Available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/ijhydene

Catalytic hydrothermal gasification of cellulose and glucose

Zhen Fang[a,*], *Tomoaki Minowa*[b], *Chun Fang*[c], *Richard L. Smith, Jr*[d], *Hiroshi Inomata*[d], *Janusz A. Kozinski*[e]

[a]*Biomass Group, Xishuangbanna Tropical Botanical Garden, Chinese Academy of Sciences, 88 Xuefulu, Kunming, Yunnan province 650223, China*
[b]*Biomass Technology Research Center, National Institute of Advanced Industrial Science and Technology, 2-2-2 Hiro Suehiro, Kure, Hiroshima 737-0197, Japan*
[c]*AgWeatherNet Program, Washington State University, 24106 N Bunn Rd, Prosser, WA 99350, USA*
[d]*Department of Chemical Engineering, Research Center of Supercritical Fluid Technology, Tohoku University, Aoba-ku Aramaki Aza Aoba-04, Sendai 980-8579, Japan*
[e]*Department of Chemical Engineering, University of Saskatchewan, 57 Campus Drive, Saskatoon, Sask., Canada S7N 5A9*

ARTICLE INFO

Article history:
Received 28 May 2007
Received in revised form
26 September 2007
Accepted 28 November 2007
Available online 9 January 2008

Keywords:
Hydrothermal
Hydrogen
Cellulose
Glucose
Sub-and supercritical water
Gasification
Catalyst

ABSTRACT

An optical micro-reactor (50 nL), an autoclave (120 mL), and a flow reactor (11.3 mL) were used to study the catalytic hydrothermal gasification of cellulose and glucose. In the micro-reactor experiments, Ni catalyst had a low gasification rate, but 96 wt% rate (35 mol% H_2) was achieved in the autoclave when Ni/silica–alumina and cellulose were mixed well during slow heating to 350 °C (30 min). It was found from the micro-reactor that cellulose completely dissolved in water at 318 °C upon fast heating, and that Pt was the most active catalyst for glucose reactions. Gasification of glucose with Pt/γ-alumina catalyst was examined in flow experiments, where it was found that 67 wt% gasification rate (with up to 44 mol% H_2) could be obtained at 360 °C and 30 MPa.

1. Introduction

Water at a temperature and pressure that is near its critical point (CP; 374 °C, 22.1 MPa) is commonly referred to as hydrothermal water (HTW), which includes sub-critical water (SubW < CP) and supercritical water (SCW > CP). HTW behaves as a weakly polar solvent with both acidic and basic characters [1,2], and has the ability to hydrolyze and dissolve biomass. HTW can provide a homogeneous phase for biomass conversions [3,4]. Therefore, HTW has been used widely to gasify many different constituents of biomass, such as glucose [5–12], cellulose [4,6,10–15], lignin [12,14–17], organic wastes [12,14,18,19], starch [11,20,21] as well as actual biomass [10,21–25] without or with catalysts (e.g., ZrO_2, NaOH, KOH, Ni, Pt, CeO_2, Pd, RuO_2, Ru, $KHCO_3$ [4,6,9,10,12,14–17,19,20,25]). The following reactions can be considered to occur in HTW:

$$\text{Cellulose:}\quad (C_6H_{10}O_5)_n + nH_2O \rightarrow nC_6H_{12}O_6, \tag{1}$$

$$\text{Glucose:}\quad C_6H_{12}O_6 \rightarrow 6H_2 + 6CO, \tag{2}$$

$$\text{Water-gas shift (WGS):}\quad CO + H_2O \rightarrow H_2 + CO_2, \tag{3}$$

$$\text{Overall:}\quad (C_6H_{10}O_5)_n + 7nH_2O \rightarrow 12nH_2 + 6nCO_2. \tag{4}$$

*Corresponding author. Tel.: +86 871 5163360; fax: +86 871 5160916.
E-mail address: zhenfang@xtbg.ac.cn (Z. Fang).

0360-3199/$ - see front matter
doi:10.1016/j.ijhydene.2007.11.023

According to Eqs. (1)–(4), theoretically, the gas produced from cellulose or glucose gasification can contain up to 66.7 mol% H_2. At moderately high temperatures (550−600 °C) and short reaction times in flow reactors, glucose can be 100% gasified with activated carbon or KOH catalyst with gas containing up to 60 mol% H_2 [5,7,19]. At lower temperatures (400−450 °C) and longer reaction times in batch reactors, 97% cellulose and 7.9% lignin can be gasified with RuO_2 (450 °C and 2 h) [14]. When Ru is used, 100% lignin can be gasified (400 °C and 3 h) [12]. In the batch gasification of cellulose with Ni (30 min), the gasification rate is very differently with 18% being obtained at 374 °C [23] and 84% being obtained at 350 °C [26].

Even though gasification technology is effective, little data concerning phase behavior of biomass decomposition with and without catalysts have been reported. Differences in the various cellulose gasification rates could be due to the phase behaviors or competing reaction kinetics that are controlled by mass transfer limitations. In this sense, a homogeneous reaction environment can be thought of as being advantageous for continuous chemical processing of water-insoluble biomass feedstocks. A homogeneous fluid can be obtained by flash-pyrolysis of biomass (wood), and subsequently reforming of the pyrolysis condensate in SCW to produce H_2 [27], which is a two-step (pyrolysis and hydrothermal) gasification process.

The purpose of this work is to produce H_2 rich gas from biomass in both batch and flow reactors. Cellulose and glucose were studied in a one-step hydrothermal process up to 400 °C with and without catalysts (Ni, Ru, and Pt). Three types of reactors were used: (i) a 50-nL optical micro-reactor, diamond anvil cell (DAC), (ii) a batch reactor (autoclave, 120 mL), and (iii) a flow reactor (11.3 mL). Catalyst activities, reactions, phase behaviors, and conditions for solubilizing cellulose were visually observed in the DAC during heating the {biomass/catalyst + water} system up to the supercritical region. These results were used to gasify glucose and cellulose in the autoclave (batch process) and in the flow reactor (continuous process).

2. Materials

Cellulose (microcrystalline powder; ~20 μm, 99.0% purity, DP = 229; Aldrich, Milwaukee, WI) and glucose (particles; >99.0% purity; Fluka, BioChemika) were used as representative biomass constituents. Aqueous solutions of 0.1- and 0.9-M glucose were made for the experiments in the DAC and flow reactor. Ni (powder; ~3 μm, 99.7% purity; Aldrich), Ru (sponge; ~20 mesh, 99.95% purity; Alfa Aesar, Ward Hill, MA) and Pt (1% Pt on γ-alumina powder; ~100 μm, Alfa Aesar) were used as the gasification catalysts in the DAC experiments. Ni catalyst used in the autoclave was prepared by crushing a commercial catalyst (Engelhard, NI-3288, ca. 50 wt% nickel on silica–alumina) to 60–200 mesh and treating it in a reducing atmosphere at 350 °C for 4 h. Pt pellets (0.5% Pt on $\frac{1}{8}$ in alumina pellets, AlfaAesar) were used as catalyst in the flow reactor.

3. Experimental approach

3.1. Reaction in DAC

An optical micro-reactor, Bassett-type [28] hydrothermal DAC was used for visual observations of {biomass + H_2O + catalyst} systems during heating process. The experimental setup and procedures are similar to our previously published works [4,29–32]. The reaction chamber (ca. 50 nL) consisted of a hole (500-μm i.d.) in an inconel gasket (250-μm thickness) and sealed by compression of two opposing diamond anvils. The micro-chamber was heated easily at slow and fast rates (0.1 to 20 °C/s) by two electric micro-heaters and can simulate reactions in batch and flow reactors at slow and fast heating rates. Temperature of the system was measured and recorded by a data acquisition unit (Strawberry Tree, Model DS-12-8-TC, Sunnyvale, CA). Water density (ρ) was adjusted by changing the size of argon gas bubbles introducing into the chamber and was calculated from the homogenization temperature (T_h), at which gas bubbles disappeared when heated.

Mixtures of {biomass + H_2O + catalyst} in the chamber were heated and observed under 110× magnification with a stereomicroscope (Olympus SZ11) with the images being recorded by a Panasonic 3-CCD camera (AW-E300). After completion of each experiment, the residues deposited on the lower and upper diamond anvils were analyzed by FT-IR microscopy (UMA 500, Bio-Rad, Cambridge, MA).

3.2. Gasification in an autoclave

Owing to micro-volume of the DAC, only microscopy techniques can be used to analyze products. Larger reactor is needed to get enough products for detailed analyses. A 120-mL autoclave (18-mL head space) was used to gasify cellulose. Cellulose (5 g), water (30 mL) and Ni catalyst (2 g) were loaded in the reactor. After being sealed, the autoclave with initial 3-MPa N_2 pressure was heated to 200−350 °C (4.3–16.5 MPa) at a heating rate of 0.18 °C/s and stirred by a magnetic stirrer. After reaching the desired temperature and holding time (0, 30 min, 1 h), the autoclave was cooled by cutting the electrical power. The gas volume was measured using a gas meter (Shinagawa-sheiki, W-NK-0.5B), and its composition was analyzed by gas chromatography (Shimadzu, GC-12A-TCD or GC-9A-FID). The reaction mixture was separated into three phases: (i) aqueous phase, (ii) oil phase (acetone-soluble), and (iii) water-insoluble fraction (residue). The aqueous phase was analyzed for total organic carbon (TOC) with a Yanaco TOC-8L analyzer and for glucose with a Shimadzu UV-160A absorption spectrometer. After freeze-drying, sugars in the aqueous phase (their trimethylsilyl derivatives) were analyzed with a GC (Hewlett-Packard, 5890A; CBP-10 column). Organic elements (C, H) of the oil and residue were analyzed by an elemental analyzer (AMCO NA-1500).

3.3. Gasification in the flow reactor

Continuous flow reactors are important for commercial applications of hydrothermal gasification technology. Stirred tank, transpiring wall, and tubular flow reactors operating under hydrothermal and supercritical conditions have been reported in the literature [33,34]. In this work, we used a tubular flow reactor to check practical aspects and operation. The flow reactor used here was made of a $\frac{3}{8}$-inch 316-SS tube (11.3 mL; 400-mm length and 6.01-mm i.d.) loaded with 5-g Pt/Al_2O_3 pellets, which was heated by an electric tube furnace (F21100, Fisher) up to 400 °C. A high-pressure liquid chromatography pump (Model 510, Waters Associates, Milford, MA) was used to feed the prepared 0.1-M glucose solution. The solution was preheated in a $\frac{1}{16}$-inch 316-SS tube to 100 °C in 20 s and before being fed into the reactor. The reaction temperature (100–400 °C)in the center of the reactor tube, exit temperature at the end of the reactor and the preheated temperature were measured by K-type thermocouples (TJ36-Cain-116G-12, Omega). The pressure was controlled by a back-pressure regulator (Model: 54-2162D26, Tescom, MN) at 10–30 MPa. After leaving the reactor, effluent was rapidly quenched with a cooling water jacket to terminate the reaction. After reaction, products of three phases (gas, aqueous, and oil) were collected, separated, and analyzed as described similar to the above autoclave section.

4. Results and discussion

Three series of experiments have been conducted. The first series was carried out in the DAC. It focused on visual observations, activities of catalysts, phase behaviors, conditions for re-polymerization of glucose (residue formation) as well as complete dissolution of cellulose. These results were further used to gasify biomass to H_2 rich gas in batch (autoclave) and flow reactors. In the second series of experiments, gasification rates of insoluble cellulose with Ni catalyst were studied at low temperatures (⩽350 °C) and long reaction times (up to 1 h) in the autoclave. However, this batch-type process is not practical for commercial applications. Therefore, the third series of experiments were conducted in the flow reactor in order to produce H_2 continuously in short reaction times (e.g., 1 min). In the DAC, two types of phase behavior experiments were conducted: (i) slow heating rates (0.18 °C/s) (tests 1–2) and (ii) fast heating rates (9.5–14.5 °C/s) (tests 3–6) (Table 1). In the autoclave, two types of experiments were performed at the temperature and pressure conditions ranging from (200 °C, 4.3 MPa) to (350 °C, 16.5 MPa): (i) non-catalytic decomposition of cellulose and (ii) gasification of cellulose with Ni. In the flow reactor, a series of experiments was performed for continuous gasification of glucose with Pt from 100 to 400 °C.

Visual experimental conditions in the DAC are summarized in Table 1 (tests 1–6). Visual observations of the reactive phase behavior of cellulose and glucose are given in Fig. 1 (for slow heating tests 1–2), and Figs. 2–5 (for fast heating tests 3–6), respectively. Images and FT-IR spectra of the residues on lower and upper anvils are given in Figs. 6–8. Figs. 9–10 give carbon yields (%) for the four phase products (gas, oil, aqueous, and residue) from the cellulose decomposition in the autoclave without and with Ni catalyst. Carbon balances reported are based on the four phases. The gas compositions from both autoclave (Ni) and flow (Pt) gasification are given in Fig. 11. In the continuous Pt gasification of 0.1-M glucose, concentrations of glucose and TOC are given in Figs. 12 and 13, respectively. Results are discussed in detail in the below sections.

4.1. *Slow heating experiments*

Slow heating are widely used in batch processes. Biomass was catalytically gasified in HTW by slow heating (0.18 °C/s) to the reaction temperatures between 200 and 350 °C from room temperature. Total heating time to 350 °C was about 30 min. Ni was used as the catalyst because it has been shown to be effective for reforming biomass to hydrogen [26,35,36]. The DAC images are shown below.

4.1.1. *Visual observations (tests 1–2) with DAC*

In test 1, {cellulose + Ni + H_2O} with an argon gas bubble (Fig. 1A, a) was heated to 350 °C. Cellulose became yellow and transparent at 287 °C (Fig. 1A, b) and then dissolved at 293 °C maximum dissolution was reached at 320 °C (Fig. 1A, c and d). As temperature increased further to 350 °C, little change occurred for the non-dissolved cellulose (Fig. 1A, d and e).

Table 1 – Summary of experimental conditions in the diamond anvil cell

Experiments	Slow heating (0.18 °C/s)		Fast heating (9.5–14.5 °C/s)			
	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6
Sample	Cellulose	Glucose	Cellulose	Glucose	Glucose	Glucose
Catalyst	Ni	Ni	None	Ni	Ru	Pt
Conditions						
Max. T (T_{max}, °C)	350	350	319	400	400	400
Density of water at T_h (kg/m^3)	945	837	808	799	675	660
Average heating rate (°C/s)	0.18	0.18	11.1	9.5	14.4	14.5
T_h (homogenization T, °C)	118	223	244	250	317	323
Run time (s)[a]	1782	1811	26.5	39.0	26.0	26.0

[a] Heating time to the maximum temperature.

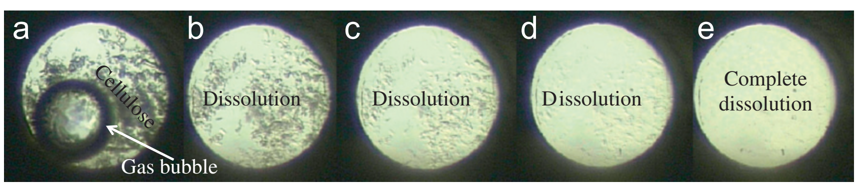
A

0 s, 25 °C 1456.8 s, 287 °C 1536.0 s, 300 °C 1658.0 s, 320 °C 1781.5s, T_{max} = 350 °C

B

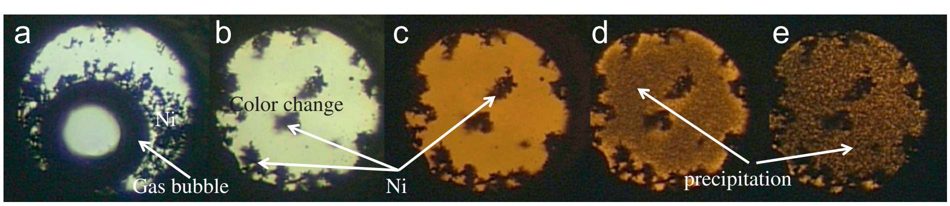
1068 s, T_h = 223 °C 1423.5 s, 280 °C 1522.0 s, 300 °C 1622.5 s, 320 °C 1810.0s, T_{max} = 350 °C

Fig. 1 – Visual observation of biomass for slow heating tests (Table 1; heating rate = 0.18 °C/s): (A) test 1: {cellulose + Ni + H_2O}, T_h = 118 °C, ρ = 945 kg/m^3; (B) test 2: {glucose + Ni + H_2O}, T_h = 223 °C, ρ = 837 kg/m^3.



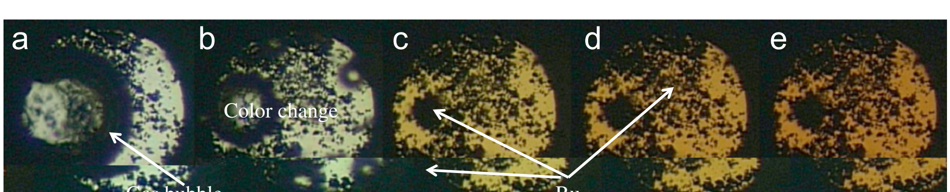
0 s, 25 °C 24.4 s, 309 °C 25.1 s, 314 °C 25.5 s, 316 °C 26.1 s, 318 °C

Fig. 2 – Visual observation of cellulose complete dissolution in water for fast heating test 3 (Table 1): heating rate = 11.1 °C/s, T_h = 244 °C, ρ = 808 kg/m^3.



0 s, 25 °C 19.7 s, 280 °C 25.0 s, 320 °C 29.7 s, 350 °C 38.4s, T_{max} = 400 °C

Fig. 3 – Visual observation of {glucose + Ni + H_2O} for fast heating test 4 (Table 1): heating rate = 9.5 °C/s, T_h = 250 °C, ρ = 799 kg/m^3.



0 s, 25 °C 14.0 s, 280 °C 17.6 s, 320 °C 20.1 s, 350 °C 26.0s, T_{max} = 400 °C

Fig. 4 – Visual observation of {glucose + Ru + H_2O} for fast heating test 5 (Table 1): heating rate = 14.4 °C/s, T_h = 317 °C, ρ = 675 kg/m^3.