(RESEARCH ARTICLE)

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Assessment of the thermal degradation kinetics of fresh green coconut husk (*Cocos nucifera L.*) powder and after methyl levulinate production

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Abstract

This study describes the recycling of green coconut husk powder (CHP) aimed at the sustainable production of methyl levulinate. The preliminary step involved thermogravimetric analysis of green (CHP) and residues after synthesis of methyl levulinate with the catalyst's aluminum sulfate (CHP-AS) and titanium dioxide (CHP-TD), based on a degradation and determination of activation energy using the Ozawa-Flynn-Wall (OWF) method. Thermogravimetric analyses showed significant differences between the main constituents of CHP, CHP-AS and CHP-TD residues: hemicellulose (18.18, 9.78 and 12.17%), cellulose (44.65, 26.18 and 44.23%) and lignin (20.09, 19.89 and 19.58%), respectively. The methyl levulinate concentration obtained by the reaction between CHP and aluminum sulfate was 16.53 g.L^{-1}, due to the participation of hemicellulose and cellulose. The results showed that the activation energies calculated using the OFW method were 142 kJ.mol^{-1} (CHP), 125 kJ.mol^{-1} (CHP-AS) and 180 kJ.mol^{-1} (CHP-TD).

Graphical abstract
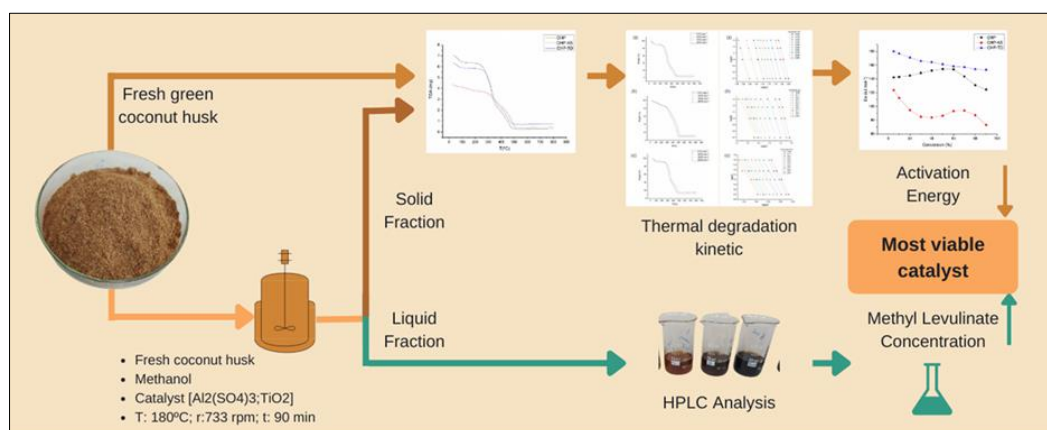
* Corresponding author: Leonete Cristina de Araújo Ferreira Medeiros Silva; E-mail: leonete.cristina@ufersa.edu.br
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1. Introduction

The transition to a low-carbon energy matrix requires searching for bioproducts and renewable energies, deemed limitless and with less environmental impact. Considered a renewable source, biomass is a viable alternative to the indiscriminate use of fossil fuel derivatives, responsible for greenhouse gas emissions and climate disorders [1]. The use of biomass favors cleaner and more sustainable production processes, thereby ensuring the development of chemical products, additives, biofuels and bioenergy in line with decarbonizing policies [2]. Thus, agricultural waste can be reintroduced into new bioproduct and bioenergy production chains, transforming an environmental liability into an energy asset [3,4]. Since it is highly resistant to degradation, numerous agricultural residues can cause incalculable damage to ecosystems and human life [5].

Brazil is the fifth largest coconut producer in the world, with a harvested area of approximately 223,000 hectares and estimated production of 1.05 billion fruits in 2020, the Northeast being the largest producer [6,7]. Given that each fruit produces 1 Kg of solid waste and has a decomposition time of around 10 years, its disposal in inappropriate areas, even sanitary landfills, results in high management costs and causes significant environmental impact [8]. Reusing this waste is an alternative to mitigate these problems by producing powder and fiber with specific properties that favor several applications. Fiber is used as raw material for crafts or agricultural input [9] and green coconut husk powder (CHP) as a biosorbent to remove metallic ions resulting from the presence of functional groups containing oxygen, hydroxyl and carbonyl [10-13] and in the formulation of additives and bioproducts since it is a source of lignin, cellulose and hemicellulose [4,14,15].

Currently, the scientific community is studying the transformation of lignocellulosic biomass into valuable, sustainable environmentally friendly products, such as 5-hydroxymethylfurfural, levulinic acid and levulinate esters [16]. The latter are a promising class of biomass derivatives with low toxicity, high lubrication, moderate flow at low temperatures and low vapor pressure [17]. Methyl levulinate (MLev) is a target product in biorefining and widely used as an additive in gasoline, diesel and biofuels, in addition to acting as a raw material for the manufacture of spices, coatings, herbicides, plasticizers, fragrances and pharmaceutical products, among others [2,18].

Thermogravimetric analysis (TGA) is becoming a widely used method due to its simplicity, precision and determination of broad spectrum of properties, particularly composition and thermal degradation [19;20]. This technique involves specific studies on the output of the transesterification reaction aimed at biodiesel production [21], in addition to compositional determination of hemicellulose, cellulose, and lignin present in several biomass sources, such as "dendezeiro" (oil palm) waste (empty fruit trusses, mesocarp fiber and palm husk), forest residues (wood shavings and powder), peanut shells, date palm petioles and alamo wood [20,22,23].

Isoconversional methods have been widely used to determine the non-kinetic parameters in pyrolysis processes and conversion reactions of solid raw materials and biomass [24,25,26]. It is presumed that the activation energies of kinetic degradation reactions are represented by activation energy distribution as a function of conversion degree [27]. Some authors combined TGA with isoconversional models aimed at determining kinetic parameters in different biomass sources (pineapple, orange and mango peel, rice husk, and açai berries) [23,28].

As such, this study proposes an unprecedented and innovative investigation on methyl levulinate production from green CHP for use as additives in biofuels, such as biodiesel. A preliminary step was to determine the energy potential of green CHP and after the conversion reaction into methyl levulinate using aluminum sulfate and titanium dioxide catalysts. To that end, decomposition analysis of green CHP was conducted and kinetic degradation assessed, in addition to determining activation energy using TGA and the Ozawa-Flynn-Wall (OFW) method.

2. Material and methods

2.1. Materials

Fresh green coconut *(Cocos nucifera L.)* husk powder was obtained from the Brazilian Agriculture Research Corporation (Embrapa), Embrapa Tropical unit (Ceará, Brazil). The synthesis reactions of methyl levulinate from green CHP were carried out with methanol (Dinâmica, 98%), and aluminum sulfate (Vetec, 98%) and titanium dioxide catalysts (Vetec, 98%).

2.2. Green coconut husk powder preparation

Embrapa Tropical developed the green coconut process to obtain powder for reuse in specific applications. The experimental procedure to produce green CHP with a particle size of 0.841 - 2.0 mm followed the methodology created by Embrapa [5], consisting of the following processes: pre-drying, grinding, drying and particle size classification. This methodology makes it possible to obtain CHP with the following textual properties: specific surface area - 1.86 $m^2.g^{-1}$, total pore volume - 0.0028 $cm^3.g^{-1}$, average pore volume - 2.9 nm and average particle diameter - 161.1 nm [29](Nascimento et al., 2020).

2.3. Methyl levulinate production

The conversion reactions of green CHP into methyl levulinate were conducted in the presence of methanol and catalysts, in line with the methodology applied in the synthesis of carbohydrate additives or directly from bamboo or wheat straw [28,30-32]. The reactions were conducted in a 300 mL pressurized stainless steel cylindrical reactor, with temperature adjusted by a coil and monitored by a thermocouple (Parr instrument, USA). The reactions were processed using 12.0 g of green CHP, 78.0 g of methanol and 1.2 g of aluminum sulfate [$Al_2(SO4)_3$] or titanium dioxide (TiO_2) catalyst for 15 minutes at an agitation speed of 733 rpm, with temperature controlled at 180 ºC. At the end of the reaction, the products were removed and filtered, obtaining a liquid phase (methyl levulinate) and solid fraction (green CHP waste). The methyl levulinate concentration was determined by liquid chromatography using a CTO-10ASvp chromatograph (Shimadzu) equipped with a CLC shim-pack column (4.5mm x 15cm), operating at a temperature of 65 °C. The mobile phase, consisting of a 2.5 mM sulfuric acid solution with a flow rate of 0.6 $mL.min^{-1}$, was responsible for transporting 10 µL of methyl levulinate, its detection ensured by the refractive index (RI) detector. Solid fraction composition was determined by TGA and activation energy estimated by the association between TGA and the Ozawa-Flynn-Wall (OFW) isoconversional method. It is important to underscore that the solid fraction was determined according to its condition: green CHP, green CHP after the reaction with aluminum sulfate (CHP-AS) and green CHP after the reaction with titanium dioxide (CHP-TD).

2.4. Thermogravimetric analysis

Thermogravimetric analysis (TGA) has been used to determine the composition of different types of biomass [33-35]. Thus, the study of decomposition green CHP was carried out by thermogravimetry using a TG/DTG analyzer (Shimadzu, DTG-60) with FC-60 flow controller and TA Acquisitions Status data acquisition software. Analyses were conducted with 6.0 ± 1.0 mg of the sample in inert nitrogen atmosphere, under the following conditions: temperature range between 25 and 800 ºC, heating rate of 10 $ºC.min^{-1}$ and flow rate of 50 $mL.min^{-1}$. The green CHP degradation curve was used to obtain the weight percentage of cellulose, cellulose, lignin, carbon, ashes, moisture and volatile material.

2.5. Isoconversional method

Thermogravimetric analysis combined with the isoconversional model makes it possible to determine apparent activation energy (Ea) [36]. The Ozawa-Flynn-Wall (OFW) and Kissinger-Akahira-Sunose (KAS) models are the most widely used [26] and can be applied to calculate kinetic parameters such as the degradation reaction rate, considering that conversion is only a function of temperature [37]. The Ozawa-Flynn-Wall (OFW) isoconversional method has been used to estimate activation energy values irrespective of the expressions of reaction speed. The success of the application is attributed to the approximate expressions used to integrate the Arrhenius equation. Activation energy was calculated with the OFW method, using a range of E/RT values from ambient temperature to 800 ºC and heating rates of 5, 10, 15 and 20 $°C.min^{-1}$. Applying different heating rates ensures a useful estimate of activation energy using the OFW method [38]. This method was developed for non-isothermal analyses and applies Doyle's approximation to determine activation energy without the need of knowing the order of the reaction. The OFW equation is expressed by Equation 1[39]:

$$\log \beta + 0.4567(Ea/RT) = constant \qquad (1)$$

Where β is the heating rate, Ea the activation energy, R the universal constant of ideal gases and T the reaction temperature (K).

3. Results and discussion

3.1. Composition of green coconut husk powder

The composition of biomass is one of the most relevant factors in identifying its energy potential in order to guarantee its application as a source of sustainable energy [24]. The thermogravimetric technique was used in the samples (CHP,

CHP-AS and CHP-TD) to obtain the content of the main constituents of green CHP (Table 1). The three residues exhibited moisture content below 10%, considered an acceptable limit to convert biomass in thermochemical processes [40]. In addition, these results corroborate the moisture content found in other lignocellulosic sources, such as tucumã seeds (7.6 %), banana trunk (6.67 %), and castor bean waste (11.14 %) [18,41,42]. Ash content was within the classic range for lignocellulosic biomass, namely, between 0.1 and 20 % [44]. Finally, hemicellulose and cellulose percentages declined for the CHP-AS residue, since they were consumed during the reaction. The decrease of these components is because one of the methyl levulinate production routes is through cellulose [18,30-32].

Table 1 Fresh green coconut husk powder (CHP) constituents and after the methyl conversion reaction (CHP-AS and CHP-TD)

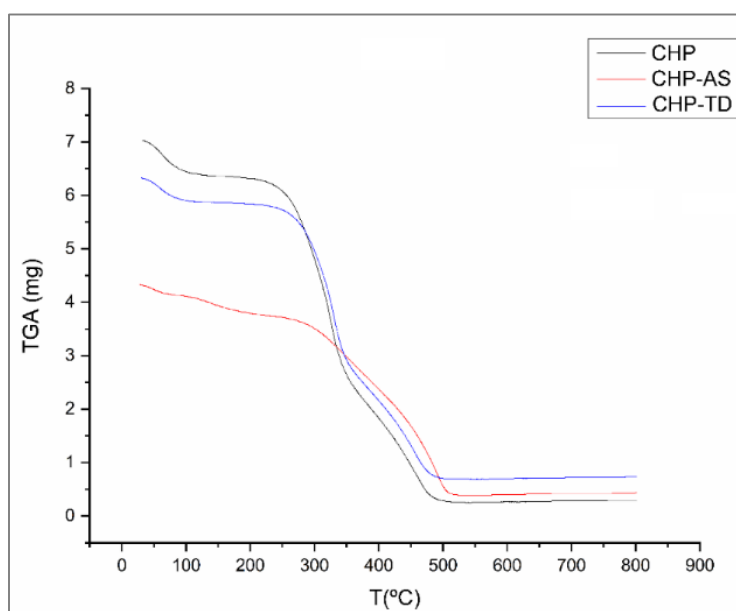| Constituents		Biomass		
Description	**Temperature Range**	**CHP**	**CHP-AS**	**CHP-TD**
Moisture (%)	0 - 100 ºC	8.946	5.149	6.729
Extractables (%)	100 - 250 ºC	4.963	9.051	2.764
Hemicellulose (%)	250 - 300 ºC	18.182	9.779	12.178
Cellulose (%)	300 - 400º C	44.651	26.183	44.227
Lignin (%)	400 - 470 ºC	20.093	19.89	19.586

Figure 1 Thermogravimetric profile of green coconut husk powder (CHP, CHP-AS and CHP-TD)

The evolution of the thermal degradation of green coconut husk powder (CHP, CHP-AS and CHP-TD) is shown in Figure 1. The first decomposition stage occurred up to a temperature of 100 ºC, indicating water evaporation, and the second, between 100 and 250 ºC, demonstrates the release of volatile constituents (water and holocellulose). The thermal degradation of cellulose and hemicellulose was observed at a temperature range between 250 and 450 ºC, exhibiting the highest weight loss from 35 to 62.83%. The last thermal degradation stage, which occurred between 450 and 800 ºC, represents lignin decomposition and ash formation, with a weight loss of less than 20%. With respect to the thermal degradation of hemicellulose, it is suggested that its structure amorphizes randomly and is richly branched, thereby facilitating removal of the main stem and contributing to the degradation of volatile compounds. In addition, with a structure displaying low polymerization, thermal degradation of hemicellulose may occur at low temperatures. On the other hand, cellulose, considered a long chain polymer, decomposes at temperatures above 300 °C, thermal energy capable of breaking cellulose bonds [22,36]. In the case of lignin, the significant presence of aromatic rings with several branches in its structure requires higher temperatures for total decomposition [45,46]. The behavior of green CHP

decomposition is similar to the degradation of other biomass sources, such as rice husk, pine sawdust, areca nut shell, hazelnut shell and plantain flower petals [23,27,36].

3.2. Thermal degradation assessment

A single heating rate may not describe the real nature of the reaction and could lead to mistaken interpretations [47]. Thus, a study based on four heating rates was performed (5, 10, 15 and 20 °C.min^{-1}) in order to ensure a robust interpretation of TGA profiles, showing weight loss in the samples (CHP, CHP-AS and CHP-TD) in the 100- to-800 °C temperature range (Figure 2). In all the cases studied, an increase in heating rate did not significantly change the thermal decomposition pattern of green coconut husk powder waste (CHP, CHP-AS and CHP-TD). However, an increase in heating rate causes a slight displacement of the degradation curve towards higher temperatures in a faster time frame. This behavior was also reported in thermal degradation studies conducted with açai and millet husk [28,48].
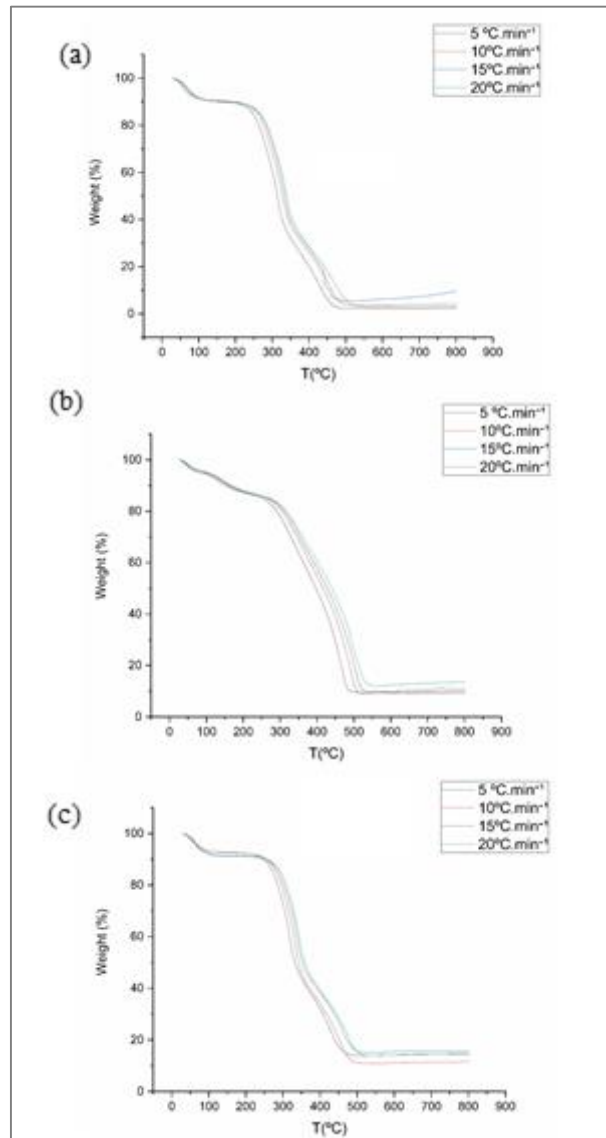

Figure 2 Thermal degradation profile as a function of different heating rates: a) CHP, b) CHP-AS and c) CHP-TD

3.3. Activation energy using the OFW method

The OFW model is used to measure the multiple scanning rate, ensuring kinetic analysis based on several green CHP residue TGA curves (CHP, CHP-AS and CHP-TD) obtained at different heating rates (5, 10, 15 and 20 °C.min^{-1}) (Figure 3). The behavior of straight lines related to the OWF model shows greater parallelism in values between 1.65 and 1.80 (Figure 3a), 1.40 and 1.60 (Figure 3b) and 1.40 and 1.45 (Figure 3c), suggesting hemicellulose and cellulose decomposition and the onset of thermal decomposition of lignin contained in green coconut husk powder waste (CHP,

CHP-AS and CHP-TD). This behavior was also observed in the thermal decomposition of lignocellulosic waste from sugarcane bagasse, sugarcane straw, rice husk and wood residue [49].
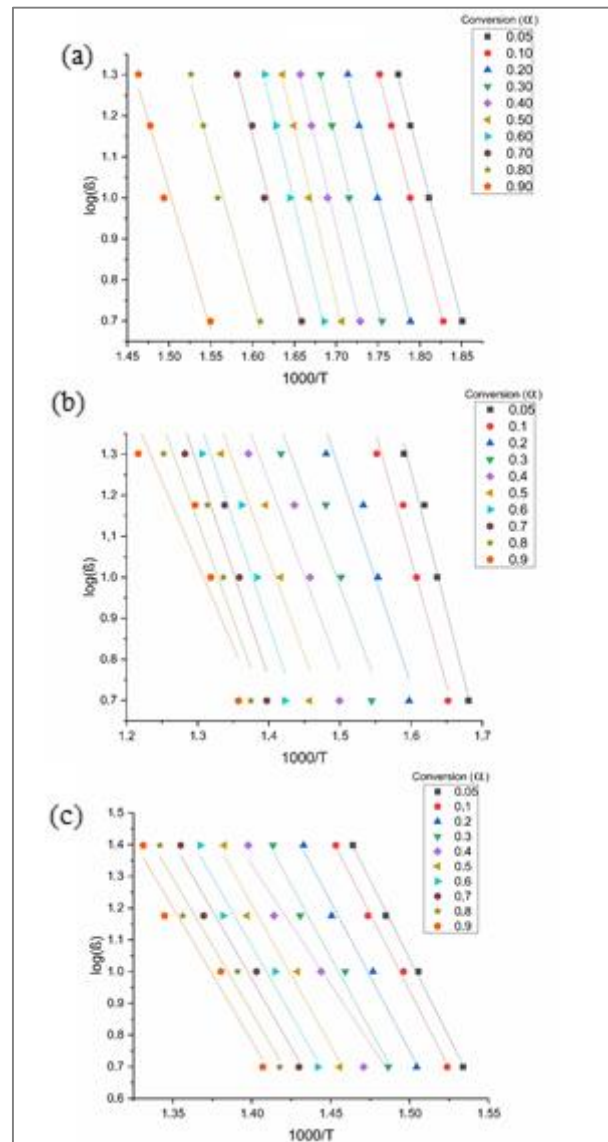

**Figure 3** Conversion evolution by analyzing the Ozawa-Flynn-Wall model: a) CHP, b) CHP-AS and c) CHP-TD

The coefficient of correlation (R^2) of each conversion reaction (α) was based on previously reported heating rates (Figure 3). In all the models, R^2 values ≥ 0.90 were obtained, confirming that the equations were reliably adjusted. The conversion rate used to obtain activation energy distribution, applying the isoconversional method, was 5-90 %, as reported in other studies [50,51]. In this respect, activation energy was obtained using the OFW method via equation 1. Table 2 presents the activation energy values of CHP, CHP-AS and CHP-TD residues, as a function of the conversion rate.

The kinetic properties of green CHP degradation were assessed based on activation energy (Ea) behavior as a function of the conversion rate (**Error! Reference source not found.**). This approach involved only the region of greatest weight loss, considered the pyrolysable fraction, as reported in kinetic studies of different biomasses, such as corn husk, wheat straw and hazelnut shells [27]. Given that activation energy depends on the conversion rate, the reaction mechanism is not identical in all the decomposition processes, but complex with multiple stages. However, according to studies on the kinetics of biomass degradation, the average Ea values reflect the preponderant influence of hemicellulose, cellulose and lignin [52].

Table 2 Activation energy (E_a) as a function of the conversion rate obtained by the OFW method

Conversion (α)	CHP	CHP-AS	CHP-TD
	E_a (kJ.mol^{-1})	E_a (kJ.mol^{-1})	E_a (kJ.mol^{-1})
0.05	142.30	123.78	180.05
0.1	142.79	112.20	176.75
0.2	144.86	94.58	170.94
0.3	148.49	84.91	165.87
0.4	152.23	83.88	164.36
0.5	154.30	86.43	161.36
0.6	153.80	93.11	158.31
0.7	143.43	93.96	157.14
0.8	130.82	87.30	154.16
0.9	124.51	73.15	153.27

It is important to underscore that the conversion range of α = 0.10 - 0.30 represents the onset of organic compound decomposition with initial activation energy of 143 kJ.mol^{-1} (CHP), 180 kJ.mol^{-1} (CHP-TD) and 125 kJ.mol^{-1} (CHP-AS). The thermal degradation of hemicellulose and onset of cellulose decomposition occurs primarily in the conversion range of α = 0.30 - 0.50, where the lowest activation energy was obtained with CHP-AS waste, Ea = 125 kJ.mol^{-1}, indicating the conversion of these constituents into methyl levulinate. The region representing the conversion of α = 0.50 - 0.80 shows cellulose decomposition and the onset of lignin decomposition. The increase in the activation energy of CHP residue in the conversion range of α = 0.50 - 0.80 may be due to the fact that green CHP is highly heterogeneous and its structural constituents have a specific degradation temperature range. The conversion rate of α = 0.80 indicates the start of the decline in degradation, demonstrated by the decrease in activation energy.
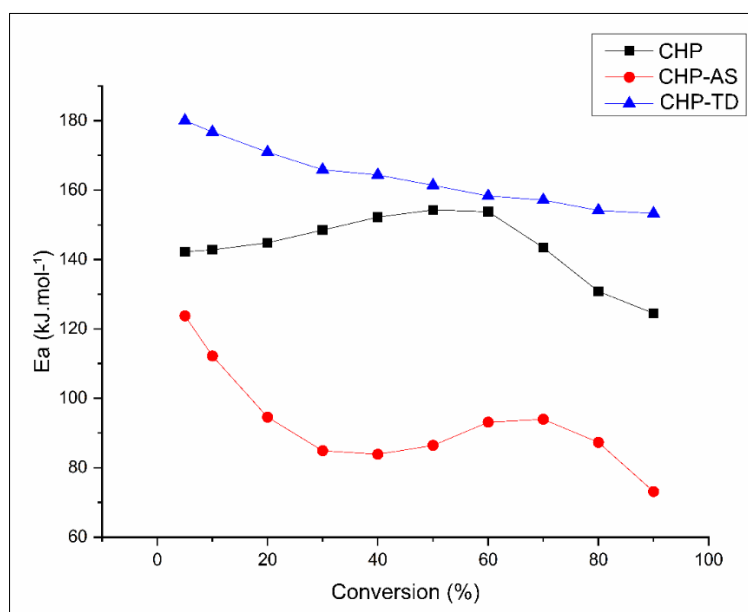
Figure 4 Evolution of activation energy versus the converted fraction of the samples (CHP, CHP-AS and CHP-TD)

In addition, the lower activation energy values obtained with the CHP-AS residue reveal the small amount of hemicellulose and cellulose, because of its conversion into methyl levulinate, a behavior previously observed in a compositional study using thermogravimetry. With respect to hemicellulose, activation energy decreased from 148 kJ.mol^{-1} (CHP) to 84 kJ.mol^{-1} (CHP-AS). In the case of cellulose, the activation energy declined from 154 kJ.mol^{-1} (CHP) to 86 kJ.mol^{-1} (CHP-AS). Thermogravimetry was used to determine the activation energy of different biomasses, producing the following results: Lagerstroemia speciosa (pride of India) seed husks (Ea = 164.00 - 141.93 kJ.mol^{-1}) (Nawaz et al., 2021), oil-free yeast (Ea = 111.32 - 211.50 kJ.mol^{-1}) [53] and açai seeds from the Amazon (Ea = 159.12 kJ.mol^{-1}) [28].

3.4. Methyl levulinate production

The methyl levulinate obtained from the reaction between green CHP and the aluminum sulfate catalyst [$Al_2(SO4)_3$] exhibited a concentration of 16.53 g.L^{-1}, while the methyl levulinate concentration obtained with the titanium dioxide (TiO$_2$) catalyst was 0.16 g.L^{-1}. These results corroborate the changes observed in the composition of CHP residue (CHP-AS and CHP-TD). In the case of CHP-AS, the hemicellulose and cellulose content declined, indicating they were consumed, favoring the production of methyl levulinate. The composition of CHP-TD did not change significantly, suggesting that hemicellulose and cellulose did not actively participate in the methyl levulinate conversion reaction. Thus, the TiO$_2$ catalyst was unable to accelerate this reaction. A number of studies used biomass waste to produce methyl levulinate from wheat straw and bamboo, achieving outputs of 20.22 and 30.75%, respectively [30,31]. Supplementary studies on the efficiency of methyl levulinate production will be conducted in future research, where experimental planning will be developed as a function of the main variables that control the green coconut powder conversion reaction (time, temperature, amount of catalyst, among others), in order to establish conditions that are favorable to methyl levulinate production from green CHP.

4. Conclusion

The present study explored the composition and activation energy of green coconut residues (CHP, CHP-AS and CHP-TD). The results demonstrate that aluminum sulfate was more favorable to methyl levulinate production, since TGA revealed a decline in cellulose and hemicellulose: 18.18 % (CHP) to 9.77% (CHP-AS) and 44.65% (CHP) to 26.18% (CHP-AS), respectively. These results were confirmed by the methyl levulinate concentration of 16.53 g.L^{-1} obtained by the CHP conversion reaction with the aluminum sulfate catalyst. With respect to the thermal stability of the samples, the increase in heating rate caused the degradation peak to displace to regions with higher temperatures, but without affecting degradation performance. The OFW model demonstrated that activation energy is related to the presence of hemicellulose and cellulose, as shown by the activation energy of 143 kJ.mol^{-1} (CHP), 180 kJ.mol^{-1} (CHP-TD) and 125 kJ.mol^{-1} (CHP-AS).

Compliance with ethical standards

Disclosure of conflict of interest

There are no conflicts to declare.

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