## Abstract

Wet air oxidation (WAO) pre-treatment conditions for rice husk were statistically optimized by using the Response Surface Methodology (RSM). Composition of pretreated rice husk was determined to be (in wt%): cellulose (66.97±1.86), hemicellulose (8.47±2.87), lignin (2.89±2.11), and ash (21.10±0.72). The wet air oxidation pretreatment was coupled with alkaline peroxide pre-treatment. This methodology was named Alkaline Peroxide Assisted Wet Air Oxidation (APAWAO). The intensive structural breakdown of rice husk following APAWAO was visualized by Scanning Electron Microscopy (SEM). The degradation products (which are the main inhibitors to subsequent enzymatic hydrolysis and fermentation) formed during pre-treatment were analyzed by High Performance Liquid Chromatography (HPLC). The concentrations of carboxylic acids in the pre-treatment liquid were (in g/l):  $(4.62\pm0.75)$  after WAO and (5.42±0.84) after APAWAO. The concentration of furan aldehydes (furfural and HMF) were (in ppm): 10.86±2.34 after WAO and 1.13±0.28 after APAWAO. The concentration of furan aldehydes formed after WAO and APAWAO were substantially less than that from conventional biomass pre-treatment methods viz. acid hydrolysis and steam explosion. The potential of ionic liquids for pre-treating rice husk was also investigated. Two ionic liquids, viz. 1-Ethyl-3-methylimidazolium acetate (EMIM Ac) and 1-Butyl-3-methylimidazolium chloride (BMIM Cl) were studied. The cellulose content in IL pre-treated rice husk was (in wt%): 75.51±1.25 (EMIM Ac-treated) and 95.20±0.78 (BMIM Cl-treated). The enzymatic digestibility of pre-treated rice husk was investigated, and was found to increase from (in wt%)  $4.11\pm0.40$  in untreated rice husk, to 28±0.29 in WAO pre-treated rice husk, 82.10±4.03 in APAWAO pre-treated rice husk, and 50.05±1.84 (EMIM Ac-treated) and 54.46±1.49 (BMIM Cl-treated). Maximum glucose concentration of 55 g/l was obtained, when 10% dry matter of APAWAO pre-treated rice husk was enzymatically hydrolysed. It was shown that the liquid fraction from APAWAO pre-treatment could be reused for enzymatic hydrolysis, without detoxification. Fermentation of pre-treated, saccharified rice husk was performed by five different strategies using Saccharomyces cerevisiae. Concentration of produced ethanol was determined by Gas Chromatography (GC). The maximum ethanol concentration achieved was 28.74 g/l, corresponding to 3.65 vol% of ethanol. The process of rice husk to ethanol bioconversion was technoeconomically analyzed by conceptually scaling up the process to commercial scales.

**Keywords:** Bioethanol, Pre-treatment, Enzymatic saccharification, Fermentation, Rice husk, Lignocellulose, Biomass, Process optimization, HPLC, GC, Wet air oxidation, Ionic liquids, Cellulases, High dry matter loading, Conceptual process integration, Process economics