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Short communication

# Flame retardant properties of the bark powder of *Anadenanthera peregrina* var. *falcata* (Benth.) Altschul (angico) studied by coupled thermogravimetry–Fourier transform infrared spectroscopy

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ABSTRACT

In this research, the bark powder of *Anadenanthera peregrina* var. *falcata* (angico) was characterized by means of simultaneous thermogravimetry–differential scanning calorimetry (TG–DSC) and differential scanning calorimetry (DSC) in order to investigate the chemical features responsible for the flame retardant properties of this plant. The TG–DSC and DSC data evidenced that dehydration occurs between 40 and 140 °C and that the anhydrous solid is stable up to 195 °C, when thermal decomposition begins. Coupled thermogravimetry–Fourier transform infrared spectroscopy (TG–FTIR) techniques were used to identify the volatile products evolved during the decomposition of the sample, showing that water and carbon dioxide are the majority products formed by its decomposition even at temperatures as low as 200 °C. The strong endothermic peak associated with the release of water provides a reasonable explanation for the fire retardant properties of angico.



## 1. Introduction

The *Anadenanthera peregrina* var. *falcata* (angico) is a plant species of the family Fabaceae and is a characteristic tree of the Brazilian Cerrado with high frequency and dispersion in this type of land, occurring in primary and secondary formations. It is a rustic plant resistant to droughts and even forest fires [1] and is widely used in construction, joinery and carpentry. The fire resistance exhibited by these structures is often attributed to the morphological features of this plant in such a way that the bark would exert a physical protection, functioning as a thermal insulator during fires and thus protecting the sapwood of the stem [2]. However, it is questionable whether other factors associated with bark would participate in such protection.

The occurrence of fires in the Brazilian Cerrado is one of the major environmental concerns due to the rich biodiversity of this ecosystem, constituted by more than 10,000 species of plants, being that around 4400 ones are endemic [3]. Every year, public and private sectors make many efforts in operations for both prevention and firefighting.

Among the several thermal methods of analysis employed to characterize solid compounds, evolved gas analysis (EGA) using coupled thermogravimetry–Fourier transform infrared spectroscopy (TG–FTIR) is widely used to evaluate properties of organic compounds since it can provide extremely useful information about the volatile products generated during thermal decomposition processes [4]. EGA studies using coupled TG–FTIR analysis have already been used, for example, to investigate the pyrolysis of wood lignin and the pyrolysis of poplar wood sawdust [5,6].

*A. peregrina* var. *falcata* stands out amid the various tree species in Cerrado for its high resistance against fires. This unique feature encouraged us to explore this plant using TG–FTIR techniques. In the present paper, we present some evidences about the mechanism adopted by this tree to survive in the arid habitat of Cerrado [7].

## 2. Experimental

Simultaneous thermogravimetry–differential scanning calorimetry (TG–DSC) curves were recorded on a TGA/DSC 1 STAR[e] System from Mettler-Toledo under the following experimental conditions: open α-alumina crucibles, heating rate of 20 °C $min^{-1}$, in an air atmosphere with flow rate of 100 mL $min^{-1}$ and samples of about 7 mg. Differential scanning calorimetry (DSC) curves were recorded using a DSC Q10 modulus from TA instruments under an air flow of 100 mL $min^{-1}$, at a heating rate of 20 °C $min^{-1}$, using covered aluminum crucibles with a pin hole ($\phi$ = 0.7 mm) and sample masses of about 2 mg. The DSC modulus

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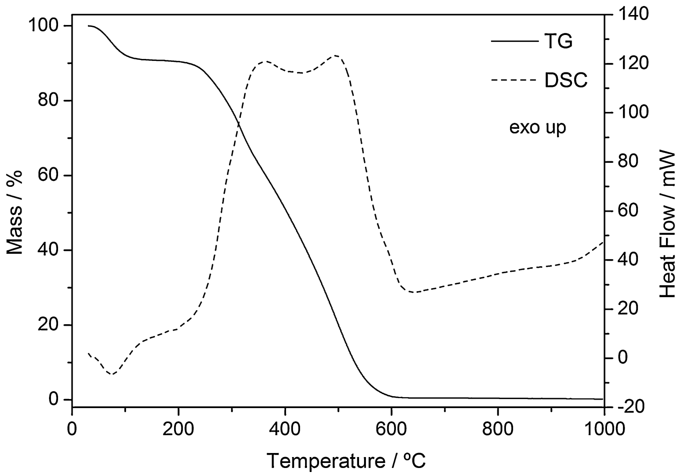


**Fig. 1.** TG–DSC curves of *Anadenanthera peregrina* var. *falcata* bark powder ($m$ = 7.080 mg).

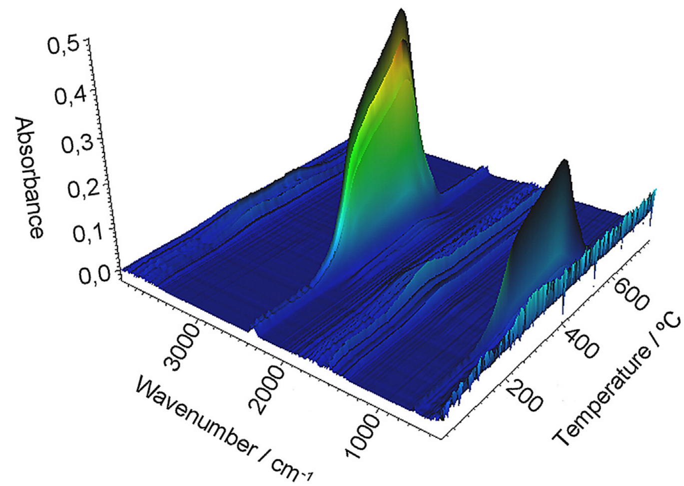


**Fig. 3.** 3D infrared spectra of the gases evolved from the thermal decomposition of *Anadenanthera peregrina* var. *falcata* bark powder between 30 and 700 °C.

was calibrated using indium metal (99.99+%) for temperature and enthalpy. Coupled TG–FTIR analyses were performed with a Nicolet iS10 IR spectrophotometer from Thermo Scientific coupled to the gas exhaust of the TGA/DSC 1 STAR$^e$ System. The attenuate total reflectance infrared spectra of the bark powder were recorded on a Nicolet iS10 IR (Thermo Scientific) an ATR accessory with Ge window.

## 3. Results and discussion

The TG–DSC curves of the *A. peregrina* var. *falcata* bark powder are shown in Fig. 1. The TG curve shows that the sample is stable up to 195 °C, when thermal decomposition begins, occurring as a single step up to 620 °C. The first mass loss, between 40 and 140 °C, is associated with the endothermic peak at 74 °C and corresponds to the dehydration of the sample ($\Delta m_1$ = 9.10%). The second step is observed between 195 and 620 °C ($\Delta m_2$ = 90.36%), with exothermic peaks at 363 and 495 °C, and is attributed to the oxidation of the organic matter. The final residue of 0.54% is due to ashes and non-volatile inorganic compounds.

The DSC curve of *A. peregrina* var. *falcata* bark powder is shown in Fig. 2. The endothermic peak at 84 °C, which is associated with a mass loss in the TG, was firstly attributed to the dehydration of the sample ($\Delta H$ = 200.5 J g$^{-1}$). However, the TG–FTIR analysis indicated that the release of carbon dioxide may give a contribution to this endothermic event.

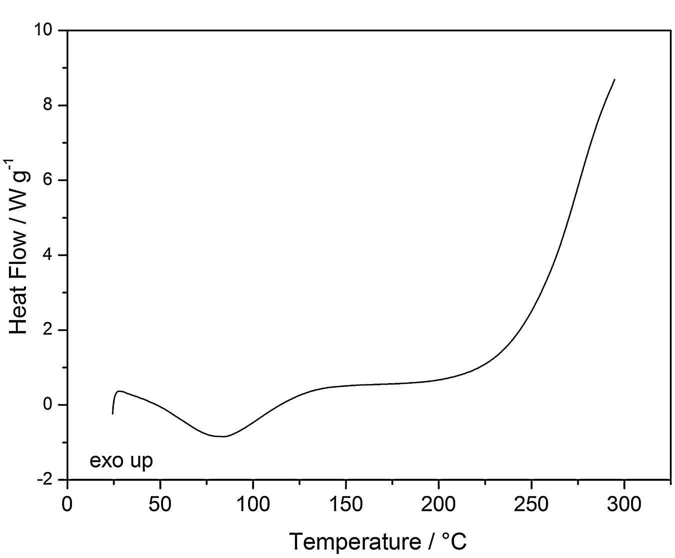


**Fig. 2.** DSC curve of *Anadenanthera peregrina* var. *falcata* bark powder ($m$ = 2.075 mg).

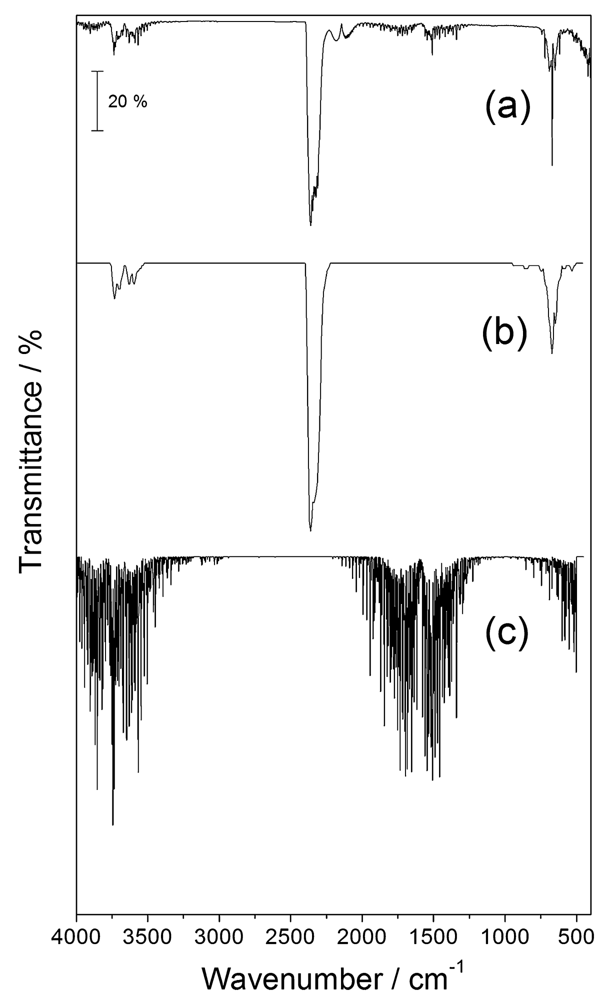


**Fig. 4.** FTIR infrared spectra of (a) gas collected at 140 °C, (b) $CO_2$ spectrum from the HR TGA vapor phase Thermo Fisher Scientific Inc. [8] and (c) $H_2O$ spectrum from the HR TGA vapor phase Thermo Fisher Scientific Inc. [8].

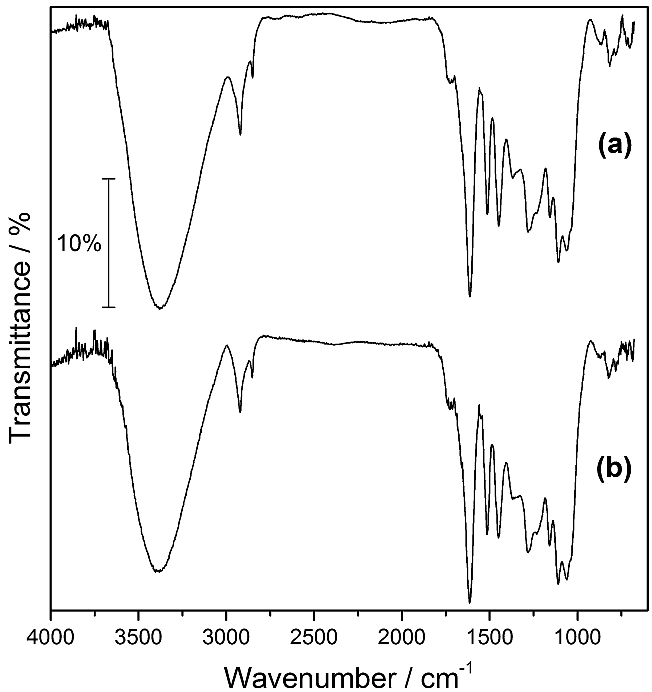


**Fig. 5.** FTIR infrared spectra of (a) raw bark powder of *Anadenanthera peregrina* var. *falcata* and (b) bark powder of *Anadenanthera peregrina* var. *falcata* after being heating to 150 °C.

Fig. 3 shows a 3D graphic consisting of the continuously collected FTIR spectra of the gases evolved during the heating of the sample from 30 to 700 °C. The selected FTIR spectrum of the gases collected at 140 °C is presented in Fig. 4. The results indicate that, up to 200 °C, carbon dioxide (Fig. 4b) and water (Fig. 4c) are the main volatile compounds released by the bark powder of angico.

A comparison between the FTIR spectra of the raw bark powder of *A. peregrina* var. *falcata* and of a sample previously heated to 150 °C is shown in Fig. 5. The results show a considerable decrease in the relative intensities of the absorption bands of water (3400 and 1610 $cm^{-1}$) when they are compared with other bands of the organic groups of the material (1510, 1450, 1270 and 1110 $cm^{-1}$ [6]).

## 4. Conclusion

The TG–DSC curves supplied information about the thermal stability and thermal decomposition of the *A. peregrina* var. *falcata* bark powder. The DSC curves allowed us to determine the enthalpy associated with the release of water and carbon dioxide ($\Delta H = 200.5\,J\,g^{-1}$), whose eliminations in the first mass loss were evidenced in the EGA analysis by coupled TG–FTIR. A sample of the bark powder of angico was heated to 150 °C and its FTIR spectrum showed a decrease in the amount of water (absorption bands at 3400 and 1610 $cm^{-1}$). The strong endothermic peak associated with the release of $H_2O$ and $CO_2$ at low temperatures may be responsible for the flame retardant properties of this plant.

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