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Supercritical water gasification of glycerol and methanol mixtures as model waste residues from biodiesel refinery

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ABSTRACT

The eco-friendly processing in biodiesel refineries is feasible with effective utilization of the byproducts and waste residues. The motive of this research is to convert the model byproducts of biodiesel refineries to H₂. In this study, different glycerol–methanol mixtures were gasified in supercritical water at variable temperatures (450–600 °C) and pressures (23–25 MPa) for 45 s in a continuous-flow tubular reactor. Glycerol and methanol concentrations were varied from 5 to 20 wt% individually in the mixtures, and their impacts on gas yields were investigated both experimentally and thermodynamically. The thermodynamic simulations were performed using Aspen Plus based on Gibbs free energy minimization method. The thermodynamic yield (25.3 mmol/g) of H₂ was higher compared to experimental yields (19 mmol/g) at 600 °C, 25 MPa and 1:1 glycerol-to-methanol feed solution. To enhance the gas yields, the effects of four alkali catalysts such as KOH, NaOH, K₂CO₃ and Na₂CO₃ at 0.5 wt% concentration were examined. Among all the catalyst, 0.5 wt% K₂CO₃ resulted in highest H₂ yields (24.8 mmol/g), total gas yields (1.24 g/L) and carbon gasification efficiency (96.7%) at 600 °C and 25 MPa with 1:1 glycerol-to-methanol feed solution. The results suggest that effluents from biodiesel refineries can be used as potential feedstock for waste-to-energy conversion.

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1. Introduction

The growing energy demands have led to the overwhelming consumption of fossil fuels which is a major reason for increasing greenhouse gases emissions and global warming. Waste lignocellulosic biomass, algae and oil seed crops being carbon neutral are the next generation renewable resources of energy. The synthesis of biodiesel through transesterification of waste vegetable oils produces large quantities of byproducts

(Pagliaro et al., 2007). The byproducts of biodiesel refineries include free fatty acids, methanol, and water and glycerol mixed with alkalis (Pagliaro and Rossi, 2010). In a biodiesel refinery, the typical biodiesel-to-glycerol weight ratio is 9:1 (Guo et al., 2012). A greater alcohol-to-oil (6:1) mole ratio is employed to facilitate the reaction for completion (Thompson and He, 2006). The unreacted methanol ends up in glycerol phase and forms the key components of crude glycerol (Chiu et al., 2005). Nearly 80% of methanol in the byproduct stream is

Abbreviations: CGE, carbon gasification efficiency; CFTR, continuous-flow tubular reactor; Pc, critical pressure; Tc, critical temperature; GTM, glycerol-to-methanol ratio; LHV, lower heating value; NIST, National Institute of Standards and Technology; SCW, supercritical water; SCWG, supercritical water gasification; TCD, thermal conductivity detector; TGY, total gas yield.

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recovered and recycled back to the reactor while the remaining becomes a part of crude glycerol (Ortiz et al., 2011b). Several studies have demonstrated that methanol undergoes decomposition and reforming reactions to produce fuel gases in supercritical water (SCW) (May et al., 2010; Van Bennekom et al., 2011; Bouquet, 2012).

As the production of biodiesel is continuously increasing worldwide, large quantities of crude glycerol (mainly glycerol + methanol) are also generated. Nearly 1.6 million tons of crude glycerol were produced as byproduct of biodiesel plants in 2009 (Wendisch et al., 2011). In Canada, about 43,860 tons of crude glycerol are generated from 500 million liters of biodiesel production facilities per annum (Levin and Chahine, 2010). This has a potential to generate nearly 6700 tons of H₂ sufficient enough to fuel 26,800 vehicles for a year. The polyalcohol glycerol in its pure form finds many applications in food processing industries, cosmetics and pharmaceuticals (Ortiz et al., 2011a). Furthermore, glycerol has also been tested for its conversion to value-added products such as diols, acrolein, hydroxyl acetone and synthesis gas (Chiu et al., 2006; Corma et al., 2008; Gungormusler et al., 2011). However, the techniques involved in the purification of glycerol from waste effluents are highly expensive, which becomes a challenge toward the economics and sustainability of biodiesel refineries. Considering the process expenditures in the biodiesel plants, different routes to convert the crude glycerol into valuable products have been considered over the past few years (Ayoub and Abdullah, 2012).

Hydrogen (H₂) having a high heating value of 120 MJ/kg is considered as a clean fuel as it produces water upon combustion. Currently, one of the main sources (96% of the total H₂ supply) of H₂ is steam reforming of CH₄ that has a production cost of US\$ 1.5–3.7 per kg (Ewan and Allen, 2005; Balat and Kurtay, 2010). Glycerol is one of the potential renewable sources for H₂ generation (Markočić et al., 2013). Different methods to convert glycerol to fuel gases through fermentation, steam reforming, aqueous phase reforming, autothermal reforming and supercritical water gasification (SCWG) have been reviewed by Adhikari et al. (2009). The synthesis of fuel gases by thermochemical gasification route is widely in practice; however, the drying of biomass is a prerequisite and a major constraint (Nanda et al., 2014). H₂ production through SCWG of glycerol has attracted attention over the conventional routes due to distinct reasons such as: (i) direct processing of wet biomass/effluent with moisture content greater than 50%, (ii) availability of H₂ gas at high pressure, (iii) scope of energy recovery from the high temperature product gases, and (iv) high yields of H₂ with lower chances of tar and char formations (Van Bennekom et al., 2011).

The abundant availability of water with its non-toxic nature and flexibility in altering its thermo-physical properties beyond the critical point (T_c: 374 °C and P_c: 22.1 MPa) has directed its implementation as a medium for biomass gasification (Watanabe et al., 2004; Kruse and Dinjus, 2007). The shift in the nature of water from polar to non-polar due to the switch in its dielectric constant from 80 to 1–2 paves the path for the organic processing to happen in homogeneous phase thus eliminating any mass transfer resistances (Guo et al., 2010; Reddy et al., 2014a). The deceleration of hydrogen bonds in the supercritical environment at higher densities promotes H⁺ and OH⁻ ions, resulting in acid–base chemistry during the degradation of organic complexes (Boero et al., 2004; Kritzer, 2004). Water also acts as a reactant in the gasification of organics, contributing to H₂ production at

supercritical environments as the experiments done with D₂O instead of H₂O confirm this phenomenon (Kuhlmann et al., 1994). Moreover, experimental yields equivalent to theoretical yields were obtained with glucose (~12 mol/mol of glucose) indicating that water acts as a key reactant at 767 °C and 25 MPa (Susanti et al., 2012). Low densities with high diffusivities and negligible surface tension of SCW make it a prime component in reforming and degradation of organics into useful chemicals (Kruse, 2008; Knez et al., 2015).

Many investigations have been performed to understand the principles behind the conversion of pure glycerol to H₂ (Markočić et al., 2013). Depending on the operating conditions employed in SCWG of glycerol, ionic and free radical mechanisms prevail (Bühler et al., 2002). The key liquid intermediates of glycerol gasification in SCW are acetaldehyde, propionaldehyde, acrolein, allyl alcohol, hydroxyl acetone, ethanol, formaldehyde and propionic acid while the product gas comprises of H₂, CO, CO₂, CH₄ and C₂H₆ (Guo et al., 2012, 2013; Pairojpiriyakul et al., 2014). Qadariyah et al. (2011) demonstrated that valuable liquid products such as acetaldehyde and acrolein are obtained at subcritical conditions, whereas allyl alcohol along with acrolein is generated at supercritical conditions (Qadariyah et al., 2011). In addition to the decomposition mechanism, glycerol also follows steam reforming route to produce H₂ (Guo et al., 2012; Byrd et al., 2008).

The steam reforming of crude glycerol (methanol + fatty acid methyl esters + glycerol) has been performed with in situ sorption of CO₂ using dolomite to attain pure H₂ at atmospheric pressure (Dou et al., 2010). The byproduct of biodiesel refineries was subjected to reforming with water at subcritical (300 °C) and supercritical (450 °C) temperatures in a pressure range of 8.5–31 MPa to yield fuel gases, oil and solid products (Onwudili and Williams, 2010). The reaction mechanisms of reforming of methanol, pure glycerol and crude glycerol in the presence of alkali catalyst (Na₂CO₃) have also been elucidated at supercritical conditions (Van Bennekom et al., 2011). The H₂ yields of 15 and 10 mmol/g were obtained for pure glycerol and bioglycerol (C_{4.3}H_{9.7}O_{1.8} Na_{0.1}Si_{0.08}), respectively, at 525–600 °C and 25 MPa (Yu-Wu et al., 2012). SCWG at 500 °C, 45 MPa and 2.39 M KOH has shown to produce maximum H₂ (27.9 mol%) from crude glycerol (Yang et al., 2013). SCWG conducted with pure and crude glycerol both in batch and continuous reactor obtained H₂ yields of 26.4 and 35.8 mmol/g for two kinds of crude glycerol (Dianningrum et al., 2014). A recent investigation on the economic assessment from the reforming of glycerol at supercritical conditions confirms that it is a promising feedstock for H₂ generation (Galera and Ortiz, 2015).

The product gas composition of SCWG of crude glycerol varies tremendously depending on the operating parameters. Due to the expensive recovery processes, significant quantities of alkalis add up into biodiesel refinery effluents along with methanol and crude glycerol. With this objective, this gasification study on glycerol and methanol mixtures were carried out both in the presence and absence of catalysts. The temperatures are tuned from 450 to 600 °C at pressures of 23 and 25 MPa. The concentrations of methanol and glycerol were altered to understand the gas yields in SCW. Two types of feed solution have been investigated and their compositions (i.e. glycerol and methanol proportions) are mentioned in Table 1 to understand the impact of each component on H₂ yields. Furthermore, the experimental results were compared with the thermodynamic analysis of the feeds at the abovementioned parameters. Additionally, four different alkali catalysts such

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