Ignition and Combustion Characteristics of Single Droplets of a Crude Glycerol in Comparison with Pure Glycerol, Petroleum Diesel, Biodiesel and Ethanol

Hendrix Y. Setyawan, Mingming Zhu*, Zhezi Zhang and Dongke Zhang

Centre for Energy (M473), The University of Western Australia, 35 Stirling Highway,
Crawley, WA 6009, Australia

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* Corresponding author:

Dr Mingming Zhu

Email: mingming.zhu@uwa.edu.au

Phone: +61 8 6488 5528

Fax: +61 8 6488 7622

Abstract

The ignition and combustion characteristics of single droplets of a crude glycerol were experimentally studied and compared with those of pure glycerol, a petroleum diesel, a biodiesel, and ethanol. A single fuel droplet was suspended at the tip of a silicon carbide fibre undergoing heating, ignition and combustion in an electrically heated horizontal tube furnace at an air temperature ranging from 948K to 1048 K. The ignition and combustion behaviour of the droplet were recorded using a CCD camera. Ignition delay time, total combustion time, burning rate, and flame standoff ratio were estimated. At a same temperature, the ignition delay time and total combustion time followed the order of pure glycerol > crude glycerol > ethanol > biodiesel > diesel, while the burning rate followed the order of crude glycerol > diesel > biodiesel > ethanol > pure glycerol, suggesting that the impurities, mainly water and methanol, had a profound influence on the combustion characteristics of crude glycerol. The flame standoff ratio slightly decreased after ignition but continuously increased with time afterwards for the crude glycerol and remained almost unchanged for the pure glycerol, indicating the significant influence of impurities on the quasi-steadiness of the flame.

Keywords: Biodiesel; Combustion Characteristics; Diesel; Ethanol; Glycerol; Ignition

1. Introduction

Biodiesel, an alternative liquid transport derived from renewable sources of fatty acids such as vegetable oils and animal tallow, has become of worldwide interest, often advocated by environmental and conservation movements and special interest groups [1, 2]. The global biodiesel production has increased rapidly in recent years, reaching 28.3 million metric tonnes (MMT) in 2014 [3]. A by-product of the biodiesel production process is glycerol and, with approximately 0.1 kg of crude glycerol being created for every 1 kg of biodiesel produced [4], the global crude glycerol production in 2014 was estimated to be 2.8 MMT, which is significantly greater than the glycerol market, currently at 2 MMT globally, could possibly absorb [4]. Hence, it is necessary to search for alternative uses of the overproduced glycerol.

A number of processes, such as pyrolysis, fermentation and steam reforming have been proposed to convert glycerol into products of certain values such as hydrogen [5], acrolein [6], syngas [7], and chemicals [8]. However, these conversion technologies are either expensive, or the product volume and value too low, or require large throughputs to make an economical sense, while the crude glycerol supplies are incompatibly small and scattered over different regions.

However, direct combustion of glycerol in utility boilers or internal combustion engines for combined heat and power and heat (CHP) is a plausible alternative [9]. Direct combustion of glycerol offers a few advantages over the other technologies such as simplicity, flexible scale operation, maturity, and cost effectiveness.

As an alternative fuel, glycerol has been tested for combustion using burners and diesel engines [9, 10]. Pure glycerol was shown to burn effectively in a heating boiler with the use of a high-swirl refractory burner [10]. In a set of tests with a diesel engine generator rated at 43 kW, the generator fuelled with pure glycerol produced a continuous power of 41.5 kW [9]. However, the combustion of glycerol is inherently challenging due to the high viscosity, low energy density, high auto-ignition temperature, and low heating value [11].

In addition, the combustion of crude glycerol is further complicated by the impurities brought in during the biodiesel production process, which would be too costly to remove. The impurities include, depending on the process and operating conditions, methanol (6.2– 12.6 wt%), water (6.5– 28.8 wt%), soap (up to 26.5 wt%), fatty acid methyl ester (FAME) (up to 28.8 wt%), glycerides (up to 7.0 wt%), free fatty acid (FFA) (up to 3.0 wt%), as well as ash (2.7 – 3 wt%) [12]. Of particular note is that crude glycerol also contains high concentrations of sodium as a result of excess catalyst used in the transesterification process [12], which could have significant and adverse effect on the flame, combustion equipment, and environment [13]. Thus, in order to better utilise the glycerol as a fuel, it is important to study its ignition and combustion characteristics in comparison to those of other, better understood fuels and to especially understand the effect of the impurities on the combustion behaviour of crude glycerol.

The present preliminary experimental work was aimed to gain a fundamental understanding of the ignition and combustion behaviour of single droplets of crude glycerol and compare them with those of several well studied liquid fuels including diesel biodiesel and ethanol. The experimentation was performed by suspending single droplets in hot air in an electrically heated furnace. The ignition delay time, combustion time, burning rate, and flame standoff ratio were determined with the aid of a CCD camera imaging technique. The effect of air temperature on the ignition and combustion characteristics was studied. This approach would provide a useful means to understand the combustion characteristics of glycerol, which would ultimately lead to better use of crude glycerol in combustion applications. The results would shed light on the feasibility of utilising crude glycerol in diesel engines for power generation as one of the simplest and easiest means of crude glycerol utilisation. Since diesel, biodiesel and ethanol are well studied for their application in diesel engines [14 – 16], comparing the ignition and combustion characteristics of crude glycerol against these fuels will also provide essential guidance in utilising glycerol in diesel engines.

99 2. Experimental

100 Employed in the current study were pure glycerol and ethanol acquired from Sigma Aldrich (Perth
101 Australia), a crude glycerol and biodiesel provided by Wilmar International (Gresik, Indonesia) and
102 a petroleum diesel (Caltex No.2) obtained from a local service station. The chemical compositions
103 and physical properties of these fuels are shown in Table 1 and the composition of the crude
104 glycerol is listed in Table 2.

105 The ignition and combustion behavior of these fuels were studied using a single droplet combustion
106 technique as schematically shown in Figure 1 and described elsewhere [20, 21]. Briefly, the
107 experimental set-up consists of a droplet suspension system, a horizontal tube electric furnace (600
108 mm in length and 40 mm in diameter) with temperature control for providing a hot air environment,
109 a step motor for delivering the droplet into the furnace, and a CCD camera for capturing the images.
110 In a typical experimental run, the furnace was preheated to a desired temperature from 948K to
111 1048K, the typical combustion temperatures in diesel engines. A droplet was produced by a micro
112 pipette of 10 μ L and was deposited on the tip of a silicon carbide fibre of 0.142 mm in diameter.

113 Aided by the step motor, the droplet was transported to the centre of the furnace at a linear velocity
114 of 1ms^{-1} . The high speed CCD camera with an exposure time of $1000\mu\text{s}$ (50fps) captured the time-
115 sequenced images of the droplet during its ignition and combustion process. The step motor and
116 camera were controlled from a computer. In order to capture the evolution of the droplet size, a
117 halogen lamp was used to backlit the images of the burning droplet. Note that when the droplet was
118 attached to the tip of the silicon carbide fibre, it was deformed to an ellipsoidal shape due to gravity.
119 The equivalent droplet diameter was determined from the height (d_{max}) and width (d_{min}) of the
120 droplet measured from the CCD images according to the following equation [22, 23]:

$$121 \quad d = \sqrt[3]{(d_{\text{max}})(d_{\text{min}})^2} \quad (1)$$

122 The initial equivalent droplet diameter was approximately 1 mm.

The ignition delay time and total combustion time of a burning droplet were estimated by analysing the CCD images taken without backlit. The ignition was defined as the moment when the first visible flame was observed [23 – 27]. The ignition delay time (t_i) was defined as the time difference between the moment when the droplet reached the centre of the furnace and the ignition. The period from the ignition until the extinction of the flame was taken as burnout time (t_b). The total combustion time (t_c) was the sum of ignition delay time and the burnout time.

The process of the single droplet combustion may be described as follows. When a droplet (R_d) is subjected to the hot ambience at a certain temperature (T), it starts to vaporise. The vapour diffuses outwards and mixes with oxygen. Once the ignition criterion is met, the ignition occurs and a thin flame is formed enveloping the droplet. Ideally, there is no oxygen inside the flame front and there are no unburnt fuel species outside the flame. As combustion proceeds, the droplet size shrinks continuously through evaporation due to the heat received from the flame [28].

Figure 2 (a) schematically shows a generic structure of a burning droplet with a diffusion flame enveloping the droplet. The definition of the droplet radius and flame radius is also shown. The flame radius of the droplet (R_f) was determined by measuring the radius of the flame, the distance from the centre of droplet to the flame front, during the stable combustion phase, which is approximately 0.1 - 0.3 s after ignition.

Figure 2 (b) shows a real image of an actual burning droplet of pure glycerol. A horizontal line passing through the centre of the droplet was drawn and displayed on Figure 2(b) and the colour intensity along the line shown in Figure 2(b) was estimated from monochrome signal using a self-developed Matlab code. The result was shown in Figure 2(c). The centre of the line corresponds to the position of fibre and the position at which the colour intensity reached the highest was taken as the flame front. The flame should ideally be symmetric but the shape of the actual flame deformed a little throughout the experiment because of buoyancy induced convection. The sudden decrease of the colour intensity at the centre was due to the presence of the fibre. With the actual width of the fibre (0.142 mm) being used as a reference, the actual flame radius was then calculated.

The backlit images of a burning droplet were used to determine the burning rate. Backlit by the halogen lamp, the rate of imaging was set at 200 fps. From the time sequenced images and with the aid of Matlab, the burning rate (k) then was determined using the d^2 -Law [28]:

$$k = \frac{d(d^2)}{dt} \quad (2)$$

3. Results and Discussion

The ignition and combustion characteristics of the crude glycerol, including the time-sequenced droplet size, ignition delay time, total combustion time, burning rate, flame standoff ratio, and flame radius, were compared to those of pure glycerol, biodiesel, diesel and ethanol.

Figure 3 shows the temporal variation of the square of the normalised droplet diameter $(d/d_0)^2$ at 973K for the different fuels studied. The droplet sizes for the five fuels respectively were measured from the moment of occurrence of ignition until the completion of combustion. A significant observation can be made from Figure 3, that is, the linear trend of reduction in the droplet size during combustion, implying that the droplet combustion conformed to the d^2 -law [28].

It was also observed that the droplet size fluctuated noticeably for the crude glycerol but not so significant for the other fuels. This is mainly due to the fact that the crude glycerol contained several impurities including methanol and water whose boiling points were 337 K and 373 K respectively, lower than that of glycerol, at 563 K. Table 2 shows that the crude glycerol contains 2.2% methanol and 22.6% water. When the crude glycerol droplet was heated and the temperature of the droplet reached the boiling points of methanol and water, which would then evaporate before glycerol reached its boiling point, resulting in the formation of bubbles of methanol and water steams [29, 30]. The bubbles thus formed would grow, collapse and even explode, leading the observed fluctuations of the shape and size of the droplet during combustion [31].

The temporal variation curves of the droplet size in Figure 3 were linearly fit to obtain the burning rates of the five fuels following d^2 -law, respectively. The theoretical burning rates (k_c) of the droplets at 973K were also calculated based on the classic d^2 -law [28]:

$$k_c = \frac{8\lambda_g}{c_{p,g}\rho} \ln(1+B) \quad (3)$$

where λ_g is the thermal conductivity of air, $c_{p,g}$ the specific heat of air/vapour mixture, B the Spalding number, and ρ the fuel density.

Figure 4 shows good agreements between the theoretical and experimental burning rates of the five fuels, with only small deviations. These deviations are expected due to the experimental errors, simplification of the model, complexity of the actual droplet combustion processes, and effect of the fibre [32].

Two pieces of information of interest were obtained from Figure 4. Firstly, the burning rate of pure glycerol was lower than that of diesel, biodiesel and ethanol. Referring to the Equation 3, the burning rate is mainly influenced by the density and Spalding transfer number of the fuel since the thermal conductivity and heat capacity of fuel vapour/air mixture varied, insignificantly, with temperature [28]. The density of pure glycerol, diesel, biodiesel, and ethanol are 1261 kg m^{-3} , $820\text{--}850 \text{ kg m}^{-3}$, 883 kg m^{-3} , and 789 kg m^{-3} , respectively and their calculated Spalding transfer numbers are 4, 9, 8, and 3 respectively. As expected, the burning rate of pure glycerol was indeed lower than the other fuel as it is denser and has a relatively low Spalding number.

The second interesting observation from Figure 4 is that the burning rate of the crude glycerol was the highest among the fuels tested, suggesting the impurities had accelerated the burning rate. The crude glycerol contained methanol, water, sodium (soap) and FAME, all of which contributed to the higher burning rate [29, 30]. Equation 3 implies that the burning rate of a fuel increases as the latent heat of evaporation and fuel boiling point decrease [28]. The latent heat of evaporation of crude glycerol was higher than that of pure glycerol as the major impurities (methanol and water) have higher latent heat of vaporisation than glycerol. Due to the differences in latent heats, the

temperature rise would be faster in glycerol compared to methanol and water. However, the vapour pressures of methanol and water are higher than that of glycerol. Consequently, methanol and water vaporized faster than glycerol at the surface of the droplet, leading to the high observed burning rate of crude glycerol.

The other impurities such as FAME, sodium and ash may also affect the burning rate of glycerol. For instance, the burning rate of FAME, the main constitute of biodiesel is slightly higher than that of glycerol as indicated in Figure 4. The sodium addition in glycerol may enhance the soot formation propensity, which will in turn affect the burning rate [13, 16, 33]. However, the effect of these impurities on the burning rate would be very limited due to their very low concentrations in the crude glycerol as shown in Table 2.

Figure 5 compares the results of ignition delay time of the fuels at different temperatures. The ignition delay time decreased with increasing furnace temperature as expected. At the same temperature, the ignition delay times followed the order of pure glycerol > crude glycerol > ethanol > biodiesel > diesel and this order remained unchanged in the temperature range from 948K to 1048K.

The ignition delay time is a result of pre-combustion reactions in the fuel/air mixture, consisting of a physical delay (droplet heating, evaporation, molecular diffusion and mixing with air) and a chemical delay (subsequent chemical reaction of gas phase between fuel and oxygen) [24, 25, 34]. The ignition delay time of a fuel can also be correlated with the Cetane number of the fuel [35]. A higher Cetane number affords a shorter ignition delay [35]. Table 1 displays that the Cetane number of pure glycerol is 5, being the lowest as compared to that of biodiesel (51.7), diesel (47.4 - 63.9), and ethanol (12), respectively. The crude glycerol had a slight higher Cetane number (6.7) than pure glycerol. The Cetane numbers of those fuels were consistent with the result of the ignition delay times measured using single droplet combustion method. Glycerol, which has a low Cetane number, required more time to burn, whereas the other fuel ignited faster.

It is also evident that the ignition delay time of the crude glycerol was slightly longer than that of pure glycerol, particularly at higher temperatures, due to the presence of impurities such as water, methanol, sodium and FAME. Our previous studies found that water can significantly delay the ignition time of glycerol droplets [30]. Due to its low boiling points, water on the surface of the droplet would evaporate prior to the evaporation of glycerol and the water vapour (steam) dilutes the glycerol/air mixture in the gas phase, thus it would require a longer time for the ignition to occur when more fuel is accumulated in the boundary layer of the droplet, resulting in a delay of the ignition of glycerol. In the interior of the crude glycerol droplets, water would delay the increase of temperature by increasing heat capacity of the droplets as the heat capacity of water is $4200 \text{ J kg}^{-1} \text{ K}^{-1}$, much higher than that of glycerol ($2400 \text{ J kg}^{-1} \text{ K}^{-1}$). Also, it is well known that the presence of water in the hydrocarbon fuels could suppress the ignition [36]. Likewise, the water content in the crude glycerol would delay the ignition as observed in the present experimentation. On the contrary, methanol, sodium and FAME would accelerate the ignition time of glycerol [29]. Methanol vapour is combustible which could result in a shorter ignition time of crude glycerol droplets, but its flame may not be visible. It was also reported in the literature that the ignition time of liquid sodium droplets was stable under 0.2s in an air temperature above 800K [37]. However, their effects on the ignition delay time were suspected to be insignificant due to their low concentrations in the crude glycerol.

Figure 6 displays the total combustion times of the fuels at different temperatures. Overall, the total combustion time decreased when temperature increased. Pure glycerol showed the longest total combustion time followed by the crude glycerol, ethanol, biodiesel and diesel. This trend was the same at temperatures ranging from 948K to 1048K. The total combustion time is dependent on the ignition delay time and the burning rate of the droplet after ignition. Figure 6 shows that pure glycerol had longer total combustion time due to its longer ignition delay time and lower burning rate as compared to the diesel, biodiesel and ethanol.

246 The total combustion time of the crude glycerol was shorter than that of pure glycerol. Although the
247 ignition delay time of crude glycerol was longer than that of pure glycerol as shown in Figure 6, the
248 crude glycerol droplet had a much higher burning rate than pure glycerol, as discussed in the
249 previous section, which consequently lead to shorter total combustion time for the crude glycerol.
250 Figure 7 compares the flame standoff ratio profiles as a function of time for the different fuels tested
251 at 948K and 1023K, measured from ignition to the end of combustion. The flame standoff ratio is
252 an important parameter in characterising the combustion process of single droplets, such as the
253 flame size, whether the combustion is quasi-steady, and fuel vapour accumulation rate in the
254 boundary layer of the droplet [38, 39]. Shown in Figure 7, the flame standoff ratio of the fuels
255 studied varies over time. For crude glycerol, diesel and biodiesel, the flame standoff ratio slightly
256 decreased shortly after ignition and then continuously increased with the increase being faster
257 towards the end of the droplet lifetime. Before the ignition occurred, the fuel vapour gradually
258 accumulated in the boundary layer around the droplet due to fuel evaporation, resulting in a slight
259 temperature reduction in the gas phase due to evaporative cooling [40]. As ignition occurred, the
260 flame was formed, and the temperature in the boundary layer increased accordingly [40]. The
261 increasing gas temperature exponentially raised the rate of combustion, which in turn drove the
262 flame gradually towards the droplet surface, causing a decrease in the flame standoff ratio [40].
263 The increase of the flame standoff ratio afterwards mainly attributed to the fuel vapour
264 accumulation effects [38]. The instantaneous rate of fuel vaporisation is greater than that of fuel
265 consumption in the flame front, resulting in accumulation of the fuel vapour in the inner region of
266 the flame which slightly pushed the flame away from the droplet surface [33, 41, 42]. Similar
267 behavior of flame standoff ratio has been observed for alkane fuels [43]. For pure glycerol and
268 ethanol, the flame standoff ratio remained constant during the combustion. The high oxygen content
269 in both pure glycerol and ethanol might suppress the soot precursors to form carbon atoms [14, 15,
270 33], resulting in a smaller and less sooty flame observed.

The different trends of the flame standoff ratio during combustion process for crude glycerol and pure glycerol was caused by the impurities contained in the crude glycerol. As discussed previously, methanol and water affected the ignition delay time, total combustion time and burning rate. It follows that the impurities also affected the flame size, pushing the flame front outwards a little. It is can also be seen from Figure 7 that the flame standoff ratio decreased slightly with increasing ambient temperature. At a given temperature, the descending order of the flame standoff ratio from the largest follows: diesel > biodiesel > crude glycerol > ethanol > pure glycerol.

4. Conclusions

The ignition delay times, total combustion times, burning rates, and flame standoff ratios of single droplets of a crude glycerol, pure glycerol, a petroleum diesel, a biodiesel and ethanol were experimentally studied and compared, as follows:

- The ignition delay time and total combustion time decreased while, correspondingly, the burning rate increased with increasing air temperature.
- At a given temperature, the ignition delay time and total combustion time followed the descending order of pure glycerol > crude glycerol > ethanol > biodiesel > diesel.
- The crude glycerol showed the highest burning rate while the pure glycerol the lowest among the fuels studied. The presence of methanol and water in the crude glycerol was shown to have a profound influence on the combustion characteristics of the crude glycerol. While methanol reduced the ignition delay time, water would suppress the ignition by increasing the heat capacity of the glycerol, evaporating prior the glycerol on the droplet surface and delaying the fuel accumulation in the boundary of the glycerol droplets. Methanol and water reduced the total combustion time of crude glycerol droplets by increasing the burning rate, which was caused by the decrease of latent heat and boiling point, the increase of vapour pressure and the micro-explosion.

- The flame standoff ratio slightly decreased after ignition for all fuels and afterwards continuously increased with time for crude glycerol, diesel and biodiesel but remained constant for the pure glycerol and ethanol.

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418 **Figure Captions**

419 Figure 1 A schematic diagram of the apparatus for experimentation of single droplet combustion

420 Figure 2 A typical structure and characteristics of a burning droplet: (a) a schematic diagram of a
421 typical single droplet enveloped by a flame; (b) a typical image of an actual burning
422 glycerol droplet; (c) colour intensity profile along the indicated line shown on (b)

423 Figure 3 Measured temporal variation of the square of the normalized droplet diameter of fuels
424 during combustion

425 Figure 4 Comparison of the burning rates of pure glycerol, crude glycerol, biodiesel, diesel, and
426 ethanol

427 Figure 5 The ignition delay times at different temperatures for droplets of different fuels

428 Figure 6 Total combustion times at different temperatures of single droplets of different fuels

429 Figure 7 Flame standoff ratios for different fuels at 948K and 1023K

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463 Figure 6 Total combustion times at different temperatures of single droplets of different fuels

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465 Figure 7

466
467 Figure 7 Flame standoff ratios for different fuels at 948K and 1023K

468

469 **Table Captions**

470 Table 1 Key physical and thermodynamic properties of fuels tested

471 Table 2 The properties of crude glycerol

472

473

474 Table 1 Key physical and thermodynamic properties of fuels tested

Fuel property	Fuels				
	Crude glycerol	Pure glycerol	Biodiesel	Diesel	Ethanol
Formula	n/a	C ₃ H ₈ O ₃	n/a	n/a	C ₂ H ₆ O
Molecular weight (gmole ⁻¹)	n/a	92.09	~308	~200	46.07
Density (kgm ⁻³)	1205*	1261*	878*	840*	789*
Heating value (MJkg ⁻¹)	14.84*	18*	42.2*	44.8*	29.7*
Boiling point (K)	403*	563*	628*	533*	350*
Cetane number	~6.7	5	51.7	52	12
Heat of vaporization (MJkg ⁻¹)	n/a	0.67	0.30	0.34	0.92
Viscosity (mPa.s)	1200*	1500*	3.42*	2.02*	1.144*
Auto-ignition temperature (K)	673*	796*	646*	588*	638*
Flash point (K)	463*	450*	422*	328*	282*
Specific heat capacity (kJ kg ⁻¹)	~2.8	2.43	2.2	1.8	2.72
Thermal conductivity (Wm ⁻¹ K ⁻¹)	n/a	0.2900	0.1490	0.1169	0.2040
Adiabatic flame temperature (K @973K)	n/a	2201	2291	2413	2078
Stoichiometric					
fuel/air ratio (w/w)	n/a	5	11	12	9
Spalding number	n/a	4	9	8	3

475 * indicates that the data were measured by the authors. The other data were taken from the literature
 476 [17-19].

477

478

479 Table 2 The properties of crude glycerol

480	<i>Composition</i>	<i>(wt%)</i>
	Free glycerol	68.2
481	Methanol	2.2
	Water	22.6
482	Soap	1.3
	Fatty acid methyl ester (FAME)	0.5
483	Free Fatty Acids (FFA)	1.8
484	Ash	3
	<i>Elemental Analysis</i>	<i>(wt%)</i>
	C	31.85
	H	10.25
	N	0.32
	Na	0.76
	P	0.11
	S	0.02

485

486

**Ignition and Combustion Characteristics of Single Droplets of a
Crude Glycerol in Comparison with Pure Glycerol, Petroleum Diesel,
Biodiesel and Ethanol**

Hendrix Y. Setyawan, Mingming Zhu*, Zhezi Zhang and Dongke Zhang
Centre for Energy (M473), The University of Western Australia, 35 Stirling Highway,
Crawley, WA 6009, Australia

(A manuscript offered to “*Energy*”)

* Corresponding author:

Dr Mingming Zhu

Email: mingming.zhu@uwa.edu.au

Phone: +61 8 6488 5528

Fax: +61 8 6488 7622

Abstract

The ignition and combustion characteristics of single droplets of a crude glycerol were experimentally studied and compared with those of pure glycerol, a petroleum diesel, a biodiesel, and ethanol. A single fuel droplet was suspended at the tip of a silicon carbide fibre undergoing heating, ignition and combustion in an electrically heated horizontal tube furnace at an air temperature ranging from 948K to 1048 K. The ignition and combustion behaviour of the droplet were recorded using a CCD camera. Ignition delay time, total combustion time, burning rate, and flame standoff ratio were estimated. At a same temperature, the ignition delay time and total combustion time followed the order of pure glycerol > crude glycerol > ethanol > biodiesel > diesel, while the burning rate followed the order of crude glycerol > diesel > biodiesel > ethanol > pure glycerol, suggesting that the impurities, mainly water and methanol, had a profound influence on the combustion characteristics of crude glycerol. The flame standoff ratio slightly decreased after ignition but continuously increased with time afterwards for the crude glycerol and remained almost unchanged for the pure glycerol, indicating the significant influence of impurities on the quasi-steadiness of the flame.

Keywords: Biodiesel; Combustion Characteristics; Diesel; Ethanol; Glycerol; Ignition

1. Introduction

Biodiesel, an alternative liquid transport derived from renewable sources of fatty acids such as vegetable oils and animal tallow, has become of worldwide interest, often advocated by environmental and conservation movements and special interest groups [1, 2]. The global biodiesel production has increased rapidly in recent years, reaching 28.3 million metric tonnes (MMT) in 2014 [3]. A by-product of the biodiesel production process is glycerol and, with approximately 0.1 kg of crude glycerol being created for every 1 kg of biodiesel produced [4], the global crude glycerol production in 2014 was estimated to be 2.8 MMT, which is significantly greater than the glycerol market, currently at 2 MMT globally, could possibly absorb [4]. Hence, it is necessary to search for alternative uses of the overproduced glycerol.

A number of processes, such as pyrolysis, fermentation and steam reforming have been proposed to convert glycerol into products of certain values such as hydrogen [5], acrolein [6], syngas [7], and chemicals [8]. However, these conversion technologies are either expensive, or the product volume and value too low, or require large throughputs to make an economical sense, while the crude glycerol supplies are incompatibly small and scattered over different regions.

However, direct combustion of glycerol in utility boilers or internal combustion engines for combined heat and power and heat (CHP) is a plausible alternative [9]. Direct combustion of glycerol offers a few advantages over the other technologies such as simplicity, flexible scale operation, maturity, and cost effectiveness.

As an alternative fuel, glycerol has been tested for combustion using burners and diesel engines [9, 10]. Pure glycerol was shown to burn effectively in a heating boiler with the use of a high-swirl refractory burner [10]. In a set of tests with a diesel engine generator rated at 43 kW, the generator fuelled with pure glycerol produced a continuous power of 41.5 kW [9]. However, the combustion of glycerol is inherently challenging due to the high viscosity, low energy density, high auto-ignition temperature, and low heating value [11].

In addition, the combustion of crude glycerol is further complicated by the impurities brought in during the biodiesel production process, which would be too costly to remove. The impurities include, depending on the process and operating conditions, methanol (6.2– 12.6 wt%), water (6.5– 28.8 wt%), soap (up to 26.5 wt%), fatty acid methyl ester (FAME) (up to 28.8 wt%), glycerides (up to 7.0 wt%), free fatty acid (FFA) (up to 3.0 wt%), as well as ash (2.7 – 3 wt%) [12]. Of particular note is that crude glycerol also contains high concentrations of sodium as a result of excess catalyst used in the transesterification process [12], which could have significant and adverse effect on the flame, combustion equipment, and environment [13]. Thus, in order to better utilise the glycerol as a fuel, it is important to study its ignition and combustion characteristics in comparison to those of other, better understood fuels and to especially understand the effect of the impurities on the combustion behaviour of crude glycerol.

The present preliminary experimental work was aimed to gain a fundamental understanding of the ignition and combustion behaviour of single droplets of crude glycerol and compare them with those of several well studied liquid fuels including diesel biodiesel and ethanol. The experimentation was performed by suspending single droplets in hot air in an electrically heated furnace. The ignition delay time, combustion time, burning rate, and flame standoff ratio were determined with the aid of a CCD camera imaging technique. The effect of air temperature on the ignition and combustion characteristics was studied. This approach would provide a useful means to understand the combustion characteristics of glycerol, which would ultimately lead to better use of crude glycerol in combustion applications. The results would shed light on the feasibility of utilising crude glycerol in diesel engines for power generation as one of the simplest and easiest means of crude glycerol utilisation. Since diesel, biodiesel and ethanol are well studied for their application in diesel engines [14 – 16], comparing the ignition and combustion characteristics of crude glycerol against these fuels will also provide essential guidance in utilising glycerol in diesel engines.

99 2. Experimental

100 Employed in the current study were pure glycerol and ethanol acquired from Sigma Aldrich (Perth
101 Australia), a crude glycerol and biodiesel provided by Wilmar International (Gresik, Indonesia) and
102 a petroleum diesel (Caltex No.2) obtained from a local service station. The chemical compositions
103 and physical properties of these fuels are shown in Table 1 and the composition of the crude
104 glycerol is listed in Table 2.

105 The ignition and combustion behavior of these fuels were studied using a single droplet combustion
106 technique as schematically shown in Figure 1 and described elsewhere [20, 21]. Briefly, the
107 experimental set-up consists of a droplet suspension system, a horizontal tube electric furnace (600
108 mm in length and 40 mm in diameter) with temperature control for providing a hot air environment,
109 a step motor for delivering the droplet into the furnace, and a CCD camera for capturing the images.
110 In a typical experimental run, the furnace was preheated to a desired temperature from 948K to
111 1048K, the typical combustion temperatures in diesel engines. A droplet was produced by a micro
112 pipette of 10 μ L and was deposited on the tip of a silicon carbide fibre of 0.142 mm in diameter.

113 Aided by the step motor, the droplet was transported to the centre of the furnace at a linear velocity
114 of 1ms^{-1} . The high speed CCD camera with an exposure time of $1000\mu\text{s}$ (50fps) captured the time-
115 sequenced images of the droplet during its ignition and combustion process. The step motor and
116 camera were controlled from a computer. In order to capture the evolution of the droplet size, a
117 halogen lamp was used to backlit the images of the burning droplet. Note that when the droplet was
118 attached to the tip of the silicon carbide fibre, it was deformed to an ellipsoidal shape due to gravity.
119 The equivalent droplet diameter was determined from the height (d_{max}) and width (d_{min}) of the
120 droplet measured from the CCD images according to the following equation [22, 23]:

$$121 \quad d = \sqrt[3]{(d_{\text{max}})(d_{\text{min}})^2} \quad (1)$$

122 The initial equivalent droplet diameter was approximately 1 mm.

The ignition delay time and total combustion time of a burning droplet were estimated by analysing the CCD images taken without backlit. The ignition was defined as the moment when the first visible flame was observed [23 – 27]. The ignition delay time (t_i) was defined as the time difference between the moment when the droplet reached the centre of the furnace and the ignition. The period from the ignition until the extinction of the flame was taken as burnout time (t_b). The total combustion time (t_c) was the sum of ignition delay time and the burnout time.

The process of the single droplet combustion may be described as follows. When a droplet (R_d) is subjected to the hot ambience at a certain temperature (T), it starts to vaporise. The vapour diffuses outwards and mixes with oxygen. Once the ignition criterion is met, the ignition occurs and a thin flame is formed enveloping the droplet. Ideally, there is no oxygen inside the flame front and there are no unburnt fuel species outside the flame. As combustion proceeds, the droplet size shrinks continuously through evaporation due to the heat received from the flame [28].

Figure 2 (a) schematically shows a generic structure of a burning droplet with a diffusion flame enveloping the droplet. The definition of the droplet radius and flame radius is also shown. The flame radius of the droplet (R_f) was determined by measuring the radius of the flame, the distance from the centre of droplet to the flame front, during the stable combustion phase, which is approximately 0.1 - 0.3 s after ignition.

Figure 2 (b) shows a real image of an actual burning droplet of pure glycerol. A horizontal line passing through the centre of the droplet was drawn and displayed on Figure 2(b) and the colour intensity along the line shown in Figure 2(b) was estimated from monochrome signal using a self-developed Matlab code. The result was shown in Figure 2(c). The centre of the line corresponds to the position of fibre and the position at which the colour intensity reached the highest was taken as the flame front. The flame should ideally be symmetric but the shape of the actual flame deformed a little throughout the experiment because of buoyancy induced convection. The sudden decrease of the colour intensity at the centre was due to the presence of the fibre. With the actual width of the fibre (0.142 mm) being used as a reference, the actual flame radius was then calculated.

149 The backlit images of a burning droplet were used to determine the burning rate. Backlit by the
150 halogen lamp, the rate of imaging was set at 200 fps. From the time sequenced images and with the
151 aid of Matlab, the burning rate (k) then was determined using the d^2 -Law [28]:

$$152 \quad k = \frac{d(d^2)}{dt} \quad (2)$$

153 3. Results and Discussion

154 The ignition and combustion characteristics of the crude glycerol, including the time-sequenced
155 droplet size, ignition delay time, total combustion time, burning rate, flame standoff ratio, and flame
156 radius, were compared to those of pure glycerol, biodiesel, diesel and ethanol.

157 Figure 3 shows the temporal variation of the square of the normalised droplet diameter $(d/d_0)^2$ at
158 973K for the different fuels studied. The droplet sizes for the five fuels respectively were measured
159 from the moment of occurrence of ignition until the completion of combustion. A significant
160 observation can be made from Figure 3, that is, the linear trend of reduction in the droplet size
161 during combustion, implying that the droplet combustion conformed to the d^2 -law [28].

162 It was also observed that the droplet size fluctuated noticeably for the crude glycerol but not so
163 significant for the other fuels. This is mainly due to the fact that the crude glycerol contained
164 several impurities including methanol and water whose boiling points were 337 K and 373 K
165 respectively, lower than that of glycerol, at 563 K. Table 2 shows that the crude glycerol contains
166 2.2% methanol and 22.6% water. When the crude glycerol droplet was heated and the temperature
167 of the droplet reached the boiling points of methanol and water, which would then evaporate before
168 glycerol reached its boiling point, resulting in the formation of bubbles of methanol and water
169 steams [29, 30]. The bubbles thus formed would grow, collapse and even explode, leading the
170 observed fluctuations of the shape and size of the droplet during combustion [31].

The temporal variation curves of the droplet size in Figure 3 were linearly fit to obtain the burning rates of the five fuels following d^2 -law, respectively. The theoretical burning rates (k_c) of the droplets at 973K were also calculated based on the classic d^2 -law [28]:

$$k_c = \frac{8\lambda_g}{c_{p,g}\rho} \ln(1+B) \quad (3)$$

where λ_g is the thermal conductivity of air, $c_{p,g}$ the specific heat of air/vapour mixture, B the Spalding number, and ρ the fuel density.

Figure 4 shows good agreements between the theoretical and experimental burning rates of the five fuels, with only small deviations. These deviations are expected due to the experimental errors, simplification of the model, complexity of the actual droplet combustion processes, and effect of the fibre [32].

Two pieces of information of interest were obtained from Figure 4. Firstly, the burning rate of pure glycerol was lower than that of diesel, biodiesel and ethanol. Referring to the Equation 3, the burning rate is mainly influenced by the density and Spalding transfer number of the fuel since the thermal conductivity and heat capacity of fuel vapour/air mixture varied, insignificantly, with temperature [28]. The density of pure glycerol, diesel, biodiesel, and ethanol are 1261 kg m^{-3} , $820\text{--}850 \text{ kg m}^{-3}$, 883 kg m^{-3} , and 789 kg m^{-3} , respectively and their calculated Spalding transfer numbers are 4, 9, 8, and 3 respectively. As expected, the burning rate of pure glycerol was indeed lower than the other fuel as it is denser and has a relatively low Spalding number.

The second interesting observation from Figure 4 is that the burning rate of the crude glycerol was the highest among the fuels tested, suggesting the impurities had accelerated the burning rate. The crude glycerol contained methanol, water, sodium (soap) and FAME, all of which contributed to the higher burning rate [29, 30]. Equation 3 implies that the burning rate of a fuel increases as the latent heat of evaporation and fuel boiling point decrease [28]. The latent heat of evaporation of crude glycerol was higher than that of pure glycerol as the major impurities (methanol and water) have higher latent heat of vaporisation than glycerol. Due to the differences in latent heats, the

temperature rise would be faster in glycerol compared to methanol and water. However, the vapour pressures of methanol and water are higher than that of glycerol. Consequently, methanol and water vaporized faster than glycerol at the surface of the droplet, leading to the high observed burning rate of crude glycerol.

The other impurities such as FAME, sodium and ash may also affect the burning rate of glycerol. For instance, the burning rate of FAME, the main constitute of biodiesel is slightly higher than that of glycerol as indicated in Figure 4. The sodium addition in glycerol may enhance the soot formation propensity, which will in turn affect the burning rate [13, 16, 33]. However, ~~it is speculated that~~ the effect of these impurities on the burning rate would be very limited due to their very low concentrations in the crude glycerol as shown in Table 2.

Figure 5 compares the results of ignition delay time of the fuels at different temperatures. The ignition delay time decreased with increasing furnace temperature as expected. At the same temperature, the ignition delay times followed the order of pure glycerol > crude glycerol > ethanol > biodiesel > diesel and this order remained unchanged in the temperature range from 948K to 1048K.

The ignition delay time is a result of pre-combustion reactions in the fuel/air mixture, consisting of a physical delay (droplet heating, evaporation, molecular diffusion and mixing with air) and a chemical delay (subsequent chemical reaction of gas phase between fuel and oxygen) [24, 25, 34]. The ignition delay time of a fuel can also be correlated with the Cetane number of the fuel [35]. A higher Cetane number affords a shorter ignition delay [35]. Table 1 displays that the Cetane number of pure glycerol is 5, being the lowest as compared to that of biodiesel (51.7), diesel (47.4 - 63.9), and ethanol (12), respectively. The crude glycerol had a slight higher Cetane number (6.7) than pure glycerol. The Cetane numbers of those fuels were consistent with the result of the ignition delay times measured using single droplet combustion method. Glycerol, which has a low Cetane number, required more time to burn, whereas the other fuel ignited faster.

It is also evident that the ignition delay time of the crude glycerol was slightly longer than that of pure glycerol, particularly at higher temperatures. ~~Speculation as to reasons, the, due to the presence of~~ impurities such as water, methanol, sodium and FAME ~~might change the ignition delay time of crude glycerol. Our previous studies found that Water-water~~ can significantly delay the ignition time of glycerol droplets [3036]. Due to its low boiling points, water on the surface of the droplet would evaporate prior to the evaporation of glycerol and the water vapour (steam) dilutes the glycerol/air mixture in the gas phase, thus it would require a longer time for the ignition to occur when more fuel is accumulated in the boundary layer of the droplet, resulting in a delay of the ignition of glycerol. In the interior of the crude glycerol droplets, water would delay the increase of temperature by increasing heat capacity of the droplets as the heat capacity of water is $4200 \text{ Jkg}^{-1}\text{K}^{-1}$, much higher than that of glycerol ($2400 \text{ Jkg}^{-1}\text{K}^{-1}$). Also, it is well known that the presence of water in the hydrocarbon fuels could suppress the ignition [36]. Likewise, the water content in the crude glycerol would delay the ignition as observed in the present experimentation. On the contrary, methanol, sodium and FAME would accelerate the ignition time of glycerol [29]. Methanol vapour is combustible which could result in a shorter ignition time of crude glycerol droplets, but its flame may not be visible. It was also reported in the literature that the ignition time of liquid sodium droplets was stable under 0.2s in an air temperature above 800K [37]. However, their effects on the ignition delay time were suspected to be insignificant due to their low concentrations in the crude glycerol.

Figure 6 displays the total combustion times of the fuels at different temperatures. Overall, the total combustion time decreased when temperature increased. Pure glycerol showed the longest total combustion time followed by the crude glycerol, ethanol, biodiesel and diesel. This trend was the same at temperatures ranging from 948K to 1048K. The total combustion time is dependent on the ignition delay time and the burning rate of the droplet after ignition. Figure 6 shows that pure glycerol had longer total combustion time due to its longer ignition delay time and lower burning rate as compared to the diesel, biodiesel and ethanol.

247 The total combustion time of the crude glycerol was shorter than that of pure glycerol. Although the
248 ignition delay time of crude glycerol was longer than that of pure glycerol as shown in Figure 6, the
249 crude glycerol droplet had a much higher burning rate than pure glycerol, as discussed in the
250 previous section, which consequently lead to shorter total combustion time for the crude glycerol.
251 Figure 7 compares the flame standoff ratio profiles as a function of time for the different fuels tested
252 at 948K and 1023K, measured from ignition to the end of combustion. The flame standoff ratio is
253 an important parameter in characterising the combustion process of single droplets, such as the
254 flame size, whether the combustion is quasi-steady, and fuel vapour accumulation rate in the
255 boundary layer of the droplet [38, 39]. Shown in Figure 7, the flame standoff ratio of the fuels
256 studied varies over time. For crude glycerol, diesel and biodiesel, the flame standoff ratio slightly
257 decreased shortly after ignition and then continuously increased with the increase being faster
258 towards the end of the droplet lifetime. Before the ignition occurred, the fuel vapour gradually
259 accumulated in the boundary layer around the droplet due to fuel evaporation, resulting in a slight
260 temperature reduction in the gas phase due to evaporative cooling [40]. As ignition occurred, the
261 flame was formed, and the temperature in the boundary layer increased accordingly [40]. The
262 increasing gas temperature exponentially raised the rate of combustion, which in turn drove the
263 flame gradually towards the droplet surface, causing a decrease in the flame standoff ratio [40].
264 The increase of the flame standoff ratio afterwards mainly attributed to the fuel vapour
265 accumulation effects [38]. The instantaneous rate of fuel vaporisation is greater than that of fuel
266 consumption in the flame front, resulting in accumulation of the fuel vapour in the inner region of
267 the flame which slightly pushed the flame away from the droplet surface [33, 41, 42]. Similar
268 behavior of flame standoff ratio has been observed for alkane fuels [43]. For pure glycerol and
269 ethanol, the flame standoff ratio remained constant during the combustion. The high oxygen content
270 in both pure glycerol and ethanol might suppress the soot precursors to form carbon atoms [14, 15,
271 33], resulting in a smaller and less sooty flame observed.

The different trends of the flame standoff ratio during combustion process for crude glycerol and pure glycerol was caused by the impurities contained in the crude glycerol. As discussed previously, methanol and water affected the ignition delay time, total combustion time and burning rate. It follows that the impurities also affected the flame size, pushing the flame front outwards a little. It is can also be seen from Figure 7 that the flame standoff ratio decreased slightly with increasing ambient temperature. At a given temperature, the descending order of the flame standoff ratio from the largest follows: diesel > biodiesel > crude glycerol > ethanol > pure glycerol.

4. Conclusions

The ignition delay times, total combustion times, burning rates, and flame standoff ratios of single droplets of a crude glycerol, pure glycerol, a petroleum diesel, a biodiesel and ethanol were experimentally studied and compared, as follows:

- The ignition delay time and total combustion time decreased while, correspondingly, the burning rate increased with increasing air temperature.
- At a given temperature, the ignition delay time and total combustion time followed the descending order of pure glycerol > crude glycerol > ethanol > biodiesel > diesel.
- The crude glycerol showed the highest burning rate while the pure glycerol the lowest among the fuels studied. The presence of methanol and water in the crude glycerol was shown to have a profound influence on the combustion characteristics of the crude glycerol. While methanol reduced the ignition delay time, water would suppress the ignition by increasing the heat capacity of the glycerol, evaporating prior the glycerol on the droplet surface and delaying the fuel accumulation in the boundary of the glycerol droplets. Methanol and water reduced the total combustion time of crude glycerol droplets by increasing the burning rate, which was caused by the decrease of latent heat and boiling point, the increase of vapour pressure and the micro-explosion.

- The flame standoff ratio slightly decreased after ignition for all fuels and afterwards continuously increased with time for crude glycerol, diesel and biodiesel but remained constant for the pure glycerol and ethanol.

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419 **Figure Captions**

420 Figure 1 A schematic diagram of the apparatus for experimentation of single droplet combustion

421 Figure 2 A typical structure and characteristics of a burning droplet: (a) a schematic diagram of a
422 typical single droplet enveloped by a flame; (b) a typical image of an actual burning
423 glycerol droplet; (c) colour intensity profile along the indicated line shown on (b)

424 Figure 3 Measured temporal variation of the square of the normalized droplet diameter of fuels
425 during combustion

426 Figure 4 Comparison of the burning rates of pure glycerol, crude glycerol, biodiesel, diesel, and
427 ethanol

428 Figure 5 The ignition delay times at different temperatures for droplets of different fuels

429 Figure 6 Total combustion times at different temperatures of single droplets of different fuels

430 Figure 7 Flame standoff ratios for different fuels at 948K and 1023K

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466 Figure 7

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468 Figure 7 Flame standoff ratios for different fuels at 948K and 1023K

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470 **Table Captions**

471 Table 1 Key physical and thermodynamic properties of fuels tested

472 Table 2 The properties of crude glycerol

473

474

475 Table 1 Key physical and thermodynamic properties of fuels tested

Fuel property	Fuels				
	Crude glycerol	Pure glycerol	Biodiesel	Diesel	Ethanol
Formula	n/a	$C_3H_8O_3$	n/a	n/a	C_2H_6O
Molecular weight ($gmole^{-1}$)	n/a	92.09	~308	~200	46.07
Density [‡] (kgm^{-3})	1205 [*]	1261 [*]	878 [*]	840 [*]	789 [*]
Heating value [‡] ($MJkg^{-1}$)	14.84 [*]	18 [*]	42.2 [*]	44.8 [*]	29.7 [*]
Boiling point [‡] (K)	403 [*]	563 [*]	588-630-628 [*]	433- 633-533 [*]	350 [*]
Cetane number	~6.7	5	51.7	52	12
Heat of vaporization ($MJkg^{-1}$)	n/a	0.67	0.30	0.34	0.92
Viscosity ($mPa.s$) [‡]	1200 [*]	1500 [*]	3.42 [*]	2.02 [*]	1.144 [*]
Auto-ignition temperature [‡] (K)	673 [*]	796 [*]	646 [*]	588 [*]	638 [*]
Flash point [‡] (K)	463 [*]	450 [*]	422 [*]	328 [*]	282 [*]
Specific heat capacity ($kJ kg^{-1}$)	~2.8	2.43	2.2	1.8	2.72
Thermal conductivity ($Wm^{-1}K^{-1}$)	n/a	0.2900	0.1490	0.1169	0.2040
Adiabatic flame temperature (K @973K)	n/a	2201	2291	2413	2078
Stoichiometric fuel/air ratio (w/w)	n/a	5	11	12	9
Spalding number	n/a	4	9	8	3

476 * indicates that the data were measured by the authors. The other data were taken from the literature
477 [17-19].
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479

480 Table 2 The properties of crude glycerol

481	<i>Composition</i>	<i>(wt%)</i>
	Free glycerol	68.2
482	Methanol	2.2
	Water	22.6
483	Soap	1.3
	Fatty acid methyl ester (FAME)	0.5
484	Free Fatty Acids (FFA)	1.8
485	Ash	3
	<i>Elemental Analysis</i>	<i>(wt%)</i>
	C	31.85
	H	10.25
	N	0.32
	Na	0.76
	P	0.11
	S	0.02

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