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A synergetic pretreatment technology for woody biomass conversion

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HIGHLIGHTS

- Kinetics of hot-water extraction is analogous to surface renewal.
- Synergy of hot-water extraction stems from pretreatment and fractionation.
- Hot-water extraction improves biomass conversion efficiency, rate and yield.
- Hot-water extraction enables multiple products recovery and sequential deconstruction.

A R T I C L E I N F O

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ABSTRACT

Conversion of woody biomass to chemicals, materials and energy requires at least three steps: pretreatment, cracking and conversion. Size reduction is the minimum required pretreatment step prior to further processing. Cracking step is the middle step in woody biomass conversion whereby solid woody biomass is reduced to small building blocks (molecules) or intermediates. The last step in woody biomass conversion is the generation of desired products from the building blocks or intermediates. Reactions involve woody biomass usually as a solid. The (solid-liquid or solid-gas) surface reactions have an apparent zeroth order owing to the complete renewal of surfaces during the dissolution. A vast array of products (chemicals, energy and materials) can be produced from woody biomass based on its four major components: extractives, hemicellulose, lignin and cellulose. Each of these four components has a different degree of resistance to chemical, thermal and biological degradation. The pretreatment step is designed to improve the efficiency of the cracking step. Waste products are commonly produced during pretreatment step for a sugar-based biorefinery due in part to the desire to maximize (or degrade cellulose to) glucose production. Non cellulose components in a sugar-based biorefinery were commonly discarded, starting from the pretreatment step. A synergetic approach is to eliminate the waste generation in pretreatment and inserting a step to turn the otherwise waste into value-added product(s). Hot-water extraction can serve this purpose. With a hot-water extraction process as a pretreatment step, size reduction can be enhanced after the high pressure operation. Value-added products can be produced from the hot-water extraction and the treated woody biomass can be more efficiently transformed in the cracking step: either be sugar-based, or gasification, or pyrolysis, or direct conversion to solid wood products. The synergy stems from the selective separation/removal of components from woody biomass. The reaction of solid component dissolutions from the woody biomass is of zeroth order, following a surface renewal mechanism during the bulk of the hot-water extraction process.

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1. Introduction

Climate change has led to the increased interest in biomass utilization for chemicals, energy and materials. Although humanity started with using exclusively biomass as the source of chemicals and energy, fossil chemicals have overtaken the role as the dominant energy and chemical source since the industrial revolution. Petroleum, natural gas, and coal have been regarded as toxic waste materials from the distant past. They have been the cheapest sources of energy and chemicals for over half a century. The use of fossil sources has caused a steep increase in atmospheric carbon dioxide. The current level of CO₂ is nearly 400 ppm up from about 330 ppm just 40 years ago. The rise in atmospheric carbon dioxide has accompanied an increase in the atmospheric temperature and other noticeable changes in the climate of earth. The climate change has led the way of discussion on sustainability. Fossil use is not sustainable from both extremes: (1) depletion of source and (2) monotonous increase in atmospheric carbon dioxide concentration. The sustainability of humanity is at threat from the fossil use. Elimination of fossil use and base our needs of chemicals, energy and materials entirely on renewable resources have become the hot-topic. Woody biomass is renewable and sustainable [1]. Although fossil sources may be rich in energy and lean in carbon dioxide, use of woody biomass in place of petroleum, coal and natural gas is highly desirable. Further increase in atmospheric carbon dioxide level is expected until sustainable state is reached [2]. Use of woody biomass has seen increasing interest in industrial applications.

While there are numerous ways of converting woody biomass to chemicals that can be utilized by mankind with the established infrastructures, we shall focus on the conversions in liquid, in particular water. Conversion technologies based on water as solvent can be either biological or chemical. Ability to produce a desired product and minimum environmental impact all favor the use of water as a solvent. Product diversity and green processing are important to a sustainable economy. The importance of biomass conversion has attracted widespread attention and there have been numerous reviews and book chapters dedicated in the area of biomass conversion. A few reviews have been focused on the pretreatment technologies alone [3–8].

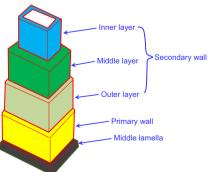
The objective of this paper is to provide a review on the various routes of conversion of woody biomass, in particular, to elucidate the synergetic characteristics of the hot-water pretreatment technology as well as the kinetics behind hot-water extraction.

2. Chemical composition of woody biomass

Plant cells are the main source of chemicals, energy and materials for human use. While differences remain for different species: grassy plants, shrubs, and trees. They all contain woody biomass, or more precisely, lignocellulosic biomass. The term lignocellulosic biomass stem from the four main components in woody biomass: extractives, hemicellulose, lignin and cellulose. Together, lignin and cellulose form the majority of the dry mass of a plant cell. A schematic of a plant cell is shown in Fig. 1.

One can observe that there is no space between cells in Fig. 1. Cellulose is main component, followed by hemicelluloses and lignin. All the inter-cell spaces (middle lamellae) are filled with substances such as lignin (>80%), hemicellulose and extractives. The fiber/cell walls on the other hand are consisted of mostly cellulose, with lignin and hemicellulose being the minor components. Despite the high content of lignin in the middle lamellae, over 60% of the lignin is in the cell walls due to the relative "thickness" of the different layers as shown in Fig. 2.

Lignin is an amorphous macromolecule of phenylpropanoid units: coniferyl alcohol, sinapyl alcohol, and phenolpropylene alcohol. The lignin present in softwood is composed almost entirely of coniferyl alcohol, while that in hardwood is composed of both

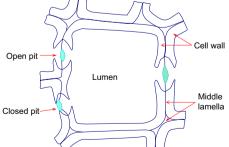


(b) Cross-section of a plant cell. The cells are "glued" together by middle lamella, which contains most lignin and some hemicellulose. Pits serve as channels connecting the lumen of adjacent cells. During biomass conversion, the pits serve as the conduit for

the transport of reaction agents and products.

(a) "Layers" of plant cell wall. The center of the cell is hollow (lumen). The outermost of the cell is the primary wall, which borders adjacent cells with middle lamella. The secondary wall is normally divided into three layers.

Fig. 1. Schematics of a plant cell.



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