Online residence time distribution measurement of thermochemical biomass pretreatment reactors

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HIGHLIGHTS

- Online electrical conductivity instrumentation rapidly quantifies RTD.
- NaCl is an effective tracer for thermochemical pretreatment of biomass slurry.
- Significant cost and time savings and more accurate compared with offline analysis.
- Mean residence time is significantly longer than theoretical.
- Model developed to predict true mean residence time.

GRAPHICAL ASBTRACT
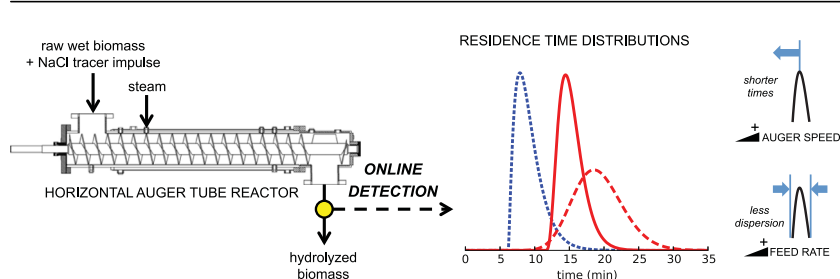
ABSTRACT

Residence time is a critical parameter that strongly affects the product profile and overall yield achieved from thermochemical pretreatment of lignocellulosic biomass during production of liquid transportation fuels. The residence time distribution (RTD) is one important measure of reactor performance and provides a metric to use when evaluating changes in reactor design and operating parameters. An inexpensive and rapid RTD measurement technique was developed to measure the residence time characteristics in biomass pretreatment reactors and similar equipment processing wet-granular slurries. Sodium chloride was pulsed into the feed entering a 600 kg/d pilot-scale reactor operated at various conditions, and aqueous salt concentration was measured in the discharge using specially fabricated electrical conductivity instrumentation. This online conductivity method was superior in both measurement accuracy and resource requirements compared to offline analysis. Experimentally measured mean residence time values were longer than estimated by simple calculation and screw speed and throughput rate were investigated as contributing factors. A semi-empirical model was developed to predict the mean residence time as a function of operating parameters and enabled improved agreement.

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1. Introduction

Thermochemical pretreatment is a key step in the overall process of refining lignocellulosic biomass into sugars and ultimately alcohol or hydrocarbons for transportation fuels. Dilute acid-catalyzed thermochemical pretreatment physically disrupts the biomass structure and hydrolyzes most of the hemicellulose fraction and some of the cellulose fraction into fermentable sugar monomers prior to enzymatic hydrolysis of the remaining cellulose (Esteghlalian et al., 1997; Mosier et al., 2005). One key chemical reaction is hydrolysis of xylan to the desired intermediate, xylose monomer, which further degrades to fermentation-inhibiting furfural and other byproducts as the reaction proceeds. Xylan hydrolysis reaction rate is primarily controlled by acid concentration and temperature, and the extent of reaction is governed by residence time. Since the desired monomeric sugar is an intermediate

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reaction product, effective reactor residence time control is necessary to target reactor conditions that favor high sugar yield.

Bench scale pretreatment experimentation is typically performed using batch reactors in which system residence time is carefully controlled within a narrow window by application of steam and quick depressurization to quench the reactions (Nguyen et al., 1998). As pretreatment is scaled to the pilot plant and beyond, continuous flow reactors are preferred for plant operations and cost (Humbird et al., 2011). Residence time in continuous reactors is controlled by various mechanical conveyance means, including variable speed auger-screws within horizontal tubes. Continuous reactors generally have imperfect flow characteristics, where undesired back mixing and flow stratification lead to variations in residence time from those predicted from theoretical plug flow (Froment and Bischoff, 1990). This variation is characterized by the residence time distribution (RTD) that describes the probability that a particle or chemical species will spend a specific time at desired reaction conditions. Maximal xylose yield is achieved at a specific residence time, but non-ideal flow inside continuous pretreatment reactors distributes species about the targeted reaction time, which ultimately reduces the desired product yield (Schell et al., 2003). A continuous reactor with a sharp, low-variance RTD with the mean residence time value at the target reaction time is favorable for translating from bench-scale batch reactor conditions and allows more precise control of reaction extent and ultimately the ability to maximize desired intermediate product yield. It is desirable to measure the RTD of these pretreatment reactors to verify residence time and also to enable study of main factors affecting RTD control.

Recent studies have reported measurements of the residence time in a biomass-fed pyrolysis reactor (Xi et al., 2015) and screw conveyor (Nachenius et al., 2015). Although these papers have brought valuable information to the literature for biomass processing equipment, the methods did not permit measurement at live reaction conditions. Xi et al. (2015) measured RTD in a biomass pyrolysis reactor using the impulse response method by injecting a tracer and measuring the amount of tracer in samples collected over regular intervals. It is important to note, however, that this method was employed in an ambient environment instead of at real reaction conditions. This is suitable only if system rheology remains the same at ambient conditions and during the course of actual reaction. In the case of biomass pretreatment to sugars, the slurry rheological characteristics change dramatically during pretreatment and measurement of RTD at reaction conditions is absolutely necessary for accurate results. Nachenius et al. (2015) measured the RTD of pine chips, rice, and sand in a horizontal screw conveyor at ambient conditions via step-change experiments by stopping the inlet flow and observing the flow response of the outlet by collecting samples at regular intervals. This equipment is similar to pretreatment reactors; however, when at operating conditions, the inlet biomass flow may not simply be stopped without process upset. Steam is injected to rapidly heat the incoming feedstock, drive the reaction, and also compensate for heat loss. A step-change approach stopping all feed streams would confound RTD measurement as a constant slurry composition could not be maintained. Furthermore, it is unclear if deviating from steady-state flow in the reactor will provide a valid RTD for the pretreatment reactor, as fill fraction may affect the RTD itself. Finally, explosive flashing of biomass slurry at the reactor outlet presents difficulty and a serious safety hazard for manual sample collection to make use of offline analytical methods previously presented. The ability to perform *online* RTD measurements in a biomass thermochemical pretreatment reactor at live, steady-state reaction conditions is critical.

The online RTD measurement methods reported in the literature focus on polymer screw extruders (Gao et al., 1999; Lee et al., 2005; Hu and Kadri, 1999) and food processing equipment (Ramaswamy et al., 1995; Tulsiyan et al., 2009). These methods include ultrasonic, photo-detected dye, magnetic, and radiofrequency identification (RFID) techniques. The machinery used in these examples is similar to pretreatment reactors, but the inhomogeneity, elevated temperature and pressure, and chemistry of pretreatment conditions present special challenges for the implementation of these online measurement techniques. For example, the RTD of chicken chow-mein inside an ohmic heater sterilization system was measured online using RFID by Tulsiyan et al. (2009) as a more accurate alternative to the industry-accepted magnetic method. Unfortunately, the RFID and magnetic methods do not translate well to biomass pretreatment reactors because RFID tags cannot withstand temperatures above 150 °C and both RFID tags and magnets would likely suffer mechanical damage during screw conveying. Acid pretreatment reactors are primarily constructed of high-nickel alloys for corrosion resistance and do not readily attract magnets as they are paramagnetic. However, several minor parts are cold-worked 316L stainless steel, which exhibits some ferromagnetism and would capture magnets fed through the system and render the magnetic RTD detection method ineffective. Lee et al. (2005) presented an online RTD measurement method for a polymer extruder involving a calcium carbonate tracer detected using ultrasound. This required the homogeneous polymer melt to completely fill the space between the emitting and receiving transducers. Unfortunately, pretreated biomass is a heterogeneous wet-granular slurry consisting of moist variable-sized biomass particles with steam-filled voids that renders the ultrasonic RTD method also ineffective. Photo-detection is another attractive method, but again suffers from the incompatibility of cameras/photo-sensors with reactor conditions involving high temperature and condensing steam.

This study provides a novel, rapid online RTD measurement method suitable for the harsh and non-ideal conditions within biomass pretreatment reactors where RTD measurement techniques previously reported would fail to perform. Electrical conductivity-based quantification of sodium chloride tracer was developed into a fast online detection technique that is applicable to pilot- and full-scale biomass pretreatment reactors and also other processes that involve high solids aqueous slurries such as wood pulping and food processing, to name a few. A pilot-scale thermochemical pretreatment reactor served as a platform for demonstrating this method and is analogous to other pilot- and full-scale reactors. The method developed in this work is applicable beyond biomass pretreatment to any process where electrical conductivity can be manipulated and measured online at process conditions.

2. Measurement methodology

Our RTD measurement method was developed working with a Metso, Inc. (Norcross, GA, USA) continuous pilot-scale horizontal auger-tube pretreatment reactor used for research activities (Shekiro et al., 2014). This Hastelloy C-2000 constructed reactor, represented in Fig. 1, was maintained at 160 °C by saturated steam injection. Tub ground and hammer milled (with a 19 mm rejection screen) corn stover was pre-wetted with 1.0 wt% sulfuric acid to attain ~50 wt% total solids content and was fed into the reactor at a rate of 600 dry kg/d. A small amount of liquid was involuntarily pressed from the wetted feedstock within the tapered screw feeder and was discarded. However, additional fresh water was injected inside the shredder conveyor to maintain a reactor exit total solids content of 28%.

Theoretical plug-flow residence time within the entire reactor (t_{th}) was calculated by summing individual component residence times using

$$t_{th} = \sum \frac{V_i}{v_i},$$ (1)

where V is the active volume inside each tube (cm^3) and v is the