



Kinetic study of vetiver grass powder filled polypropylene composites

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ABSTRACT

Polypropylene composites containing vetiver grass powder as filler are used in Thailand in many applications, i.e. household articles, furniture and office appliances. A widely used method of disposal of these composites after use is through pyrolysis in incinerators, gasification plants, or combustion systems. A knowledge of the pyrolysis kinetics of these composites is useful for the efficient design of these disposal plants. In this paper, the results of an experimental study of the pyrolysis kinetics of polypropylene (PP), vetiver grass, and PP composites containing vetiver grass powder are presented and mathematical models of the kinetics are developed. A thermogravimetric analysis of the PP, vetiver grass and PP composites has been carried out. Mass loss data for the thermal decomposition process have been obtained for PP, vetiver grass and PP composites at four different heating rates of 5, 10, 15 and 20 °C min⁻¹ in a nitrogen atmosphere. The kinetics of the PP decomposition has been modeled by a single-stage reaction describing the degradation of hydrocarbon polymer. The kinetics of the vetiver grass decompositions are modeled with three independent decomposition reactions describing the degradation of hemicellulose, cellulose and lignin. The kinetics of the decompositions of the vetiver grass filled PP composites are modeled by both a three series reaction process and by a process involving three independent reactions. One of the three independent reactions modeled the decomposition of hemicellulose and cellulose, the second modeled the main decomposition of PP and remaining cellulose, and the third modeled the decomposition of lignin and remaining cellulose and PP. Values of the kinetic parameters (activation energy, pre-exponential factor and reaction order) are obtained which give a good fit between the kinetic models and the experimental data.

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1. Introduction

Polymers are widely used in many applications. Commonly used polymers include resin, thermoplastic starch and polyolefins (polyethylene (PE), polypropylene (PP)). PP is one of the fastest growing general-purpose thermoplastics in use today as it is lightweight, and has relatively low cost, excellent chemical resistance, moderately high melting temperature and good processability. Compared to PE, PP provides higher thermal stability and lower cost [1].

Polymers are often reinforced with various filler materials. In the past decade, the use of lignocellulosic materials as reinforcing fillers in polymer composites has attracted increased attention [2–7]. These naturally occurring fillers are of interest since the production of composites using them is inexpensive and their use can reduce environmental problems caused by the use of artificial fillers. In Thailand, a widely used natural filler is vetiver grass. Vetiver grass

is a tropical plant that grows naturally in Thailand in an extensive range of areas from lowlands to highlands and polypropylene composites containing vetiver grass powder as filler are used in many applications such as household articles, outdoor furniture, door panels, decking, fencing, window parts and office appliances.

Most plastics take a very long time to decompose in nature. Therefore the disposal of polymers after use is an important problem in waste disposal. Commonly used methods involve thermal decomposition in incinerators, gasification plants or combustion systems. TGA is a widely used method for studying the mass loss and thermal decomposition of solid materials as it gives an understanding of the devolatilization kinetics of solid and liquid materials during combustion and pyrolysis. The thermal decomposition of synthetic polymeric materials was studied by many authors and the kinetics of the degradation process has been determined for some important polymers. Most of these studies focused on the kinetic parameters of a PP matrix [1,8–10] or PP alone [11,12]. However, a limited number of studies reported the thermal decomposition of polymer composites filled with a variety of materials [1,9,13]. For example, Wielage et al. [1] studied the thermal degradation of PP grafted with 1% maleic anhydride using

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thermogravimetric analysis (TGA) and a differential scanning calorimeter (DSC). Gersten et al. [9] studied the pyrolysis of a mixture of PP and oil shale in order to improve the effectiveness of oil shale processing and decrease waste problems. Day et al. [13] studied the thermal degradation of PP among other polymers in the presence of copper, iron oxide and dirt.

TGA has been used to study the decomposition process of biomass during combustion or pyrolysis (see, e.g. [14–17]). TGA has also been used to study the non-isothermal decomposition kinetics of residue with plastics (PP and bakelite) and to compare the kinetics with that of the individual components in order to understand the cracking reactions that occur during co-processing [15].

Several authors [15–21] have emphasized that the knowledge of the kinetics of the chemical and thermal processes during pyrolysis of biomass, fuel or polymers is very important for the design and operating conditions of the incinerators, combustion furnaces or gasification plants used for the pyrolysis or combustion of these materials. TGA is a useful tool for determining the kinetics of pyrolysis. Conesa et al. [22] questioned themselves on the validity and utility of the different methods for kinetic analysis of thermogravimetric data concluding that if the model has been obtained correctly, i.e. a model that fits runs performed in different conditions (such as different heating rates), with a correct treatment of the data, it will reproduce experimental data properly, allowing a reactor to be designed.

The aim of the present work is to model the kinetics of PP and PP composites containing vetiver grass by the thermal decomposition in TGA under nitrogen atmosphere, at four different heating rates. Satisfactory models are summarized and the optimized kinetic parameters are reported and discussed.

2. Experiments

2.1. Materials

PP homopolymer (P400S, Thai Polyethylene Co., Bangkok, Thailand) with a melt flow index of 4.13 g 10 min⁻¹ and density of 0.903 g cm⁻³ was used as a matrix polymer. Vetiver grass (*V. zizanioides*) obtained from the Royal Project Foundation (Thailand) was used as a lignocellulosic filler. The dry leaves of the vetiver grass were ground into fine powder using a grinder. Composites of PP filled with 10% weight vetiver grass powder were prepared by melt-mixing in a co-rotating twin-screw extruder (Prism TSE 16, UK). The temperatures used were in the range of 180–200 °C. The extruder was operated at 150 rpm.

2.2. Methodology

The thermogravimetric studies were carried out in dynamic (non-isothermal) mode at four different heating rates of 5, 10, 15 and 20 °C min⁻¹ in nitrogen atmosphere. The equipment used for conducting the thermal decomposition experiments was a PerkinElmer thermobalance Module Pyris-1 TGA. The sample masses used were about 4–5 mg. The operating conditions were as follows. The nitrogen flux was set at approximately 60 ml min⁻¹ with a 90 min purge time used to ensure that the air was evacuated from the system and that the atmosphere was inert. The initial temperature was chosen as 50 °C and the final temperature as 850 °C.

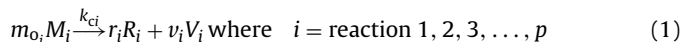
3. Kinetic analysis

3.1. Kinetic models

Two different kinetic models were examined to obtain a kinetic law for each sample.

The first kinetic model assumed independent processes for the decomposition of the different constituents of the PP polymer, the vetiver grass and the polymer composite. The second kinetic model assumed series reaction processes for the constituents.

The independent process model is as follows. If there are p independent processes, then the reactions can be written as:



where i varies from 1 to p , and p denotes the number of reactions; M_i is the initial solid which follows reaction i ; R_i and V_i are the residue and the volatiles generated in reaction i , respectively; m_{o_i} is the initial reactant mass fraction coefficient in individual independent reaction i ; r_i and v_i are, respectively, the yield coefficients of residue R_i and the volatiles V_i expressed as grams of R_i or V_i divided by grams of reacted solid. The yield coefficient v_i is the maximum amount of volatiles evolved by reaction i and is equal to $(m_{o_i} - r_i)$. Thus, the kinetic rate can be written as:

$$\frac{d(m_{M_i}/m_{o_i})}{dt} = -k_{c_i} \left(\frac{m_{M_i}}{m_{o_i}} \right)^{n_i} \quad \text{where } \sum_{i=1}^p m_{o_i} = 1 \quad (2)$$

and k_{c_i} represents the kinetic constant of reaction i and m_{M_i} is the mass fraction of non-reacted individual material.

Using the Arrhenius law, the kinetic constant, k_{c_i} , can be calculated as:

$$k_{c_i} = k_{o_i} \exp \left(-\frac{E_i}{RT_i} \right) \quad (3)$$

or

$$k_{c_i} = k_{c_i}^* \exp \left(-\frac{E_i}{R} \left(\frac{1}{T_i} - \frac{1}{T_i^*} \right) \right) \quad (4)$$

with $k_{c_i}^*$ being calculated as:

$$k_{c_i}^* = k_{o_i} \exp \left(-\frac{E_i}{RT_i^*} \right). \quad (5)$$

Here, $k_{c_i}^*$ represents the corresponding kinetic constant of the reaction i at a reference temperature T_i^* ; T_i^* is a temperature within the range of significant weight loss rate; k_{o_i} is the kinetic pre-exponential factor or frequency factor; E_i is the activation energy; R is the universal gas constant and is equal to 8.314 J mol⁻¹ K⁻¹; T_i denotes the temperature read by the system thermocouple at time t .

The experimental weight recorded by TGA is the sum of non-reacted solid and the residue formed, without distinguishing the two fractions. Thus, typically, this kinetic law is represented as:

$$\frac{dm_i}{dt} = -k'_{c_i} (m_i - m_{i\infty})^{n_i} \quad (6)$$

where m_i indicates the sum of non-reacted solid mass fraction (m_{M_i}) and the residue mass fraction (m_{R_i}) formed by reaction i ($m_{M_i} + m_{R_i}$); k'_{c_i} is a kinetic constant for rate of mass loss; n_i is the reaction order of reaction i and $m_{i\infty}$ is the final solid at time infinity in the same reaction. Therefore

$$-\frac{dm}{dt} = -\sum_{i=1}^p \frac{dm_i}{dt} = \sum_{i=1}^p [k'_{c_i} (m_i - m_{i\infty})^{n_i}]. \quad (7)$$

Another way of avoiding the problem of the mixture of “non-reacted” and “residue” solids is by using the concept of conversion degree (α_i) [23]. The conversion degree is defined as the decomposed fraction of composite solid at a given time relative to the decomposed fraction at time infinity. The decomposed fraction is obtained by measuring the mass loss of the solids as a function of time. The mass of volatiles evolved are defined by the parameters

v_i and $v_{i\infty}$, where v_i is the mass fraction volatilized in reaction i at time t and $v_{i\infty}$ is the mass fraction volatilized in reaction i at time infinity. The α_i parameter is defined as follows:

$$\alpha_i = \frac{v_i}{v_{i\infty}} = 1 - \frac{m_i}{m_{o_i}} \quad (8)$$

The overall conversion ' α ' is defined by

$$\alpha = \frac{v}{v_{\infty}} = \frac{1 - m}{1 - m_{\infty}} \quad (9)$$

where v is the total volatile evolved by the sample used at time t and v_{∞} represents the total mass fraction volatilized at time infinity. Then, the kinetics can be calculated in terms of the conversion rate as:

$$\frac{d\alpha_i}{dt} = k_{c_i}(1 - \alpha_i)^{n_i} \quad (10)$$

By using the Euler method of numerical integration, Eq. (10) becomes

$$\alpha_{i,t+\Delta t} = \alpha_{i,t} + k_{c_i}\Delta t(1 - \alpha_{i,t})^{n_i} \quad (11)$$

An alternative formula to Eq. (11) can be obtained by formally integrating Eq. (10) and then approximating the integral by replacing it by a sum over equal intervals with the integrand assumed constant on each interval. The result obtained is:

$$\alpha_{i,t+\Delta t} = 1 - [(1 - \alpha_{i,t})^{1-n_i} - k_{c_i}\Delta t(1 - n_i)]^{1/1-n_i} \quad \text{when } n_i \neq 1 \quad (12)$$

Both expressions (Eqs. (11) and (12)) lead to the same results when $n_i \neq 1$.

The overall or total conversion (α) can be calculated by

$$\frac{d\alpha_{\text{tot}}}{dt} = \frac{1}{v_{\infty}} \left[v_{1\infty} \frac{d\alpha_1}{dt} + v_{2\infty} \frac{d\alpha_2}{dt} + v_{3\infty} \frac{d\alpha_3}{dt} + \dots + v_{i\infty} \frac{d\alpha_i}{dt} \right] \quad (13)$$

where v_{∞} is equal to $(v_{1\infty} + v_{2\infty} + \dots + v_{i\infty})$.

The value of α_{tot} obtained from the Euler method is:

$$\alpha_{\text{tot},t+\Delta t} = \alpha_{\text{tot},t} + \frac{1}{v_{\infty}} \left[v_{1\infty} \left(\frac{d\alpha_1}{dt} \right)_t + v_{2\infty} \left(\frac{d\alpha_2}{dt} \right)_t + v_{3\infty} \left(\frac{d\alpha_3}{dt} \right)_t + \dots + v_{i\infty} \left(\frac{d\alpha_i}{dt} \right)_t \right] \Delta t \quad (14)$$

In the case of the p series reactions, a similar mathematical scheme can be used, although some changes must be included. In this case, the definition of α_i in Eq. (8) can only be used for the first reaction ($i=1$). For the later reactions ($i=2, 3, \dots, p$), the formulae in Eqs. (8), (10) and (11) must be changed to the following [23]:

$$\alpha_i = \frac{v_i}{v_{i\infty}} = \frac{v_i}{r_{i-1} - r_i} \quad i = \text{reaction } 2, 3, \dots, p \quad (15)$$

$$\frac{d\alpha_i}{dt} = k_{c_i}(\alpha_{i-1} - \alpha_i)^{n_i} \quad i = \text{reaction } 2, 3, \dots, p \quad (16)$$

$$\alpha_{i,t+\Delta t} = \alpha_{i,t} + k_{c_i}\Delta t(\alpha_{i-1,t} - \alpha_{i,t})^{n_i} \quad i = \text{reaction } 2, 3, \dots, p \quad (17)$$

Obviously both models are coincident for the case of a single reaction.

A summary of the details of the independent process and series reaction models is presented in Table 1.

3.2. Estimation of kinetic parameters

The main kinetic parameters were estimated by fitting the kinetic models to the experimental data. The relevant kinetic parameters estimated for the independent processes model and the series reaction model will be described in Section 4.

The experimental data used for the estimation of kinetic parameters was obtained by combining the experimentally determined conversion fractions $\alpha_{i,\text{exp}}$ at a given set of N discrete times at four different heating rates. Relevant kinetic parameters for the independent processes model and the series reaction model were determined by minimizing the mean square error between the experimental measurements of the conversion fractions $\alpha_{i,\text{exp}}$ and the model values $\alpha_{i,\text{cal}}$. The objective function (O.F.) used for minimization of the mean square error is:

$$\text{O.F.} = \sum_{j=1}^4 \sum_{i=1}^N (\alpha_{i,\text{exp}} - \alpha_{i,\text{cal}})^2 \quad (18)$$

where $i = 1, 2, \dots, N$ denotes the set of times, $j = 1, 2, 3, 4$ represents the four heating rates, and the subscripts 'exp' and 'cal' indicate experimental and calculated values, respectively. The mean relative error (ε_r) was also calculated using the following equation:

$$\varepsilon_r(\%) = \sum_{j=1}^4 \sqrt{\frac{\sum_{i=1}^N ((\alpha_{i,\text{exp}} - \alpha_{i,\text{cal}}) / \bar{\alpha}_{i,\text{exp}})^2}{N}} \times 100 \quad (19)$$

where $\bar{\alpha}_{i,\text{exp}}$ represents the mean degree of conversion over the four different heating rates at a given time i .

4. Results and discussion

As previously stated, this present work is aimed at determining the thermal degradation of PP composite and its individual materials using TGA. The data of mass loss (TG or thermogravimetric curve) as a function of temperature and time was obtained for the three materials (pure PP, vetiver grass, and the PP composite with vetiver grass) at four different heating rates of 5, 10, 15 and 20 °C min⁻¹. The derivative thermogravimetric (DTG) curves and the conversion rate thermogravimetric (CRTG) curves of materials were then calculated as a function of temperature and time. Values of the kinetic parameters in the kinetic models were then determined by a least squares curve fitting procedure.

Table 2 shows the temperature ranges corresponding to the experimental data observed for the main decomposition processes of the materials studied at the four heating rates analyzed, as well as the values of the temperature at the maximum decomposition rate (DTG peak maxima, T_{peak}). As was expected, for all materials the maximum rate of mass loss shifts to higher temperatures as the heating rate is increased. The general features of the curves for all materials are similar but there are differences in detail. Figs. 1–3 show the TG, DTG and CRTG curves for pure PP, vetiver grass and PP composites, respectively. The initial point of the degradation appears to be independent of the heating rate. According to the results in Table 2, the initial degradation temperature of the PP composites, around 250–260 °C, is higher than that of pure vetiver grass, around 150 °C. This fact can be due to the composite preparation process, which takes place at 180–200 °C. At this temperature the first volatiles can be released, for what they are not detected in the thermal degradation. This aspect, together with the low proportion of vetiver grass in the composites, leads to a negligible weight loss at temperatures lower than 250 °C in the composite degradation.

Table 1
Kinetic expressions used in series and independent reactions in an inert atmosphere.

	Series reactions	Independent reactions
1	$m_i M_i \rightarrow r_i R_i + v_i V_i$ where $i = 1$ $r_i R_i \rightarrow r_{i+1} R_{i+1} + v_{i+1} V_{i+1}$ \vdots $r_{p-1} R_{p-1} \rightarrow r_p R_p + v_p V_p$	$m_i M_i \rightarrow r_i R_i + v_i V_i$ where $i = 1, 2, 3, \dots, p$
2	$\frac{d\alpha_i}{dt} = k_{c_i} (1 - \alpha_i)^{n_i}$ where $i = 1$ and $\frac{d\alpha_i}{dt} = k_{c_i} (\alpha_{i-1} - \alpha_i)^{n_i}$; where $i = \text{reaction } 2, 3, \dots, p$	$\frac{d\alpha_i}{dt} = k_{c_i} (1 - \alpha_i)^{n_i}$ where $i = \text{reaction } 1, 2, 3, \dots, p$
3	$\alpha_{i,t+\Delta t} = 1 - [(1 - \alpha_{i,t})^{1-n_i} - k_{c_i} \Delta t (1 - n_i)]^{1/1-n_i}$ when $n_i \neq 1$ and $i = \text{reaction } 1$ or $\alpha_{i,t+\Delta t} = \alpha_{i,t} + k_{c_i} \Delta t (1 - \alpha_{i,t})^{n_i}$ where $i = \text{reaction } 1$ and $\alpha_{i,t+\Delta t} = \alpha_{i,t} + k_{c_i} \Delta t (\alpha_{i-1,t} - \alpha_{i,t})^{n_i}$ where $i = \text{reaction } 2, 3, \dots, p$	$\alpha_{i,t+\Delta t} = 1 - [(1 - \alpha_{i,t})^{1-n_i} - k_{c_i} \Delta t (1 - n_i)]^{1/1-n_i}$ when $n_i \neq 1$ and $i = \text{reaction } 1, 2, 3, \dots, p$ or $\alpha_{i,t+\Delta t} = \alpha_{i,t} + k_{c_i} \Delta t (1 - \alpha_{i,t})^{n_i}$ where $i = \text{reaction } 1, 2, 3, \dots, p$
4		$\frac{d\alpha_{\text{tot}}}{dt} = \frac{1}{v_{\infty}} \left[v_{1\infty} \frac{d\alpha_1}{dt} + v_{2\infty} \frac{d\alpha_2}{dt} + v_{3\infty} \frac{d\alpha_3}{dt} + \dots + v_{i\infty} \frac{d\alpha_i}{dt} \right]$
5		$\alpha_{\text{tot},t+\Delta t} = \alpha_{\text{tot},t} + \frac{1}{v_{\infty}} \left[v_{1\infty} \left(\frac{d\alpha_1}{dt} \right)_t + v_{2\infty} \left(\frac{d\alpha_2}{dt} \right)_t + v_{3\infty} \left(\frac{d\alpha_3}{dt} \right)_t + \dots + v_{i\infty} \left(\frac{d\alpha_i}{dt} \right)_t \right] \Delta t$

4.1. Degradation of polypropylene

In the present paper, data of four different heating rates (5, 10, 15 and 20 °C min⁻¹) were simultaneously optimized. The calculated results showed that PP TG curves were fitted satisfactorily to a single fraction model. The three fitting parameters used were:

- kinetic constant at a reference temperature, 700 K ($k_{c_1,700K}^*$);
- activation energy parameter (E_1);
- reaction order (n_1).

As explained by Font et al. [23], the use of $k_{c_1}^*$ as fitting parameter instead of the kinetic pre-exponential factor (k_{01}), reduces the interrelation between the k_{01} and E_1 values in Eq. (3). k_{01} was then calculated from $k_{c_1,700K}^*$ and E_1 , and the maximum value of volatiles evolved, i.e. volatiles generated by the reaction ($v_{1\infty}$), was calculated as ($m_{01} - m_{1\infty}$) from the experimental data. The value of the objective function (O.F.) and the mean relative error (ε_r) were also computed. Table 3 shows the fitted values of the kinetic parameters of pure PP and Table 4 shows the calculated values for the decomposition temperature ranges and DTG peak maxima obtained from the model using these fitted values.

Comparisons of experimental and calculated values of mass loss versus temperature (TG curve), DTG and CRTG curves of pure PP in nitrogen atmosphere are shown in Fig. 1a–c, respectively, for the four different heating rates. It is clear that the estimated results are in good agreement with the experimental data. The DTG curves in Fig. 1b show clear peaks which correspond to the maximum rate of mass loss shown in Fig. 1a and the maximum conversion rate shown in Fig. 1c. The curves show that most of the decomposition of the PP occurs in a narrow temperature range and that, as noted before, the temperature of maximum rate of mass loss shifts to a higher temperature as the heating rate increases.

Table 2
Experimental decomposition temperature ranges and DTG peak maxima.

Sample	Temperature range (°C), T_{peak} (°C)			
	5 °C min ⁻¹	10 °C min ⁻¹	15 °C min ⁻¹	20 °C min ⁻¹
PP	375–482, 461.8	375–500, 478.5	375–508, 485.7	375–516, 491.5
Vetiver grass	150–606, 306.4	150–620, 314.8	150–650, 319.0	150–663, 325.2
Vetiver grass filled PP composites	250–490, 462.1	250–505, 476.8	260–515, 487.5	260–524, 496.9

According to the PP experimental data in Table 2, the PP pyrolytic degradation begins at about 375 °C, and finishes at around 482–516 °C, depending on the heating rate. The DTG peak temperature is in the range 462–492 °C as a function of the heating rate. As shown in Table 3, the activation energy of PP optimized from the four heating rates data is approximately 231 kJ mol⁻¹. Compared to previous literature, all of these values seem to be reasonable, since most of the activation energies and temperature ranges of the PP decomposition reported in the literature are in the range 184–271 kJ mol⁻¹ and 340–496 °C, respectively [1,8,9,24,25]. For example, Gersten et al. [9] obtained that the decomposition of PP was in the temperature range 340–494 °C, depending on the heating rate, with the activation energy and reaction order of about 250 kJ mol⁻¹ and 0.99, respectively. Wu et al. [24] used the Friedman method to calculate the kinetic parameters for the pyrolysis of PP, obtaining values at about 184 kJ mol⁻¹ for the activation energy with the reaction order of 0.90. Additionally, Peterson et al. [12] surveyed literature data of the activation energy and found values in the range 214–244 kJ mol⁻¹, which show good agreement with the value of 231.4 kJ mol⁻¹ obtained in this work. Most of the previous authors have obtained values for the reaction orders between 0.9 and 1.0. In the present study, the reaction order was estimated as approximately 0.43 which was appreciably less than previously reported values. However, Marcilla et al. [25] reported an activated energy of 209 kJ mol⁻¹ and a reaction order of 0.12 for the thermal degradation of PP. As noted previously by García and Font [19], the reaction order can be affected by the variation of sample surface exposed during pyrolysis.

Comparing the peak temperature of PP TG curves obtained in this study with those reported by other researchers, a total similarity has been found [9,21,24]. Thus, Gersten et al. [9] observed a single peak corresponding to the decomposition reaction of PP. Sørnum et al. [21] also proposed a single-reaction model for the thermal decomposition of PP, PE and polystyrene (PS), however, a high

Table 3
Values of the optimized parameters for the pyrolysis of PP.

$k_{c_1,700K}^*$ (s^{-1})	k_{01} ($s^{-1}(\text{mass fraction})^{1-n}$)	E_1 (kJ mol^{-1})	n_1	$\nu_{1\infty, \text{exp}}$	ε_r (%)
5.74×10^{-4}	1.06×10^{14}	231.4	0.429	0.994	10.2

activation energy value of $336.7 \text{ kJ mol}^{-1}$ for PP was obtained. Wu et al. [24] reported sharp peaks in the DTG curves similar to those in Fig. 1b and explained that these peaks correspond to the weight loss of hydrocarbons, where the breaking down of C–C bonds is the determining reaction.

4.2. Degradation of vetiver grass

Vetiver grass is a lignocellulosic material whose major constituents are hemicellulose, cellulose and lignin. Pyrolysis of biomass containing these three constituents has been widely studied and is still a subject of current interest (see, e.g. [21,26–28]). Most of these studies have shown that hemicellulose started to decompose at a lower temperature than the cellulose and lignin. Thus, for example, Müller-Hagedorn et al. [29] reported fractionated pyrolysis experiments of three different wood species containing hemicellulose, cellulose and lignin in the temperature range of $100\text{--}500^\circ\text{C}$ using TGA and Gas Chromatography/Mass Spectroscopy (GC/MS) analysis. Their results showed that the decomposition products changed with temperature indicating that the main decomposition of the three materials occurred at different temperatures. The decomposition products at the lowest temperatures could be mainly attributed to the first stage of hemicellulose decomposition. As the temperature increased the decomposition products could be attributed mainly to cellulose and lignin and a second stage of hemicellulose decomposition. Chen et al. [30] concluded from their pyrolysis experiments that the main devolatilization observed during decomposition occurred at temperatures lower than 450°C and could be attributed to the decomposition of cellulose and hemicellulose while a continuous slight devolatilization observed at temperatures higher than 450°C could be attributed to the decomposition of lignin and remaining cellulose and hemicellulose. Orfão et al. [27] also reported similar results to those of Chen et al. [30]. However, Sørsum et al. [21] reported that the decomposition of hemicellulose and cellulose typically occurred in the temperature ranges of $200\text{--}400$ and $275\text{--}400^\circ\text{C}$, respectively, while lignin degradation occurred over a broad temperature range, $200\text{--}500^\circ\text{C}$.

In the present paper, the thermal decomposition of vetiver grass is simulated by an independent processes model and a series reaction process model. In both cases three reactions are included in order to model the decomposition of the constituents. As found, an independent processes model with three independent reactions

fits the experimental data better than a series reaction model, so only the results for the three independent processes model are discussed in this paper. The use of an independent processes model was also in agreement with the assumption of Müller-Hagedorn et al. [29] that the hemicellulose, cellulose and lignin in their wood samples decomposed independently.

The following parameters were calculated from the simultaneously optimized data of the four heating rates (5 , 10 , 15 and $20^\circ\text{C min}^{-1}$) for three independent processes using a least squares fitting method. The calculated parameters were:

- three kinetic constants at 3 reference temperatures (k_{c_1, T_1}^* , k_{c_2, T_2}^* and k_{c_3, T_3}^*);
- three activation energy parameters (E_1 , E_2 and E_3);
- three reaction orders (n_1 , n_2 and n_3);
- two maximum amount of volatiles evolved from the first and second reactions ($\nu_{1\infty}$, $\nu_{2\infty}$).

The pre-exponential factors (k_{01} , k_{02} and k_{03}) were calculated from k_{c_i, T_i}^* and E_i . The amount of volatiles evolved from the third reaction ($\nu_{3\infty}$) was calculated from the observed values of the total volatiles at infinite time (ν_{∞}) and the $\nu_{1\infty}$ and $\nu_{2\infty}$ values for the first two reactions.

The calculated TG, DTG and CRTG curves for vetiver grass are compared in Fig. 2 with the experimental curves for the four heating rates of 5 , 10 , 15 and $20^\circ\text{C min}^{-1}$. The curves show good agreement between the experimental data and the values calculated from the three independent processes model. As expected, the decomposition ranges shift to higher temperatures as the heating rate increases. This fact can be seen more clearly from the T_{peak} values.

Fig. 4 shows an example of the experimental total DTG curve as well as DTG curves calculated from the three independent processes model for the vetiver grass degradation at a heating rate of 5°C min^{-1} . The experimental DTG curve can be modeled as the overlapping of three calculated DTG curves corresponding to decomposition of three fractions. As can be seen, there are two relatively narrow peaks in the DTG curves. A single broad peak can also be seen that spreads over a range of higher temperatures (up to 700°C , approximately). As mentioned previously, the hemicellulose started to decompose at the lowest temperature followed by cellulose and lignin at higher temperatures, so the first peak can be attributed to decomposition of hemicellulose, the second peak can

Table 4
Calculated decomposition temperature ranges and DTG peak maxima.

Sample		Temperature range ($^\circ\text{C}$), T_{peak} ($^\circ\text{C}$)			
		5°C min^{-1}	$10^\circ\text{C min}^{-1}$	$15^\circ\text{C min}^{-1}$	$20^\circ\text{C min}^{-1}$
PP	Single peak	375–477, 467.2	375–490, 478.5	375–498, 487.6	375–502, 494.0
Vetiver grass by independent reaction model	1st peak	170–357, 256.0	170–390, 273.5	170–407, 280.1	170–410, 288.6
	2nd peak	245–377, 306.4	245–396, 314.8	245–410, 323.0	245–425, 325.2
	3rd peak	255–700, 380.5	255–700, 403.2	255–700, 409.0	255–700, 415.2
Vetiver grass filled PP composites by series reaction model	1st peak	175–364, 296.1	175–388, 316.0	175–405, 326.8	175–417, 335.7
	2nd peak	375–481, 467.0	375–496, 481.8	375–505, 489.4	375–510, 496.9
	3rd peak	420–521, 477.1	432–537, 492.2	440–554, 501.3	447–561, 507.5
Vetiver grass filled PP composites by independent reaction model	1st peak	175–364, 296.1	175–388, 316.0	175–405, 326.8	175–417, 335.7
	2nd peak	375–481, 467.0	375–496, 481.8	375–505, 489.4	375–510, 496.9
	3rd peak	392–521, 472.1	392–541, 485.3	392–554, 493.3	392–559, 496.9

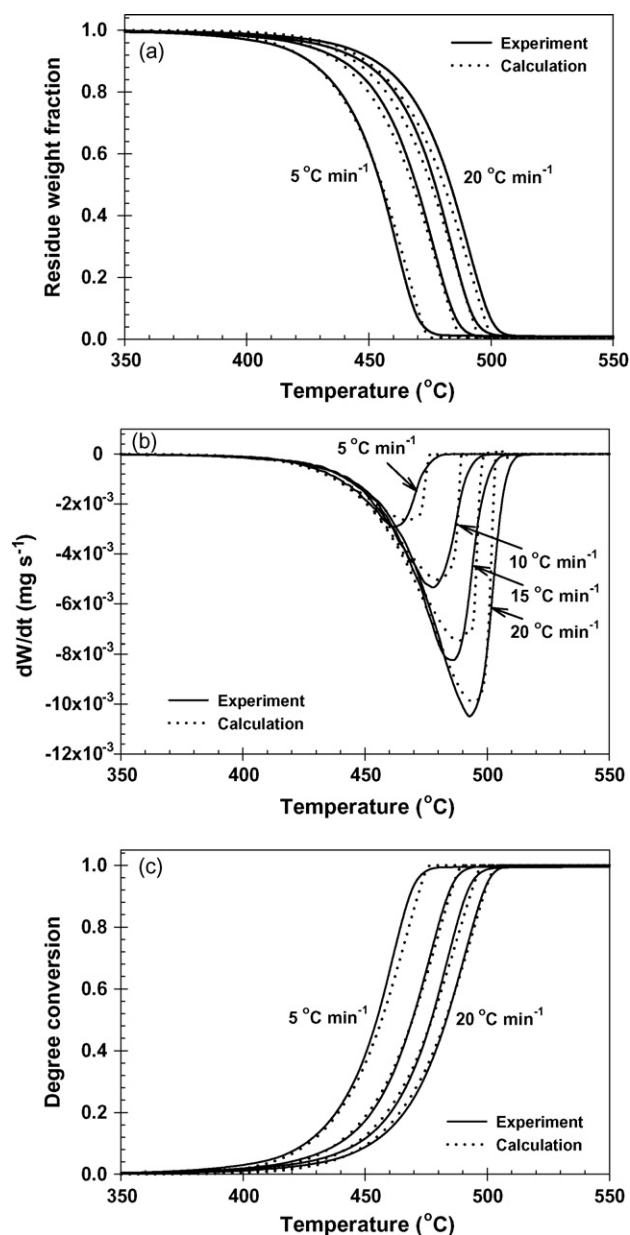


Fig. 1. Comparison of experimental (—) and calculated (···) data using a single fraction model for pure PP at 5, 10, 15 and 20 °C min⁻¹ in N₂: (a) TG curve; (b) DTG curve; (c) CRTG curve.

be attributed to decomposition of cellulose and remaining hemicellulose and the broad third peak can be attributed to decomposition of lignin and remaining hemicellulose and cellulose.

The values calculated from the model using these fitted parameters are shown in Table 4 for the decomposition temperature range as well as the temperatures of the three DTG peak maxima (T_{peak}) for the 1st peak (hemicellulose), 2nd peak (cellulose) and 3rd peak (lignin) for the four heating rates studied.

Table 5 shows the values of the kinetic parameters obtained. Unfortunately, the comparison of these parameters to those obtained in the literature is not straight forward, since most authors assumed first-order kinetic reactions [21,27,28] in their kinetic models and many authors also considered the models in different ways. Kinetic models with three independent parallel first-order reactions were used by Sørum et al. [21] to represent the decomposition of individual cellulosic fractions – newspaper, cardboard,

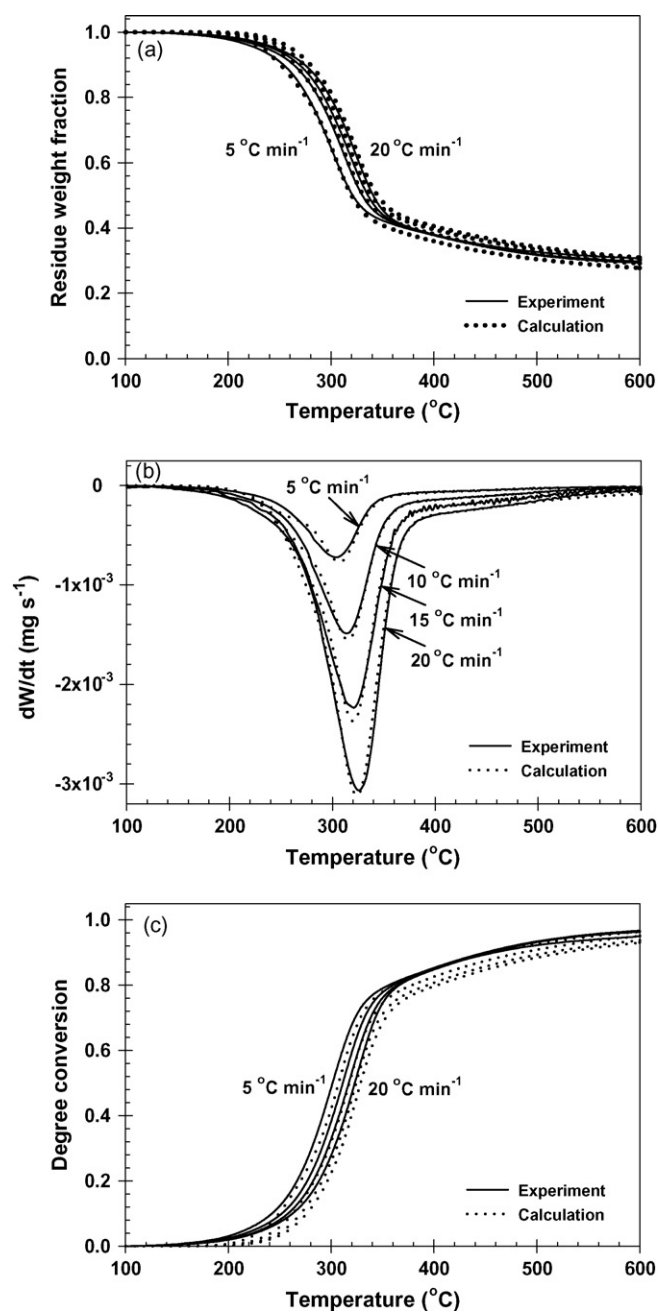


Fig. 2. Comparison of experimental (—) and calculated (···) data using the three independent processes model for vetiver grass at 5, 10, 15 and 20 °C min⁻¹ in N₂: (a) TG curve; (b) DTG curve; (c) CRTG curve.

recycled paper and spruce – in municipal solid wastes. They found that three peaks were obtained when they modeled their data over narrow temperature ranges of 200–400, 275–400 and 200–500 °C, respectively. They also showed that, depending on type of sample tested, the activation energies for the first, second and third peaks were between 96.7 and 136.2, 214.0 and 274.7, and 41.3 and 55.1 kJ mol⁻¹, respectively. In their study, Órfão et al. [27] assumed that the decomposition of cellulose in their samples was equivalent to the decomposition of Avicel cellulose and that the kinetic parameters of Avicel cellulose decomposition could be used to represent the cellulose fraction. Manyà et al. [28] employed a three independent processes model to fit the experimental data of the decomposition of two sugarcane bagasses and two waste wood samples. They used a summative model of three pseudocompo-

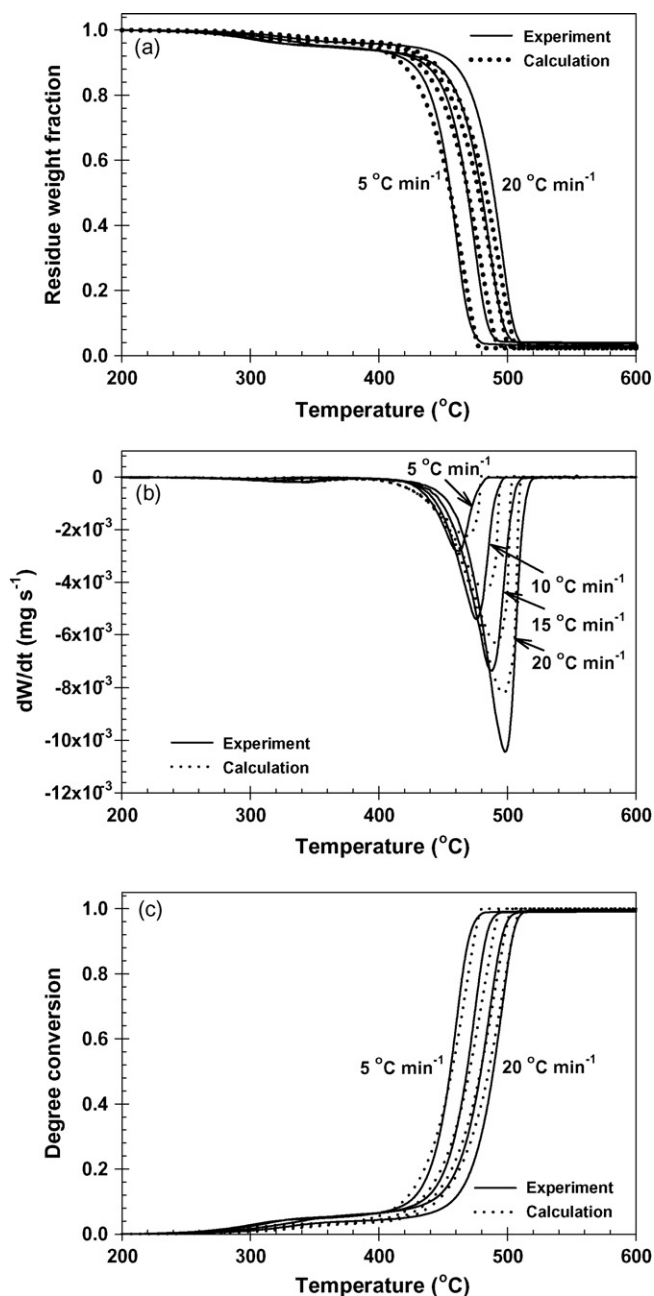


Fig. 3. Comparison of experimental (—) and calculated (···) data using the three independent processes model for vetiver grass powder filled PP composites at 5, 10, 15 and 20 °C min⁻¹ in N₂: (a) TG curve; (b) DTG curve; (c) CRTG curve.

nents obtained by a reformulation of a model of Teng and Wei [31] and found that their model yielded good agreement with the experimental data. They estimated activation energies for three pseudocomponents in their two sugarcane bagasse samples and two waste wood samples in the ranges 194.0–200.0, 243.3–250.8 and 53.6–60.9 kJ mol⁻¹, respectively.

The values shown in Table 5 for the activation energies for the first, second and third peaks in the decomposition are approximately 106, 214 and 140 kJ mol⁻¹, respectively. And those of the reaction orders for the three processes are approximately 1.62, 1.93 and 7.4 respectively. The results for the activation energies of peaks 1 and 2 are in good agreement with those reported previously in the literature [21,32]. Although the activation energy obtained for peak 3 of 140.2 kJ mol⁻¹ is higher than most values reported

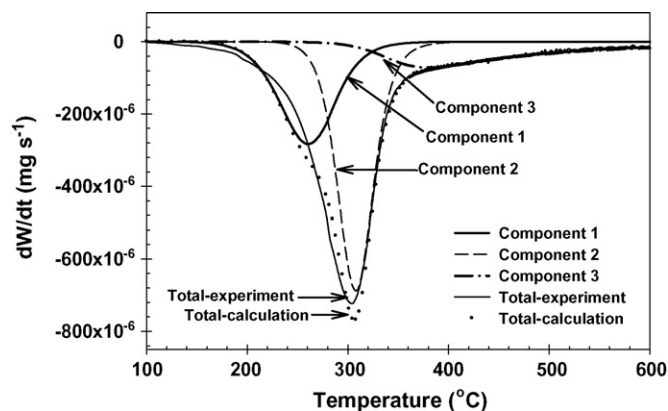


Fig. 4. DTG curve showing the overlapping three independent processes of vetiver grass at a heating rate of 5 °C min⁻¹.

previously, Caballero et al. [26] also obtained high values for the activation energies of the third peak for almond shell and olive stone of 193.5 and 188.1 kJ mol⁻¹ respectively. As noted above, most previous authors have assumed first-order kinetics for the three processes. The values of the reaction order for the first and second peaks obtained in this work appear to be reasonable, but the value for the third peak seems to be high. However, Urban and Antal [33] reported very high reaction order values of 10 and 15 for the two independent decomposition reactions of an undigested sludge, while Caballero et al. [26] obtained high reaction order values of 10.991 and 7.210 for the third peak of almond shells and olive stones, respectively.

From the $v_{i\infty}$ values obtained, the decomposition of the hemicellulose fraction generates around 20% of volatiles, the cellulose fraction 34.5% and the lignin fraction around 18.5%. Around 27% of the original mass remains as residue.

Although a direct comparison of the kinetic parameters with values reported in the literature is difficult, the calculated results show that the values of the kinetic parameters in the present paper are reasonable. In general, these types of models proposed are pseudo-mechanistic models. As already reported [22,25], the parameters of these types of kinetic models are interrelated together and it is not easy to verify the actual degradation mechanisms without any doubt, however, we are able to obtain a set of fitting parameters which allows us to reproduce experimental data properly and to use them in the design of reactors.

Table 5
Values of the optimized kinetic parameters for the pyrolysis of vetiver grass.

Parameters	Vetiver grass (by independent reaction model)
$k_{c1,500K}^*(s^{-1})$	8.77×10^{-4}
$k_{o1}(s^{-1}(\text{mass fraction})^{1-n})$	1.05×10^8
$E_1(kJ mol^{-1})$	106.0
n_1	1.621
$v_{1\infty}$	0.198
$k_{c2,625K}^*(s^{-1})$	1.51×10^{-1}
$k_{o2}(s^{-1}(\text{mass fraction})^{1-n})$	1.15×10^{17}
$E_2(kJ mol^{-1})$	213.9
n_2	1.926
$v_{2\infty}$	0.345
$k_{c3,773K}^*(s^{-1})$	1.17×10^{-1}
$k_{o3}(s^{-1}(\text{mass fraction})^{1-n})$	3.47×10^8
$E_3(kJ mol^{-1})$	140.2
n_3	7.400
$v_{3\infty}$	0.188
v_{∞}	0.731
$\varepsilon_T(\%)$	18.6

Table 6

Values of the optimized kinetic parameters for the pyrolysis of vetiver grass filled PP composites.

Parameters	Vetiver grass filled PP composites (by series and independent reaction models)
$k_{c1,460K}^*$ (s^{-1})	2.96×10^{-5}
k_{o1} ($s^{-1}(\text{mass fraction})^{1-n}$)	1.02×10^6
E_1 ($kJ\ mol^{-1}$)	92.8
n_1	1.013
$\nu_{1\infty}$	0.030
$k_{c2,700K}^*$ (s^{-1})	5.88×10^{-4}
k_{o2} ($s^{-1}(\text{mass fraction})^{1-n}$)	3.99×10^{12}
E_2 ($kJ\ mol^{-1}$)	212.2
n_2	0.436
$\nu_{2\infty}$	0.927
$k_{c3,750K}^*$ (s^{-1})	6.06×10^{-3}
k_{o3} ($s^{-1}(\text{mass fraction})^{1-n}$)	7.10×10^{14}
E_3 ($kJ\ mol^{-1}$)	245.1
n_3	1.270
$\nu_{3\infty}$	0.017
ν_{∞}	0.974
ε_f (%)	22.7 (series), 22.4 (independent)

4.3. Vetiver grass filled PP composites

The experimental and model fitting methods used for the PP composite are similar to those described in Sections 2 and 3.1, respectively. The experimental data was fitted to both a three independent processes model and a series reaction model.

Fig. 3 shows experimental and calculated TG, DTG and CRTG curves for the four heating rates of 5, 10, 15, 20 °C min⁻¹. The calculated curves were obtained from a three independent processes model using parameter values obtained by a least squares fit to the experimental data. Similar results were obtained when a series reaction model was tested. Table 4 gives the temperature ranges calculated from the kinetic models for both series reactions and independent processes models of decomposition of the PP composite at four different heating rates. For fractions 1 and 2, both models lead to the same temperature range and T_{peak} . Differences between them are only observed in fraction 3. According to the results obtained, the series reaction model reproduces the third fraction decomposition at higher temperatures than the independent reaction model.

From the values shown in Table 4, it can be deduced that the small shoulder peak in the temperature range 175–417 °C (corresponding to four heating rates) can be attributed to degradation of hemicellulose and cellulose in the vetiver grass. The large peak in the temperature range 375–510 °C can be attributed to the main degradation of PP, as this range is in good agreement with that observed for pure PP, 375–502 °C. This peak will probably also include decomposition of some remaining cellulose. The third small fraction in the temperature range of 392–559 °C can be attributed to the degradation of lignin and remaining cellulose, as this range is in the ranges with those observed for lignin (255–700 °C, vetiver grass 3rd peak) and cellulose (245–425 °C, vetiver grass 2nd peak).

The calculated kinetic parameters for vetiver grass filled PP composites are shown in Table 6. As expected, the main decomposition process corresponds to the second peak (around 93% of volatiles generated). Peaks 1 and 3 only represent around 3% and 2% of the total weight loss, respectively. Although the decomposition temperature range of the third fraction is not simulated in the same way by both models, the low percentage of this fraction in the composite does not allow us to distinguish between the models, since both of them lead to similar kinetic parameters and relative errors.

By comparing the kinetic data of pure PP (Table 3) with those of second peak parameters in PP composites (Table 6), significant similarities are observed. Thus, the 'n' value is almost the same in both cases and there is a small difference in the activation energy value. Due to the interrelationship between activation energy and pre-exponential factor, small differences in activation energy values can lead to higher differences in the pre-exponential factor, but as can be seen, the values of kinetic constant are very similar in both cases.

For the PP composite, the experimental and calculated data showed that good agreement could be obtained with both an independent processes and a series reactions process model. This contrasts with the case of vetiver grass where the three independent processes model gave a good fit with the experimental data but an acceptable fit could not be obtained between the experimental and calculated values with a series reaction model. This difference between the composites and the vetiver grass modeling is probably due to the low percentage of grass used in the composites (10%). In the composite solid, the major component is PP and therefore the degradation of the three components of the low percentage of vetiver grass is expected to make only a relatively small contribution to the experimentally observed decomposition data, which does not allow us to distinguish between both models. Therefore, we believe that an independent processes model for the PP composite is preferable to a series reaction model as the vetiver grass component cannot be satisfactorily modeled by a series reaction model.

5. Conclusions

The pyrolysis of PP, vetiver grass, and PP composites containing 10% vetiver grass powder as filler was investigated using TGA for a range of heating rates in an inert nitrogen atmosphere. Kinetic models, based on Arrhenius type temperature behavior, were developed to describe the rate of thermal decomposition. The PP was modeled by a single reaction model. The vetiver grass and the PP composite were modeled by a three independent processes model and a three series reaction model. The kinetic parameters in the models were estimated by a least squares fitting procedure.

For the PP the experimental data could be fitted with a single reaction model which showed one clear peak in the DTG curve.

For the vetiver grass the experimental data could be fitted to a three independent processes model. An attempt was also made to fit a three series reaction model but the fit was appreciably worse than a three independent processes. The DTG curve could be fitted by a superposition of three peaks, one dominant peak and two small shoulder peaks. The lower temperature shoulder peak could be associated with decomposition of hemicellulose, the dominant peak could be associated with decomposition of cellulose and remaining hemicellulose and the higher temperature shoulder peak could be associated with decomposition of lignin and remaining cellulose and hemicellulose. The initial point of the degradation seemed to be almost independent of the heating rate, although as was expected, the peaks shifted to higher temperatures as the heating rate was increased.

For the composite solid (PP/grass=90/10), the experimental data could be fitted either to a three independent processes model or a three series reaction model. As for the vetiver grass, the DTG curves could be modeled by a superposition of three peaks, but in this case, due to the low percentage of vetiver grass in the composite, one of the peaks is clearly dominant over the other two peaks.

A comparison of the vetiver grass and the PP composite data shows that the initial degradation temperature of the PP composite is appreciably higher than that of pure vetiver grass (250 °C in

composite and 150 °C in vetiver grass). This could be due to the fact that the composite is prepared at temperatures between 180 and 200 °C. At these temperatures, some degradation of the vetiver grass can be occurred and the first volatiles can be released from samples. This fact, together with the low proportion of vetiver grass in the composite, means that there is negligible decomposition of the already partially degraded vetiver grass in the PP composite at temperatures lower than 250 °C.

For all samples, good agreement was obtained between the experimental data and the data calculated from the kinetic models. A comparison of the kinetic models and the experimental results led to an improved understanding of the decomposition kinetics of PP composite containing vetiver grass as filler.

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