



Research Paper

Investigating the applicability of Athabasca bitumen as a feedstock for hydrogen production through catalytic supercritical water gasification

Rachita Rana^a, Sonil Nanda^b, Janusz A. Kozinski^b, Ajay K. Dalai^{a,*}

^a Department of Chemical and Biological Engineering, University of Saskatchewan, Saskatoon, SK, Canada

^b Department of Earth and Space Science and Engineering, Lassonde School of Engineering, York University, Toronto, ON, Canada



ARTICLE INFO

Keywords:

Bitumen
Hydrogen
Supercritical water gasification
Catalyst
Process optimization

ABSTRACT

Supercritical water gasification has been a promising technique for hydrogen production using several lignocellulosic biomasses and organic wastes. Various organic wastes such as sewage sludge, lignocellulosic biomass, municipal solid waste, industrial effluents and cattle manure that have been used as feedstocks for supercritical water gasification. With the objective of hydrogen production from alternative and less explored resources, Canadian Athabasca bitumen was used as a feedstock for supercritical water gasification in this study. Bitumen was gasified in supercritical water to examine the impacts of temperature (550–700 °C), feedstock concentration (20–35 wt%) and reaction time (15–60 min) at the reactor pressure of 23 MPa. The improvements in hydrogen yields with the use of four different heterogeneous catalysts such as FeCl₃, ZnCl₂, Ni/Si-Al₂O₃ and Ru/Al₂O₃ at 5 wt% loading were targeted. Prior to gasification in a tubular batch reactor, bitumen was characterized for determining its ultimate composition (carbon-hydrogen-nitrogen-sulfur-oxygen, CHNSO analysis), surface organic functional groups (Fourier-transform infrared spectroscopy, FTIR) and devolatilization behavior (thermogravimetric analysis, TGA). In non-catalytic gasification, the highest hydrogen yields (2.26 mmol/g) and total gas yields (4.68 mmol/g) were obtained at 700 °C in 60 min of reaction time with 20 wt% feed concentration. 5 wt% ZnCl₂ enhanced the gasification rate with hydrogen yields up to 3.57 mmol/g. The overall catalyst activity towards maximizing hydrogen yields was in the order of ZnCl₂ > FeCl₃ > Ru/Al₂O₃ > Ni/Si-Al₂O₃. This study is an initial attempt to determine the candidacy of bitumen as a possible resource for hydrogen generation.

1. Introduction

Fossil fuels have been serving as the most preferred and prominent energy source to the world since the industrial revolution. There have been different forms of fuel such as sweet crude (or the conventional oil) and synthetic crude (or the unconventional oil) [1]. Depleting conventional oil reserves have proven an immediate need to explore unconventional sources of energy. These unconventional sources of energy are abundant to meet the growing energy needs. Among the various sources of unconventional crude, shale gas and bitumen are copiously present in North America. The Canadian oil sand reserves in Alberta are believed to be the third largest oil reserve in the world after Venezuela and Saudi Arabia. In 2016, the total reserves of oil in Alberta were about 165.4 billion barrels [2].

According to the Canadian Energy Research Institute, the Western

Canadian oil reserves can contribute close to \$1.5 trillion in federal and provincial revenues over the next 20 years [3]. It has become extremely essential to develop alternate technologies to generate energy from the domestic oil reserves in Canada. According to the International Energy Agency (IEA), the global demand for energy would escalate by 31% by 2040 due to the improved living standards of the people in the developing nations and the growth of the emerging nations [4].

Oil sands are found mostly in Venezuela, the U.S., Canada and Russia, but the Athabasca deposit in Alberta, Canada is the largest using the most advanced production processes [5]. Oil sand is usually a mixture of sand, water, clay minerals and bitumen. Bitumen is extracted from oil sands through techniques such as steam-assisted gravity drainage and hot water extraction. Bitumen is quite viscous and has American Petroleum Institute (API) gravity < 10, which necessitates its processing and upgrading to produce commercially useable fuels and

Abbreviations: API, American Petroleum Institute; CHNSO, Carbon-hydrogen-nitrogen-sulfur-oxygen; P_C, Critical pressure; T_C, Critical temperature; FID, Flame ionization detector; FTIR, Fourier-transform infrared spectroscopy; HHV, Higher heating value; K_w, Ion product value; LHV, Lower heating value; SCW, Supercritical water; SCWG, Supercritical water gasification; TCD, Thermal conductivity detector; TGA, Thermogravimetric analysis

* Corresponding author at: Department of Chemical and Biological Engineering, University of Saskatchewan, Saskatoon, Saskatchewan, S7N 5A9, Canada.

E-mail address: ajay.dalai@usask.ca (A.K. Dalai).

petroleum-based products. The extracted bitumen undergoes upgrading to produce synthetic crude oil as the end product. The production cost of oil in Canada (U.S. \$11.56/bbl) is the second highest after the U.K. (U.S. \$17.36/bbl) [6]. There are constant efforts towards bringing in new technologies for oil producers to make this treatment of bitumen efficient. Bitumen from the Athabasca region of Canada is a hydrocarbon mixture (~83%) with high sulfur content (~4%) and traces of nitrogen and oxygen [7]. The high sulfur content makes processing of bitumen-derived gas oil challenging.

There have been different approaches for the utilization of bitumen as a potential fuel. Karimi and Gray [8] studied the steam gasification of coke from oil sands bitumen at atmospheric pressure and 600–800 °C in the presence of catalysts (e.g., CaCO₃, CaO, MgO, Na₂CO₃, KCl and K₂CO₃). It was reported that the alkali metal catalysts showed better activity due to the higher mobility of the compounds within the coke phase. Karimi et al. [9] further studied the kinetics of catalytic steam gasification of bitumen coke and found that the portion of the catalyst that penetrated in the coke particles promoted the high reaction rates. Murugan et al. [10] studied the pyrolysis kinetics of Athabasca bitumen mixed with sands from different sources. It was found that the source of sand did not affect the pyrolysis of bitumen. However, the coke yields and activation energies were considerably impacted in the pyrolysis of pure bitumen when compared with bitumen-sand mixture. Wahyudiono et al. [11] studied the non-catalytic liquefaction of bitumen using the hydrothermal or solvothermal process as an efficient technology for upgrading bitumen to valuable chemicals. Stanlick et al. [12] studied the effect of mixing and vapor residence time on the thermal fluid cracking of bitumen in a mechanically fluidized bed reactor. Longer vapor residence times increased the conversion of vapors to gases, whereas shorter residence times improved liquid distribution and oil yield. Furthermore, distribution of liquid on coke particles reduced coke yield as a result of cracking.

Supercritical water gasification (SCWG) for hydrogen-rich syngas production is a striking technology that has proven its success for the conversion of lignocellulosic biomass and other organic compounds [13–17]. The thermo-physical properties of water change beyond its critical pressure ($P_C \sim 22$ MPa) and critical temperature ($T_C \sim 374$ °C). Liquid water transforms into a homogeneous fluid with its viscosity similar to gases and density similar to liquids [18]. Water in its supercritical state is an excellent solvent that enhances its mass transfer and solvation properties [19]. High mass transfer and thermal conduction rates, low dielectric constant and absolute miscibility of hydrocarbons are a few advantageous properties of supercritical water (SCW). The gas-like viscosity of water at supercritical conditions increases its diffusion coefficient and reaction rates. Furthermore, a pressure higher than the critical pressure of water enhances particle collision and the possibility of chemical reaction to occur within the reactants [20]. Operating conditions such as temperature, pressure, reaction time, feed concentration, catalyst loading and reactor geometry are a few factors that influence the gasification efficiency and product yields [21].

The application of supercritical water can be extended to the environmentally friendly conversion of bitumen to hydrogen appears promising. Considering the large reserves of bitumen in Canada, such a conversion technology that uses water as the medium for gasification can address several oil sand related issues such as environmental pollution, wastewater management and fuel crisis. There is no noteworthy attempt made to generate hydrogen using bitumen as the feedstock in hydrothermal gasification. In the present study, the catalytic SCWG process was employed for the conversion of Athabasca bitumen to produce hydrogen-rich syngas. The gasification process parameters such as temperature (550–700 °C), feed concentration (20–35 wt%) and reaction time (15–60 min) were thoroughly evaluated for gas yields from bitumen. The roles of metal catalysts (*viz.* FeCl₃, Ni/Si-Al₂O₃, Ru/Al₂O₃ and ZnCl₂) were also investigated in maximizing hydrogen yields.

2. Materials and methods

2.1. Feedstock and catalysts

Bitumen used as the feedstock in this study was sourced from the Athabasca oil sands deposit in northern Alberta, Canada. It was generously supplied by Syncrude Canada Ltd., which is one of the world's leading producers of synthetic crude oil from oil sands in Edmonton, Canada. Bitumen used in this study was non-distilled and did not contain any sand particles. The catalysts used in this study *viz.* FeCl₃ (CAS: 7705-08-0; PubChem SID: 24868641), ZnCl₂ (CAS: 7646-85-7, PubChem SID: 24853766), Ni/Si-Al₂O₃ (PubChem SID 24852528), and Ru/Al₂O₃ (PubChem SID 24867548) were purchased from Sigma Aldrich, Oakville, ON, Canada.

2.2. Feedstock characterization

The ultimate composition (carbon, hydrogen, nitrogen, sulfur and oxygen contents) of bitumen was determined using an Elemental vario EL III CHNOS analyzer (Elementar Analysensysteme, Hanau, Germany). The surface organic functional groups in bitumen were resolved through Fourier-transform infrared (FTIR) spectroscopy using a Bruker Alpha FTIR spectrometer (Bruker Optics Ltd, Milton, ON, Canada). Each spectrum was an average of 32 scans in the range of 500 to 3500 cm⁻¹ obtained at a resolution of 2 cm⁻¹. The higher heating value (HHV) of bitumen was calculated using the modified Dulong's formula as mentioned in Eq. (1) [22].

$$\text{HHV}(\text{MJ/kg}) = \frac{33.5 \times \text{C}(\text{wt}\%)}{100} + \frac{142.3 \times \text{H}(\text{wt}\%)}{100} - \frac{15.4 \times \text{O}(\text{wt}\%)}{100} \quad (1)$$

Thermogravimetric analysis (TGA) of bitumen was conducted using a TGA Q500 instrument (TA Instruments-Waters LLC, New Castle, DE, USA). About 10–15 mg of bitumen was heated up to 700 °C at a heating rate of 10 °C/min to record its devolatilization pattern. The thermal degradation behavior of bitumen was studied under nitrogen atmosphere with a gas flow rate of 40 mL/min. The trend of weight loss with the rise in temperature was monitored to elucidate the specimen's thermal stability and fraction of volatile components.

2.3. Supercritical water gasification reactor

Supercritical water gasification was carried out in a tubular batch reactor setup made of stainless steel SS316 (length: 40.5 cm, inner diameter: 0.94 cm and outer diameter: 1.27 cm). The volume of the SCWG batch reactor was ~28 cm³. A schematic representation of the reactor setup is shown in Fig. 1. The gasification unit was assembled using SS316 tubing and fittings (*i.e.*, pressure gauges, pressure relief valves, back pressure regulator, 2 μm filter, gas-liquid separating cylinder and tubular reactor) supplied by Swagelok (Swagelok Central Ontario, Mississauga, ON, Canada) in addition to an ATS Series 3210 furnace and ATS temperature control system (Applied Test Systems, Butler, PA, USA), Omega Type-K thermocouples (Spectris Canada Inc., Laval, QC, Canada) and desiccant column (Praxair Canada Inc., Mississauga, ON, Canada).

The gasification experiments were performed in the tubular batch reactor under inert atmosphere created by nitrogen. Further to nitrogen purging, the entire system (except for the reactor) was vacuumed to vent out any nitrogen gas from the system. The presence of inert gas nitrogen in the reactor was obligatory to create an initial pressure via the ideal gas law. Nitrogen was also used to create an initial pressure inside the reactor in the range of 10–15 MPa depending on the reaction temperature. The heating rate of the gasification system was 20 °C/min. After reaching the desired temperature and pressure (~23 MPa) inside the reactor, it was maintained for the desired reaction time. A back pressure regulator was installed to maintain the pressure inside the

Download English Version:

<https://daneshyari.com/en/article/6664075>

Download Persian Version:

<https://daneshyari.com/article/6664075>

[Daneshyari.com](https://daneshyari.com)