Combustion characteristics of a Pinewood Pyrolysis Bio-oil droplet at high ambient temperatures

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1 Introduction

Fast pyrolysis has been used for longer and can result in products of different characteristics when using varied reactors or source materials [1]. Because bio-oils produced using fast pyrolysis tend to considerably affect the power equipment that uses them, various studies have been conducted to determine how their undesirable effect on such equipment can be decreased; the most notable solutions so far proposed include physical, catalytic, and chemical upgrading [2,3]. Although bio-oils generally have very different properties from petroleum fuels, most commercially available bio-fuels are fairly similar to them and thus are easily applied to existing power equipment. Because existent burner designs are sensitive to the quality of bio-oil used, which can make burners prone to ignition, flame detection, and flame stabilization problems, an adequate bio-oil burner design and the corresponding bio-oil composition have become the focus of numerous studies [4,5]. To this end, our previous study [6] used fast pyrolysis to decompose various biomass residues and investigated the bio-oil properties under varied operating parameters. This was followed by a diesel engine test using a diesel fuel diluted with various concentrations of bio-oil [7]. The results indicated that the addition of bio-oil both enhanced the diesel's combustion efficiency and reduced pollutant emissions: however, as the bio-oil concentration and operating time were increased, the efficiency of the diesel engine decreased, with slagging produced in its cylinders. Therefore, bio-oil in varying concentrations was subsequently added to kerosene for a spray combustion test through actual measurement [8] and numerical simulation [9]. These results indicated that the presence of bio-oil not only changed the properties of the spray, it also shortened the length of the flame produced, which was mainly caused by the premature ignition of volatile substances in the bio-oil. To verify the added bio-oil's effect on spray combustion, the present study conducted a combustion test on multicomponent droplets of a bio-oil/kerosene mixture [10] and

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identified numerous phenomena including micro-explosions, puffing, and slagging that could be attributed to how the composition of the bio-oil induced combustion behavior and speed different from those of single-component droplets. With the objective of producing bio-oil of high quality and quantity using pyrolysis, the study further investigated the effect of fluidization velocity on the yield [6] and quality [11] of produced bio-oil by adopting various fluidization velocities in a fluidized bed reactor. Emulsification technology that enables the adequate mixing of bio-oil and petroleum fuels is essential for this purpose [7,12,13].

From the aforementioned studies, the spray combustion properties of bio-oil are clearly affected by the varied pyrolysis processes that the biomass is subjected to and the varied petroleum fuels that the bio-oil is mixed with. If the difference between the different bio-oil/petroleum fuel mixtures used for spray combustion is to be investigated, the magnitude of combustion is a critical factor that substantially affects the spray combustion achieved. To alleviate problems concerning bio-oil combustion, the present study mixed butanol with bio-oil produced through the slow pyrolysis of pinewood. The burning rate and thermochemical properties of the resulting mixtures were determined, and the properties of bio-oil created through the pyrolysis of biomass were elucidated, as well as the combustion properties of the mixture's multicomponent droplets.

2 Approaches

This study used slow pyrolysis to produce bio-oil from pinewood. A droplet combustion test platform were then used to investigate the thermochemical characteristics of the bio-oil/butanol mixture.

Figure 1illustrates the test platform used in the droplet combustion tests. The system consisted primarily of a droplet generator, a combustion chamber, an igniter, and an image capturing system. First, a digital delay generator sent a pulsating direct current to activate the piezoelectric chips, whose deformation would (in a technique similar to ink-jet printing) squeeze the fuel in the tank into the droplet generator. The fuel mixture was ejected from the glass nozzle in the form of a droplet approximately 0.9 mm in diameter, which was then caught and fixed in place by crossed (90°) low-thermal-conductive ceramic fibers in the combustion chamber. A glow plug igniter (operated at 12 V, 7 A, and 84 W) was subsequently extended beneath the droplet for $0.3-0.8 \pm 0.3$ s and then quickly withdrawn to ignite the droplet. The resultant combustion was then captured using a Phantom v7.3 high-speed camera using backlighting method. The high-speed camera operated at 1000 fps and had a resolution of 384×384 pixels, spatial resolution of 0.022 mm/pixel, and exposure time of 1 µs. A Phantom M310 color high-speed camera with a 4× optical lens was also used to capture magnified images at 2000 fps, with a resolution of 512×512 pixels and exposure time of 100 µs.

3 Results and Discussions

The present study produced bio-oil through the pyrolysis of pinewood and measured the characteristics of bio-oil using methods such as ultimate and proximate analyses. The bio-oil was then mixed with butanol, and droplet combustion tests were performed to determine the bio-oils properties and explore the relationship between the evaporation and combustion behavior of bio-oil droplet.

3.1 Fuel Preparation

Pyrolysis partially converted pinewood, which had been shredded, sieved, and dried in advance, to bio-oil, the properties of which are listed in Table 1. Specifically, the bio-oil had relatively low moisture content (8.1 wt.%) but a high heat value (LHV, 17.12 MJ/kg) and viscosity (7600 cP). The bio-oil had a pH of approximately 3, indicating that it would corrode mechanical components and cause malfunctions if used alone. Certain properties of butanol nullify the need for an emulsifier in its mixture with the bio-oil, which

together with the increased pH of a bio-oil/butanol mixture compared with pure bio-oil indicates that a bio-oil/butanol mixture would be suitable for fueling power equipment.

3.2 Photographic of bio-oil/butanol droplet combustion

Figure 2 illustrates the combustion of the bio-oil/butanol droplets. The diameters of the droplets were between 0.92 and 0.97 mm. As the igniter approached the droplet, the droplet suddenly burst into flames because of the intense heat, and its diameter gradually decreased as it burned. BO0 exhibited steady combustion. Compared with BO0, BO10 took almost an equal amount of time to ignite but the droplet's shape became irregular at 0.98 s/mm², which clearly indicated the combustion of the residue. Increasing the bio-oil concentration further lengthened the time needed for the droplet to ignite and the duration of the combustion. Puffing occurred to the BO30 droplet as early as 1.15 s/mm².

3.3 Change in droplet diameters of the various mixtures

The images in Figure 2 reveal that in some circumstances the droplet did not shrink with combustion time and in at least one instance even expanded noticeably. Figure 3 records the changes in the diameter of the various droplets from first ignition at 723 K to their gradual shrinkage owing to evaporation caused by combustion. The BO0, BO10, BO30, and BO50 droplets all began with an initial diameter of 0.94 ± 0.03 mm. The combustion process occurred in four distinct stages: the heating stage (I), steady burning stage (II), swelling stage (III), and residue burning stage (IV). According to Figure 3a, the stage I of BO0 was fairly short, which can be attributed to the high volatility and low boiling point of butanol; the droplet must have been ignited as soon as the igniter approached (50 µs), after which the droplet burned steadily until it was all consumed. The stage I (heating) of BO10 was longer than for BO0, but stage II was nearly the same length, and a substantial stage III (expansion and puffing) occurred from 1.22 s/mm² onward, caused by the heavy fraction in the bio-oil that changed the butanol's boiling point (Figure 3b). The droplet's different composition and volatility is also supported by the data in Figure 2, in which the droplet was observed to leave a residue after burning. Stage I for the BO50 droplet was notably longer than those of the other droplets, with ignition only occurring after heated for 1400 µs.

These results suggest that the water, volatiles, non-saturated and saturated aliphatic acids, and aromatics in the bio-oil all had a different effect on the combustion of the droplet, as did the concentration of bio-oil in the mixture. The droplet evaporated and burned mostly because of the non-saturated and saturated aliphatic acids in the bio-oil and some of the aromatics. Micro-explosions were mostly caused by moisture, and some of the aromatics polymerized during evaporation, leading to residue formation and subsequent combustion. Aside from the effect on droplet composition, different concentrations of bio-oil changed the internal and external heat transfer characteristics of the droplet, which is also a crucial factor in droplet combustion.

3.4 Internal convection of droplets with varying bio-oil concentrations

Figure 4 displays the combustion of a droplet observed through the $4 \times \text{lens}$ of a high-speed camera. The internal heat transfer mechanism, altered by the mixture's differences in volatility, can plainly be discerned from the images. The droplet diameter was decreased slightly upon heating because the light fraction of the droplet (i.e., butanol) evaporated first. Stage I was extended when the butanol percentage in the droplet was decreased. The droplet was ignited after 1.42 s, after which it burned steadily because of the high volatility of butanol. By the time the droplet was heated beyond boiling point of butanol, the boiling inside the droplet had caused some constituents in the bio-oil to reach their superheating limits and vaporize, as indicated by the bloated droplet at 1.55 s. In this particular image, the droplet is significantly deformed by the increasing vapor within it that was prevented from escaping by the droplet's high viscosity. Because the droplet contained a large amount of macromolecular compounds that had a high boiling point and were difficult to decompose, continued heating eventually caused the liquid phase cracking of these compounds, which

resulted in the formation of residue and marked the beginning of stage IV, as was suggested in a previous study [10].

3.5 Burning rate of the droplet with varying bio-oil concentration

The burning rate of a droplet is prone to be affected by the volatility of its constituents, and the combustion characteristics of a droplet are closely associated with its constituent compounds. The burning rate of the droplets with varying concentration of bio-oil is plotted in Figure 5. The equation for the burning rate is as follows:

 $d^2 = d_0^2 - Kt$

where d, d_0 , t, and K are the droplet diameter (mm), initial droplet diameter (mm), time (s), and burning rate (mm^2/s) , respectively. Given the same ignition temperature of 723 K, the steady burning stage (II), swelling stage affected by bio-oil constituents (III), and residue burning stage (IV) were investigated with the following results: Pure butanol had the highest burning rate $(1.03 \text{ mm}^2/\text{s})$, and the rate decreased as the concentration of bio-oil was increased. For a concentration of 50%, the burning rate was at its lowest point of 0.713 mm²/s. The combustion of droplets with mid-to-high bio-oil concentration lead to extensive droplet swelling caused by the trapping of macromolecular vapor inside the droplet because of the droplet's high viscosity. The last stage of combustion was the combustion of the residue, the burning rate of which exhibited a trend inverse to that of the droplet; specifically, the residue burning rate increased when the biooil concentration was increased. This can be explained by the smaller gaseous molecules created by the macromolecules decomposed during the residue combustion, which in turn released large amounts of volatiles that then increased the burning rate. These results suggest that the complex composition of the biooil affected the processes of evaporation and combustion. When mixed with butanol, the non-saturated and saturated aliphatic acids burned with the butanol, and the heat released during this burning in turn heated the droplet. The moisture and aromatics in the droplet, however, caused micro-explosions and led to the formation of surface residue; the former increased the burning rate, whereas the latter decreased it and produced soot. Consequently, the burning rate of the droplet decreased with the increase in bio-oil concentration, but the residue burning rate increased.

4 Conclusions

To understand the combustion properties of bio-oil, the present study used slow pyrolysis to produce pinewood bio-oil whose composition and characteristics were then investigated through ultimate and proximate analysis. A droplet combustion test was performed to determine the combustion and soot formation processes of butanol/bio-oil mixtures in varying proportions. The following conclusions were drawn from the results. Compared with bio-oil acquired through fast pyrolysis, the pinewood bio-oil acquired through slow pyrolysis had low moisture content but high heat value. However, the high viscosity of the bio-oil made it unsuitable to be used alone. Therefore, it should be mixed with petroleum fuel.

An increase in bio-oil concentration extended the combustion duration of the droplet. When 10% of bio-oil was added (BO10), irregularity in droplet shape occurred at 0.98 s/mm², accompanied by the formation of considerable residue. When a concentration of 50% was used (BO50), the droplet expanded dramatically during combustion, and residue was formed at 2.02 s/mm², which was subsequently combusted until consumed. The droplet burning rate decreased when the bio-oil concentration was increased. Contrarily, the residue burning rate increased with an increase in bio-oil concentration.

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References

[1] A. V. Bridgwater, S. Czernik, J. Piskorz. Progress in thermochemical biomass conversion (2001) 977-997.

[2] S. Czernik, A. V. Bridgwater, Overview of applications of biomass fast pyrolysis oil, Energy Fuels 18 (2004) 590-598.

[3] A. V. Bridgewater, Review of fast pyrolysis of biomass and product upgrading, Biomass Bioenergy 38 (2012) 68-94.

[4] J. Lehto, A. Oasmaa, Y. Solantausta, M. Kytö, D. Chiaramonti, Fuel oil quality and combustion of fast pyrolysis bio-oils. VTT Technology, (2013), 87.

[5] J. Lehto, A. Oasmaa, Y. Solantausta, M. Kytö, D. Chiaramonti, Review of fuel oil quality and combustion of fast pyrolysis bio-oils from lignocellulosic biomass, Appl Energy 116 (2014) 178-190.

[6] S. I. Yang, M. S. Wu, C. Y. Wu, Application of Biomass Fast Pyrolysis Part I: Pyrolysis Characteristics and Products, Energy 66 (2014) 162-171.

[7] S. I. Yang, T. C. Hsu, C. Y. Wu, K. H. Chen, Y. L. Hsu, Y. H. Li, Application of Biomass Fast Pyrolysis Part II: The Effects That Bio-oil Has on the Performance of Diesel Engines, Energy 66 (2014) 172-180.

[8] S. I. Yang, M. S. Wu, T. C. Hsu, Spray combustion characteristics of kerosene/bio-oil part II: Experimental study, Energy 119 (2017) 26-36.

[9] S. I. Yang, T. C. Hsu, M. S. Wu, Spray combustion characteristics of kerosene/bio-oil part II: Numerical study, Energy 115 (2016) 458-467.

[10] M.S. Wu, S. I. Yang, Combustion characteristics of multi-component Cedar Bio-oil/kerosene droplet, Energy 113 (2016) 788-795.

[11] H. Kuo, B. Hou, A. Huang, The influences of the gas fluidization velocity on the properties of biooils from fluidized bed pyrolyzer with in-line distillation, Appl Energy (2017), doi.org/10.1016/j.apenergy.2016.10.102.

[12] B. Lin, W. Chen, W. M. Budzianowski, C. T. Hsieh, P. H. Lin, Emulsification analysis of bio-oil and diesel under various combinations of emulsifiers, Appl Energy 178 (2016) 746-757.

[13] S. Xiu, A. Shahbazi, Bio-oil production and upgrading research: A review, Renew Sustain Energy Rev 16 (2012) 4406-4414.

[14] Y. Xu, I. Keresztes, A. M. Condo, D. Phillips, P. Pepiot, C. T. Avedisian, Droplet combustion characteristics of algae-derived renewable diesel, conventional# 2 diesel, and their mixtures, Fuel 167 (2016) 295-305.

[15] N. Hashimoto, H. Nomura, M. Suzuki, T. Matsumoto, H. Nishida, and Y. Ozawa, Evaporation characteristics of a palm methyl ester droplet at high ambient temperatures, Fuel 143 (2015) 202–210.

[16] S. Singh, C. Wu, P. T. Williams, Pyrolysis of Waste Materials Using TGA-MS and TGA-FTIR As Complementary Characterisation Techniques, J. Anal Appl Pyrol. 94 (2012) 99–107.

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Figure 1. Droplet combustion equipment.



concentrations.

Table 1. Bio-oil properties.

Feedstock	Pinewood	Test method
Viscosity, cPt	7600	Brookfield(USA), LVT, UL-adopter
pH	3	Micro-compter pH-Vision Datalogger 6091
Moisture, wt.%	8.1	Karl-Fischer Moisture Titrator MKS-500
Carbon, wy.%	52.1	
Hydrogen, wt.%	6.6	ASTM D5291
Nitrogen, wt.%	0.5	
LHV, MJ/kg	17.12	ASTM D240



Figure 2. Combustion of the droplets.



Figure 4. Internal convection of the droplet.



Figure 3. Droplet diameters with varying bio-oil Figure 5. Droplet burning rates with varying concentration of bio-oil.