REVIEW ARTICLE

Thermogravimetric Stability Behavior of Less Common Lignocellulosic Fibers - a Review

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A review on the thermogravimetric behavior of some less-common natural lignocellulosic fibers is presented. The review was limited to works analyzing results on the weight loss variation with temperature by means of the thermogravimetric (TG) curve and its derivative (DTG) for uncommon fibers such as curaua, rice, wheat straw, henequen, piassava, fique, date palm, buriti, artichoke, grass, okra, sponge gourd, caroa and olive husk. Relevant parameters obtained from corresponding TG/DTG curves were discussed to highlight distinctions and similarities in the thermal stability of these fibers. The concept of fiber thermal degradation is critically examined in view of the decomposition stages associated with the main constituents: water, hemicellulose, lignin and cellulose. The effect of fiber thermal degradation on possible application as polymer composite reinforced is remarked.

KEY WORDS: Lignocellulosic fibers, Thermogravimetric behavior, Less common fibers, TG/DTG analysis.

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1. Introduction

Natural fibers obtained from both animals and plants have been used since the primordium of humankind and are still extensively considered for large scale production of items such as textiles and papers. In the beginning of the past 20th century, there was a clear tendency towards replacing natural fibers as engineering materials throughout the 20th century. At the end of the century, the use of these energy-intensive and long lasting synthetic materials was questioned as contributors to generalized pollution and global warming. The particular case of fiber reinforced composite materials was illustrated by Bledzki and Gassan[1] as well as Mohanty et al.[12] in their classical review articles. Some of their examples are worth revisiting. As earlier as 1896, airplane seats and fuel-tanks were made of natural fibers bound with polymers. In 1908, the first large quantities of natural cellulose-based fibers (paper or cotton) reinforcing polymeric (phenol- or melamine-formaldehyde) composites were applied for fabrication of sheets, tubes and pipes in the electronic industry. With the introduction of glass fiber, all-synthetic composites with unsaturated polyester matrices reached commodity status in the 40's[2]. The application of natural fibers in composites then came to a near-halt[13]. However, in few cases such as the late Germany car industry, in which textile wastes were used to reinforce the plastic body of the Trabant model and that of the Indian government Madras-House project with jute reinforced polyester plates used in building construction, natural fiber composites persisted for decades after mid last century.

The beginning of this new millennium witnesses a revival in the use of natural fibers as composite reinforcement. Environmental issues are currently a relevant reason, which favor natural fiber extracted from plants, also known as biofibers or lignocellulosic fibers (LCF), and is motivating numerous publications and industrial applications[3–10]. Additionally, economical and technical advantages related to lower cost as well as societal benefits in providing income to local producers in Africa, Latin America, and South Asia, contribute to the tendency of LCF substitution for synthetic fibers. For instance, some of the LCF’s technical properties, such as low density and superior toughness, represent important advantages over the glass fibers, in “fiberglass” composites, as the reinforcement phase[11,12].

Today an expansion in industrial uses of LCF composites as engineering materials is taking place and occupying traditional “fiberglass” niches such as automobiles components, building plates, packaging, sport gears, electrical parts, and medical prosthesis[9]. The vehicles manufacturing sector, in particular, is adopting LCF composites at a fast rate in both interior and exterior components[13–16].

For the reader it is also relevant to be aware of drawbacks exhibited by the LCF’s that could also affect their incorporation into polymer composites. As any biomaterial, their dimensions are not only anatomically restricted but also display an accentuated statistical dispersion[10]. By contrast, synthetic fibers are fabricated within precise dimensional characteristics. The LCF hydrophilic nature is another drawback responsible for the weak adhesion to hydrophobic polymers, usually considered as composite matrices[1–10]. Several types of LCF surface modifications[17,18], especially by means of chemical treatments, may improve the fiber/matrix adherence. However, it is worth mentioning that any treatment is associated with additional cost and thus decreases the competitiveness of the LCF. Still another shortcoming is the limited thermal stability of any LCF, which restricts its applications at temperatures that causes significant degradation of the fiber organic structure, particularly in combination with a polymeric matrix. Review works[1–2] generally stated that the processing temperatures for most LCF’s are limited to about 200°C. Bledzki and Gassan[1] indicated that at normal thermoplastic composites processing temperatures, 180-200°C, critical decomposition of a reinforcing LCF may occur. In the case of cotton, a notable degradation at 100°C-130°C takes place after 80 days. By contrast, Sanadi et al.[11,12] found that in some fibers it is possible to use temperatures higher than 200°C for short periods.

Several less-common LCF’s have been investigated as potential reinforcement of polymer composites and an overview on these composites thermal stability was recently published[10]. Now, the thermogravimetric response of these fibers, as isolated entities, will be the subject of the present review. A brief overview in the TG/DTG characteristics common to all LCF’s with emphasis on the thermal behavior of the main constituents is presented.

2. General Characteristics of the LCF’s

Natural cellulose-based fibers extracted from plants, the LCF’s, have in common a complex structure composed
of several biocells formed out of crystalline microfibrils based on cellulose. Spiraling microfibrils are connected by amorphous lignin and hemicellulose comprising a cylindrical layer. A LCF is actually composed of multiples of such layers in one primary and three secondary cell walls stick together\[11]. For the interested reader, the chemical characteristics of these main constituents of a LCF, namely, cellulose, hemicellulose and lignin, are presented in the review article of Bledzki and Gassan\[11]. Owing to this complex arrangement, the LCF’s are sometimes referred as ‘natural composites’. Differences in these microstructure and chemical aspects among the LCF’s are relevant to justify distinct properties. Structural parameters such as the spiral angle of the microfibril\[11,12] and the LCF dimensions, especially its equivalent diameter\[10], significantly affects the mechanical properties. The relative amount of cellulose also conditions the properties. In fact, cellulose may vary from 31 wt\% in the kenaf fiber to 83 wt\% in cotton\[2], which is a comparatively stronger fiber. Additionally, as indicated by Mohanty et al.\[13], synthetic fibers like glass, carbon and aramid can be produced with a definite range of properties. By contrast, the properties of the same LCF may vary considerably depending on the plant age and location as well as climatic seasonal conditions and processing procedures.

Not only the mechanical but also the thermal behavior of LCF’s are distinctly affected by their microstructural, dimensional, chemical, plant condition, and processing differences. In 1981, Nguyen et al.\[21,22] presented a two-part review on the thermal analysis of lignocellulosic materials with several earlier references on the subject that will not be revisited in this work. In short, the main conclusions of that first comprehensive review including neat cellulose, hemicellulose and lignin as well as wood and bark, were the following: Neat cellulose decomposition occurred from 210°C to 260°C in non-oxidative atmosphere and from 160°C to 250°C under air. Neat hemicellulose decomposes from 159°C to 280°C. Lignin starts decomposing from 220°C and continues above 400°C. Wood, as a LCF, shows water release at 107°C under helium and 87°C under air. The wood constituents decompose at comparatively higher temperatures; cellulose from 343°C to 367°C and hemicellulose from 207°C to 330°C. Since this first review\[21,22], in spite of the considerable number of papers dedicated to the thermal behavior of LCF’s, only the general review of Saheb and Jog\[23], in a short section, dealt with the thermal stability of LCF’s. As main conclusions, these authors indicated that the thermal degradation of LCF’s is a two stage process at 220°C-280°C, due to hemicellulose, and 280°C-300°C, due to lignin. No indication of the cellulose degradation was provided by Saheb and Jog\[23]. Moreover, these authors stated that the degradation of LCF’s is crucial in the development of composites and thus has a bearing on the curing temperature in the case of thermostet and extrusion temperatures in thermoplastic composites. The thermal degradation of the fibers also results in production of volatiles at processing temperatures above 200°C, which leads to porous polymer composites with inferior mechanical properties.

An attempt to review the thermal behavior of LCF’s is faced with the challenge posed by the numerous published works. Recently, the authors of the present review published an overview on the thermal behavior of common natural fibers reinforced polymer composites\[24] and are submitting another review on the thermogravimetric analysis of common LCF’s, including jute, sisal, hemp, flax, coir, cotton, kenaf, wood, pineapple, bamboo, rami, banana, and bagasse. As a continuation, the present review extends the thermogravimetric analysis to less-common, and in some respect uncommon, LCF’s. The selected LCF’s were curaua, rice, wheat straw, henequeen, piassava, fique, date palm, buriti, artichoke, grass, okra, sponge gourd, caroa and olive husk. The reader might be asking why not include other less-common fibers. The reason is the apparent absence of consistent works on TG/DTG results published in well established sources of information.

### 3. Thermogravimetric Results of Less-Common LCF’s

For the purpose of organization the names of specific fibers are used as subtitles for the corresponding review on related articles showing TG/DTG results. It should also be mentioned that temperature data will be shown with numerical approximation to avoid decimals.

#### 3.1 Curaua Fiber

Curaua is a bush-like plant native of the Amazon region, which belongs to the same ananas gender of the common pineapple. The fibers extracted from the leaves of curaua are relatively soft and strong, reaching tensile strength of above 1,000 MPa\[6,10,25]. This has motivated, in recent years, not only research works on the possible use of the curaua fiber as reinforcement of polymer composites\[10,26] but also application in the automotive industry\[19]. The reader may not yet be familiar, but applications of curaua fiber composites are expected to increase owing to their superior engineering performance, including thermal behavior.

Mothé and Araujo\[27] evaluated the thermogravimetric performance of curaua fibers by TG/DTG analysis at a heating rate of 10°C/min in nitrogen. Three stages of weight loss were observed. The initial around 60°C corresponds to the released of moisture, which occurs for all lignocellulosic fibers. The second, as a small DTG shoulder peak at about 290°C, was attributed to the beginning of lignin decomposition. The third, as the main DTG peaks at 360°C, was assigned to the hemicellulose depolymerization and cleavage of the glycosidic links in the cellulose. Santos et al.\[28] presented TG/DTG curves of curaua fibers analyzed at a heating rate of 10°C/min in air. The moisture loss was found to occur around 80°C followed by two other weight loss events. The first, a slight shoulder around 270°C, was attributed to lignin and hemicellulose degradation. The second, at 310°C, was related to the cellulose degrada- tion. A final weight loss at 414°C was ascribed to residues, quoting Mothé and Araujo\[27]. The authors\[28] mentioned that the shoulder in the first peak of the derivative of the TG (DTG) curve indicates a third thermal degradation reaction. However, the shoulder at about 270°C corresponds to the only shoulder in the DTG curve, which is certainly not a third thermal degradation.
Tomczak et al.\textsuperscript{[29]} showed TG/DTG curves of untreated curaua fibers obtained at a heating rate of 20°C/min in both nitrogen and oxygen atmospheres. They revealed in nitrogen an initial DTG peak at 62°C, attributed to the elimination of absorbed or combined water, followed by two weight loss events at 337°C and 519°C, probably due to the degradation of lignin and cellulose. A possible shoulder at about 270°C was not mentioned by the authors. Under oxygen atmosphere, DTG peaks were reported to occur at 72°C, 275°C, and 300°C, and were indicated by Tomczak et al.\textsuperscript{[29]} as representing decomposition process of the fiber constituents. The authors\textsuperscript{[29]} did not mention specifically the degradation of hemicellulose nor explained the disappearance of the corresponding nitrogen 519°C peak under oxygen atmosphere.

Araujo et al.\textsuperscript{[30]} carried out thermogravimetric analysis at a heating rate of 10°C/min in argon. They indicated two weight loss processes for the curaua fiber. The first started at 266°C, with a DTG shoulder around 280°C, which was ascribed to the thermal degradation of pectin, lignin and hemicellulose, quoting Tomczak et al.\textsuperscript{[29]}. The main peak at 363°C was associated with the decomposition of the α-cellulose. Although not mentioned by the authors\textsuperscript{[30]}, the DTG curve apparently displays an initial peak at 60°C.

D’Almeida et al.\textsuperscript{[31]} described the thermal behavior of curaua, caroa, piassava and sponge gourd fibers by TG/DTG curves using several heating rates up to 40°C/min in nitrogen. The set of DTG curves at 10°C/min are reproduced in Fig. 1. All investigated fibers showed an initial DTG peak around 50°C, probably due to water release. The other peaks are listed in the insert of Fig. 1 together with corresponding values for the activation energy. In the particular case of the curaua fiber, the authors\textsuperscript{[31]} indicated only a single peak at 365°C, which was associated with the thermal decomposition of α-cellulose. However, a slight shoulder peak appears to exist around 280°C. The authors justified the existence of only one DTG peak as related to a more homogeneous thermal degradation of the curaua fiber. As shown in the insert of Fig. 1, the activation energy of the curaua fiber was the highest among the others, but according to D’Almeida et al.\textsuperscript{[31]}, similar to the ones reported for the other lignocellulosic fibers.

Silva and Aquino\textsuperscript{[32]} presented TG curve, obtained at a heating rate of 10°C/min in nitrogen, for two types of curaua fibers; white and purple. As a general result, the authors indicated that the thermogravimetric analysis did not show significant change in the thermal stability of both types of curaua fiber. In common, TG curves display a first weight loss stage around 80°C corresponding to water evaporation. A second stage, around 235°C, was attributed to lignin decomposition, quoting Mothé and Araujo\textsuperscript{[33]}, and a third around 380°C, indicated as the lignin final combustion. Silva and Aquino\textsuperscript{[32]} mentioned that the percentage of the final carboniferous residue was somewhat higher for the white (19 wt%) than the purple (17 wt%) curaua fiber. This was considered common for lignocellulosic fibers in the analyzed conditions.

Spinacé et al.\textsuperscript{[34]} studied the thermal degradation of curaua fibers that were untreated (C), washed (CW), treated with sodium hypochlorite (CH), and treated with cold oxygen plasma (CP). Similar DTG curves were obtained at a heating rate of 10°C/min in argon. The authors\textsuperscript{[34]} reported an initial weight loss at 75°C due to absorbed moisture. This was followed by three other processes. The first with maximum decomposition rate, a shoulder at 268°C, was ascribed to the decomposition of hemicellulose. The second, with a maximum at 335°C-345°C, was attributed to cellulose degradation. The third with a maximum at 439°C-476°C was assigned to the decomposition of lignin. By comparing these results\textsuperscript{[34]} with those from the same research group\textsuperscript{[29,30]}, the reader will notice that the DTG peaks, maximum thermal decomposition rate, were somewhat different. This certainly could be a consequence of different lots of curaua fibers, although not discussed by Spinacé et al.\textsuperscript{[34]}. More intriguing, however, is the fact that in previous works\textsuperscript{[28,30]}; they attributed the first DTG peak (220°C-266°C) to lignin degradation and the final degradation (414°C) to residues.

3.2 Rice Husk and Straw Fibers

The rice plant is cultivated worldwide as one of the most used grains for human consumption. Both the rice husk and the rice straw are usually disposed as a residue from rice milling process or leftover as crop waste. As by-products, the rice husk and rice straw can be incinerated to generate energy in thermal power plants. Their potential...
as composite reinforcement is also being investigated and for this purpose the thermal behavior of the rice husk and straw fibers need to be assessed.

Mansaray and Ghaly\cite{34} subjected rice husk to thermogravimetric analysis at heating rates of 10°C/min, 20°C/min, and 50°C/min under nitrogen. Although not mentioned by the authors, their only example of DTG curve shows an initial peak around 50°C, possibly due to water release. Two other steps associated with shoulder peak, 300°C–325°C, and main peak, 348°C–363°C, varied depending on the rice husk variety and heating rate. Apparently, a slight tail peak may exist around 420°C. As a general conclusion, Mansaray and Ghaly\cite{34} indicated that, during thermal decomposition of rice husk, the degradation rate increased as the heating rate was increased.

Yao et al.\cite{35} investigated the thermal decomposition kinetics of several common LCF’s as well as the rice husk and straw fibers. TG/DTG curves were obtained at 2, 3.5, 5, 7.5, 10, and 15°C/min under nitrogen. Fig. 2 exemplifies curves obtained at a heating rate of 2°C/min for the rice husk, Fig. 2(a), and rice straw, Fig. 2(b). In these figures, shoulder peaks were found at 297°C (husk) and 274°C (straw). Moreover, main peaks at 322°C (husk) and 311°C (straw) were assigned to the decomposition of cellulose. Since the TG/DTG curves were recorded above 100°C, it was not possible to infer the existence of an initial water release peak.

Table 1 reproduces results of Yao et al.\cite{35} on the activation energy calculated according to different experimental methods. In this table, one sees that the activation energy varies from 166 kJ/mol to 168 kJ/mol for the rice husk and from 176 kJ/mol to 198 kJ/mol for the rice straw. Yao et al.\cite{35} indicated that the rice straw shows the highest activation energy among the investigated fibers. The authors concluded that the decomposition activation energy range in Table 1 can help understand the thermal stability of natural fibers used as reinforcement in polymer composites.

![Fig. 2](image_url) TG/DTG of several LCF’s including rice husk (a) and rice straw (b). Reproduced from Yao et al.\cite{35}

### Table 1 Average apparent activation energy of selected natural fibers calculated by three methods. Reproduced from Yao et al.\cite{35}

<table>
<thead>
<tr>
<th>Natural fiber</th>
<th>Firedman $E_a$ (kJ/mol)</th>
<th>R²</th>
<th>F-W-O $E_a$ (kJ/mol)</th>
<th>R²</th>
<th>Coats-Redfern (modified) $E_a$ (kJ/mol)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bagasse</td>
<td>168.5 (7.5)$^a$</td>
<td>0.9972 (0.0022)</td>
<td>169.5 (4.8)</td>
<td>0.9967 (0.0019)</td>
<td>168.7 (4.9)</td>
<td>0.9963 (0.0021)</td>
</tr>
<tr>
<td>Bamboo</td>
<td>164.1 (2.2)</td>
<td>0.9982 (0.0003)</td>
<td>162.8 (2.5)</td>
<td>0.9989 (0.0003)</td>
<td>161.9 (2.3)</td>
<td>0.9987 (0.0003)</td>
</tr>
<tr>
<td>Cotton stalk</td>
<td>165.3 (8.5)</td>
<td>0.9953 (0.0010)</td>
<td>169.9 (5.1)</td>
<td>0.9959 (0.0005)</td>
<td>169.1 (5.7)</td>
<td>0.9954 (0.0006)</td>
</tr>
<tr>
<td>Hemp</td>
<td>180.9 (9.4)</td>
<td>0.9939 (0.0042)</td>
<td>177.9 (3.9)</td>
<td>0.9925 (0.0065)</td>
<td>177.7 (4.1)</td>
<td>0.9918 (0.0072)</td>
</tr>
<tr>
<td>Jute</td>
<td>183.1 (9.4)</td>
<td>0.9993 (0.0008)</td>
<td>184.2 (5.8)</td>
<td>0.9991 (0.0011)</td>
<td>184.3 (6.3)</td>
<td>0.9990 (0.0012)</td>
</tr>
<tr>
<td>Kenaf</td>
<td>169.8 (3.5)</td>
<td>0.9964 (0.0006)</td>
<td>170.3 (1.6)</td>
<td>0.9965 (0.0009)</td>
<td>169.6 (1.9)</td>
<td>0.9960 (0.0010)</td>
</tr>
<tr>
<td>Rice husk</td>
<td>168.2 (2.5)</td>
<td>0.9926 (0.0050)</td>
<td>167.4 (2.2)</td>
<td>0.9944 (0.0036)</td>
<td>166.5 (2.1)</td>
<td>0.9938 (0.0040)</td>
</tr>
<tr>
<td>Rice straw</td>
<td>197.6 (3.0)</td>
<td>0.9814 (0.0047)</td>
<td>195.9 (1.5)</td>
<td>0.9812 (0.0055)</td>
<td>169.9 (1.3)</td>
<td>0.9812 (0.0060)</td>
</tr>
<tr>
<td>Wood-maple</td>
<td>156.0 (2.7)</td>
<td>0.9865 (0.0050)</td>
<td>155.8 (3.8)</td>
<td>0.9857 (0.0028)</td>
<td>154.3 (3.6)</td>
<td>0.9838 (0.0031)</td>
</tr>
<tr>
<td>Wood-pine</td>
<td>161.5 (3.0)</td>
<td>0.9965 (0.0041)</td>
<td>161.8 (3.2)</td>
<td>0.9946 (0.0060)</td>
<td>160.4 (3.1)</td>
<td>0.9940 (0.0067)</td>
</tr>
<tr>
<td>All fiber average$^b$</td>
<td>171.5 (12.3)</td>
<td>0.9928 (0.0064)</td>
<td>171.5 (11.7)</td>
<td>0.9935 (0.0058)</td>
<td>170.9 (12.5)</td>
<td>0.9928 (0.0064)</td>
</tr>
</tbody>
</table>

$^a$Values from 50 conversion fractions with mean value and standard deviation.

$^b$Values from 10 types of fibers with mean and standard deviation.

3.3 Wheat Straw Fiber

Wheat straw is another crop waste generated in huge amounts in many producing countries. Its application as polymer composite reinforcement has been studied and promising results obtained. As for other LCF’s, this application requires information on thermal stability.

Hornsby et al.\[36\] presented thermogravimetric curves for both isothermal weight loss and TG obtained at a heating rate of 5 °C/min in both air and nitrogen for flax and wheat straw fibers. The isothermal curves obtained in air revealed that flax has a much greater thermal stability than the wheat straw fiber. TG curves in both nitrogen and air show an initial weight loss of 7.3–7.8 wt.%, which was associated with moisture. Major thermal decomposition temperatures for the wheat straw were 283°C in nitrogen and 264°C in air. The authors\[36\] pointed out that the thermal behavior of wheat straw fiber lies between those of lignin and α-cellulose. Residues remaining after heating at 725°C were found as 24.2 wt.% in nitrogen and 70 wt.% in air. It was indicated that the value for air is consistent with reported silica levels typically contained in the wheat straw fiber.

3.4 Henequen Fiber

Henequen fiber is a relatively uncommon LCF, native from Mexico and Central America, similar to sisal and pita fiber. The fibers extracted from the leaves of the henequen plant are traditionally used in baskets, roofing and carpets. Nowadays, these fibers are considered as composite reinforcement and their thermal behavior investigated.

Sgircia and Hawley\[37\] conducted thermogravimetric analysis, at a heating rate of 25°C/min in nitrogen, of untreated hemp, flax, kenaf, and henequen fibers. Based on TG curves, degradation temperatures were shown in association with 5 wt.%, 25 wt.%, 50 wt.%, and 75 wt.%. DTG curves were neither shown nor discussed. The degradation temperatures (weight loss %) for the untreated henequen fibers were found as 61°C (5 wt.%); 301°C (25 wt.%); 337°C (50 wt.%); and 392°C (75 wt.%). These values were somewhat lower than the corresponding ones for the other investigated LCF’s. No discussion was offered by Sgircia and Hawley\[37\] on possible degradation mechanism. However, they indicated that the relatively lower degradation temperatures of these LCF’s, particularly the henequen fiber, place restriction on possible reinforcement of epoxy composites that may undergo microwave thermal curing.

3.5 Piassava Fiber

Piassava palm tree is native of Brazil from which stiff and long fibers can be extracted. These fibers have traditionally been used in simple items such as broom, sweep, and kiosk roofing. The mechanical properties of the piassava fiber motivated research works on the incorporation in polymer composites, which also required investigations related to its thermal stability.

As already presented in section 3.1, D’Almeida et al.\[31\] showed TG/DTG curves, Fig. 1, obtained at 10°C/min in nitrogen for the curaua fiber, as well as for caroa, sponge gourd and piassava. Although not mentioned by the authors\[31\], all investigated fibers showed an initial DTG peak around 50°C, which should be certainly related to the release of moisture. The other peaks are listed in the insert of Fig. 1, together with the corresponding activation energies. In the case of the piassava fiber, a peak at 304°C was associated with the decomposition of hemicellulose. The authors mentioned that this value is higher than the usual range, 260°C-281°C, attributed to the hemicellulose thermal decomposition. They also mentioned that previous works on different LCF’s\[38,39\], with common co-authors, obtained lower values for the first peak. A second peak at 377°C was attributed to the thermal decomposition of α-cellulose.

Nascimento et al.\[40\] showed TG/DTG curves obtained at a heating rate of 10°C/min in nitrogen, for untreated piassava fibers. They reported an initial DTG peak at 62°C due to moisture release. A second peak at 288°C was ascribed to the cellulose decomposition. A third peak at 357°C was assigned to the decomposition of lignin. The authors failed to comment on a possible tail peak seen in their DTG curve around 425°C.

The same authors, D’Almeida et al., of an above-discussed paper\[31\], in a more recent work\[41\], presented TG/DTG curves obtained at a heating rate of 10°C/min in nitrogen, of untreated (raw) and alkali (10 wt.% and 15 wt.% NaOH) treated piassava fibers. The curves show an initial DTG peak around 50°C, same as in their first work\[31\], due to a loss of absorbed moisture or combined water. A clear DTG peak around 300°C for the untreated fiber was attributed to the thermal decomposition of hemicellulose and rupture of glycoside link of the cellulose, quoting Wielage et al.\[42\] and Nair et al.\[43\]. This peak was attenuated and became a shoulder for the 10% NaOH, but completely disappeared for the 15 wt.% NaOH treated fibers. D’Almeida et al.\[41\] indicated that these results are in close agreement with the fact that an alkali treatment removes hemicellulose and causes fibrillation of lignocellulose fibers. The major DTG peak at 372°C was also indicated to be in close agreement with the value reported by Mohanty et al.\[44\] for the thermal decomposition of α-cellulose of jute fiber. This peak decreased to 353°C and 340°C for the 10 wt.% and 15 wt.% alkali treatments, respectively. The authors\[41\] attributed this to hemicellulose removal, which split the fiber into microfibers and causes an increase in the fiber surface available for the reaction and favoring thermal degradation. In the same work\[41\], fibers subjected to acetylation showed almost similar TG/DTG curves to those for the untreated piassava fiber.

3.6 Fique Fiber

Fique fiber is extracted from the leaves of a plant, bearing the same name, which is a native of Colombia. The fiber has a flexible manufacturing process for producing fabrics of diversified textures. The thermal properties of the fique fiber were found to withstand temperature up to 200°C without degradation\[45\].

Gañán and Mandragon\[46\] presented thermogravimetric results at a heating rate of 10°C/min in helium, for both untreated as well as maleic anhydride (MA); acrylic acid (AA); and silane treated fique fibers. The untreated fiber presented three weight loss regions. An initial DTG peak around 65°C was associated with elimination of superficial
water. A second DTG shoulder peak at 298°C was attributed to the thermal depolymerization of hemicellulose and separation of the glycosidic linkages of cellulose, quoting Nair et al.[47]. A main DTG peak occurred at 355°C and was assigned to the decomposition of cellulose. Regarding the treated fique fibers, the authors[46] indicated that the temperature of the initial peak increases for the different treatments, especially with the silanization. Silane treatment was the only one to increase the temperature of the other peaks. Therefore, the authors concluded that the most effective treatment for thermal stabilization of fique fibers is silanization.

In another work, Gañán and Mandragon[48] presented thermogravimetric results at a heating rate of 10°C/min in nitrogen, for both untreated and treated with maleic anhydride (MA); propionic acid (PA), formaldehyde (F), and glycidyl methacrylate (G), fique fibers. The untreated fiber presents three weight loss regions, associated with DTG peaks. The first at 65°C corresponds to release of moisture. The others, at 301°C and 356°C, were associated with the decomposition of hemicellulose, lignin, and cellulose, but not specified by the authors[46]. For the treated fique fibers, a significant reduction in moisture content was attributed to the presence of new groups in the fiber surface, reducing the moisture access to the fiber. The first peak, nevertheless, did not change much for the treated fibers. The other peaks experiment a slight increment with treatment. In particular, for the G treated, the second peak was increased to 342°C and the third to 391°C. For Gañán and Mandragon[48], this was an indication of higher thermal stability of the G treated fique fibers.

3.7 Date Palm Fiber

Date palm tree is normally found in temperate regions from the Middle East to California, in the USA. The palm tree stem is covered with a mesh of fibers used to make ropes and baskets. The possibility of finding uses for these fibers in composites is motivating research works on their mechanical and thermal properties.

Alawar et al.[49] presented TG curves, obtained at a heating rate of 10°C/min in air, for untreated (raw) and alkali (5% NaOH) treated date palm fibers. Except for the graphs, no quantitative parameters were provided. Based on an approximately 20°C shift to higher temperature of the second and most effective stage of weight loss in the TG curve, the authors[49] indicated that the alkali treated fiber has a comparatively higher resistance to thermal degradation than the raw date palm fiber. No discussion on the possible mechanism of thermal degradation was presented.

3.8 Buriti Fiber

Fibers extracted from the leaves of the buriti palm tree, native of Brazil, have shown a potential as polymer composite reinforcement. Recent investigations have disclosed the properties of these buriti fibers including their thermal behavior.

Santos et al.[50] presented TG curves (no experimental procedure on thermogravimetric analysis was provided) for untreated as well as mercerized (20% NaOH) and silane treated buriti fibers. Based on these curves, the authors indicated that all fibers display two main weight loss processes. The first occurs between 60°C-100°C with 8 wt.% of loss, and is attributed to elimination of water due to the hydrophilicity of the lignocellulosic fiber. The second starts at 150°C for the untreated and silane treated fibers. This was attributed to thermal decomposition of the pectin, lignin and hemicellulose in the buriti fiber. A significant shift to a higher temperature, 230°C, for the mercerized fiber, suggested to Santos et al.[50] a comparative increase in thermal stability. No additional discussion on the possible degradation of cellulose was provided.

3.9 Artichoke Fiber

Artichoke is a well known plant, whose capitula is consumed worldwide as a gastronomic item. Investigations are under way to recover the stem of the plant in order to extract its fiber for composite reinforcement. Research works are thus being conducted to assess these artichoke fibers properties, including the thermal stability.

Fiore et al.[51] showed TG/DTG curves obtained at a heating rate of 10°C/min in air for untreated artichoke fibers extracted from the stem of the plant. Fig. 3 reproduces these curves from the original in Fiore et al. paper[51]. As seen in this figure, the DTG curve has an initial peak at 46°C due to the vaporization of water. The authors indicated that the thermal degradation started at 230°C and is apparently finished around 700°C when about 12 wt.% of residue is left. A shoulder peak at 285°C was credited to the thermal depolymerization of hemicellulose, pectin and glycosidic linkages of cellulose. The major peak at 352°C was assigned to the decomposition of cellulose. Fig. 3 also depicts six small tail peaks, from which the authors[51] identified the prominent ones at 454°C and 510°C as resulting from the oxidative degradation of the charred residue. As a general comment, Fiore et al.[51] mentioned that the decomposition of lignin, whose structure is a complex composition of aromatic rings with various branches, takes place at a very low weight loss rate within the whole temperature range, from ambient up to 700°C, quoting the work by Yang et al.[52].

3.10 Grass Fiber

Grass is a generic name given to herbaceous or gramineous plants typical of prairies that are abundant all over the
world. Research works are now given attention to fibers extracted from the stem of selected grasses as potential reinforcement of composites with desirable mechanical properties and thermal stability.

Liu et al.\[53\] presented TG/DTG curves for untreated (raw) and alkali (several conditions) treated grass fibers extracted from the stem of a specific type known as 'Indian Grass', a native of the USA, which grows throughout most North America. No indication of heating rate or test atmosphere was given in the paper\[53\]. Even though DTG curves display shoulder peaks around 340°C, only the main peaks were considered by the authors. They reported maximum decomposition rate temperatures of 352°C and 384°C for the raw and 10% NaOH grass fibers treated for 16 hours, respectively. According to Liu et al.\[53\], this indicated that the alkali treatment improved the thermal stability of the grass fiber. They attributed this fact to the relative decrease of lignin and hemicellulose in the grass fiber after the alkali solution treatment. Moreover, they pointed out that the thermal stability of the alkali treated grass fiber was dependent on the concentration of alkali solution and treatment time.

3.11 Okra Fiber

Okra is another vegetable which is part of the diet of most countries. The fibers extracted from the bark of the okra plant display chemical similarities with other LCF's used as polymer composite reinforcement, like the pineapple fiber. Therefore, works are evaluating the properties of the okra fiber, including the thermal stability.

De Rosa et al.\[39\] performed a thermal characterization of the okra fiber by means of TG/DTG analysis at a heating rate of 10°C/min in nitrogen. They found three weight loss steps associated with DTG peaks. The initial peak at 55°C was attributed to the vaporization of water. The onset degradation for the okra fiber was precisely determined after 220°C. A shoulder peak at 303°C was assigned to the thermal depolymerization of hemicellulose and pectin as well as the cleavage of glycosidic linkages of cellulose. The main peak at 359°C was attributed to the degradation of α-cellulose. No tail peaks are observed in the DTG curve for the okra fiber but a residual weight of 7.6% was related by De Rosa et al.\[39\] to carbonaceous residues and possible undegraded fillers, quoting Arbeloa et al.\[54\].

3.12 Sponge Gourd Fiber

Luffa is a plant with oblong cylindrical fruits. The fibrous vascular system of the dried fruit forms a natural reticulate of fibers known as vegetable sponge or sponge gourd. Nowadays, the use of these fibers is restricted to hygiene pads but recent investigations revealed a potential to enhance the toughness of polymer composites with acceptable thermal stability.

D’Almeida et al.\[59\] investigated the effect of derivatization on sponge gourd fibers using thermogravimetric analysis at a heating rate of 10°C/min under nitrogen. From raw and acetylated fibers, TG/DTG curves were presented and discussed. Both fibers show a low temperature weight loss with initial DTG peaks at 49°C (raw) and 37°C (acetylated). The authors reported that the initial weight loss of the raw fiber (18 wt.%) was significantly lower than that of the acetylated fiber (9.4 wt.%) as an indirect indication that the treatment was effective in reducing the fiber hydrophilic character. Shoulder peaks can be seen in the DTG curves for both fibers but only that of the acetylated (217°C) was considered by the authors\[59\] and attributed to the elimination of acetyl groups. They indicated, however, that between 250 and 315°C the weight loss of the raw fibers could be attributed to the thermal decomposition of hemicellulose and rupture of glycoside link of the cellulose molecule\[42,43\]. The main peaks reported at 380°C (acetylated) were not discussed by D’Almeida et al.\[59\] but they indicated that the weight loss occurring between 315°C-430°C involves the decomposition of cellulose oligomers, changing into levoglucosans and low molecular weight volatile compounds like ketones, aldehydes, furans, and pyrans, quoting Wielage et al.\[42\]. As a conclusion, D’Almeida et al.\[59\] stated that the acetylation not only increased the hydrophobic character of the sponge gourd fiber but also reduced the amount of lignin and hemicellulose, contributing to the homogeneity of the fiber microstructure.

In the already discussed work of D’Almeida et al.\[31\], TG/DTG curves obtained at different heating rates, from 5 to 40°C/min, in nitrogen were shown for curaua (see section 3.1) piassava (see section 3.5), caroa and sponge gourd untreated fibers. Fig. 1 illustrated these curves for the heating rate of 10°C/min as well as an insert with DTG peak temperatures and activation energies. For the specific case of the sponge gourd fiber, an initial peak is seen around 50°C and corresponds to the loss of humidity. A decomposition shoulder peak at 303°C was attributed to hemicellulose, although the values are higher than the usual range, 260°C-281°C for hemicellulose thermal decomposition, quoting the works of Ramiah\[54\] and Órfão et al.\[31\]. The main temperature peak at 374°C was assigned to the thermal decomposition of α-cellulose. D’Almeida et al.\[31\] indicated that, after this main thermal decomposition event, possibly around 400°C, the decomposition of cyclic rings begins and, at even higher temperatures, carbonization of levoglucosan can occur, quoting the work of Trindade et al.\[58\]. The activation energy of 165 kJ/mol was considered within the reported for other lignocellulosic fibers, quoting Wielage et al.\[42\].

3.13 Caroa Fiber

Caroa is a plant of the bromeliaceae family, same as the pineapple, native of Brazil. The fibers extracted from the leaves of the plant are being traditionally used to fabricate ropes as well as rough fabrics and papers. The mechanical properties of the caroa fibers are motivating its use as composite reinforcement. Thermal properties are beginning to be assessed.

In the same work of D’Almeida et al.\[31\], presented in section 3.1, TG/DTG curves for caroa fiber were also shown. The initial DTG peak around 50°C, due to moisture release, was followed by a major peak at 357°C, which was attributed to decomposition of α-cellulose, quoting the work of Das et al.\[99\]. The absence of a shoulder decomposition peak at lower temperature, see Fig. 1, was not an indicative of the existence of fiber earlier degradation. According to the au-
thors[31], the weight loss of approximately 30 wt.% between 200°C and the peak temperature, 357°C, can be credited to the thermal decomposition of cellulose and the rupture of the glycosidic link of the cellulose molecule, quoting Wielage et al.[40] and Nair et al.[41]. The rupture of α- and β-arylalkyl-ether linkages originated from the thermal degradation of lignin were also indicated by D’Almeida et al.[38] to contribute to the weight loss of the caroa fiber.

3.14 Olive Husk Fiber

Olive husk is an agricultural waste generated during the olive milling process that extracts the oil. Significant amounts of olive husk are disposed every crop in Mediterranean countries both in South Europe and North Africa. A possible alternative to incineration, which today is the only destiny to olive husk, is its incorporation into polymer composites. Preliminary investigations on mechanical and thermal properties were recently being conducted.

Amar et al.[60] carried out thermogravimetric analysis of both untreated and silane treated olive husk fibers at a heating rate of 10°C/min in nitrogen. Each TG/DTG curve was very similar for both fiber types. An initial DTG peak was found around 100°C and attributed to water evaporation. A shoulder peak was localized at 260°C for the untreated and 250°C for the treated fiber. According to the authors[60], this shoulder corresponds to the temperature of decomposition of hemicellulose and glycedic bonds of cellulose. A main common peak at 325°C was ascribed to the decomposition of cellulose, while a tail peak at 350°C was assigned to the decomposition of lignin.

4. Concluding Remarks

It is not the intention of this review paper to be just a list of weight loss stages and degradation temperatures for some less common LCF’s, as presented so far. This list must be translated into meaningful results that could characterize the thermal stability of the fibers and indicate their temperature limits for a possible engineering application, especially as reinforcement of polymer composites. Therefore, a critical discussion will attempt to establish these limits in the reviewed papers.

The first obstacle for any general conclusion on the thermogravimetric behavior of less common LCF’s is the fragmented data available. Not only the testing conditions such as heating rate and the atmosphere vary among the papers, but also relevant parameters were not obtained from the TG/DTG curves. This required, sometimes, that relevant data be estimated directly by the authors of this review from displayed figures. For instance, the first well recognized level of thermal degradation associated with the transition temperature from the initial stage of slow weight loss, usually less than 10%, to the faster weight loss stage, more than 50%, was not indicated in most papers. The method of two tangent intercept was manually used to give an approximated value, whenever the data was not available.

The influence of the heating rate was analyzed for the cases of curaua, piassava, sponge gourd and caroa[31] as well as rice husk and straw[33] fibers. Regardless of the method, it was generally found that main DTG peaks are shifted towards higher temperatures with increasing heating rate according to thermally activated mechanism with distinct activation energies for each different fiber. Curaua, with 199 kJ/mol, showed the highest activation energy, while caroa, with the lowest 135 kJ/mol, was identified as the fiber with greater amounts of hemicellulose as compared to cellulose.

The test atmosphere also played a significant role. For fibers thermally analyzed under both inert (argon or nitrogen) or oxidative (air or oxygen) atmospheres, the former displayed thermogravimetric parameters associated with higher temperatures. In other words, under inert atmosphere the fibers tend to be more thermally stable. For example, comparing the curaua degradation temperatures for inert, 260°C–280°C[31,33], their average value is higher than that for oxidative, 238–250°C[28,29], atmosphere. Moreover, the final residue left at 700°C under inert, 10-13 wt.%, is superior to that under oxidative, 1 wt%, atmosphere.

A comparison of the thermal stability between the less common LCF’s by their thermogravimetric parameters also reveals relevant distinctions. Both caroa[31] and olive husk[60] fibers appears to be the less stables, with degradation temperatures of 190°C and 201°C, respectively. By contrast, henequen[27] and grass[32], with corresponding 301°C and 300°C, are the most stable. Comparing the DTG main peak temperatures, in average, the sponge gourd in nitrogen, with 374°C–386°C[31,39], would be the most thermally resistant. On the contrary, the main peak found for curaua in air at 300°C-310°C[28,29] would be the less resistant.

Water release may also be considered an important thermal event for LCF’s, particularly if they are used as polymer composite reinforcement. Based on the reviewed results, all less common fibers show water release small DTG peaks around 45°C[31] to 100°C[60]. The only exception was the grass fiber, for which no initial DTG peak apparent-ly exists. A possible explanation could be a more efficient preliminary drying procedure. Polymer composites incorporated with any of these water containing LCF’s could be subjected to porosity caused by vapor accumulation during exposure to temperatures slightly above 100°C.

As a general conclusion from this review work, the less common LCF’s are expected to resist temperatures above 200°C. In the case of curaua fiber, the degradation temperature may be shortly below, 190°C[31]. However, fibers like henequen[27], grass[32], and sponge gourd[39] may resist up to 300°C. In spite of limited data, the results on less common LCF’s apparently indicate that fiber treatments[39,41] fail to improve some fiber thermal stability. By contrast, in other LCF’s[45,50,53] the applied chemical treatments improved the thermal resistance.

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