Valorization of Cellulosic Biomass via Solvent Processing

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Biomass is an abundant, sustainable and low-cost resource that it is currently utilized to a rather small extent for the production of fuels, platform chemicals, and functional polymers (Agbor et al., 2011). A key issue in exploiting biomass is its competition with food production. This motivates the utilization of cellulosic biomass that is not part of human nutrition. However, cellulosic biomass remains vastly underutilized mainly because of the extended noncovalent interactions and crystalline structure of cellulose molecules that render cellulosic biomass recalcitrant to valorization (Gross & Chu, 2010). Currently, cellulosic biomass is converted to liquid chemicals and energy through breaking of chemical bonds (conversion to sugars) in thermochemical (e.g., pyrolysis, gasification, and high-pressure liquefaction) or enzymatic hydrolysis processes that have high energy consumption and low efficiency (Nzihou, 2010). An efficient way to improve the processing of this renewable resource is solvent treatment of biomass through disrupting the interaction network of crystalline cellulose, so that the polymer chains become readily accessible to reagents and enzymes (Alexandridis et al., 2018). Further, for the preparation of high value-added cellulosic polymers (Chronakis & Alexandridis, 2001), fibers, films, and composites, the direct dissolution of cellulose is often preferred than its conversion to sugars. However, very few solvent systems are effective for the direct (molecular) dissolution of cellulose, and the cellulose dissolution mechanism remains elusive (Alexandridis et al., 2018). To this end, we focus on dissolution of cellulose and we utilize knowledge on molecular interactions, transformations, and transport phenomena involved in this process in order to improve the processing of semicrystalline cellulose and the valorization of cellulosic biomass.

In cellulose dissolution, the intra- and inter-molecular interactions (hydrophobic and hydrogen bonding) operating in cellulose are modulated by solvent molecules, and the crystalline structure of cellulose is disrupted (Medronho et al., 2012). However, experimental observations suggest that it is not sufficient for the cellulose chains to be non-crystalline but, rather, chains must perform local conformational movements that result in chain disentanglement (Le Moigne et al., 2010). This suggests that there might be different types of interactions that affect disentanglement from those that affect decrystallization. Therefore, the dissolution of semicrystalline cellulose involves the two inter-related phenomena of decrystallization and chain disentanglement, the balance of which determines the overall kinetics of dissolution (Ghasemi et al., 2017a).

Following solvent diffusion into solid cellulose, the crystalline network of cellulose is gradually destroyed and conformational chain movement is facilitated. This results in a transformation of the solid cellulose into a gel-like medium and a swelling of the cellulosic particles (Wang et al., 2014). After a certain induction time, cellulose chains gradually become disentangled and move out of their network into the bulk solution. Therefore, the dissolution of cellulose involves several steps (Figure 1) including solvent diffusion, cellulose decrystallization, specimen swelling, cellulose chain disentanglement, and diffusion of disentangled chains toward the bulk solution (Ghasemi et al., 2017a).

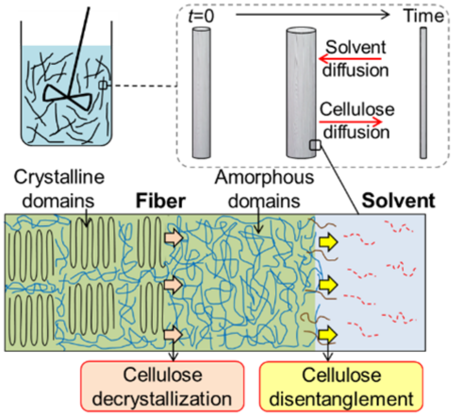

Figure 1. Dissolution of cellulosic fibers.

We developed a phenomenological model that captures the phenomena governing the homogeneous swelling and dissolution of semicrystalline cellulose (Ghasemi et al., 2017a; Ghasemi et al., 2017b). The model incorporates experimental data on the initial conditions of cellulose fiber (i.e., degree of polymerization, degree of crystallinity, fiber diameter, heterogeneous internal structure of the fiber), diffusion coefficients of solvent in cellulose and of cellulose chains in solution, and dissolution induction time (Ghasemi et al., 2017a). The model allows the translation of macroscopic experimental observations of time evolution of cellulose fiber diameter and degree of crystallinity into fundamental microscopic understanding of cellulose dissolution. We further developed a dissolution ensemble model (Ghasemi et al., 2018a; Ghasemi et al., 2018c), in which the behavior of a polydisperse population of cellulose particles is predicted from an ensemble of individual particle dissolution models, in order to addresses the kinetics of cellulose dissolution at conditions emulating large-scale processing.

The single-particle model quantifies the solvent effectiveness in cellulose decrystallization and chain disentanglement (captured by the decrystallization constant, k_{dec}, and disentanglement rate, r_{dis}, respectively) as two important factors that can control the rate and extent of cellulose dissolution (Ghasemi et al., 2017a). k_{dec} can be used to estimate the activation parameters of cellulose decrystallization in order to assess the temperature sensitivity of this process (Ghasemi et al., 2017a). The model provides further microscopic/internal information on the cellulose fibers during dissolution, including the concentration profiles of solvent and cellulose (amorphous and crystalline) over time (Ghasemi et al., 2017c). This information, coupled with the time variation of the fiber solubility, can identify the diffusion mechanism of solvent in micrometer-diameter cellulosic fibers (Ghasemi et al., 2017c). The model also provides macroscopic/integrated information such as the time evolution of fiber diameter, degree of crystallinity, and fraction of un-dissolved fiber, as well as the time required for the total dissolution of the cellulose fiber, and the time required for fiber decrystallization (Ghasemi et al., 2017c).

In the model, different solvent systems correspond to different effectiveness toward cellulose decrystallization (k_{dec}) and chain disentanglement (r_{dis}) (Ghasemi et al., 2017c). Mapping out this parameter space allows the identification of conditions where cellulose dissolution is constrained by the lack of solvent ability in decrystallization or in chain disentanglement (Ghasemi et al., 2017c). It has been found that conditions that facilitate cellulose decrystallization increase the cellulose fiber swelling and result in a faster fiber dissolution. Furthermore, conditions that facilitate cellulose chain disentanglement, in addition to increasing the rate of dissolution, can result in faster decrystallization. The solvent effectiveness in chain disentanglement is the only factor that determines the decrease of the cellulose fiber radius (Ghasemi et al., 2017a).

In order to select efficient biomass pretreatment options (e.g., reduce the crystallinity or reduce the particle size) the model has been employed to quantify the impact of the degree of crystallinity and of the fiber diameter on the kinetics of cellulose swelling and dissolution (Ghasemi et al., 2018b). The obtained results lead to the assessment on how and under what conditions the reduction of crystallinity and fiber diameter can change the mechanism of cellulose dissolution between disentanglement-controlled and decrystallization-controlled, thus providing guidelines for efficient pretreatment strategy (e.g., whether to reduce crystallinity or to mill and decrease particle size) in order to increase the fraction of cellulose that is dissolved (Ghasemi et al., 2018b).

The population ensemble model provides novel results on the (i) cellulosic biomass particle size distribution and polydispersity evolution over the time course of dissolution, and (ii) effect on cellulose dissolution of the particle size distribution width and mean particle size at different conditions (Ghasemi et al., 2018c). It has been found that particle size reduction (e.g., via milling) is always an effective procedure to increase biomass solubility when dissolution is controlled by chain disentanglement. However, when dissolution is controlled by decrystallization, particle size reduction is an efficient procedure only for short dissolution times, whereas, for relatively long dissolution times, pretreatment to decrease the crystallinity would be more effective.

The obtained results provide guidelines for the selection of solvent systems and experimental conditions that can improve the extent and speed of biomass dissolution. The findings also provide recommendations for an efficient pretreatment strategy to facilitate an enhanced conversion of cellulosic biomass. The obtained insights offer useful suggestions for effectively processing of cellulosic biomass (grinding and milling coarse particles and controlling the polydispersity of the mixture) in order to enhance valorization of this renewable resource. Further, the developed models have broad applications in the dissolution of polydisperse system of polymers, of interest, for example, in plastic recycling (Zhao et al., 2018) and drug delivery (Peppas & Narasimhan, 2014).

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