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An integrated process for the production of platform chemicals and diesel miscible fuels by acid-catalyzed hydrolysis and downstream upgrading of the acid hydrolysis residues with thermal and catalytic pyrolysis

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HIGHLIGHTS

- ▶ Integrated process for miscanthus hydrolysis and residues (AHRs) pyrolysis.
- ► Hydrolysis parameters effect study on levulinic acid production and AHR nature.
- ► Cellulose, hemicellulose and lignin content of AHRs effect on bio-oil production.
- ▶ In situ catalytic upgrading of AHR pyrolysis vapors.

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ABSTRACT

This study evaluates an integrated process for the production of platform chemicals and diesel miscible biofuels. An energy crop (*Miscanthus*) was treated hydrothermally to produce levulinic acid (LA). Temperatures ranging between 150 and 200 °C, sulfuric acid concentrations 1–5 wt.% and treatment times 1–12 h were applied to give different combined severity factors. Temperatures of 175 and 200 °C and acid concentration of 5 wt.% were found to be necessary to achieve good yield (17 wt.%) and selectivities of LA while treatment time did not have an effect. The acid hydrolysis residues were characterized for their elemental, cellulose, hemicellulose and lignin contents, and then tested in a small-scale pyrolyzer using silica sand and a commercial ZSM-5 catalyst. Milder pretreatment yielded more oil (43 wt.%) and oil O_2 (37%) while harsher pretreatment and catalysis led to more coke production (up to 58 wt.%), less oil (12 wt.%) and less oil O_2 (18 wt.%).

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1. Introduction

Biomass has been identified as the prime candidate to replace fossil resources. There is now a major focus worldwide on chemical conversions of lignocellulosic biomass to organic (bulk-) chemicals and alternative fuels (Gallezot, 2012; Sanders et al., 2012). Special emphasis is given to acid catalysis conversions at elevated temperatures (100–250 °C). In this hydrolysis process, the cellulose fraction is depolymerized to glucose, which is subsequently converted to 5-hydroxymethyl furfural (HMF) as the intermediate product. Further conversion of HMF in the presence of the acid catalyst yields levulinic acid (LA) and formic acid in a 1:1 mol ratio (Girisuta et al., 2006). LA is a versatile building block for the

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0960-8524/\$ - see front matter © 2012 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.biortech.2012.09.013 synthesis of various organic compounds that can be used as fuel additives, biodegradable herbicides or precursors in the polymer and resin industries (Bozell and Petersen, 2010). Several reviews describe the properties and potential industrial applications of LA and its derivatives (Leonard, 1956; Rackemann and Doherty, 2011).

The hemicelluloses are converted to the monomer of hexose and pentose sugars. The hexoses (mainly glucose, mannose, and galactose) follow the same reaction path as the glucose from cellulose and the pentoses, composed mainly of xylose and with lesser amounts of arabinose, are converted to furfural (Antal et al., 1991; Weingarten et al., 2010). During hydrolysis, some lignin is released as acid soluble lignin (ASL), while the major part survives as an insoluble residue. These solid residues are mixed with the insoluble condensation reaction products (often referred to as 'humins') formed during the conversions (Patil and Lund, 2011). These solid mixtures can be separated by filtration from the water-soluble stream and are defined as the acid hydrolysis residue (AHR). To the best of our

