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Hydrogen production from lignin, cellulose and waste biomass via supercritical water gasification: Catalyst activity and process optimization study

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ABSTRACT

Process optimization for catalytic biomass supercritical water gasification process (SCWG) was performed. By catalysts screening using cellulose and lignin as biomass model compounds, K_2CO_3 and 20Ni—0.36Ce/Al_2O_3 were identified as the best catalysts. Then, an optimization study based on Taguchi experimental design was conducted, and waste biomass including wheat straw, canola meal, and timothy grass were used as feedstock. The effect of different parameters are studied. For these parameters, the order of relative importance for hydrogen production is: temperature > catalyst loading > catalyst type > biomass type. High temperature (~650 °C), and high catalyst loading (~100%) are favorable for hydrogen production. The average hydrogen yield using different waste biomass was in the order of: canola meal > wheat straw > timothy grass.

1. Introduction

Global environment and energy concerns – raised by the usage and potential depletion of fossil fuels drive the research on hydrogen production as a clean energy source [1]. Production of hydrogen from biomass could perfectly bridge the gap between the current fossil fuel based strategy and the practical water splitting in future [2]. Supercritical water gasification (SCWG) refers to gasification with the presence of supercritical water (SCW), which is obtained at pressures above 22.1 MPa and temperatures above 374 °C. SCWG is considered as a key technology for directly converting wet biomass into a pressurized and clean gas with high hydrogen content [3].

Catalysis is important for hydrogen production from SCWG. Specifically, without catalysts, reactions in SCWG suffer from high activation energy. On the contrary, use of catalysts can potentially achieve promising conversion of biomass at lower temperature, which is crucial for reducing the cost of this process [4]. Both hetero/homogenous catalysts have been tested in SCWG in previous studies. For the homogenous category, catalytic effects of alkaline salts such as K_2CO_3, Na_2CO_3, $KHCO_3$, and NaOH have been evaluated for subcritical and supercritical water gasification [4]. The mechanism of hydrogen production using alkali salts as catalysts involving production of simpler intermediates which could be easily converted to hydrogen. Also, via absorption of produced carbon dioxide, alkali catalysts could also enhance the water–gas shift reaction to generate hydrogen [5]. In terms of heterogeneous catalysts, both Ni and Ru based catalysts were proved to be effective for SCWG [4,6]. The main route for hydrogen production from these catalysts is through the steam reforming reactions of different hydrocarbons [5]. The promising activity of Ni–Ru bimetallic catalysts for SCWG of indole was reported in a recent published work [7]. The main advantage of Ru based catalyst is its high activity whereas Ni based catalyst is favorable because of the low cost and considerable activity.

In literature, different biomass model compounds were used as feedstocks for SCWG to understand the process. Also, technology for hydrogen production from real waste biomass via SCWG process is under development [8]. In our previous studies, lignin was used as a model biomass to optimize the reaction parameters for a batch type SCW reactor, and the screening/modification of various Ni based catalysts was conducted. As the first step, parameters for non-catalytic SCWG of lignin, three parameters including temperature, pressure, and water to biomass ratio was optimized using Central Composite Design (CCD) with parameters varied in the range of 400–650 °C, 23–29 MPa, and 3–8, respectively. It was found that up to 650 °C, higher temperature is desirable for hydrogen production; however, change of pressure did not show significant effect [9]. Similar effect of temperature was observed on the

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SCWG of marine biomass, where the increase in temperature from 300 to 600 °C improved the hydrogen yield [10]. Then, for catalytic SCWG of lignin, under the operation conditions of 650 °C, 26 MPa and water to biomass mass ratio of five, it was observed that: using different supports, the activity of Ni-based catalysts were in the order of Al_2O_3 > TiO_2 > AC > ZrO_2 > MgO. Regarding promoters, the activity of the catalysts were in the order of Ce > Co > Cu [11].

Generally, studies based on model biomass provide more fundamental information about the process whereas studies on real biomass provides more information on the performance of the SCWG reactors at various operating conditions [12]. The objective of this study is to further understand the effects for reaction parameters in the catalytic SCWG process, and optimize the process operating conditions.

Based on the literature, several gaps need to be filled: first, the performances of promising catalysts identified in the literature need to be compared under identical reaction conditions; also, the performances of catalysts should be evaluated for real biomass rather than model biomass; what's more, the optimization of the process parameters is critical to determine the favorable process conditions to achieve maximum hydrogen production. To fill the knowledge gaps, we present the results from SCWG test of different catalysts, catalyst characterization, biomass characterization, and parameter optimization study of hydrogen yield using Taguchi approach.

One contribution of this work is its comprehensiveness by the wide coverage of biomass materials. Specifically, for the catalyst comparison, lignin and cellulose are used as feedstock. Lignin and cellulose are two main components of biomass, yet, in plant body they have different functions. Specifically, cellulose functions as the dominant reinforcing phase in plant structures [13], whereas lignin fills the spaces between cellulose and hemicellulose, and functions resin to hold the lignocellulose matrix together [14]. Therefore, the effects of the structural difference between them on the catalyst performance provide more insight knowledge for application of each catalyst for real biomass. In addition, for the optimization study, three types of waste biomass such as canola meal (CM), wheat straw (WS), and timothy grass (TG) were used. Wheat straw and timothy grass are all abundant biomass in the province of Saskatchewan. Canola meal is the by-product of biodiesel industry and is generally used for animal feed, however, the issue of oversupply drive the need to utilize canola meal as renewable energy source [15]. To the best of our knowledge, the effects of timothy grass and canola meal for hydrogen production via SCWG were studied first time. Also, the characterization data presented in this paper provides better insight into the role of different biomass in the process, and the information would also be valuable for researcher with different research interests.

As another novelty, Taguchi experimental design is applied for the first time for optimization of the SCWG process. Taguchi experimental design is a classic experimental design method dedicated to optimization of process performance, quality and minimize its cost [16]. In recent years, application of Taguchi method has been introduced into many research fields, such as chemical engineering, and thermal engineering [17]. The method involves use of Taguchi orthogonal array (OA), which is developed based on factorial design [18]. The use of orthogonal array enables researcher to optimize process parameters with a minimum number of experiments [19]. Also, Taguchi method effectively maintains the statistical accuracy of the experiments [20]. Specifically, statistical analysis of the data including analysis of variance (ANOVA) as well as effects of parameters/interactions provide information about statistical significance of different parameters/interactions and helps to determine optimum combination of reaction parameters [21]. In addition, the application of the Taguchi method enables the evaluation of relative importance of different reaction parameters.

The work presented in this paper is also significant due to the wide range of catalysts used. First, the effect of different methods including impregnation and coprecipitation, on the performance of Ni—Ce/Al_2O_3 are reported for the first time. In addition, this paper reports results from SCWG tests of various homo/heterogeneous catalysts combined with data from systematic characterizations of both catalysts and biomass samples. Information in this paper should be helpful to explore the mechanism of each catalyst function for gasification of biomass model compounds and real biomass under supercritical water condition.

2. Materials and method

2.1. Catalyst preparation

Catalysts tested in this study were prepared by impregnation (Imp.) or coprecipitation (Cop.) method. Precursors used for the preparation including $Ni(NO_3)_2{\cdot}6H_2O$, $CeCl_3{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$ were supplied by Sigma Aldrich (Oakville, Canada). Ruthenium (III) nitrosylnitrate was supplied by Alpha Aser (Ward Hill, USA). Catalyst supports such as Al_2O_3 and TiO_2 in pellet form both were supplied by Alpha Aesar (Ward Hill, USA).

Before preparation, the amount of precursors used were calculated based on the composition of the catalyst. For the impregnation, the precursor was dissolved in water. Then, a 1-mL syringe was used to impregnate the solution into the support. Before calcination, the catalyst was dried in an oven at 105 °C for 8 h. The catalyst was then calcined in flowing air at 650 °C for 6 h. The coprecipitation (marked as Cop. with their name) method was employed for precipitating Ni, Ce and Al in their nitrate solution with aqueous ammonia. After filtration, the precipitate was washed and dried and calcined under the same condition with the impregnated catalysts.

2.2. Material, SCW reactor, and procedure for SCWG tests

Model biomass sample including lignin and cellulose were purchased from Sigma Aldrich (Oakville, ON, Canada). Waste biomass samples used were canola meal, wheat straw, and timothy grass. Canola meal was provided by Milligan Biofuels Inc. (Foam Lake, SK, CANADA). Wheat straw and timothy grass were all collected from a local farm (Saskatoon, SK, Canada). The compressed nitrogen gas (N_2) with high purity (>99.9%) was purchased from Praxair Canada Inc. (Saskatoon, SK, Canada).

The batch-type SCW reactor was made from 316 stainless steel. Detailed specifications and schematics of the tubular batch SCW reactor could be found in our previous work [9]. For the screening tests, operating conditions were all kept at 650 °C, and at 26 MPa with a water to biomass mass ratio of five.

For each catalytic SCWG test, 0.65 g biomass sample and calculated amount of catalyst were loaded in the reactor together with distilled water, the reactor was then sealed followed by the leak test before the experiment. After removal of air by using a vacuum pump, the reactor was purged with N_2 to a certain initial pressure to reach the final pressure of 26 MPa. During the run, the reactor was heated by an electrical furnace with a fixed heating rate of 30 °C/min to 650 °C and 50 min residence time (including the time used for reactor heating up and reaction time at the desired temperature). The temperature was controlled by a temperature controller and monitored/calibrated by a K type thermocouple.

For product separation and collection, detailed descriptions are given in our previous work [11]. Briefly, the gas phase products were released to the condenser and collected using a Tedlar bag. The liquid and solid products were collected from the reactor by rinsing with distilled water and HPLC grade acetone into clean