

## Kinetic Model of Wheat Straw Autohydrolysis Considering Heating and Cooling Phases

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Thermochemical and fractionation processes are promising ways for energy valorization and recovery of biomass and waste. An example is given by the application of a lignocellulosic fractionation process to recover both antioxidant phenolic compounds and cellulose from wheat straw, where a first hydrolysis step is carried out as a novel and green auto-hydrolysis process instead of conventional mild acid hydrolysis. Regarding this, the development of kinetic and reactor models that can represent the autohydrolysis process is crucial to exploit the potential of the agricultural residues (e.g., wheat straw). Several mathematical models were investigated, but the more suitable models for optimization purposes seem to be those based on a non-isothermal kinetic model. However, these models have several shortcomings. For instance, in the autohydrolysis process for the recovery of cellulose and lignin from by-products, the heating and cooling phases are not taken into account. Hence, from the point of view of energy optimization, closely linked also to economical optimization, this aspect becomes extremely important.

Therefore, the aim of this work was to briefly present and comment, similarly to review work, the severity factor model and the kinetic model already investigated in the scientific literature in order to enable their comparison with the newly developed method in the current work in terms of different key performance indicators (e.g., cellulose recovery or sugar release). Specifically, our model includes new equations that consider both heating and cooling phases during autohydrolysis of wheat straw, as well as the isothermal step. In this way, it could be possible to use the obtained kinetic parameters not only for a specific case but also for different situations involving a wide range of operating conditions.

### 1. Introduction

In the last decades, the utilization of alternative energy sources in replacement to highly environmental impacting fossil fuels has increasingly gained attention, due to the possibility to meet both the energy and chemical feedstock demands (Ertas et al., 2014). Within this frame, lignocellulosic biomass such as wheat straw (WS) could represent a good candidate to be implied in biorefinery applications (Bassani et al., 2020a). Specifically, WS is one of the most abundant agricultural residues produced worldwide (Han et al., 2015), whose composition (cellulose: 33–40 % dry weight (DW), hemicellulose: 20–25 % DW, and lignin: 15–20 % DW) may enable its potential exploitation for the production of basic chemicals (e.g., sugars), lignin and bioethanol (Rossberg et al., 2014). However, in order to maximize the yield of products obtained while reducing the amount of generated emissions and waste streams, a simple, low-cost, and environmentally-friendly biomass pre-treatment is strictly required (Sipponen et al., 2014). To this purpose, the successful capability of autohydrolysis processes to enhance the selective depolymerization of cellulose and hemicellulose from wheat straw has been previously demonstrated, as a viable alternative to the conventional acid hydrolysis step (Bassani et al., 2020a; Ertas et al., 2014; Ruiz et al., 2012). In particular, the former process only requires the usage of water at elevated temperatures (160–240 °C) to disrupt acetyl groups of cellulosic components, thus increasing their susceptibility to the subsequent enzymatic attack for mono-sugars production (Sipponen et al., 2014). Additionally, in comparison with acid-assisted hydrolysis, it allows a lower

generation of undesired components and a significant reduction of operative costs since the neutralization step could be avoided (Carvalheiro et al., 2009).

Previous authors have developed mathematical models to better understand the kinetics of the autohydrolysis process, as well as to find optimal operating conditions to increase reaction rates/yields at minimum energy expenditures. In particular, Carvalheiro et al. (2009) used an index called severity factor ( $R_0$ ) to compare different experimental data (yield of mono- and oligosaccharides, lignin, and pH) obtained as a function of a combination of processing temperature and reaction time. Instead, Sidiras et al. (2011) developed a non-isothermal kinetic model which allowed to more accurately simulate the kinetics of the single-step batch autohydrolysis of wheat straw cellulose and hemicellulose with respect to the severity factor models.

The aim of this work, carried out in the frame of the “Newpack” project (792261-NEWPACK-H2020-BBI) which dealt with the fabrication of new bio-based plastic materials starting from food wastes, was to furtherly improve the model proposed by Sidiras et al. (2011). Specifically, additional equations, taking into account the effect of temperature rise and decay immediately before and after the isothermal zone of the autohydrolysis step, were implemented. The model developed will be utilized to properly define the set of operating conditions yielding the maximum amount of interest reaction products, as well as to reduce the energetic consumption associated with the process itself.

## 2. Material and Methods

In this section, the equations of the model aimed to predict the concentrations of the main species involved in the autohydrolysis step as a function of reaction time, are presented and briefly described. Summarizing, the set of equations indicate with a capital letter A is referred to in the work of Sidiras et. al. (2011), while the one with capital letter B to Carvalheiro et al. (2009). The idea, as already mentioned, is to start from the kinetic scheme and the related equations reported by Sidiras et al. (2011) and improve that scheme including equations to predict temperature variation in the different phases of the process. The system includes the equations from (1A) to (10A) which are the same reported by Sidiras et al. (2011) excepted for equation (10A), in which  $U$  is the global heat transfer coefficient,  $S$  is the surface area of the reactor and  $T_j$  is the external temperature, generated by the thermal resistance during the heating phase and by the cooling jacket during the cooling phase. Each coefficient,  $U$  and  $T_j$ , is estimated in order to obtain the same temperature profile reported by Sidiras et al. (2011). It is important to underline that each equation, from (1A) to (8A), is referred to the change of the concentration of the same components reported by Sidiras et al. (2011). In the same way, equation (9A) is used to assess the change in pH in the liquid phase. For instance, the concentration of crystalline cellulose is  $C_{cel}^{CC}$  and of amorphous cellulose is  $C_{cel}^{AC}$ , while the concentration of reaction resisting hemicellulose is  $C_{hem}^{RR}$  and of easily reacting hemicellulose is  $C_{hem}^{ER}$ . Each concentration is reported as a weight (w/w) fraction of the respective initial dry material. Since the study becomes more valuable if validated on a different set of experimental data, the work of Carvalheiro et al. (2009) is considered because it is the only one found in the literature, from the author's knowledge, that present some indication of how autohydrolysis reactor was heated and cooled. This is necessary in order to set the coefficient,  $U$  and  $T_j$  for equation (10B). However, Carvalheiro et al. (2009) investigated the process of autohydrolysis starting from a solid to liquid ratio equal to twice if compared to the one used by Sidiras et. al. (2011). Therefore, having to take into account the different concentrations of water, an additional equation for water consumption (11B) was introduced. In this way, the different amount of water is taken into account, which could result, for example, in a different pH value at the same operating conditions. Additionally, for each equation from (1B) to (9B) the water concentration dependence ( $C_{h2o}$ ) was added. The latter is reported as a w/w fraction of the respective initial compound. Since the purpose of this work was not to evaluate the effects of different water concentrations, but rather the effects of the heating and cooling phases, equation (13B) was applied only in the case of Carvalheiro et al. (2009) validation. Finally, it is useful to highlight that the kinetic constants ( $k$ ), with the related frequency factors ( $p$ ) and activation energy ( $E_a$ ), were kept equal in both cases because the model has to be standardized as much as possible.

$$A) \frac{dC_{hem}^{RR}}{dt} = -k_1 C_{hem}^{RR} \quad B) \frac{dC_{hem}^{RR}}{dt} = -k_1 C_{hem}^{RR} C_{h2o} \quad (1)$$

$$A) \frac{dC_{hem}^{ER}}{dt} = -k_2 C_{hem}^{ER} \quad B) \frac{dC_{hem}^{ER}}{dt} = -k_2 C_{hem}^{ER} C_{h2o} \quad (2)$$

$$A) \frac{dC_{WSOH}}{dt} = k_1 C_{hem}^{RR} + k_2 C_{hem}^{ER} - k_3 C_{WSOH} \quad B) \frac{dC_{WSOH}}{dt} = k_1 C_{hem}^{RR} C_{h2o} + k_2 C_{hem}^{ER} C_{h2o} - k_3 C_{WSOH} (C_{h2o})^\alpha \quad (3)$$

$$A) \frac{dC_{xyl}}{dt} = k_3 C_{WSOH} - k_4 C_{xyl} \quad B) \frac{dC_{xyl}}{dt} = k_3 C_{WSOH} (C_{h2o})^\alpha - k_4 C_{xyl} (C_{h2o})^\beta \quad (4)$$

$$A) \frac{dC_{cel}^{CC}}{dt} = -k_5 C_{cel}^{CC} \quad B) \frac{dC_{cel}^{CC}}{dt} = -k_5 C_{cel}^{CC} C_{h2o} \quad (5)$$

$$A) \frac{dC_{cel}^{AC}}{dt} = -k_6 C_{cel}^{AC} \quad B) \frac{dC_{cel}^{AC}}{dt} = -k_6 C_{cel}^{AC} C_{h2o} \quad (6)$$

$$A) \frac{dC_{WSOC}}{dt} = k_5 C_{cel}^{CC} + k_6 C_{cel}^{AC} - k_7 C_{WSOC} \quad B) \frac{dC_{WSOC}}{dt} = k_5 C_{cel}^{CC} C_{h2o} + k_6 C_{cel}^{AC} C_{h2o} - k_7 C_{WSOC} (C_{h2o})^\alpha \quad (7)$$

$$A) \frac{dC_{glu}}{dt} = k_7 C_{WSOC} - k_8 C_{glu} \quad B) \frac{dC_{glu}}{dt} = k_7 C_{WSOC} (C_{h2o})^\alpha - k_8 C_{glu} (C_{h2o})^\beta \quad (8)$$

$$A) \frac{da}{dt} = k_A (a_\infty - a) \quad B) \frac{da}{dt} = \frac{k_A (a_\infty - a)}{C_{h2o}} \quad (9)$$

$$A) \frac{dT}{dt} = UA(T - T_j) \quad B) \frac{dT}{dt} = US(T - T_j) \quad (10)$$

$$A) - \quad B) \frac{dC_{h2o}}{dt} = -k_{h2o} C_{h2o} \quad (11)$$

Where:

$$k_i = p_i * a * \exp\left(-\frac{E_{ai}}{RT}\right) \quad i = 1, 2, \dots, 8 \quad (12)$$

$$k_a = p_a * \exp\left(-\frac{E_{aa}}{RT}\right) \quad (13)$$

$$k_{h2o} = p_{h2o} * \exp\left(-\frac{E_{ah2o}}{RT}\right) \quad (14)$$

### 3. Results and Discussions

As already described above, Sidiras et al. (2011) proposed a kinetic model to take into account different maximum temperatures reached at which the autohydrolysis reactor can operate. However, each simulation at the different maximum temperatures (i.e., 160 °C, 180 °C, 200 °C, 240 °C), was done considering the reactor as isothermal, neglecting the heating and cooling phases.

Table 1: Kinetic parameters of the proposed model for non-isothermal autohydrolysis

Reactions	Frequency factor (P)	Activation Energy (E <sub>a</sub> )	Frequency factor (P)	Activation Energy (E <sub>a</sub> )
	Sidiras et al. (2011)	Sidiras et al. (2011)	New	New
1	1.9300E+15	1.0400E+02	2.1486E+15	1.0366E+02
2	1.4000E+16	1.0400E+02	1.3717E+16	1.0347E+02
3	4.3000E+21	1.5650E+02	4.9155E+21	1.5508E+02
4	4.5000E+29	2.3250E+02	4.7646E+29	2.3157E+02
5	7.8200E+14	1.1640E+02	8.2984E+14	1.1630E+02
6	5.2200E+15	1.1640E+02	5.4429E+15	1.1483E+02
7	1.4000E+17	1.2500E+02	1.4840E+17	1.2453E+02
8	1.2300E+20	1.6400E+02	1.3771E+20	1.6403E+02
9	1.8900E+04	5.8000E+01	1.3538E+04	5.9970E+01
11	-	-	8.7305E+02	3.4115E+01

Therefore, as a first attempt, a simulation was performed with the kinetic data reported by Sidiras et al. (2011) and in Table 1 but considering also the heating and cooling phases (i.e., including equation (10-A)). The activation energy is expressed as  $\frac{kJ}{mol}$ , while frequency factor dimensions is related to the reaction order. For instance, for reaction (1-B) the frequency factor is expressed as  $\frac{1}{min}$ .

Subsequently, another simulation was made, again considering all the process phases, with new kinetic parameters (reported in Table 1) obtained from a regression on the experimental data reported by Sidiras et al. (2011). To perform the regression, the numerical libraries BzzMath (Buzzi and Manenti, 2012) were used, which are particularly well suited for the purpose, as well as for solving ordinary differential equations system.

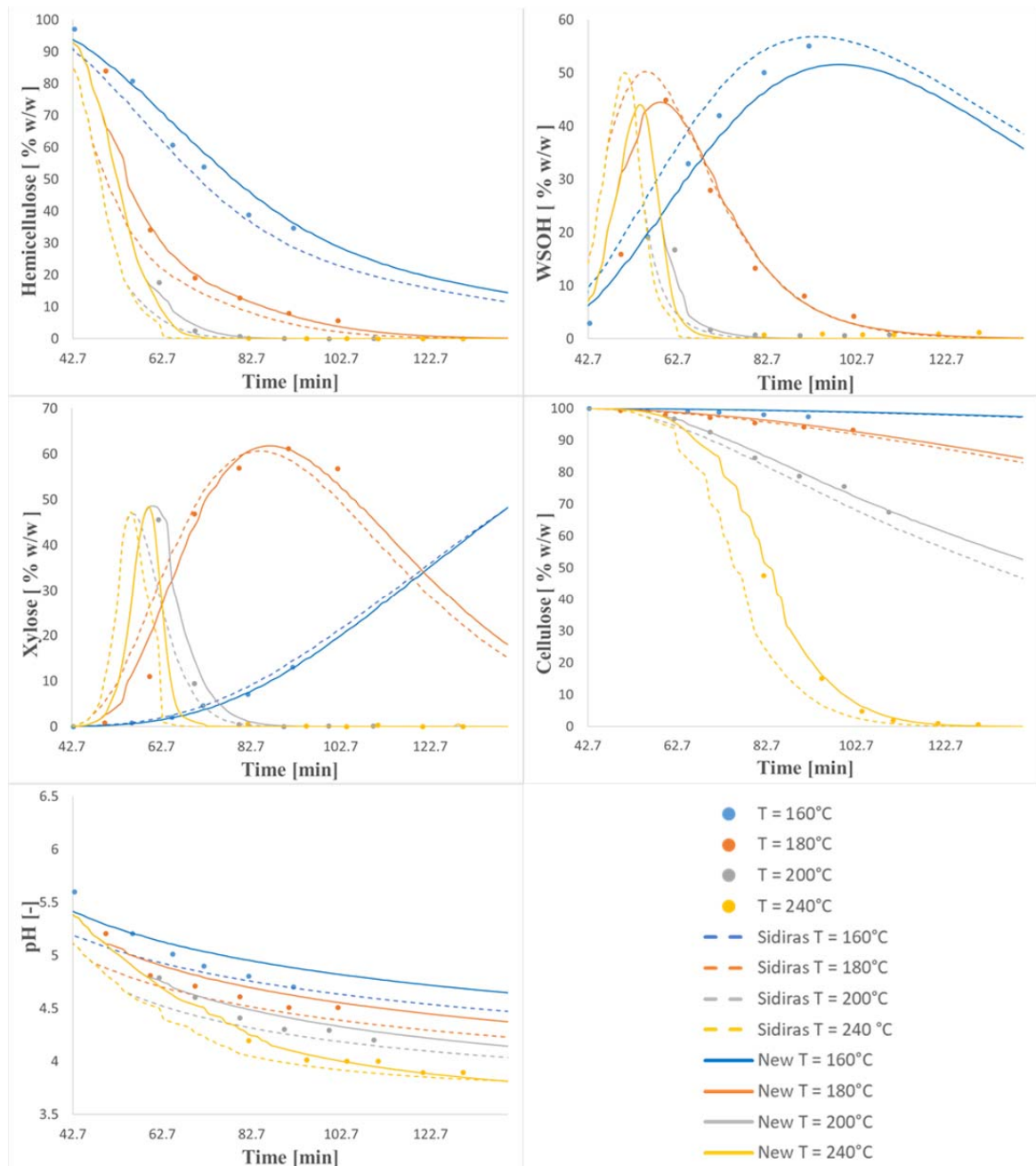


Figure 1: Comparison between the new model (solid line) and the one proposed by Sidiras et al. (2011) (dashed line) based on experimental data proposed by Sidiras et al. (2011).

As shown in Figure 1, the experimental data are better predicted by the model with regressed kinetic parameters (solid line) than those proposed by Sidiras et al. (2011) (dashed line). Although the improvement

obtained in the simulations is slight, it is possible to affirm that considering the heating and cooling phases could be a crucial point for possible energy optimization of the process. Indeed, Sidiras et al. (2011) used very fast heating and cooling systems, which therefore lead to a lower influence of these phases on the final composition of both solid and liquid.

This is the main reason why only a slight difference is noticed between the two simulated cases. However, rapid heating and cooling are directly related to higher energy consumption. For example, cooling by simply taking advantage of the room temperature would certainly be slower, but at almost zero cost. However, in the latter case, precisely, a correct prediction of the reactions occurring in this phase becomes crucial to optimize the correct process times. Moreover, further experimental data would be needed, especially for high temperatures and low total process times, in order to better verify some simulated trends (e.g., 240 °C and 45 minutes for xylose production). For this reason, during the Newpack project, further experimental tests will be scheduled to better investigate the above operating conditions also exploiting, if necessary, the model-based design of experiment to minimize the number of tests to further validate the proposed model.

Then, the model has been validated also on the data set proposed by Carvalho et al. (2009). It is interesting to underline that, in this case, correctly evaluate the heating and cooling phases is fundamental because Carvalho et al. (2009) heat the solid and the water up to a series of desired temperatures (e.g., 150 °C, 170 °C, 190 °C, etc.) and then once reached they cool down rapidly the reactor. Therefore, there is no phase where the reactor remains in isothermal conditions. As mentioned, the kinetic constants are the same as for the previous case and the frequency factor and activation energy for equation (11-B) are reported in Table 1. The latter were derived through regression to predict the pH change in Carvalho et al. (2009) process.

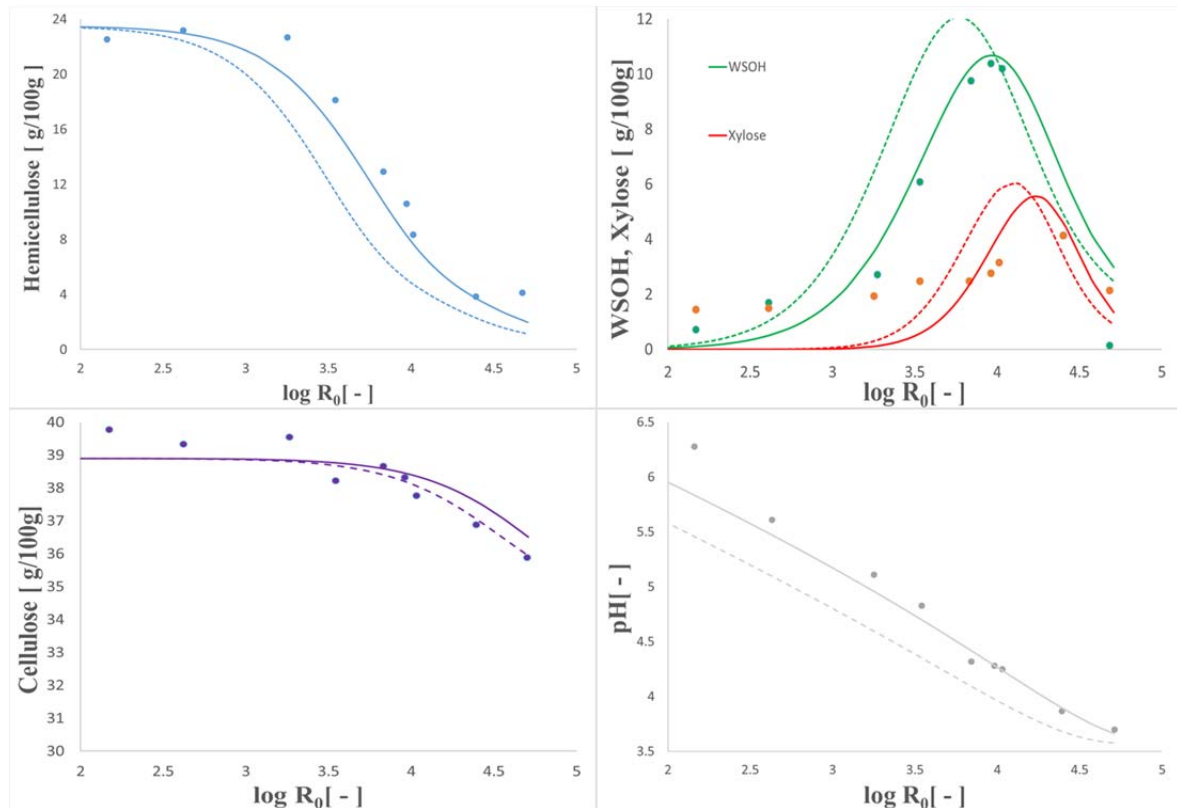


Figure 2: Comparison between the new model (solid line) and the one proposed by Sidiras et al. (2011) (dashed line) based on experimental data proposed by Carvalho et al. (2011).

In this case, the graphs in Figure 2 show a more marked improvement because, as described above, there is no phase in which the reactor is in isothermal condition. In other words, it is not possible to neglect the effects of the heating and cooling phases. In this case, the trends are reported as a function of  $\log(R_0)$ , where  $R_0$  is called severity factor. The latter is expressed as

$$R_0 = \int_0^t \exp\left(\frac{T(t) - 100}{14.75}\right) dt \quad (15)$$

where  $t$  is the reaction time (min),  $T$  is the reactor temperature ( $^{\circ}\text{C}$ ), and 14.75 is an empirical parameter related to activation energy and temperature.

#### 4. Conclusions

In conclusion, this work was a first attempt to evaluate the effects of heating and cooling phases on the final product compositions in the process of autohydrolysis of agro-food residues, with particular reference to wheat straw. The simulations, carried out based on experimental data present in scientific literature, initially showed only a slight improvement in the prediction of experimental data because there was a predominant isothermal and high-temperature phase compared to the rapid heating and cooling phases. However, based on another set of experimental data where the heating phase becomes predominant, more marked improvements in the prediction given by the model were highlighted.

For these reasons, this work will be the base for future developments, first of all, the inclusion of equations able to predict the different behavior of the process related to different inlet solid to liquid ratio. In this way, it will be possible to optimize the process also from the point of view of the downstream separations to be performed, where a lower quantity of liquid is often associated with lower costs. As already mentioned several times, another future development will regard the energy optimization of the process and then directly testing the optimal operating conditions found. In addition, the process will be optimized to maximize the yields of the components (e.g., cellulose recovery yield). Finally, some studies could be also conducted to predict the concentration of polyphenols that are released in the liquid phase (Vadivel et al. 2017) and models could also be developed for other agro-food residues like, for instance, grape skins (Bassani et al. 2020b).

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