



Article

Modification of Orange Bagasse with Reactive Extrusion to Obtain Cellulose-Based Materials

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Abstract: Orange bagasse (OB) could be considered a sustainable, renewable, and low-cost biomass for the extraction of cellulose. In this context, reactive extrusion can be considered an excellent, eco-friendly, alternative process for the extraction of cellulose from lignocellulosic materials. Thus, the present study aimed to obtain cellulose-based materials with a reactive extrusion process and also to investigate the impact of pectin on the delignification process. Two groups of samples (OB and depectinized OB) were submitted to extrusion with sulfuric acid or sodium hydroxide in one-step processes. The cellulose content of extruded materials was highly affected by pectin content in the raw material; the thermal profile (TGA curves) and crystallinity also changed. The cellulose content of modified materials ranged from 18.8% to 58.4%, with a process yield of 30.6% to 79.2%. The alkaline reagent provided the highest cellulose content among all extrusion treatments tested, mainly for OB without pectin. The extrusion process was considered an efficient and promising process for extracting cellulose from citrus residue. Materials produced in this study can be used as sources of cellulose fiber for various products and processes, such as in the food industry, fermentation substrates, or refined applications after subsequent treatments.



Citation: Mantovan, J.; Yamashita, F.; Mali, S. Modification of Orange Bagasse with Reactive Extrusion to Obtain Cellulose-Based Materials. *Polysaccharides* **2022**, *3*, 401–410. <https://doi.org/10.3390/polysaccharides3020024>

Academic Editor: Cédric Delattre

Received: 25 March 2022

Accepted: 2 May 2022

Published: 6 May 2022

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Keywords: one-step process; eco-friendly; pectin; alkaline treatment

1. Introduction

In general, each type of agro-industrial residue requires specific studies to optimize its use for cellulose production due to great variations in the chemical composition of agro-industrial residues, as well as preferably meeting the current demands for sustainable and competitive technological solutions. Conventional processes use a considerable amount of energy and an abundant number of reagents, including chlorinated agents, thus resulting in toxic effluents [1,2].

In this context, reactive extrusion can be considered an excellent alternative process for extracting cellulose from lignocellulosic biomass because it promotes high productivity, lower effluents generation, low overall processing costs, and short-duration processes [3–5]. Extrusion is an important technique in polymers and the food industry and is efficiently employed for cereal brans modification, but little has been explored for the obtainment of cellulose-rich materials from fruit wastes, including orange bagasse [6,7].

Orange bagasse (OB) is generated in large amounts by the orange (*Citrus × sinensis* (L.) processing industry for juice extraction. It contains peel, albedo, and seed, which corresponds to approximately 50% of the fruit weight [8,9]. This most popular citrus fruit has a well-established global consumer market, with Brazil being the leading country in orange and orange juice production [10]. Usually, it is destined as an animal feed supplement; however, its production requires expensive energy resources and shows few nutritional benefits. Furthermore, its improper disposal generates greenhouse gases and risk of pollution for watercourses due to citrus residue characteristics, such as low pH

(between 3 and 4), water content of about 80–90%, and high organic matter concentration (about 95% of total solids) [11,12].

Orange bagasse has a complex composition, which varies according to species and seasonality. The fibrous structure contains cellulose, hemicellulose, and lignin, as insoluble fibers, and pectin and gums as soluble fibers [8,13]. Both fibrous fractions confer several beneficial effects on human health, boosting a range of applications in the food industry [14]. In addition, the residue can find applications in the areas of smart materials, fuels, environmental solutions, etc. Thus, several studies propose applications to this residue, such as the production of adsorbent biomaterials for pollutants [15], production of biogas and bioethanol [16], and hesperidin extraction [8], and as sources of pectin and soluble sugars [17]. The lignocellulosic structure of OB also provides cellulose fibers and nanocellulose through specific extraction methods [18–23].

Cellulose-based materials have many applications, acting as precursors for obtaining various products of industrial interest, such as membranes, hydrogels, nanocellulose, and modified cellulose [24], and they can also be applied as dietary fibers and as substrates in fermentation processes [23,25,26]. Cellulose-based materials obtained with reactive extrusion have shown promising characteristics, such as thermal stability and higher crystallinity indexes [27], as well as hypoglycemic, cholesterol-lowering, and fermentation capacities. The chemical and functional modifications caused by extrusion are capable of adapting the raw material to various applications, thus producing materials with high added value [7].

In this study, orange bagasse and depectinized orange bagasse were subjected to reactive extrusion with sulfuric acid or sodium hydroxide in one-step processes to obtain cellulose-based materials. Composition, crystallinity, and thermal stability were analyzed. The use of an abundant amount of residue as raw material, as well as the one-step extrusion process, is key to producing economically competitive and eco-friendly materials. In addition, the extracted pectin can be used in future food applications.

2. Materials and Methods

2.1. Material

Defatted orange bagasse (OB) was donated by an orange juice industry (Integrada Cooperativa, Paranaíba, PR, Brazil). The residue was dried at 50 °C for 24 h in an air circulation oven (MA 415, Marconi, Piracicaba, Brazil) and milled to ensure homogeneity in particle size (yield particles < 0.3 mm) using a basic analytical mill (IKA-A11, Merck, Darmstadt, Germany). All reagents used in this study have analytical grade (Synthlab, Diadema, Brazil).

2.2. Methods

2.2.1. Extraction of Cellulose-Based Materials Using Reactive Extrusion

Two initial materials were employed to study the production of cellulose-based materials: raw OB (OB) and depectinized OB (OBP). The reagents employed were NaOH (10% *w/w*) and H₂SO₄ (2% *w/w*); water was used as control. The samples were labeled, respectively, as EXNaOH, EXH₂SO₄, EXH₂O for OB samples, and EXPNaOH, EXPH₂SO₄, and EXPH₂O for OBP samples subjected to reactive extrusion.

Pectin removal was performed according to the method reported by Kratchanova et al. [28], with some modifications. Specifically, the extraction was carried out in a hydrochloride acid solvent bath (HCl 0.05 M) under continuous stirring at 80 °C (OB: HCl solution ratio, 1:40 *w/v*). The solution extraction was filtered for solid fraction separation (insoluble fibers), added with an equal volume of absolute ethanol, and kept for two hours in a refrigerator. The pellet was collected and washed with a sequence of alcoholic solutions: 70% acidic ethanol (0.5% HCl), 70% ethanol, and 96% ethanol. Samples were dried at 50 °C to constant weight in a ventilated oven (035 Marconi MA—São Paulo, SP, Brazil) and milled to a fine powder (basic analytical mill, IKA-A11, Merck, Darmstadt, Germany). Pectin content was

calculated from the dry weight of pectin and compared with the initial OB sample. All experiments were conducted in triplicate.

The reactive extrusion process was performed using a single-screw extruder (AX Plastics, Diadema, SP, Brazil), with a diameter of 1.6 cm and a screw length/diameter ratio (L/D) of 40, with four heating zones and a matrix of 0.8 cm in diameter. The temperature in all zones was fixed at 120 °C, and the screw speed was 50 rpm. One hour before sample extrusion, reagents were dissolved in distilled water and homogenized with the raw OB and OBP in sealed plastic bags. All samples (120 g) were extruded with an initial moisture content of 40% (*w/w*). After extrusion, the samples were washed with water and neutralized to pH 5–6, dried in a ventilated oven at 40 °C (035 Marconi MA, Brazil), and milled (particles 0.3 mm).

2.2.2. Cellulose, Hemicellulose, Lignin, and Pectin Contents

The chemical composition of raw OB and cellulose-based materials were analyzed for cellulose, hemicellulose, and lignin concentrations. Cellulose and hemicellulose were measured by the Van Soest method [29], and lignin content was measured by the standard method of the Technical Association of Pulp and Paper Industry-TAPPI T222 om-88 [30].

The pectin content of raw OB was determined in the raw OB according to the method of Kratchanova et al. [28].

2.2.3. Fourier Transform-Infrared Spectroscopy (FTIR)

FTIR analysis was carried out using a Shimadzu FT-IR-8300 equipment (Tokyo, Japan), with a spectral resolution of 4 cm^{−1} and a spectral range of 4000–500 cm^{−1}. Dried samples were mixed with potassium bromide and compressed into tablets.

2.2.4. X-ray Diffraction (XRD)

The crystallinity of untreated and treated sample fibers was obtained using an X-ray diffractometer system (PANalytical X'Pert PRO MPD, Almelo, The Netherlands), with copper K α radiation ($\lambda = 1.5418 \text{ \AA}$) operating at 30 mA and 40 kV. The relative crystallinity index (CI) was calculated as follows: CI (%): $([I_{002} - I_{am}]/I_{002}) \times 100$, where I_{002} is the diffraction intensity at approximately $2\theta = 20\text{--}22^\circ$ (crystalline region), and I_{am} is the diffraction intensity at approximately $2\theta = 16\text{--}18^\circ$ (amorphous region) [31].

2.2.5. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was employed as a technique in which the thermal stability of samples was evaluated under a controlled temperature program. The materials were scanned at a heating rate of 20 °C min^{−1}, from 30 to 900 °C under a nitrogen atmosphere to prevent any thermoxidative degradation, using a Shimadzu thermogravimetric analyzer (Kyoto, Japan). T_{10} is considered the temperature corresponding to a 10% mass loss and was calculated from TGA curves.

2.2.6. Statistical Analysis

R software (SR Core Team. R, Vienna, Austria, 2016) was employed to perform an analysis of Tukey's mean comparison tests ($p \leq 0.05$).

3. Results

3.1. Extraction of Cellulose-Based Materials with Extrusion

In this study, the raw OB showed $12.4 \pm 0.6\%$ cellulose, $7.5 \pm 0.1\%$ hemicellulose, $8.9 \pm 0.5\%$ lignin, and $12.3 \pm 0.7\%$ pectin (Table 1). Cellulose, hemicellulose, lignin, and pectin contents in related studies in the literature are approximately 18–20, 6–14, 4–6, and 18%, respectively [8,13]. Such variations in the composition of OB can be explained to be due to fruit variety, harvest time, and conditions for juice extraction. The cellulosic fraction of OB has great potential for exploration, as the residue has high availability in Brazil.

Table 1. Insoluble fibers (cellulose, hemicellulose, lignin) contents, process yield, cellulose yield, and crystallinity index (CI) of raw OB and cellulose-based materials from OB obtained with extrusion.

Treatment	Cellulose Content (%)	Hemicellulose Content (%)	Lignin Content (%)	Process Yield (%) *	Cellulose Yield (%) **	CI (%)
OB	12.4 ± 0.4 ^f	7.5 ± 0.1 ^{cd}	8.5 ± 0.4 ^e	-	-	18
OBP	27.9 ± 0.5 ^c	6.5 ± 0.9 ^d	27.1 ± 0.9 ^a	55.6	100	42
EXH ₂ O	18.8 ± 1.6 ^e	10.6 ± 0.6 ^a	22.5 ± 1.2 ^b	79.2	100	38
EXH ₂ SO ₄	19.9 ± 0.5 ^{de}	7.4 ± 0.2 ^{cd}	23.7 ± 0.8 ^b	37.7	60.5	37
EXNaOH	21.2 ± 0.3 ^d	8.8 ± 0.9 ^{bc}	20.1 ± 0.2 ^{cd}	43.5	73.4	45
EXPH ₂ O	31.8 ± 0.5 ^b	10.4 ± 1.1 ^{ab}	18.6 ± 0.2 ^d	68.5	100	42
EXPH ₂ SO ₄	33.3 ± 0.6 ^b	8.1 ± 0.4 ^c	20.8 ± 0.3 ^c	30.6	82.3	43
EXNaOH	58.4 ± 0.6 ^a	3.7 ± 0.2 ^e	19.4 ± 0.1 ^{cd}	35.5	92.8	51

^{a-f} Different letters in the same column indicate significant differences ($p \leq 0.05$) between means (Tukey's test).

* Process yield: the amount of cellulose-based material obtained for each 100 g of raw OB or raw OBP (dry basis).

** Cellulose yield: cellulose content in relation to the original cellulose content of raw OB (dry basis) or raw OBP (dry basis).

The OBP showed $27.9 \pm 0.5\%$ cellulose, $6.5 \pm 0.9\%$ hemicellulose, and $27.1 \pm 0.9\%$ lignin. The initial acid treatment employed for pectin extraction possibly removed soluble sugars, gums, and aqueous extracts, among other non-fibrous components, which increased the cellulose and lignin concentrations and reduced the process yield, without affecting cellulose yield (Table 1). Pectin is the most complex polysaccharide that makes up the primary cell walls of all plants [32]; it is especially abundant in orange, and its content can vary from 13% to 35% depending on the extraction method used [33,34]. Pectin has been widely used in the food industry, as a thickener, emulsifier, and stabilizer, and in addition, it has shown many benefits for human health [35,36]. We suggest that the pectin fraction extracted in this study can be employed for future applications, although it is not the focus of this article.

Raw OB (OB) and depectinized OB (OBP) were modified with reactive extrusion to obtain cellulose-based materials. Table 1 shows the modifications on lignocellulosic fractions caused by extrusion. Extrusion processing significantly increased the cellulose content in all samples, including the control treatment (with water). The extrusion process is an energy-efficient, thermomechanical treatment for lignocellulose, combining heat, compression, and shear forces in a single process, which increases the surface area and pore size of the material, thus leading to physical and chemical disruption [3,4,27,37].

Mantovan et al. [1] reported that cellulose content of OB processed by an isolated alkaline treatment increased from 12.4% to 54.7%, with a process yield of 25%, a value close to that observed in this study for the EXPNaOH sample (58.4%); however, in this study, the process yield was 35% (Table 1). The combined (physical and chemical) processes in one step are promising approaches to reducing environmental impacts and overall costs [2,38].

The hemicellulose contents of extruded samples were close to those of the OB sample, ranging from 7.4% to 10.6%, except for the EXPNaOH sample (OBP extruded with NaOH), which presented the lower hemicellulose content (3.5%) (Table 1). Lignin content for all samples increased in relation to raw OB. The elimination of pectin increased the relative proportion of lignin and hemicellulose in extruded samples, even though mass loss occurred, which resulted in decreased process yields for these samples (Table 1). Possibly, a certain amount of cellulose is also degraded during reactive extrusion; only samples extruded with water (EXH₂O and EXPH₂O) did not show losses in their cellulose yields, with both samples presenting 100% cellulose yields (Table 1). Generally, treatments do not achieve absolute selectivity for the non-cellulosic fraction [1,19], resulting in decreased cellulose yields. Alkaline treatment combined with pectin extraction (EXPNaOH) resulted in a sample with higher cellulose content without a reduction in cellulose yield.

Pectin extraction processes from orange bagasse have been extensively studied under different conditions [33,34,39], but few studies characterize the fibrous material remaining after the pectin extraction. In this study, it was observed that the depectinized OB samples presented significant increases in their cellulose content after being subjected to treatments with water, acid, or alkali when compared to samples obtained from raw OB (Table 1). Pectin plays a role as a physical barrier restricting access to the cellulosic fraction [40]. According to Garcia-Amezquita et al. [6] and Larrea et al. [41], extrusion modifies the fiber composition of orange peel by increasing soluble fibers at the expense of a decrease in insoluble fibers. This same trend was also reported by other authors for soybean hulls [42] and oat bran [43] subjected to extrusion.

Alkaline treatment provided the highest cellulose content among all extrusion treatments, mainly for the OBP sample (Table 1). According to the cellulose yield data (Table 1), it is possible to verify that alkaline treatment was more selective in the degradation of non-cellulosic fractions, preserving cellulose fibers. Alkaline treatments have low cost and show excellent results in removing lignin and hemicellulose, without causing major environmental impacts [19,44]. Melikoğlu et al. [45] also reported the efficiency of this reagent for extracting cellulose from apple pomace.

For both EX and EXP materials, the use of sulfuric acid (H_2SO_4) did not significantly affect cellulose and lignin contents when compared with water treatment; hemicellulose content showed a slight decrease (Table 1).

3.2. Extruded Cellulose-Based Materials Characterization

3.2.1. Fourier Transform-Infrared Spectroscopy (FTIR)

FTIR spectra of the cellulose-based materials are shown in Figure 1. As can be seen, all spectra appeared to be rather similar, which indicates that cellulose, hemicellulose, and lignin fractions were preserved. This corroborates the chemical composition shown in Table 1.

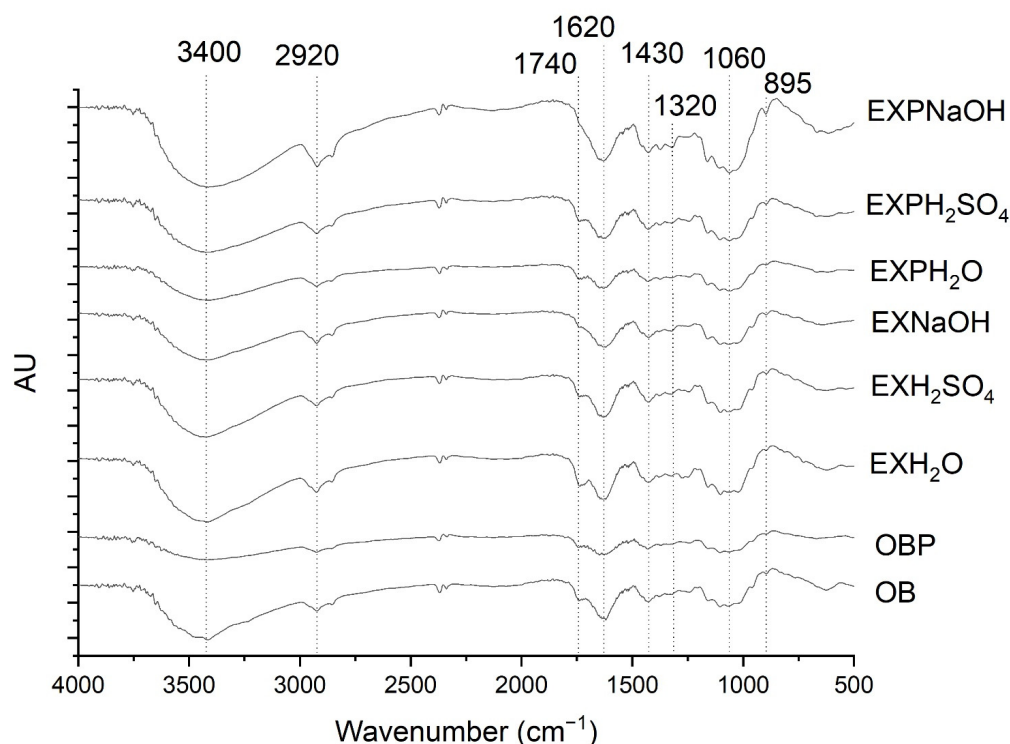


Figure 1. FTIR spectra of raw orange bagasse (OB), depectinized OB, and cellulose-based materials obtained with reactive extrusion.

All samples showed bands at 3400 cm^{-1} for intramolecular and intermolecular hydrogen bonds (OH), and 2920 cm^{-1} for C–H group stretching vibrations. The band at 1740 cm^{-1} can be attributed to ester and acetyl groups [46], and it was less evident in the spectra of materials treated with NaOH, suggesting that the alkali treatment removed higher contents of hemicelluloses and lignin, as observed by other authors [1,46].

The prominent band at 1620 cm^{-1} observed for all samples is attributable to cellulose–water absorption [5]. The band at 1320 cm^{-1} represents CH_2 stretching vibration. Cellulose β -glycosidic linkage was observed at 1060 and 895 cm^{-1} . The band at 1430 cm^{-1} can be related to lignin, and it was found in all samples [5,47].

3.2.2. X-ray Diffraction (XRD)

In XRD analysis (Figure 2), it was possible to observe that all the tested samples presented the typical patterns of semicrystalline materials, with the main crystalline peaks at $2\theta = 22^\circ$ and an amorphous region at $2\theta = 16\text{--}18^\circ$. In addition, a new peak was observed at $2\theta = 34.5^\circ$ for extruded samples.

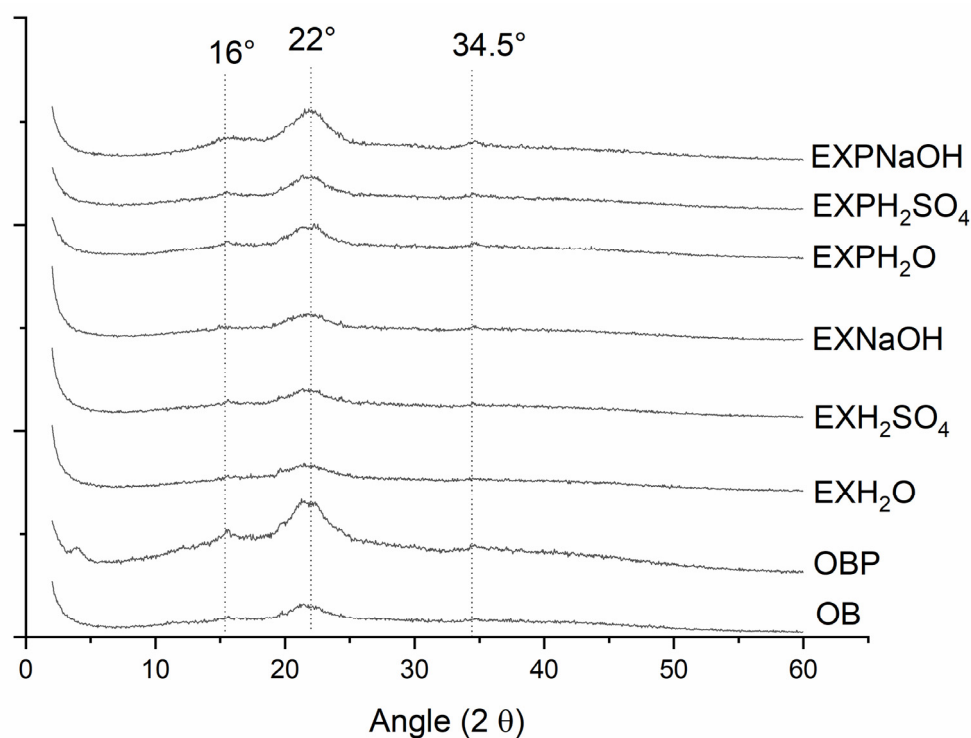


Figure 2. X-ray diffractograms of raw orange bagasse (OB), depectinized OB, and cellulose-based materials obtained with reactive extrusion.

The crystalline peak at $2\theta = 22^\circ$ increased for all extruded materials and for OBP samples, due to the physical and chemical treatments; consequently, the crystallinity index (CI) also increased (Table 1), indicating the partial removal of the amorphous regions from the residue [48].

CI was 18.1% for raw OB and changed according to the treatment employed (Table 1). The EXPNaOH sample showed the highest CI value (50.57%) due to its higher cellulose content (58.4%), while the EXNaOH sample showed a higher CI among the EX samples. The depectinized materials showed higher CI values when compared with the respective treatments in samples containing pectin. Pectin is an amorphous polysaccharide, and it also provides some resistance to the disruption of the lignocellulosic matrix [40].

3.2.3. Thermogravimetric Analysis (TGA)

In Figures 3 and 4, thermograms of cellulose-based materials are presented. The small weight changes of up to 100 °C were assigned to the evaporation of water from the samples. All samples showed double-peak decomposition patterns at 268–295 °C and 335–372 °C. A similar, two-stage decomposition was observed for orange bagasse treated with different alkaline extraction methods [2]. A third distinct decomposition stage was observed at temperatures above 450 °C for EX samples (obtained from raw OH), which could be associated with lignin degradation [49].

Materials that were not subjected to the pectin extraction process presented more complex chemical compositions, which resulted in more complex peak distributions; the same trend was also observed by other authors [4]. The decomposition of lignocellulosic products can be grouped into three stages: (1) hemicellulose degradation (110 to 290 °C), (2) degradation of cellulose (290 to 390 °C), and (3) lignin degradation (above 390 °C) [49].

T_{10} values corresponded to the initial decomposition temperatures at 10% degradation of the samples, and these values were obtained from TGA curves. All samples showed T_{10} values in the range of 110 to 121 °C, except the EXPNaOH sample, which showed a higher value (170 °C, Figure 4), and this probably occurred due to its more homogeneous chemical composition, with a higher cellulose content, as well as due to its higher CI.

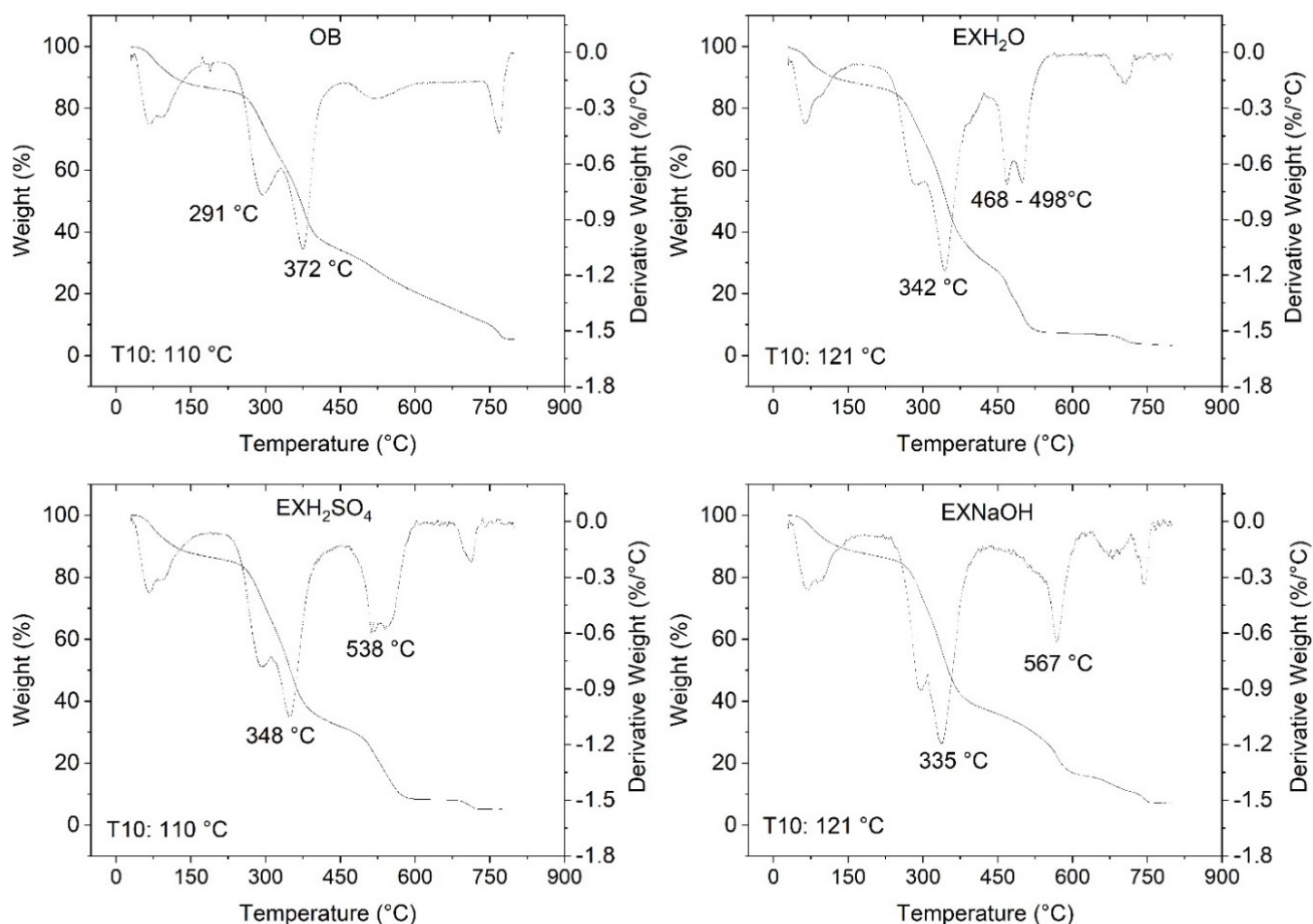


Figure 3. TGA and DTGA curves of raw orange bagasse (OB) and cellulose-based materials obtained with reactive extrusion (EX).

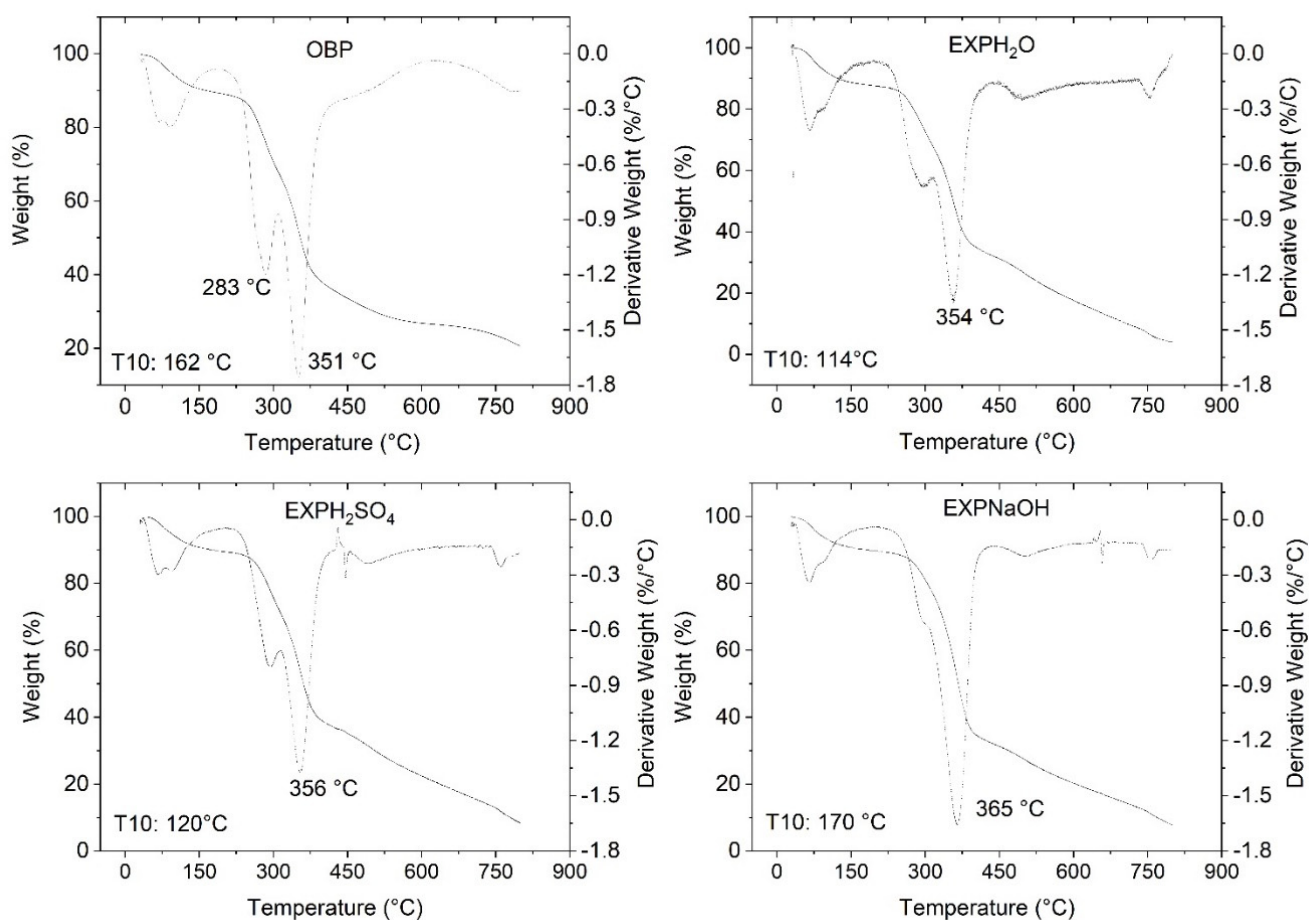


Figure 4. TGA and DTGA curves of depectinized OB (OBP) and cellulose-based materials obtained with reactive extrusion (EXP).

4. Conclusions

In this study, reactive extrusion was used as a green and simple route to prepare cellulose-based materials from orange bagasse. The modification of OB using an extrusion process was successfully accomplished and resulted in materials with 18.8% to 58.4% cellulose. Previous pectin extraction from OB effectively improved cellulose extraction. The alkaline treatment with NaOH was more efficient in removing non-cellulosic fractions from OB samples. The materials showed partial crystallinity and relative thermal stability.

One-step treatments were crucial to the determination of the economic viability and sustainable aspect of this study. Pectin and cellulosic fraction can be used for several applications and are aligned with concepts of biorefinery and circular economy.

Author Contributions: Conceptualization, J.M. and S.M.; methodology, J.M., S.M. and F.Y.; software, J.M.; formal analysis, J.M. and S.M.; investigation, J.M., S.M. and F.Y.; writing—original draft preparation, J.M. and S.M.; writing—review and editing, J.M. and S.M.; supervision, S.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by FINEP 01.21.0126.00.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors would like to thank the Universidade Estadual de Londrina-UEL facilities at the Multiuser Laboratories Center (CMLP-UEL FINEP), where X-ray, FTIR, and microscopy analyses were performed.

Conflicts of Interest: The authors declare no conflict of interest.

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