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Short communication

# Ignition temperatures of various bio-oil based fuel blends and slurry fuels

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## HIGHLIGHTS

- Ignition temperatures of slurry fuels are higher than the corresponding fuel blends.
- Crude glycerol improves the ignition of bio-oil based fuels due to sodium salt.
- The ASTM-based method measures the ignition temperature of vapour phase.
- The TGA method measures the ignition temperature of solid residue after evaporation.

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## ABSTRACT

Ignition temperatures of a series of bio-oil based fuel blends or slurry fuels prepared from bio-oil, bio-oil water soluble fraction (WSF), crude glycerol and/or biochar are measured via thermogravimetric analysis (TGA) method and a modified method based on ASTM standard. Bio-oil has an ignition temperature of 506 °C while WSF has a slightly higher ignition temperature (511 °C) due to negative effect of water on ignition. Fuels with crude glycerol (CG) have lower ignition temperatures due to the presence of sodium salts in CGs. For example, the ignition temperatures of the CG/methanol/bio-oil/biochar (CGMBB) slurry fuels range from 445 to 470 °C while that of the glycerol/methanol/bio-oil/biochar (GMBB) slurry is 510 °C. Although biochar has a lower ignition temperature (375 °C), slurry fuels have higher ignition temperatures than the respective blends. This is attributed to the formation of less volatile and more carbonaceous solid by the interactions between bio-oil components and biochar. The results show that the ASTM-based method measures ignition temperatures with emphasis on ignition of vapour phase but the TGA method provides that with emphasis on ignition of the solid residue after evaporation.


## 1. Introduction

Utilisation of crude glycerol is challenging but of critical importance to the economic and environmental performance of biodiesel production plants [1–5]. Recent studies [4–9] indicated that crude glycerol can be mixed with fast pyrolysis bio-oil or its water soluble fraction (WSF), with or without the introduction of fine biochar particles, to prepare new classes of bio-oil based fuel blends or slurry fuels. The reported fuel properties of these fuel blends or slurry fuels meet the specifications on various aspects for stationary applications (e.g. combustion in boilers) [5,7,9]. Ignition behaviour is an important consideration for safety during fuel storage and transport as well as combustion performance during applications [10]. Glycerol was reported to have an ignition temperature of 370 °C [11,12]. However, little is known on the ignition behaviour of the fuel blends and slurry fuels prepared from bio-oil (or bio-oil WSF) and glycerol, with or without biochar addition. Therefore, the objective of this study is to investigate the ignition temperatures of these bio-oil based fuel blends or slurry fuels. The ignition temperatures were determined via two methods, ie. thermogravimetric analysis (TGA) [13] and an ASTM-based method modified from ASTM standard E659.

## 2. Experimental

### 2.1. Sample preparation

Bio-oil was supplied by a commercial producer and it was produced by fast pyrolysis of pine wood biomass at 500 °C. Bio-oil was mixed with water at a weight ratio of 1:0.5, which is known to produce optimal bio-oil WSF that is suitable for preparing stable fuel

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mixture with crude glycerol and has a relatively low water content [5]. Both the bio-oil and WSF samples were kept at 4 °C in a fridge before use. Biochar was prepared by fast pyrolysis of pine wood biomass at 500 °C (detailed given elsewhere [8]). Then biochar was ground using a ball mill (Retsch MM400) and then sieved to below 75 μm. Glycerol (G5516) and sodium oleate (26125, represents soap) were both purchased from Sigma-Aldrich. Analytical grade methanol, sodium hydroxide (NaOH) and sodium chloride (NaCl) were bought from Chem-Supply. Six crude glycerol samples (referred to as CG1−3 and CG4−6) were formulated (according to the compositions of crude glycerols [7]) as listed in Table 1. CG1−3 were used to prepare CG/methanol/bio-oil (CGMB) blends with composition of 4.6% CG, 7% methanol and 88.4% bio-oil. CG4−6 were used for preparing CG/WSF (CGWSF) blends with composition of 40% CG and 60% WSF. Glycerol/methanol/bio-oil (GMB) blend and glycerol/WSF (GWSF) blend with same compositions were also prepared as blanks. Bioslurry fuels were prepared by further adding 10% biochar to the CGMB and CGWSF blends. The fuel blends or slurries were mixed using magnetic stirrer in plastic containers at room temperature. In addition, CG7 and CG8 without sodium salts (while keep the same concentrations of other impurities as those in CG3 and CG6, respectively) were also prepared to understand the effect of sodium salts.

### 2.2. Sample characterization

Proximate analysis for biochar was conducted using thermogravimetric analysis (TGA, Mettler TGA/DSC 1 STAR). Ultimate analysis of biochar and bio-oil samples were performed by an elemental analyzer (Perkin-Elmer 2400 Series II). The higher heating value (HHV) of the fuel samples were calculated based on elemental analysis [14]. The water content and total acid number (TAN) of fuel samples were performed via a Karl Fisher titrator (Metter V30) and an acid-base titrator (MEP Oil Titrino plus 848) respectively, following the previous methods [6]. The determination of surface tension, density and viscosity follows previously reported methods [9] by Surface tensiometer (KSV Sigma 701), volumetric flask and rheometer (model Haake Mars II) respectively.

The ignition temperatures of bio-oil based fuel samples were determined using a TGA (Mettler TGA/DSC 1 STAR). In each run, 15–20 mg of sample was put into a platinum pan. Air was used as purge gas with a flow rate of 100 mL/min. In the TGA, the sample was heated from 40 to 1000 °C at 10 °C/min. All experiments were carried out in at least duplicate. The ignition temperatures of fuel samples were defined following an intersection method [15,16]. The standard deviations of ignition temperatures determined by the TGA method is within 3 °C. A modified test method based on ASTM standard E659 (hereafter referred to as ASTM-based method) was also deployed. Briefly, a portion of fuel sample is placed in a muffle furnace at known temperatures and observed inside the furnace over a ten minute period to determine whether ignition occurs. Auto ignition is evidenced by the sudden appearance of a flame inside the vessel. If ignition is not observed, the temperature of furnace will be raised by a 20 °C interval until ignition is observed. All tests were carried out at least in duplicate.

## 3. Result and discussion

Table 2 presents the data on fuel properties of the CGMB fuel blends and CG/methanol/bio-oil/biochar (CGMBB) slurry fuels benchmarking against biochar, bio-oil, GMB blend, bio-oil/biochar (BB) slurry and glycerol/methanol/bio-oil/biochar (GMBB) slurry. CGMBB slurry fuels have a slightly higher HHV (~19.5 MJ/kg), lower water content (19.8–20.3%) and TAN (35.9–36.1 mgNaOH/g) in comparison to those of CGMB blends (HHV: ~18.7 MJ/kg; water content: ~21.7%; and TAN: 42.1–43.0 mgNaOH/g, respectively). The viscosity, surface tension and density of CGMBB slurry are 222–268 mP.s, 33.5–35.5 mN/m and 1.19 g/cm$^3$ respectively. Due to the addition of biochar particles, these are higher than those of CGMB blend being 82.4–86.6 mP.s, 33.1–34.8 mN/m and 1.17 g/cm$^3$ respectively, leading to much higher Ohnesorge numbers for the CGMBB slurry fuels compared to the CGMB blends. Such observations are consistent with those on GMB blends and GMBB slurries [9], as well as bio-oil and BB slurry [17].

Table 3 shows the ignition temperatures of the bio-oil based blend and slurry fuels measured by TGA method. First, the results show that bio-oil or WSF alone has high ignition temperature being 506 and 511 °C, respectively. The difficulty in the ignition of bio-oil or WSF is likely due to the formation of carbonaceous solid by cracking reactions at high temperature (such residue solid is known to be hard to ignite [16]). The slightly higher ignition temperature of WSF in comparison to bio-oil can be attribute to the negative effect of higher water content in WSF. Second, ignition temperatures of the slurry fuels containing CG are lower compared to those slurries with only bio-oil, WSF or glycerol. For example, CGMBB slurry fuels have ignition temperatures in a range of 445–470 °C while BB slurry and GMBB slurry ignited at 497 and 510 °C, respectively. Third, the ignition temperatures of CGWSFB slurry fuels (424–445 °C) tested by TGA method are lower than that of GWSFB slurry (456 °C). This is attributed to the presence of sodium salt in CGs may have catalytic effect on ignition. It was known that inorganic species decreases the ignition temperatures of solid fuels [18]. To prove this point for these liquid/slurry fuels, further experiments were undertaken to measure the ignition temperatures of fuels prepared from CGs without sodium salts. It was found that the ignition temperatures are 502 and 469 °C for CG7MBB slurry and CG8WSFB slurry, respectively. Such ignition temperatures are considerably higher than the corresponding fuels prepared from CGs with sodium salts, i.e. 447 and 443 °C for CG3MBB slurry and CG6WSFB slurry, respectively. Last, GMBB or CGMBB slurry fuels demonstrate higher ignition temperatures compared with their corresponding blends. Although biochar has an ignition temperature of 375 °C, lower than that of the GMB or

**Table 1**
Compositions of different types of formulated crude glycerol samples for use in this study (wt%).

| Crude glycerol | Glycerol | Soap | Water | NaOH | NaCl | Methanol |
|---|---|---|---|---|---|---|
| CG1 | 83.3 | 10.4 | 4.2 | 2.1 | | |
| CG2 | 81.2 | | 14.6 | | 4.2 | |
| CG3 | 66.7 | 10.4 | 20.8 | 2.1 | | |
| CG4 | 80.0 | 10.0 | 4.0 | 2.0 | | 4.0 |
| CG5 | 78.0 | | 14.0 | | 4.0 | 4.0 |
| CG6 | 64.0 | 10.0 | 20.0 | 2.0 | | 4.0 |
| CG7 | 76.2 | | 23.8 | | | |
| CG8 | 72.7 | | 22.7 | | | 4.6 |

CG: crude glycerol.