Structural Effects of Cellulose on Hydrolysis and Carbonization Behavior during Hydrothermal Treatment

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ABSTRACT: This study aims to investigate how the morphology of cellulose influences the hydrolysis and carbonization during hydrothermal treatment at temperatures between 180 and 240 °C. The morphology of cellulose, especially different crystallinities and degrees of polymerization, is represented by microcrystalline cellulose and α-cellulose. Kinetic analysis is considered a tool to allow the determination of the mechanisms of the two types of cellulose during the hydrothermal process. A kinetic model, in which cellulose is assumed to be hydrolyzed to a limited extent, is proposed. Five scenarios are used as models for pyrolysis of nonhydrolyzed cellulose that forms primary char, along with reaction pathways of hydrolyzable cellulose and its derivatives that latterly form secondary char. The morphologies of solid products are in good agreement with the results of the proposed model.

1. INTRODUCTION

Lignocellulosic biomasses, such as agricultural residues, energy crops, and forestry wastes, are important resources beyond the field of application as renewable energy to substitute fossil fuels. Moreover, they are also a source for the production of biobased chemicals. Lignocellulosic biomass is abundant on the earth and carbon neutral if it is burned, which validates its sustainability and significant role in bioeconomy. There are several technologies enabling the conversion of biomass to more valuable products. Such biomass always contains high moisture content, which is a major challenge due to direct combustion not being a feasible idea. Therefore, hydrothermal treatment, in which hot compressed water at temperatures around 200 °C is involved,1 is a suitable technology for conversion of wet biomass. Hydrothermal carbonization (HTC) is an attractive process that converts biomass into carbonaceous materials. The high versatility of HTC products allows their utilization in many applications such as electrode materials in energy storage technologies,2 materials used as sensors and fuel cell catalysts,3 and soil amendments in agriculture.4 Furthermore, hydrochar derived from HTC can be applied as a solid fuel to replace lignite due to similar heating values.5

Cellulose is frequently used to represent lignocellulosic biomass because it is a primary structural component of the plant cell wall, which makes up 40−60 wt % besides hemicellulose and lignin.6,7 It is a polysaccharide linked by β-1,4-glycosidic bonds between D-glucopyranose units forming chains. These chains are linked by hydrogen bonds that are formed between its hydroxyl groups, which results in various orders of crystallinity.8 As a result of these inter- and intramolecular forces, cellulose is resistant to various treatments.9 Hydrothermal treatment allows hot compressed water to access the inner structures of cellulotic biomass. Essentially, an arrangement of molecules of cellulose develops its structure into crystalline and amorphous domains. The amorphous fraction in cellulose is more reactive than the crystalline fraction.10 Crystalline-to-amorphous transformation of cellulose takes place when water penetrates the inner structure at different temperatures depending on its crystallinity.11 In fact, crystalline cellulose swells only in supercritical water. Here, the conversion of cellulose from the crystalline to amorphous domain occurs, leading to fast reaction rates to form oligomers.12 In addition, the crystallinity of the unreacted cellulose was almost unchanged by the extent of conversion.13,14 Following hydrolysis, dehydration of hydrolyzed C6 and C5 sugars leads to the production of 5-hydroxymethylfurfural (HMF) and furfural, respectively.15 These carbon-rich intermediates consecutively polymerize to form secondary char, whereas lignin likely forms primary char via solid-to-solid conversion.16,17 Both chars are called hydrochar when they are formed by HTC, despite their different chemical structures.

Although many studies have investigated the HTC of biomass and cellulose, it is yet unclear how to design...
operational conditions for HTC processes because the reaction pathway and kinetics are yet largely unknown.18 Until now, different kinetic models have been presented for the HTC of cellulose. So far, kinetic analysis has been conducted following Arrhenius behavior under the assumption of a first-order reaction for hydrolysis and liquid-phase reactions (i.e., dehydration, retro-aldol condensation, etc.).19−24 However, secondary char formation was found to be favored at a high concentration of HMF; hence, the reaction order of the polymerization should be higher than unity.25−28 A key challenge in this field is that the HTC of cellulose consists of not only the secondary char formation through dissolved intermediates but also another parallel reaction pathway, namely, the solid-to-solid char formation, to form the so-called primary char.29 Falco et al. argued that the solid-to-solid pathway dominates during the HTC of cellulose due to the presence of large aromatic clusters in the char.30 The authors further stated that more furanic structures should be present similar to glucose-based char to prove the presence of secondary char. Their conclusion might be questionable due to the high presence of spherical particles visible in the scanning electron microscopy (SEM) pictures.30,31 These are usually regarded as secondary char.25 In another study, it was concluded that spherical particles were dominant if higher acid concentrations were applied, which promoted hydrolysis of the cellulose.32 All in all, it is difficult to analytically distinguish secondary and primary char since both appear as one bulk of char. Current kinetic models handle this aspect with different approaches. Some authors simply neglect secondary char formation and model the primary char formation in terms of a first-order rate equation, which converts cellulose into char.23,24 However, a first-order rate equation might also not completely fit for the HTC of cellulose, since a certain concentration dependency has already been observed.31 In other studies, hydrochar formation in real biomasses was solely modeled based on the amount of dissolved compounds,32 and in other cases, both reaction pathways were included.25,34,35

However, none of these studies have taken structural effects of biomass on kinetic reaction rates into account, which should essentially influence the rate of hydrolysis due to the different crystalline fractions and degrees of polymerization (DP) of crystalline and amorphous cellulose. Thus, a kinetic rate analysis of two celluloses representing crystalline (micro-crystalline cellulose (MC)) and amorphous (α-cellulose (AC)) properties was executed. Also, this study is aimed at investigating the hydrolysis and carbonization behavior during HTC with a special focus on the solid products. To the best of our knowledge, this is the first work that parallelly determined the reaction kinetics of both primary and secondary char formations of cellulose as a feedstock material. Five scenarios for char production were proposed and the best model was statistically selected as an approach to explain the reaction mechanisms.

2. RESULTS

2.1. Intermediate Products. To see whether cellulose degradation happened during the heating period before reaching the target temperature (180−240 °C), additional observations at lower temperatures of 140 and 160 °C were carried out. Each experimental run started from room temperature and then the reactors were removed from the oven, right after the temperature was reached. By visual observation, each product had no changes in its appearance, namely, the solid products were white and the liquid effluent was clear as they were at the beginning. It was confirmed by high-performance liquid chromatography (HPLC) that no degradation of the liquid eluent had taken place below the temperature of 180 °C. No degradation products (sugars, furans, or acids) were detectable.

Low amounts of hydrolyzed products (less than 12% conversion of cellulose) were observed for both α-cellulose (AC) and microcrystalline cellulose (MC) at 180 °C when the reaction time was long enough. The products became more profound at 200 °C, where a higher product yield could be observed from AC than MC. A higher yield of glucose in AC depicts faster hydrolysis of cellulose, which is the rate-limiting step. Only very low concentrations of fructose were detected, possibly because of its fast conversion directly after the production. 5-Hydroxymethylfurfural (HMF) and furfural were produced subsequently from fructose by dehydration. These reaction steps were delayed when MC was employed as feedstock. A dramatic change in cellulose conversion could be seen when the temperature shifted from 200 to 220 °C, where AC and MC completely converted in 180 and 120 min, respectively. At this temperature, glucose yield became higher in the case of MC. At 240 °C, AC and MC started to hydrolyze even before the reaction time was set to zero (before the temperature reached 240 °C). However, the amount of intermediate products was lower than that at 220 °C and at a longer reaction time. It is also noteworthy that the major organic acids were formic acid and levulinic acid, where the latter was stable even at a longer reaction time. At higher temperatures (200−240 °C), the amount of detectable furfurals increased slightly. This was already reported in the literature for temperatures close to 200 °C but at higher concentrations and with a catalyst. Low concentrations due to either the small degree of conversion of cellulose or the high conversion rate are autocatalyzed by resulting acids whose concentration increases throughout the conversion process.36

2.2. Solid Product Characterization. Figure 1 shows differential thermogravimetry (DTG) curves, which demonstrate the relative mass loss of the compound during a temperature change. The peak depicts the main decomposition
temperature of a single compound. It shows that raw AC and raw MC decomposed at temperatures of 354 and 339 °C, respectively. DTG curves of HTC products from AC and MC treated at 200 and 220 °C displayed peaks shifted to a lower temperature range of 320–330 °C and the height of the peak decreased with longer reaction time. Concurrently, peaks at a temperature of around 415 °C, corresponding to char, appeared when the reaction time was long enough.

To quantify the fraction of char products in unreacted cellulose, an estimation was made by defining the carbon content of cellulose and char as 44 and 65%, respectively. Therefore, the carbon, hydrogen, and oxygen contents of the product were measured by elemental analysis as can be found in Table 1.

The results of the elemental analysis are represented by the van Krevelen diagram in Figure 2, which depicts that high severity of operating conditions (high temperature and long reaction time) leads to lower O/C and H/C. Spectra derived from Fourier transform infrared (FTIR) spectroscopy, as shown in Figure 3, depict peaks of O–H (3300 cm⁻¹), C–H (2900 cm⁻¹), C=O (1740 cm⁻¹), C=C (1600 cm⁻¹), and C–C (1000 cm⁻¹). The scanning electron microscopy (SEM) images of solid products produced at the longest reaction time of each temperature are shown in comparison with their raw material (AC or MC) in Figure 4, and the morphology of the solid products is discussed in Section 3.1.

### Table 1. Elemental Contents of Solid Product from the HTC of AC and MC at Different Temperatures and Reaction Times

| temp (°C) | time (min) | C   | H   | O   | C   | H   | O   |
|----------|------------|-----|-----|-----|-----|-----|-----|
|          | 0          | 180 | 42.47 | 6.78 | 50.76 | 43.30 | 6.79 | 49.91 |
|          | 15         | 15  | 42.68 | 6.82 | 50.50 | 43.26 | 6.93 | 49.81 |
|          | 30         | 45  | 42.63 | 6.83 | 50.55 | 43.16 | 6.61 | 50.24 |
|          | 60         | 30  | 43.37 | 6.96 | 49.68 | 43.21 | 6.72 | 50.07 |
|          | 120        | 45  | 42.51 | 6.78 | 50.70 | 43.37 | 6.76 | 49.87 |
|          | 180        | 60  | 42.57 | 6.89 | 50.55 | 43.42 | 6.78 | 49.80 |
|          | 120        | 180 | 42.45 | 6.80 | 50.75 | 43.40 | 6.77 | 49.84 |
|          | 240        | 220 | 42.80 | 6.78 | 50.42 | 42.69 | 6.82 | 50.49 |

Figure 2. Van Krevelen diagram of solid products from the HTC of (a) AC and (b) MC.

2.3. Kinetic Analysis. From eqs 1–10, the kinetic rate constants (k₁–k₉) were computed on five different scenarios of pyrochar formation. These calculations are done to mainly...
prove our possible explanations of the results found. A refinement of these calculations may be necessary to evaluate the predictions. Therefore, the confidence interval of the results is given in the Supporting Information in Tables S1 and S2. The first assumption is that all of the cellulose could have been hydrolyzed and no pyrochar formation has taken place. Hence, the term $k_{pf}([\text{Cel}])$ in eqs 1 and 6 is zero. When pyrolysis is involved, it is important to understand that it is a heterogeneous chemical reaction consisting of several processes, such as nucleation, adsorption, desorption, interfacial reaction, and diffusion. To simplify the pyrolysis reaction, the assumptions for the second to the fifth scenarios are based on the solid-state pyrolysis in a single step. This is according to what was suggested by Antal et al. when they did their research on the pyrolysis of pure Avicel cellulose. Nonetheless, this is only applicable for the solid-to-solid degradation of cellulose because in every other case, the models need to be customized concerning parallel or subsequent reactions. The second scenario assumed a pseudo-first-order reaction for pyrochar, and thus the term $k_{pf}([\text{Cel}])$ is $k_{p}[\text{Cel}]$. However, in the third scenario, a nucleation-growth model is considered, which is based on the Prout–Tompkins rate equation that is analogous to a cumulative probability distribution showing sigmoidal behavior. This rate equation infers that the rate of formation of char product depends on both the amount of cellulose and the product itself. The term is hence $k_{p}[\text{Cel}](1 − [\text{Cel}]/3.5)$, where 3.5 is approximated for the carrying capacity, which limits the maximum yield of char. Furthermore, scenarios four and five share an idea similar to the third one, whereas the fourth one takes into account a forcing function and the fifth one includes a nucleation parameter, which represents how fast the nucleation is. The nucleation parameter was assumed to have a value of 2. All five scenarios are summarized, including their quality of fitting represented as root mean square error (RMSE) in Table 1.

From Table 2, we derived the quality of the fitting of the scenario (5) > (4) > (3) > (1) > (2) by a decrease in RMSE. Therefore, the best plots of the scenario (5) compared to experimental data sets are shown in Figure 5. As shown, there is no significant difference of product distribution between AC and MC at 180 °C. That is, hydrolysis of celluloses was very slow in both cases, and thus no intermediate compounds of interest and char product were observed. At 200 °C, the model predicted that AC produced hydrochar and partially pyrochar, while MC produced only pyrochar. Hydrolysis of MC might

Figure 3. FTIR spectra of solid products compared to raw material (AC or MC) at different temperatures and reaction times: (a) AC 200 °C, (b) AC 220 °C, (c) AC 240 °C, (d) MC 200 °C, (e) MC 220 °C, and (f) MC 240 °C.
still not be fast enough to produce the hydrochar precursor in the liquid phase. At 220 °C, MC seems to hydrolyze better than AC, as could be inferred from a higher yield of sugar and furans at an earlier reaction time. Consequently, at 240 °C, MC mostly hydrolyzed, and thus the main product was hydrochar. On the other hand, the model predicted that pyrochar was dominant in the case of AC.

Table 3 shows the optimized values of the kinetic rate constants ($k_1$–$k_9$) from scenario (5), whose pyrochar formation is presumed to be analogous to the nucleation-growth model with the nucleation parameter. It is noteworthy that including the nucleation parameter in the differential rate equations, eqs 1 and 6, gave rise to L2 (mol C)−2·min−1 as the unit of $k_9$. The unit of pre-exponential factors is similar to those of the kinetic rate constants. Table 4 displays the activation energies and the pre-exponential factors obtained from the correlation and slope of the Arrhenius plots derived from eq 11. These are the plots of the logarithm of the rate constant as a function of the inverse of the absolute temperature. That is, the reaction rate constants at different temperature data points correspond to the activation energy and the pre-exponential factor of a specific reaction. The coefficient of determination or $R^2$ expresses how well kinetic rate constants correlate with the reaction temperature.

### Table 2. Summary of the Five Scenarios for Pyrochar Formation Mechanisms and RMSE of Each Scenario

| Scenario | Equation | AC RMSE (mol C·L−1) | MC RMSE (mol C·L−1) |
|----------|----------|---------------------|---------------------|
| (1) no pyrochar | $k_9f([Cel]) = 0$ | 6.1723 | 7.1390 |
| (2) pseudo-first order | $k_9f([Cel]) = k_9[ Cel ]$ | 6.2638 | 6.9010 |
| (3) nucleation-growth | $k_9f([Cel]) = k_9[ Cel ](1 - [ Cel ]/3.5)$ | 5.3521 | 5.5260 |
| (4) nucleation-growth with forcing function | $k_9f([Cel]) = k_9[ Cel ](1 - [ Cel ]/3.5)$ | 5.7203 | 5.1095 |
| (5) nucleation-growth with nucleation parameter | $k_9f([Cel]) = k_9[ Cel ](1 - [ Cel ]/3.5)^2$ | 5.1971 | 4.6902 |

## 3. DISCUSSION

### 3.1. Morphology of the Solid Products

DTG results in Figure 1 present the temperature-dependent transformation of solid products from both raw materials, AC and MC, for different reaction temperatures and times. The thermogravimetric analysis (TGA) curve of raw AC compared to raw MC depicts a broader left-skewed peak, indicating diverse structures in AC, i.e., an amorphous structure in between a crystalline structure, the so-called semicrystallinity. Therefore, the peak of MC whose structure is more purely crystalline is slightly narrower. After hydrothermal treatment, it is likely that the amorphous regions were destroyed. Consequently, the structure of the products from both AC and MC became more uniform and thus their peaks became narrower and shifted to the left. Here, the peaks represent the conversion of cellulose with respect to the reaction time. An increase of generated peaks at temperatures around 415 °C, which correspond to char formation after the conversion of cellulose, could be observed. The decrease of the cellulose peaks and the increase of char peaks are more pronounced at 200 °C for MC. This result correlates well with the finding that more char is produced from MC than AC, which is due to the higher stability against hydrolysis and, thus, lower reactivity of MC during HTC, resulting from its crystalline structure. The structure of MC is the reason for the lower accessibility of...
water, while the amorphous regions and AC are easily converted.

In Figure 5, the concentration of products from AC at (a) 180 °C, (b) 200 °C, (c) 220 °C, and (d) 240 °C and from MC at (e) 180 °C, (f) 200 °C, (g) 220 °C, and (h) 240 °C as a function of the reaction time (●: cellulose, □: sugars, ◇: furans, ○: char; solid lines: model predicted yield, dotted lines: predicted pyrochar, and dashed lines: predicted hydrochar).

In Figure 2, the van Krevelen diagrams of products obtained from AC and MC conversion show lower O/C and H/C ratios.
at higher reaction temperatures and longer residence times. This is the result of dehydration of cellulose during pyrolysis, as well as that of sugar to HMF. In addition, carbonization is associated with the elimination of water and carbon dioxide, which is the reason for the different compositions of the products. It was assumed that a maximum 4-fold dehydration took place in one sugar molecule, increasing the carbon content of hydrochar to 65%. Beyond this carbon content, decarboxylation further increased the H/C ratio slightly.

### Table 3. Reaction Rate Constants of Proposed Scheme in AC and MC at Different Temperatures

| reaction rate constant | 180 °C | 200 °C | 220 °C | 240 °C |
|-----------------------|--------|--------|--------|--------|
| $k_1$                 | 4.85 × 10^{-4} | 1.31 × 10^{-3} | 7.79 × 10^{-3} | 3.03 × 10^{-2} |
| $k_2$                 | 2.27    | 1.40 × 10^{-2} | 8.53 × 10^{-2} | 2.76 × 10^{-1} |
| $k_3$                 | 2.50 × 10^{-14} | 7.03 × 10^{-9} | 1.98 × 10^{-2} | 4.24 × 10^{-2} |
| $k_4$                 | 2.23 × 10^{-6} | 9.05 × 10^{-3} | 3.69 × 10^{-2} | 1.44 × 10^{-1} |

### Table 4. Activation Energy and Pre-exponential Factor of Specific Reactions in the Proposed Scheme

| reaction | $E_a$ (kJ mol⁻¹) | $A$ (mol C)⁻¹·min⁻¹ | $R$ (°C) |
|----------|------------------|----------------------|---------|
| $k_{1,AC}$ | 1.37 × 10⁵ | 2.25 × 10¹² | 0.98 |
| $k_{1,MC}$ | 2.00 × 10⁵ | 2.44 × 10⁹ | 0.98 |
| $k_2$ | 1.26 × 10⁸ | 1.09 × 10¹² | 0.87 |
| $k_3$ | 1.27 × 10⁸ | 6.83 × 10¹¹ | 0.63 |
| $k_{2,AC}$ | 1.39 × 10⁵ | 2.22 × 10⁵ | 0.97 |
| $k_{2,MC}$ | 8.16 × 10⁵ | 1.70 × 10⁶ | 1.00 |

“Units of pre-exponential factors (A) are similar to those of associated kinetic reaction constants (k).

The small pieces shown in Figure 4 are mostly pyrolyzed MC, which, in this work, is stated as pyrochar. These pieces of evidence support the prediction in Figure 5 very well as hydrochar dominates over pyrochar with the existence of unreacted AC, while pure pyrochar is produced from MC. This implies that pyrolysis mainly takes place on the crystalline areas because of a comparatively low hydrolysis rate and a more stable structure of MC compared to that of AC. As shown in the SEM images, the products of AC and MC treated at temperatures over 200 °C are similar. That is, spherical particles accumulated across the whole surface in the form of larger particles. Most likely, it can be inferred that the spherical particles are hydrochar and the larger particles inside are pyrochar. In addition, large, loose spherical particles (~3 μm) could be observed beside fiber strings that are covered by very small spheres (~100 nm). This observation is due to the fact that free particles (not settled on pyrochar) can grow through Ostwald ripening as well as coalescence, whereas particles that are settled on the surface of the pyrolyzed fiber string are immobilized and cannot grow further, thus remaining very small. Their size is in a range of a few hundred nanometers, which is in agreement with what has been observed as primary nanoparticles in the aggregation of HMF. Nevertheless, previous research discovered a similar morphology of hydrochar produced from a homogeneous reaction, where HMF was an intermediate for the hydrochar formation to obtain spherical particles. On the other hand, particles crack due to the release of volatiles from pyrolyzed biomass but the morphology of pyrochar still resembles original cellulose.

3.2. Mechanisms of Hydrolysis and Char Formation in the Liquid Phase (Hydrochar). As mentioned in Section 2.1, intermediate compounds detected in the liquid phase were evidence of the hydrolysis of cellulose. Once cellulose starts to hydrolyze, glucose is released and subsequently isomerized to fructose. The isomerization of glucose and fructose is a reversible reaction, which, at equilibrium, is dominated by glucose. In addition, fructose converts rapidly via dehydration to produce HMF, and thus fructose could hardly be found. Intermediate products reached the highest yield at 220 °C, most likely because, at a high temperature, the conversion to hydrochar is preferred.

The kinetic rate constants $k_1$, $k_2$, and $k_3$ correlated well with a function of temperature following Arrhenius behavior, as depicted in Table 4. The activation energy of the hydrolysis of cellulose (reaction associated with $k_4$) is 137 kJ mol⁻¹ for AC and 200 kJ mol⁻¹ for MC. According to previous reports in the literature, Schwald and Bobleter, for example, treated cotton cellulose in a batch reactor at temperatures ranging from 245 to 275 °C and found that cellulose hydrolysis is a first-order reaction with an activation energy of 129 kJ mol⁻¹. It should
be mentioned here that cotton cellulose is analogous to AC because cotton cellulose also exhibits an amorphous structure, as well as similar crystallinity and DP. Therefore, their activation energies and those reported in the present work are comparable. Yang et al. reported that the activation energy of MC was 226.5 kJ mol⁻¹ in a temperature range of 205—245 °C. In the same temperature range, their result showed good comparability with our. Interestingly, the reaction kinetic parameter $k_1$ of AC was higher than that of MC at temperatures up to 200 °C and then became lower at temperatures above 200 °C. This could be explained by the accessibility of the amorphous regions in AC to water that consequently enhanced the hydrolysis of glycosidic bonds. On the other hand, MC, whose amorphous portion was removed, rarely had hydrolyzable sites available for the access of water and resulted in a lower rate of hydrolysis (close to zero). When the temperature shifted above 200 °C, water could likely have better access to the crystalline regions of cellulose. Regardless of the crystallinity, the reaction rate of hydrolysis of both AC and MC dramatically increased. This could be because the activation temperature for splitting the glycosidic bonds was reached in this range of temperature. Referring to the lower DP of MC, less hydrolyzable bonds in MC could be inferred. Once the cellulose is hydrolyzed, there should not be any influence of the structure of cellulose on the reactions in the liquid phase. By further assuming equality between AC and MC together.

It is noteworthy that the reactions to determine $k_d$, $k_o$, $k_p$, $k_f$, and $k_s$ are not the focus of this study because they correspond to the production of acids and unknown residues, which, according to the measurements carried out, seem to be no part of char production pathways. Thus, the calculated rate constants are included in the Supporting Information in Table S3 together with the confidence intervals of all of the rate constants in Tables S1 and S2. Furthermore, the reaction that converts furans to organic acids ($k_d$) did not correlate well with different temperatures, meaning that Arrhenius behavior is not favored. This is possibly a result of the almost not occurring decomposition of furans to form organic acids but rather condensation to produce hydrochar, and thus a low sensitivity of $k_f$ could be expected. As such, the low sensitivity might result in a wrong interpretation of the activation energy, and therefore, it is not considered.

The formation of hydrochar corresponds to the formation of carbon spheres, the mechanism of formation of which is likely a polycondensation of HMF molecules. It is assumed that HMF reacts to 2,5-dioxo-6-hydroxyhexanal (DHH), which further reacts to an oligomer via aldol condensation of several HMF molecules. The oligomer precipitates probably due to hydrophobic ripening and further agglomerates with other oligomers to form spherical particles. These spheres can further grow through coalescence. In this course, several water molecules are split, increasing the carbon content to approx. 65—66 wt % This, in fact, is the minimum carbon content observable in the synthesis of carbon spheres from sugars, and thus also for hydrochar. Sample dots in the van Krevelen plot also indicate that the change in elemental composition from the sugar to the carbon spheres accurately follows dehydration lines at the beginning of the reaction, which is further affiliated by a drift along the decarboxylation lines. These circumstances motivated us to develop an adapted HTC model, which is based on an approach presented by Jatzwauk and Schumpe. As mentioned in the Methods section, they assumed that hydrochar has a maximum carbon content of 72 wt % and further calculated the fraction of char in the solid phase. In this approach, a solid sample with carbon content lower than 72 wt % still contains residual feedstock material. Therefore, their method was developed in the present study by assuming that above 65 wt % carbon, no feedstock material is left in the solid bulk. In addition, carbonization proceeds via decarboxylation from that point on. It can be assumed that this calculation procedure, which is derived from the mechanism of formation of hydrochar, can also be applied to the solid-to-solid pathway to form pyrochar. This is because intramolecular dehydration reactions, followed by decarboxylation, take place in the solid-to-solid pathway similar to the formation of hydrochar.

### 3.3. Mechanism of Char Formation in the Solid Phase (Pyrochar)

To investigate further what the pyrolytic reaction mechanism looks like, the term $k_d([Cel]) = k_d([Cel])(1 - [Cel]/3.5)^2$ was considered to have an analogy to the Prout—Tompkins equation, which is widely used for the explanation of solid-state kinetics. The Prout—Tompkins equation can also represent an autocatalytic expression, where the final product $(Y)$ catalyzes the reaction starting with reactant $X$.

$$X + Y \rightarrow 2Y$$

Upon assuming $\alpha$ and $\beta$ to be reaction orders, then the rate equation can be written as

$$\frac{d[X]}{dt} = -k[X]^\alpha[Y]^\beta = -k[X]([X]_0 - [X])^\beta$$

or

$$\frac{d[X]}{dt} = -k[X]^\beta[X]_0(1 - [X]/[X]_0)^\beta$$

(1)

Because $[X]_0$ is the initial concentration of a reactant, which is a constant number, the equation can be rewritten as

$$\frac{d[X]}{dt} = -k'[X]_0^\beta(1 - [X]/[X]_0)^\beta$$

(2)

Equation 14 is analogous to the second term in $k_d([Cel]) = k_d([Cel])(1 - [Cel]/3.5)^2$, where $k'$ is $k_d$, $\alpha$ is 1, and $\beta$ is 2.

Although there was no significant difference between the product yields of pyrochar formation between AC and MC at 180 and 220 °C, interesting predictions from the scenario (5) at 200 °C, as depicted in Figure 5b,f, and 240 °C, as depicted in Figure 5d,h, were observed. At 200 °C, AC produced more hydrochar than pyrochar, whereas MC produced only pyrochar. At 240 °C, pyrochar was dominant among char products when AC was the starting material. MC mostly hydrolyzed at this temperature, as discussed in the previous section, which resulted in dominant hydrochar formation. Char formation via a pyrolytic reaction mechanism in the inner fibers that were not exposed to water gave a good correlation between $k_d$ and temperature. This led to the conclusion that the pyrolytic reaction in an HTC system obeys Arrhenius behavior, even though the autocatalytic effect may result in an inconstant kinetic parameter. From the Arrhenius equation in eq 11, activation energies ($E_a$) and pre-exponential factor ($A$) were calculated and are reported in Table 4.
It was found that the activation energy of pyrolysis in AC was higher than that in MC. This means that pyrolysis in AC is thermodynamically harder to achieve than MC, which supports the finding that pyrochar was dominant in products from MC, especially at low temperatures.

4. CONCLUSIONS

The model shown in this study is a closer approach for the fundamental understanding of reactions that take place during hydrothermal carbonization compared to previous studies. Hydrolysis and carbonization behavior for the calculation of the kinetic reaction rate during hydrothermal treatment of two cellulosics are considered. A first-order reaction is assumed for all reactions except the formation of pyrochar to simplify the model during computation. In addition, the kinetic rate analysis considered the formation of char by two parallel pathways. One pathway resulted in the formation of pyrochar produced from unhydrolyzable cellulose. Both the pyrochar and hydrochar formation pathways represent a good model of the real behavior of cellulose. In the case of pyrochar formation, five different approaches are considered. These approaches allow us to understand the formation of the secondary chars based on the initial nucleation-growth model associated with nucleation parameters that represent how fast the reaction proceeded. In addition, the selection of the most suitable pyrochar pathway was evaluated and studied statistically. Morphological analysis and the prediction of the kinetic model were consistent.

It was found that when the temperature was up to 200 °C the amorphous fraction of cellulose was hydrolyzed, while the crystalline fraction remained resistant to water, and thus a higher char yield was observed for microcrystalline cellulose. As the temperature shifted above 220 °C, the effect of crystallinity became less pronounced as demonstrated by a lesser extent of pyrolysis taking place in microcrystalline cellulose. In contrast, α-cellulose was even more pyrolyzed than microcrystalline cellulose, which suggested that the effect of the degree of polymerization was more significant in terms of a hindrance for water to hydrolyze cellulose.

Further investigations on the morphology of hydrochar and pyrochar are necessary to be confident about their distinction. In addition, one can further explore the effects of temperature and pressure of water on its thermal conductivity and heat transfer inside the cellulose structure.

5. MATERIALS AND METHODS

5.1. Materials. Two different types of cellulose (microcrystalline cellulose (MC) of Merck KGAa and α-cellulose (AC)) obtained from Sigma-Aldrich were used as received without any prior treatments. MC is typically prepared from AC by treating amorphous regions with acid. As a result, MC has more crystalline fragments and shorter chain lengths, while the molecular mass of the repeating unit remains basically the same. Therefore, MC represents cellulose with high crystallinity and a low DP as opposed to AC.

5.2. Hydrothermal Carbonization (HTC). HTC experiments were carried out with the experimental setup previously described by Körner et al., which is a 12.2 mL cylindrical stainless steel autoclave (ID = 10 mm, L = 160 mm) equipped with a thermocouple and a temperature logger. MC (0.85 g) or AC with 8.5 mL of deionized water (70% of total reactor volume) was loaded into the autoclave reactor. Then, the reactors were put into a modified gas chromatography oven and heated up to the desired temperature (180–240 °C). The pressure of the reactor was in the range of 1.2–3.7 MPa corresponding to the amount of water inside the reactor and reaction temperatures. After reaching the reaction temperature, reaction times between 0 and 240 min were recorded. For further conversion of cellulose at 200 °C, the reaction time was extended to 480 min. The reaction was terminated by quenching the autoclave reactors in a cold-water bath. Solid and liquid products were separated by vacuum filtration using 0.45 μm nylon membrane filter (Whatman). Solid particles were washed with deionized water and dried in an oven at 105 °C overnight.

5.3. Analysis. 5.3.1. Solid Phase. Dried solid products were removed from the membrane papers and ground to ensure the homogeneity of the sample prior to elemental analysis using an elemental analyzer (Euro EA-CHNSO, Hekatech). These solid products are simplified as remaining cellulose and char in the present work due to the methodology of the kinetic studies; thus, the preparation of the kinetic model is simplified. While the real composition of the solid products was therefore not determined in the present study, proof was given that these consist of polycyclic aromatic hydrocarbons. Their determination was carried out in an indirect method adapted from the ones described in the work of Jatzwauk and Schumpe. They assumed that the carbon content of the solid phase is the mean value between the mass fraction of cellulose having a carbon content of 44 wt % and hydrochar with 72 wt %. This procedure can be improved by considering the fact that the so-called carbon spheres (secondary char), produced from monomeric sugars, commonly have a carbon content of 65–66%, which most likely arises from a 4-fold dehydration of a monosaccharide. Therefore, it can be assumed that, once the solid phase after HTC (of cellulose) reached a carbon content of 65%, no original cellulose is present anymore. A further rise in carbon content is only possible through solid-to-solid reactions, such as decarboxylation.

Thermogravimetric analysis (TGA) of raw material and product samples was carried out using a STA 449 F5 thermogravimetric balance from NETZSCH-Geratebau GmbH (Ahlden, Germany). Samples of around 15 mg were weighed out into Al₂O₃ crucibles to fulfill the regulation of the International Confederation for Thermal Analysis and Calorimetry. They propose a sample mass times heating rate of less than 100 mg·°C⁻¹·min⁻¹ to avoid limitations of heat and mass transfer. The initial moisture content was removed by heating samples up from room temperature to 105 °C with a heating rate of 10 °C·min⁻¹ over 10 min. Subsequently, the samples were heated up to 900 °C with a constant heating rate of 10 °C·min⁻¹ under a N₂ flow of 100 mL·min⁻¹.

Fourier transform infrared (FTIR) spectroscopy was performed using Bruker α II PLATINUM-ATR (Germany). Wavenumbers in between 400 and 4000 cm⁻¹ were scanned by averaging 24 scans. The background was recorded and subtracted from the measurements of raw material and HTC products to prevent the signals from the surroundings and get a smooth baseline.

A scanning electron microscopy (SEM; Inspect F50; FEI, Eindhoven, Netherlands) analysis was conducted to study the morphological features of raw material and selected solid samples. Each sample was attached to the metal mounting of
the SEM using carbon double-sided tape. All of the samples were coated with Pd (Leica EM ACE200 coater).

5.3.2. Liquid Phase. Liquid products were obtained after vacuum filtration without dilution. The identification of specific intermediate products in the liquid phase, as specified later, was done by a high-performance liquid chromatograph (HPLC, Shimadzu) equipped with a refractive index detector (RID) and a BioRad Aminex column (300 × 7.8 mm² ID). The analytical conditions were as follows: 4 mM aqueous sulfuric acid solution as mobile eluent, a flow rate of 0.6 mL·min⁻¹, and an oven temperature of 35 °C.

5.4. Kinetic Model. The kinetic model of the HTC of cellulose is proposed and expressed in Scheme 1. From this point on, the primary char and secondary char are called “pyrochar” and “hydrochar”, respectively, to reflect the mechanisms that produce them. The parts of the cellulose that are considered nonhydrolyzable during HTC are called pyrochar (PC). This is due to the solid-to-solid mechanism through which they are converted, which is similar to pyrolysis previously described by several authors such as Léde et al. and Antal et al. However, the present mechanism for the solid-to-solid conversion in this study is more likely comparable to the resulting solids of wet torrefaction or low-temperature pyrolysis. Hydrochar (HC) is the solid formed by secondary char reactions during the hydrolysis of cellulose to intermediates and the simultaneous dehydration, decarboxylation, and polymerization reactions, as shown by previous studies. Such low torrefaction temperature is possible here because water is a very good heat transfer medium due to its high thermal conductivity compared to air, which is the medium in conventional pyrolysis. Additionally, the decomposition of cellulose during HTC occurs at a lower temperature compared to dry torrefaction because it is performed in water under subcritical conditions.

Importantly, the amount of solved intermediates was comparatively lower than the solid products. Therefore, the products that have similar functional groups are lumped together for better evaluation. That is, glucose and fructose are lumped into sugar (S), HMF and furfural are lumped into furans (F), and all of the detectable organic acids are lumped into acids (A). In detail, this model was proposed based on the knowledge that cellulose was partially hydrolyzed to oligomers and consequently glucose is produced. It was not possible to quantify the oligomers; thus, they were implicitly included in the residuals (R₂). In fact, the kinetic rate constant of the conversion of cellulose (Cél) to oligomers (R₂) differs from that of oligomers to glucose. Presumably, the change should not be significant because both conversions are hydrolyses that are similar cleavage of the glycosidic bonds. This was supported by Calvini et al. who proposed that the most accurate way to describe the degradation of cellulose would be a sum of first-order reactions. Beyond this, they also reported that a simplification should be made by the approximation of quite equal reaction rates. Therefore, these two consecutive conversions share the same kinetic rate constant (κ₂). Glucose further isomerizes to fructose, from which consequently HMF and furfural are generated by the dehydration of fructose. Hydrochar is formed from the polymerization of HMF and furfural, which is supposed to have a reaction order greater than 1 according to evidence that char production increased with substrate concentration observed by many previous studies. However, it is not reasonable to assume a higher reaction order for hydrochar formation in this work because the hydrochar was produced from low-concentration intermediates and not from the initial substrate. In other words, the concentration of char precursors is not a controllable variable; hence, the reaction order should not be considered a variable in the model. Furthermore, a significant determination of the reaction order was not possible because only one starting concentration of cellulose was used. Thus, every reaction order between 1 and 2 is possible to fit the data together with the corresponding rate constant. It may also cause overfitting by assuming too many variables. In addition, organic acids are well known as byproducts in hydrothermal processes of lignocellulosic biomass. Levulinic acid is the main decomposition product of HMF, while the other light carboxylic acids (formic, acetic, lactic acids) are formed as degradation products of sugars. In addition to this, organic acids possibly gasify. These gas products were negligible because the operating conditions in this study were not severe enough for the gasification to occur and therefore did not produce a significant amount of gas. While not all compounds could be identified and quantified and interconnected liquid and solid reactions taken into consideration, it is necessary to perform the calculation on a basis of mole carbon atoms instead of the mole of each compound. In addition, the concentration of cellulose does not exist because cellulose particles actually just submerge in the water without dissolving. Here, the concentration of cellulose means the total mole carbon atoms of cellulose molecules per specific volume. All of the HPLC analyses were performed in mol C·L⁻¹ to use the same unit for both liquid and solid products because the carbon balance is easy to calculate for both. Regarding this, the carbon balance of the liquids is close due to the separation of only water during the conversion; thus, the rate constants are comparable with both units. Furthermore, the activation energy of the liquid samples could be calculated using mol C·L⁻¹ instead of g·L⁻¹. The unidentified compounds were quantified as residuals, which make up the missing percentages to even the carbon balance to 100%. The residuals can be degradation products of sugars, furans, and acids specified as R₃, R₄, and R₅, respectively.

To fit the rate equations, the results of HPLC and EA were used. Assuming first order for all reactions except pyrochar formation, reaction rate equations for each compound were

Scheme 1. Proposed Reaction Pathway of Hydrothermal Conversion of Cellulose
derived. That is, the change of concentration of reactants or products with time is proportional to the concentration of the reactants.

\[
\frac{d[\text{Cel}]}{dt} = -k_1[\text{Cel}] - k_{fg}([\text{Cel}]) \quad (3)
\]

\[
\frac{d[S]}{dt} = k_1[R_1] - (k_2 + k_3 + k_4)[S] \quad (4)
\]

\[
\frac{d[F]}{dt} = k_2[S] - (k_4 + k_5 + k_6)[F] \quad (5)
\]

\[
\frac{d[A]}{dt} = k_3[S] + k_4[F] - k_5[A] \quad (6)
\]

\[
\frac{d[\text{HC}]}{dt} = k_5[F] \quad (7)
\]

\[
\frac{d[\text{PC}]}{dt} = k_{fg}([\text{Cel}]) \quad (8)
\]

\[
\frac{d[R_1]}{dt} = k_1[\text{Cel}] - k_{2a}[R_1] \quad (9)
\]

\[
\frac{d[R_2]}{dt} = k_3[S] \quad (10)
\]

\[
\frac{d[R_3]}{dt} = k_4[F] \quad (11)
\]

\[
\frac{d[R_4]}{dt} = k_5[A] \quad (12)
\]

The kinetic rate constants \((k_1 - k_5)\) were computed by MATLAB R2018b using the lsqnonlin function to minimize nonlinear least-squares errors of experimental and predicted values. The term \(k_{fg}([\text{Cel}])\) represents solid-state conversion of cellulose, where \(f([\text{Cel}])\) is a function of the concentration of cellulose substrate. This term was yet unknown in its pattern, and therefore, different theories and mathematical models were applied until the best curve fitting was obtained. The selected model was then used to explain possible mechanisms in the solid-to-solvent conversion. Afterward, the Arrhenius behavior is considered to determine the activation energy \((E_a)\) and pre-exponential factor \((A)\) of the reactions of interest. In general, chemical reactions are limited to the number of molecules interacting with each other, whose energy is larger than \(E_a\). For the mentioned reasons, determining several rate constants for the same reaction at different temperatures allows obtaining \(E_a\) and \(A\) in a graphical way. In a nutshell, this means that the kinetic rate constant is dependent on \(e^{-E_a/RT}\); thus, \(E_a\) and \(A\) are specific constants for each reaction. According to the Arrhenius equation \((eq 13)\), \(E_a\) and \(A\) were determined by plotting each kinetic rate constant against the corresponding inversed absolute temperature \((1/T)\).

\[
k(T) = A \exp\left(\frac{-E_a}{RT}\right) \quad (13)
\]

The accuracy of fitting is represented by the root-mean-square error \((RMSE)\), which is formulated as expressed in \(eq 14\).

\[
RMSE = \sqrt{\frac{\sum \text{(predicted value - actual value)}^2}{\text{number of experimental runs}}} \quad (14)
\]
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ABBREVIATIONS USED

| Symbol | Description |
|--------|-------------|
| [Cel] | concentration of cellulose (mol C·L⁻¹) |
| [S]   | concentration of sugars (mol C·L⁻¹) |
| [F]   | concentration of furans (mol C·L⁻¹) |
| [A]   | concentration of acids (mol C·L⁻¹) |
| [HC]  | concentration of hydrochar (mol C·L⁻¹) |
| [PC]  | concentration of pyrochar (mol C·L⁻¹) |
| [R]   | concentration of residuals (mol C·L⁻¹) |
| t     | reaction time (min) |
| A     | pre-exponential factor (min⁻¹ or L²·(mol C)⁻²·min⁻¹) |
| Eₐ    | activation energy (J·mol⁻¹) |
| R     | gas constant (J·mol⁻¹·K⁻¹) |

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