



## Research paper

# Microwave pretreatment effects on switchgrass and miscanthus solubilization in subcritical water and hydrolysate utilization for hydrogen production

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## ABSTRACT

Microwave pretreatment is an energy-efficient and environmentally benign technology that can be used to reduce the recalcitrance of complex biomass structure. Switchgrass (*Panicum virgatum* L.) and miscanthus (*Miscanthus x giganteus*) are perennial C4 grasses that are being developed as bioenergy crops because they have high yield potential and desirable agronomic traits. These materials are promising candidates for biofuels, bioproducts and green chemicals production from biomass.

In the present study, miscanthus and switchgrass biomass were solubilized in subcritical water after pretreatment by microwave at different processing temperatures. The hydrolysates obtained were evaluated for hydrogen-rich gas production by aqueous-phase reforming (APR).

Higher temperature microwave processing reduced the biomass recalcitrance resulting in microwave treated materials having 7–10% higher solubility in subcritical water than untreated materials. However, gasification of pretreated biomass hydrolysates produced less gaseous products compared to untreated biomass for both switchgrass and miscanthus. Miscanthus biomass was more vulnerable to destruction by microwave treatment and recalcitrance of this biomass was achieved at lower temperature compared to switchgrass. Miscanthus biomass that was not microwave treated produced the highest gas yield. Microwave pretreatment caused significant increases in the formation of ungasified solid carbon residue in the APR process.

## 1. Introduction

Among alternative biomass resources, switchgrass (*Panicum virgatum*) and miscanthus (*Miscanthus x giganteus*) are promising potential sources for production of value-added products. They are non-edible biomass materials with high total carbohydrate contents. These sources are C4 warm-season perennial grasses and both crops have a tolerance for cold weather and are highly adaptable to varying soil conditions [1,2].

Pretreatment is an essential prerequisite to make biomass accessible to deconstruction by altering structural features such as removing lignin and reducing cellulose crystallinity, thereby increasing porosity. Successful production of biofuels and other bioproducts from lignocellulosic biomass depends on the pretreatment and deconstruction methods applied as well as the physical and chemical properties of the

biomass. An efficient pretreatment method followed by solubilization in aqueous media without using toxic and hazardous chemicals is necessary to obtain reduced molecular weight of carbohydrates from biomass to produce various biofuels and bioproducts.

Microwaves are in the region of the electromagnetic spectrum between infrared radiation and radio frequencies, in the 1 mm to 1 m wavelength range (300 MHz–300 GHz). This electromagnetic radiation is used to generate heat by the oscillation of molecules upon radiation absorption. Microwave-based pretreatment causes both thermal and non-thermal effects generated by an extensive intermolecular collision as a result of realignment of polar molecules with microwave oscillations [3]. Selectively heating polar parts of lignocellulosic biomass with microwave radiation can reduce the recalcitrance of complex biomass structure. On the other hand, disrupting the crystallinity and altering the compact and rigid biomass structure can be achieved in an

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electromagnetic field of microwaves [3]. Microwave treatment has enhanced the surface disruption and the breaking of lignin structures in switchgrass and improved enzymatic saccharification 53% more compared to conventional heating [4]. Microwave pretreatment was used for solubilization of lignocellulosic biomass in combination with acid and alkali treatments followed by enzymatic hydrolysis [4–6]. Chimentão et al. (2014) investigated hydrolysis of dilute acid-pretreated cellulose in a conventional oven and under microwave heating [7]. Although the method was called “mild hydrothermal conditions”, the hydrolysis process was accelerated by using acids (sulfuric and oxalic acids). Thangavelu et al. (2014) used a one step process in hydrothermal conditions using a domestic microwave oven in which hydrolysis was accelerated by carbon dioxide, but it did not lead to complete solubilization of biomass [8]. On the other hand, use of subcritical water as hydrolysis medium under appropriate temperature and pressure conditions could be an effective method to solubilize microwave pretreated biomass without using any acid, base, enzyme or chemical catalysts. Applying microwave irradiation before hydrolysis in subcritical water could make the lignocellulosic biomass vulnerable to thermochemical solubilization.

In previous studies, the maximum solubilization yield of wheat (*Triticum aestivum*) straw and kenaf (*Hibiscus cannabinus*) biomass were 70–75% which was achieved in subcritical water medium at 250 °C and 27.58 MPa carbon dioxide pressure conditions [9,10]. However, the hydrolysates obtained in this process contained high molecular weight polysaccharides that were difficult to utilize for producing value-added products such as hydrogen. The diversity in the chemical composition and molecular weight distribution of lignocellulosic biomass hydrolysates considerably affect the method employed for biofuel or useful chemicals production. The more degraded organics containing biomass hydrolysate showed better selectivity for hydrogen production by aqueous-phase reforming (APR) [11].

Using microwave pretreatment with subcritical water as a hydrolysis medium could be an effective method to solubilize biomass in an environmentally friendly way without use of any acid, base, enzyme or chemical catalysts. Subcritical water process that combined with innovative microwave irradiation pretreatment can be defined as ‘green treatment’ since it utilizes renewable biomass materials as feeds, uses water as solvent and eliminates the use and generation of hazardous substances in the treatment process [12,13]. Although many studies have been reported on microwave pretreatment for enhancing the enzymatic hydrolysis [14–17], there are no reports of solubilization of the microwave treated biomass samples in *subcritical water* and *evaluation of the hydrolysates for gasification*. The objectives of the present study are to 1) develop an effective solubilization method for lignocellulosic biomass using microwave pretreatment and subcritical water solubilization technologies, 2) evaluate solubilization performances of two non-edible biomass feedstocks, switchgrass and miscanthus, and 3) investigate the utilization of the hydrolysates for hydrogen biofuel production by APR. APR is compatible with water-soluble feedstocks such as hydrolysates produced in the present study and it produces less CO by-product due to facilitated water-gas shift reaction. This process has several advantages compared with steam reforming, such as gasification occurring at considerably lower temperatures (~225 °C) [10].

## 2. Experimental

### 2.1. Biomass materials

Switchgrass and miscanthus biomass materials used in this study were provided by USDA-ARS, University of Nebraska-Lincoln. The Kanlow N1 switchgrass was harvested at anthesis and *Miscanthus x giganteus* was harvested after a killing frost. Harvested samples were dried in a forced-air oven at 50 °C to a constant weight and dhj ry weight determined. Biomass samples were ground through a 2-mm screen with a Wiley Mill (Thomas-Wiley Mill Co., Philadelphia, PA)

**Table 1**  
Hemicellulose, cellulose, and acid detergent lignin composition of biomass samples.

Biomass	Cellulose, %	Hemicellulose,%	Acid detergent lignin,%	Ash,%
Switchgrass	36.47	27.90	2.07	3.72
Miscanthus	37.52	25.26	4.41	3.99

then a subsample was ground through a UDY cyclone mill (UDY Corp., Ft. Collins, CO) with a 1-mm screen for analyses. The ground switchgrass and miscanthus contained  $7.56 \pm 0.68\%$  and  $3.24 \pm 0.64\%$  moisture, respectively. Biomass samples were analyzed by the USDA-ARS Forage Research Laboratory at Lincoln, NE. All ground samples were scanned on NIRSystems Model 6500 near-infrared reflectance spectrophotometer (NIRS; Foss NIRSystems Inc, Laurel, MD). The compositions of the biomass samples were predicted using the warm-season perennial grass equation with a global H value of 1.06. Hemicellulose, cellulose, and acid detergent lignin are reported on a dry matter (DM) basis and were corrected for ash (Table 1). All chemicals used in this study were either analytical or reagent grade.

### 2.2. Microwave pretreatment

MarsXpress microwave system (CEM Corporation) was used for microwave pretreatment of biomass. The system consisted of two magnetrons that can control the temperature of samples up to 300 °C. The system has no sensor for pressure. Ground biomass weighing 0.5 g and 12 cm<sup>3</sup> distilled water were placed in a closed-teflon vessel. A total of 10 vessels were used in a turning carousel for each run. The pretreatment was applied for a range of temperatures (60, 80, 100, 120, 150, 180, 210 °C) at 800 W. The 10 min ramp time was used to reach the target temperature and heating rate changed accordingly. The microwave system was held at constant temperature for 35 min. Some pretreatments were performed at 1600 W for comparison. After pretreatments were completed, the samples were cooled to room temperature and the liquid and solid fractions were separated by filtration.

Microwave treated samples were examined by Hitachi S4700 field-emission scanning electron microscope (FE-SEM) and Perkin Elmer Spectrum RX-I infrared spectroscopy for morphological changes in the biomass structures.

### 2.3. Hydrolysis in subcritical water

Microwave pretreated dry solid biomass samples were subjected to subcritical water treatment for solubilization. The experiments were performed using 5 g ground biomass material and 350 cm<sup>3</sup> water in a 500 cm<sup>3</sup> stainless steel high pressure reactor (Parr Model 4575 HP/HT, Parr Instrument Co., Moline, IL, USA) equipped with magnetic drive stirrer and temperature controller system. The mixture was heated with a rate of 4.7 °C min<sup>-1</sup> until it reached desired temperature, 220 °C. Then, the reactor was pressurized with CO<sub>2</sub> using ISCO 260D pump (Isco Inc., Lincoln, Nebraska, USA) to 25.51 MPa. The contents of the reactor were mixed at 500 rpm via the magne-drive for 120 min. In the next step, the reactor was taken out of the heating system and quenched in ice-cold water. The hydrolysate solution was collected and filtered through 0.2 µm nylon filter and clear solution was analyzed for total organic carbon (TOC) using a Tekmar Dohrmann Apollo 9000 instrument.

Statistical analysis of the data was performed by Microsoft excel by applying one way analysis of variance (ANOVA) at significance level of 5% (P = 0.05), and significant differences among means were defined by using the Student t-test.

### 2.4. Hydrogen production from hydrolysates

The biomass hydrolysates were evaluated for hydrogen production by APR gasification technique using carbon supported Pt catalyst (Alfa

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