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Title: BIOMASS VALORIZATION BY USING A SEQUENCE OF ACID HYDROLYSIS AND PYROLYSIS PROCESSES. APPLICATION TO LEUCAENA LEUCOCEPHALA

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Keywords: Leucaena; hydrolysis; pyrolysis; activation energy

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Abstract: Among main ways to provide an environmentally friendly energy and platform chemicals are the lignocellulosic conversion processes. The proper execution of this way will depend on the correct selection of lignocellulosic materials. A compelling plant is Leucaena leucocephala because its great variety of uses, its high biomass production and its leguminous nature. In this study, acid hydrolysis (130-170°C and 0.5-2% H2SO4, to extract valuable hemicelluloses) as pretreatment and pyrolysis of the solid residue (to get a gaseous fuel) as treatment have been used in its valorization. A laboratory-scale reactor was used for the pyrolysis experiments (550°C, N2) for both Leucaena leucocephala, as raw material, and the solid residues after hydrolysis process and raw material. The amounts of CO, CO2 and H2 found in the raw material are similar to those found in the solids obtained after the different studied hydrolysis conditions. Moreover, the thermal behavior of studied solids has been studied by thermogravimetric analysis under nitrogen atmosphere at different heating rates (5, 10, 15 and 20 °C min-1). Activation energy for all samples has been obtained by the Flynn-Wall-Ozawa method. The optimum value, in which a high relationship between recoverable hemicelluloses fraction and H2 concentration is found, under medium hydrolysis temperature (150°C) has been obtained and was independent of the amount of acid added to the hydrolysis process.

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Huelva, 15 March, 2017

Dear Dr. Patrick

I am enclosing the revised version of our article **"BIOMASS VALORIZATION BY USING A SEQUENCE OF ACID HYDROLYSIS AND PYROLYSIS PROCESSES. APPLICATION TO *LEUCAENA LEUCOCEPHALA*".**

In the new version we have taken into account the comments the reviewer suggestions.

The more important changes we have made are included in the following pages.

We think that after this revision, attending to your comments and suggestions, many points in the paper were clarified and the whole paper improved.

We would like to thank the Editor and the reviewers for your help and to express our readiness to take into account any further observations you may consider necessary.

With best regards,

Sincerely yours,

Dr. Manuel Jesús Díaz Blanco
Corresponding author

BIOMASS VALORIZATION BY USING A SEQUENCE OF ACID HYDROLYSIS AND PYROLYSIS PROCESSES. APPLICATION TO LEUCAENA LEUCOCEPHALA

Reviewer #1:

Abstract: There are serious grammatical errors in the abstract. Missing point FWO method.

The abstract has been rewritten.
Deleted:
"A main way to provide an environmentally friendly energy and platform chemicals is the lignocellulosic conversion processes. A compelling plant is *Leucaena leucocephala* because its great variety of uses, high biomass production and its leguminous nature. In this study, acid hydrolysis (130-170°C and 0.5-2% H_2SO_4, to extract valuable hemicelluloses) as pretreatment and pyrolysis of the solid residue (to obtain a gaseous fuel) as treatment have been used in its valorization. In this work, an experimental kinetic study of *Leucaena Leucocephala* hydrolysis plus pyrolysis is presented. The amounts of CO, CO_2 and H_2 found in the raw material are similar to those found in the solids obtained after the different studied hydrolysis conditions. Thermogravimetric analysis was investigated under nitrogen atmosphere at different heating rates of 5, 10, 15 and 20ºC min^{-1}. Activation energy for all samples were obtained by the FWO method The optimal values in which a fraction of recoverable hemicelluloses and higher H_2 concentration is obtained, is found in the medium temperature hydrolysis process and are independent of the amount of acid added."

Included:
"Among main ways to provide an environmentally friendly energy and platform chemicals are the lignocellulosic conversion processes. The proper execution of this way will depend on the correct selection of lignocellulosic materials. A compelling plant is *Leucaena leucocephala* because its great variety of uses, its high biomass production and its leguminous nature. In this study, acid hydrolysis (130-170°C and 0.5-2% H_2SO_4, to extract valuable hemicelluloses) as pretreatment and pyrolysis of the solid residue (to get a gaseous fuel) as treatment have been used in its valorization. A laboratory-scale reactor was used for the pyrolysis experiments (550ºC, N_2) for both *Leucaena leucocephala,* as raw material, and the solid residues after hydrolysis process and raw material. The amounts of CO, CO_2 and H_2 found in the raw material are similar to those found in the solids obtained after the different studied hydrolysis conditions. Moreover, the thermal behavior of studied solids has been studied by thermogravimetric analysis under nitrogen atmosphere at different heating rates (5, 10, 15 and 20 ºC min-1). Activation energy for all samples has been obtained by the Flynn-Wall-Ozawa method. The optimum value, in which a high relationship between recoverable hemicelluloses fraction and H_2 concentration is found, under medium hydrolysis temperature (150ºC) has been obtained and was independent of the amount of acid added to the hydrolysis process.

Highlights: Replace the second sentence by: TGA was utilized to determine the kinetic parameters using FWO methods.

Highlight has been replaced

Introduction: The authors said: The obtained kinetic parameters will be used to modelling activation energy under different acid hydrolysis process and get the suitable process conditions to for the optimum energetic valuation. But, the work doesn't obtain the optimum condition for the acid hydrolysis (See Figure 1).

> The aim of the paper is not to achieve the highest hemicellulose extracted or the greatest amount of hydrogen. In this respect, the objective is to find the right balance between hemicelluloses extracted and the amount of hydrogen in the gas obtained. In this way, the energy valorization is maximized.

2.1. Characterization and storage of raw material: Describe the sampling of raw material collected from several experimental plots

> *Deleted*: Leucaena branches and twigs with 0.5-5 cm in diameter were used. These pieces were obtained by trimming Leucaena plants from which leaves and non-wood twigs were removed prior to grinding in a hammer mill.
>
> *Included*: Leucaena branches and twigs with 0.5-5 cm in diameter were used. These pieces were obtained by using a random trimming of Leucaena plants from which leaves and non-wood twigs were removed. To assure homogeneity and reproducibility of the experiments, these samples were air-dried during a day at room temperature, grinded and sieved to 250–500 μm.

2.2. Acid hydrolysis processing of wood samples. The liquid/solid ratio (LSR) of 8 kg water/kg raw material was repeated twice in this section.

> *Deleted*: using a liquid/solid ratio (LSR) of 8 kg water/kg raw material, on dry basis (the moisture content of material was considered as water).

2.4 Laboratory-scale reactor and TGA pyrolysis processing of samples. In this section put the following expression: In this study four replicates of each material were tested to prevent these errors.

> *In Section 2.5 Deleted*: In this study, four replicates of each material were tested to prevent these errors.
>
> *In Section 2.4 Included*: In this study, four replicates of each material were tested to prevent these errors.

2.5.Kinetic analysis by Flynn-Wall-Ozawa method. Correct the following paragraph because it is not understood: Therefore, for…

> *Deleted*: Therefore, for different heating rates (β) and a given degree of conversion (α), a linear relationship is observed by plotting of natural logarithm of heating rates (ln β), versus (1/T) obtained from thermal curves recorded at different heating rates will be a straight line whose slope (-0.4567 (Ea/RT)) will calculate the activation energy.
>
> *Included*: Therefore, under a given degree of conversion (α) and for different heating rates (β), a linear relationship could be obtained by plotting the heating rates logarithm (ln β), versus (1/T). Temperatures have been obtained from thermal curves recorded at different heating rates. This will result in a straight line whose slope (-0.4567 (Ea/RT)) will calculate the activation energy.

3.2. Thermogravimetric analysis of the pyrolysis process. Correct the following expression:

Deleted: It can be due to the higher cellulose and lignin content in the solid residue, is well know that wood polymers of biomass (cellulose, hemicellulose and lignin) interact during pyrolysis and in the temperature range of 150°C to 180°C, the stability of cellulose is reduced.

Included: It can be due to the higher cellulose and lignin contents in the solid residue, is well know that wood polymers of biomass (cellulose, hemicellulose and lignin) interact during pyrolysis and in the temperature range of 150°C to 180°C, the stability of cellulose is reduced.

3.3 Gases obtained Improve the English redaction in the following paragraph:

Deleted: By what the hydrolysis temperature, in a similar way to that exposed in the hydrolysis and extraction process, is the main factor in the H_2 production during the pyrolysis of the solid tested. Obtaining, under high hydrolysis temperature (170ºC) a solid from which a higher amount of hydrogen with respect to those found in the material original could be obtained.

Included: Accordingly to that exposed in the hydrolysis and extraction process, hydrolysis temperature is the main factor in the H_2 production in hydrolysis solid residues pyrolysis. This leads to higher amount of hydrogen, with respect to those found in the raw material, from the solid residue obtained under high hydrolysis temperature (170ºC).

3.4. Kinetic analysis The authors work in the <alpha> values between 0.05 to 0.75. Explain the reason to work in this range.

The non-isothermal method kinetic method (FWO) used in this study has become a common analytical technique. Therefore, Equation 3 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 (0.05 to 0.75) are widely used to represent the evolution of Ea as a function of the major components in lignocellulosic materials (cellulose, hemicellulose and lignin).

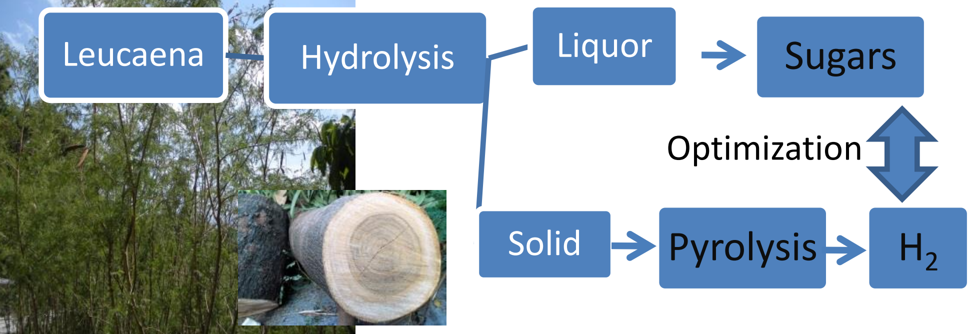
4. Conclusions. Clarify that these values are optimal only for the studied range of operation variables considering the acid hydrolysis.

Included: Under the studied range variables in acid hydrolysis, the optimal values, in which a fraction of recoverable hemicelluloses and higher H_2 concentration is obtained, is found at medium temperature hydrolysis process and is independent of the amount of acid added.

Highlights

- Thermal behaviour of hydrolyzed solid from *Leucaena leucocephala* under pyrolysis process.
- TGA was utilized to determine the kinetic parameters using FWO methods.
- Optimal parameters of acid hydrolysis were 170°C, 2% H_2SO_4
- TGA and DTA are useful in the interpretation of the kinetic results.

Graphical Abstract (for review)



Leucaena

Hydrolysis

Liquor

Sugars

Optimization

Solid

Pyrolysis

H_2

BIOMASS VALORIZATION BY USING A SEQUENCE OF ACID HYDROLYSIS AND PYROLYSIS PROCESSES. APPLICATION TO *LEUCAENA LEUCOCEPHALA*

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Abstract

Among main ways to provide an environmentally friendly energy and platform chemicals are the lignocellulosic conversion processes. The proper execution of this way will depend on the correct selection of lignocellulosic materials. A compelling plant is *Leucaena leucocephala* because its great variety of uses, its high biomass production and its leguminous nature. In this study, acid hydrolysis (130-170°C and 0.5-2% H_2SO_4, to extract valuable hemicelluloses) as pretreatment and pyrolysis of the solid residue (to get a gaseous fuel) as treatment have been used in its valorization. A laboratory-scale reactor was used for the pyrolysis experiments (550ºC, N_2) for both *Leucaena leucocephala,* as raw material, and the solid residues after hydrolysis process and raw material. The amounts of CO, CO_2 and H_2 found in the raw material are similar to those found in the solids obtained after the different studied hydrolysis conditions. Moreover, the thermal behavior of studied solids has been studied by thermogravimetric analysis under nitrogen atmosphere at different heating rates (5, 10, 15 and 20 ºC min-1). Activation energy for all samples has been obtained by the Flynn-Wall-Ozawa method. The optimum value, in which a high relationship between recoverable hemicelluloses fraction and H_2 concentration is found, under medium hydrolysis temperature (150ºC) has been obtained and was independent of the amount of acid added to the hydrolysis process.

Keywords

Leucaena; hydrolysis; pyrolysis; activation energy

1. Introduction

Lignocellulosic biomass is the most abundant renewable feedstock and low-cost raw materials. Therefore, its optimal utilization could be perceived as one of the key approaches to contribute to sustainable industrial progress, consequently, to low-carbon economy. In this sense, a huge amount of lignocellulosic biomass can potentially be converted into different high value products including value added chemicals and energy sources [1, 2].

Lignocellulosic biomass fractionation into reactive intermediates is a critical process prior to further development into valuable products. In this sense, it is a complex carbohydrate polymer. Mainly is composed of cellulose (major structural component), hemicellulose (copolymer of different C5 and C6 sugars) and lignin (a three-dimensional, highly cross-linked macromolecule, is the second most abundant natural polymer), as well as other minor components. To get an integral valorization of lignocellulosic several steps must be are involved (deconstructing the three-dimensional structure of lignocellulose, getting high yields of sugars and/or chemicals and lignin valuation) jointly a cost-effective process [3].

The intrinsic complexity of biomass calls for a biorefinery approach, which is adapted to the feedstock. A direct conversion of the whole biomass by thermal degradation (combustion, gasification or pyrolysis) is commonly used. However, to achieve an economic, social and environmental sustainability for the lignocellulosic materials valorisation, fractionation and subsequent valuation of its main component, is the essential point [4] and, then, unconventional solutions are needed.

The main purpose of fractionation is to get fractions that could be processed further into less complex product mixtures with higher concentrations of the desired compounds [5] and subsequent processing of the other non-extracted compounds.

Among the different pretreatment methods to enhance the extraction of carbohydrates in the process from lignocellulosic materials, hot water or weak acid hydrolysis are among the most suitable first step typically used to hydrolyze carbohydrates from lignocellulosic materials [1, 6]. Moreover, acid hydrolysis has proved one of the most efficient choices for this purpose inasmuch as it facilitates the dissolution of hemicellulose polymers, which can be used to obtain a variety of oligomers with high applicability in the chemical, pharmaceutical and food industries [6, 7].

On the other hand, and for energetic valorization, pyrolysis is a technology sector, which has a global expansion in terms of volume and production due to the need for renewable energy new sources [8]. The pyrolysis process involves the thermal degradation of lignocellulosic materials in the absence of oxygen in order to produce a mixture of char (ash), pyrolysis oil (bio-fuel), and synthetic gas (syngas) and, in addition, a gas mixture of carbon monoxide, hydrogen, carbon dioxide, and methane could be found [9]. The biomass pyrolysis is an advisable treatment for lignocellulosic materials because solid biomass which are very difficult and costly to manage. It can be converted into a low char volume, liquid and gas valuable products. These products have advantages in transport, storage, combustion, retrofitting and flexibility in production [8].

Respect to raw material selected in this work, *Leucaena leucocephala* (Leucaena) is a very fast-growing tree. Young trees reach a height of more than 6 meters in two to three years [10]. It was known as the 'miracle tree' because of its worldwide success as a long-lived and highly nutritious forage tree, and its great variety of other uses. [11]. Leucaena species showed high biomass productivity (more than 50 ton ha-1 year-1 under Mediterranean conditions [12, 13]. Moreover, this plant is extensively used as forage, fuel (direct combustion) and reforestation material [11, 14]. Previous use of Leucaena thermal valuation as pyrolysis liquid-phase [15, 16] and as char was described by Maneewan et al., [17] and Idrus et al., [18].

The goals of this work are to obtain the optimum hydrolysis conditions to get the maximum hemicelluloses derivatives concentration in the liquor and determine kinetic parameters during pyrolysis decomposition of *Leucaena leucocephala* as raw material and solid obtained after hydrolysis under different process conditions. The obtained kinetic parameters will be used to modelling activation energy under different acid hydrolysis process and get the suitable process conditions to for the optimum energetic valuation.

2. Materials and methods

2.1. Characterization and storage of raw material

Leucaena branches and twigs with 0.5-5 cm in diameter were used. These pieces were obtained by using a random trimming of Leucaena plants from which leaves and non-wood twigs were removed. To assure homogeneity and reproducibility of the experiments, these samples were air-dried during a day at room temperature, grinded and sieved to 250–500 μm. The material was collected from several experimental plots in Campus La Rábida, Huelva University (Huelva, Spain). This raw material used, which was prepared in accordance with Tappi T-257 [19], was analyzed for the following parameters: ethanol-benzene extractives (TAPPI-204) [20], ash (TAPPI T-211) [21], holocellulose [22], monosaccharides and acetyl groups contents.

To this end, portions of the homogenized wood chips were subjected to quantitative acid hydrolysis with 72% sulphuric acid (TAPPI T-249) [23]. The solid residue after hydrolysis was recovered by filtration and considered as Klason lignin. The monosaccharides and acetic acid contained in hydrolysates were determined by HPLC in order to estimate (after corrections for stoichiometry and sugar decomposition) the contents of samples in cellulose (as glucan), hemicelluloses (as xylan and araban), and acetyl groups.

The chemical characterization of Leucaena used in this study and the characterization of the others materials by various authors are shown in Table 1. The major fraction is cellulose (analyzed as glucan), to 32.2% (at TAPPI T-203) [28], followed by the Klason lignin to 21.5 % (after quantitative acid hydrolysis) and hemicelluloses fraction (calculated as the sum of xylan, araban, acetyl groups and others) to 18.6%.

2.2. Acid hydrolysis processing of wood samples.

Raw material and water were mixed in the desired proportions and treated in a 2 dm^3 stainless steel reactor (Parr Instruments Company, Moline, Illinois, USA). The reactor was fitted with four-blade turbine impellers, heated by an external fabric mantle and cooled by cool water circulating through an internal loop. The reaction media stirred at 150 rpm and heated to reach the desired temperature. Time zero was considered the beginning of the isothermal stage and the hydrolysis process was considered finished at 60 minutes of operating time according to previous bibliographic data [24, 25, 27]. The operating conditions were 130, 150 and 170°C temperature and 0.5, 1.25 and 2% H_2SO_4 content and a liquid/solid ratio of 8 kg water by kg raw material, on a dry basis. When the pretreatment was finished, the reactor was immediately cooled down by cooling water and then removed from heating jacket.

After treatment, solid residues were recovered by filtration, washed with water, air-dried, weighed for yield determination. Aliquots of the solid phase were analyzed for moisture and composition (duplicate) using the same methods as for raw material analysis. An aliquot of the liquors was filtered through 0.45 mm membranes and used for direct HPLC determination of monosaccharides, oligomers and Hemicelluloses extracted.

2.3. Experimental design for acid hydrolysis processes. Multiple regression models.

In order to relate the dependent (yield, hemicelluloses extracted) and independent variables (temperature 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 1.

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

Where X is the absolute value of the independent variable concern, X 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 to previous work (data not shown). The number of tests required was calculated as N = 2^n + 2n + nc, 2n being the number of points constituting the factor design, 2n that of axial points, and nc that of central points. Under our conditions, N = 9. The experimental results were fitted to the following second-order polynomial (Eq. 2):

$$Y = a_0 + \sum_{i=1}^{n} b_i\, X_{ni} \ + \sum_{i=1}^{n} c_i\, X_{ni}^2 \ + \sum_{i=1;\, j=1}^{n} d_i\, X_{ni}\ \ X_{nj}\ \ (i < j) \quad \text{Eq.2}$$

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

2.4 Laboratory-scale reactor and TGA pyrolysis processing of samples

Leucaena and its hydrolyzed solid residues chips with diameter of about 50 mm were milled into smaller chips with the diameter of about 1-2 mm. Milled chips were stored in a small glass bottle to prevent the contact with air moisture.

A laboratory-scale reactor was used for the pyrolysis experiments. The experimental system consists of a quartz tube, 10 mm wide, where the sample (approximately 2g) is uniformly introduced inside a tube of 35 cm length. A horizontal actuator introduces the tube with the biomass into a furnace maintained at 550ºC at constant velocity, 2 s of residence time was selected [29, 30]. N_2 (20 cm^3 min^{-1}) was used as transport gas. H_2, CO and CO_2 determinations was performed by using a previously calibrated multi-gas analyser (MultiRAE IR PGM-54, RAE Systems, San José, CA, USA) and were done in triplicate by using its integrated sampling pump with a flow rate of 0.2 L min^{-1}. This instrument incorporated sensors, among other gases, to determine the concentrations of gases. In this study, four replicates of each material were tested to prevent these errors.

Thermo-chemical decomposition behavior was assessed using a thermo-gravimetric analyzer (TGA) (Mettler Toledo TGA/DSC1 STARe System). The TGA experiments were performed by heating a 50-130 mg sample from 25°C to 800°C under four heating rates of 5, 10, 15 and 20°C min^{-1} under a nitrogen flow of 20 cm^3 min^{-1}. Data obtained from thermo-gravimetric analysis were analyzed or any changes in thermo-chemical decomposition behavior. The TGA data were analyzed to determine the Arrhenius activation energy (E) and pre-exponential constant (A) using their isoconversion method described by Flynn-Wall-Ozawa.

2.5.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. The ability to follow the changes in activation energy as a function of conversion is of great interest to the thermal analyst. In the present study, the obtained Ea values could be used to determine acid hydrolysis optimum conditions for maximum energy efficiency (H_2) with the minimum Ea value.

Activation energy has been studied by several differents mathematical methods [31, 32]. In this sense, the use of the isoconversion method has been successfully documented for pyrolysis kinetics determination [33, 34].

For a single-reaction mechanism, activation energy should be a constant value throughout the weight loss region. The activation energy values for the degradation process were determined by the isoconversional Flynn-Wall-Ozawa (FWO) method [35, 36] defined by Eq. 3.

$ln\ (\beta) = ln(\frac{A\ Ea}{R\ g(\alpha)}) - 2.315 - 0.4567\ \frac{Ea}{R\ T}$ (Eq 3)

Where β is the heating rate, A is the pre-exponential factor, g(α) is a function of the conversion, E_a is the activation energy, T is the temperature and R is the gas constant.

Therefore, under a given degree of conversion (α) and for different heating rates (β), a linear relationship could be obtained by plotting the heating rates logarithm (ln β), versus (1/T). Temperatures have been obtained from thermal curves recorded at different heating rates. This will result in a straight line whose slope (-0.4567 (Ea/RT)) will calculate the activation energy. The underlying assumption is that the reaction model, g(α), is identical at a given degree of conversion (α) for a reaction under different thermal conditions. Moreover, this method can be used for determination of the Ea values without any knowledge of the reaction mechanisms [34]. Disadvantage of this method is a series of measurements at different heating rate that must be made for the same samples mass and the same volume flow of inert gas and their fluctuation can cause of errors [37].

3. Results and discussion

3.1. Acid hydrolysis stage

The normalized values of independent variables (temperature and acid concentration), the solid yield and 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 nonisothermal process between 130ºC and 170°C has not been considered due to the short time heating the reactor, between both temperatures, elapsed compared to both heating from ambient temperature.

Among the obtained results, the variation ranges in solid phase: 59.2-87.8% of the solid yield and 43.41-80.73% of the hemicellulose extracted is found. The error in mass balance was less than 5% in all components. It is assumed to be a considerable difference because the working hypothesis was to maximize the extraction of hemicellulose derivatives while minimizing that of cellulose derivatives to get the maximum power capacity.

According with Section 2.3, to assess the relative influence of the selected independent variables (temperature and acid concentration) on each dependent variable (solid yield and total hemicelluloses extracted), the polynomial mathematical models were obtained (Table 3) by substituting the values of the measured independent variables for each dependent variable, and applying a polynomial model analysis. Each value used to obtain the equations is the average of three measurements. The differences between the experimental values and those that were estimated using the previous equations never exceeded 5% for the solid yield, glucose and xylose and 10% in total hemicellulose extracted. Suitable fits with values of F-Snedecor >32 and R^2 greater than 0.92 in all cases have been obtained.

In order to estimate the influence of operational variables on solid yield after raw material hydrolysis, and to compare different conditions, the surface response in Fig.1 has been plotted.

Solid yield decrease with increasing temperature. It could be due to the oligomers depolymerization and some glucose extraction from the solid. A medium yield variation with respect to acid concentration can be observed under low temperature. Nevertheless, as expected, a high yield decrease is observed under high acid concentration and temperature.

A low hemicellulose liquor content variation under the different acid concentration is observed (Fig. 2). However, a strong increase in the extracted hemicellulose contents can be observed under high temperature (170ºC). In general, there was a decline of oligomers for increased acid concentration and temperature, and conversely an increase in extracted content is observed. Although, under medium temperature (150ºC), lower extracted hemicellulose values than that obtained for low temperature (130ºC) are observed. This is probably due to the speed of the reaction at high temperature, which increased the rate of oligomers degradation and low total extraction is found.

The results in this work can be comparable with the data shown by Feria et al., (2011) (20-80% hemicellulose extracted) and López et al., [27] (30-85% hemicellulose extracted) in *Eucalyptus globulus*.

3.2. Thermogravimetric analysis of the pyrolysis process.

Ten solid residues have been obtained after hydrolysis process to compare its thermal behavior regarding to the original raw material. However, because of the process conditions, each obtained solid has undergone a different hemicellulose extraction, is for that reason why, to perform the thermogravimetric comparison we have only taken the raw material, as reference, the minimum (-1, -1) and the maximum hemicellulose extraction (+1, +1) conditions of acid hydrolysis to compare them.

Effect of the heating rate on thermal degradation (TGA) and differential mass loss (DTG) thermograms of thermal decomposition of Leucaena and solid residues obtained under high (+1, +1) and low (-1,-1) acid hydrolysis process extraction pyrolysis, at four heating rates 5, 10, 15, 20 ºC min^{-1} under nitrogen atmosphere are shown in Figure 3-5 respectively.

As expected, the three typical regions are evident which correspond to water evaporation, active and passive pyrolysis in the figures is found. The first region from 60 ºC to 150 ºC is related to the extraction of moisture and adsorbed water in samples. The main pyrolysis process proceeds in a range from 150 ºC to 400 ºC for the solid residue, although it began a little later for raw material (180 ºC). In this region (active pyrolysis), two main peaks (related to hemicellulose and cellulose decomposition) [38] for the raw material (Figure 2) are observed, nevertheless, the first peak (hemicellulose peak) is not observed for the solid obtained after the hydrolysis. Data and stages found for the selected solid materials (Fig 3-5) are in agreement with Gašparovič et al., [39] that examined the TGA for various wood chips and revealed that thermal decomposition of biomass proceeds in three stages: water evaporation, active and passive pyrolysis. Moreover, the decomposition process depends on the composition and concentration of its main biomass components (cellulose, hemicellulose and lignin). In that form, the decomposition of hemicelluloses and cellulose take place in active pyrolysis in the temperature from 200-400ºC and 250-380ºC, respectively, lignin is decomposed in both stages [40] in range from 180-850 ºC without characteristic peaks. In this study, Leucaena as raw material its thermal degradation begins at 200ºC, however for both the hydrolyzed solids, this degradation begins at 150ºC. Under the process conditions, part of hemicelluloses has been extracted. By what the TGA hemicelluloses shoulder is not observed in Figures 4 and 5. Furthermore, the lower temperature to which producing the weight loss could be due to the lower polymerization level of both hemicelluloses and cellulose remaining in the solid. Is known that acid hydrolysis pre-treatment breaks down the lignin protection and produces cellulose depolymerization creating the conditions for hydrolysis of polysaccharides [40].

It is known that the heating rate affects both location of the TGA and DTG curve positions, maximum decomposition rate and location of maximum temperature peaks and, as expected, for all the studied samples, the maximums of the decomposition rates are also slightly shifted towards higher temperatures [41]. When heating rate increases, starting and final temperature of active and passive pyrolysis region also increase. As can be seen in these figures, there is a shift in conversion lines caused by various heating rates. For all the studied solids, at higher heating rates, individual conversions are reached at higher temperatures. These phenomena can be explained on the basis of heat transfer limitation [42]. At low heating rate, a higher instantaneous thermal energy is provided in the system and a longer time may be required to reach equilibrium and the maximum rate curve to shift to the right [43].

The maximum peak temperature for raw material is found at 342°C (at 20ºC min^{-1}), with a maximum weight loss rate of 17.2% min^{-1} and at 333°C (at 20ºC min^{-1}), with a maximum weight loss rate of 14.9% min^{-1} for the hydrolyzed material (+1, +1). In this sense, cellulose decomposed dramatically in the temperature range of 300°C to 400°C with a large decomposition peak at 340°C [44] and the reported decomposition temperature range for xylan was between 200°C and 350°C with a decomposition peak at 260°C. Nevertheless, higher derivative weight values are found for the solid residue after hydrolysis with respect to the raw material is found after 400 ºC. It can be due to the higher cellulose and lignin contents in the solid residue, is well know that wood polymers of biomass (cellulose, hemicellulose and lignin) interact during pyrolysis and in the temperature range of 150°C to 180°C, the stability of cellulose is reduced. Nonetheless, residual cellulose is protected by lignin after the temperature reaches 350°C [38, 45]. Above 450 ºC there is only a small drop of mass (passive pyrolysis). Lignin is decomposed in both regions of active and passive pyrolysis without characteristic peaks [46]. The differences in final content among samples could be attributed to the different ash concentration. This data are coherent with the data obtained for similar biomass [47, 48].

3.3 Gases obtained

In Table 4 gases content (CO, CO_2 and H_2) obtained for pyrolysis of Leucaena and the solid residues obtained after the hydrolysis under different process conditions are shown. Is well known that the composition of syngas depends on the biomass properties and gasifier operating conditions [49]. However, under fixed conditions data obtained may be useful for comparison among different treatments.

The amounts of CO, CO_2 and H_2 found in the Leucaena are similar to those found in the solids obtained after the hydrolysis. At this point, only the solid samples (1, 0) and (- 1, 0) have higher CO_2 and H_2 content than that found in the other samples as well as a lower amounts of CO. Both points correspond to samples in which they have a medium temperature (150ºC) in the hydrolytic process. Furthermore, both points have higher and lower acid concentration respectively. Accordingly to that exposed in the hydrolysis and extraction process, hydrolysis temperature is the main factor in the H2 production in hydrolysis solid residues pyrolysis. This leads to higher amount of hydrogen, with respect to those found in the raw material, from the solid residue obtained under high hydrolysis temperature (170ºC).

3.4. Kinetic analysis

While determination of pyrolysis kinetics is critical to the understanding of the pyrolysis process for a given biomass, few works have documented the effects of physico-chemical pretreatments on the pyrolysis process [48, 50, 51]. The activation energy (Ea) for the raw material and the hydrolysis solid residues were obtained using FWO method. The kinetic parameters obtained by FWO were calculated according to Eq. (3) for a given value of conversion (α). Each of the shown experimental results is an average value of at least 3 determinations. The deviations of each one of those parameters with respect to their averages are smaller than 5% in all the cases. To determine the kinetic parameters, we chose the same value of α from range 0.05 to 0.75 for all curves at different heating rate and we found the corresponding temperature. The FWO equations of $\ln(\beta_i)$ versus $1/T_{\alpha i}$ $^{o}C^{-1}$ for different values of conversion are shown in Table 5. The regression equations and the square of the correlation coefficient (R^2) is also presented and high R^2 values for all of the equations in Table 5 is observed. The apparent activation energies were obtained from the slope.

The activation energies (Ea) were derived from the slope. The results obtained from for *Leucaena leucocephala* was 172, 187 and 168 kJ mol^{-1} for α=0.25; 0.50 and 0.75 respectively. In this sense, the activation energy was not similar for all conversion indicates the existence of a complex mechanism that occurs in the solid state. By applying an ANOVA analysis for each one of the dependent variable obtained as a function of the independent variables. To determine the values of the independent variables giving the minimum Ea for each solid residue (with respect to the raw material) the response surfaces of Ea for a given value of conversion (α) were plotted (Figures 6-8).

In Figure 6, we can observe that activation energy for the solid residue after hydrolysis as a function of temperature and acid concentration was dependent of these parameters and, over the entire range of these parameters, the value of Ea is always greater than that obtained by the raw material. The activation energy ranged from 180 kJ mol^{-1} to 270 kJ mol^{-1} for the fractional conversion range of 0.25. A similar result for the hemicellulose activation energy (213 kJ mol^{-1}) was presented by Lv et al. [52] by the same kinetic method. As Figure 3 shows, acid concentration is the most influential variable on Ea values evolution. This range corresponds to the thermal degradation of the hemicellulose and the onset of cellulose degradation [44]. Lower variations with respect to temperature have been found. However, a decline in temperature causes an increase Ea. Therefore, lower-to-medium temperature values (130-150ºC) and lower acid concentration (0.5%) are desired to obtain lower Ea values, similar to that found for the raw material. This behavior could be due to the fact that under these conditions a low amount of hemicelluloses is extracted (Table 2). And, as it is known [39] the hemicelluloses activation energy is smaller than the one corresponding to the cellulose, reason why the solid activation energy is low if the amount of hemicelluloses remaining in the solid is high.

Figure 7 shows the activation energy for $\alpha=0.5$. The activation energy ranged from 170 kJ mol^{-1} to 265 kJ mol^{-1} for this fractional range, a similar result for the cellulose activation energy (185 kJ mol^{-1}) was presented by Sonobe and Worasuwannarak [53] using an isothermal method. Conversely, Jin et al., [54] reported activation energy values of 381 kJ mol^{-1} for cellulose at 300°C under isothermal heating conditions. Acid concentration is the most influential variable on Ea evolution. Higher values could be found under high acid concentration (2% H_2SO_4) and low temperature values (130ºC). However, lower values than that found for the raw material is found at lower acid concentration (0.5% H_2SO_4) and medium temperature values (150ºC).

It's clear that under this parameter low glucan is extracted from the original raw material a similar behaviour to that found in Figure 6 is found in Figure 8. The activation energy ranged from 190 kJ mol^{-1} to 217 kJ mol^{-1} for this fractional range. Lignin activation energy was reported in the range of 237.1- 266.6 kJ mol^{-1} by Cai et al., [55] under isothermal heating conditions and 284 kJ mol^{-1} by Murugan et al., [56]. In this sense, different activation energy values of lignin may be attributed to the calculation methods and source of lignin. In this figure, Acid concentration is the most influential variable and higher acid addition (2% H_2SO_4) implies higher Ea values. Moreover, over the entire studied range of acid concentration and temperature, the value of Ea is always greater than that obtained by the raw material.

Figure 9 shows the hydrogen obtained versus activation energy when $\propto$=0.5 which corresponds, in most of cases, to the maximum activation energy of the process. In the figure it is observed that the point that offers highest obtained hydrogen for a minimum activation energy corresponds to the point (-1,0). Leucaena (raw material) corresponds to the group of low activation energy, but the quantities of hydrogen obtained are also in the lower range of the samples tested. Moreover, all of the maximum value of hydrogen obtained and minimum activation energy correspond to samples obtained under medium values temperature.

4. Conclusions

In the proposed acid hydrolysis process, experimental design variations among 59.2-87.8% of the solid yield and 43.41-80.73% of the hemicellulose extracted is observed.

The thermal degradation of the studied materials (raw material and hidrolized solids) is influenced by its composition. The amounts of CO, CO_2 and H_2 found in the raw material are similar to those found in the solids obtained after the different studied hydrolysis conditions. The activation energy ranged from 180-270 kJ mol^{-1} for α=0.25, 170-265 kJ mol^{-1} for α=0.5 and 190-217 for α=0.75.

Leucaena (raw material) has a medium-to-low activation energy (with respect hydrolyzed solids), however, low hydrogen has been obtained. Under the studied range variables in acid hydrolysis, the optimal values, in which a fraction of recoverable hemicelluloses and higher H_2 concentration is obtained, is found at medium temperature hydrolysis process and is independent of the amount of acid added.

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Table

Table 1. Average chemical composition for *Leucaena leucocephala* used and other similar lignocellulosic residues bibliographic composition[a].

	Leucaena leucocephala (present study)	Leucaena leucocephala (Feria et al., 2011)	Leucaena diversifolia (Alfaro et al., 2009)	Paulownia fortunei (Caparrós et al., 2008)	Eucalyptus globulus (López et al., 2014
Ethanol extract., %	nd.	nd.	1.7	nd.	2.7
Ash, %	1.4	1.3	nd.	nd.	0.7
Holocellulose, %	72.8	70.6	65.8	56.9	nd.
Glucan, %	32.2	37.2	38.0	34.2	42.8
Klason lignin, %	21.5	22.4	24.8	27.2	21.2
Xylan, %	15.5	17.4	15.8	18.3	17.1
Araban, %	1.0	1.0	1.5	1.1	0.7
Acetyl groups, %	2.1	1.8	3.3	3.3	3.5

[a] Raw material percentages (100 kg dry matter)

Table 2. Variation of yield and hemicelluloses content extracted from solid phase as a function of sulphuric acid concentration (Xc) and temperature (X_T) in a acid hydrolysis process

X_c	X_T	*Y*ield (%)	Total hemicellulose extracted* (%)
1	1	69.21	78.1
1	-1	87.80	43.4
-1	1	59.22	75.5
-1	-1	72.01	53.1
1	0	78.17	56.6
-1	0	65.31	57.9
0	1	59.13	80.7
0	-1	75.17	55.6
0	0	65.70	53.7
0	0	65.73	53.7

Where X_C: normalized value for sulphuric acid concentration (-1) 0.5%, (0) 1.25% and (1) 2% H_2SO_4; X_T: normalized value for temperature (-1) 130°C, (0) 150°C and (1) 170°C

*Percentages with respect to initial content in solid raw material)

Table 3. Polynomial models obtained for the selected dependent variables in the hydrolysis process.

Equation	R^2	F-Snedecor
3. $YI = 66.67 + 6.44 X_C - 7.90 X_T + 5.28 X_C X_C - 1.45 X_C X_T$	0.99	438.76
4. $Hem = 55.86 + 13.60 X_T + 8.65 X_T X_T + 3.02 X_C X_T$	0.92	33.50

Where: YI= solid yield percentage with respect to initial content; Hem= total hemicellulose reminded with respect to initial content in solid; X_C: normalized value for sulphuric acid concentration (-1) 0.5%, (0) 1.25% and (1) 2% H_2SO_4; X_T: normalized value for temperature (-1) 130°C, (0) 150°C and (1) 170°C

Table 4. Gases obtained in laboratory pyrolysis process for Leucaena raw material (Leuc) and the solid residues after hydrólysis process in the experimental design (all values are expressed as volume percentage).

	Leuc		Solid Residue after hydrolysis (X_c and X_T: Hydrolysis conditions)									
		X_c	1	1	-1	-1	1	-1	0	0	0	0
		X_T	1	-1	1	-1	0	0	1	-1	0	0
CO	28.5		27.6	26.9	25.9	28.4	25.3	25.1	28.8	29.0	27.4	27.5
CO_2	21.1		22.0	21.2	21.1	21.9	25.1	25.0	19.1	19.1	22.6	22.3
H_2	6.52		6.7	7.1	7.1	6.9	7.9	8.0	5.9	6.0	7.3	7.6

Where X_C: normalized value for sulphuric acid concentration (-1) 0.5%, (0) 1.25% and (1) 2% H_2SO_4; X_T: normalized value for temperature (-1) 130°C. (0) 150°C and (1) 170°C

Table 5. The FWO equations of ln(β_i) versus 1/$T_{\alpha i}$ $^oC^{-1}$ for different values of conversion.

	α=0.25		(Y = a X + b)	α=0.50		(Y = a X + b)	α=0.75		(Y = a X + b)
	a	B	R^2	a	b	R^2	a	b	R^2
Leuc	-26.58	19.54	0.89	-21.66	40.99	0.95	-15.45	29.54	0.92
X_C X_T									
(1, 1)	-24.07	46.31	0.84	-21.43	39.06	1.00	-23.19	40.12	0.99
(1, -1)	-18.79	37.67	0.99	-21.17	39.29	0.96	-28.74	41.17	0.99
(-1, 1)	-20.06	39.46	0.99	-19.04	35.56	0.99	-20.56	36.27	0.99
(-1,-1)	-24.50	46.48	0.98	-21.89	40.26	0.99	-20.59	35.02	0.99
(1, 0)	-19.05	38.10	0.99	-21.92	39.70	1.00	-23.93	41.35	1.00
(-1, 0)	-24.06	46.77	0.99	-19.66	35.73	0.99	-20.40	35.55	0.98
(0, 1)	-17.85	33.77	0.98	-22.96	41.79	1.00	-20.51	36.32	0.99
(0,-1)	-19.09	39.01	0.96	-19.63	38.47	0.99	-20.92	37.17	0.99
(0, 0)	-16.80	32.62	0.98	-18.62	34.64	0.99	-20.93	35.38	0.99
(0, 0)	-21.30	37.46	0.99	-21.79	38.26	0.98	-21.06	33.21	0.98

Figure 1. Variation of solid yield as a function of acid concentration and temperature under acid hydrolysis process.

Figure 2. Variation of total hemicellulose content extracted as a function of acid concentration at three temperature.

Figure 3: Pyrolysis TGA and DTG dependencies of Leucaena raw material at various heating rates: 5ºC/min, 10ºC/min, 15ºC/min, 20ºC/min.

Figure 4: Pyrolysis TGA and DTG dependencies of solid residue obtained under high acid hydrolysis extraction (+1, +1) at various heating rates: 5ºC/min, 10ºC/min, 15ºC/min, 20ºC/min.

Figure 5: Pyrolysis TGA and DTG dependencies of solid residue obtained under low acid hydrolysis extraction (-1, -1) at various heating rates: 5ºC/min, 10ºC/min, 15ºC/min, 20ºC/min.

Figure 6: Activation energy evolution for the solid residue after hydrolysis as a function of Temperature and Acid Concentration with respect to the Leucaena leucocephala as raw material at α=0.25.

Figure 7: Activation energy evolution for the solid residue after hydrolysis as a function of Temperature and Acid Concentration with respect to the Leucaena leucocephala as raw material at α=0.50.

Figure 8: Activation energy evolution for the solid residue after hydrolysis as a function of Temperature and Acid Concentration with respect to the Leucaena leucocephala as raw material at α=0.75.

Figure 9. Obtained hydrogen versus activation energy (α=0.5).

Figure 1

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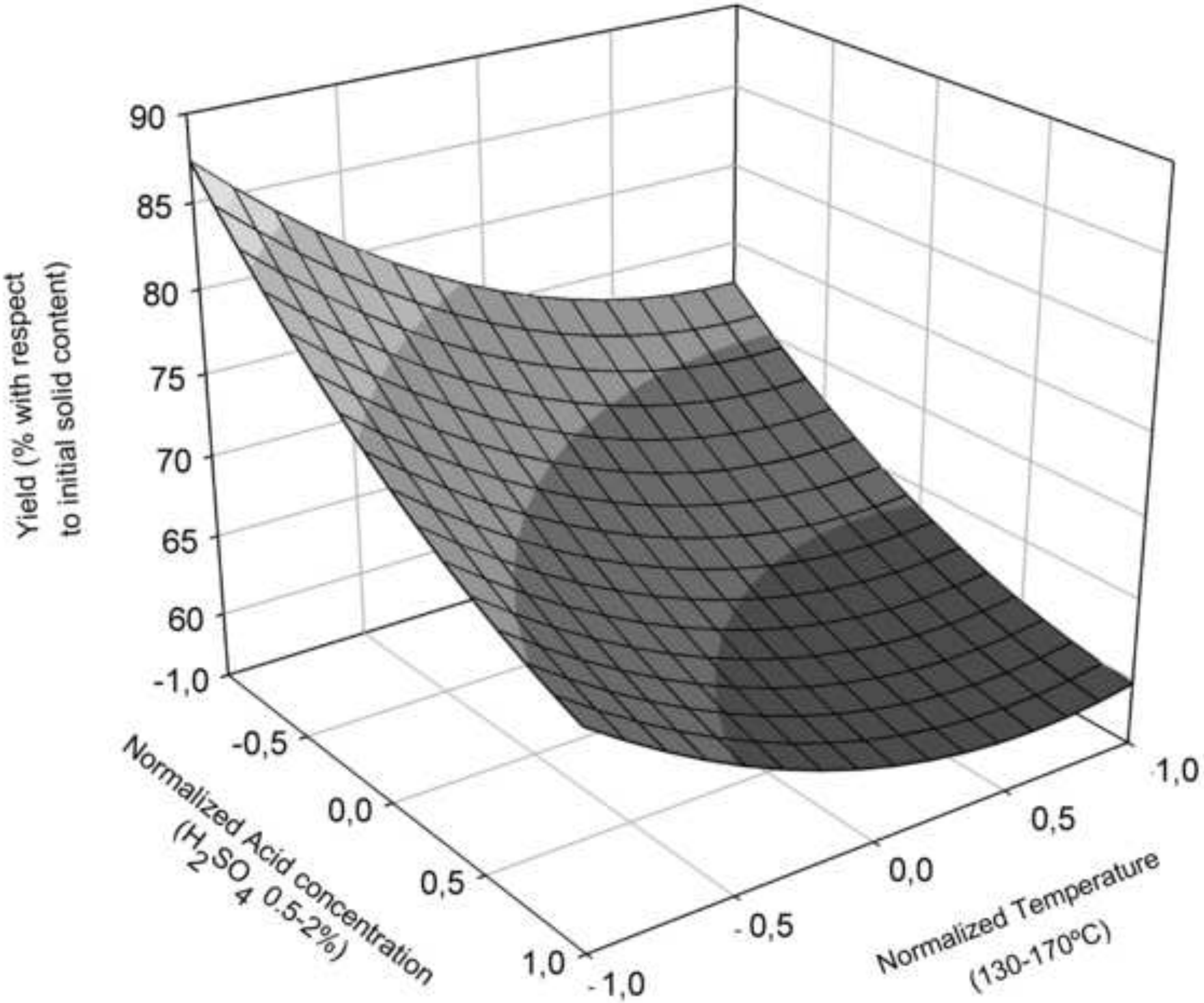

Figure 2

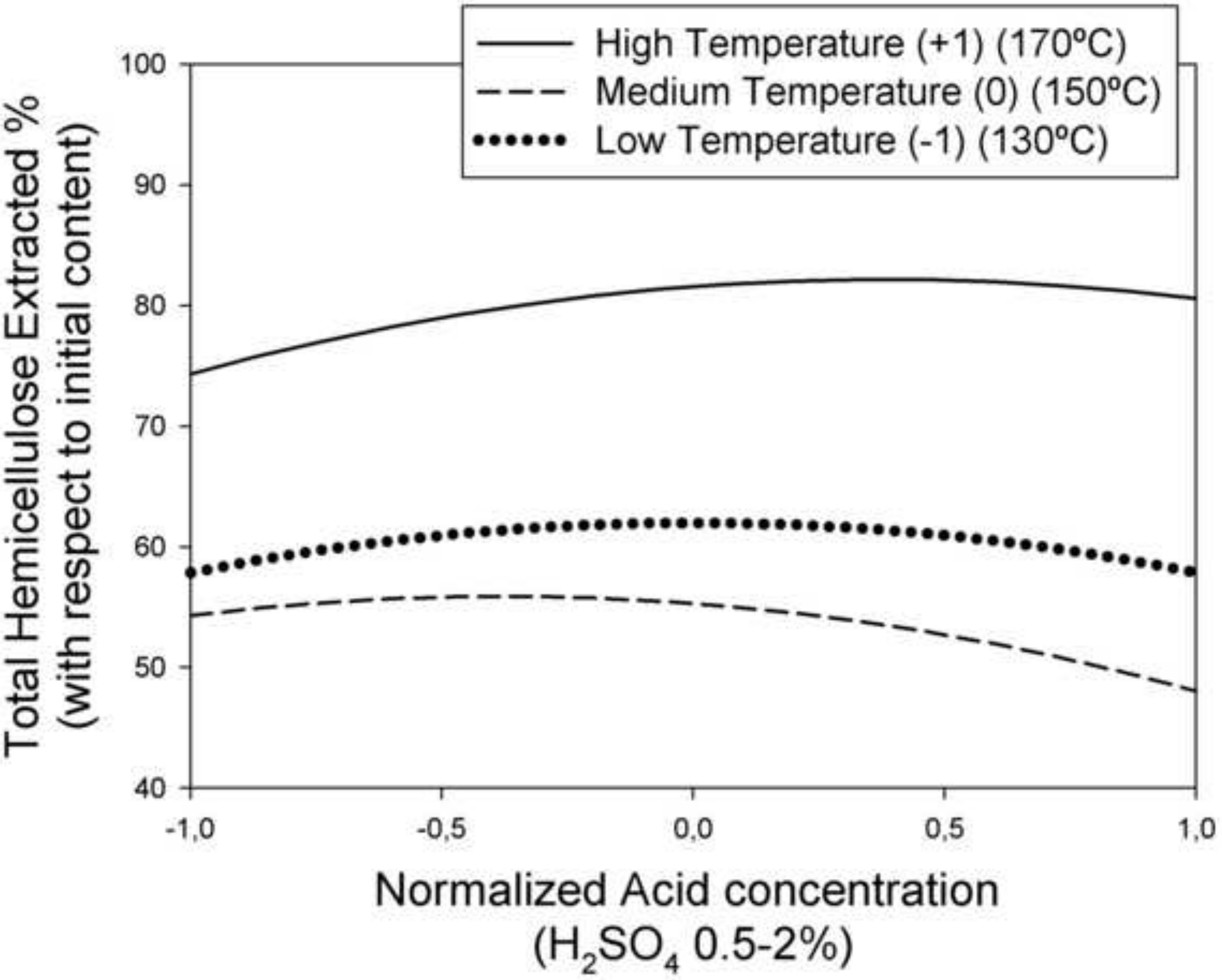
High Temperature (+1) (170ºC)
Medium Temperature (0) (150ºC)
Low Temperature (-1) (130ºC)
Total Hemicellulose Extracted %
(with respect to initial content)
100
90
80
70
60
50
40
-1,0
-0,5
0,0
0,5
1,0
Normalized Acid concentration
(H_2SO_4 0.5-2%)

Figure 3

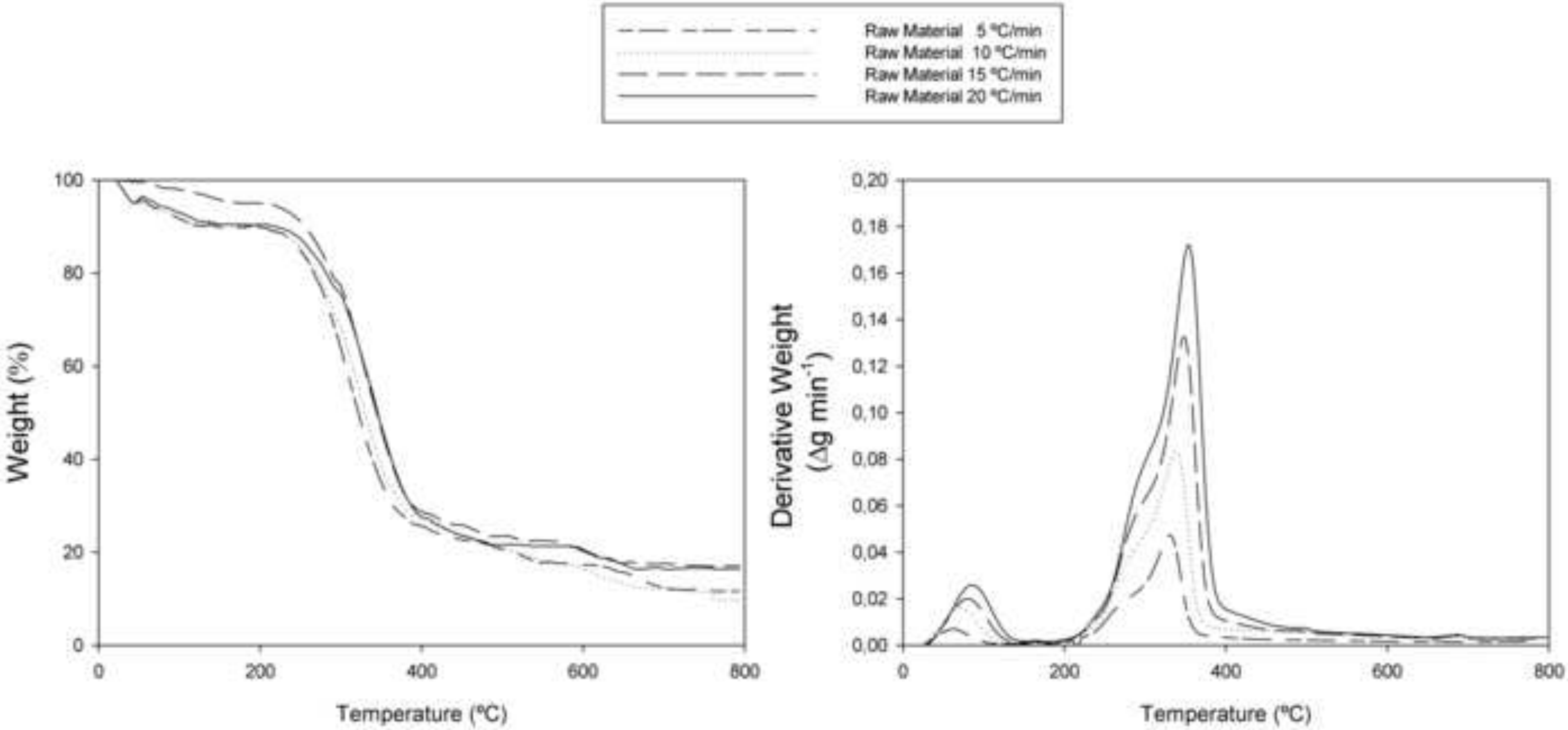
Raw Material 5 °C/min
Raw Material 10 °C/min
Raw Material 15 °C/min
Raw Material 20 °C/min
Weight (%)
100
80
60
40
20
0
0
200
400
600
800
Temperature (°C)
Derivative Weight
(Δg min^{-1})
0,20
0,18
0,16
0,14
0,12
0,10
0,08
0,06
0,04
0,02
0,00
0
200
400
600
800
Temperature (°C)

Figure 4

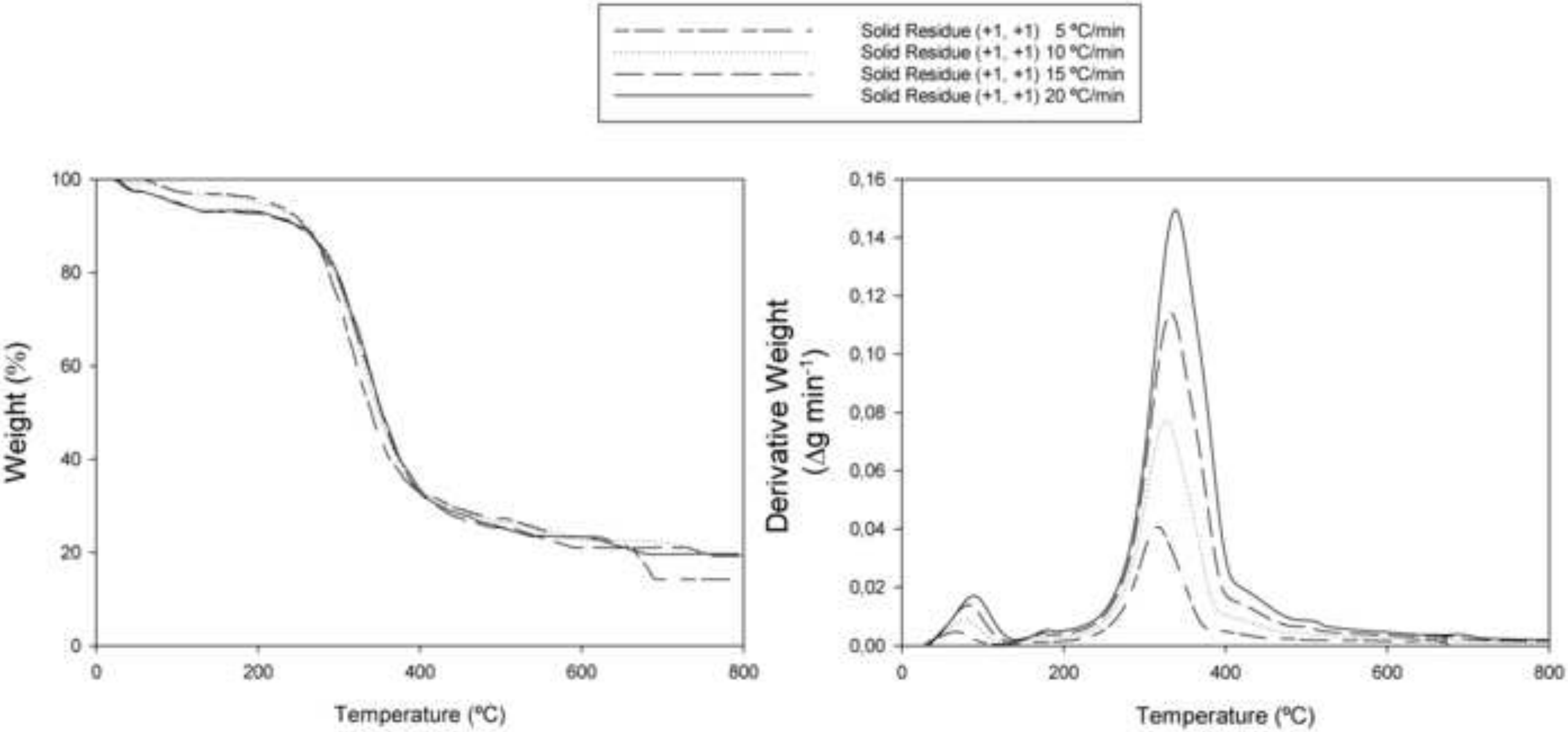
Solid Residue (+1, +1) 5 ºC/min
Solid Residue (+1, +1) 10 ºC/min
Solid Residue (+1, +1) 15 ºC/min
Solid Residue (+1, +1) 20 ºC/min
Weight (%)
100
80
60
40
20
0
0
200
400
600
800
Temperature (ºC)
Derivative Weight
(Δg min⁻¹)
0,16
0,14
0,12
0,10
0,08
0,06
0,04
0,02
0,00
0
200
400
600
800
Temperature (ºC)

Figure 5

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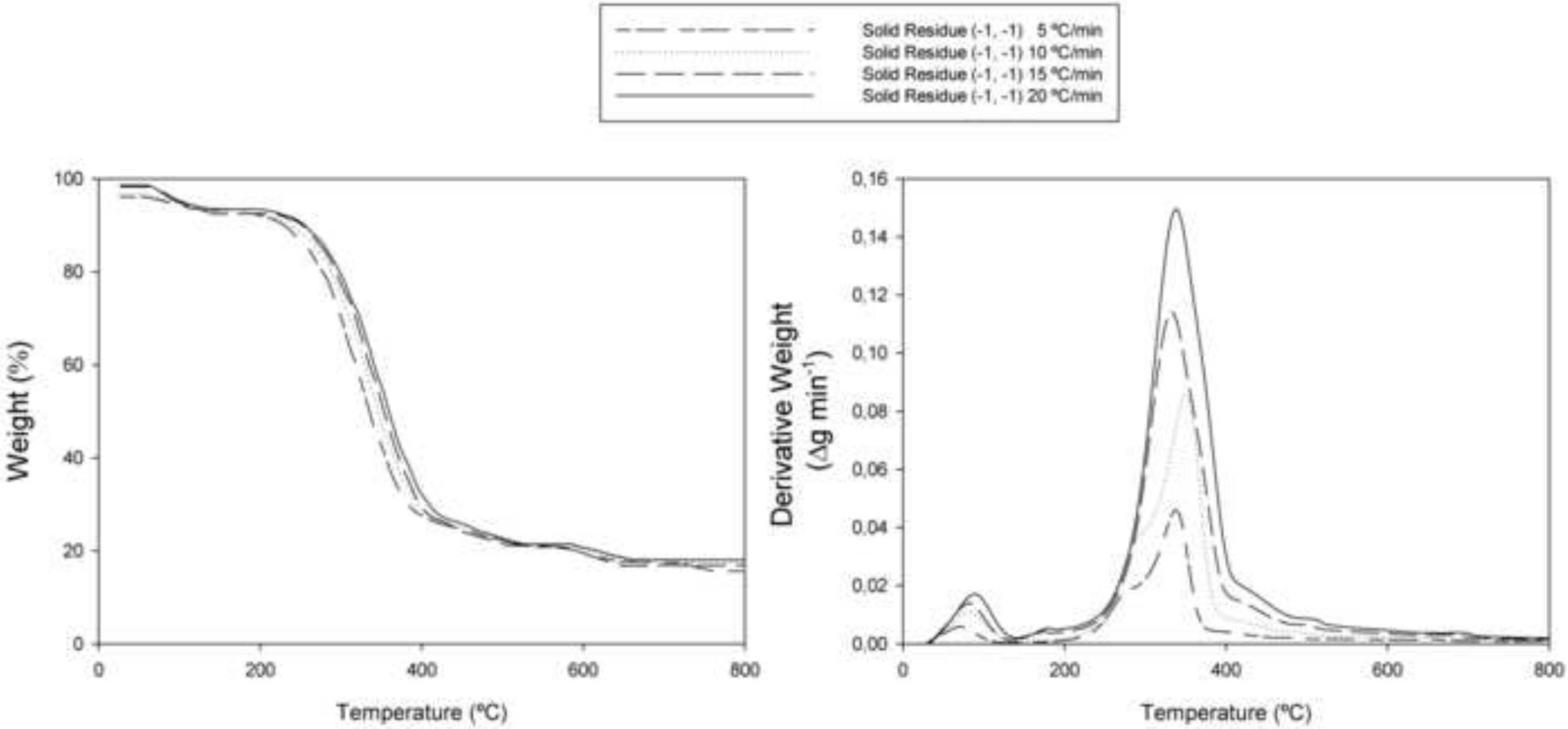

Figure 6

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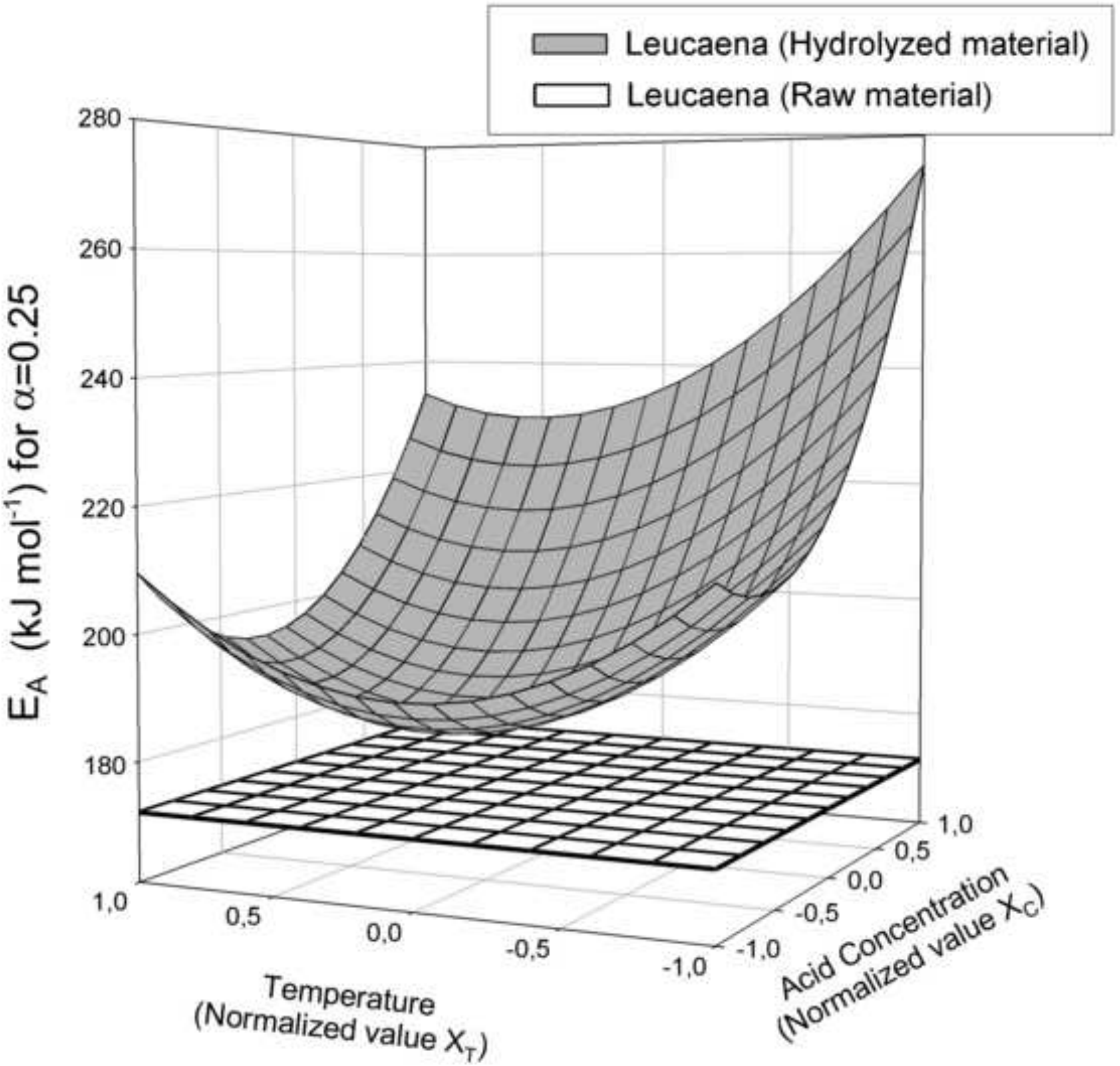

Figure 7

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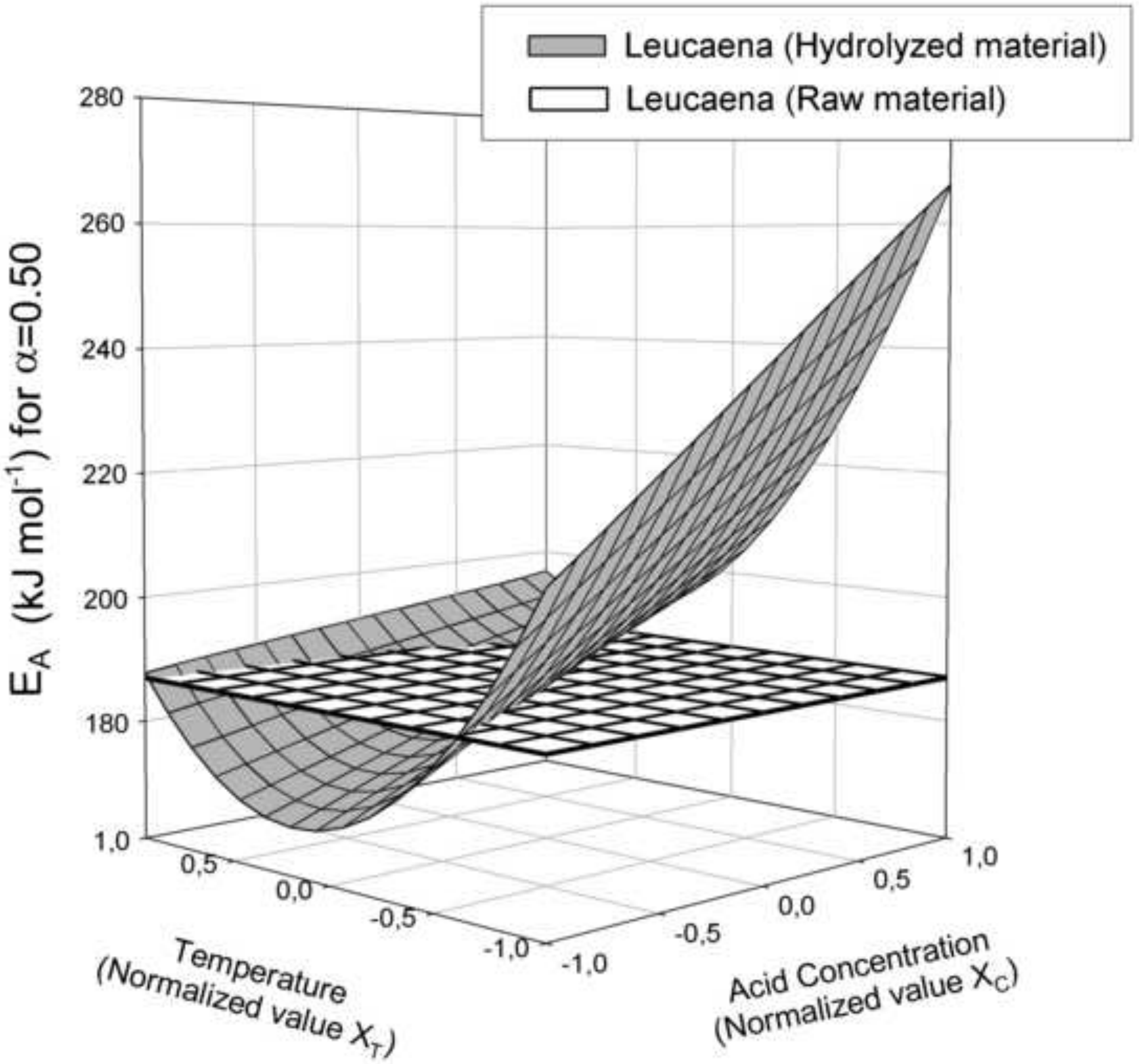


Figure 8

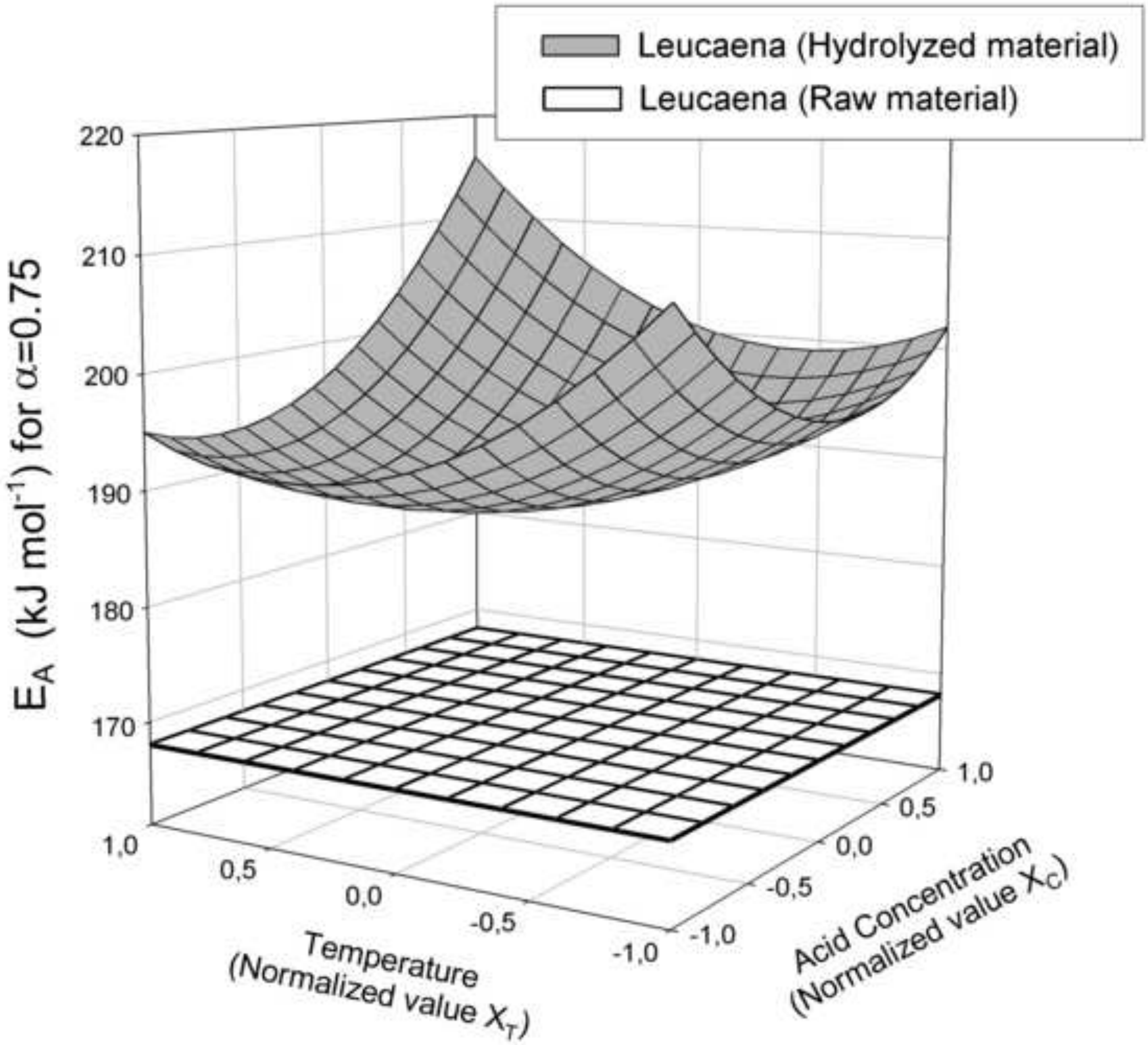
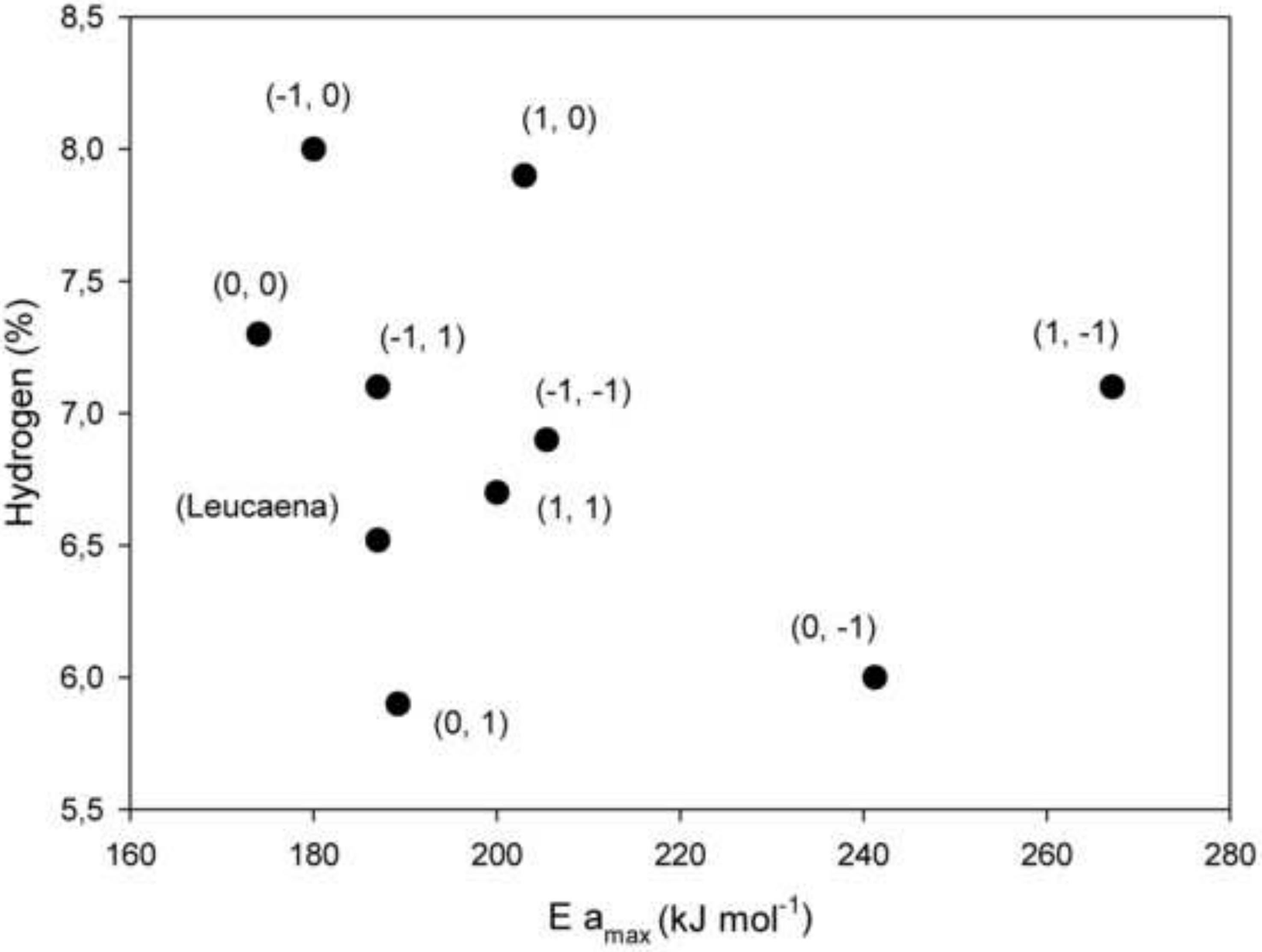

▨ Leucaena (Hydrolyzed material)
☐ Leucaena (Raw material)
E_A (kJ mol^{-1}) for α=0.75
220
210
200
190
180
170
1,0
0,5
0,0
-0,5
-1,0
Temperature
(Normalized value X_T)
1,0
0,5
0,0
-0,5
-1,0
Acid Concentration
(Normalized value X_C)

Figure 9


Hydrogen (%)
8,5
8,0
7,5
7,0
6,5
6,0
5,5
160
180
200
220
240
260
280
E a$_{max}$ (kJ mol^{-1})
(-1, 0)
(1, 0)
(0, 0)
(-1, 1)
(1, -1)
(-1, -1)
(Leucaena)
(1, 1)
(0, -1)
(0, 1)