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# On the thermal degradation of cellulose in cotton fibers

**Luis Cabrales · Noureddine Abidi**

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**Abstract** Thermal decomposition of cellulose has been widely studied for the past several years. It has been reported that the source of cellulose and its composition greatly affect its pyrolysis. One of the most widely used analytical tools for the study of cellulose pyrolysis is thermogravimetric (TG) analysis. Several model-fitting methods have been employed to study cellulose pyrolysis kinetics. An alternative to the model-fitting approach is the so-called model-free method developed by Vyazovkin. This isoconversional technique calculates the activation energy as a function of the degree of the conversion. In this article, the pyrolysis of cellulose in cotton fibers compared to microcrystalline cellulose (Avicel, PH 105) was investigated. TG curves were acquired as a function of the heating rates (4, 5, 8, 10, and 16 °C min$^{-1}$) and the model-free method was used to analyze the data. Activation energies of cotton fibers and Avicel were obtained, and compared to the data reported in the literature. In addition, models for isothermal decomposition were calculated and compared with experimental data at the same temperature.

**Keywords** TG · Cellulose · Activation energy · Cotton · Model-free kinetics

## Introduction

Cellulose is the most abundant polymer on the earth. Understanding the cellulose thermal degradation is of great importance in a vast array of areas such as generation of energy from biomass and the improvement of flame retardants of cellulosic fibers. Although there has been extensive research focused on cellulose pyrolysis, it is not yet fully understood. Thermogravimetric (TG) analysis is a widely used technique in this area [1]. It is useful for the thermal characterization of both inorganic and organic materials, including polymers (such as cellulose). It provides quantitative results regarding the loss of mass of a sample as a function of increasing temperature or time [2]. Moreover, TG measurements provide basic information regarding the thermal properties of the material and its composition. The first derivative thermogravimetry (DTG) can be used to investigate the differences among TG curves [3].

As reported by Antal et al. [1], the goal of cellulose pyrolysis kinetics is to describe mathematically the thermal decomposition of a small and homogeneous sample of pure cellulose. In order to calculate the activation energy, several model-fitting methods have been used previously. An alternative to the model-fitting methods are the so-called model-free methods. The advantage of using a model-free approach is that it permits the calculation of the activation energy at different degrees of conversion without assuming any particular reaction model [4]. In this study, the model-free method used was developed by Vyazovkin [5–7]. This method has been applied to study several polymers and energetic materials. To our knowledge, limited research study has been published on cellulosic materials pyrolysis using this method [8]. The advantage of Vyazovkin's method over one of the most popular isoconversional methods, Flynn–Wall–Ozawa method, is that it performs the integration over small time segments, which eliminates a systematic error [9].

L. Cabrales · N. Abidi (✉)
Department of Plant and Soil Science, Fiber and Biopolymer Research Institute, Texas Tech University, P.O. Box 45019, Lubbock, TX 79403, USA
e-mail: n.abidi@ttu.edu

In this article, the pyrolysis of cellulose in cotton fibers compared to microcrystalline cellulose (Avicel, PH 105) was investigated. TG curves were acquired as a function of heating rates (4, 5, 8, 10, and 16 °C $\mathrm{min}^{-1}$) and the model-free method was used to analyze the data.

## Experimental

### Materials

Microcrystalline cellulose Avicel PH 105 (FMC biopolymer, Philadelphia, PA) was used as received. The moisture content was 3.5%, the loose bulk density was 0.28 g $\mathrm{cm}^{-3}$, and the degree of polymerization was 221. Cotton fiber samples (*Gossypium hirsutum* L cv. TX55) were collected at 24 and 56 days post anthesis (dpa) [10]. No treatment was performed to remove the noncellulosic materials. The fibers were pulverized in a Wiley mill to pass a 20 mesh.

### Experimental methods

Thermogravimetric analysis of cellulose samples was performed using Pyris1TGA equipped with a 20-sample autosampler (PerkinElmer Shelton, CT). Temperature calibration of TG was performed with the curie point of alumel and nickel alloys at 10 °C $\mathrm{min}^{-1}$. TG curves were recorded between 150 and 600 °C with the following heating rates: 4, 5, 8, 10, and 16 °C $\mathrm{min}^{-1}$ in a flow of nitrogen at 20 mL $\mathrm{min}^{-1}$. The mass of each sample was between 2 and 3 mg. Samples were stabilized at 150 °C for 5 min before starting the heating program to eliminate the absorbed water. A baseline was performed by running an empty ceramic crucible at each heating rate and baseline curves were subtracted from the curves of the sample. This procedure was done to avoid the effect of buoyancy on the results. Three independent replications were performed from each sample. The Pyris software was used to calculate the first derivatives of the curves (DTG) and to determine the percent mass loss for each sample.

Experimental degree of conversion was determined for each sample. For this purpose, cellulose samples were placed in the crucible at room temperature. Samples were pre-dried; the temperature was increased from 150 to 300 °C at 100 °C $\mathrm{min}^{-1}$, which was then maintained at 300 °C for 180 min. Three independent replications were performed from each sample.

Statistical analysis of the data was performed using Statistica Software (StatSoft Inc, Tulsa). Factorial ANOVA (Analysis of variance) was performed to test any statistically significant effects, and the mean separation was determined according to Newman–Keuls tests (with $\alpha = 5\%$).

### Kinetic analysis

In order to calculate the activation energy, we used the method developed by Vyazovkin et al. [5]. This method is based on the following equations. First, the rate of a solid-state decomposition can be described by this relationship [10]:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = kf(\alpha), \tag{1}$$

where $k$ is the rate constant, $f(\alpha)$ represents the reaction model, and $\alpha$ represents the conversion fraction. The rate constant is temperature dependent as described by Arrhenius equation [10]:

$$k = A\mathrm{e}^{-E_\mathrm{a}/RT}, \tag{2}$$

where $A$ is the pre-exponential factor, $E_\mathrm{a}$ the activation energy, $T$ the absolute temperature, and $R$ the universal gas constant. By substituting Eq. 2 in Eq. 1, we can derive Eq. 3 [10]:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A\mathrm{e}^{-E_\mathrm{a}/RT}f(\alpha). \tag{3}$$

At a constant heating rate for non-isothermal conditions, the explicit temporal/time dependence in Eq. 3 is eliminated by the following transformation:

$$\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T} = A\mathrm{e}^{-E_{\mathrm{a}\alpha}/RT}f(\alpha) \tag{4}$$

where $\beta$ is the heating rate, $E_{\mathrm{a}\alpha}$ the activation energy as a function of the conversion factor ($\alpha$), and $\mathrm{d}\alpha/\mathrm{d}T$ the rate of the reaction [11].

Vyazovkin developed an advanced isoconversional method where the activation energy can be determined by finding the value of $E_{\mathrm{a}\alpha}$ for which the objective function $\Omega$ in Eq. 5 is minimized at any particular value of $\alpha$, where $n$ is the number of heating rates:

$$\Omega = \sum_{i=1}^{n}\sum_{j\neq 1}^{n}\frac{I(E_{\mathrm{a}\alpha}, T_{\alpha i})\beta_j}{I(E_{\mathrm{a}\alpha}, T_{\alpha j})\beta_j}, \tag{5}$$

where

$$I(E_{\mathrm{a}\alpha}, T_{\alpha i}) = \int_0^{T_{\alpha i}} \mathrm{e}^{-E_{\mathrm{a}\alpha}/RT}\mathrm{d}T. \tag{6}$$

The $I(E_{\mathrm{a}\alpha}, T_{\alpha i})$ values in Eq. 6 may be found by numerical integration as well with the help of the Senum–Yang approximation [12]. In other isoconversional methods, the value of $E_{\mathrm{a}\alpha}$ is assumed to be constant throughout the whole interval of integration. This assumption introduces a systematic error if the actual value of $E_{\mathrm{a}\alpha}$ changes with $\alpha$. In the method developed by Vyazovkin, the systematic error is eliminated by performing the integration over small temperature segments. Thus, the constancy of $E_{a\alpha}$ is assumed for only a small interval of conversions [5].

In this article, we used MFK Software from PerkinElmer (CT, USA). This program is based on the method developed by Vyazovkin [12]. Three plots of the dependency of the activation energy to the degree of conversion were obtained from each sample. Calculated values of the degree of conversion as a function of time at isothermal conditions ($T$ = 300 °C) were also obtained using the MFK software.

## Results and discussion

Representative TG curves of Avicel and cotton fibers at 56 and 24 dpa obtained at five different heating rates (4, 5, 8, 10, and 16 °C min$^{-1}$) are shown in Figs. 1, 2, and 3, respectively. Two major differences could be noticed when comparing these TG curves: the onset temperature of the decomposition, and the amount of mass remaining at 600 °C. The onset of decomposition temperature is lower in cotton fibers harvested at 24 dpa compared to that of cotton fibers harvested at 56 dpa. Avicel sample has the highest onset of decomposition temperature. The difference observed in the onset of decomposition temperatures could result from the noncellulosic materials of cotton fibers located primarily in the cuticle and the primary cell wall. These noncellulosic materials are mostly waxes, pectin substances, organic acids, sugars, and ash-producing organic salts. These materials are reported to have a lower decomposition temperature than cellulose [3]. Cotton fibers from TX55 cultivar harvested at 24 dpa have a cellulose content of 68.3%, which is lower than the cellulose content of fibers harvested at 56 dpa (estimated at 88.4%) [13]. The lower cellulose content indicates a higher proportion of noncellulosic materials and, thus, younger fibers have a lower onset decomposition temperatures compared to fibers harvested at 56 dpa. The difference observed in the remaining mass at 600 °C could be due to the reaction between the noncellulosic material decomposition by-products and cellulose (Tables 1, 2, 3). It was reported that small amounts of metal ions could influence the amount of char produced in cellulose pyrolysis [1]. The lowest remaining mass was obtained for the Avicel sample (~4%) and the highest was obtained for the cotton fibers harvested at 56 dpa (~17%).

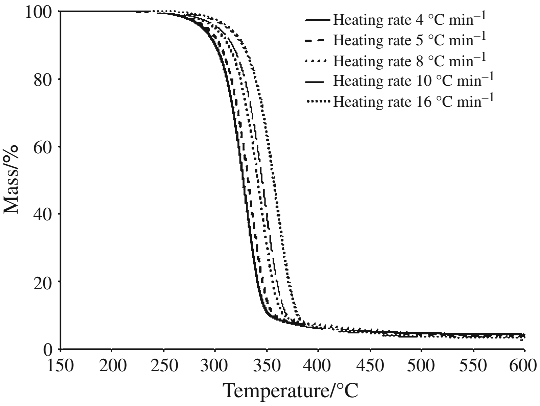

**Fig. 1** TG curves of Avicel at different heating rates

It has been documented that the model-free method developed by Vyazovkin may not be applied in decomposition reactions where the amount of the remaining product depends on the heating rate [14]. Analysis of variance of the mass percent remaining was performed to evaluate the dependence of mass percent remaining as a function of the heating rate. Tables 1, 2, 3 show the analysis of variance of the mass percentage remaining when the temperature has reached 600 °C at different heating rates for Avicel and cotton fibers at 24 and 56 dpa, respectively. The percent remaining at the heating rate 5 °C min$^{-1}$ for Avicel is in agreement with the value reported in the literature [15]. Although the results in Table 1 present a

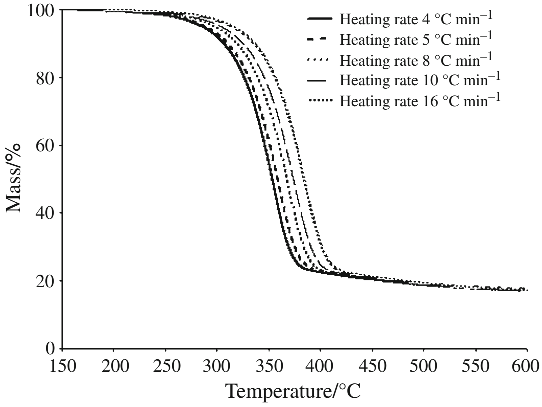

**Fig. 2** TG curves of cotton fibers harvested at 56 dpa at different heating rates

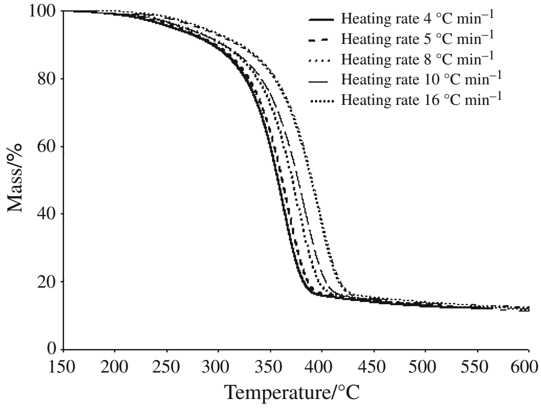

**Fig. 3** TG curves of cotton fibers harvested at 24 dpa at different heating rates

**Table 1** Variance analysis: effect of heating rate on the mass percent remaining for Avicel sample

| Parameter | df | *F* | Probability | % Remaining[a] |
|---|---|---|---|---|
| Intercept | 1 | 6844.19 | 0.000000 | |
| Heating rate/°C $min^{-1}$ | 4 | 16.83 | 0.000194 | |
| 4 | | | | 4.05a |
| 5 | | | | 3.79a |
| 8 | | | | 3.72a |
| 10 | | | | 3.40b |
| 16 | | | | 3.02c |
| Error | 10 | | | |

*df* Degrees of freedom, *F* variance ratio

[a] Values not followed by the same letter are significantly different with $\alpha = 5\%$ (according to Newman–Keuls tests)

**Table 2** Variance analysis: effect of heating rate on the mass percent remaining for cotton fibers at 56 dpa

| Parameter | df | *F* | Probability | % Remaining[a] |
|---|---|---|---|---|
| Intercept | 1 | 1017575.50 | 0.000000 | |
| Heating rate/°C $min^{-1}$ | 4 | 1.10 | 0.396803 | |
| 4 | | | | 17.29a |
| 5 | | | | 17.27a |
| 8 | | | | 17.12a |
| 10 | | | | 17.11a |
| 16 | | | | 16.98a |
| Error | 10 | | | |

*df* Degrees of freedom, *F* variance ratio

[a] Values not followed by the same letter are significantly different with $\alpha = 5\%$ (according to Newman–Keuls tests)

**Table 3** Variance analysis: effect of heating rate on the mass percent remaining for cotton fibers at 24 dpa

| Parameter | df | *F* | Probability | % Remaining[a] |
|---|---|---|---|---|
| Intercept | 1 | 19696.31 | 0.000000 | |
| Heating rate/°C $min^{-1}$ | 4 | 0.61 | 0.666908 | |
| 4 | | | | 11.72a |
| 5 | | | | 11.80a |
| 8 | | | | 11.83a |
| 10 | | | | 11.91a |
| 16 | | | | 12.11a |
| Error | 10 | | | |

*df* Degrees of freedom, *F* variance ratio

[a] Values not followed by the same letter are significantly different with $\alpha = 5\%$ (according to Newman–Keuls tests)

statistical difference in the mass percent remaining for Avicel, this is a small difference in mass remaining, and it would not affect the results of the activation energy. However, in cotton fibers, the analysis of variance does not show any statistically significant effects of the heating rate on the remaining mass percent.

In order to compare the TG curves, the average inflection points (peak temperature) of the first derivative of TG curves were calculated and are presented in Table 4. The data in this table reveal that the increase of the heating rate leads to an increase in the peak temperatures. It should be pointed out that, the peak temperature of Avicel at a heating rate of 5 °C $min^{-1}$ is in agreement with previously reported values [15]. Furthermore, the peak temperatures of Avicel are lower than the peak temperatures of the decomposition of cotton fibers. This could be attributed to higher molecular weight of cellulose macromolecules in cotton fibers. Indeed, it has been reported that the thermal stability of cellulose increases with increasing molecular weight [16]. For this particular sample of Avicel, the reported value of the degree of polymerization was 221. However, for mature cotton fibers, the degree of polymerization was reported to range from 9,600 to 14,000 [17]. Therefore, it is reasonable to hypothesize that the higher peak temperatures of cotton fibers compared to Avicel is caused by the higher molecular weight. However, cotton fibers harvested at 24 dpa present a higher peak temperature compared to that of fibers harvested at 56 dpa. Cellulose in fibers at 24 dpa has lower molecular weight compared to cellulose in fibers at 56 dpa. In a previously reported study, cotton fibers of Texas Marker-1 cultivar at 25 dpa have been reported to have a broad distribution of molecular weight, which includes a higher proportion of lower molecular weight material present in the primary cell wall compared to fibers at 40 dpa [18]. In fibers at 25 dpa, the high molecular weight characteristic of secondary cell wall cellulose is also present [18]. The high peak temperature of cotton fibers at 24 dpa cannot be assigned only to the molecular weight. It is reasonable to assume that the higher content of noncellulosic materials in fibers at 24 dpa compared to 56 dpa, leads to a shift of the peak temperature of cellulose to higher temperatures. It was reported that a small amount of NaCl added to Avicel sample influences the pyrolysis reactions of cellulose in Avicel sample, and the peak temperature is shifted to higher temperatures by 5 °C [19].

The calculation of the activation energy as a function of the degree of conversion was calculated from different TG curves for Avicel and cotton fibers harvested at 56 and 24 dpa (Figs. 4, 5, 6). In the case of Avicel, the activation energy remains constant between 5 and 85% conversion level with an average value of 164 kJ $mol^{-1}$ (Fig. 4). At higher conversion level (>85% conversion), an increase in the activation energy with the conversion level is observed. The activation energy for cotton fibers at 56 dpa starts at lower values, compared to Avicel, between 5 and 10%

**Table 4** Evolution of the peak temperature as a function of the heating rate for Avicel and cotton fibers

| Heating rate/°C min$^{-1}$ | Avicel | | Cotton 56 dpa | | Cotton 24 dpa | |
|---|---|---|---|---|---|---|
| | Peak temperature/°C | STD/°C | Peak temperature/°C | STD/°C | Peak temperature/°C | STD/°C |
| 4 | 330.33 | 0.34 | 356.86 | 0.22 | 366.213 | 0.438 |
| 5 | 334.11 | 0.90 | 361.34 | 0.40 | 370.637 | 1.043 |
| 8 | 343.87 | 0.16 | 370.24 | 0.13 | 379.097 | 0.297 |
| 10 | 347.51 | 0.23 | 374.60 | 0.97 | 385.027 | 0.990 |
| 16 | 355.57 | 0.23 | 381.79 | 1.04 | 393.473 | 1.606 |

*STD* standard deviation

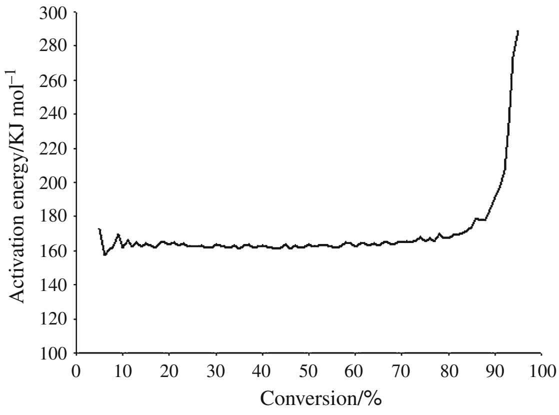

**Fig. 4** Activation energy (expressed in kJ mol$^{-1}$) as a function of the conversion level for Avicel

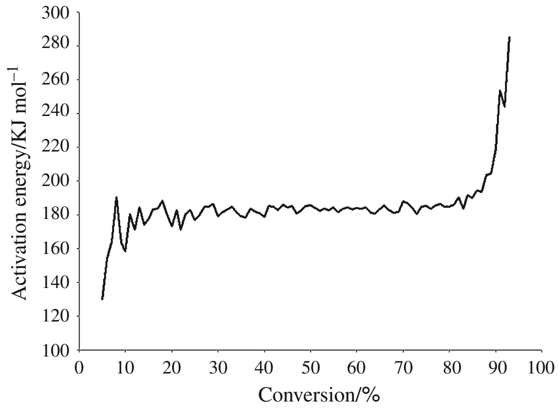

**Fig. 5** Activation energy (expressed in kJ mol$^{-1}$) as a function of conversion level for cotton fibers harvested at 56 dpa

conversion level (Fig. 5). This could be attributed to the presence of noncellulosic materials in the cotton fibers. After 10% conversion level, the activation energy remains constant until 85% conversion level with an average value of 178 kJ mol$^{-1}$. The activation energy increases at higher conversion level (>85%). The average value of the activation energy of fibers at 56 dpa (178 kJ mol$^{-1}$) is higher than the Avicel value (164 kJ mol$^{-1}$). As indicated above,

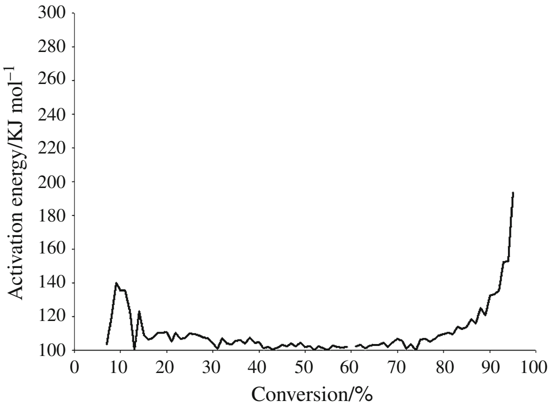

**Fig. 6** Activation energy (expressed in kJ mol$^{-1}$) as a function of conversion level for cotton fibers harvested at 24 dpa

the high activation energy of fibers at 56 dpa is associated with the high molecular weight. For fibers at 24 dpa, the average activation energy value is 109 kJ mol$^{-1}$ (Fig. 6). Previously reported values of the activation energy for different samples of cellulose vary widely, from 48 to 282 kJ mol$^{-1}$, depending on the sample origin and processing, the experimental conditions, and the method used to calculate the activation energy [20]. Activation energy values above 200 kJ mol$^{-1}$ for Avicel PH-105 using model-fitting methods have been reported [21]. Values of the activation energy around 200 kJ mol$^{-1}$ [22] and even lower values (183–189 kJ mol$^{-1}$) were reported for cellulose powder samples (not Avicel PH 105) using other model-free methods [23]. Kokot et al. studied the thermal degradation of cellulosic fabrics with a TG at similar conditions performed in this study. The activation energy values obtained for different cotton fabric samples were from 113 to 185 kJ mol$^{-1}$ in the temperature range of 306–348 °C [24]. Moreover, Mack and Donaldson performed TG, DSC, and DTA tests on cotton fabric. Their results showed an activation energy of 171.54 kJ mol$^{-1}$ calculated from DSC curves, and that of 204 kJ mol$^{-1}$ calculated from TG curves [25]. However, the heating rate used by them was different from the heating rate used in our study. In addition, Chatterjee and Conrad [26] using TG isothermal measurements on cotton samples obtained values of the activation energy of 138.07 and 227.19 kJ mol$^{-1}$ for the initiation reaction and propagation reaction, respectively, although the mass of the samples in their study were one order of magnitude higher than the mass used in this investigation. Yao et al. studied the activation energy of several natural fibers with TG at different heating rates and different model-free methods. Activation energy values from 154.30 to 197.6 kJ mol$^{-1}$ were obtained [27]. Using a model-free method, Mamleev et al. investigated the decomposition of cotton in air and obtained values of the activation energy of 90–167 kJ mol$^{-1}$ for 5% of conversion, 195.9 kJ mol$^{-1}$ over the range $0.2 \leq \alpha \leq 0.62$, and 153.1 kJ mol$^{-1}$ over the range of $0.7 \leq \alpha \leq 1$. Their results at low degree of conversion are in agreement with our results. Mamleev et al. attributed the initial value of the activation energy to the formation of ether bond between hydroxymethyl groups and hydroxyls in adjacent chain ends and the products of cellulose decomposition. Corradini et al. studied the activation energy of several cotton fibers with TG and the Flynn–Wall–Ozawa method. Their results indicated that there was a relationship between the degree of crystallinity and the activation energy value. For cotton samples having a crystallinity index (CI) of 77%, the activation energy values obtained were around 150 kJ mol$^{-1}$. However, for cotton samples with a CI of 63%, the activation energy values obtained were around 137.7 kJ mol$^{-1}$ [28]. Consequently, the range of reported activation energy values are in agreement with the values obtained in our study.

It is important to point out that all the samples showed constant activation energy as function of conversion level, between 5 and 85% for Avicel and between 10 and 85% for cotton samples. This could mean that the reaction is a single-step process or that the activation energy is governed by the slowest step of a multistep process [9, 29]. However, cellulose thermal decomposition has been reported to be a multistep process [3]. It is generally understood that the thermal degradation of cellulose can follow competitive reaction pathways. The Broido–Shafizadeh multistep model for cellulose pyrolysis states that the first step of cellulose degradation is the formation of “active cellulose” followed by two parallel pathways. One of the competitive reactions is the formation of volatiles, and the other one is the formation of char and gases [30]. Thus, the calculated activation energy for the cellulose decomposition in both Avicel and cotton fibers presented in this study, could originate from the slowest step in the overall reaction process.

The comparison of the experimental degree of conversion to the calculated degree of conversion at isothermal conditions $T = 300$ °C shows a good agreement for Avicel and cotton fibers at 56 dpa (Fig. 7). In addition, cotton fibers at 56 dpa require longer time to reach the same degree of conversion compared with Avicel samples at isothermal conditions. For example, to achieve a degree of conversion of 40%, 62 min are needed for mature cotton fibers, while only 20 min are needed for Avicel. It is concluded that the cause of this behavior is the higher activation energy of the decomposition of cotton, which has already been attributed to its high molecular weight. For fibers at 24 dpa, there is a good agreement between the calculated values and the experimental values up to 50% of conversion. At higher degree of conversion, there is a divergence between the calculated and the experimental values. Since cotton fibers at 24 dpa have lower activation energy than Avicel, it was expected that these fibers exhibit faster isothermal decomposition times compared to Avicel. However, the calculated values and the experimental values for cotton fibers at 24 dpa are below than those determined for Avicel, which means that these fibers exhibit longer decomposition times.

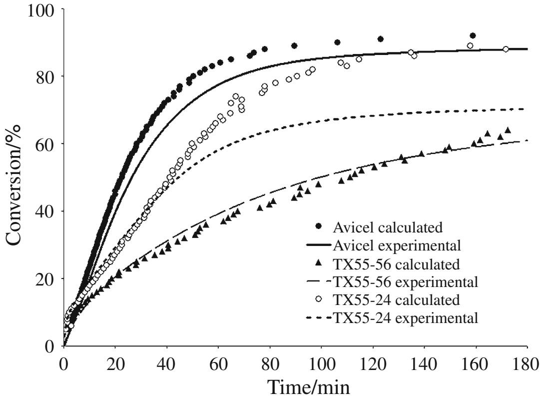

**Fig. 7** Comparison between experimental and calculated conversion level as a function of time at isothermal conditions ($T = 300$ °C)

## Conclusions

In this study, the pyrolysis of cellulose in Avicel and cotton fibers was investigated using TG and a model-free method. The results showed that cotton fibers harvested at 56 dpa have higher peak temperatures and higher activation energy (178 kJ mol$^{-1}$) compared to cellulose in Avicel. The constant activation energy seems to indicate that cellulose pyrolysis is governed by the slowest step in the multistep decomposition process. Moreover, the experimental values of the isothermal decomposition showed a good agreement with the calculated values, which validate the obtained activation energies. These results indicate that the method developed by Vyazovkin is useful in predicting the decomposition values at isothermal conditions and calculating the activation energy and its dependency with the conversion level.

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