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# Saccharification of lignocellulosic biomass for biofuel and biorefinery applications – A renaissance for the concentrated acid hydrolysis?

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#### Abstract

Hydrolysis of lignocelluloses using concentrated acids achieves near-theoretical sugar yields, and with fewer degradation products than the more commonly employed dilute acid hydrolysis process. In this paper, the dependence of sugar yield and the production of fermentation inhibitors on central process parameters is investigated, and the "severity factor" concept of one single process parameter characterizing the extent of the reaction is applied for the first time to concentrated acid hydrolysis of lignocellulosic biomass. Selected hydrolyzates have been fermented in the laboratory to investigate the effect of analyzed and unknown fermentation inhibitors in the hydrolyzates on fermentation performance. The concentrated acid hydrolysis process appears to be an interesting process for saccharification of lignocellulosic biomass for biofuel and biorefinery applications, with high sugar yields, low levels of fermentation inhibitors, good fermentability and good robustness towards changes in raw material quality.

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Keywords: Sulfuric acid; Hydrolysis; Concentrated acid Hydrolysis; Decrystallization; Lignocellulosic biomass; Lignocelluloses; Lignocellulosics; Aspen; Pine; Generalized severity parameter; Severity parameter; Fermentation; Biofuels; Biorefinery; Bioethanol

#### 1. Introduction

The increased concern for anthropogenic  $CO_2$  emissions and limited availability of petroleum resources in the future has spurred a steadily increasing interest in energy and fuel based on renewable

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resources. Although currently exploited biomass resources don't seem to be sufficient to cover the world's transport energy needs, much less the world's total energy needs [1,2], lignocellulosic biomass is still regarded by many as the only large-scale currently available non-fossil carbon source for energy carriers, chemicals and materials. Thus, there is still a strong motivation for research into industrially and economically viable processes for conversion of biomass to energy, fuels, chemicals, and materials.

Currently investigated technologies for conversion of lignocellulosic biomass to fuels and chemicals are diverse; however the main interest in the research community seems to focus on either gasification followed by hydrocarbon synthesis, or saccharification followed by biochemical or catalytic processing of sugars and/or lignin. The use of simple monosaccharides as process intermediates may enable the production of a diverse range of compounds, either by fermentation [3] or by catalytic hydrodeoxygenation [3,4] and is thus a very interesting approach for a biorefinery producing a diverse range of products, of which the fuel components may not necessarily provide the highest income for the biorefinery [5]. However, successful and effective production of monosaccharides in high yields is still a challenge. The main saccharification methods currently being investigated are acidic or enzymatic hydrolysis of biomass polysaccharides after a pretreatment stage, followed by chemical or biochemical conversion of the sugar intermediates. Another approach is the simultaneous saccharification and fermentation (SSF), or consolidated bioprocessing (CBP) [6] to overcome feedback inhibition of the hydrolytic enzymes employed.

### 1.1. Saccharification methods

Dilute acid pretreatment and hydrolysis is extensively investigated, and the technology is today at the pilot plant level. However, dilute acid hydrolysis has some drawbacks, namely the acid-catalysed dehydration of the sugar intermediates into furfural-type components, decreasing sugar yields and inhibiting biochemical conversion of the sugars into *e.g.* fuel ethanol [7]. Due to the mild conditions employed during enzymatic hydrolysis, furfural production is essentially negligible, and enzymatic saccharification is therefore an appealing alternative to acid hydrolysis. However, the recalcitrance of lignocellulosic substrates and the cost of currently available enzyme preparations are regarded as the major obstacles to an economically viable lignocellulose-based biorefinery employing enzymatic hydrolysis. Also, finding appropriate pretreatment methods to increase substrate availability is a challenge for successful employment of enzymatic hydrolysis in a lignocellulose-based biorefinery [7]. It is believed, however, that improved pretreatment methods and enzyme preparations may overcome this challenge in the future.

Concentrated acid saccharification is a process which was in industrial use during the early 20<sup>th</sup> century [8,9], but it is now discontinued due to the large consumption of acid making the process less economically favorable. However, the development of effective acid recovery solutions for the concentrated acid hydrolysis process [10,11,12] has renewed the interest [11,13-21] in this process, which previously was regarded as economically not viable due to the large amounts of acid required. In concentrated acid saccharification, concentrated mineral acids effectively de-crystallize the cellulose, making the reaction system during subsequent hydrolysis more homogeneous and thus less vulnerable to monosaccharide degradation before complete hydrolysis is obtained.

#### 1.2. The severity factor and its applicability to concentrated acid hydrolysis

The severity factor concept has been used as a single-parameter characterization of the extent of reaction in lignocellulose processes like pyrolysis [22], delignification [23,24], or autohydrolysis [25,26], but has seen its most widespread use for characterization of dilute acid hydrolysis [22,27].

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