

Materials Produced from Plant Biomass. Part I: Evaluation of Thermal Stability and Pyrolysis of Wood

Matheus Poletto, Juliane Dettenborn, Vinícios Pistor, Mara Zeni, Ademir José Zattera*

Laboratory of Polymers – LPOL, Center of Exact Sciences and Technology – CCET,
Caxias do Sul University – UCS, Caxias do Sul, RS, Brazil

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This paper compares the thermal stability of the sawdust of different wood species, an important factor in producing reinforced polymers. The compositions of two wood species, *Pinus taeda* and *Eucalyptus grandis*, were determined to evaluate the influence of the main wood components on the thermal stability of this material. The two species were submitted to thermogravimetric analysis at different heating rates to calculate the activation energy (E_a) using the Flynn-Wall-Ozawa (FWO) and Kissinger methods. The results suggest that larger quantities of holocellulose and lignin associated with lower extractive contents give the wood greater thermal stability. The E_a values calculated for the two species were in the range of 146-165 kJ.mol⁻¹. Evaluation of the activation energy values offers a simplified means to better understand the thermal decomposition of the sawdust of different wood species used in developing composites.

Keywords: lignocellulosic materials, thermal analysis, thermal stability, apparent activation energy

1. Introduction

The use of plant biomass materials, such as wood chips and sawdust, to reinforce thermoplastic polymers has gradually increased in recent years^{1,2}. These materials are biodegradable, are obtained from renewable sources, and have low density and high mechanical properties compared to glass fiber^{1,2}. However, they present limitations, such as low thermal stability and absorption of humidity³.

The thermal stability of wood is an important parameter for the production of reinforced polymers. Wood is used as an added load and improves the mechanical resistance of polymers that are processed at temperatures close to 200 °C³. The degradation of wood due to high temperatures at the time of processing may lead to undesirable properties, such as odor and discoloring, along with a reduction in mechanical properties³. The main chemical components of wood are cellulose, hemicellulose and lignin. Generally, the thermal degradation of wood involves a number of complex reactions^{3,4}. At heating rates below 100 °C/min there are four stages in the thermal decomposition of wood: evaporation of the water present; volatilization of the extractives; decomposition of the hemicelluloses; and subsequent decomposition of cellulose, while lignin is decomposed more slowly within a greater temperature range⁴. Cellulose presents crystallinity which makes it more thermally stable. Hemicellulose and lignin, on the other hand, are amorphous and their degradation begins at lower temperatures than in the case of cellulose⁴. Thermogravimetric analysis (TGA) is one of the most widely used techniques to evaluate the thermal decomposition of materials. The kinetic parameters of degradation such as activation energy (E_a) can be determined using this technique. These parameters can be determined experimentally, isothermally, with time variation⁵, or varying the heating rate (ϕ). This latter method is known as non-isothermal and is generally used to measure mass loss as a function of temperature⁶. Examples of non-isothermal techniques commonly used to determine E_a are the Kissinger method⁷, which assumes a maximum rate of conversion, and the methods proposed by Avrami^{8,9}, Ozawa¹⁰, and Flynn and Wall¹¹ which are based on the isoconversion method. Knowledge of the kinetic parameters associated with the thermal properties is an

important factor in estimating the thermal behavior of the polymers and composites¹². Wu and Dollimore¹³ studied the thermal degradation of several wood species at 200 to 650 °C using thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTGA) in an inert atmosphere. They obtained activation energy values varying from 160 to 180 kJ.mol⁻¹, using the method proposed by Arrhenius^{6,11}. D'Almeida et al.¹⁴, evaluating the thermal behavior of lignocellulosic fibers, obtained activation energies between 135 and 199 kJ.mol⁻¹ through the method proposed by Kissinger. The objective of this study is to investigate the thermal decomposition process of two different wood species and determine their activation energies with thermogravimetry using the methods proposed by Flynn-Wall-Ozawa (FWO)^{10,11} and by Kissinger⁷.

2. Experimental

2.1. Materials

The wood samples used in this study were obtained from wastes of the lumber industry in the northeast of the state of Rio Grande do Sul, Brazil. The species were *Pinus taeda* (*P. taeda*) and *Eucalyptus grandis* (*E. grandis*), which are also widely used to produce cellulose. The pine woods are known as softwoods (gymnosperms) and eucalyptus woods as hardwoods (angiosperms), because of the difference in their cell composition. The wastes were characterized by granulometric analysis using Tyler series sieves¹⁵. Samples with a particle size between 0.841-0.595 mm were used to perform the thermogravimetric analysis.

The basic constituents of the wood samples were determined according to the Klason method¹⁶, following the TAPPI Test Method T222 om-02 standard¹⁷, in triplicate, on dry samples kept in an oven for 24 hours at 105 °C. The extractives content was determined through three successive extractions (Soxhlet) with ethanol/benzene, ethanol and water. The determination of the acid-insoluble lignin was performed in triplicate using sulfuric acid and the ash content was determined by calcination at 600 °C for 2 hours.

*e-mail: ajzatter@ucs.br

2.2. Thermogravimetric analysis

Thermogravimetric analyses were performed on a Shimadzu TGA-50 analyzer in an N₂ atmosphere with a 50 cm³/min flow. Dynamic experiments were conducted using heating rates of 5, 10, 20 and 40 °C/min from ambient temperature (approx. 23 °C) to 600 °C. The mass used in each experiment was around 10 mg.

2.3. Theoretical considerations

The kinetic study of degradation consists of determining the degree of conversion of decomposed fractions (α). In non-isothermal experiments, (α) can be calculated using Equation 1^[18]:

$$\alpha = \frac{m_0 - m}{m_0 - m_\infty} \quad (1)$$

where m_0 is the initial mass, m is the mass at each time instant t at a temperature T and m_∞ is the final mass. The conversion rate of a kinetic reaction in the solid state $d\alpha/dt$ can be described as a function of $k(T)$ and $f(\alpha)$ as illustrated in Equation 2.

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (2)$$

where $d\alpha/dt$ expresses the conversion rate as a function of time, k is the rate constant and is a function of temperature, $f(\alpha)$ is a function of the reaction mechanism.

The rate constant is generally given by the Arrhenius equation (Equation 3):

$$k(T) = Ae^{\frac{-E_a}{RT}} \quad (3)$$

where E_a is the apparent activation energy (kJ.mol⁻¹), R is the gas constant (8.314 J.K⁻¹.mol⁻¹), A is the pre-exponential factor (min⁻¹), and T is the absolute temperature (K). Combining Equations 2 and 3 the Equation 4 is obtained:

$$\frac{d\alpha}{dt} = Af(\alpha)e^{\frac{-E_a}{RT}} \quad (4)$$

Since in this method one can vary the heating rate (ϕ), it can be observed that, in this case, the temperature and time are dependent on the heating rate (ϕ) of the experiment. This dependence can be described as (Equation 5):

$$\left(\phi = \frac{dT}{dt} \right) \quad (5)$$

Thus, the reaction rate of a non-isothermal event is described as (Equation 6):

$$\frac{d\alpha}{dT} = \frac{A}{\phi} e^{\frac{-E_a}{RT}} f(\alpha) \quad (6)$$

Several approaches have been proposed to solve the general equation (Equation 6), using different kinetic models to determine the kinetic parameters through thermogravimetric analysis. The method of Ozawa, Flynn and Wall^{10, 11} is one of the isoconversion methods used to estimate the activation energy, and it is based on Doyle's integral approach¹⁹ using the Equation 7:

$$\log(\phi) = \log\left(\frac{AE_a}{R}\right) - \log(g(\alpha(T))) - 2.315 - 0.4567 \frac{E_a}{RT} \quad (7)$$

where $g(\alpha(T))$ is an integral function of the conversion.

The isoconversion principle of FWO is based on the assumption that the rate of reaction in a given conversion is a function only of

temperature. At different heating rates with a constant conversion ($\alpha(T)$) a linear relation is observed on plotting $\log(\phi)$ vs. $1/T$, where the activation energy E_a is calculated according to the slope of the straight line obtained²⁰.

In the Kissinger method⁷, $\ln(\phi/T_p^2)$ vs. $1/T_p$ is used for different heating rates according to Equation 8, with the peak temperature (T_p) obtained from the peak of the DTGA curve, and is valid for first-order reactions. The activation energy is calculated from the slope of the straight line obtained.

$$\ln\left(\frac{\phi}{T_p^2}\right) = \ln\left(\frac{AR}{E_a}\right) + \left(\frac{1}{T_p}\right)\left(\frac{-E_a}{R}\right) \quad (8)$$

3. Results and Discussion

3.1. Chemical composition of wood

In order to determine the effect of the chemical composition of different types of wood sawdust on the thermal stability, the amounts of holocellulose (cellulose + hemicellulose), lignin and extractives were determined for the two samples. The wood degradation temperature is expected to be related to the thermal stability of its individual components and the differences in the thermal stability of the sawdust samples can be attributed to variations in the chemical composition of wood^{3, 21}. The chemical composition of the sawdust samples of the two wood species used is shown in Table 1.

According to Table 1, differences can be observed in the composition of the two wood species. *E. grandis* presented greater quantities of holocellulose and lignin than *P. taeda* wood. The quantity of extractives, composed of waxes, grease, resins, tannins, sugars, gums and pigments, for the wood of *P. taeda* was around twice that for *E. grandis*. At 600 °C no significant differences were observed in the amount of ash for the two species analyzed. The holocellulose content of untreated wood is generally around 60-70% that of dry wood²². The lignin content usually varies between 18-25% for hardwoods and between 25 and 35% for softwoods²². In general, the extractives content is between 4 and 10%^[23].

3.2. Thermal stability of wood

The thermal stability of the two wood species was determined by thermogravimetry. The mass loss increases with temperature, for a heating rate of 20 °C/min, are shown in Figure 1. The curves show a mass loss at below 100 °C, which can be attributed to the evaporation of water present in the sample. The mass loss increases gradually up to approximately 200 °C, and then a more marked mass loss occurs between 200 and 400 °C. The two samples showed a mass loss of around 75% on reaching 400 °C.

The degradation of the *E. grandis* wood presents two peaks and a shoulder at approximately 285 °C, and the *P. taeda* wood showed only two degradation peaks, as seen in the DTGA curves. In the region between 200 and 400 °C two distinct events occur. The first event, observed at 210-300 °C, can be associated with the decomposition of hemicellulose and the slow degradation of lignin. The second event at approximately 350 °C can be attributed to the

Table 1. Chemical composition of the sawdust samples of the wood species investigated.

Wood species	Holocellulose (%)	Lignin (%)	Extractives (%)	Ash (%)
<i>P. taeda</i>	61.2 ± 0.2	25.6 ± 0.1	9.3 ± 0.7	3.9 ± 0.3
<i>E. grandis</i>	64.4 ± 0.3	27.6 ± 0.7	4.2 ± 0.2	3.7 ± 0.2

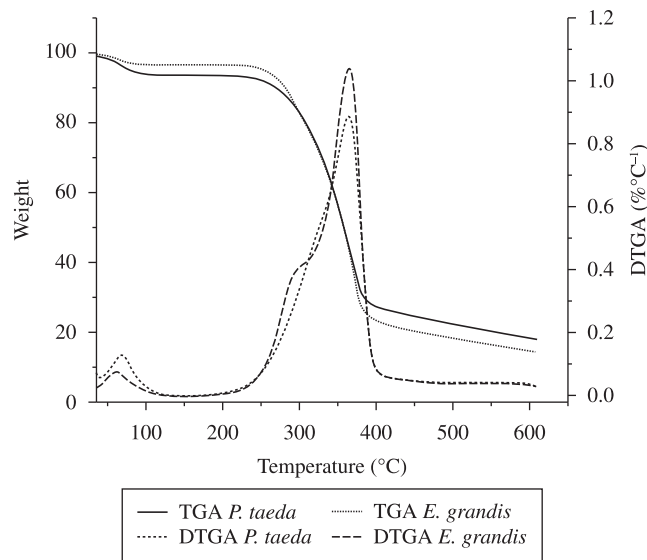


Figure 1. Thermal decomposition of the wood samples studied.

degradation of cellulose. These results are consistent with previously published data^{3,18,21}. According to Kim et al.²⁴, the depolymerization of hemicellulose occurs at 150-350 °C, the random cleavage of the glycosidic linkage of cellulose at 275-350 °C, and the degradation of lignin at 250-500 °C. However, the differences observed in the DTGA results may be associated with the amount of extractives in the wood samples (Table 1). The higher amount of extractives in *P. taeda* may account for the difficulties encountered in identifying the distinct degradation phenomena³. At lower temperatures *P. taeda* is less stable than *E. grandis*, as show in Figure 1. This behavior can be attributed to the higher extractives content. The *E. grandis* sample had higher holocellulose and lignin and lower extractives contents than *P. taeda* (Table 1). Shebani et al.³ and D’Almeida et al.¹⁴ demonstrated that higher cellulose and lignin content in lignocellulosic materials leads to a greater thermal stability. This factor thus contributes to the greater thermal stability at temperatures close to those of the processing of thermoplastic composites reinforced with wood (around 200 °C).

3.3. Apparent activation energy (E_a)

The TGA thermograms obtained at several heating rates for the *P. taeda* and *E. grandis* samples are shown in Figures 2 and 3, respectively. A gradual displacement of the curves to higher temperatures is observed with increasing heating rate. This phenomenon is expected because the low heating rates generate large intervals of time to obtain the curves. It can be seen in Figure 2 that there is an anomaly in the rate of 20 °C/min until at least 20% of weight loss, which may be related to analytical error. However, a conversion range of 0.2 to 0.7 was evaluated in this study, thus validating the curves presented.

The activation energy calculated according to the FWO method, through TGA analysis, is called the apparent activation energy, because it is the sum of the activation energies of the chemical reactions and physical processes that occur simultaneously during thermal degradation⁶. In Figures 4 and 5, the curves resulting from applying the FWO method to *P. taeda* and to *E. grandis* can be observed, showing conversions of between 0.2 and 0.7. It can be also be observed that the correlation coefficients (R) were between 0.982 and 0.999, and that the lines are positioned close and parallel to each other, indicating small variations in the activation energy according to the conversion¹⁸. The degradation kinetics of wood can be summarized

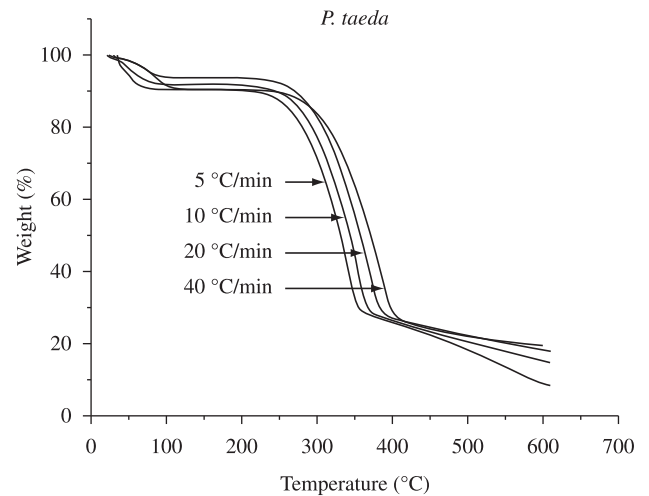


Figure 2. Thermograms (TGA) with different heating rates for *P. taeda*.

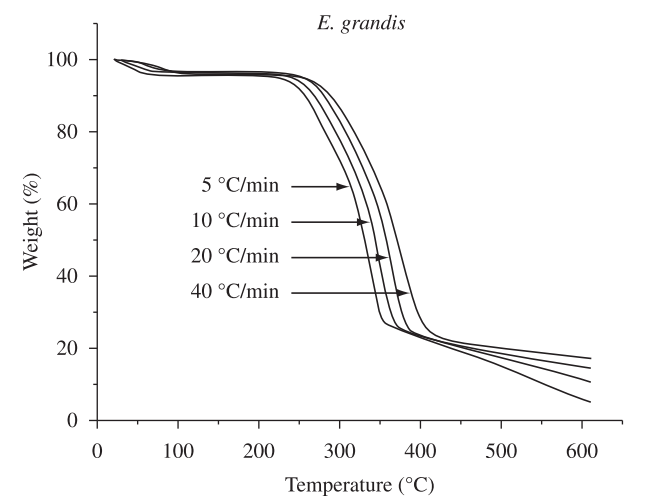


Figure 3. Thermograms (TGA) with different heating rates for *E. grandis*.

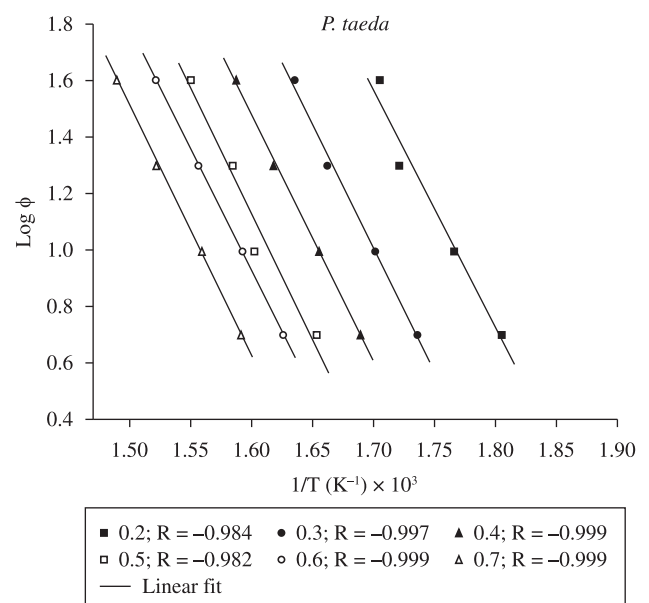


Figure 4. FWO method applied to *P. taeda* wood.

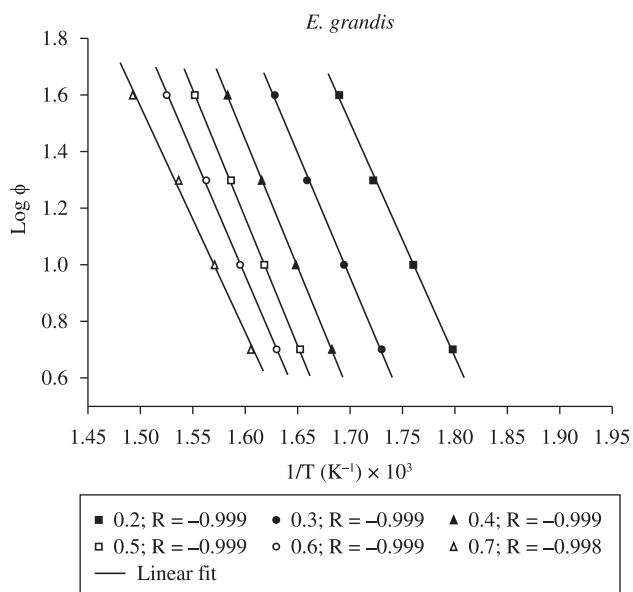


Figure 5. FWO method applied to *E. grandis* wood.

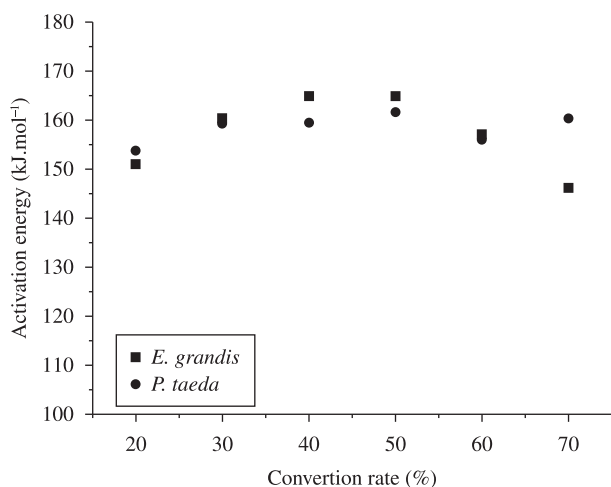


Figure 6. Variation of the activation energy with conversion for the investigated samples.

by three independent first-order reactions²⁵, corresponding to the decomposition of the three main components of wood: the most reactive fractions of hemicellulose, cellulose, and lignin, and lastly the remaining fraction of carbohydrates²⁵. In this study, the conversion range analyzed relates to the decomposition of cellulose.

The activation energy values varied between 153–163 kJ.mol^{-1} for *P. taeda* and 146–165 kJ.mol^{-1} for *E. grandis*, thus being almost the same for the two wood species, as is clear in Figure 6. Yao et al.¹⁸ studied ten different types of natural fibers and obtained activation energy values of 150–170 kJ.mol^{-1} , indicating that in the thermal decomposition of natural fibers the activation energy does not vary, or varies minimally after the initial mass loss stage, and remains practically constant up to $\alpha = 0.6$. When the more volatile components are degraded at below $\alpha = 0.2$, differences in the activation energy values can be observed. Thus, in the range of degradation of cellulose studied for the two woods significant changes were not observed.

The method proposed by Kissinger was also used to determine the activation energy. Figures 7 and 8 show the derivative

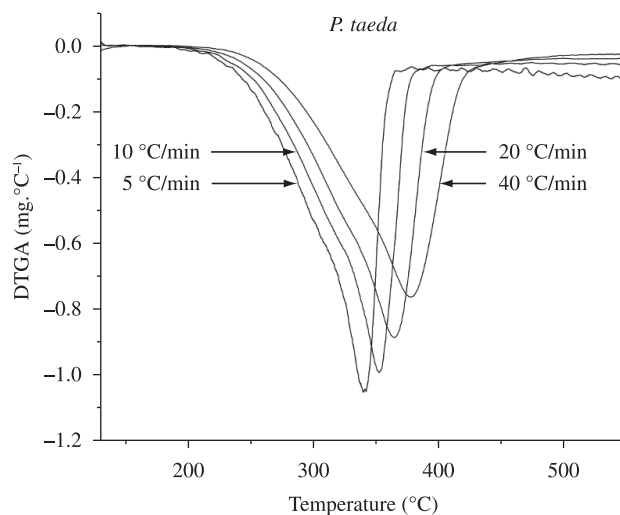


Figure 7. DTGA curves for *P. taeda* applying the Kissinger method.

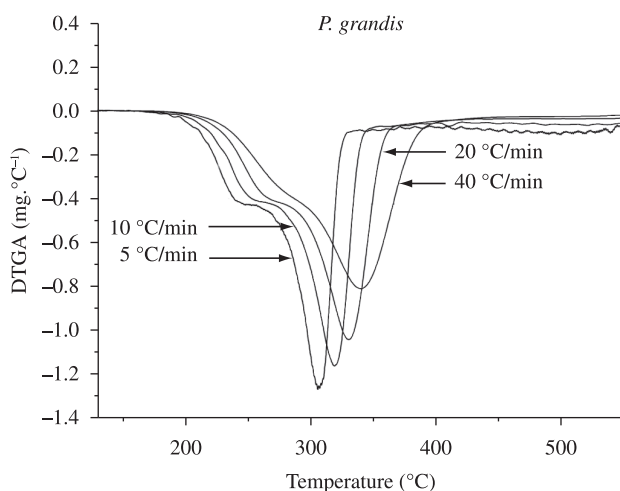


Figure 8. DTGA curves for *E. grandis* applying the Kissinger method.

thermogravimetric curves used to calculate E_a applying the Kissinger method. The values assumed for the calculation are the maximum peak values of the derivatives⁷. Figure 9 shows the curves resulting from applying this method. The correlation coefficients are also close to unity. For *P. taeda* the E_a was 148.6 kJ.mol^{-1} and the R value was 0.994, and for *E. grandis* the respective values were 165.9 kJ.mol^{-1} and 0.998. The activation energy value calculated by the Kissinger method for *P. taeda* is below that calculated using the FWO method, whereas for *E. grandis* the value obtained is within the previously calculated range. Although the model proposed by Kissinger is valid for first-order reactions and considers the peak temperature of the DTGA, the values obtained, even with a more distant average value, seems to be consistent with the range of values obtained by the FWO method.

As suggested by Brown et al.²⁶ the different methods of kinetic analysis are complementary and not competitive. Wood is an anisotropic material and the quantity of principal components in its composition, as well as the presence of inorganic components, varies according to factors such as geographical location and complexity of growth, directly affecting the degradation process and the activation energy. However, despite these factors the two woods showed very similar thermal behavior.

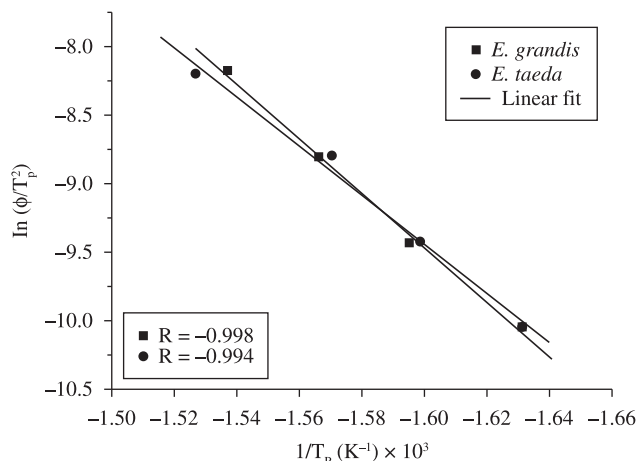


Figure 9. Graph of $\ln \phi / T_p^2$ vs. $1/T_p$ obtained by the Kissinger method.

4. Conclusions

Thermogravimetric analysis (TGA) was used to determine the thermal stability and activation energy of *P. taeda* and *E. grandis* woods, which are commonly used as applied loads in polymers and also in the lumber and paper pulp industries. The results showed that degradation of sawdust samples of these wood species begins at between 210 and 230 °C, with a high mass loss of around 75% on reaching 400 °C. At temperatures above 400 °C the lignin decomposition processes occur. The *E. grandis* wood was found to have better thermal stability than *P. taeda* at temperatures near the processing temperatures of thermoplastic composites reinforced with wood, probably due to greater amounts of holocellulose and lignin associated with lower contents of extractives in the former. The activation energy values for the two samples are between 146-165 kJ.mol⁻¹. These data are important in order to gain a better understanding of the degradation mechanisms of different types of woods and supply information which can be used to determine the best polymer processing conditions when wood is used as a reinforcement material.

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