

Treatment Variable Effects on Supercritical Gasification of High-Diversity Grassland Perennials

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Abstract Low-input high-diversity (LIHD) mixtures of native grassland perennials were subjected to a supercritical treatment process with the aim of obtaining hydrogen-rich gases. The process was studied based on the following treatment variables: reaction temperature (374 °C to 575 °C, corresponding to a pressure range of 22.1 to 40 MPa), residence time (10 to 30 min), biomass content in the feed, and catalysts (0% to 4% NaOH and solid alkali CaO–ZrO₂). The gaseous phase produced from gasification of LIHD primarily consisted of hydrogen (H₂), with a mixture of carbon monoxide (CO), methane (CH₄), and carbon dioxide (CO₂). The statistical significance of treatment variables was evaluated using analysis of variance (ANOVA). It showed that at the level of $P < 0.05$, temperature, catalysts, and biomass content in the feed significantly affected gas yields, while residence time was not significant.

Keywords Supercritical gasification · Biodiversity · Hydrogen · Statistical significance

Introduction

Hydrogen is considered a clean fuel that provides a promising method to help the United States achieve energy independence, make strides in environmental stewardship, and develop a thriving economy. It is manufactured from either fossil fuels such as natural gas, naphtha, and coal or nonfossil energy sources, such as water by electrolysis, photolysis, or thermolysis. Other methods of renewable hydrogen production include the high temperature gasification and low-temperature pyrolysis of lignocellulosic biomass [1].

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Supercritical Fluid extraction (SFE) is a separation technology using supercritical fluids such as the extracting solvent. A supercritical fluid is any substance at a temperature and pressure above its thermodynamic critical point, which is defined in terms of the critical temperature and critical pressure. Water (H₂O) is a supercritical fluid above 374 °C and 22.1 MPa. Recently, a supercritical fluid treatment has been considered to be an attractive alternative in science and technology as the solvent for extraction. The molecules in the supercritical fluid have a high kinetic energy (like the gas) and a high density (like the liquid). Therefore, it is expected that the chemical reactivity can be high as well. In addition, the ionic product and dielectric constant of supercritical water, which are important parameters for chemical reactions, can be continuously controlled by regulating pressure and temperature. In addition, the supercritical water can be realized from the ionic reaction field to the radical reaction field [2]. Therefore, supercritical water gasification of biomass is expected as a possible system for producing renewable hydrogen, which is beneficial to exploit biomass resources and to develop a highly efficient, clean method for large-scale hydrogen production [3].

In comparison with other biomass thermochemical gasification, such as air gasification or steam gasification, the supercritical water gasification can deal directly with the wet biomass without drying and have high gasification efficiency in lower temperatures [4]. Previous supercritical gasification research of feedstock including glucose, acetic acid, formic acid, wood, etc, has been reviewed by Mozaffarian, et al. [5]. For this study, the supercritical water gasification of high-diversity mixtures of plants grown with low inputs on agriculturally degraded land [6], which shows the potential as a major source of biofuel biomass, was studied in a batch pressure vessel equipped with an induction heating system and based on the following treatment variables: reaction temperature, residence time, biomass content in the feed, and catalysts. The statistical significance of treatment variables was evaluated using analysis of variance (ANOVA) *F* test.

Material and Methods

Materials

High diversity biomass [low-input, high-diversity (LIHD)], which contains 18 perennial herbaceous grassland species, was provided by the Department of Ecology, Evolution, and Behavior at the University of Minnesota, St. Paul, Minnesota [6]. LIHD was ground in a mill (Thomas Scientific of Swedesboro, NJ, USA) to pass through a screen with a 0.5-mm aperture.

Biomass Analytical Procedures

Composition analysis of biomass was carried out by the laboratory analytical procedures (LAPs) developed by the National Renewable Energy Laboratory. The moisture content of biomass was determined by the method of LAP #001. The ash content of biomass was determined by the method of LAP #005. Structural analyses of the samples were carried out according to the methods of LAP #002, LAP #003, LAP #017, and LAP #019 [7]. The compositions of LIHD are listed in Table 1.

Apparatus and Process

A 75-ml Parr high pressure reactor (Parr Instrument of Moline, IL, USA) was used for supercritical treatment of the feedstock. The reactor consisted of a reaction cylinder and a

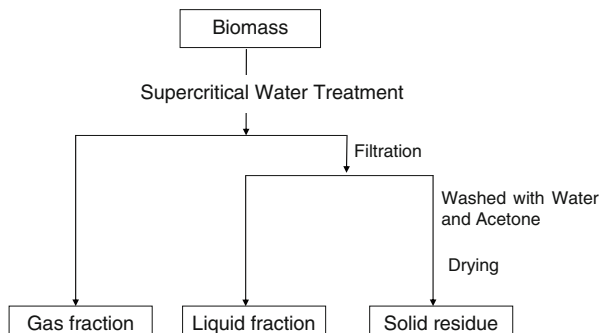
Table 1 The composition of LIHD^a (air dried, % by weight).

	LIHD
Glucan	27.7
Xylan	10.7
Galactan	1.3
Arabinan	1.6
Mannan	0.3
Klason lignin	29.8
Moisture	3.6
Ash	8.0

^a Biomass contained acid-soluble lignin, extractives, acetyl acid groups and uronic acid groups.

pressure gauge/valve assembly. An induction heating system, which allows for the reduction of heat-up times by approximately two orders of magnitude, was customized by L.C. Miller Company of Monterey Park, CA, USA [8]. For a typical run, 1.5 g of feedstock and 40 ml chemical solution containing 0–4% of sodium hydroxide were placed inside the cylinder. When using solid alkali CaO–ZrO₂ as the catalyst, CaO–ZrO₂ was directly added to the cylinder. The cylinder was then sealed and purged with nitrogen gas at a flow rate of 80 ml/min in order to remove air and prevent secondary reactions, such as thermal cracking and repolymerization. The reactor was heated to 374 °C to 575 °C at a heating rate of about 120 °C/min, and this desired temperature was held for 10–30 min.

After completing the reaction, the cylinder was cooled down by soaking in an ice bath for 5 min. Gases were sampled into a gas bag for later GC analysis. The gas fraction was determined by measuring the weight difference of the reactor before and after gas sampling. The liquid, including both water fraction and heavy oil fraction, was collected into a sample bottle for later analysis. The procedure for products separation after supercritical treatment is shown in Fig. 1. The aqueous phase was filtered to separate the water solution and the water insoluble fraction. The water insoluble fraction and the wall of the pressure reactor were washed with 10 ml acetone three times and then separated through a filtration process. The total amount of the acetone solution containing heavy oil and the aqueous phase were referred to as the liquid fraction. The acetone insoluble fraction was then air-dried at room temperature for 48 to 72 h to become a constant weight to yield the char residue. Constant weight is defined as less than ±0.01 g change in the weight upon 12 h of re-drying the residue.

Fig. 1 Process for products separation after supercritical treatment

The yield percentage of each fraction from supercritical treatment is defined as:

$$\text{Gas yield (\%)} = \left(\frac{\text{weight of gas}}{\text{weight of starting biomass}} \right) \times 100$$

$$\text{Residue yield (\%)} = \left(\frac{\text{weight of residue}}{\text{weight of starting biomass}} \right) \times 100$$

$$\text{Liquid yield (\%)} = \left(1 - \frac{\text{weight of gas}}{\text{weight of starting biomass}} - \frac{\text{weight of residue}}{\text{weight of starting biomass}} \right) \times 100$$

All experiments and analysis were performed in triplicate.

Catalysts Preparation

Solid alkali CaO–ZrO₂ was prepared as follows: hydroxides of Zr and Ca were obtained by dissolving chloride of Zr and Ca in water (atom ratio 7:3), hydrolyzing with aqueous ammonia to pH=9~10 in solution, washing the precipitate and drying at 110 °C. The precipitates were calcinated in a furnace at 570 °C for 4 hours, and then powdered.

Chemical Analysis

The gaseous samples were analyzed using GC with MS5A, PPQ, and WAX columns and a thermal conductivity detector for the analysis of hydrogen, carbon monoxide, carbon dioxide, methane, and other gases [9]. The volume concentration of each gas of interest was calculated based on an external standard method.

Chemical compositions of the liquid products were identified using an HP 6890 GC/5973 mass spectrometer with a DB-5 capillary column. The GC was programmed at 40 °C for 30 s and then increased at 10 °C/min to 300 °C and finally held with an isothermal for 10 min. The injector temperature was 300 °C, and the injection size was 1 µl. The flow rate of the carrier gas (helium) was 0.6 ml/min. The ion source temperature was 230 °C for the mass selective detector [10]. The compounds were identified by a comparison with the NIST Mass Spectral Database.

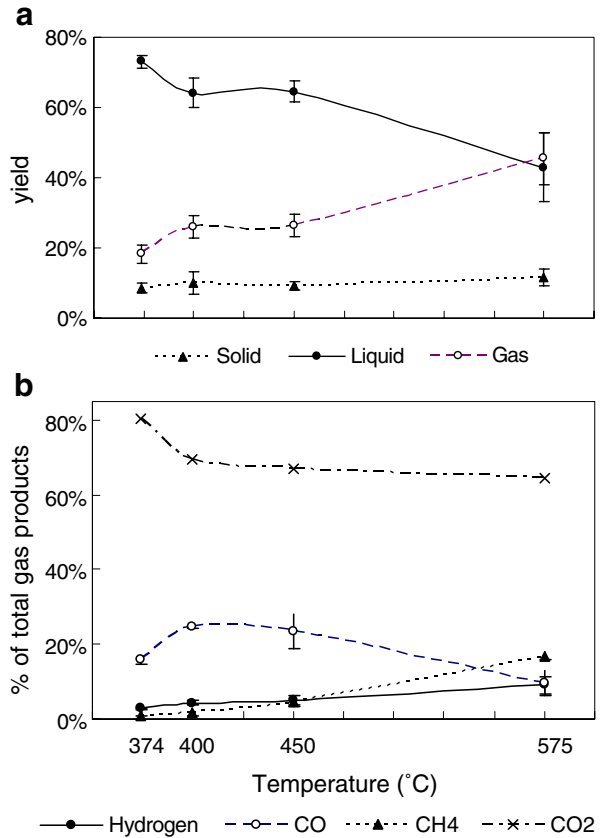
Results and Discussion

Effect of Treatment Temperature

While no catalyst was added into the reaction mixtures, the final temperature for supercritical treatment of high diversity biomass (LIHD) varied from 374 °C to 575 °C, which corresponds to a pressure range of 22.1 to 40 MPa. The products of treating LIHD contained 18% to 46% gas, 42% to 73% liquid, and 8% to 12% residue. According to Fig. 2a, it is clear that the yield of gaseous products obtained from the separation of supercritical treatment products increased with an increasing treatment temperature.

The gaseous phase from supercritical treatment of LIHD primarily consisted of hydrogen (H₂), carbon monoxide (CO), methane (CH₄), and carbon dioxide (CO₂), which were 2.8% to 9%, 9% to 24%, 1% to 17%, and 65% to 80% of the total gaseous products, respectively. While the supercritical treatment temperature was raised from 374 °C to 575 °C, the yield of H₂ also increased to 9% (see Fig. 2b). This demonstrates that the final temperature had an obvious influence on the supercritical treatment yields.

Fig. 2 Effect of temperature on the yields of supercritical treatment and gaseous products. **a** The yields of LIHD. **b** The yield of gaseous products from LIHD *error bars* represent standard deviations calculated from the data obtained from three duplicated experiments



Effect of Catalysts on Yield

LIHD was treated at 450 °C and 575 °C for 10 min in the presence of the following catalysts: 1% NaOH, 4% NaOH, and solid alkali CaO–ZrO₂. When NaOH concentration increased from 0% to 4%, the yield of gaseous products and hydrogen increased significantly (see Table 2). Ergo, the catalyst is another important factor that needs to be considered in the supercritical treatment process.

At 450 °C and 575 °C, the hydrogen yields were 12.8% and 7% of total biomass [79.8% and 52.1% of total gaseous products (mol)], respectively. During biomass gasification, a complex combination of reactions occurs including pyrolysis, hydrolysis, steam reforming (water and biomass react to produce CO, CO₂, and H₂), the water–gas shift (WGS) reaction (water and CO react to form H₂ and CO₂), and methanation (CO and H₂ react to form CH₄ and H₂O). At a higher temperature of 575 °C, methanation reaction seems to be more dominant, and CH₄ yield is 46.6% of total gaseous products. In order to achieve high hydrogen production, the key factor is the presence of a proper catalyst.

When liquefying biomass, solid alkali CaO–ZrO₂ was shown to have similar activity as sodium hydroxide (NaOH) [11]. During supercritical treatment, the residues were slightly reduced from 11.5% to 6.6% of the total biomass, but the gas yields were not significantly affected (see Table 2).

Table 2 Effect of catalysts on supercritical treatment of LIHD (biomass content 3.8%).

Final temperature (°C)	Catalyst	Supercritical treatment yield (% of total mass)			Gas yield (% of the total gaseous products)			
		Solid	LIQUID	GAS	H ₂	CO	CH ₄	CO ₂
575	None	11.6±2.3	42.8±9.8	45.5±7.5	9.0±2.4	9.6±3.3	16.9±1.0	64.5±6.7
575	1% NaOH	11.7±3.1	26.7±4.3	61.7±5.6	16.3±8.8	1.4±1.9	32.8±1.7	49.5±9.0
575	4% NaOH	11.5±2.2	27.5±5.2	61.1±7.4	52.1±2.4	–	46.6±0.5	1.3±1.9
575	CaO–ZrO ₂	6.6±2.0	37.2±4.0	56.1±4.2	8.8±2.3	7.7±0.9	22.5±0.3	60.9±1.1
450	None	9.0±1.2	64.2±4.2	26.4±3.3	5.0±1.1	23.5±4.5	4.4±1.1	67.1±2.7
450	4% NaOH	9.1±0.7	50.6±1.8	40.3±3.1	79.8±11.8	1.2±2.1	19.0±10.0	-

– not detectable

Effect of Treatment Time

LIHD was treated at 575 °C and 40 MPa for 10 or 30 min in the presence of 4% NaOH as the catalyst. A longer treatment time of 30 min resulted in more gaseous products than 10 min treatment, which was 70.0% and 61.1% of the total biomass, respectively (see Fig. 3a). However, the hydrogen concentration in the total gaseous phase was almost unaffected by the treatment time. A possible reason for this is the gas reaction may already reach the steady state within 10 min.

Effect of Biomass Content in the Feed

When the biomass concentration in water decreased from 7.5% (w/w) to 1.3% (w/w), the products gradually contained more gaseous products, but less liquid products (see

Fig. 3 Effect of time on yields. LIHD was treated at 575 °C for 10 min (a) and 30 min (b)

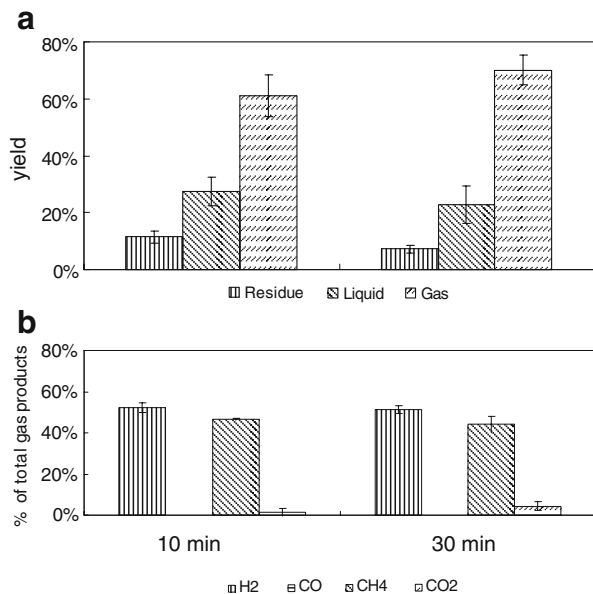


Table 3 Effect of biomass content on supercritical treatment of LIHD (575 °C, 4% NaOH).

Biomass content (% w/w)	Supercritical treatment yield (% of total mass)			Gas yield (% of the total gaseous products)			
	Solid	Liquid	Gas	H ₂	CO	CH ₄	CO ₂
1.3	9.3±3.9	21.7±9.8	69.1±5.1	59.5±1.3	0.1±0.1	40.4±0.3	–
3.8	11.5±2.2	27.5±5.2	61.1±7.4	52.1±2.4	–	46.6±0.5	1.3±1.9
7.5	8.0±1.2	51.7±4.7	40.4±5.0	24.5±5.9	2.0±0.5	68.8±5.2	4.8±1.2

– not detectable

Table 3). A decreasing hydrogen yield was also observed with an increasing biomass content.

Statistical Assessment

The statistical significance of the four experimental factors, reaction temperature, residence time, biomass content in the feed, and catalysts on gas yields was assessed using ANOVA. When each factor is considered, the experimental conditions for other factors are identical to minimize the factor–factor interaction effects. The significance test was done for each factor using one-way ANOVA *F* test. The null hypothesis is that the population means measured at different levels of the experimental factor are all equal. The alternative is that they are not all equal, or the factor is significant. The *P* values for each factor were calculated as follows: temperature, 0.0002; catalysts, 0.0185; biomass content, 0.0005; residence time, 0.0722. If a statistical significance level cutoff is chosen as *P*=0.05, it is concluded that temperature, catalysts, and biomass content were significant factors, while residence time was not significant at a level of *P*<0.05.

Conclusions

This paper presents an initial screening of the experimental variables relevant for supercritical gasification processing of low-input high-diversity (LIHD) mixtures of native grassland perennials. The process was studied based on the following treatment variables: reaction temperature, residence time, biomass content in the feed, and catalysts. The gaseous phase from gasification of LIHD primarily consisted of hydrogen, with a mixture of carbon monoxide, methane, and carbon dioxide. The statistical significance of treatment variables was evaluated using analysis of variance *F* test. It showed that temperature, catalysts, and biomass content in the feed significantly affected gas yields at the level of *P*< 0.05, while residence time was not significant (*P*>0.05). Though the experimental dataset was relatively small, considering the factors and experimental levels examined, the statistical assessment of the experimental data is useful to evaluate the experimental factor effects: whether it is due to true factor effects or experimental errors. In the future, parameter optimization techniques, such as response surface methodology and machine learning methods, will be employed for enhanced supercritical gasification yields.

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