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Research paper

Supercritical water gasification of timothy grass as an energy crop in the presence of alkali carbonate and hydroxide catalysts

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ABSTRACT

This study is focused on identifying the candidature of timothy grass as an energy crop for hydrogen-rich syngas production through supercritical water gasification. Timothy grass was gasified in supercritical water to investigate the impacts of temperature (450–650 °C), biomass-to-water ratio (1:4 and 1:8) and reaction time (15–45 min) in the pressure range of 23–25 MPa. The impacts of carbonate catalysts (e.g., Na_2CO_3 and K_2CO_3) and hydroxide catalysts (e.g., NaOH and KOH) at variable mass fractions (1–3%) were examined to maximize hydrogen yields. In the non-catalytic gasification of timothy grass, highest hydrogen (5.15 mol kg^{-1}) and total gas yields (17.2 mol kg^{-1}) with greater carbon gasification efficiency (33%) and lower heating value (2.21 MJ m^{-3}) of the gas products were obtained at 650 °C with 1:8 biomass-to-water ratio for 45 min. However, KOH at 3% mass fraction maximized hydrogen and total gas yields up to 8.91 and 30.6 mol kg^{-1}, respectively. Nevertheless, NaOH demonstrated highest carbon gasification efficiency (61.3%) and enhanced lower heating value of the gas products (4.68 MJ m^{-3}). Timothy grass biochars were characterized through Fourier transform infrared spectroscopy, Raman spectroscopy and scanning electron microscopy to understand the behavior of the feedstock to rising temperature and reaction time. The overall findings suggest that timothy grass is a promising feedstock for hydrogen production via supercritical water gasification.

1. Introduction

The dedicated energy crops are the plant species that are explicitly cultivated as biofuel feedstocks. Some lignocellulosic plants identified as energy crops include alfalfa, bamboo, elephant grass, hybrid poplar, jatropha, reed canary grass, ryegrass, silvergrass, switchgrass and timothy grass. Conservative estimates suggest that the annual availability of energy crops in Canada can range up to 17.3 million tonnes, which has a potential to produce 4.7 billion litres of bioethanol per annum [1]. It should be noted that the availability of energy crop biomass largely depends upon the feedstock value and their propensity for biofuel production.

The salient features of an ideal energy crop are: (i) low cost and fast growth; (ii) short rotation harvesting; (iii) non-seasonal or perennial availability; (iv) high yield, i.e. maximum dry matter production per hectare; (v) lower requirement of intensive agricultural practices; (vi) reduced accumulation of environmental contaminants, e.g. chemical fertilizers, pesticides and heavy metals; (vii) no competition with food crops for nutrients or sunlight; (viii) ability to grow and regenerate in marginal or degraded lands; and (ix) resistance to extreme weather conditions. As the energy crops are non-food or non-cash crops cultivated on marginal soil, they usually do not pose any threat to the food supply and arable lands [2,3].

Timothy grass is a perennial grass native to Europe and North America that grows well in heavy soil and is resistant to drought as well as humid, cold and hot weather conditions. Recently, a few studies have demonstrated the bioenergy potential of timothy grass. The physicochemical characterization of timothy grass is almost analogous to that of wheat straw [4,5], which suggests that

Abbreviations: BTW, Biomass-to-water; CGE, Carbon gasification efficiency; FTIR, Fourier transform infrared; GC, Gas chromatography; HHV, Higher heating value; LHV, Lower heating value; SEM, Scanning electron microscopy; SCW, Supercritical water; SCWG, Supercritical water gasification; WGS, Water-gas shift.

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perennial grasses can potentially supplement the demand for agricultural biomass in biorefineries. Mohanty et al. [6] performed slow and fast pyrolysis of timothy grass at variable heating rates of 275 K min^{-1} and 723 K min^{-1}, respectively. While fast pyrolysis led to the mass fractions of 42% bio-oil, 22% gas and 22% biochar, slow pyrolysis resulted in mass fractions of 18% bio-oil, 27% gas and 43% biochar from timothy grass. Nanda et al. [7] performed dilute acid pretreatment and enzymatic hydrolysis of timothy grass followed by bioconversion to ethanol (22.6 g L^{-1} in 36 h) and butanol (10.8 g L^{-1} in 60 h) using *Saccharomyces cerevisiae* and *Clostridium beijerinckii*, respectively.

Supercritical water gasification (SCWG) is an attractive hydrothermal technology for the conversion of lignocellulosic biomass to produce combustible syngas. SCWG employs supercritical water (SCW) as a homogeneous reaction medium and indigenous catalyst. The thermophysical properties of water transform beyond its critical temperature (≥374 °C) and critical pressure (≥22.1 MPa) that imparts enhanced mass transfer and solvation properties [8]. SCW has liquid-like viscosity and gas-like density along with high diffusivity, low dielectric constant and excellent heat transfer properties [9]. The efficiency of SCWG, as well as gas yields and composition, are determined by the applied temperature, pressure, feed concentration and reaction time [10]. H_2-rich syngas obtained from SCWG can act as a direct fuel or be used to produce hydrocarbon fuels, green diesel and synthetic chemicals via Fischer-Tropsch process [11]. As a fuel, H_2 enriched syngas can be used in high-efficiency power generation systems, combustion engines and fuel cells for both vehicular transportation and distributed electricity generation.

Currently, the primary routes for commercial H_2 production from fossil fuels or hydrocarbons are via steam reforming, alkaline-enhanced reforming, partial oxidation and autothermal reforming. Nearly 59% of industrial H_2 production is through steam methane reforming of natural gas, which contributes about 30 million tonnes of CO_2 per annum [12]. The cost of H_2 production through steam methane reforming is also sensitive to the price of natural gas. For instance, the cost of generating H_2 by steam methane reforming of natural gas (10.30–13.5 \$ GJ^{-1}) is nearly three times higher than the price of natural gas (3.43–4.50 \$ GJ^{-1}) [12]. The cost of H_2 obtained through pyrolysis and gasification is expected to be 1.47–2.57 \$ kg^{-1} and 1.44–2.83 \$ kg^{-1}, respectively [13]. Balat and Balat [14] reported that the cost of H_2 obtained from biomass pyrolysis ranges between 8.86 and 15.52 \$ GJ^{-1}. Hamelinck and Faaij [15] reported that the cost of biomass-derived H_2 ranges from 10 to 14 \$ GJ^{-1}, with a net energy efficiency of 56–64%. However, H_2 price could fluctuate depending on production capacity of the refinery, the cost of feedstock, co-product marketability and carbon trading.

Although the potential of dedicated energy crops for biorefining is well-known, yet their applied conversion is scarcely available in the literature. Hence, the current paper attempts to better understand the candidacy of timothy grass for H_2 production during SCWG. Several parameters governing the SCWG of timothy grass such as temperature, feed concentration and reaction time along with homogeneous catalysts have been systematically investigated.

2. Materials and methods

2.1. Energy crop biomass

Timothy grass (*Phleum pratense* subsp. *pratense*) was used as a representative energy crop biomass in this gasification study. Timothy grass bales weighing about 3–5 kg were procured from a local farm in Saskatchewan, Canada. The grass species was in the later flowering stage during harvest. The height of the cut was between 0.8 and 1.2 m in length that included leaves with a few flower heads. Any visible contaminants such as sand, soil or shell particles were manually removed by threshing the grass bales. The feedstock was then air-dried under ambient conditions for over three months and pulverized to a particle size of 0.5 mm using an IKA MF 10 Basic S1 grinder (ThermoFisher Scientific Inc., Mississauga, Ontario, Canada). The pulverized biomass was stocked in clean glass jars at room temperature and used as necessary.

2.2. Supercritical water gasification

SCWG experiments were performed in a SS316 stainless steel batch tubular reactor (length: 40.5 cm, outer diameter: 1.27 cm and inner diameter: 0.94 cm). The schematics of the SCWG reactor and its operational procedures have been meticulously described by Nanda et al. [16]. The SCWG reactor assembly consisted of pressure gauge, pressure relief valve, split furnace, tubular reactor, Type-K thermocouple, check valve, 2 μm filter and gas-liquid separator. The tubing and accessories of SS316 grade were purchased from Swagelok® (Swagelok Central Ontario, Mississauga, Ontario, Canada).

Nitrogen was used as the inert gas to create an initial reactor pressure of 10–15 MPa depending on SCWG temperature. The tubular reactor was placed inside an ATS Series 3210 furnace (Applied Test Systems, Butler, Pennsylvania, USA) and controlled by an ATS Type-K temperature control system. After completion of the experiments, the gas was filled in the gas-liquid separator and finally collected in gas sampling Tedlar® bags (Environmental Sampling Supply, San Leandro, California, USA).

SCWG of timothy grass was performed at a pressure range of 23–25 MPa to investigate the impacts of temperature (450–650 °C), biomass-to-water or BTW ratio (1:4 and 1:8) and reaction time (15–45 min). Two BTW feed ratios were studied, especially 1:4 (2.3 g dry biomass with 9 cm^3 deionized water) and 1:8 (1.1 g dry biomass with 9 cm^3 deionized water). For catalytic SCWG experiments, carbonate salts (e.g., Na_2CO_3 and K_2CO_3) and hydroxide salts (e.g., NaOH and KOH) were employed at mass fractions of 1–3%. The catalysts were purchased from Sigma-Aldrich Canada Co., Oakville, Ontario, Canada. All the experiments were performed in triplicates with standard error < 3%.

2.3. Gas chromatography

The gases were analyzed in an Agilent 7820A gas chromatography (GC) system (Agilent Technologies, Santa Clara, California, USA). The GC was equipped with a thermal conductivity detector having three packed columns and one capillary column. The Ultimetal HayesepQ T 80/100 mesh column identified H_2, CO and CH_4, whereas the Ultimetal Hayesep T 80/100 mesh column quantified CO_2 and C_2H_6. Argon was used as the carrier gas with the column temperature of 60 °C. Agilent OpenLAB CDS ChemStation software was used to quantify the individual gases.

The individual gas yield was determined as the moles of each gas per gram of timothy grass. The total gas yield was calculated as the moles of total gas products collected per gram of timothy grass. Carbon gasification efficiency or CGE was estimated as the total moles of carbon in the gas phase per total moles of carbon in timothy grass (equation (1)). The lower heating value or LHV of the gas product was estimated using the compositions of H_2, CO, CH_4 and C_2H_6 (equation (2)).