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TORREFACTION OF CELLULOSE: VALIDITY AND LIMITATION OF THE TEMPERATURE/DURATION EQUIVALENCE

Pin Lv,^a Giana Almeida,^b and Patrick Perré^{c,*}

During torrefaction of biomass, equivalence between temperature and residence time is often reported, either in terms of the loss of mass or the alternation of properties. The present work proposes a rigorous investigation of this equivalence. Cellulose, as the main lignocellulosic biomass component, was treated under mild pyrolysis for 48 hours. Several couples of T-D (temperature-duration) points were selected from TGA curves to obtain mass losses of 11.6%, 25%, 50%, 74.4%, and 86.7%. The corresponding residues were subjected to Fourier transform infrared spectroscopy for analysis. According to the FTIR results, a suitably accurate match to global T-D equivalence is exhibited up to 50% mass loss: in this domain, mass loss is well correlated to the treatment intensity (molecular composition of the residue) except for slight differences in the production of C=C and C=O. For mass loss levels of 74.4% and 86.7%, distinct degradation mechanisms take place at different combinations of temperature and duration, and the correlation fails. Compared to the mass loss at 220°C and 250°C, the equivalent molecular composition can be achieved through treatment at 280°C with shorter treatment time and less depolymerization and oxidation. The main conclusion drawn is that mass loss can be used as a synthetic indicator of the treatment intensity in the temperature range of 220°C to 280°C up to a mass loss of 50%.

Keywords: Cellulose; Biomass; Mass loss; Torrefaction; Kinetics

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INTRODUCTION

Torrefaction that changes the chemical and physical properties of biomass is a transformation process able to improve the properties of solid wood (such as hydrophobicity, durability and stability, grindability, and energy density). Torrefaction has been recognized as a feasible pretreatment for future biofuel production in the BtL (Biomass to liquid) chain, which integrates various technology stages, including torrefaction, gasification, purification of the synthesis gas, and its ultimate conversion to second generation biofuels using Fischer-Tropsch synthesis (Zwart *et al.* 2006; Prins *et al.* 2006; Deng *et al.* 2009; Watson *et al.* 2010; Meng *et al.* 2012). Moreover, torrefied biomass is found suitable for (co-)combustion in coal fired power plants, and the combination of torrefaction and pelletization processes are widely discussed to produce “coal like” fuel pellets that can replace coal in existing power plants (Biagini *et al.* 2002; Weststeyn 2004; Bergman *et al.* 2005; Bergman 2005; Dai *et al.* 2008).

In the study of torrefaction and conversion processes of biomass, many experimental investigations reveal no significant interactions among three main components of biomass (cellulose, hemicelluloses, and lignin) and thus, thermal behavior of biomass materials can be summatively characterized by these individual components. (Cozzani *et al.* 1995; Alén *et al.* 1996; Várhegyi, *et al.* 1997; Svenson *et al.* 2004; Biagini *et al.* 2006; Yang *et al.* 2006; Chen and Kuo 2011).

In addition, interesting findings related to mass loss of wood have been reported during torrefaction. The loss of mass has been used as a criterion in identifying the stages of wood degradation when submitted to heat (Vovelle and Mellottee 1982; Brito *et al.* 2008). Mass loss is considered the most important parameter related to the reduction of modulus of rupture during heat treatment of *Grevillea robusta* wood (Mburu *et al.* 2008). In the temperature range from 220°C to 250°C, treatment intensity, assumed equal to mass losses, is strongly correlated with wood elemental composition, which would be a valuable tool in estimating the durability of commercially heat-treated wood against fungal decay (Šušteršič *et al.* 2010).

During a torrefaction study of maritime pine and pedunculate oak woods (at 220°C, 250°C, and 280°C for 1 or 5 hours), a lab scale thermal analyzer was utilized to investigate alterations in the chemical composition and energy properties (Colin 2007; Pierre *et al.* 2011). It was demonstrated that mass loss can be an excellent indicator in predicting treatment extent on energy and composition properties. Moreover, linear regressions have been developed that relate energy properties as a function of mass loss caused by various torrefaction processes in the study of three eucalyptus species and barks (Almeida *et al.* 2010). Accordingly, mass loss played an important role in the biomass torrefaction study; however, it seems that the limits of mass loss as an indicator have not been examined so far.

Cellulose, one of three primary constituents in lignocellulosic biomass materials, is an important component involved in many processes, and thus many studies have developed kinetic models for predicting the pyrolysis behavior of cellulose (Bradbury *et al.* 1979; Agrawal 1988; Di Blasi 1994; Marongiu *et al.* 2005). Nevertheless, there is little consensus concerning the kinetics of wood and cellulose pyrolysis due to various processes and final applications, as well as different properties of species (Di Blasi 1996; Grønli and Melaaen 2000; Moghtaderi 2006; Di Blasi 2008). Understanding the pyrolysis behavior of cellulose is fundamental to biomass thermo-chemical conversions; therefore, the present study focused on the time-temperature equivalence for the heat-treatment of cellulose.

Throughout the experiment, two parameters, the plateau temperature (T) and the duration (D), were highlighted to investigate the mass loss of cellulose under mild pyrolysis with each treatment being characterized by its T-D couple. Sampling of ten residues for different T-D couples leading to five values of mass loss (11.6%, 25%, 50%, 74.4%, and 86.7%) were duplicated and analyzed by Fourier transform infrared spectroscopy.

EXPERIMENTAL

Methods

Torrefaction of microcrystalline cellulose (Sigma Aldrich Chemical Co., France) was carried out using a Mettler TGA-DSC 1. Initially, samples were heated at a rate of 5°C/min from ambient temperature to 110°C, and dried for 30 minutes at 110°C. The mass recorded at the end of this drying segment was used as the initial mass to determine the mass loss due to pyrolysis. The temperature was then increased at 5°C/min to a final temperature and was held, thereafter, for 48 hours (2880 min). All treatments were performed in a nitrogen atmosphere with a gas flow of 50 mL/min.

Aluminum crucibles, 70 µL, were used in the TGA experiments. Samples weighed approximately 5 mg and were placed in the open crucible. At least three blank tests were carried out, and the curves presented in this work show data after the blank was subtracted. Figure 1 shows TGA curves collected after the drying segment. Cellulose exhibited stable behavior when treated at 220°C, while it decomposed rapidly and even sharply when subjected to the treatment at 250°C and 280°C. The mass loss (ML) of the sample was calculated using the following equation,

$$ML = [(M_0 - M_t) / M_0] \times 100\% \quad (1)$$

where, M_0 is the mass obtained at the end of the drying segment and M_t is the mass obtained after the drying segment.

Several couples of T-D points were selected from the TGA curves based on the mass at the end of the treatment. An interior baseline was then extended from those points, where intersections with other curves identify T-D couples that give the same mass loss (Fig. 1).

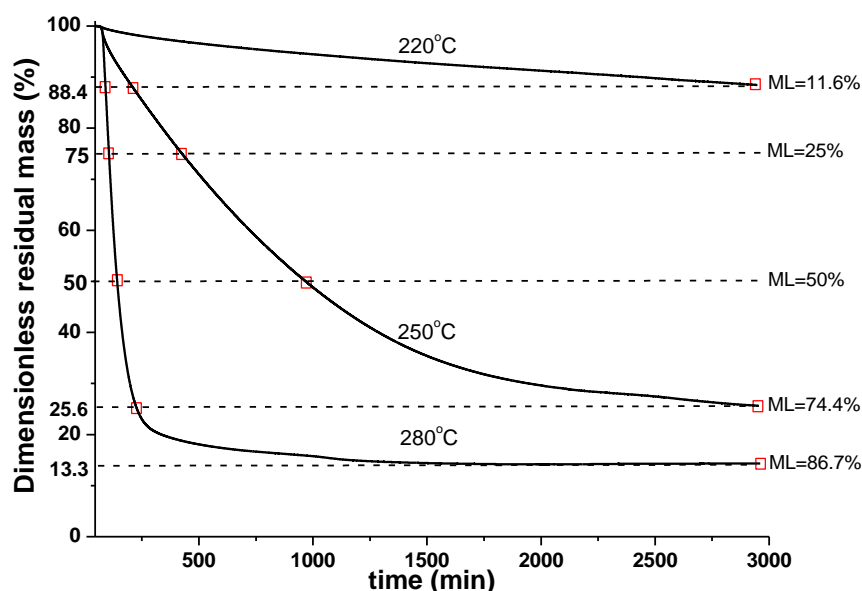


Fig. 1. TG curves of the pyrolysis of cellulose under different treatments for 48h (□ symbols indicate the T-D points selected and analyzed by FTIR; ML: mass loss)

Four other T-D points were also selected at mass loss levels of 25% and 50% for more comprehensive data and analysis. These T-D points are listed in Table 1. Torrefactions were then carried out to duplicate each T-D point and stopped at a specific time.

The obtained residues were examined with a Nicolet 6700 combined with an ATR unit (SMART, iTR, Thermo SCIENTIFIC) at a resolution of 4 cm^{-1} for 64 scans in the range from 4000 to 650 cm^{-1} . A background spectrum was recorded prior to each spectrum.

Table 1. Temperature and Duration Selected at the Same Mass Loss Level

Treatments Mass loss	Duration		
	220°C	250°C	280°C
11.6%	2880 min	127.7 min	8.95 min
25%	/	350.9 min	24.6 min
50%	/	893 min	60.5 min
74.4%	/	2880 min	142.3 min
86.7%	/	/	2880 min

RESULTS AND DISCUSSION

From Fig. 1, 10 specific torrefied cellulose samples at different mass loss levels were examined, and the recorded infrared spectra are presented in Fig. 2 (a-d) and Fig. 3. Typical absorptions of untreated cellulose as shown in Fig. 2a include 3335 cm^{-1} (ν OH), 2896 cm^{-1} (ν C-H), 1426 cm^{-1} (ρ CH₂ sym.), 1365 cm^{-1} (δ CH), 1333 cm^{-1} (δ CH in-plane), 1310 cm^{-1} (δ CH), 1201 cm^{-1} (ρ OH; δ CH), 1160 cm^{-1} (ν bridge -O- asym.), 1103 cm^{-1} (cyclic ether, asym.), 1054 cm^{-1} (ν C-O), 1027 cm^{-1} (ν C-O), 895 cm^{-1} (ν bridge C-O-C sym), 709 cm^{-1} (ω OH out-of-plane), and 665 cm^{-1} (ω OH out-of-plane), which is in agreement with results reported in the literature (Baeza and Freer 1991).

T-D Couples With 11.6% Mass Loss

Compared with the untreated cellulose, all the absorption peaks of the treated cellulose, at the mass loss level of 11.6%, are in the same position, which implies that the main molecular structure retains its original form even after 48 h at 220°C (Fig. 2a). Analogous results have been reported that cellulose in *Eucalyptus* and *Pinus* woods does not change under treatment for 9 hours at 180°C (Brito *et al.* 2008). Moreover, it is visually apparent that the relative intensities of the treated samples were almost equivalent, which implies a similar degradation behavior whatever the T-D couple applied to obtain this level of mass loss. However, two new peaks arising at 1715 and 1633 cm^{-1} give evidence of the degradation of the cellulose; the absorbances which are ascribed to C=O and C=C groups, respectively (Maschio *et al.* 1992).

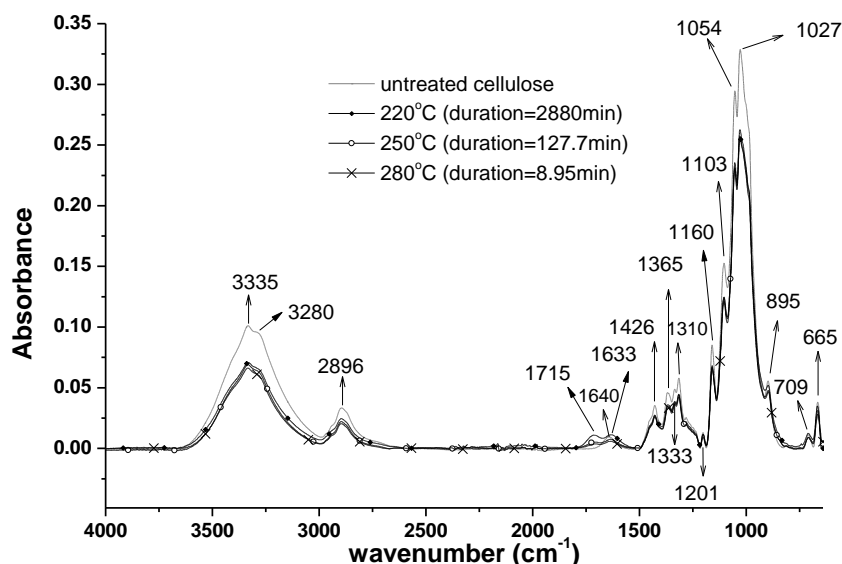


Fig. 2a. FTIR-ATR spectra of cellulose at the mass loss of 11.6% under different treatments

T-D Couples With 25% or 50% Mass Loss

At 250°C and 280°C, the degradation of cellulose increases rapidly with the prolongation of residence time. From Fig. 2 (b-c), the relative intensities of O-H (3000 to 3600 cm^{-1}), C-H (2700 - 3000 cm^{-1}), and C-O (1000 - 1200 cm^{-1}) obviously decrease while accompanied by an increase of C=O and C=C (especially at 50% mass loss), while the positions of characteristic peaks continue to be nearly the same as untreated cellulose. From this result, it can be concluded unexpectedly that dehydration dominates during the degradation until 50% mass loss of the cellulose.

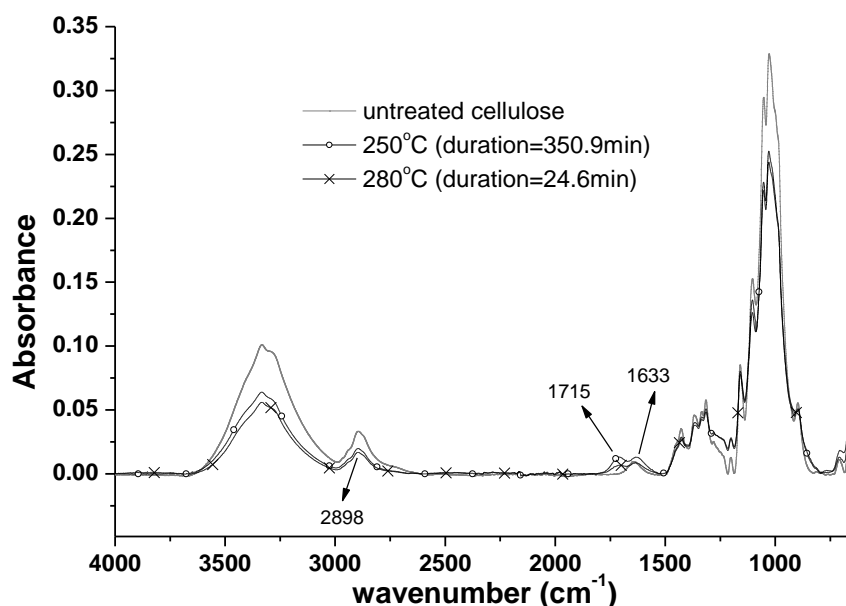


Fig. 2b. FTIR-ATR spectra of cellulose with a mass loss of 25% under different treatments

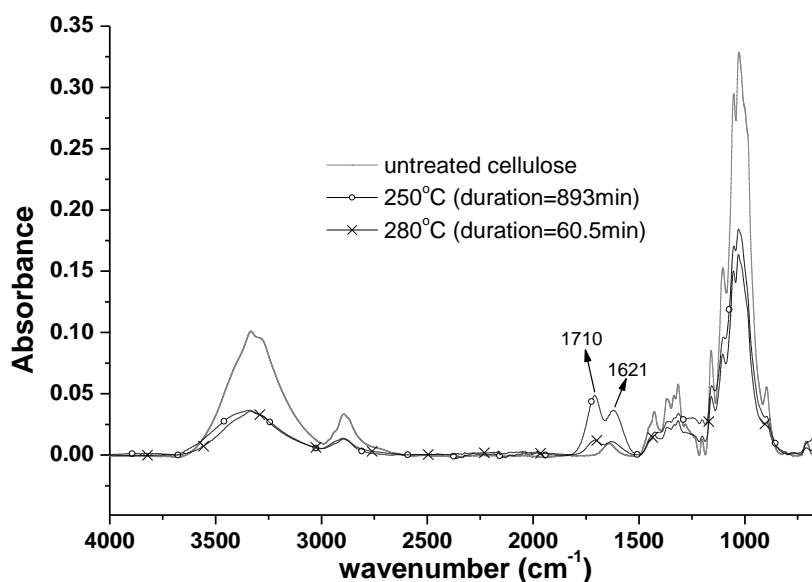


Fig. 2c. FTIR-ATR spectra of cellulose with a mass loss of 50% under different treatments

T-D Couples With 74.4% Mass Loss

In the case of treatment at 250°C for 48 h, which had a mass loss of 74.4% (Fig. 2d), a shoulder appears at 1767 cm⁻¹, which denotes the generation of carboxylic groups (Socrates 2001). Simultaneously, disappearance of characteristic absorptions and arising of a series of broad bands in the range of 650 to 1500 cm⁻¹ demonstrate that cleavage of C-O bond predominates, resulting in the rearrangement of the molecular structure. It is from this stage that the corresponding T-Ds at the same mass loss level are no longer equivalent.

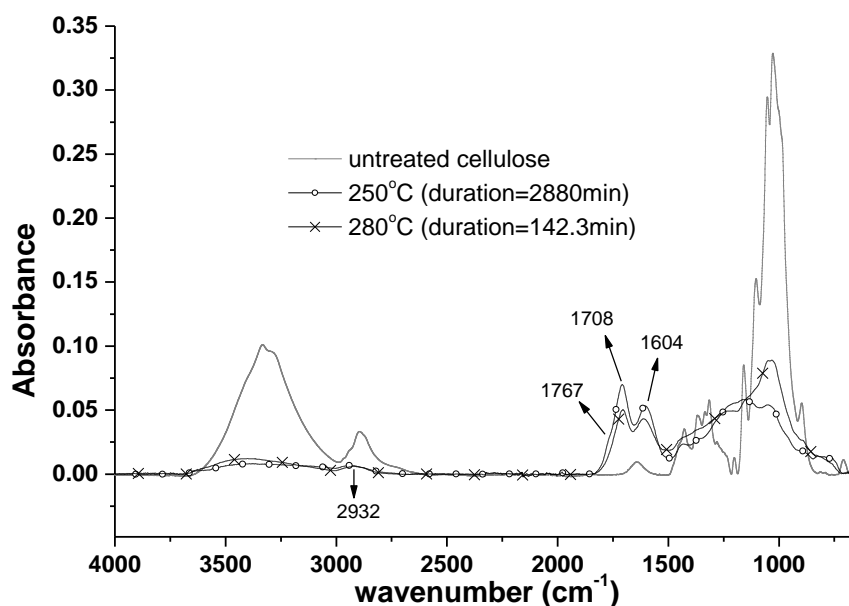


Fig. 2d. FTIR-ATR spectra of cellulose with a mass loss of 74.4% under different treatments

As the degradation continues up to a mass loss of 86.7%, the absorption of cyclic carboxylic acid anhydride appears at 1842 cm^{-1} ($\nu\text{ C=O asym.}$), 1767 cm^{-1} ($\nu\text{ C=O sym.}$), 1200 cm^{-1} ($\nu\text{ C-O-C}$), and 899 cm^{-1} ($\nu\text{ C-O-C}$) under the treatment at 280°C for 48h (Fig. 3) (Marquardt 1966; Socrates 2001). The production of carboxylic acid indicates that cellulose undergoes a more severe degradation. Evident yield of carbonized cellulose is found for new peaks developing at 1599 , 1427 , and 737 cm^{-1} , which are typically ascribed to aromatic skeletal stretching vibrations and aromatic $=\text{C-H}$ out-of-plane deformation, respectively.

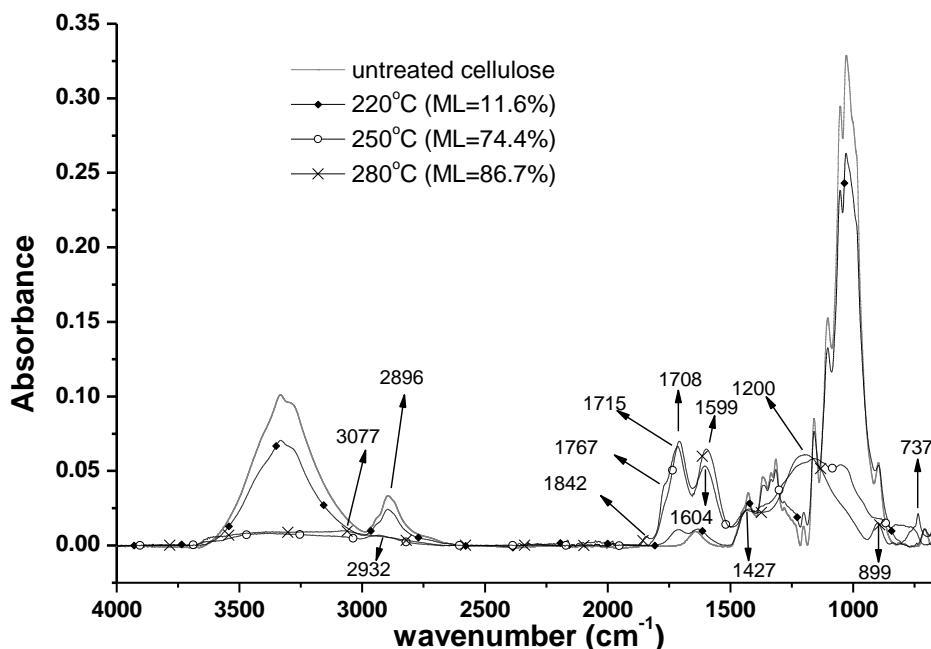


Fig. 3. FTIR-ATR spectra of pyrolyzed cellulose under different treatments for 48h

On closer inspection, the alkyl group shifts to a higher wavenumber while the naissance of C=C absorption shifts to a lower wavenumber during the treatments. In order to get a better knowledge of the kinetics of cellulose, it is worthwhile to explain these shifts. Alkyl groups in cellulose (Fig. 2a) absorb at 2986 cm^{-1} (assigned to C-H in methine), and then this absorption shifts to 2932 cm^{-1} and 3077 cm^{-1} at higher mass loss treatments (Fig. 2d, Fig. 3), indicating that alkyl groups change from C-H in methine to C-H in methylene and the hydrogen atom becomes adjacent to unsaturated carbon atoms. In addition, the absorption initially at 1633 cm^{-1} is attributed to C=C through intra-molecular dehydration (Gribov and Popov 1963). At a mass loss of 50%, the absorption shifts to 1621 cm^{-1} as a result of the production of vinyl ketone groups (Socrates 2001). This can be verified by the increase in intensity of C=O (1715 cm^{-1} at 11.7% mass loss), which shifts to a lower wavenumber at 1710 cm^{-1} because of the conjugation with C=C . The absorption at 1604 cm^{-1} with a mass loss of 74.4% after the treatment at 250°C for 48 h is characteristic of C=C-C=C (Noack 1962a,b). It is associated with the generation of carboxylic acids and favours carbonization, which can be confirmed by the sudden decrease in alkyl and hydroxyl groups. The absorption at 1599 cm^{-1} after the treatment at 280°C for 48 h, together with the new peak at 3077 cm^{-1} assigned to aromatic C-H

stretching vibrations, demonstrates the process of carbonization, which explains the flattening out of the mass loss curve at 280°C after about 1500 min of treatment. This carbonization mechanism agrees with other investigations (Arseneau 1971; Broido and Nolson 1975; Koullas *et al.* 1991).

It is clear that at higher treatment temperatures less residence time is needed to reach the same mass loss level (Table 1). For example, at a mass loss level of 50%, the residence time at 250°C (893 min) was 14 times greater than that at 280°C (60.5 min). Furthermore, when comparing the T-Ds at the same mass loss level up to 50%, it is observed that cellulose maintained its characteristic structure even though the chemical properties were not exactly the same (Fig. 2 a-c). Higher absorption intensities of C=O and C=C were detected in the case of lower temperature treatment compared with those under higher temperature treatment, which can be due to the effect of longer residence time; therefore, for a same mass loss level, torrefaction at higher temperatures takes less time with less depolymerization whereas torrefaction at lower temperatures enables cellulose to produce more C=O and C=C groups but at the cost of longer duration. Also, the disappearance of the characteristic absorptions under the conditions at 250°C and 280°C after 48 h indicates differing kinetics from what was observed at 220°C after 48 h (Fig. 3). Chemical changes of the functional groups that prevail in the degradation mechanism in this study are presented sequentially as follows:

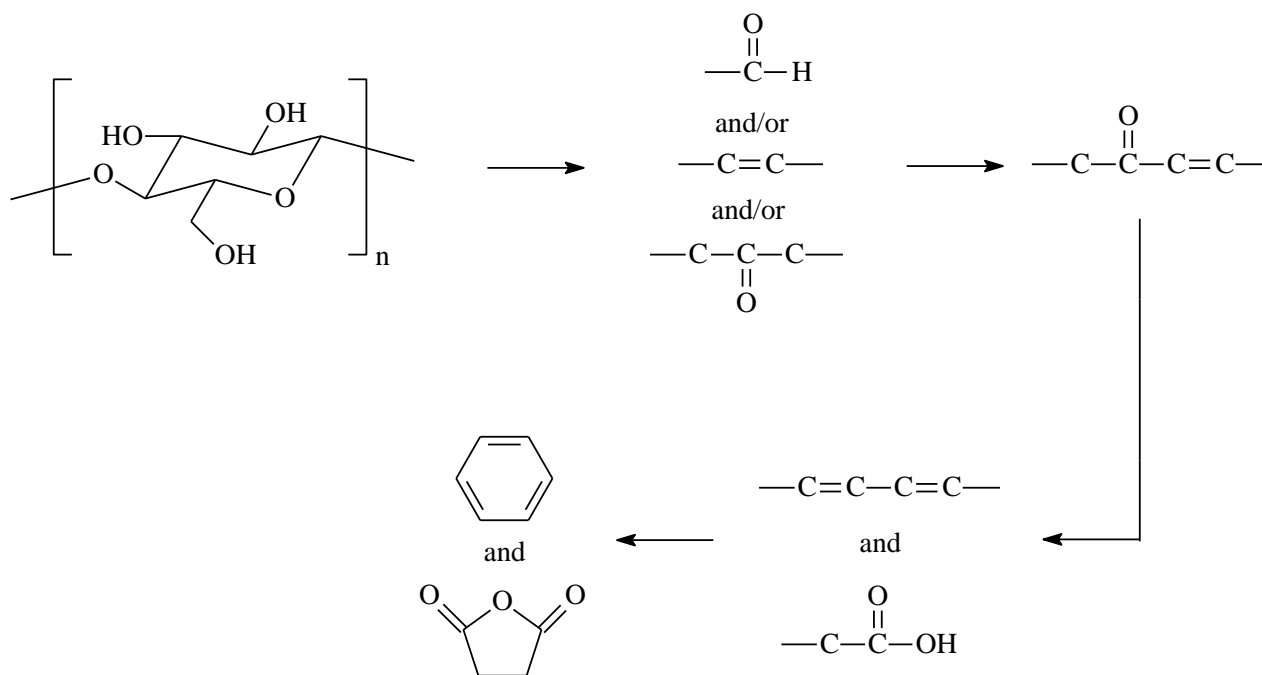


Fig. 4. Reaction scheme to account for the findings of this study

CONCLUSIONS

The aim of this work was to test the temperature-duration (T-D) equivalence regarding thermal degradation of cellulose. Thermogravimetric tests were performed to choose T-D couples able to produce the same values of mass loss (11.6%, 25%, 50%, 74.4%, and 86.7%) at different plateau temperatures. Subsequently, tests were reproduced to obtain the final product for each T-D couple. The residues were analysed by FTIR under the ATR mode.

1. The T-D points selected were in good equivalence at the same mass loss level up to 50% mass loss. At mass losses of 74.4% and 86.7%, rearrangement of the molecules dominates and breaks the equivalence. Consequently, interaction between temperature and duration leading up to 50% mass loss is regarded as the limit of the equivalence within this study. Mass loss appears to be a suitable indicator of treatment intensity in the temperature range of 220°C to 280°C up to a mass loss of 50%.
2. Under the same treatment intensity, torrefaction at higher temperatures takes less time with less depolymerization, whereas torrefaction at lower temperatures enables cellulose to produce more C=O and C=C groups but at the cost of longer required duration.
3. Dehydration predominates in the kinetics of cellulose treated at 220°C, whereas condensation predominates at treatments of 250°C and 280°C with long duration (more than 50% mass loss).

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