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Research article

Energy balance of biofuel production from biological conversion of crude glycerol

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ABSTRACT

Crude glycerol, a by-product of biodiesel production, has gained significant attention as a carbon source for biofuel production. This study evaluated the energy balance of biodiesel, hydrogen, biogas, and ethanol production from 3.48 million L of crude glycerol (80% w/v). The conversion efficiency (energy output divided by energy invested) was 1.16, 0.22, 0.27, and 0.40 for the production of biodiesel, hydrogen, biogas, and ethanol respectively. It was found that the use of crude glycerol for biodiesel production was an energy gain process, with a positive energy balance and conversion efficiency of greater than 1. The energy balance revealed a net energy gain of 5226 GJ per 1 million kg biodiesel produced. Production of hydrogen, biogas and ethanol from crude glycerol were energy loss processes. Therefore, the conversion of crude glycerol to lipids and subsequently to biodiesel is suggested to be a better option compared to hydrogen, biogas, or ethanol production with respect to energy balance.

1. Introduction

Global biodiesel production has sharply increased from 500×10^8 to 7.5×10^9 gallons/year within 10 years (2004–2013), and it is predicted that the production will continuously grow (Annie, 2006; Ang et al., 2014). Generally, vegetable oils and fats are employed as feedstock. However, the large demand for the oils/fats induced an increase in their prices. On the other hand, microbial oils from microalgae, yeast, and fungus have been extensively studied for biodiesel production. The most applied method of biodiesel production from vegetable oils, animal fats, and microbial oils is transesterification. In this process, glycerol is simultaneously generated as a by-product at a rate of about 1–1.4 kg glycerol per 10 kg of biodiesel produced. As biodiesel production largely increases, glycerol management is becoming a concern. The glycerol is often called as crude glycerol whose composition varies from one biodiesel production plant to another and is mainly determined by the feedstock oil composition and quality, the oil and methanol molar ratio, catalyst, and the production process. Generally, the major fraction of the crude glycerol is glycerol (20–96% w/w), with some impurities such as water, methanol, soap (in alkaline catalytic process), and catalyst (Hansen et al., 2009; Hu et al., 2012).

Proper handling and use of crude glycerol is gaining attention due to its availability in large amount. Purification was the most applied method on crude glycerol before the boom of biodiesel production and utilized primarily in the cosmetic industry (Yang et al., 2012b). However, the energy intense process of glycerol purification has become unfavorable on cost revenue basis due to a decrease of the price of purified glycerol (1.54 US $/kg before 2000 and 0.66 US $/kg after 2007). Crude glycerol direct use as an energy source (combustion, or blending with fuel) has been reported (Johnson and Taconi, 2007; Gupta and Kumar 2012). Crude glycerol can be considered as a fuel since it burns. Several problems are reported in its application as fuel. Firstly, it has a high auto ignition temperature of 400 °C and generally requires mixing with gasoline for ignition. Additionally, it cannot burn in current existing oil burners due to its high viscosity. Moreover, a carcinogenic agent, acrolien, is produced if the combustion is unstable and incomplete. Therefore, using glycerol directly as fuel has been banned in Europe since 2006 (Slinn et al., 2008). Crude glycerol blending with solid fibrous materials or fuel (gasoline, ethanol, propanol, and propanediol) can be used as fuel, but the problem of acrolien generation during combustion is still a great concern.

Apart from being directly used as fuel, crude glycerol can also be converted to other energy sources such as biogas, ethanol,

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hydrogen, and biodiesel (Argun and Kargi, 2011; Viana et al., 2012; Yang et al., 2012a; Feng et al., 2014). Production of biofuels using crude glycerol would mitigate the pressure of its handling as well as the shortage of fossil fuels. Crude glycerol is proposed as a carbon source for lipid production employing oleaginous microorganisms, such as *Schizochytrium limacinum*, *Yarrowia lipolytica*, *Rhodotorula glutinis*, and *Cryptococcus curvatus* (Meesters et al., 1996; Papanikolaou and Aggelis, 2002; Easterling et al., 2009; Liang et al., 2010). The produced lipids can be further converted to biodiesel through transesterification. The use of crude glycerol, produced along with biodiesel, as a carbon source for oleaginous microorganisms and subsequent conversion of lipids to biodiesel completes the crude glycerol utilization and production cycle. In addition, crude glycerol has been investigated for microbial hydrogen production by fermentation (Kivistö et al., 2011; Liu et al., 2013). Several microorganisms such as *Rhodopseudomonas palustris* and *Thermotoga neapolitana* are found to provide a high hydrogen yield of up to 0.17 g H_2/g glycerol (Sabourin-Provost and Hallenbeck, 2009; Lo et al., 2010; Ngo et al., 2011). Crude glycerol has also been studied for biogas production by anaerobic fermentation, along with animal waste and/or sludge (Robra et al., 2010; Castrillón et al., 2011). It was observed that the biogas yield of crude glycerol and sludge based digestion was 825 mL/g volatile suspended solids (495 mL biogas from sludge and 330 mL from glycerol); however, only 269 mL/g VSS was achieved without the addition of crude glycerol to sludge (Johansson et al., 2004). Crude glycerol as substrate for ethanol production has also been reported (Choi et al., 2011; Oh et al., 2011).

Therefore, the aim of this study was to evaluate energy balance of various biofuel productions using crude glycerol as raw material. Based on the energy balance investigation, the study provided an insight of the management of crude glycerol.

2. Methods

2.1. Crude glycerol based biofuel production systems

2.1.1. Biodiesel production systems

The biodiesel production process is similar as described in our previous study (Zhang et al., 2013). It includes the fermentation, lipid extraction, transesterification, and biodiesel purification. Instead of solvent extraction from dry biomass, bead milling lipid extraction from wet biomass was adopted in this study (Ferraz et al., 2004).

2.1.2. Crude glycerol based hydrogen production process

Dark, photo, sequential dark and photo, and combined dark and photo fermentation were adopted for hydrogen production from crude glycerol (Sabourin-Provost and Hallenbeck, 2009; Ngo et al., 2011; Sarma et al., 2013). Researchers have reviewed and compared the types of fermentation processes for hydrogen production and revealed that the dark fermentation is the most suitable process for industrial scale production as it is easy to operate and provides a competitive hydrogen yield (Argun and Kargi, 2011). Thus, hydrogen production through dark fermentation was adopted in this study (Sarma et al., 2013).

2.1.3. Crude glycerol based biogas production process

Crude glycerol can be used as a substrate or co-substrate of organic solid waste for biogas production through anaerobic digestion. A recent review on biogas production has reported that crude glycerol as a substrate could provide a higher biogas yield than when used as a co-substrate (Viana et al., 2012). However, when crude glycerol was used as a sole substrate, nutrient addition (nitrogen) was required and biogas production wasn't stable for long term processing. It was found that crude glycerol as a co-substrate of wastewater sludge and animal waste digestion produced stable operation and comparable biogas yield. In addition, as a co-substrate, crude glycerol could increase methane content in the biogas (Robra et al., 2010). Wastewater sludge is widely and abundantly produced all over the world. It is a zero cost nutrient source, which can replace the supply of expensive chemical nutrients. Therefore, in this study, crude glycerol (10 g/L) addition to wastewater sludge (50 g/L) was considered to investigate the energy balance for biogas production, and the process was adopted from Robra et al. (2010).

2.1.4. Crude glycerol based ethanol production process

Fermentation of corn crops is the current process of biofuel ethanol production in practice. Ethanol has also been generated by aerobic and anaerobic fermentation of crude glycerol using microorganisms, such as *Kluyvera cryocrescens*, *Enterobacter Aerogenes*, and *Escherichia coli* (Choi et al., 2011; Chaudhary et al., 2012). Anaerobic fermentation is preferable as it consumes less energy (without aeration) and provides comparable ethanol yield to aerobic fermentation (Ito et al., 2005; Chaudhary et al., 2012). Equation (1) shows the stoichiometry of ethanol generation from glycerol by anaerobic fermentation.

$$C_3H_8O_3 \rightarrow CH_3CH_2OH + HCHO_2 \quad (1)$$

The fermentation of crude glycerol to produce ethanol and hydrogen simultaneously has been reported (Eq. (2)) in anaerobic fermentation when certain microorganism such as *Enterobacter Aerogenes* are used (Ito et al., 2005). In this study, the process introduced by Ito et al. (2005) was used to perform the energy balance of crude glycerol to produce ethanol.

$$C_3H_8O_3 \rightarrow CH_3CH_2OH + H_2 + CO_2 \quad (2)$$

2.2. Evaluation: basics and definitions

The energy balance evaluation was based on 3.48×10^6 L of 80% (w/v) crude glycerol utilization per year, which is ~10% of the total annul crude glycerol produced in Canada (Evans, 2013).

During the biofuel production process, the energy input was from the utilization of chemical, fuels, electricity, and steam. The energy content of fuels, electricity, and steam was directly used in the calculation as input (invested) energy. For instance, the energy content of diesel is 35.86 MJ/kg, thus the energy input from the utilization of fuel would be equal to the diesel quantity used multiplying with the energy content (35.86 MJ/kg). The energy input due to chemical utilization was calculated based on the energy consumption to produce the chemicals. For instance, every kg of KH_2PO_4 produced required energy of 10.30 MJ. Thus the energy input from KH_2PO_4 usage will be equal to the quantity of KH_2PO_4 (in kg) multiplied with 10.30 MJ. During the process, the energy was considered to be produced in two parts. One was energy in the biofuel (direct energy output) and the other was in the by-products. The energy content of the by-products was considered as credit. The energy invested was obtained by subtracting the energy credit from total energy input. The energy balance (= energy output−energy invested) and conversion efficiency (= energy output/energy invested) were determined based on energy output and energy invested. In the study, it was also assumed that there was no energy loss during utilization of fuels, power, and steam (provided 100% energy efficiency), and 100% energy efficiency available in the produced biofuel and by-products.