 influence of operation time variable was observed. Therefore, the use of non-isothermal  
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1 conditions or short operation times, mainly if low acid concentration is used, must be  
2  
3 advisable.  
4

5 Under this condition, 2.3% glucose, 9.8% xylose, 2.5% xylo-oligomers, 0.6% arabinose,  
6  
7 1.1% furfural and 0.1% 5-OH methyl furfural in the liquid phase obtained after  
8  
9 autohydrolysis are found. These conditions could be proposed as optimum conditions  
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11 for maximum hemicelluloses extraction.  
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## 18 **3.2. Pyrolysis stage**

### 19 **3.2.1. TGA Pyrolysis behavior**

20 The weight loss curves (dry ash free basis) during the non-isothermal pyrolysis at a  
21  
22 heating rate of 20°C/min for the raw material and the selected hydrolyzed solid residues  
23  
24 discussed in this work are shown in Figure 5.  
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28 As usual, the weight loss increases with increasing the reaction temperature for all  
29  
30 materials. Also, the weight loss profiles of the Tagasaste and the hydrolyzed materials  
31  
32 show a similar behavior among themselves but with some differences attributable to  
33  
34 their different chemical composition. It can be seen that the samples display one initial  
35  
36 decrease at temperatures less than 150°C representing the removal of moisture from the  
37  
38 samples. Above this fact, the temperature at which it is produced the weight loss is  
39  
40 different for each sample.  
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47 The drop in weight is initially produced, at a lower temperature, for Tagasaste and the  
48  
49 less hydrolyzed sample (-1, -1, -1) being later, and similarly to each other, the more  
50  
51 hydrolyzed samples (0, 0, 0 and 1, 1, 1).  
52  
53

54 This behavior should be attributed to its different chemical composition. In this sense,  
55  
56 Yang *et al.* [40] proved that the hemicellulose weight loss mainly happened at 220-  
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1 315°C. Tagasaste and the less hydrolyzed sample (-1, -1, -1) show higher hemicellulose  
2 content than the more hydrolyzed samples. After that, when temperature was higher  
3  
4 than 400 °C, almost all hemicellulose and cellulose was pyrolyzed with a low solid  
5  
6 residue (ash and not pyrolyzed material) is found. The differences in final content  
7  
8 among samples could be attributed to the different lignin concentration, due to most  
9  
10 difficult to decompose compound is lignin. Its decomposition happened slowly under  
11  
12 the whole temperature range from ambient to 700°C [41-42].  
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### 21 **3.2.2. Weight loss rate**

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23 The weight loss rate curves during the non-isothermal pyrolysis at a heating rate of  
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25 20°C min<sup>-1</sup> for the raw material and the selected hydrolyzed solid residues discussed in  
26  
27 this work are shown in Figure 6.  
28

29  
30 Some differences were found among the pyrolysis behaviors of the four materials are  
31  
32 shown in Figure 6.  
33

34  
35 The thermal evolution profiles in weight loss rate curves display a common to the four  
36  
37 materials peak (100-150°C) attributable to moisture losses. The lower temperature  
38  
39 shoulder (second peak) represents the decomposition of the hemicellulose with a peak  
40  
41 temperature of 305°C and 302°C for Tagasaste (raw material) and the less (-1, -1, -1)  
42  
43 hydrolyzed sample respectively and a similar weight loss rate of 8.5 %/min. Also, the  
44  
45 maximum weight loss rates, the third and main peak, common to the four materials,  
46  
47 occur in a temperature range of 350-400°C corresponding to the data reported by  
48  
49 Velden *et al.* [41] and represents the cellulose decomposition. The maximum peak  
50  
51 temperature for this major peak is 373°C, with a maximum weight loss rate of  
52  
53 22.3%/min for medium hydrolyzed material (0, 0, 0) and lower for the others. In this  
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1 form, 373°C and 18.7%/min and 365°C and 18.1%/min are found for the higher (1, 1, 1)  
2  
3 and the lower (-1, -1, -1) hydrolyzed materials. For the raw material, the higher  
4  
5 temperature peak, with only a maximum weight loss rate of 16.6%/min, was found at  
6  
7 360°C. This decomposition continues up to a temperature of approximately 400°C.  
8  
9 Above this temperature, a slow decomposition is found and could be attributable to the  
10  
11 lignin decomposition [40], continuing up to a temperature of about 650°C beyond which  
12  
13 very little change in the weight occurs.  
14  
15

16  
17 Interestingly, the maximum weight loss rate of Tagasaste is lower than that of the  
18  
19 hydrolyzed samples. This value could be attributed to the fact that hydrolyzed samples  
20  
21 contain much lower content of volatile matter than hydrolyzed material.  
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### 27 **3.2.3 Kinetics results**

28  
29 The plots of the FWO method (Figure 7), was used for the determination of the Ea  
30  
31 values for all lignocellulosic materials studied.  
32  
33

34  
35 These materials show a general trend, the kinetic behavior was similar for all of  
36  
37 materials studied. Therefore, Fig 7.shows the results of the application of the FWO  
38  
39 method with at different degree of conversion (values from 0.25 to 0.75). The linear fits  
40  
41 obtained from the plots are also shown in this figure. The Ea values were calculated  
42  
43 from the angular coefficient obtained from the straight line fit. In Table 4 Ea evolution,  
44  
45 at different degree of conversion, for all the samples studied is shown.  
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50 Similarities, in values and evolution, to those found for other similar materials are  
51  
52 observed (Table 5).  
53

54  
55 A common trend for all materials is shown. An increment in Ea from 25% to 50%  
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57 conversion is observed. After this fact, a different trend is observed. For Tagasaste a  
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1 drop in the value of  $E_a$  is shown. This decrease is lowered for the less (-1, -1, -1)  
2  
3 hydrolyzed material and for (0, 0, 0) and (1, 1, 1) hydrolyzed materials almost is not  
4  
5 appreciated. These showed differences among the studied materials must be attributed  
6  
7 to the strength of their molecular structures. The polymers of hemicellulose, cellulose,  
8  
9 and lignin, which constitute the macromolecular structure of biomass and other woody  
10  
11 materials are linked together by relatively weak bonds [46]. These bonds are even  
12  
13 weaker in the pre-treated materials, hydrolyzated in our study. Then, higher values for  
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15 Tagasaste y and the less hydrolyzated material with respect to the others are found.  
16  
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18  
19 When the conversion is 0.25 the temperature lies at around 300°C, which is an  
20  
21 indicative that the degradation process begins for hemicelluloses and cellulose. After  
22  
23 that temperature, when the conversion is 0.5, according to Lin *et al.* [47], the  
24  
25 depolymerization of cellulose is produced and this fact can result in an increase of the  
26  
27  $E_a$  values in all studied materials.  
28  
29

30  
31 The lower  $E_a$  values for the high hydrolyzed material indicates that they have a lower  
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33 thermal stability probably due to they contain lower quantities of cellulose with respect  
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35 to raw material.  
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#### 42 **4. Conclusions**

43  
44 In this work, a sequence of acid hydrolysis, as pretreatment, and pyrolysis of the solid  
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46 residue, as treatment, has been used in its valorization. An experimental design ( $H_2SO_4$   
47  
48 acid concentration 0.5%-2%, temperature 130-170°C and time 30-60 min) has been  
49  
50 used to study the hydrolysis process. Under 170°C as operational temperature, 0.5% of  
51  
52  $H_2SO_4$  and 30 min for the operation time, a quantitative xylose extraction is observed.  
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54 The liquid phase obtained after autohydrolysis of the raw material under these  
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1 conditions 91.75 % of hemicellulose could be extracted. Some solid residues after  
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3 hydrolysis (furthest and center points in the experimental design) process and raw  
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5 material have been studied by thermogravimetric analysis under nitrogen atmosphere at  
6  
7 different heating rates (5, 10, 15 and 20 °C min<sup>-1</sup>).  
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9

10 The thermal degradation of the studied materials is influenced by its composition. In  
11  
12 this sense higher reactivity of hemicelluloses can accelerate the pyrolysis degradation  
13  
14 reaction. The maximum peak temperature for this major peak is 373°C, with a  
15  
16 maximum weight loss rate of 22.3%/min for medium hydrolyzed material.  
17  
18

19 Effect of heating rate on TG and DTG curves was also presented. Activation energy has  
20  
21 been obtained by the Flynn-Wall-Ozawa method. The values of activation energy  
22  
23 obtained under three degree of conversion (0.25-0.75) ranged between 167.3-207.2 kJ  
24  
25 mol<sup>-1</sup> for Tagasaste as raw material and 159.2-210.4 kJ mol<sup>-1</sup> for solid residues obtained  
26  
27 after hydrolysis and are consistent with the range of values obtained by similar  
28  
29 lignocellulosic materials. The higher reactivity of hemicelluloses can accelerate the  
30  
31 pyrolysis degradation reaction. However, higher cellulose content implies lower  
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33 activation energy in pyrolysis process.  
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## TABLES

Table 1. Average chemical composition for Tagasaste used and other lignocellulosic residues (composition according with bibliographic sources)

	Tagasaste Alfaro <i>et al.</i> [28]	<i>Eucalyptus globulus</i> López <i>et al.</i> [29]	<i>Leucaena diversifolia</i> Alfaro <i>et al.</i> [30]	<i>Paulownia fortunei</i> Caparrós <i>et al.</i> [31]
<sup>a</sup> Ethanol extract, %	2.3	2.7	1.7	-----
<sup>a</sup> Ash, %	0.7	0.7	---	-----
<sup>a</sup> Holocellulose, %	80.3	-----	65.8	56.9
<sup>a</sup> Glucan, %	38.9	42.8	38.0	34.2
<sup>a</sup> Klason lignin, %	19.8	21.2	24.8	27.2
<sup>a</sup> Xylan, %	19.9	17.1	15.8	18.3
<sup>a</sup> Araban, %	0.6	0.7	1.5	1.1
<sup>a</sup> Acetyl groups, %	4.4	3.5	3.3	3.3
<sup>b</sup> HHV, kcal/kg	4676	4619	4530	4743

<sup>a</sup>Raw material percentages (100 kg dry matter)

<sup>b</sup>HHV: Higher Heating Value

Table 2 Yield obtained after acid hydrolysis stage, in liquid phase, of monomeric sugars and total hemicelluloses extracted (% respect to original raw material) with respect to normalized values of independent variables ( $X_c$ : Acid concentration,  $X_t$  and  $X_T$ : time and temperature of operation, respectively).

$X_c$	$X_T$	$X_t$	Yield (%)	Glucan (%)	Xylan (%)	Hemicelluloses extracted (%)
0	0	0	68.5	86.6	47.5	62.2
0	0	0	68.6	86.1	47.6	62.0
1	1	1	52.8	82.2	16.2	87.1
1	1	-1	50.8	82.5	10.3	91.8
1	-1	1	48.9	70.6	26.1	79.1
1	-1	-1	46.6	60.6	26.2	79.1
-1	1	1	64.0	90.7	22.3	82.2
-1	1	-1	58.2	89.7	23.8	81.0
-1	-1	1	83.3	92.0	74.8	40.2
-1	-1	-1	82.3	86.8	69.4	44.6
1	0	0	53.7	79.6	35.7	71.5
-1	0	0	73.1	95.3	58.9	52.9
0	1	0	56.1	85.7	17.0	86.5
0	-1	0	68.1	78.6	42.2	66.3
0	0	1	76.0	90.3	55.2	55.9
0	0	-1	69.9	86.8	46.3	63.0

Where  $X_c$ : (-1) 0.5%, (0) 1.25% and (1) 2%  $H_2SO_4$

$X_T$ : (-1) 130°C, (0) 150°C and (1) 170°C

$X_t$ : (-1) 30 min, (0) 45 min and (1) 60 min

Table 3. Equations obtained for each dependent variable of acid hydrolysis process.

Eq	Equations	R <sup>2</sup>	Snedecor-F
4	$Yi = 68.7 - 4.7 X_T + 1.7 X_t - 10.8 X_{ac} - 6.6 X_T^2 + 4.2 X_t^2 + 5.4 X_{ac}^2 + 6.4 X_T X_{ac}$	0.995	128.98
5	$Glu = 87.5 + 4.2 X_T - 2.0 X_t - 7.9 X_{ac} - 5.5 X_T^2 - 1.8 X_T X_t + 4.0 X_T X_{ac}$	0.988	129.40
6	$Xyl = 47.3 - 14.9 X_T + 1.9 X_t - 13.5 X_{ac} - 17.4 X_T^2 + 3.7 X_t^2 + 9.0 X_T X_{ac}$	0.989	142.07
7	$Hem_{Ext} = 62.2 + 11.9 X_T - 1.5 X_t + 10.8 X_{ac} + 13.9 X_T^2 - 3.0 X_t^2 - 7.2 X_T X_{ac}$	0.990	141.91

Where  $Yi$ : yield (%);  $Glu$ : Glucan;  $Xyl$ : Xylan;  $Hem_{Ext}$ : Hemicellulose extracted, and as independent variables:  $X_c$ : Acid concentration,  $X_t$  and  $X_T$ : time and temperature of operation, respectively.

The differences between the experimental values and those estimated using the equations never exceeded 10% of the former.



Table 4.  $E_a$  evolution at a function of degree of conversion.

Material	$E_a$ (kJ mol <sup>-1</sup> ) $\alpha^* = 0.25$	$E_a$ (kJ mol <sup>-1</sup> ) $\alpha^* = 0.5$	$E_a$ (kJ mol <sup>-1</sup> ) $\alpha^* = 0.75$
Tagasaste (Raw Mat.)	180.4 ± 25	207.2 ± 21	167.3 ± 18
Hydrolyzed (-1,-1,-1)	171.0 ± 21	210.4 ± 27	196.5 ± 30
Hydrolyzed (0, 0, 0)	159.2 ± 17	185.6 ± 27	183.9 ± 36
Hydrolyzed (+1,+1,+1)	168.1 ± 31	184.8 ± 22	189.5 ± 28

\*degree of conversion

Table 5.  $E_a$  evolution for different raw materials.

Raw Material	$\alpha$ (degree of conversion)	$E_a$ (kJ mol <sup>-1</sup> )	Reference
Wood	0.20	209.60	Gašparovič <i>et al.</i> [43]
Chips	0.50	204.07	
Mixture	0.70	196.49	
Poplar	0.25	137.88	Slopiecka <i>et al.</i> [34]
	0.50	198.53	
	0.70	209.49	
Pine	0.90	150.00	Wagenaar <i>et al.</i> [44]
Cornstalk	0.90	211.60	Lv <i>et al.</i> [45]
<i>Eucalyptus grandis</i>	0.20	205.00	Poletto <i>et al.</i> [35]
	0.50	218.30	
	0.70	195.40	
<i>Pinus elliotii</i>	0.20	210.30	Poletto <i>et al.</i> [35]
	0.50	191.20	
	0.70	179.60	
<i>Mezilaurus</i>	0.20	200.60	Poletto <i>et al.</i> [35]
<i>Itauba</i>	0.50	186.00	
	0.70	173.80	

## **FIGURES CAPTIONS**

**Figure 1.** Variation of yield as a function of  $X_{ac}$ : Acid concentration and  $X_t$ : operation time.

**Figure 2.** Variation of xylan content as a function of acid concentration ( $X_{ac}$ ) and time operation ( $X_t$ ).

**Figure 3.** Variation of glucan content as a function of acid concentration ( $X_{ac}$ ) and time operation ( $X_t$ ).

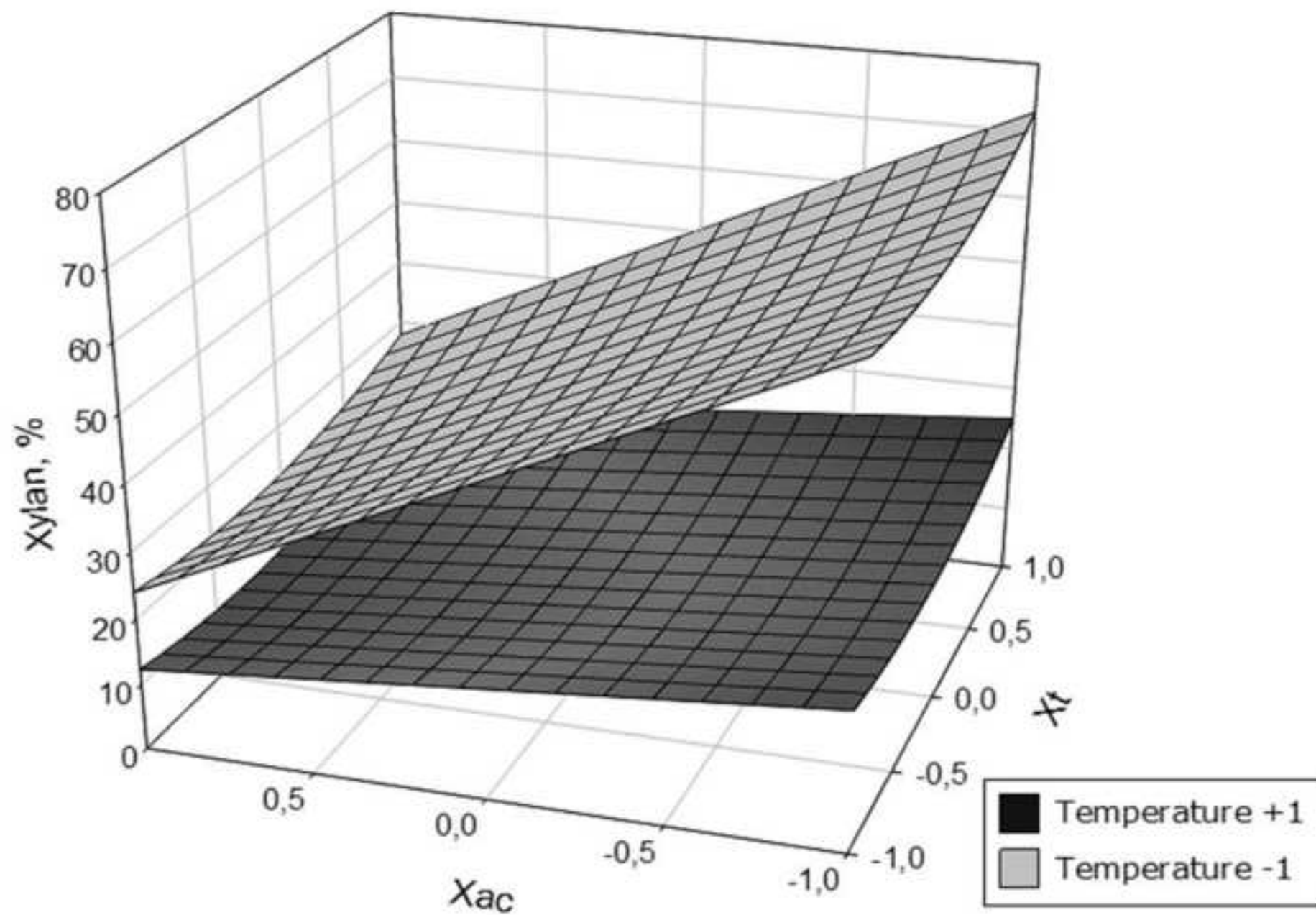
**Figure 4.** Variation of extraction hemicellulose content as a function of acid concentration ( $X_{ac}$ ) and time operation ( $X_t$ ).

**Figure 5:** Weight loss curves (%) during the pyrolysis of the raw material and the selected hydrolyzed solid residues at 20°C/min.

**Figure 6:** Weight loss rate curves (%) during the pyrolysis of the raw material and the selected hydrolyzed solid residues at 20°C/min.

**Figure 7.** FWO plots for the studied materials.





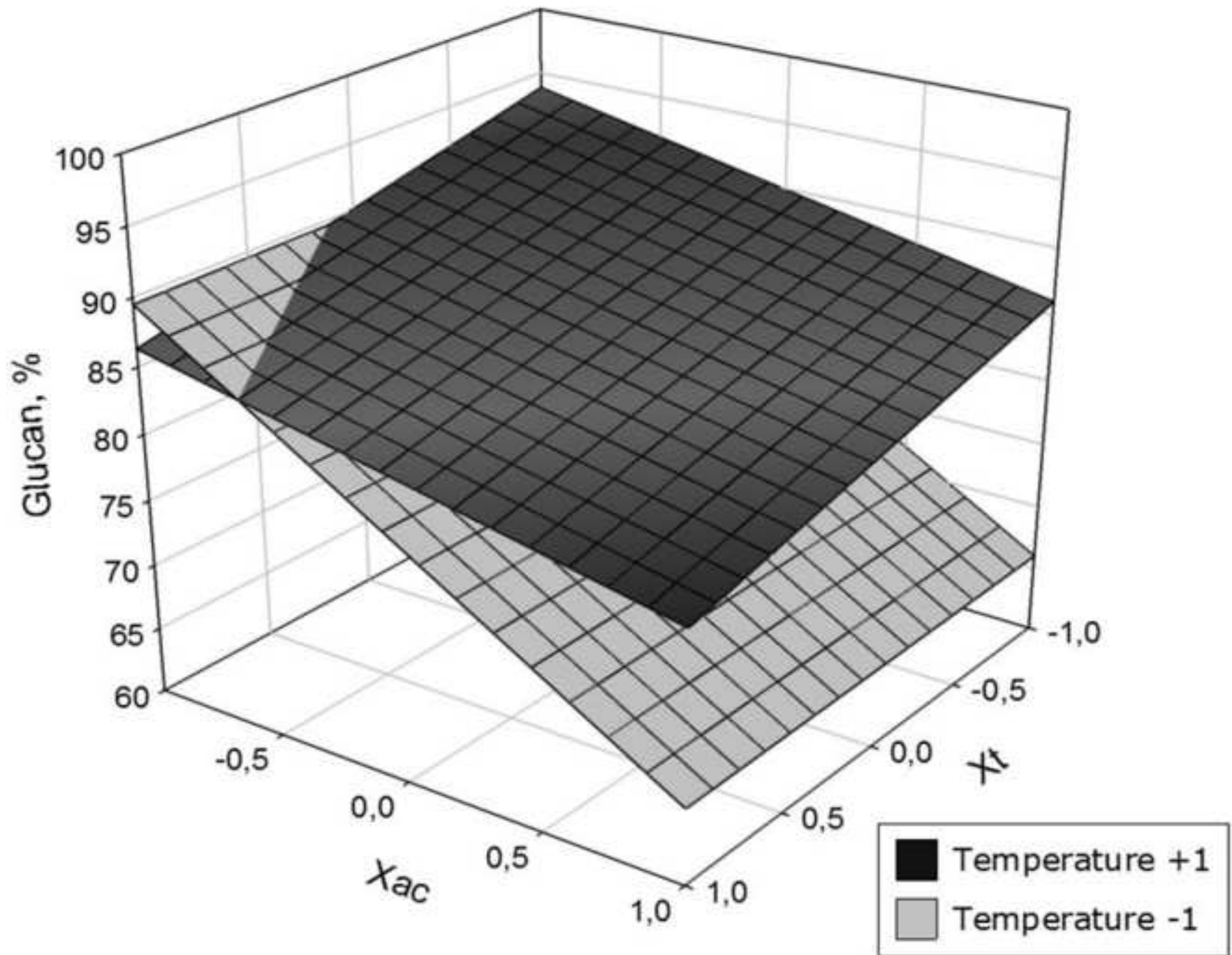
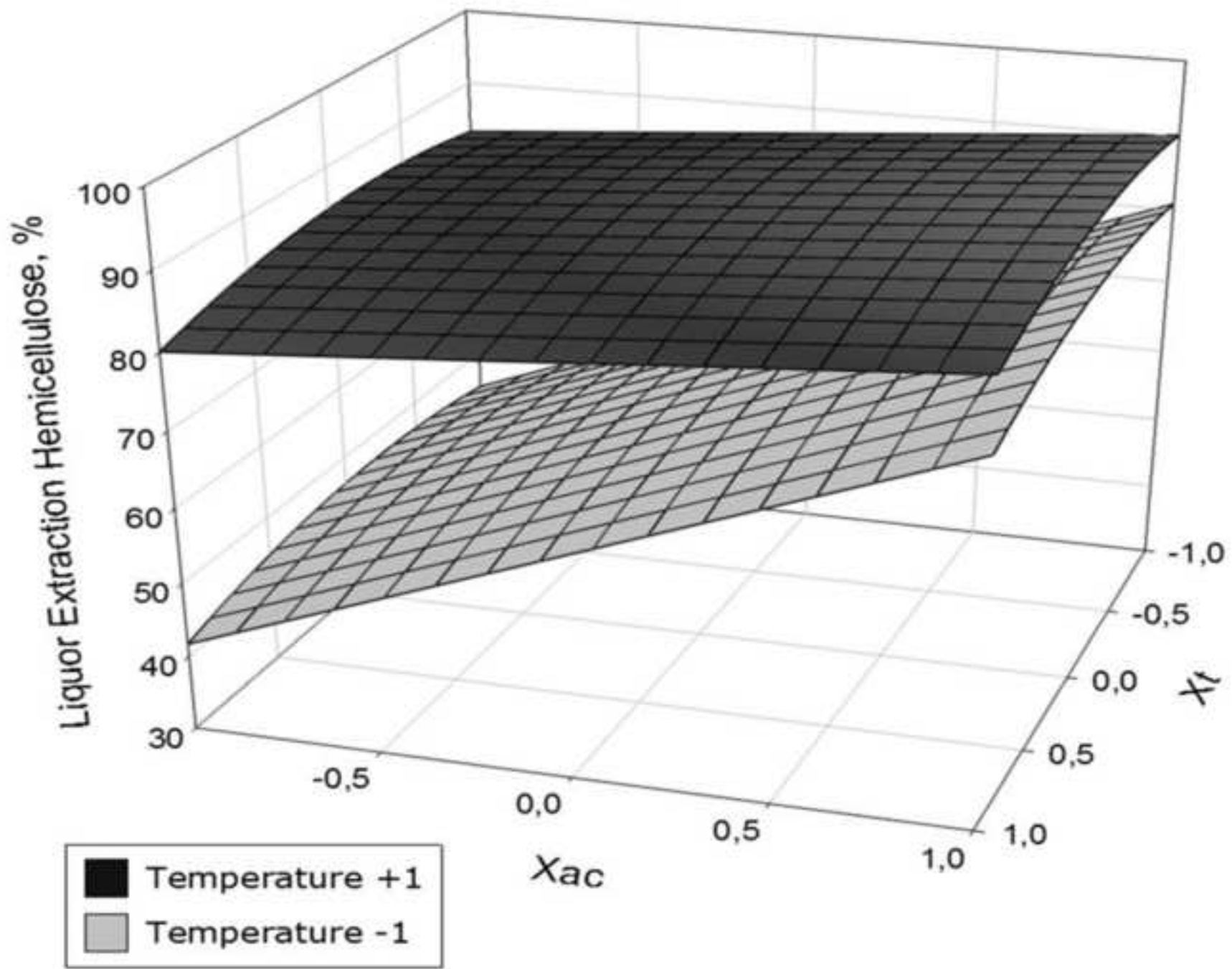
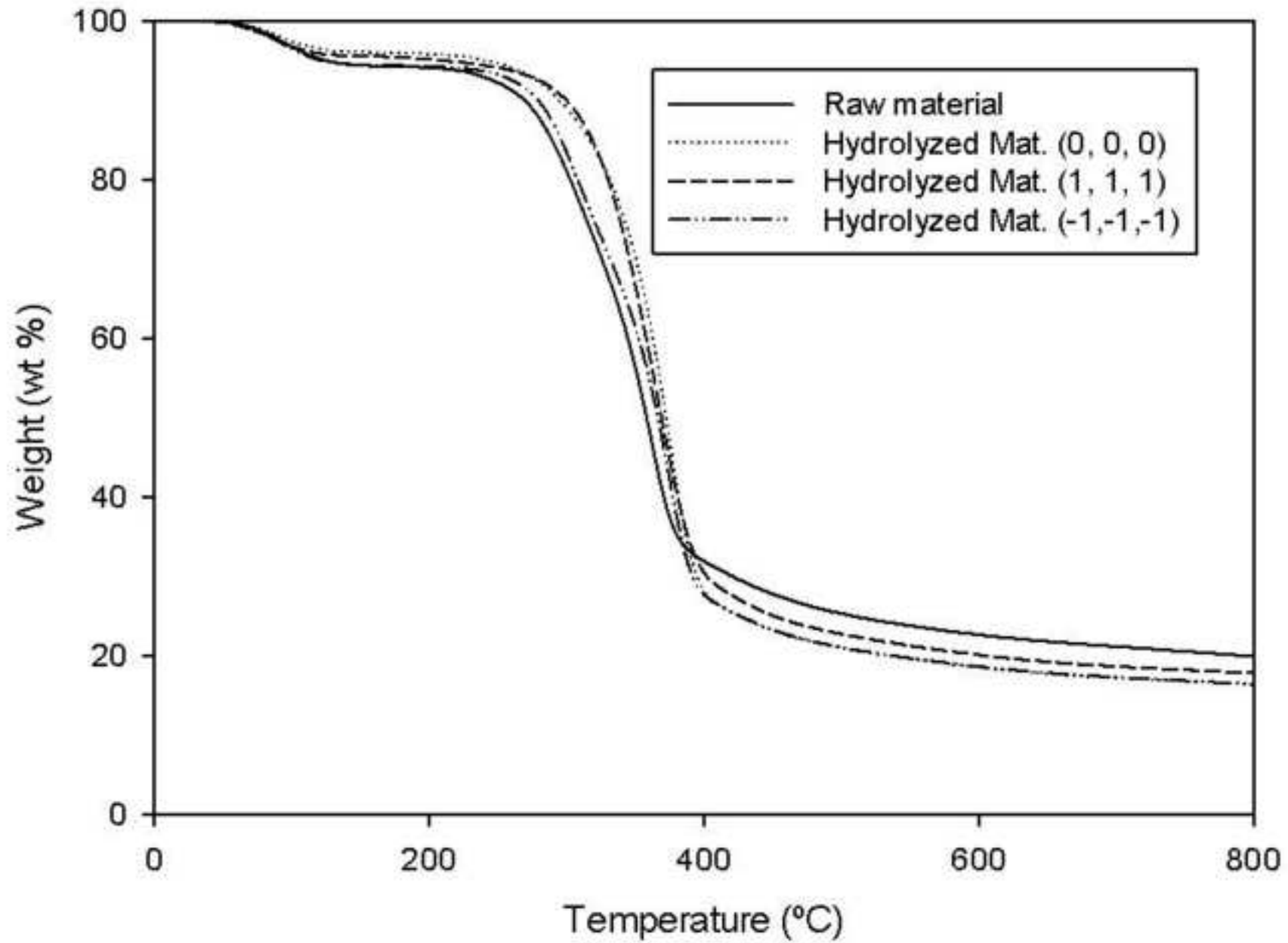


Figure 4





# Pyrolysis





# Pyrolysis

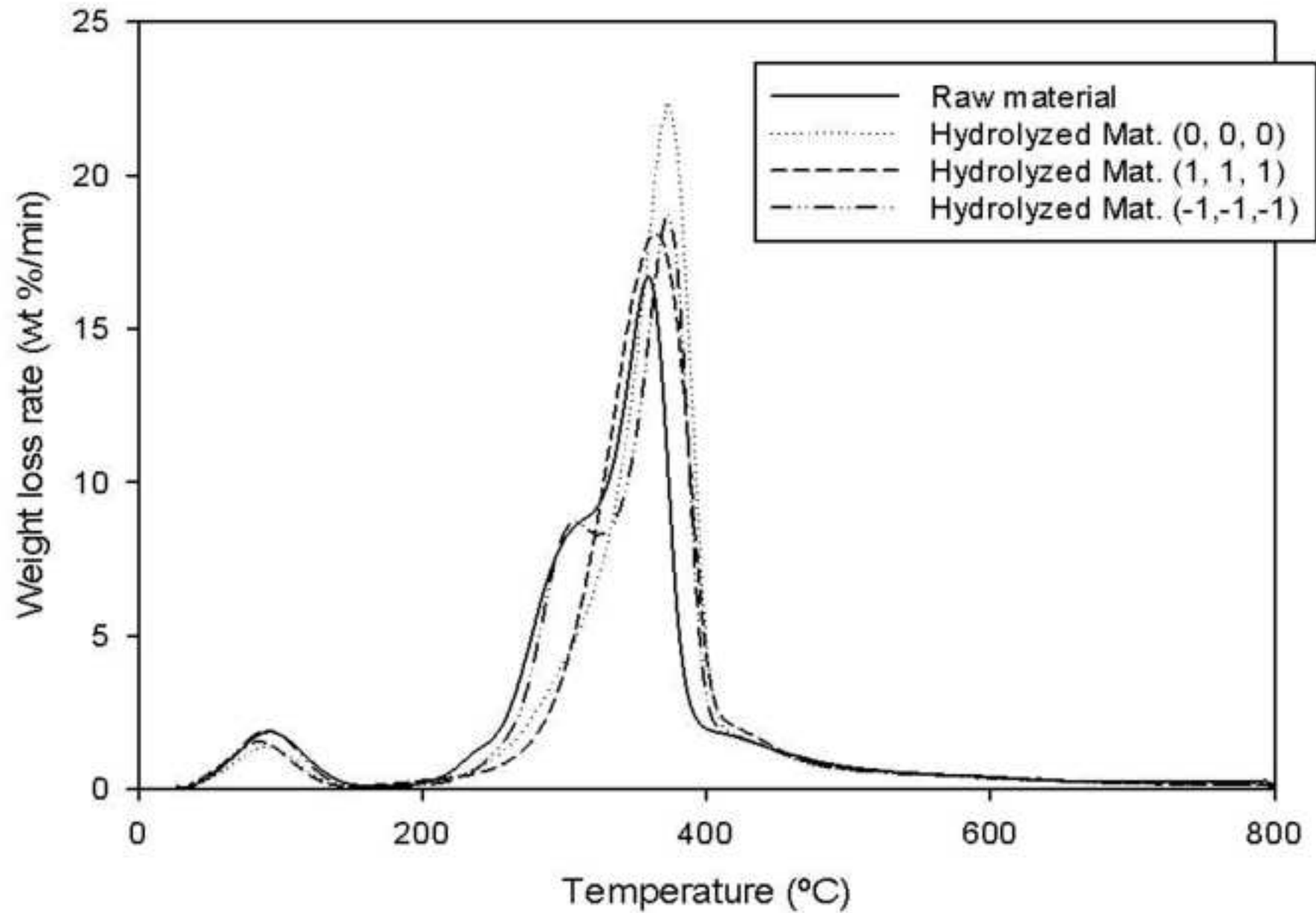


Figure 7

