



Hydrogen and methane selectivity during alkaline supercritical water gasification of biomass with ruthenium-alumina catalyst

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ABSTRACT

Ruthenium supported on alpha-alumina spheres has been employed as a catalyst for the gasification of glucose and other biomass-related samples in supercritical water at 550 °C, 36 MPa, in a batch Inconel reactor. Most of the reactions were conducted in the presence of alkaline additives particularly sodium hydroxide and calcium oxide (hydroxide). In general, over 96% carbon gasification efficiencies (CGE) were achieved in the presence of Ru/Al₂O₃, while hydrogen gasification efficiencies (HGE) based on result-derived reaction stoichiometries reached 87% for glucose. Both HGE and CGE approached 100% for the sodium carboxylates. Without alkaline additives, Ru/Al₂O₃ converted glucose into gas product with average yields of 10.8 mol hydrogen/(kg of glucose), 8.6 mol methane/(kg of glucose) and 17 mol carbon dioxide/(kg of glucose), while carbon monoxide and C₂–C₄ hydrocarbons made up only 1 mol/(kg of glucose). However, when the ruthenium catalyst was used in combination with sodium hydroxide and calcium hydroxide, the selectivity towards hydrogen gas increased, with the complete removal of carbon dioxide. Similar yields of hydrogen (14.7 mol/kg of glucose) and methane (12.8 mol/kg of glucose) were obtained with CaO and Ru/Al₂O₃. Reactions of sodium carboxylates (formate and acetate) suggested that the ruthenium catalyst was capable of catalyzing the Sabatier reversible reaction in both the forward and backward directions. The yield of each gas was found to be dependent on the concentrations of methane, hydrogen and carbon dioxide in the reactor.

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1. Introduction

Biomass represents a natural store of energy, which can be harnessed in different forms for different uses. Large scale biomass use for energy production has many advantages particularly in view of depleting fossil resources and tackling climate change. In this regard, the conversion of biomass to energy carriers has become a topical research area. Thermochemical biomass conversion processes include well-established conventional technologies such as pyrolysis, gasification, liquefaction and incineration. In addition to these, hydrothermal gasification of biomass has become an active research topic over the last few years. The main components of the gas product from hydrothermal gasification of biomass include hydrogen, methane and carbon dioxide and some carbon monoxide [1–5]. This has been largely supported by the potential of hydrogen fuel gas as the world's cleanest energy carrier. Hence, hydrothermal gasification has focused mainly on hydrogen gas production. However, chemical energy storage and utilization in the form of methane is often seen as more commercially attractive

than hydrogen. Methane produced from renewable biomass would be readily fed into the existing infrastructure. Thermochemical production of methane involves a fast process, with consequent high conversion rates [6], compared to anaerobic digestion. Therefore, hydrothermal gasification of biomass to produce a syngas composed mainly of methane and hydrogen can become an important component of the world's future energy portfolio.

Synthetic natural gas (SNG) production via hydrothermal gasification (HTG) often involves the use of metal catalysts such as nickel and ruthenium; supported on alumina or silica [7–10]. Ruthenium and nickel catalysts have been widely used for methane production via the hydrogenation of carbon dioxide and/or carbon monoxide. Waldner and Vogel [11] reported the production of synthetic natural gas (SNG) from woody biomass by a catalytic hydrothermal process using a laboratory batch reactor suitable for high feed concentrations (10–30 wt %). Their work carried out at 300–410 °C and 12–34 MPa with a Raney nickel catalyst, produced a maximum methane yield of 0.33 (g of CH₄)/(g of wood), which corresponded to the thermodynamic equilibrium yield. They achieved complete carbon gasification efficiency over an extended reaction time of about 90 min. Stucki et al. [12] reported that between 60–70% of the heating value of microalgae (*Spirulina platensis*) could be recovered as methane during HTG at 400 °C in the presence of

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ruthenium catalysts with a high overall conversion approaching 100%. More recently, Haiduc et al. [13] demonstrated the hydrothermal gasification of the microalgae *Phaeodactylum tricornutum* to a methane-rich gas at a temperature range of 400 °C and pressure of 30 MPa, using ruthenium catalysts. Carbon gasification efficiency was high (68–74%) and the combined yields of C₁–C₃ hydrocarbon was 0.2 g/g of dry feed. The biomass-released sulfur was shown to adversely affect the Ru/C catalyst performance. Azadi et al. [14] reported that Raney-nickel catalyst produced about 13 mmol of gas per gram of glucose at 350 °C. The composition of the gas product was; 69 mol% carbon dioxide; 23 mol% hydrogen and 8.5 mol% methane, at 350 °C and a pressure of 6.2 MPa. Recently, Azadi et al. [15] also demonstrated the positive effects of the addition of alkali promoters to alpha-alumina-supported nickel catalyst at 380 °C during the catalytic gasification of a 2 wt% glucose solution. Under experimental conditions of the study, about 55 mol of gas was produced per kg of glucose, with carbon and hydrogen gasification efficiencies of 99% and 127% respectively.

In several publications, the present authors [16–18] and others, for example, Kruse et al. [19] and Sinag et al. [20] have shown that the addition of alkaline compounds during hydrothermal processing of biomass leads to favourable degradation of carbohydrate-rich biomass into gasifiable intermediates. In particular, the authors found that addition of sodium hydroxide and potassium hydroxide led to the formation of gasifiable simple alkali-metal carboxylates. Potentially, hydrogen/methane ratios of 5:1 could be achieved in the gasification of carbohydrate biomass in the presence of sodium hydroxide at a ratio of 1 g glucose per 1.2 g of sodium hydroxide. No carbon dioxide is found in the gas phase, as this is removed as soluble sodium carbonate [18]. The high concentration of alkali, though beneficial for high-purity hydrogen production, can significantly affect the cost of the gasification process. A reduction in the amount of alkaline additives or the use of cheaper compounds such as calcium oxide and calcium hydroxide coupled with the use of stable metal catalysts may lower the cost of this process.

The chemistry of hydrogen production from hydrothermal biomass gasification appears to depend mainly on the water-gas shift reaction. Methane formation during alkaline hydrothermal gasification has been found to mainly depend on the decomposition reaction of metal acetates [16,21,22]. In non-alkaline hydrothermal environments, methane formation has been found to occur via methanation reactions in the presence of some supported metal catalysts [7,8].

In this work, the effect of a ruthenium/alumina catalyst has been studied during the alkaline gasification of some biomass samples and biomass model compounds. The alkaline additives used include sodium hydroxide, calcium hydroxide and calcium oxide. The effect of the catalyst on the hydrothermal reactions of sodium formate and sodium acetate was also studied. In each case, the composition analyses of the gas products have been carried out and used to explain the effect of the catalyst on the main gas components present. In addition, the stability of the ruthenium catalyst was examined.

2. Experimental

2.1. Materials

Glucose, cellulose, xylan, sodium acetate and sodium formate, sodium hydroxide, sodium carbonate, calcium hydroxide were all purchased from Sigma-Aldrich, UK. The CHNS-O analysis of the sawdust gave the following compositions; carbon, 48.3 wt%; hydrogen, 5.67 wt%; oxygen, 44.3 wt% and sulphur, 0.73 wt%. Ruthenium-alpha alumina catalyst was supplied by Catal Limited,

a UK-based SME and used as received. The nominal loading of ruthenium impregnated on 2–4 mm diameter alumina spheres was 5 wt%. The catalyst has a specific surface area of 21 m² g⁻¹ and an average pore size of 1.5 μm. The reactor used was a 75 ml batch Inconel reactor obtained from Parr Inc. U.S.A. Details of the reactor have been provided in several previous publications [17,18].

2.2. Procedure

In each case, 1.0 g of feed material (glucose, cellulose, xylan, sodium acetate or sodium formate) was loaded into the reactor containing 20 ml of distilled water. Where required, a known weight of alkaline compound (sodium hydroxide, calcium hydroxide or calcium oxide) was then added and mixed with the biomass and water in the reactor. To compare the effects of the alkaline compounds on the gasification tests, 1.20 g each of sodium hydroxide and calcium oxide, corresponding to 1.50 M NaOH and 1.07 M CaO, were used in separate alkaline gasification tests. In addition, since CaO would be transformed to Ca(OH)₂ on addition to water, one test was performed using 1.07 M Ca(OH)₂. The lower molar concentrations of Ca(OH)₂ and CaO used here was due to the consideration that both calcium compounds would form insoluble calcium carbonate by reacting with carbon dioxide in the gas products, thereby leading to reactor plugging and other complications. For tests involving ruthenium-alumina (Ru/Al₂O₃) catalyst, 1.0 g of the catalyst was placed in a wire mesh suspended inside the reactor. The reactor was closed, purged with nitrogen gas for 5 minutes and sealed. The reactor was heated quickly at a rate of 30 °C min⁻¹ up to 550 °C, such that the reaction temperature was reached after just 18 minutes; giving corresponding pressures of between 36 and 40 MPa. Once the designated temperature was reached, the reaction was allowed to stabilize for 10 minutes, after which the reactor was withdrawn from the heater and cooled rapidly with compressed air.

2.3. Gas analyses

Once cooled to room temperature, the pressure and temperature readings were noted prior to sampling the gas for analysis. The analytical equipment and procedure used for gas analysis have been previously reported in details [18,23]. The compositions of the gas products were obtained in mole percent and used to calculate the yields of the components.

2.4. Liquid analyses

The liquid effluents were analyzed for total organic carbon (TOC) and inorganic carbon (IC) which was used to indicate the extent of conversion of the feed materials during the hydrothermal gasification process. The instrument used was a Hach-Lange IL550 TOC-TN analyzer fitted with two NDIR held at 800 °C. The instrument was operated in the differential TOC determination mode, in which the same sample was analyzed consecutively for total carbon (TC) and total inorganic carbon (TIC). The difference between the TC and TIC was recorded as TOC. The analyzer was set up to make four determinations ($n = 4$) on each sample and the average results used. Typical standard deviation of replicate determinations ranged from 0.2 to 2%.

2.5. Solid analyses

In experiments, where calcium oxide was used, the formation of insoluble calcium carbonate was observed. In these cases, the insoluble solids were obtained after filtration and dried in an oven to a constant weight. The solids were pulverized and analyzed on thermogravimetric analyzer to determine the inorganic carbon content. The instrument used was a Metler Toledo TGA/DSC 1 Star System.

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