Comparative Study between the Thermal Decomposition and Biodegradation of Extruded Polystyrene by *Zophobas atratus* larval

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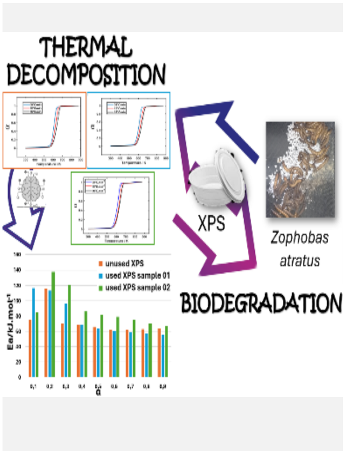
B. D. L. Ferreira[1], *R. C. O. Sebastião*[1], *Maria B. F. de Marques*[2], *J. D. Pereira*[3], *J. S. Santana*[4], *C. O de Souza*[2], *J. B. A. da Silva*[3,4], *A. A. Lucas*[6],*(1) Universidade Federal de Minas Gerais, UFMG, Belo Horizonte, Brazil. e-mail: darosbdlf@gmail.com. (2) Universidade Federal de Alfenas, UNIFAL, Alfenas, Brazil. (3) Universidade Federal da Bahia, UFBA, Salvador, Brazil. (4) Universidade do Estado da Bahia, UNEB, Salvador, Brazil. (5) Universidade Federal do Recôncavo da Bahia, UFRB, Cruz das Almas, Brazil. (6) Universidade Federal de São Carlos, UFSCAR, São Carlos, Brazil.*



Large amount of plastic waste is composed by extruded polystyrene (XPS). This polymer presents a natural slowly degradation and has become a worldwide environmental concern. This study investigates and compares the thermal decomposition process and biodegradation of XPS, by *Zophobas atratus* larval, both oxidative processes, but the larval process considered as an AOT. Non-isothermal experimental TG data and biodegradation data were used. The non-isothermal TG data are analyzed by applying isoconversional method to determine activation energy and pre-exponential factor and artificial neural network to determine the mechanism of the process. The neural network results provide an adjustment in TG curves with residual error of 10^{-4} up to 10^{-8} and the R3 model is assigned as an appropriate mechanism to describe the thermal process. The results provide information to understand and compare biodegradation and thermal decomposition processes. Energy costs were pondered, showing that although biodegradation has a higher cost, it is a sustainable better AOT.

Introduction

The accumulation of plastic waste, which is mainly produced using petroleum derivates, has become a worldwide environmental concern [1]. Conventional AOTs are promising alternatives to solve this problem in fast reaction but require high reagent consumption and have a maximum yield when associated with UV light sources [2]. Thermal decomposition and biodegradation are oxidative processes and can be an alternative without adding reagents, UV light sources and other apparatus. Studies have been conducted regarding the biodegradation of extruded polystyrene (XPS) and favorable results are obtained using larvae *Zophobas atratus* [3].

In this work, the kinetic of XPS thermal decomposition was studied and the results can be used to compare both processes, the thermal decomposition and biodegradation by larvae, as well as an economic study to evaluate the costs of both processes.

The XPS was obtained from commercial industry and this work provides an innovative procedure to compare biodegradation and thermal decomposition processes, bringing information about thermal decomposition mechanisms and alternative and sustainable biodegradation ways to promote waste reduction.

Material and Methods

The decomposition study was carried out with three different samples: one sample of unused XPS of lunch boxes and two samples of used XPS (used to pack red meat from 2 different sources). The TG curves of these three samples were obtained using Shimadzu DTG60H thermobalance with heating rates of 08, 12 and 16°C.min^{-1} under a controlled atmosphere of 50ml.min^{-1} of N_2 and sample mass of about 2.0 mg, accurately measured. The non-isothermal experimental TG curves were analyzed by isoconversional method to determine the activation energy and frequency factor, and artificial neural network to determine the contribution of kinetic models that best fit the TG data [4].

The biodegradation of XPS by *Zophobas atratus* larval study was carried out by monitoring their mass over 45 days.

Results and Discussion

The non-isothermal experimental data of α(T) obtained with heating rates of 08, 12 and 16°C.min^{-1} for the three samples are presented in graphical abstract. All curves were treated by the non-linear isoconversional method, and the activation energy values are in the Figure 1.

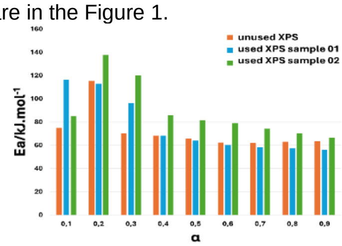


Figure 1. Activation energy along the process for the samples.

TG curves indicate the thermal decomposition event occurred in one step for the three samples and the mean values of activation energy, rate constant and frequency factor are present in Table 1.

Table 1. Mean activation energy, rate constant and frequency factor of three XPS samples.

Samples	Activation energy $kJ.mol^{-1}$	Rate constant $10^{-3}\ s^{-1}$	Frequency factor / ln(A) s^{-1}
unsed XPS	115.40	2.8929	19.979
used XPS sample 01	116.24	1.7014	19.904
used XPS sample 02	137.47	3.7208	24.883

High values for activation energy (Ea) (10-20% of conversion) are required to start the thermal decomposition process, but it is observed these values decreases along the process. The different values of Ea to the 3 samples, suggest it is depending on the composition of the food used in the lunch boxes. For the studied samples, it is noted that the used XPS samples presented superior Ea than the unused sample, which suggests that an additional energy must be supplied along the whole process in comparison to the unused sample.
The neural network fit procedure presented residual error of 10^{-5} for unsed XPS, 10^{-8} for used XPS sample 01 and 10^{-6} for used XPS sample 02. These results were obtained assuming a combination of kinetic models, which the contributions are presented in Figure 2.

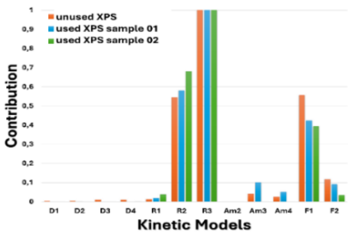


Figure 2. Normalized contribution of kinetic models.

Figure 2 shows a small modification of kinetic model contribution in the thermal decomposition process for the three samples, however the R3 model, volume contraction, presents greatest contribution in all samples, revealing itself as an appropriate mechanism to describe the process.
The heat required to thermal decompose the samples was determined from DTA curves. It was noted that, in the beginning of the process, it agrees with the Ea determined, validating the kinetic analysis performed in this work. This was verified, especially when the beginning of the process is separated in an initial event, (with a separated peak in the DTG curve). An economic study was carried out based on the heat required in the whole process, being 259 $J.g^{-1}$ (during 2859 s), 191 $J.g^{-1}$ (during 2861 s) and 180 $J.g^{-1}$ (during 2871 s) for unused XPS, used XPS sample 01 and used XPS sample 02, respectively. The costs are presented in Table 02, assuming R$1/KWh and the cost of the larvae.

Table 2. Energy costs for thermal decomposition and biodegradation of XPS.

Samples	Energy cost R$ / kg of XPS
unsed XPS	0.56
used XPS sample 01	0.23
used XPS sample 02	0.21
biodegradation	200.00

The energy costs to thermal decompose XPS on laboratory scale are lower than to perform biodegradation. Although the thermal decomposition process does not generate solid waste, it produces 3.4 kg of CO_2 per kg of XPS, which should be carefully considered. On the other hand, despite biodegradation presents superior cost, it produces solid waste that can be reused in the agricultural and food sector.
Conventional OATs, as photo-Fenton process [2], provides XPS degradation with adding reagents that can generate organic pollutants and its cost is also considerable. Considering these economic and sustainable aspects, the biodegradation presented promising results and more sustainable way in XPS degradation.

Conclusions

XPS thermal decomposition is an oxidative process and its biodegradation by *Zophobas atratus* larval is a sustainable AOT because it does not produce organic pollutants. The thermal decomposition study shows that the XPS samples presented similar behavior in the TG curves and the kinetic analysis using neural network describes the process with maximum residual error of 10^{-4}. The calculated Ea showed the process requires more energy to start and decreases along the process. Also, this energy is superior to the used XPS than to unused XPS. The heat required for the process was determined from the simultaneous DTA/TG experiments and the Ea agrees with the heat required to start the process for all samples, validating the kinetic study, that also presents the R3 model as an appropriate mechanism to describe the thermal decomposition. The biodegradation presented a higher cost than the thermal decomposition process, but sustainability is an important issue to be discussed.

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