

PATTERN FORMATION IN BIOFUEL SYSTEMS DURING BATCH HYDROLYSIS OF LIGNOCELLULOSES

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Abstract

This paper presents the first experimental evidences of pattern formation in second generation biofuel systems. These spatiotemporal patterns are observed in batch and semi-batch systems during hydrolysis of lignocelluloses and hemicelluloses, regardless of whether the hydrolysis is performed enzymatically or catalytically. Turing patterns emerge along the length of tubular batch reactors due to activator-inhibitor type reaction between the soluble sugars and the inhibitors (the monomer and the dimer) during enzymatic hydrolysis of hemicelluloses in the presence of axial diffusion. The product concentrations form limit cycles on the activator-inhibitor phase space, whose shape changes from circular to elliptical with the progress of hydrolysis. These Turing patterns are simulated using a reaction-diffusion model with activator-inhibitor type kinetics, and the simulations are validated with the experimentally-obtained spatial patterns. Temporal patterns are produced during catalytic hydrolysis of lignocelluloses in well-mixed semi-batch reactors, resulting in chaotic strange attractors with fractal dimensions and positive Lyapunov coefficients to appear on the product phase spaces. Both the spatial and the temporal patterns – driven by auto-regulatory reaction kinetics and characterized by oscillatory states existing under thermodynamic non-equilibrium – are shown to promote biofuel production by increasing the soluble sugar yields by 15-20% over their non-oscillatory counterparts.

Keywords

Turing patterns, Chaotic oscillators, Strange attractors, Lignocellulose hydrolysis, Biofuel

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Introduction

Spatiotemporal patterns – whether they are the Turing patterns (Turing, 1952) observed in nature across length scales ranging from the cellular to the galactic, or the Belousov-Zhabotinsky waves (Zaikin and Zhabotinsky, 1970) produced in chemical reactors – result from complex interactions between diffusional transport and self-regulatory (auto-catalytic or auto-inhibitory) reaction kinetics. These spatial and/or temporal oscillations usually emerge in a narrow region of the parameter space in auto-regulatory reaction systems operating under thermodynamic non-equilibrium (Lefever et al., 1967).

Here we present the first experimental evidences of spatiotemporal pattern formation in second generation biofuel systems. These oscillatory states are observed during enzymatic and catalytic hydrolyses of lignocelluloses and hemicelluloses in batch and semi-batch reactors operating far from equilibrium. The Turing patterns experimentally measured in tubular reactors during enzymatic hydrolysis of hemicelluloses have been validated by simulating a reaction-diffusion type model, while the chemical chaos produced during catalytic hydrolysis of lignocelluloses has been characterized by using Lyapunov coefficients and fractal dimensions of the chaotic strange attractors formed on the product phase spaces.

Methods

Enzymatic hydrolysis of hemicellulose (xylan) is performed for 3 days with endo-xylanase enzyme in unmixed tubular reactors of 10, 12.5 and 15 mm diameter kept in an incubator at 40°C. The concentrations of the activator and inhibitor are measured at every 3 cm interval along the reactor length at regular intervals of time by using Dinitrosalicylic Acid method and HPLC.

Catalytic conversion of lignocellulose (Sunn hemp fibre) to biofuel precursors is performed in 15 ml well-mixed (at 500 rpm) batch reactors at 110°C using ionic liquid ([Bmim]Cl) as a solvent and CuCl₂ as catalyst. Water is added every half-hour at the ten different rates ranging from 25 to 75 µl/gm/hr, and the concentrations of glucose, fructose, hydroxymethyl furfural (HMF), levulinic acid (LA) and formic acid (FA) are measured every half-hour for 24 hours of the reaction time using HPLC. The glucose separated from the reaction medium is fermented using the yeast *Saccharomyces cerevisiae* to bioethanol, whose concentration is measured using GC.

Results and Discussion

The enzymatic hydrolysis of hemicellulose produces Turing patterns of the activator and the inhibitor concentrations along the reactor length. The activators are the soluble sugars of chain-length varying from 3 to 11, while the inhibitors are the monomer (xylose) and the

dimer (xylobiose) that provide non-competitive product inhibition. We show that these Turing patterns in unmixed tubular reactors enhance reducing sugar yields by 16-20% over a well-mixed (150 rpm) hydrolysis, while the xylose yield is enhanced by 8-9%, for 1-5 mg/ml xylan loading. We simulate a reaction-diffusion model to predict these Turing patterns, and validate our simulations with the experimentally-obtained spatial patterns. Our model-experiment comparison shows that the activator and inhibitor are out-of-phase, and that the amplitudes of the activator's spatial patterns decrease with time, while those of the inhibitor increase significantly. The product concentrations form limit cycles on the activator-inhibitor phase space, whose shape changes from circular to elliptical with the progress of hydrolysis.

The catalytic hydrolysis of lignocelluloses produces chaotic strange attractors with fractal dimensions and positive Lyapunov coefficients on the product phase spaces. All the 5 products (glucose, fructose, HMF, LA, FA) exhibit aperiodic (i.e., non-repetitive) temporal oscillations, peaking at 5 hours for water-addition rates ranging from 25 to 43 µl/gm/hr, when the hydrolysis system operates in the domain of chemical chaos. 37.5 µl/gm/hr of water-addition maximizes the concentrations of glucose, LA, FA – at all times, with their average yields peaking at 5 hours to 67.5%, 12.4%, and 5%, respectively. At water-addition rates of 45 µl/gm/hr and higher, the system operates close to its thermodynamic equilibrium, resulting in the temporal oscillations to disappear completely, though the yields of glucose and HMF continue to peak at 5 hours. We show that the peak non-equilibrium yield of glucose obtained at the water-addition rate of 37.5 µl/gm/hr is 15% higher than its corresponding peak equilibrium yield at 45 µl/gm/hr of water addition, leading to a 15% increase in bioethanol production. Bioethanol yield of 78% of its theoretical value is obtained after 15 hours of *Saccharomyces cerevisiae*-mediated batch fermentation of the glucose produced.

Conclusions

Spatiotemporal oscillations in product concentrations resulting from auto-regulatory reaction kinetics and thermodynamic non-equilibrium enhance soluble sugar yields by 15-20% in enzymatic and catalytic hydrolysis of lignocelluloses and hemicelluloses for biofuel production.

References

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