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Effect of major impurities in crude glycerol on solubility and properties of glycerol/methanol/bio-oil blends

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HIGHLIGHTS

- Impurities can worsen the solubility of glycerol/methanol/bio-oil (GMB) system.
- Impurities have insignificant effect on the properties of the composed GMB blends.
- Changes in fuel properties of GMB blends due to ageing become less in presence of impurities.
- GMB blend production using crude glycerol may be integrated into biodiesel production process.

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ABSTRACT

This study investigates the effect of major impurities in crude glycerol (water, soap, NaCl and NaOH) on the solubility and fuel properties of glycerol/methanol/bio-oil blends. All the impurities considered are found to worsen the solubility of glycerol in bio-oil to some degree. The effect of water and soap on glycerol solubility in bio-oil only becomes significant when the water to bio-oil ratio or the soap to bio-oil ratio exceeds 0.3 and 0.01, respectively. However, salt (NaCl) and alkaline catalyst (NaOH) can severely worsen the solubility of glycerol in the bio-oil even at a concentration of 2% in the glycerol aqueous solutions. Compared to solubility, the rheological properties and fuel properties (including heating value, surface tension, density, etc.) of the glycerol/methanol/bio-oil blends are little influenced by these impurities, except the acidity being slightly reduced for fuel blends containing high content of NaOH (e.g. 10% of NaOH in aqueous glycerol solution). The impurities also have appreciable effect on the ageing of the composed fuel blends. In presence of alkaline matter (soap or NaOH), the changes in fuel properties (viscosity, water content and especially acidity) due to ageing become slightly less. Further investigations on solubility of formulated crude glycerol (FCG) in bio-oil and properties of the FCG/methanol/bio-oil blends suggest that the crude-glycerol/bio-oil blends production process can be potentially integrated into the existing biodiesel production process.

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1. Introduction

Glycerol is a primary by-product of biodiesel production process. In general, approximately 1 kg of glycerol can be generated along with production of 10 kg biodiesel [1–6]. The rapid growth of biodiesel industry has resulted in and will continue to lead to a large surplus of glycerol [3,7–9]. Crude glycerol, usually containing less than 88% glycerol [10,11], is of low market value [4,7,12] and is usually disposed of as a waste stream especially in small or medium scale biodiesel plants due to the high cost for purification of crude glycerol [3,13,14]. However, disposal of crude glycerol as a waste can cause severe environmental concerns and is not economic-friendly [3,12,15–17]. Therefore, glycerol utilisation is of great importance to the sustainable development of biodiesel industry.

Fast pyrolysis bio-oil can be mixed with various liquid fuels to produce mixed fuels (e.g. biodiesel/bio-oil blends [18], bio-oil/biodiesel emulsion or bio-oil/diesel emulsion [19–21] for various application. It was recently reported that blending glycerol with bio-oil (with the aid of methanol) appears to be a possible approach for producing a liquid fuel mixture with rheological and other fuel properties suitable for stationary combustion application [22]. In the industrial process for biodiesel production, it is known that methanol is present in crude glycerol [23,24] so that crude glycerol from biodiesel production process may be potentially mixed into bio-oil for manufacturing the fuel blends directly [22]. However, in addition to methanol, crude glycerol also

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contains various other impurities such as water, soap and alkaline catalyst [5,23–28]. How these impurities affect the solubility of glycerol/methanol/bio-oil system is largely unknown. It is important to understand the influence of impurities on the blending of glycerol and bio-oil, for at least three reasons. Firstly, it provides the fundamental knowledge for potentially blending crude glycerol with bio-oil to produce a liquid fuel blend for stationary applications. If the impurities can be tolerated in production of fuel blends, crude glycerol can be directly used for fuel blending so that the expensive purification process for crude glycerol in the conventional biodiesel production process may be simplified or even eliminated. This may lead to better economic performance of biodiesel production value chain. Understanding the effect of impurities can further help identify the preferable crude glycerol composition for blending with bio-oil, thereby providing guidance on optimising the integration between the biodiesel production process and the fuel blending process. Secondly, if crude glycerol can be directly mixed with bio-oil to produce fuel blends, it provides an attractive strategy for utilising crude glycerol, addressing the key issues (e.g. high viscosity and low pumpability, high alcohol content, and high content of inorganic species etc. [29–32]) associated with using crude glycerol alone as an energy source. Last but not least, it is possible that the fuel blends of crude glycerol and bio-oil may have improved acidity and stability compared to bio-oil, because not only methanol in crude glycerol can improve bio-oil properties [33,34] but also the alkaline catalysts presented in crude glycerol may neutralize the acidic compounds in bio-oil.

Therefore, this study aims to investigate the effect of several key impurities in crude glycerol on the solubility and properties of glycerol/methanol/bio-oil blends and further evaluate the possibility of mixing crude glycerol with bio-oil for producing fuel blends. A series of glycerol-impurity mixtures and formulated crude glycerol were prepared for blending with bio-oil for studying mixture solubility, fuel properties, rheological properties and ageing.

2. Experimental section

2.1. Sample preparation

The bio-oil used in this study was supplied by a commercial supplier which employed a pilot-scale pyrolysis reactor for bio-oil production via fast pyrolysis of pine wood at 500 °C. The bio-oil was kept in fridge at ~4 °C prior to experiment. The properties of the bio-oil sample are listed in Table 1. Glycerol (G5516) and sodium oleate (26,125) were purchased from Sigma–Aldrich while analytical grade methanol, NaOH and NaCl are sourced from Chem-Supply. Sodium oleate is used as a representative compound for soap [35] and referred to as soap hereafter.

A series of mixtures containing glycerol and impurities were prepared as listed in Table 3. Glycerol–water and glycerol–soap mixtures are referred to as "GWxx" and "GSxx" ("xx" represents water or soap percentage in the mixture), respectively. Certain amounts of NaOH or NaCl were added to GW35 and GW15 mixtures respectively to prepare a series of mixtures that are referred to as "GW35NaOHxx" and "GW15NaClxx" ("xx" represents the percentage of NaOH or NaCl in the mixture). Additionally, a series of four mixtures with different percentages of all the impurities (i.e. water, soap, and NaOH) were prepared as formulated crude glycerol (referred as "FCG"). The details on impurity selections and formulations were discussed in Section 3.

Table 1
Properties of the bio-oil used in this study.

Elemental analysis (wt%)					Viscosity (MPa s @25 °C)	Water content (wt%)	TAN[c] (mg NaOH/g)
C[a]	H[a]	N[a]	O[b]	Na[a]			
42.64	7.54	0.21	49.61	0.0001	130.3	23.7	48.6

[a] As received.
[b] By difference.
[c] Total acid number.

Table 2
Key considerations for formulating the compositions of crude glycerol in this study.

Parameters	Conditions and considerations
Feedstock [40,48]	Vegetable oil is represented by triolein; Free fatty acid (FFA) is represented by oleic acid; 1% ⩽ FFA content ⩽3% and water content in feedstock ⩽0.06%
Methanol to oil ratio [47]	6:1–10:1
Catalyst [40]	NaOH, 0.3–1.5%
Reactions [47,49]	Triolein (oil) + 3 methanol → 3 methyl oleate (biodiesel) + glycerol (98–100% conversion of oil) Oleic acid (FFA) + NaOH → sodium oleate (Soap) + H_2O (98–100% conversion of FFA)
Methanol recovery [59,60]	94–100%
Components distribution [4,7,35,52,53,55,56]	Catalyst, water and soap in glycerol phase: 97–100% methanol in glycerol phase: 80% unreacted oil, FFA and biodiesel in glycerol phase: negligible–1.5%
Water addition [61]	25–54 mg/g (biodiesel + glycerol)

Table 3
Compositions of series of impurity-containing glycerol used in this study (wt%).

Mixtures	Glycerol	Soap	Water	NaOH	NaCl
GW5	95.0		5.0		
GW15			15.0		
GW35			35.0		
GS5		5.0			
GS20		20.0			
GW35NaOH2	63.7		34.3	2.0	
GW35NaOH10	58.5		31.5	10.0	
GW15NaCl2	83.3		14.7		2.0
GW15NaCl6 (FCG2)	80.0		14.0		6.0
FCG1-1	80.0	15.0	3.0	2.0	
FCG1-2	87.0	8.0	3.0	2.0	
FCG3-1	60.0	15.0	20.0	5.0	
FCG3-2	67.0	8.0	20.0	5.0	

GW5, GW15 and GW35: glycerol–water mixtures with water contents of 5%, 15% and 35% respectively.
GS5 and GS20: glycerol–soap mixtures with soap contents of 5% and 20% respectively.
GW35NaOH2 and GW35NaOH10: aqueous glycerol solution GW35 with NaOH contents of 2% and 10% respectively.
GW15NaCl2 and GW15NaCl6: aqueous glycerol solution GW15 with NaCl contents of 2% and 6% respectively.
FCG: formulated crude glycerol.

2.2. Solubility and accelerated ageing experiment

Solubility tests of the impurity-containing glycerol in the bio-oil and accelerated ageing experiments were carried out following methods described elsewhere [22,34]. Briefly, at room temperature (~25 °C), an impurity-containing glycerol mixture (the GWxx, GSxx, GW15NaClxx, GW35NaOHxx or FCG mixtures) was blended with the bio-oil sample, followed by gradually adding methanol until a homogenous phase similar to that of the bio-oil was observed under an optical microscope (model: Olympus SL 60/61). Magnetic stirring was employed for mixing of these components. Accelerated ageing of selected samples was conducted in a Pyrex glass container at 80 °C for 24 h, followed by rapid cooling in an ice bath to avoid further reactions. The containers were tightly sealed and the mass of these samples were recorded before

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