

Tagasaste, Leucaena and Paulownia. Three Industrial Crops for Energy and Hemicelluloses Production

Alberto Palma

University of Huelva: Universidad de Huelva

Javier Mauricio Loaiza Rodriguez (✉ javiermauricio.loiza@diq.uhu.es)

University of Huelva: Universidad de Huelva <https://orcid.org/0000-0003-1375-1578>

Manuel J. Díaz

University of Huelva: Universidad de Huelva

Juan Carlos García

University of Huelva: Universidad de Huelva

Inmaculada Giráldez

University of Huelva: Universidad de Huelva

Francisco López

University of Huelva: Universidad de Huelva

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1 **Abstract**

2 **Background:** Burning fast-growing trees for energy production can be an effective
3 alternative to coal combustion. Thus, lignocellulosic material, which can be used to obtain
4 chemicals with a high added value, is highly abundant, easily renewed and usually
5 inexpensive. In this work, hemicellulose extraction by acid hydrolysis of plant biomass
6 from three different crops (*Chamaecytisus proliferus*, *Leucaena diversifolia* and
7 *Paulownia trihybrid*) was modelled and the resulting solid residues were used for energy
8 production.

9 **Results:** The influence of the nature of the lignocellulosic raw material and the operating
10 conditions used to extract the hemicellulose fraction on the heat capacity and activation
11 energy of the subsequent combustion process was examined.

12 The heat power and the activation energy of the combustion process were found to depend
13 markedly on the hemicellulose content of the raw material. Thus, a low content in
14 hemicelluloses resulted in a lower increased combustion efficiency and energy yield after
15 acid hydrolysis stage.

16 The process was also influenced by the operating conditions of the hydrolysis treatment,
17 which increased the superior calorific value (SCV) of the solid residue by 0.6–9.7%
18 relative to the starting material. Also, the activation energy of combustion of the
19 hydrolysis residues from tagasaste and paulownia was considerably lower than that for
20 the starting materials, the difference increasing with increasing degree of conversion as
21 well as with increasing temperature and acid concentration in the acid hydrolysis.

22 The activation energy of combustion of the solid residues from acid hydrolysis of
23 tagasaste and paulownia decreased markedly with increasing degree of conversion, and
24 also with increasing temperature and acid concentration in the hydrolysis treatment. No
25 similar trend was observed in leucaena owing to its low content in hemicelluloses.

26 **Conclusions:** Acid hydrolysis of tagasaste, leucaena and paulownia provided a
27 valorizable liquor containing a large amount of hemicelluloses and a solid residue with
28 an increased heat power amenable to efficient valorization by combustion. There are
29 many potential applications of the hemicelluloses-rich and lignin-rich fraction, for

1 example as multi-components of bio-based feedstocks for 3D printing, for energy and
2 other value-added chemicals.

3 **Keywords:** Tagasaste, leucaena, paulownia, biomass combustion, hemicellulose
4 extraction.

5

6 **1. Background**

7 Economic and social development in recent years has raised a number of problems on
8 environmental resources [1,2] and fostered a search for new types of energy to replace
9 conventional fossil fuels with cleaner, more sustainable alternatives [3,4]. Industries
10 worldwide are increasingly obtaining renewable energy from biomass [5], while
11 strengthening environmental protection. In fact, plant biomass has proved an excellent
12 source of renewable energy. This is particularly so with energy crops that are not only
13 highly productive but also efficient sinks for CO₂ or at least “neutral” as regards carbon
14 emissions to the atmosphere [3,6,7].

15 European countries are increasingly concerned with sustainable, environmentally
16 friendly production of energy, which is increasingly being obtained from renewable
17 sources. Using wood for energy production has the added advantage that it can promote
18 forest culturing in countries with a low forest area and help improve post-harvesting
19 management practices in young forests [8–10].

20 Burning fast-growing trees for energy production can be an effective alternative
21 to coal combustion [3,11]. Thus, lignocellulosic material, which can be used to obtain
22 chemicals with a high added value [12–14], is highly abundant, easily renewed and
23 usually inexpensive. At present, fast-growing biomass provides 44–65% of all renewable
24 energy used in European countries and reduces greenhouse gas emissions by 209 million
25 tons each year [15,16].

26 In this work, we assessed the potential of three different plant species (viz.,
27 *Chamaecytisus proliferus*, *Leucaena diversifolia* and *Paulownia fortunei x tormentosa x*
28 *elongata*) for energy production. *Chamaecytisus proliferus*, popularly known as
29 tagasaste, is a fast-growing bushy legume typically used as forage but can also be cropped

1 for energy production [17–21]. Tagasaste is highly productive, with more than 18 t ha⁻¹
2 yr⁻¹ in some cases. Also, it provides sheltering from the wind, helps control erosion and
3 soil salinity, fertilizes soil and contains enough protein for feeding to animals [22–25].
4 *Leucaena diversifolia* (leucaena) is a legume growing up to 6–20 m under Mediterranean
5 conditions with a high biomass productivity: usually more than 50 t ha⁻¹ yr⁻¹ [26], or even
6 up to 70 ton ha⁻¹ yr⁻¹ after 7 years [27]. This species has a high re-sprouting ability [28]
7 and provides not only wood and high-quality forage, but also energy and useful
8 biorefinery products [27,29]. *Paulownia fortunei x tormentosa x elongata* (Paulownia
9 trihybrid) is a native plant from China, where it has been known and grown for 2600
10 years. Paulownia is a fast-growing species with an average fibre length of 1.42 mm and
11 low water requirements. By virtue of its high productivity and low density, paulownia
12 trees can provide 1 m³ of wood after 5–7 years of growth [30,31]. Paulownia wood is
13 used to construct cabinets, musical instruments, mouldings, furniture and veneers, and
14 also to obtain cellulose [32,33].

15 Also, the transition to bio-economy and sustainable development requires not only
16 reducing our dependence on fossil fuels and mitigating greenhouse gas emissions [34,35],
17 but also developing the technology needed for more extensive valorization of
18 lignocellulosic biomass from energy crops [36,37].

19 In this work, we examined the extraction of hemicelluloses by acid hydrolysis for
20 their subsequent combustion. The starting hypothesis was that the hydrolysis residue
21 would have an increased heat power and combustion efficiency relative to the original
22 material, and also that the resulting liquor would contain large amounts of hemicelluloses
23 and other valorizable derivatives.

24 The primary aim of this work was to optimize the extraction of hemicelluloses
25 from biomass of three different energy crops (viz., *Chamaecytisus proliferus*, *Leucaena*
26 *diversifolia* and *Paulownia fortunei x tormentosa x elongata*) and optimize energy
27 production by combustion. For this purpose, we used the solid residue from the acid
28 hydrolysis of the three raw materials for combustion in combination with a factorial
29 experimental design and multiple regression polynomial models to examine the influence

1 of the nature of the lignocellulosic material and the operating conditions of the acid
2 hydrolysis treatment on the heat power of the solid residue and the activation energy of
3 the combustion process.

4 **2. Results and Discussion**

5 **2.1. Acid hydrolysis**

6 As noted earlier, the primary aim of this work was to optimize energy production by
7 combustion of three different lignocellulosic materials (viz., tagasaste, leucaena and
8 paulownia trihybrid) previously subjected to hemicellulose extraction by acid hydrolysis.
9 Obviously, removing some material should be expected to decrease the amount of energy
10 to be obtained; however, the hemicellulose-rich hydrolysis liquor obtained should be
11 valorizable and combustion of the resulting solid residue more energy-efficient by effect
12 of the hydrolysis pretreatment reducing its activation energy. These hypotheses were
13 tested by characterizing the raw materials, the solid residues obtained at different points
14 of the proposed experimental design and the results of the thermogravimetric analysis.
15 There are many potential applications of the hemicelluloses-rich and lignin-rich fraction,
16 for example as multi-components of bio-based feedstocks for 3D printing [38], for energy
17 [39] and other value-added chemicals [40].

18 Table 1 shows the results of the characterization of the three raw materials and
19 various others studied by Alfaro et al. (2009, 2010)[18,41] and García et al. (2011)[42],
20 as well as those for *Eucaliptus globulus*, which was used as reference. All chemical
21 determinations were made in triplicate and the coefficient of variation was less than 5%
22 in all cases. As can be seen, the xylan content of leucaena was nearly 20% lower than
23 were those of tagasaste and paulownia trihybrid, and the total hemicellulose content was
24 almost 22% lower. On the other hand, the content in mineral ash of leucaena was 75%
25 higher than that of tagasaste, but the calorific power of the former was lower than were
26 those of the other two raw materials. As shown below, the differences in composition
27 resulted in marked differences in energy yield among the raw materials.

28 Table 2 shows the composition of the solid residues from acid hydrolysis of the
29 three target raw materials. As can be seen, hemicelluloses were more efficiently extracted

1 from paulownia and tagasaste than they were from leucaena, which is consistent with the
2 decreased content of the last species in this fraction. The calorific power of the solid
3 residue exceeded that of the raw material in the three species. This result is consistent
4 with increased dissolution of the hemicellulose fraction, which was that with the lowest
5 calorific power [43].

6 The data in Table 2 were used to model the relationship between the previous
7 properties and the conditions of the acid hydrolysis treatment. For this purpose, the data
8 were subjected to multiple regression as described in Section 2.1. The equations of the
9 models thus obtained are shown in Table 3 together with their statistics (adjusted R^2 and
10 Snedecor's F -value). The values used to establish the equations were the average of 3
11 measurements each. The differences between the experimental values and those estimated
12 from the previous equations were less than 5% in all instances; also, F -values exceeded
13 51 and R^2 was greater than 0.96 in all cases.

14 The coefficients of the linear terms in the equations of Table 3 allow one to
15 envisage the influence of the independent variables on the dependent variables. Thus,
16 maximizing hemicellulose extraction and calorific value would require using high levels
17 of the two independent variables (temperature and time); on the other hand, obtaining the
18 best possible yield would entail using low levels of the previous variables.

19 Comparing the influence of independent variables by analyzing the models in
20 Table 3 is difficult. There are linear, quadratic, and interaction terms between variables.
21 So, it is easier to interpret the interaction between independent variables graphically.
22 Figures 1–3 are response surfaces intended to more clearly illustrate the relationships
23 between variables. As can be seen in Fig. 1, the calorific power of the solid residue from
24 hydrolysis of leucaena was considerably lower than were those of the other two raw
25 materials. This, however, cannot have been the sole result of leucaena containing less
26 hemicelluloses. In fact, paulownia and tagasaste had a similar calorific power despite their
27 substantial differences in hemicellulose content. Seemingly, extracting hemicelluloses by
28 acid hydrolysis of the raw material had an additional, marked effect on the calorific power
29 of the solid residue from paulownia and tagasaste. This is also apparent from Figs 2

1 (yield) and 3 (hemicellulose extraction), where the response surfaces illustrate the
2 differential influence of acid hydrolysis on the three raw materials. The patterns of
3 extracted hemicelluloses for tagasaste and leucaena are similar (see Fig. 3). For extraction
4 yield, the patterns are significantly different only at a high alkali concentration. Probably
5 due to the higher extract content and polysaccharid content in tagasaste than in leucaena.

6 Although the calorific power of a solid biofuel such as lignocellulosic biomass
7 obviously differs among raw materials, it may also differ depending on how a particular
8 material is treated prior to combustion. In theory, acid hydrolysis of lignocellulosic
9 biomass should cause the most easily hydrolysed fractions (hemicelluloses here) to be
10 removed in the hydrolysis liquor, thereby increasing the calorific power of the resulting
11 solid residue. In fact, the cellulose and lignin fractions are known to have a higher
12 calorific power than the hemicellulose fraction [44,45]. This was indeed the case with the
13 three raw materials studied. Thus, based on Eqs 3, 6 and 9 in Table 3, the superior calorific
14 value (SCV) for the solid residues from hydrolysis under extreme operating conditions of
15 tagasaste, leucaena and paulownia was 0.7–7.6%, 0.6–4.4% and 1.4–9.7% higher than
16 that for the respective raw material. As can be seen from Fig. 1, the increase in SCV for
17 paulownia exceeded those of the other two materials throughout the operating range. This
18 was partly the result of raw, untreated paulownia having an increased SCV relative to the
19 other two species (see Table 1) [18,27,41,46–48].

20 Because an increased SCV can result from increased extraction of hemicelluloses,
21 and hence from an increase in the proportions of cellulose and lignin in the hydrolysis
22 solid residue, we examined the variation of the degree of hemicellulose extraction with
23 the acid concentration and temperature used in the hydrolysis treatment preceding
24 combustion. As can be seen in Fig. 3, hemicellulose extraction from tagasaste, leucaena
25 and paulownia was 40.9, 52.6 and 37.6%, respectively, at experimental point (–1, –1),
26 and increased to 86.9, 79.8 and 94.7%, respectively at (+1, +1). The increase in SCV was
27 thus consistent with that in hemicellulose extraction from the three raw materials. SCV
28 and hemicellulose extraction were greatest for paulownia, followed by tagasaste and

1 leucaena, the last species being the least likely to benefit from acid hydrolysis in terms of
2 SCV.

3 The change in total yield included the effect of acid hydrolysis on the cellulose
4 and polyphenol fractions. As can be seen from Fig. 2, paulownia exhibited the greatest
5 decrease in extraction yield (from 65.1 to 44.8%). This result is consistent with previous
6 comments on hemicellulose extraction and SCV increase. However, as can also be seen
7 from the response surfaces for tagasaste and leucaena in Fig. 2, the raw materials
8 responded rather differently to acid hydrolysis. Thus, the results for leucaena were much
9 more strongly dependent on temperature (especially at high acid concentrations), whereas
10 those for tagasaste were more markedly dependent on the acid concentration.

11 The dependence of the SCV increase on the degree of hemicellulose extraction
12 was examined by using various correlations between the two variables in Eqs 1, 3, 4, 6,
13 7 and 9 of Table 3. Using multiple regression models to assess the dependence of SCV
14 on the independent variables revealed that the quadratic and interaction terms in the
15 equations, in combination with the hemicellulose extraction rate in linear, quadratic and
16 cubic form as an added independent variable, allowed very robust fitting with models
17 where the two independent variables of the process, hemicellulose extraction and their
18 quadratic terms were all statistically significant. Thus, adjusted- R^2 values were in the
19 region of 0.99 and F values all greater than 400. Although none of the models is shown,
20 the coefficients for the terms “hemicellulose extraction” (HE) and “hemicellulose
21 extraction squared” (HE²) were used to plot the variation of SCV with the following linear
22 combination of the two terms: $47.58 \cdot \text{HE} - 0.4415 \cdot \text{HE}^2$ for tagasaste, $-57.88 \cdot \text{HE} +$
23 $1.46 \cdot \text{HE}^2$ for leucaena and $29.85 \cdot \text{HE} - 0.23811 \cdot \text{HE}^2$ for paulownia. As can be seen from
24 Figure 4, which shows the results for the three raw materials at the central values of the
25 independent variables, the two types of variables were highly correlated, albeit with
26 differences among the three species.

27 **2.2. Thermogravimetric analysis of the combustion process**

28 As stated above, extracting hemicelluloses by acid hydrolysis alters the SCV of a raw
29 material but can also influence the activation energy of the resulting solid residue. In fact,

1 the lignocellulosic biomass pyrolysis has a complex mechanism studied by several
2 authors, for example George, A. et al. (2014) [49]. In this work, we hypothesized that
3 using appropriate hydrolysis conditions would provide solid residues subsequent
4 combustion of which would occur with a lower activation energy than in the starting
5 material, thereby increasing the combustion efficiency [50,51]. This would be an
6 additional benefit to the obtainment of a potentially valorizable hemicellulose-rich liquor
7 and a solid residue with a greater calorific power than the original material.

8 The activation energy of combustion of the hydrolysis solid residue from the three
9 raw materials was determined by thermogravimetric analysis as described in Section 2.3.
10 Tests were conducted at the central and extreme values of the experimental, design,
11 namely: (-1, -1), (0, 0) and (+1, +1). Figures 8–10 illustrate the variation of the mass loss
12 (TGA) and differential mass loss (DTG) as a function of temperature and the heating rate
13 (5, 10, 15 or 20 °C min⁻¹) for each raw material. The thermograms correspond to the
14 solid residues obtained at the central and extreme points of the experimental design for
15 the acid hydrolysis treatment. Each material exhibited the typical four TGA regions and
16 DTG peaks corresponding to mass losses by evaporation and sequential combustion of
17 the hemicellulosic, cellulosic and polyphenolic fraction (lignin). Specifically, the first
18 DTG peak, at 60–120 °C, corresponds to the removal of intrinsic and absorbed water.
19 That for the thermal decomposition of polysaccharides usually appears from 200 to 300
20 °C in hemicellulose and 350–450 °C cellulose. Our peaks for the two mass losses were
21 largely overlapped in the region from 200 to 400 °C —alternatively, a small shoulder
22 corresponding to the hemicellulosic fraction was observed, consistent with the results for
23 other materials [52,53]. The peaks for the cellulosic fraction shifted to higher temperatures
24 as the heating rate was increased from 5 to 20 °C min⁻¹.

25 The polyphenolic (lignin) fraction is a complex combination of benzene–propane
26 units spanning a broad range of molecular weights and including very large, heavily
27 reticulated structures [54,55], that are thus very thermally stable [56]. In this complex
28 situation, the polyphenolic fraction decomposes thermally over a broad temperature range
29 and gives no characteristic peaks [57]. However, our materials gave sharp peak above 400

1 °C that differed markedly depending on the heating rate and the conditions of the acid
2 hydrolysis treatment. Thus, thermal decomposition started at a lower temperature (130
3 °C) in the raw materials than in the solid residues from the hydrolysis of paulownia (130
4 °C) and tagasaste (150 °C). In leucaena, however, the degradation peaks for the
5 polyphenolic fraction appeared in the region of 400 °C in all cases. Finally, the
6 degradation peaks for the thermal degradation of lignin in the DTG curves became
7 increasingly broad as the heating rate was raised.

8 **2.3. Kinetic analysis**

9 As noted in the previous section, the activation energy of combustion of the solid
10 residue from acid hydrolysis of each raw material was determined by TGA and DTG
11 analysis in combination with the Kissinger–Akahira–Sunose (KAS) and Flynn–Wall–
12 Ozawa (FWO) methods. Thus, the slopes of the plots of mass loss against heating rate
13 allowed the kinetic parameters and activation energy for the combustion of the hydrolysis
14 solid residues to be calculated. Both the KAS method and the FWO method provided
15 well-fitted, parallel lines, which attests to the accuracy of the proposed models.

16 Figures 5–7 show the variation of the activation energy as a function of the degree
17 of conversion in the combustion of the solid residues from hydrolysis of the raw materials
18 at three different points in the experimental design. Overall, the results are similar to those
19 previously reported by other authors [58,59]; also, they differed little between the two
20 methods and the differences arose from their using different parameters. In any case, the
21 results were quite good and consistent with those of Kok et al. (2013) [60] and
22 Parthasarathy et al. (2013) [61]. As can be seen, combustion of the solid residue was a
23 typical stepwise reaction where the activation energy decreases with increasing degree of
24 conversion —this was particularly so at $\alpha > 0.50$.

25 In theory, because the raw materials had a higher hemicellulose content than the
26 solid residues obtained from their hydrolysis, the former should require a lower activation
27 energy (E_a) for combustion at low degrees of conversion [62]. In fact, the cellulosic and
28 polyphenolic (lignin) fractions have increased E_a values [59,63]. This was indeed the case
29 with tagasaste here, but, strictly, neither with paulownia nor with leucaena —the E_a values

1 at low degrees of conversion for the last species fell above those for all other combustion
2 processes at the central and extreme points of the experimental design for the hydrolysis
3 process. The differences were consistent with the decreased contents in xylan and acetyl
4 groups of leucaena relative to the other two raw materials and, also possibly, of the
5 increased mineral content of this species. In fact, acid hydrolysis removed minerals to a
6 greater extent from leucaena than it did from tagasaste or paulownia, which may have led
7 to a decreased activation energy of combustion in the resulting solid residue [64].

8 As expected, E_a in the combustion process decreased with increasing degree of
9 conversion [65], particularly in those solid residues obtained at increased temperatures or
10 acid concentrations. In fact, strong hydrolysis conditions facilitated depolymerization of
11 the cellulosic or polyphenolic fraction [58,66,67], thereby facilitating subsequent
12 combustion. This was indeed the case with tagasaste and paulownia at degrees of
13 conversion above 0.6 or 0.7, where the E_a values for combustion of the hydrolysis solid
14 residues obtained at acid concentrations higher than 1.25%, temperatures above 150 °C
15 and reaction times longer than 45 min were lower than those for the raw materials. On
16 the other hand, leucaena exhibited no well-defined operating range for acid hydrolysis
17 and provided a solid residue with a lower activation energy than the raw material itself.

18 **3. Conclusions**

19 The results obtained in this work allow us to draw the following conclusions:

- 20 – Extracting hemicelluloses by acid hydrolysis of tagasaste, leucaena and paulownia
21 prior to their valorization by combustion provides a hemicellulose-rich liquor and
22 a solid residue with a higher calorific power than the raw material.
- 23 – The hemicellulose content of the raw material had a strong influence on the
24 calorific power and activation energy of combustion of the solid residue from acid
25 hydrolysis of the three raw materials. In fact, reducing the initial hemicellulose
26 content increased the efficiency and energy yield of combustion of the hydrolysed
27 material.
- 28 – The operating conditions of the hydrolysis process also influenced the combustion
29 process, the superior calorific value (SCV) of which was increased by 0.6–9.7 %

1 relative to the starting material. The increase in SCV upon hydrolysis was strongly
2 correlated with the degree of hemicellulose extraction, albeit to a different extent
3 depending on the particular raw material.

- 4 – The activation energy of combustion of the solid residues from acid hydrolysis of
5 tagasaste and paulownia decreased markedly with increasing degree of
6 conversion, and also with increasing temperature and acid concentration in the
7 hydrolysis treatment. No similar trend was observed in leucaena owing to its low
8 content in hemicelluloses.

9 **4. Methods**

10 **4.1. Characterization and storage of the raw materials. Acid hydrolysis of wood samples**

11 Samples of tagasaste (*Chamaecytisus proliferus*) consisting of 0.5–5.0 cm thick
12 stems and branches were collected from Trigueros (Huelva), southwestern Spain.
13 Leucaena (*leucaena diversifolia*) biomass was obtained from another plantation in Huelva
14 where plots had been kept for 7 years. The plants had been planted at 3 months of age in
15 two plots of sandy loam soil of pH 6–8 to which no fertilizer was applied. The distance
16 between plants was 0.6–1.8 m and their density 10 800 plants ha⁻¹. A completely
17 randomized block design with four replicates was used.

18 Paulownia trihybrid (*fortunei x tormentosa x elongata*) was harvested after 3 years
19 of growth in the southwestern Spanish region of Extremadura and supplied by Vicedex
20 Europa (Barcelona, Spain).

21 For the three raw materials, the harvested material being ground in a hammermill
22 after removing leaves and non-wood portions. The size particle was the usual en paper
23 industry: 2-3 cm in length and 0.5 cm (approximately) in wide. For this particle size not
24 diffusional differences were appreciates. The chips were air dried until constant weight
25 and stored in hermetic bags.

26 For characterization, the three raw materials were ground to a particle size less
27 than 0.5 mm. Leucaena, tagasaste, and paulownia trihybrid were characterized chemically
28 by using TAPPI T264 cm-07 [68] for moisture content, TAPPI 211 om-02 [69] for ash
29 content and TAPPIT204-om-07 [70] with Soxhlet extraction (95% ethanol, 5 h) for

1 ethanol extractables. After characterization, the three raw materials were subjected to
2 quantitative acid hydrolysis with 72% H₂SO₄. The resulting hydrolysates were analysed
3 chemically according to TAPPI T249-em-09 [71]. Monomeric sugars (xylose, arabinose
4 and glucose) and acetic acid in the hydrolysis liquor were determined by high
5 performance liquid chromatography (HPLC), using an Aminex HPX-87H ion-exchange
6 column at 30 °C as stationary phase and 0.05 M H₂SO₄ at a flow-rate of 6 mL min⁻¹ as
7 mobile phase. Monosaccharide contents were expressed in terms of xylan, araban and
8 glucan. Klason lignin was determined according to TAPPI T222 om-11 [72].

9 ***4.2. Acid hydrolysis procedure***

10 The acid hydrolysis pretreatment used to extract hemicelluloses was performed in
11 a 2 L stainless steel reactor from Parr Instruments Co. (Moline, IL, USA). The liquid/soil
12 ratio was kept constant at 8 kg water kg raw material⁻¹ o.d.b. The independent variables
13 of the extraction process were temperature (130, 150 or 170 ° C) and acid (H₂SO₄)
14 concentration (0.5, 1.25 or 2%). Based on existing recommendations (Loaiza et al., 2017)
15 [26], the reaction time was 60 min in all tests. Once extracted, the liquid fraction with
16 hemicelluloses were separated from solid residue by filtration and washed in water, the
17 solid being air-dried and weighed to calculate the yield of the process.

18 The solid residue from the acid hydrolysis treatment was characterized for yield
19 and the amount of hemicelluloses (xylose, arabinose and acetic acid) extracted under
20 identical conditions for the three raw materials. The residue was also characterized for
21 calorific power according to standards CEN/TS 14918:2005 E (“Solid biofuels method
22 for the determination of calorific value”) [73] and UNE164001 EX. [74] A Parr 6300
23 automatic Isoperibol calorimeter, a CGA 540 connector, 99.5% pure oxygen and a
24 maximum pressure of 2500 psig were used for this purpose.

25 ***4.3. Acid hydrolysis. Multiple regression models and experimental design***

26 The acid hydrolysis process was modelled and optimized by using polynomials
27 comprising linear and quadratic terms of the process variables, and their mutual
28 interactions, the equations thus established being fitted by multiple regression. A 2ⁿ
29 central composite factor design was used to reduce the number of tests needed while

1 ensuring the absence of significant covariances between dependent variables. In this way,
 2 the dependent variables (yield, hemicelluloses extracted and superior calorific value)
 3 were related to the independent variables (temperature and acid concentration). Generally
 4 these variables and operation time had interacted during acid hydrolysis but the effect of
 5 operation time, in the range of operation selected, is significantly lower than
 6 temperature and acid concentration, [75]. Modelling required previously normalizing the
 7 ranges spanned by the independent variables according to Eq. 1 and statistically
 8 identifying the significant influences in the coefficients. Thus, no term with a coefficient
 9 $p > 0.05$ as per Student's t -test or spanning a confidence interval of less than 95% was
 10 included.

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

11 where X is the absolute value of the independent variable concerned, \bar{X} is its mean value,
 12 and X_{\max} and X_{\min} are its maximum and minimum value, respectively.

13 Three levels each of independent variable were used, namely: 0.5, 1.25 and 2%
 14 H_2SO_4 , and 130, 150 and 170 °C. The minimum number of tests needed, N , was calculated
 15 to be $2^n + 2 \cdot n + c$, where n is the number of independent variables and c that of replicates
 16 of the central point in the experimental design (Eq. 2). N was therefore $2^2 + 2 \times 2 + 2 = 10$.
 17 The experimental results were fitted to the following second-order polynomial equation:

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

18 where X denotes independent variables and Y dependent variables, the coefficients a_0 , b_i ,
 19 c_i , and d_{ij} being constant unknown characteristics estimated from the experimental data.

20 The results were assessed with the software Statistica 10.0 (StatSoft, Inc., Tulsa,
 21 OK, USA). Universal fitting statistics such as R^2 and Snedecor's F -value were also used.
 22 $R^2 > 0.85$ or $F > 5$ were taken to be acceptable.

23 **4.4. TGA and kinetic modelling**

1 Combustion of the solid residue obtained by acid hydrolysis of tagasaste, leucaena and
2 paulownia trihybrid was examined by using non-isothermal thermogravimetric analysis
3 (TGA) to determine the kinetic constants for the process. Such constants were calculated
4 from mass losses at different temperatures and times.

5 The thermo–chemical combustion of the solids was studied by using a TGA/DSC1
6 STARe System thermo–gravimetric analyzer from Mettler (Toledo, OH, USA). Tests
7 were carried out by using an amount of sample of 50–100 mg, under N₂ and O₂ streams
8 at 15 and 20 mL min⁻¹, respectively, the temperature being raised from 25 to 500 °C at 5,
9 10, 15 or 20 °C min⁻¹.

10 TGA data can be processed in different ways to estimate kinetic parameters, but
11 are usually handled with model-free fitting techniques. In fact, determining kinetic
12 parameters for combustion reactions by model-based fitting is a difficult task [76,77] and
13 better done with isoconversional methods (e.g., model-free methods such as those based
14 on single-step kinetics). Specially, prominent among such methods are the Kissinger–
15 Akahira–Sunose (KAS) and Flynn–Wall–Ozawa (FWO) methods. The FWO method,
16 which is the more commonly used [63,78], describes reaction changes as a function of
17 temperature as follows [79,80]:

18

$$\ln (\beta) = \ln \left(\frac{AEa}{Rg(\alpha)} \right) - 2,315 - 0,4567 \frac{Ea}{RT} \quad (\text{Eq. 3})$$

19 where A is the pre-exponential factor, β the heating rate, E_a the activation energy, g a
20 conversion function, T temperature and R the gas constant. Plotting the logarithm of the
21 heating rate ($\ln \beta$) against the reciprocal temperature ($1/T$) at a given degree of conversion
22 (α) and different heating rates provides a linear graph.

23 The KAS method is a modified version of the Arrhenius equation [81,82],
24 requiring no prior knowledge of the exact thermal degradation value. Rather, this method
25 integrates Eq. (4) from the initial condition ($\alpha = 0$ at $T = T_0$) to obtain Eq. (5):

$$\left(\frac{d\alpha}{dT}\right) = \frac{A}{\beta} \cdot \exp\left(\frac{-Ea}{RT}\right) \cdot f(\alpha) \quad (\text{Eq. 4})$$

$$G(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T \exp\left(\frac{-Ea}{RT}\right) \cdot dT \quad (\text{Eq. 5})$$

1 The KAS method is based on the Coats-Redfern approximation:

$$G(\alpha) = \frac{A RT^2}{\beta Ea} \exp\left(\frac{-Ea}{RT}\right) \quad (\text{Eq. 6})$$

2 rearrangement of which and conversion into natural logarithmic form yields

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{EaG(\alpha)}\right) - \frac{Ea}{RT} \quad (\text{Eq. 7})$$

3 The activation energy can be calculated from thermogravimetric curves obtained
 4 at a constant degree of conversion and variable heating rates. The TGA curves for the
 5 three raw materials were similar, which is consistent with their also similar composition
 6 (cellulosic, hemicellulosic and polyphenolic polymers).

7

8 **Abbreviations**

9 SCV: Superior calorific value; HE: Hemicellulose extraction; HE²: Hemicellulose
 10 extraction squared; TGA: Variation of the mass loss; DTG: Variation of the differential
 11 mass loss; KAS: Kissinger–Akahira–Sunose method; FWO: Flynn–Wall–Ozawa
 12 method; Ea: activation energy.

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15 **Authors' contributions**

16 AP carried out the experiments, acquired and analyzed the data and generated figures.
 17 ML carried out the experiments, acquired and analyzed the data and writing–original draft
 18 preparation. MD and FL conceived the study, designed the experiments, supervised the
 19 research and writing–review. JC and IG revised the manuscript. FL funding acquisition.
 20 All authors have read and agreed to the published version of the manuscript.

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6 **Availability of supporting data**

7 All data generated or analyzed during this study are included in this published article.

8 **Ethical approval and consent to participate**

9 Not applicable.

10 **Consent for publication**

11 Not applicable.

12 **Competing interests**

13 The authors declare that they have no competing interest.

14 **5. References**

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Table 1. Chemical composition and superior calorific value (SCV) of the three raw materials.

Property ¹	Tagasaste		Leucaena		Paulownia trihybrid		<i>Eucalyptus globulus</i>
	This work	Other authors ²	This work	Other authors ³	This work	Other authors ⁴	Other authors ⁵
Ash, %	0.8	0.7 ± 0.1	1.4	1.4 ± 0.1	n.d	0.9 ± 0.1	0.7 ± 0.1
Ethanol extract., %	2.8	2.3 ± 0.1	n.d	1.7 ± 1.1	n.d	4.6 ± 0.1	2.7 ± 0.1
Glucan, %	41.4	38.9 ± 3.4	32.2	38.0 ± 2.4	34.2	44.0 ± 3.3	42.8 ± 2.0
Lignin, Klason %	20.1	19.8 ± 1.9	21.5	24.8 ± 0.6	27.2	27.8 ± 1.1	21.2 ± 0.9
Xylan, %	18.5	19.9 ± 1.3	15.5	15.7 ± 0.1	18.3	15.7 ± 0.2	17.1 ± 0.3
Araban, %	0.6	0.6 ± 0.3	1.0	1.5 ± 0.3	1.1	1.1 ± 0.1	0.7 ± 0.1
Acetylgroups, %	3.3	4.4 ± 0.6	2.1	3.3 ± 0.5	3.3	4.4 ± 0.2	3.5 ± 0.1
SCV, kJ/kg o.d.b.	19 375	19 592 ± 28	19 060	18 981 ± 102	19 362	20 300	19 326 ± 160

n.d. not determined.

¹ All percentages are referred to dry matter.

² [18,21].

³ [27,41,83]

⁴ [30,42,84]

⁵ [46,47,85]

Table 2. Experimental design, extraction yield, amount of hemicellulose extracted and calorimetric value of the solid residues from acid hydrolysis of the three raw materials.

		Tagasaste		Leucaena		Paulownia trihybrid	
X_C	X_T	Extraction yield/Hemicelluloses extracted (%)	SVC/LCV at constant volume (J/g o.d.b.)	Extraction yield/Hemicelluloses extracted (%)	SVC/LCV at constant volume (J/g o.d.b.)	Extraction yield/Hemicelluloses extracted (%)	SVC/LCV at constant volume (J/g o.d.b.)
1	1	52.8/87.1	20 889/19 665	68.9/79.4	19 869/18 645	45.9/95.3	21 222/19 998
1	-1	48.9/79.1	19 619/18 492	84.3/42.9	19 353/18 129	45.3/87.1	20 400/19 176
-1	1	64.0/82.2	20 714/19 490	58.8/75.4	19 292/18 068	44.8/77.2	20 673/19 449
-1	-1	83.3/40.2	19 506/18 282	71.7/52.9	18 916/17 692	65.1/38.2	19 642/18 418
1	0	53.7/71.5	19 905/18 681	77.2/54.7	19 149/17 925	47.5/92.3	20 713/19 489
-1	0	76.5/50.2	19 724/18 600	65.6/56.1	19 038/17 814	56.0/41.4	20 112/18 888
0	1	61.1/86.5	20 492/19 268	59.4/77.7	19 873/18 646	51.9/60.2	20 784/19 560
0	-1	68.1/63.6	19 443/18 219	73.7/47.8	19 265/18 041	59.1/60.1	19 753/18 529
0	0	70.2/62.0	19 605/18 381	66.2/55.2	19 361/18 137	53.2/57.2	20 165/18 941
0	0	69.9/62.0	19 604/18 380	66.3/54.8	19 305/18 081	54.1/57.5	20 200/18 976

SCV superior calorific value, LCV lower calorific value

Table 3. Equations for the dependent variables (superior calorific value, extraction yield and amount of hemicelluloses extracted) as a function of the independent variables (acid concentration and temperature).

Equations		R^2	Snedecor's F -value
Tagasaste			
(1)	$SCV = 19\ 603.0 + 77.8 X_C + 587.5 X_T + 212.9 X_C X_C + 365.9 X_T X_T$	0.99	812
(2)	$Yield = 69.3 - 11.4 X_C - 3.7 X_T - 3.5 X_C X_C - 3.9 X_T X_T + 5.8 X_C X_T$	0.99	211
(3)	$HE = 62.5 + 10.8 X_C + 12.2 X_T - 2.1 X_C X_C + 12.0 X_T X_T - 8.5 X_C X_T$	0.99	325
Leucaena			
(4)	$SCV = 19\ 315.5 + 82.8 X_C + 274.8 X_T + 218.7 X_T X_T$	0.97	115
(5)	$Yield = 66.4 + 5.7 X_C - 7.1 X_T + 4.7 X_C X_C - 0.6 X_C X_T$	0.99	1460
(6)	$EH = 55.2 - 1.2 X_C + 14.8 X_T + 7.5 X_T X_T + 3.5 X_C X_T$	0.99	1633
Paulownia trihybrid			
(7)	$SCV = 20\ 186.6 + 318 X_C + 480.6 X_T + 221.8 X_C X_C + 77.8 X_T X_T - 52.2 X_C X_T$	0.99	325
(8)	$Yield = 54.5 - 4.5 X_C - 4.5 X_T - 3.8 X_C X_C + 5.2 X_C X_T$	0.96	51
(9)	$EH = 57.6 + 17.5 X_C + 10.8 X_T + 16.5 X_C X_C - 7.7 X_C X_T$	0.98	214

SCV superior calorific value, HE amount of hemicelluloses extracted, X_C acid concentration, X_T temperature.

The differences between the experimental values and those estimated by using the equations never exceeded 5% of the former.

The independent variables are expressed in coded units (Eq. 1).

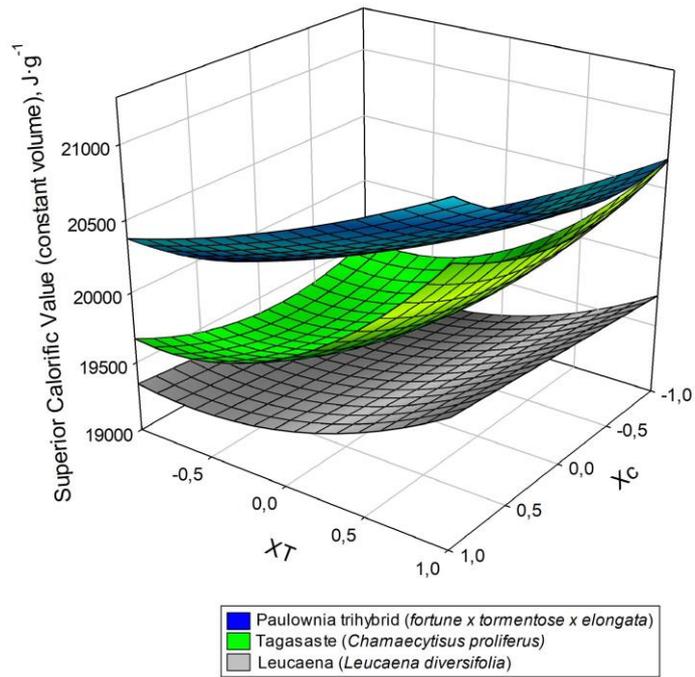


Figure 1. Variation of the superior calorific value of the three species as a function of the acid concentration and temperature.

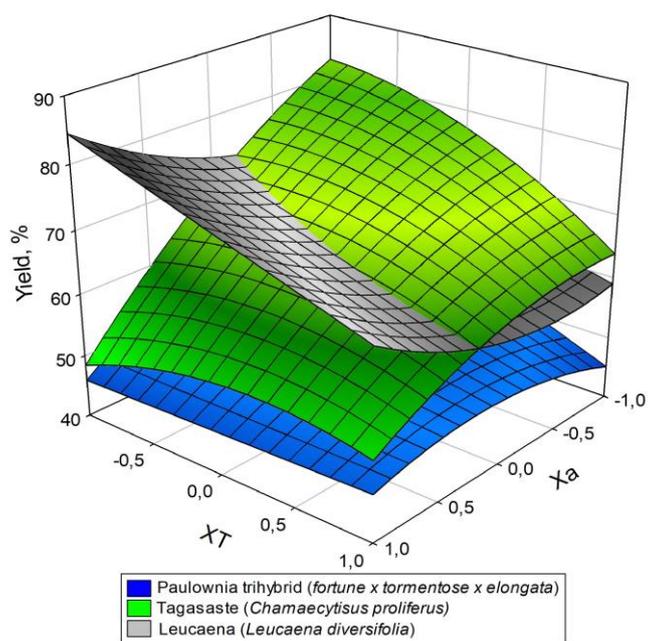


Figure 2. Variation of the extraction yield of the three species as a function of the acid concentration and temperature.

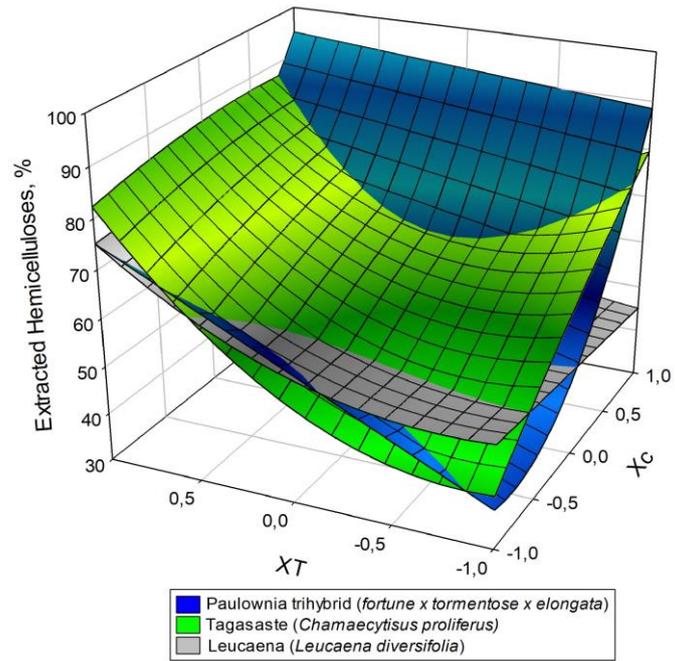


Figure 3. Variation of amount of hemicelluloses extracted from the three species as a function of the acid concentration and temperature.

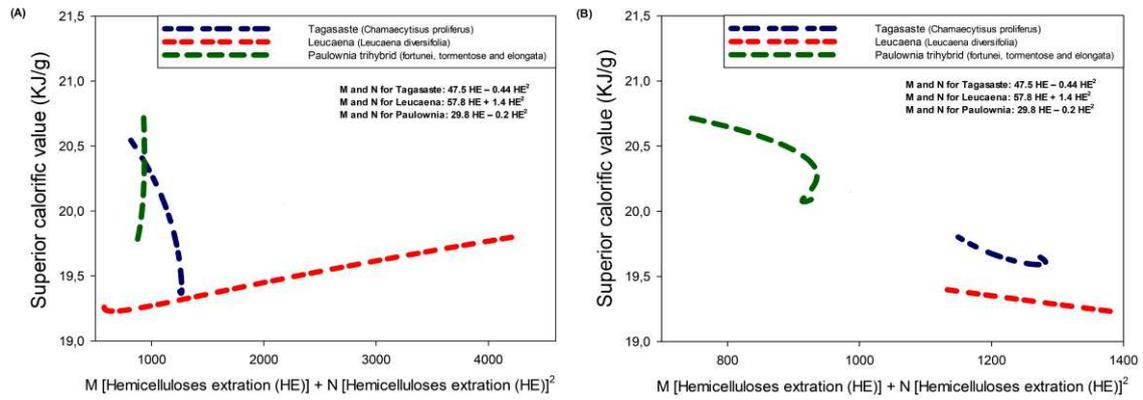


Figure 4. Correlation between the superior calorific value and hemicellulose extraction from the three species at a constant temperature of 150 °C (A) and a constant acid concentration of 1.25% (B).

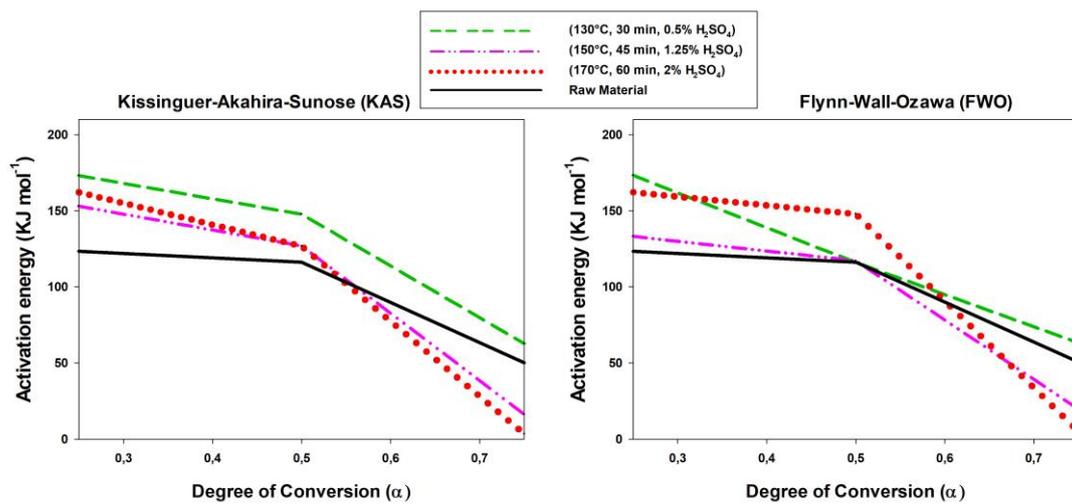


Figure 5. Variation of the activation energy of combustion of tagasaste as a function of the degree of conversion

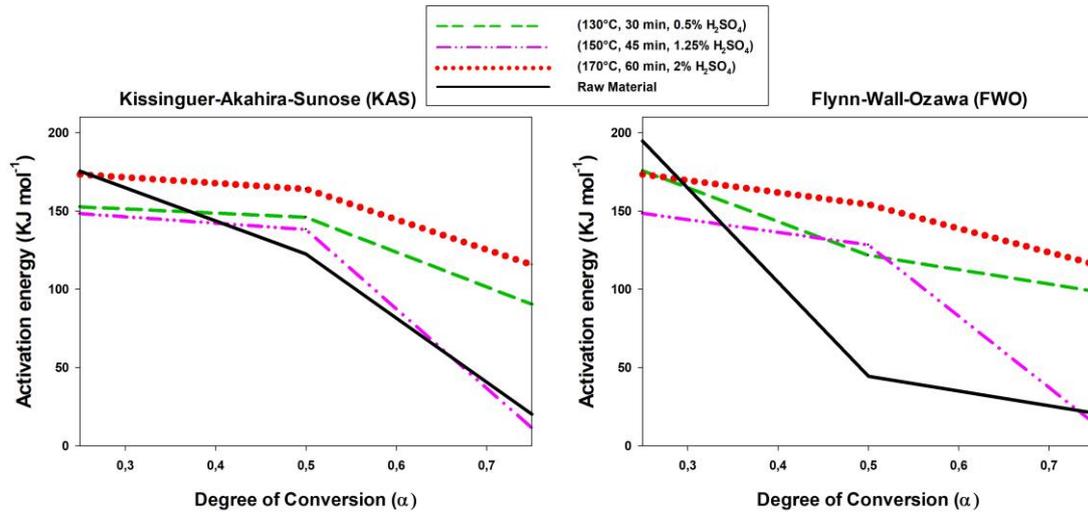


Figure 6. Variation of the activation energy of combustion of leucaena as a function of the degree of conversion.

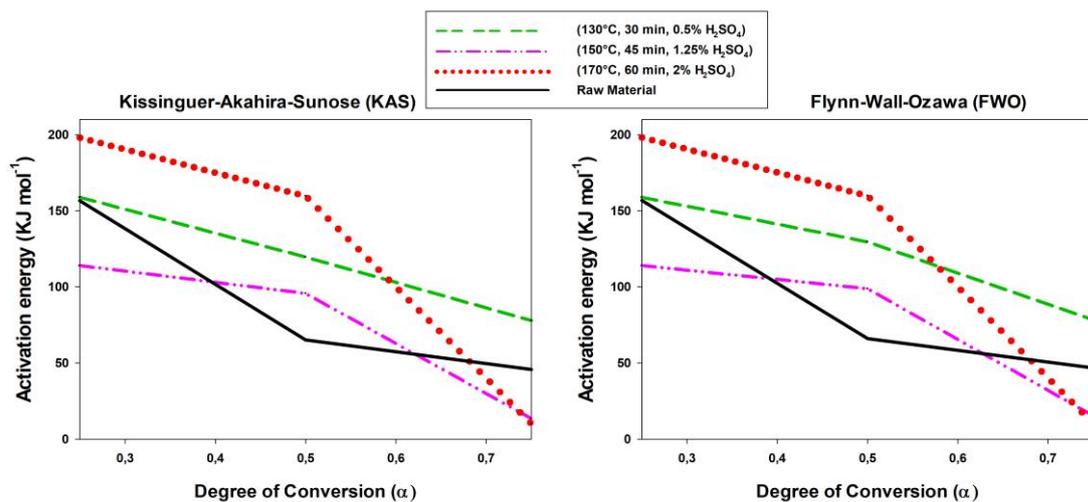


Figure 7. Variation of the activation energy of combustion of paulownia trihybrid as a function of the degree of conversion.

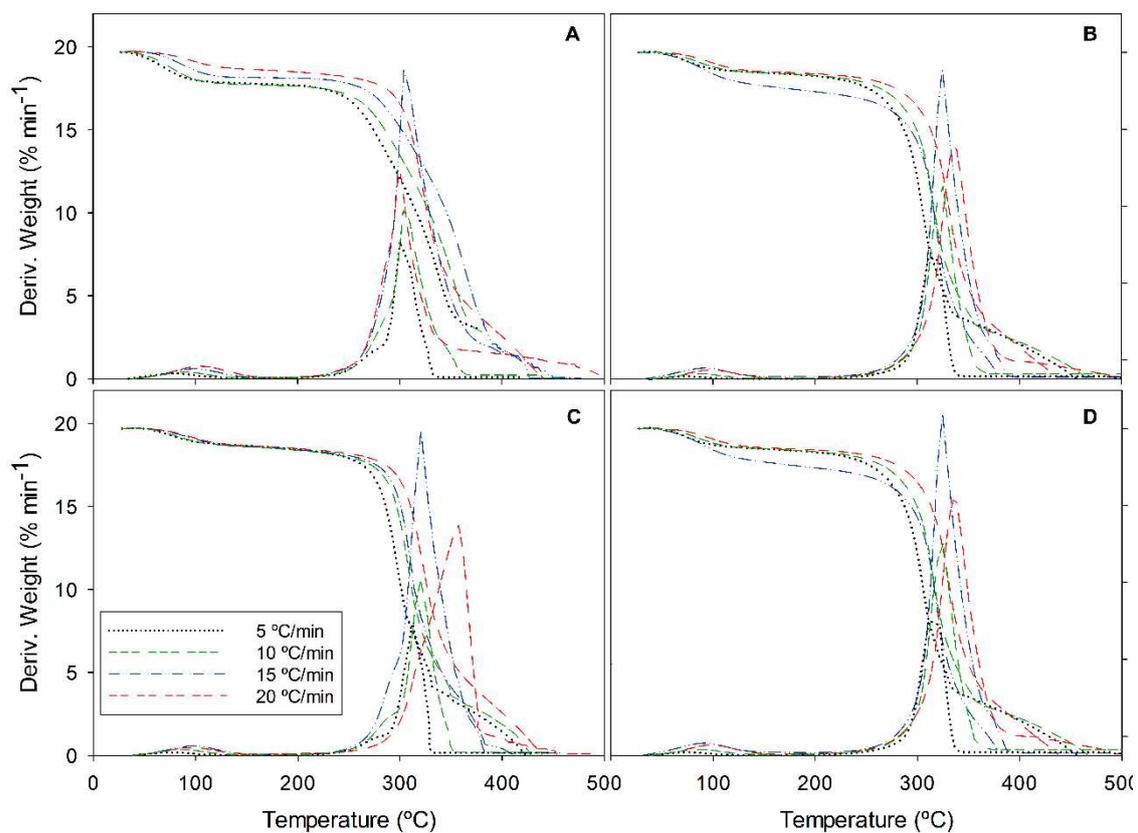


Figure 8. TGA and DTG curves for tagasaste combustion at a variable heating rate (5, 10, 15 or 20 °C/min). Raw material (A) and solid residue from hydrolysis with 2% H₂SO₄ at 170 °C for 60 min (B), 1.25% H₂SO₄ at 150 °C for 45 min (C) and 0.5% H₂SO₄ at 130 °C for 30 min (D).

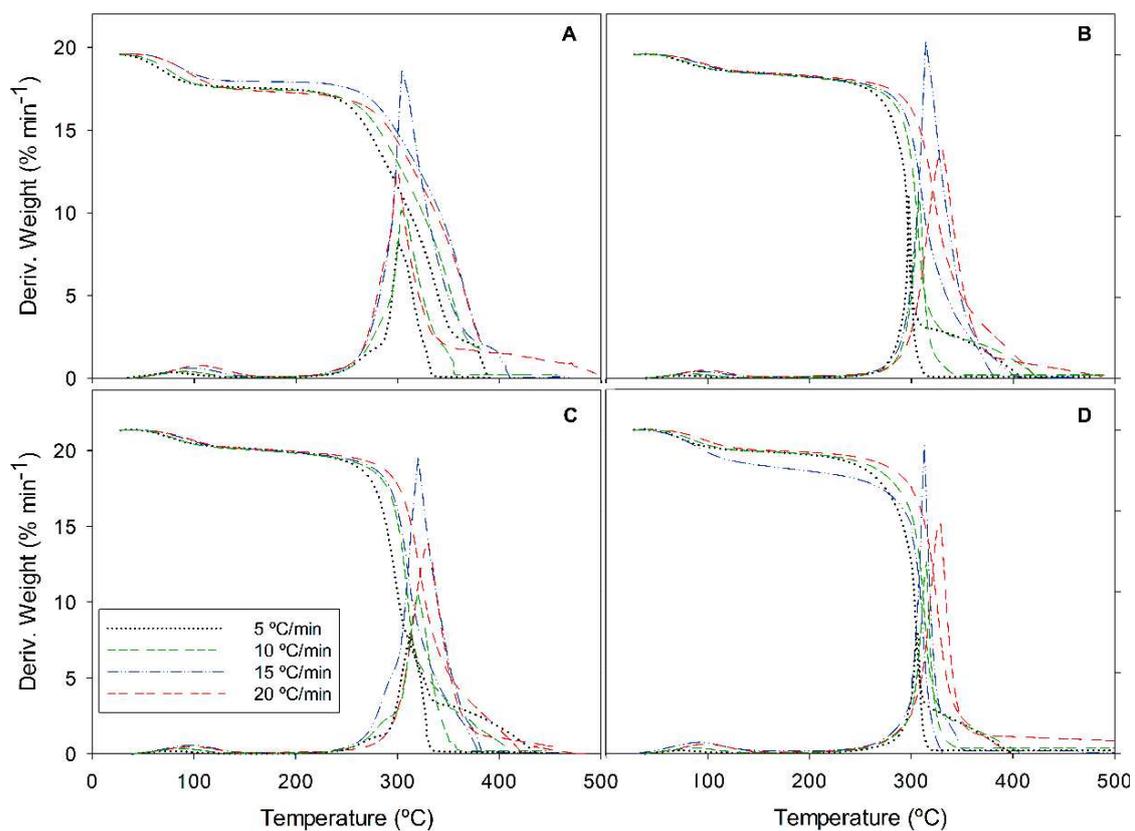


Figure 9. TGA and DTG curves for leucaena combustion at a variable heating rate (5, 10, 15 or 20 °C/min). Raw material (A) and solid residue from hydrolysis with 2% H₂SO₄ at 170 °C for 60 min (B), 1.25% H₂SO₄ at 150 °C for 45 min (C) and 0.5% H₂SO₄ at 130 °C for 30 min (D).

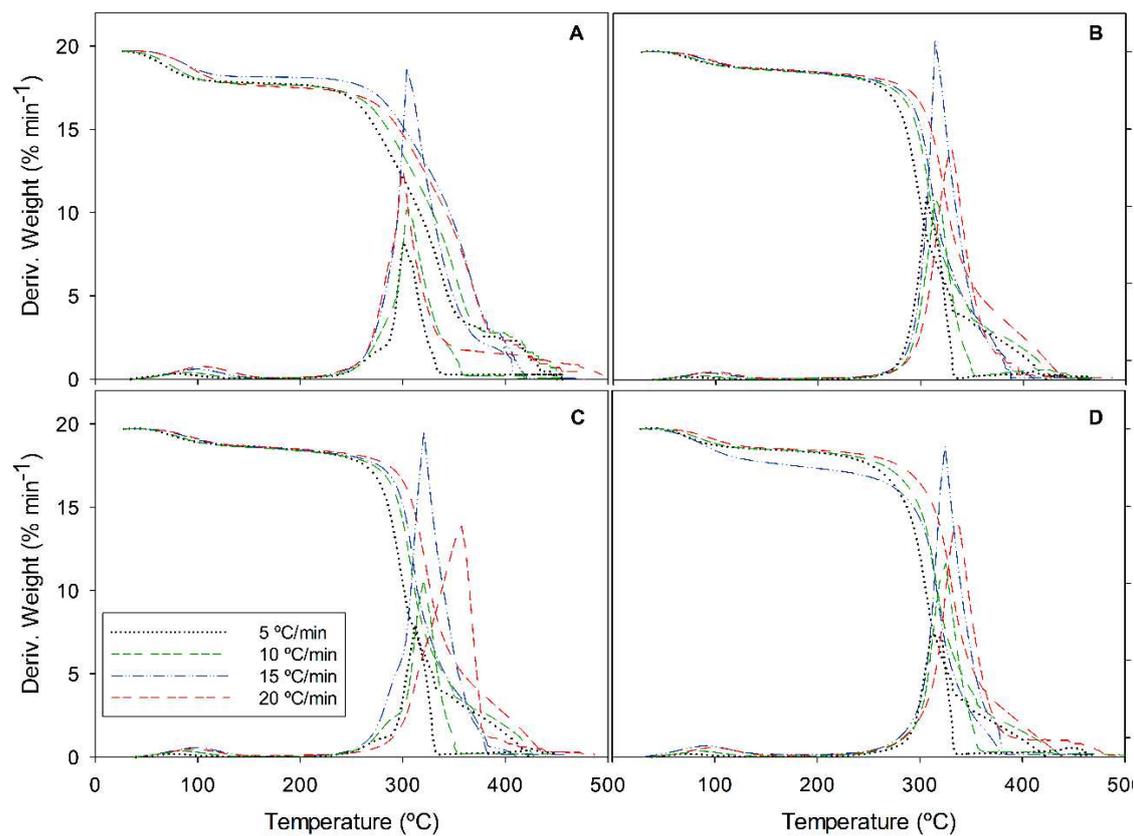


Figure 10. TGA and DTG curves for paulownia trihybrid combustion at a variable heating rate (5, 10, 15 or 20 °C/min). Raw material (A) and solid residue from hydrolysis with 2% H₂SO₄ at 170 °C for 60 min (B), 1.25% H₂SO₄ at 150 °C for 45 min (C) and 0.5% H₂SO₄ at 130 °C for 30 min (D).

Figures

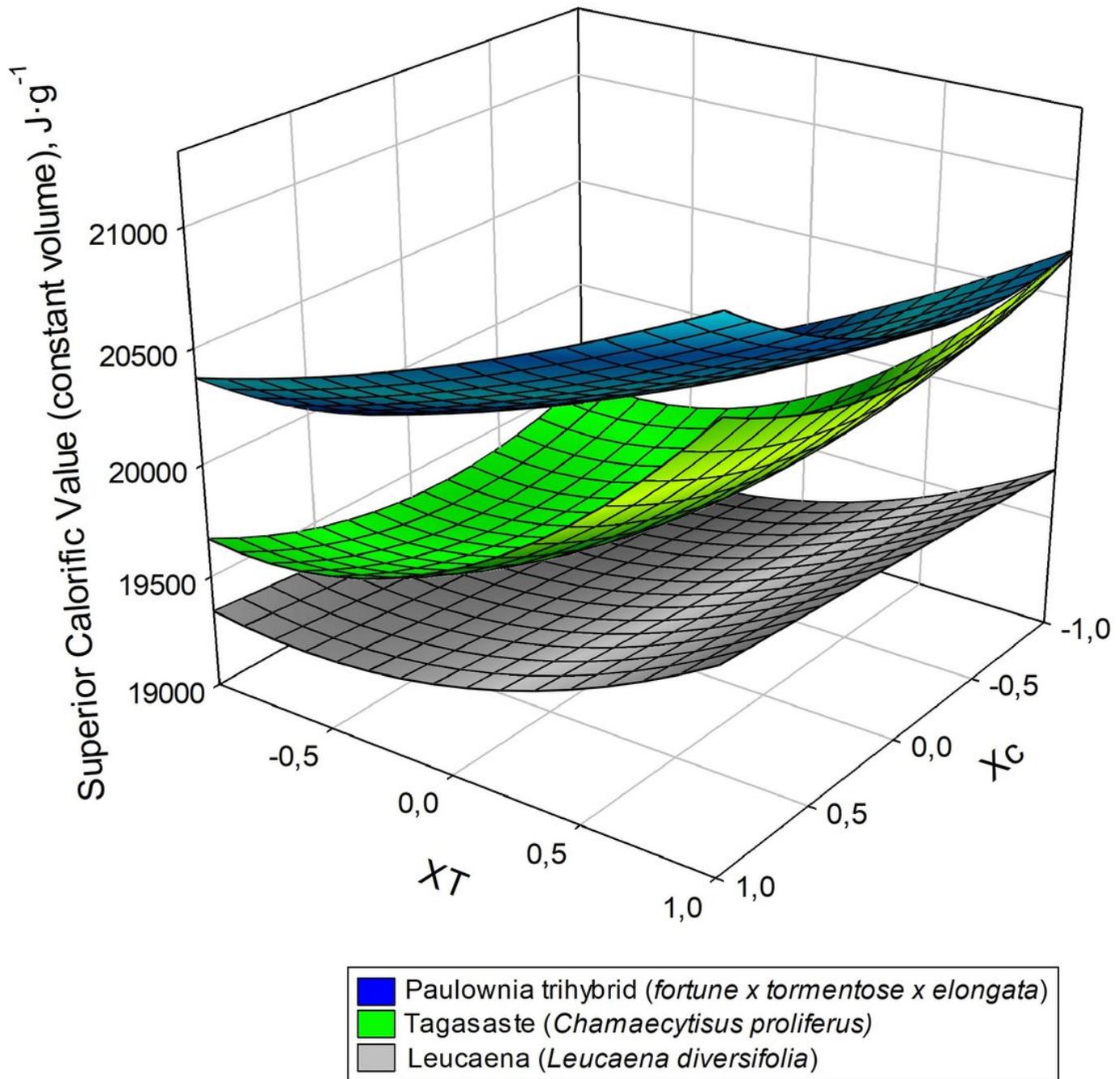


Figure 1

Variation of the superior calorific value of the three species as a function of the acid concentration and temperature.

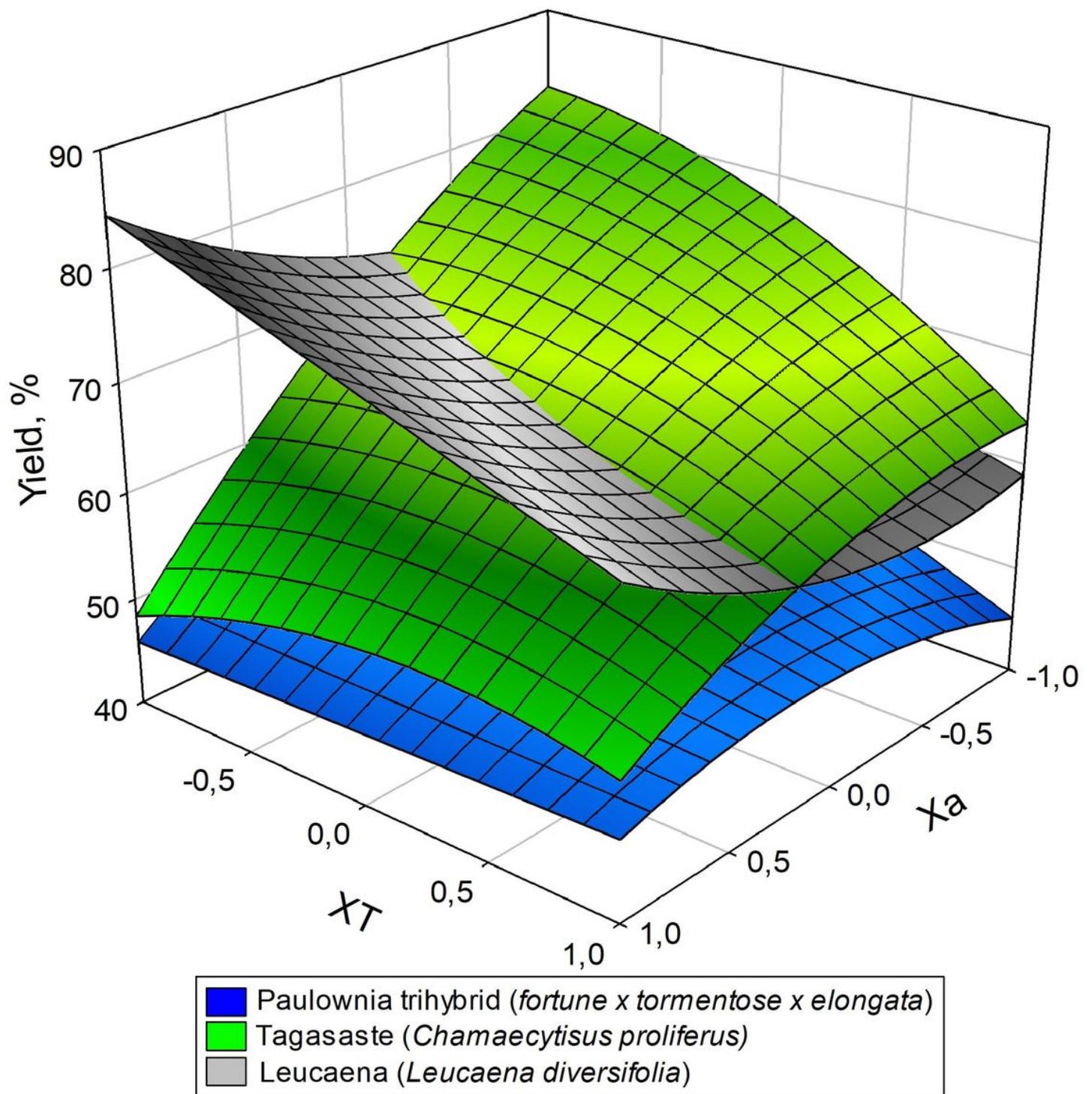


Figure 2

Variation of the extraction yield of the three species as a function of the acid concentration and temperature.

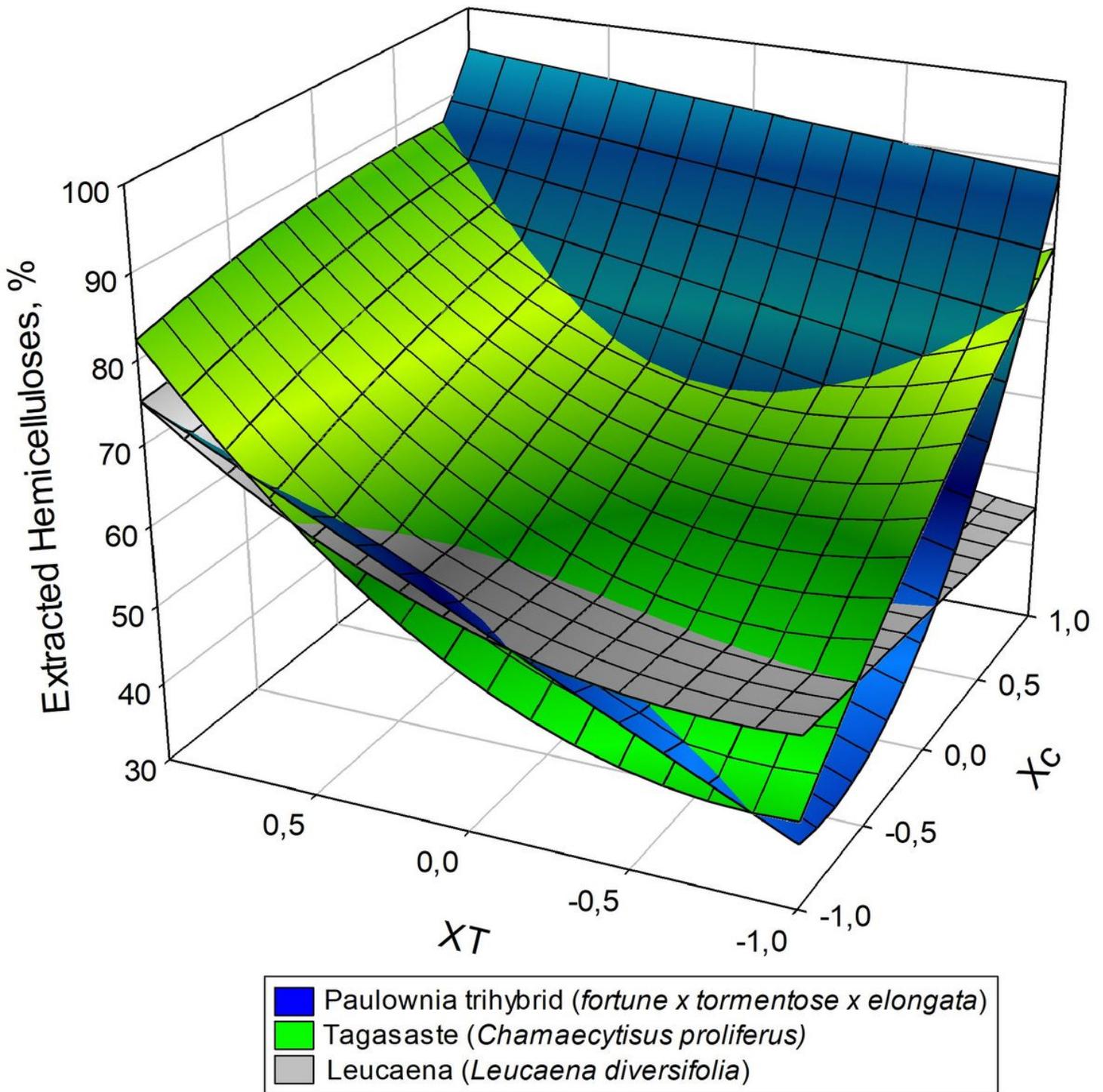


Figure 3

Variation of amount of hemicelluloses extracted from the three species as a function of the acid concentration and temperature.

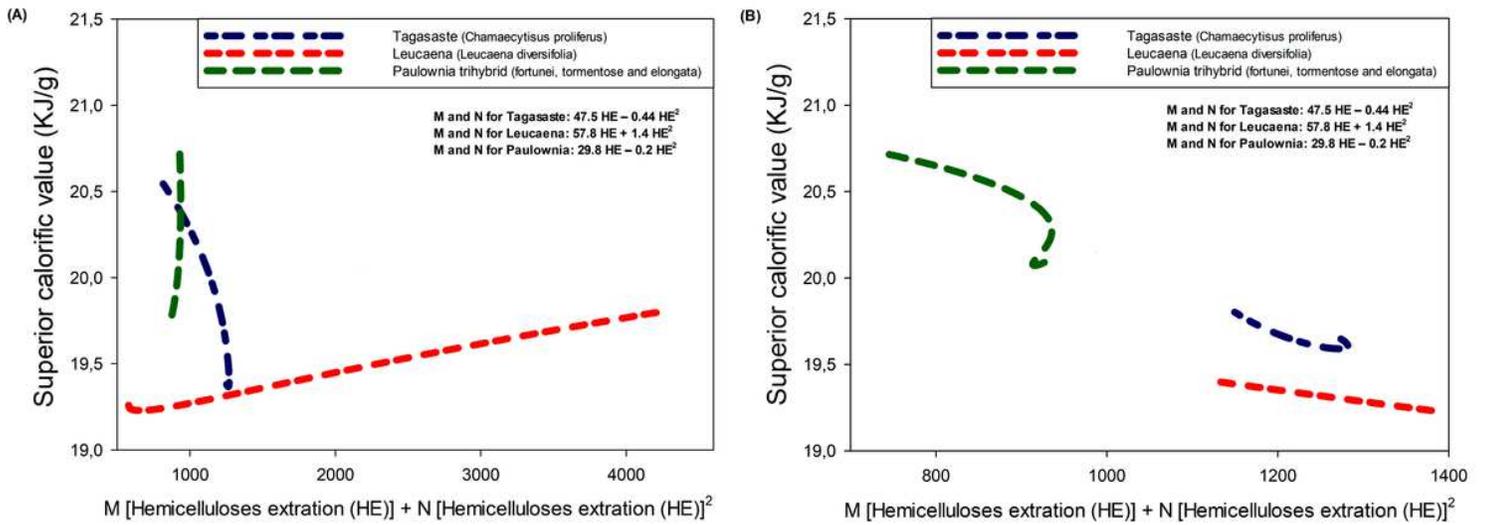


Figure 4

Correlation between the superior calorific value and hemicellulose extraction from the three species at a constant temperature of 150 °C (A) and a constant acid concentration of 1.25% (B).

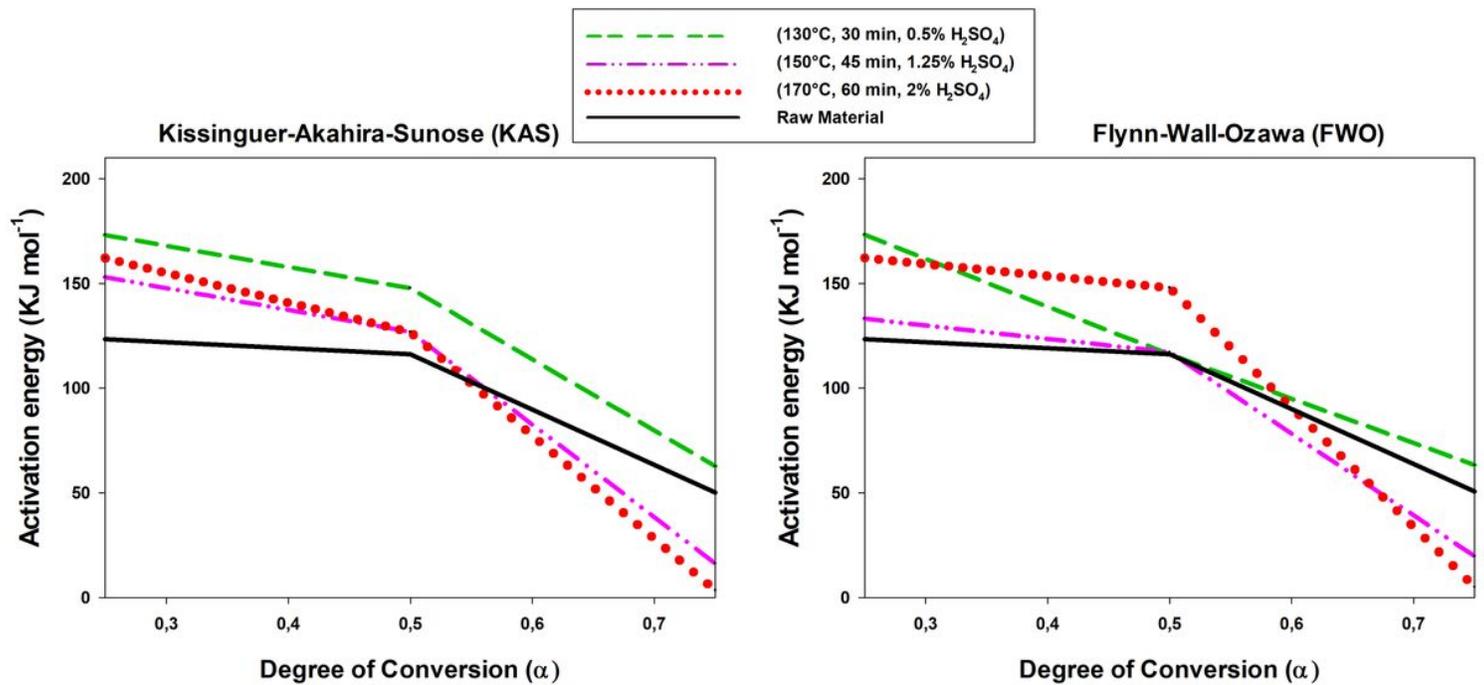


Figure 5

Variation of the activation energy of combustion of tagasaste as a function of the degree of conversion

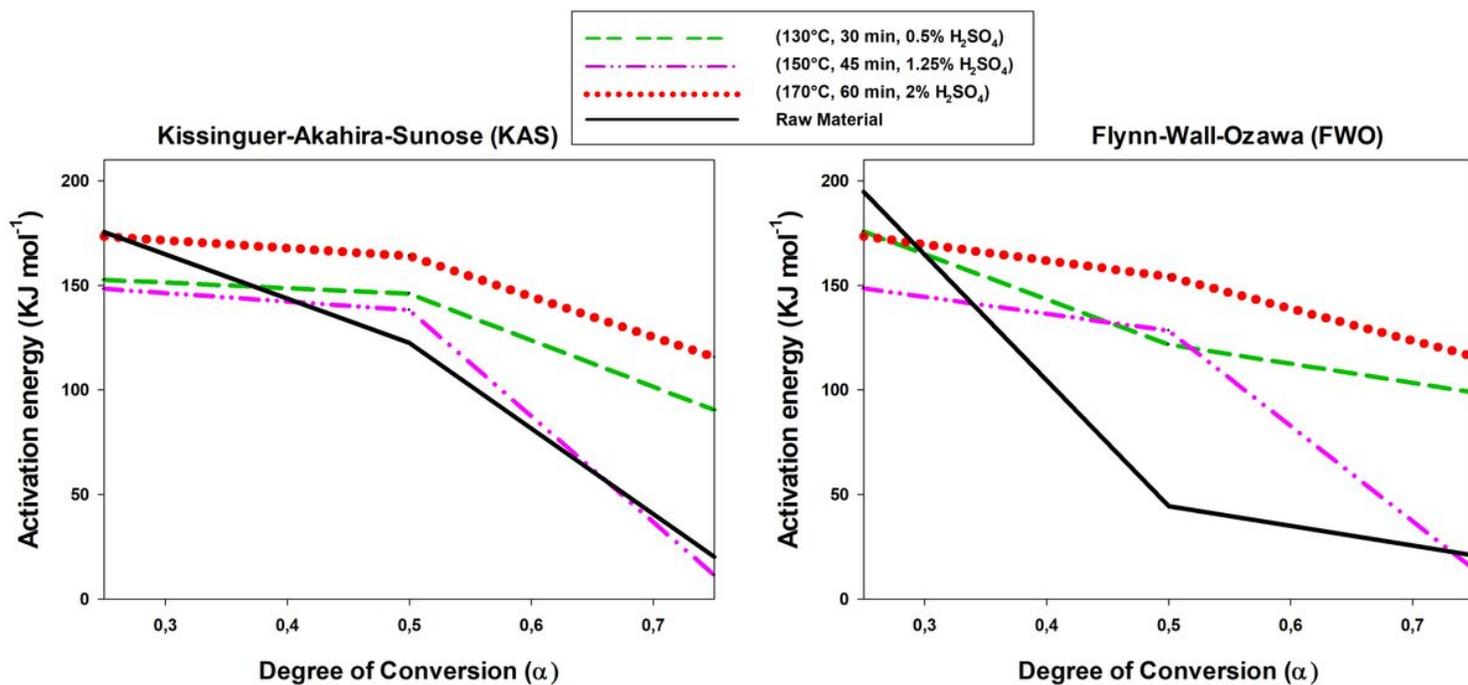


Figure 6

Variation of the activation energy of combustion of leucaena as a function of the degree of conversion.

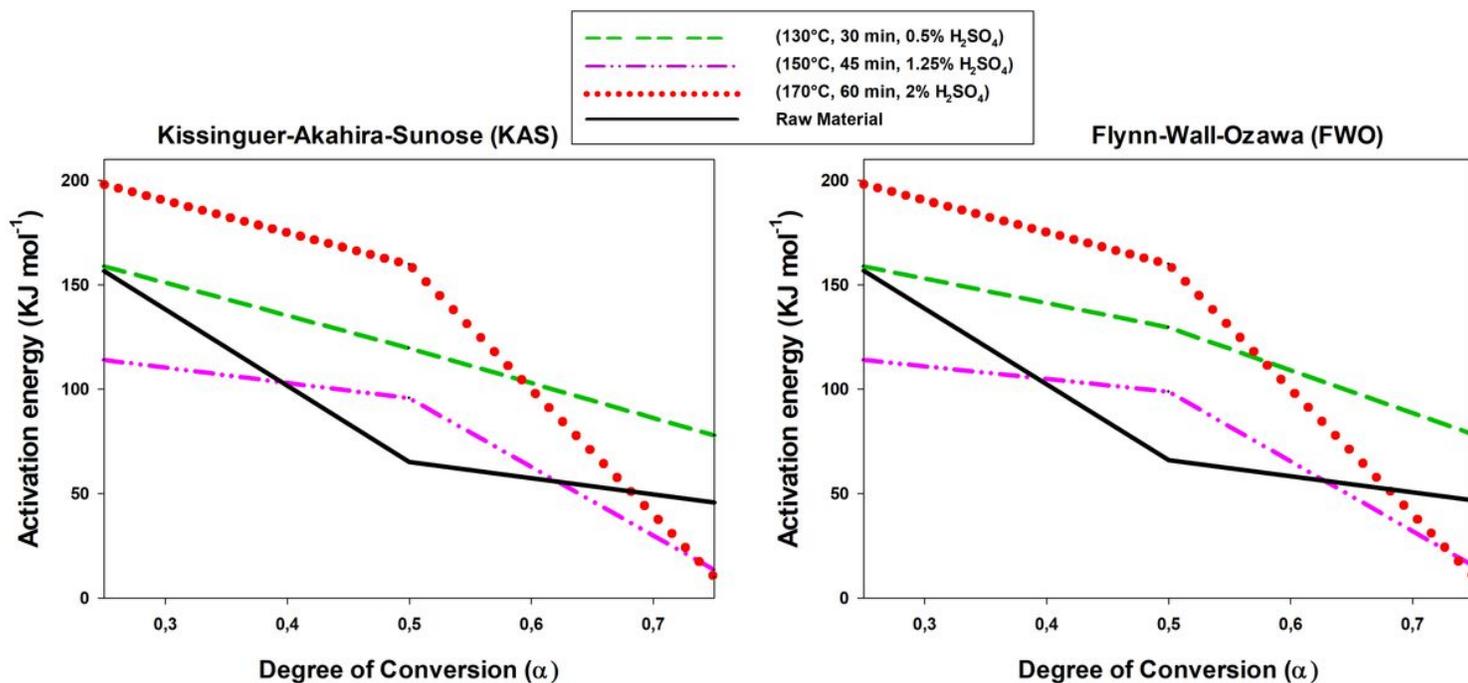


Figure 7

Variation of the activation energy of combustion of paulownia trihybrid as a function of the degree of conversion.

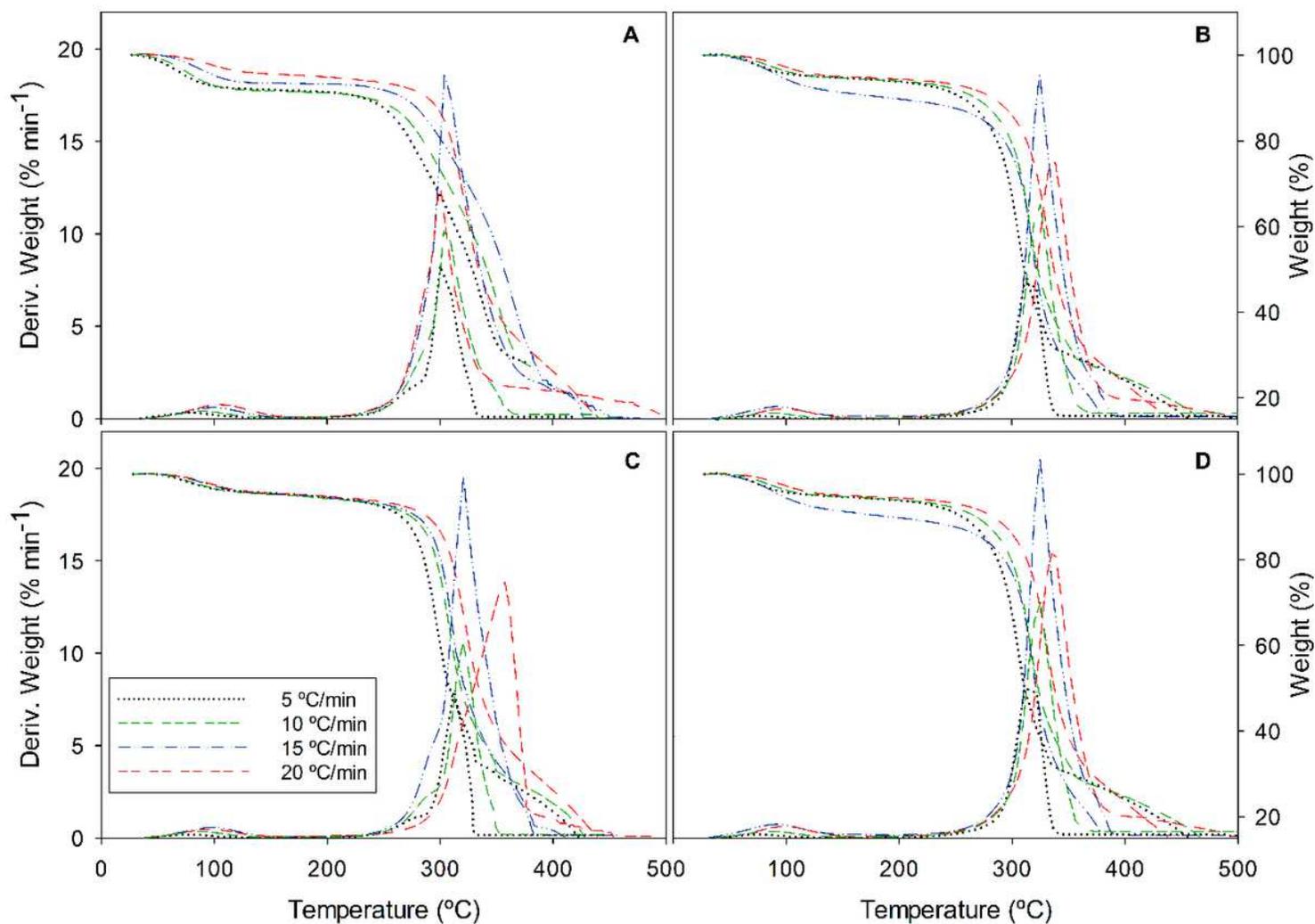


Figure 8

TGA and DTG curves for tagasaste combustion at a variable heating rate (5, 10, 15 or 20 °C/min). Raw material (A) and solid residue from hydrolysis with 2% H₂SO₄ at 170 °C for 60 min (B), 1.25% H₂SO₄ at 150 °C for 45 min (C) and 0.5% H₂SO₄ at 130 °C for 30 min (D).

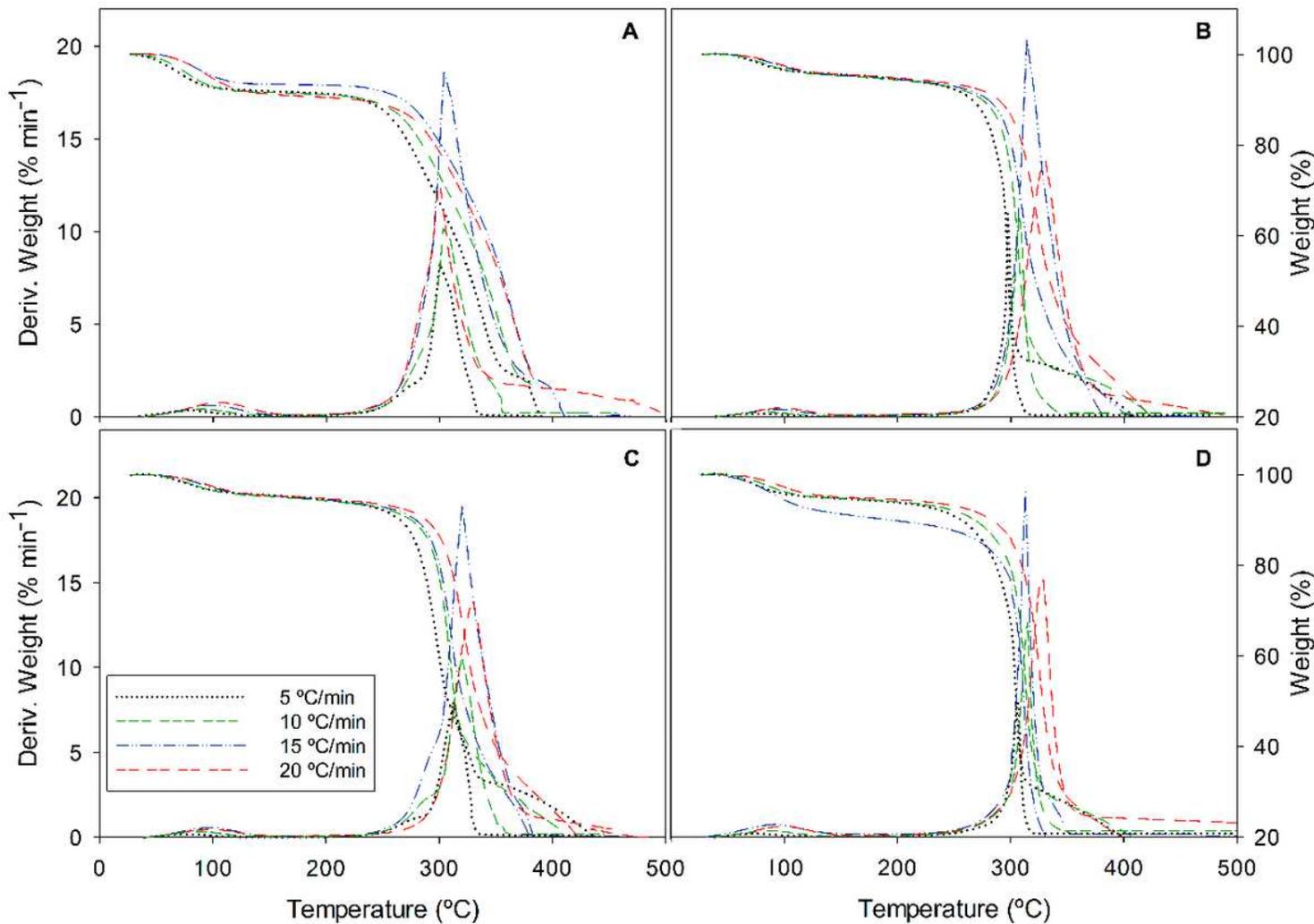


Figure 9

TGA and DTG curves for leucaena combustion at a variable heating rate (5, 10, 15 or 20 °C/min). Raw material (A) and solid residue from hydrolysis with 2% H₂SO₄ at 170 °C for 60 min (B), 1.25% H₂SO₄ at 150 °C for 45 min (C) and 0.5% H₂SO₄ at 130 °C for 30 min (D).

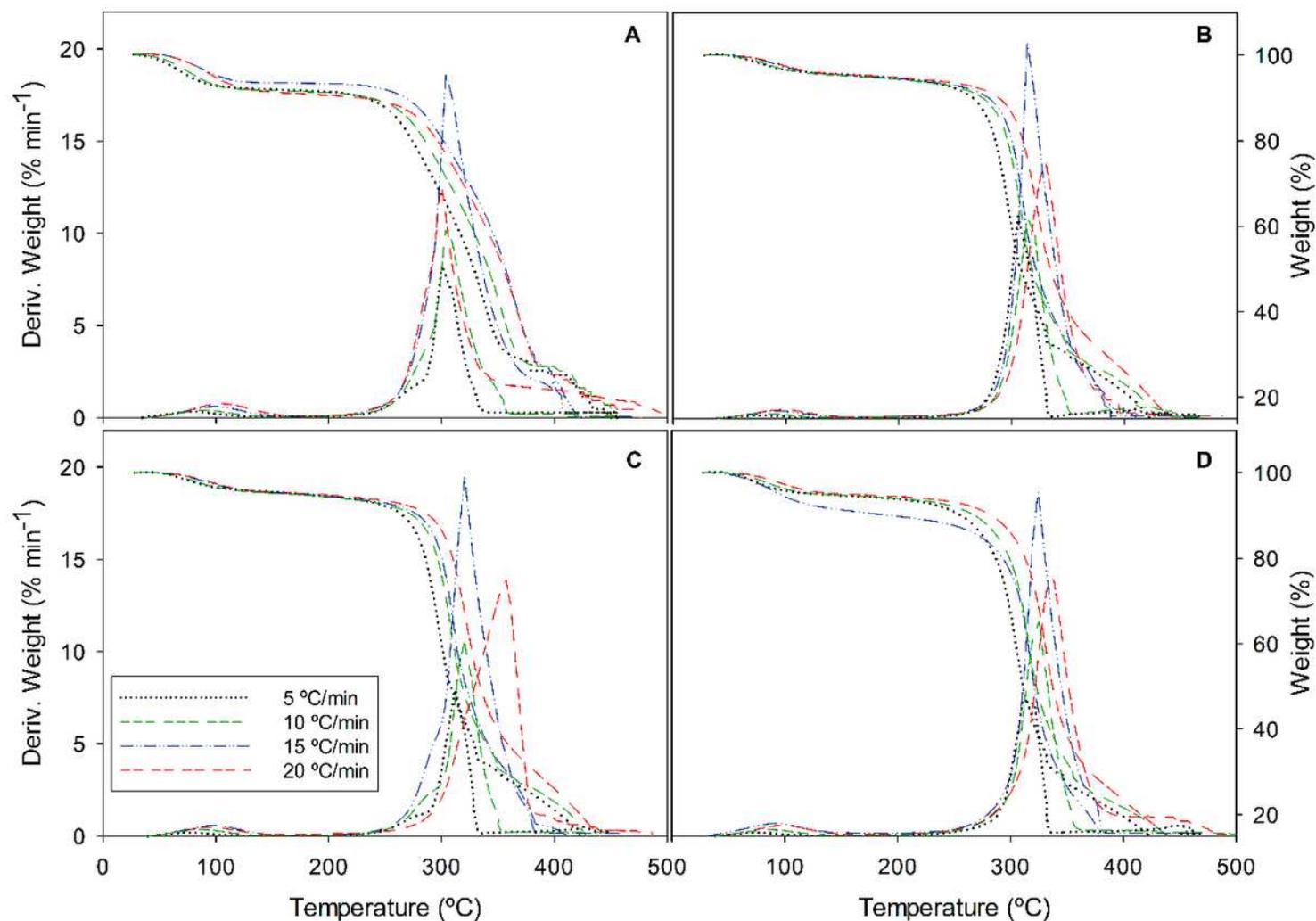


Figure 10

Figure 10. TGA and DTG curves for paulownia trihybrid combustion at a variable heating rate (5, 10, 15 or 20 °C/min). Raw material (A) and solid residue from hydrolysis with 2% H₂SO₄ at 170 °C for 60 min (B), 1.25% H₂SO₄ at 150 °C for 45 min (C) and 0.5% H₂SO₄ at 130 °C for 30 min (D).

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