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Applications of bio-oil-based emulsions in a DI diesel engine: The effects of bio-oil compositions on engine performance and emissions



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ABSTRACT

Biomass-derived bio-oil cannot be applied directly in diesel engines due to several poor fuel properties such high viscosity and instability. Emulsification could overcome the disadvantages of bio-oil. In this study, bio-oil emulsified with diesel was combusted in a DI diesel engine, and the effects of bio-oil compositions on the engine performance and emissions were investigated. Crude bio-oil has aging and instability problems, which could cause inconsistencies in the results. Synthetic bio-oil was used to avoid the limitations posed by crude bio-oil. Synthetic bio-oil was fractioned into three categories (hydroxyl compounds, aldehydes and sugars), and the corresponding emulsions were prepared. Compared with diesel, the brake-specific fuel consumption (BSFC) and brake-specific energy consumption (BSEC) were increased, and the brake power remained almost unchanged for the emulsions. For the exhaust emissions, CO and smoke emissions were decreased, while CO₂ emissions were increased. The emulsions derived from the aldehydes and hydroxyl compounds reduced NO_x emissions, whereas emulsions derived from sugars and the whole bio-oil increased NO_x emissions. The results indicated that the al-dehydes and hydroxyl compounds in bio-oil were more desirable for clean combustion than sugars. The hydroxyl compounds could result in the largest emissions reductions due to the presence of OH radicals.

1. Introduction

As one of the most reliable and efficient energy conversion devices, diesel engines are widely applied in the industrial, agricultural and transportation sectors [1]. However, the dual concerns over diesel, environment pollution and depletion [2], have driven the development of alternative energy derived from renewable biomass such as agriculture and forestry residues [3–8] Plant matter could balance out the CO_2 released from combustion through photosynthesis and, thus the greenhouse effect could be suppressed [9]. Currently, renewable bio-fuels, such as bio-oil derived from biomass pyrolysis/liquefaction, are considered a

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promising substitute for diesel due to its reproducibility and environmental friendliness [10–14]. The production and properties of pyrolysis/liquefaction bio-oil are presented in Table 1. Due to several poor fuel properties of raw bio-oil such as high water content and hydrophilic properties, bio-oil is not suitable for direction use in existing diesel engines [15]. Calabria et al. [16] found that the combustion of pyrolysis oil is prone to produce carbonaceous residuals. Denser smoke was formed when the diesel engine was fueled with coffee bean residue pyrolysis oil [17]. This was caused by the reduced heating values. Therefore, upgrading bio-oil is required before operation in diesel engines. There are many biooil upgrading technologies, such as hydro-treating, catalytic cracking, sub-/super-critical fluid, solvent addition, steam reforming and emulsification [18-21]. Compared with other upgrading technologies, emulsification is a relatively simple and viable upgrading technique [22]. The emulsification with diesel could enable bio-oil adaptation to the diesel engine without prior engine modifications [17,23]. According to Van et al. [24], pyrolysis oil

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Table 1

The processing conditions and properties of bio-oil produced by pyrolysis and liquefaction techniques.

	Pyrolysis bio-oil [16,32–34]	Liquefaction bio-oil [35]
Processing conditions	300-600 °C, inert atmosphere [15]	5-20 MPa, 250–350 °C [27]
Fuel properties		
HHV (MJ/kg)	16–19	35-45
Density @55 °C (g/cm ³)	1.1-1.3	0.8-1.2
Viscosity @50 °C (cST)	10-80	23-45
PH	~3	~4
Water content (wt.%)	16-30	13-20
Elemental composition	(%, dry basis)	(%, dry basis)
C	32 49	75.9-83.4
Н	6.9-8.6	8.4-12.4
Ν	0-0.4	0.2-0.3
0	44-60	3.9-15.4

treated by emulsification could combust easily and emit less CO. In addition, the bio-oil emulsion can introduce some improvements in the engine performance and exhaust emissions. Due to oxygenated additives and polar groups obtained in bio-oil, better friction performance could occur with the emulsified bio-oil through a frictional chemical reaction, in comparison with diesel [25]. At high temperatures, the nanoparticles of emulsion could result in microexploration, which favors fuel droplet atomization and promotes complete combustion [5]. Yang et al. [17] found that the volatility difference of water and fuel could result in micro-explosion, which facilitates the rapid vaporization of fuel droplets. The produced fine fuel droplets would experience secondary atomization and air-fuel mixing could be better.

The compositions and properties of bio-oil mainly depend on feedstock and processing conditions. More than 400 kinds of organic compounds are involved in bio-oil, such as acids, aldehydes, ketones, alcohols, esters and phenols, and some of these could induce instability and aging during storage by the polymerization reaction [26,27]. Recently, research hotspots are focusing on the suitable application of different bio-oil components classified by bio-oil multi-separation [28,29]. Ikura et al. [30] removed heavy bio-oil fractions via centrifugation and emulsified the light fractions with diesel. The as-produced emulsion had better performance than the whole bio-oil-based emulsion in terms of viscosity. corrosivity, heating value and stability. Aqueous bio-oil fractions (mainly oxygenated compounds such as alcohols, phenols, acids, aldehydes, ketones and esters) were emulsified with diesel, and the obtained stable emulsion could emit less NO_x at each power output compared with diesel [23]. Despite the desirable performance of fractional bio-oil-based emulsion fuels, little literature is available to characterize the behavior of this bio-oil emulsion on diesel engines and identify the effects of different bio-oil components. In this study, the effects of bio-oil compositions on engine performance and emissions were investigated. We considered that the instability and complex diversity on bio-oil constituents would result in inconsistencies in the results and thus cause difficulty in understanding the effects. Consequently, synthetic bio-oil was used for its simplification in chemical compositions without losing the

complexity of the physical and chemical characteristics [31].

In this study, synthetic bio-oil components were classified as hydroxyl compounds, aldehydes and sugars based on chemical structures and properties of real bio-oil. Four kinds of emulsion fuels were produced from diesel, surfactant and synthetic bio-oil or three bio-oil fractions. Then, the engine performance (including brake power, BSFC, BSEC and exhaust gas temperature) and emissions (including CO, CO_2 , NO_x and smoke) of emulsion fuels were discussed and compared with diesel. Next, the effects of bio-oil compositions on performance and emissions were evaluated. Finally, the bio-oil fractions, which were desirable as fuel for diesel engines, were assessed.

2. Materials and methods

2.1. Emulsion preparation

Considering the inconsistency of crude bio-oil constituents during storage, we employed synthetic bio-oil. This consisted of compound classes that represent best resemblance with typical pyrolysis bio-oil. A blend of methanol (5 wt%), acetaldehyde (12 wt %), acetic acid (14 wt%), glyoxal (4 wt%), acetol (8 wt%), glucose (8 wt%), guaiacol (17 wt%), furfural (4 wt%), vanillin (8 wt%) and deionized water (20 wt%) was used to prepare fresh synthetic bio-oil before each experiment. To evaluate the effects of different bio-oil compounds on engine performance and emissions, synthetic biooil was divided into three classes with respect to their chemical structures and properties: hydroxyl compounds (including methanol, acetol, guaiacol, vanillin and acetic acid), aldehydes (including acetaldehyde, glyoxal and furfural) and sugars (including glucose). Initially, the blends were formulated by mixing diesel with 5%, 10% and 15% synthetic bio-oil on a volume basis and denoted as SD05, SD10 and SD15, respectively. Nonionic surfactant Span 80 (sorbitan monooleate) was added to facilitate the miscibility of diesel and synthetic bio-oil. The diesel, bio-oil and surfactant were kept in a mechanical stirrer for homogenous mixing at 1500 rpm for 15 min. The minimum surfactant quantity for completely suspending synthetic bio-oil within diesel is displayed in Table 2.

The diesel was purchased from a local petro station. Unless otherwise stated, the chemicals used were analytically pure. After determination of the appropriate surfactant addition, four kinds of emulsions of a blend of bio-oil and its fractions with diesel were prepared. The physical properties of diesel and the emulsions are displayed in Table 3.

2.2. Experimental setup

A single cylinder, four-stroke, unmodified, air-cooled, naturally aspirated DI diesel engine was used to investigate the effects of different emulsions on engine performance and emissions (Fig. 1). The engine specifications are provided in Table 4. The engine brake torque and power were measured by an eddy current dynamometer (DW25, Chengbang China). The measurement of the fuel consumption and engine speed were conducted with an intelligent digital fuel consumption meter (ET2500, Chengbang, China) and a tachometer, respectively. An intelligent measurement and control

Table 2

Minimum surfactant quantity for emulsifying different amounts of synthetic bio-oil with diesel.

Blend	Synthetic bio-oil in blend (vol%)	Surfactant in emulsion vol%)	Surfactant efficiency (bio-oil/surfactant,vol%/vol%)	Stability (day) ^a
SD05	5	2.1	2.33	37
SD10	10	3.0	3.23	>90
SD15	15	7.3	1.90	>90

^a The time of the occurrence of the stratification during storage for 90 days at ambient temperature in a glass vial.

Table 3					
Physical	properties of	diesel	and	emulsio	ıs.

Properties	Diesel	SDE10	GDE10	ADE10	HDE10
Density @25 °C (g/cm ³)	0.843	0.875	0.860	0.851	0.860
Kinematic viscosity @40 °C (cST)	2.73	3.20	3.23	3.01	2.93
C (wt.%)	81.87	80.05	79.51	80.17	81.02
H (wt.%)	12.90	12.37	12.14	12.74	12.00
N (wt.%)	1.35	0.78	0.73	0.98	0.78
O ^a (wt.%)	3.88	6.80	7.62	6.11	6.20
HHV ^b (MJ/kg)	45.60	43.69	43.03	44.39	43.60

^a Calculated by difference.

 b The higher heating values were calculated from elemental analysis data by equation: HHV (MJ/kg) = 0.3383C + 1.442 (H - O/8).

recorded when the values of the engine power output and speed were steady. Each experiment was repeated three times to achieve high confidence in the measurements of engine performance and emissions and the average was determined for data analysis.

3. Results and discussion

3.1. Emulsification performance

As shown in Table 2, with the bio-oil percentage in the blend increasing, the surfactant quantity required to form a stable emulsion also increased. Surfactant efficiency was proposed to



Fig. 1. Schematic diagram and photograph of the test setup.

system (ET2000, Chengbang, China) was used to monitor and collect engine performance measurements and control parameters. Emissions of CO₂ (in percent volume) and NO_x (in ppm) were measured by a Testo360 gas analyzer (Germany), whereas emissions of HC (in ppm) and CO (in percent volume) were measured using a FGA-4100 (China). Smoke opacity (in m^{-1} , the light absorption coefficient *k*) was measured by an FTY-100 opacimeter (China). The measuring range and accuracy of the instruments are shown in Table 5. Fig. 1 shows the experimental setup.

The afflux of the test fuels into the engine was conducted under different loads from 15 to 80 Nm with a constant speed of 1200 rpm. At each operational condition, the engine ran for 40 min (at least) to retard the influence of the last test fuel. The data were

Table 4

Main characteristics of the diesel engine employed in this study.

Specification	Description
Туре	Horizontal four-stroke, single-cylinder, Cl
Fuel injection	Direct injection
Displacement (L)	1.093
Bore \times stroke (mm)	110×115
Compression ratio	17:1
Rated power (kW)	14.7 at 1800 rpm
Cooling	Water cooling system
Lubrication	Combined pressure and splashing

evaluate the performance of the surfactant in emulsifying bio-oil and diesel. When 10 vol% of the bio-oil was blended with diesel, the surfactant efficiency reached the peak at 3.23 vol%/vol%. The stability tests for 90 days indicated that SD05 had lower stability than SD10 and SD15. No stratification was observed for SD10 and SD15 during the 90 days of storage. In consideration of both emulsification efficiency and stability, the 10 vol% of bio-oil was chosen for the emulsion preparation. A 10 vol% of synthetic bio-oil, hydrous solution (20 wt% of water added) of glucose, aldehydes and hydroxyl compounds were blended with diesel. Subsequently, 3 vol % of the surfactant was added to emulsify the above mixtures. The emulsions were denoted as synthetic bio-oil-in-diesel emulsion

Table 5				
Range and	accuracy	of ins	strumei	nts

Instrument	Measurement	Measuring range	Accuracy
DW25 dynamometer	Brake torque	0-120 Nm	±0.5 Nm
	Brake power	0-25 kW	±0.1 kW
ET2500	Fuel consumption	_	±8 g/h
Tachometer	Engine speed	-	±1 rpm
Testo360 gas analyzer	Carbon dioxide (CO ₂)	0-20%	±1.5%
	Nitric oxides (NO _x)	0-1000 ppm	±3.8%
FGA-4100 gas analyzer	Hydrocarbon (HC)	0-10,000 ppm	±6%
	Carbon monoxide (CO)	0-9.99%	±0.06%
FTY-100 opacimeter	Smoke opacity (k)	$0-16 \mathrm{m}^{-1}$	±2.0%

(SDE10), glucose solution-in-diesel emulsion (GDE10), aldehydes solution-in-diesel emulsion (ADE10) and hydroxyl compounds solution-in-diesel emulsion (HDE10). The stability experiments of GDE10, ADE10 and HDE10 were also conducted and the results showed that no stratification was found over 90 days.

3.2. Engine performance characteristics

3.2.1. Brake power

The brake power produced by engines using diesel and emulsion fuels under various loads is presented in Table 6. Even though emulsion fuels had lower calorific values than diesel, no significant power loss occurred in the engine when operating on emulsion fuels. This can be explained by the fact that the micro-explosion in emulsions and the oxygenated additives in bio-oil and its fractions make combustion more efficient [36,37]. In addition, the emulsion fuels could output more power during the expansion stroke due to the less compression work compared to diesel [38].

As shown in Fig. 2, the maximum power loss of 3.66% was observed by the engine fueled with GDE10 at the load of 15 Nm. This can be caused by the lower energy density and higher viscosity (seen in Table 3) [39]. Due to lower heating values than other fuels, more GDE10 were needed to produce the same energy. The higher viscosity of GDE10 caused poor atomization and led to the ineffective combustion of fuels [39].

3.2.2. Brake specific fuel consumption (BSFC) and brake specific energy consumption (BSEC)

For all of the fuels, the BSFC was initially decreased with

Table 6Brake power at various loads with different fuels.

Load (Nm)	Brake power (kW)					
	Diesel	SDE10	GDE10	ADE10	HDE10	
15	1.91	1.85	1.84	1.89	1.90	
20	2.51	2.52	2.51	2.52	2.52	
30	3.78	3.76	3.77	3.77	3.77	
40	5.06	5.03	5.04	5.04	5.04	
50	6.30	6.31	6.28	6.30	6.28	
60	7.59	7.55	7.56	7.51	7.55	
70	8.81	8.79	8.80	8.77	8.78	
80	10.04	10.03	10.03	10.02	10.03	
>90	Engine stalled					



Fig. 2. Changes in the brake power of the emulsion fuels with diesel as a baseline.

increasing engine load and then increased after reaching the minimum point (Fig. 3). The BSFC for emulsion fuels was higher than that of diesel at all load conditions (except for that of HDE10 at 15 Nm). The presence of water and oxygenated additives decreased the calorific values of emulsion fuels and resulted in more fuel consumption while attaining the same output torque compared with diesel [40]. The variation trend of BSEC was similar to that of BSFC (shown in Fig. 4). The BSEC of emulsion fuels was higher than that of diesel at all load conditions (except for the 15 and 80 Nm cases). The increased BSEC resulted from the enhanced combustion efficiency which was caused by the excess of air ratio, the airenrichment in the spray and the higher premixed combustion of emulsions [36]. Yang et al. [17] also reported that water and emulsification properties of emulsion fuels could improve combustion efficiency and minimize the negative effects on fuel consumption caused by lower calorific values.

3.2.3. Exhaust gas temperature

Fig. 5 shows the variation of the exhaust gas temperature with engine load for diesel and emulsion fuels. Fig. 5(a) shows that there was no significant difference in the exhaust gas temperature between diesel and emulsions at all loads. At low loads, the existence of water in the emulsion fuels caused a heat sink, which could adsorb the heat released from fuels and thus reduce the exhaust gas temperature [41,42]. However, the difference in volatility between the water and diesel caused micro-explosions, and as a result, the mixing of the fuels with air was better and fuels atomization was more efficient [5]. Thus, complete combustion was enhanced which in turn increased the exhaust gas temperature. While the higher viscosity of emulsions could result in low quality injection and thereby lead to less complete combustion and reduction of the exhaust gas temperature [23]. As seen Fig. 5(b), there was less than a 9% change in exhaust gas temperature between diesel and emulsion fuels. This result can be considered the compromise reached different effects above. According to this result, the combustion of the emulsion fuels on diesel engines would not cause obvious changes in exhaust gas temperature.

3.3. Engine emissions characteristics

3.3.1. CO emissions

As shown in Fig. 6(a), all of the tested fuels followed the same trend, which showed that the higher engine load resulted in higher CO emissions. This was caused by the supply of more fuel-rich mixtures at higher loads [43]. As seen in Fig. 6(b), emulsion fuels had less CO emissions compared with diesel. CO is the product of incomplete combustion [44]. Bio-oil and its fractions contained extra fuel-bound oxygen, which could mitigate the formation of local fuel-rich zones and, thereby resulted in more efficient combustion than diesel [45]. For emulsion fuels, the fast evaporation of internal water droplets could cause secondary atomization and accelerate the mixing of air with fragmented fuel droplets. Therefore, less air was required and less unburned carbon was converted into CO [46]. Additionally, the fine fuel droplets formed from the micro-explosion of emulsions needed less time to burn out the carbon, which caused a shorter flame length and less possibility of flame impingement on the wall [47]. The effectiveness of emulsion fuels occurred in the following order: HDE10 > ADE10 > GDE10 > SDE10. The effects of glucose emulsified fuels on an automotive diesel engine were studied by Chen et al. [1], and the results showed that emulsified fuels had higher CO emissions than diesel. The viscosity of GDE10 and SDE10 were higher than HDE10 and ADE10, which resulted in more fuels left on the cylinder wall and suppressed the conversion of HC to CO₂ and H₂O. However, a large number of OH radicals contained in HDE10



Fig. 3. BSFC of diesel and emulsion fuels and changes in BSFC of emulsion fuels with diesel as a baseline at different loads.



Fig. 4. BSEC of diesel and emulsion fuels and changes in BSEC of emulsion fuels with diesel as a baseline at different loads.



Fig. 5. Exhaust gas temperature of diesel and emulsion fuels at different loads.



Fig. 6. CO emissions of diesel and emulsions at different loads.

accelerated the oxidation of CO [48]. Coupled with the positive effect of lower viscosity on complete combustion, HDE10 had the lowest CO emissions (Fig. 6(b)).

3.3.2. CO₂ emissions

Fig. 7(a) shows that CO₂ emissions of all of the tested fuels were increased with the increase of engine load. The CO and CO₂ formation were opposite sides of the process. CO_2 was the complete combustion product, whereas CO was the incomplete combustion product [44]. In this work, CO emissions were lower for emulsion fuels (Fig. 6(b)), and consequently, CO₂ emissions were expected increase. As seen in Fig. 7(b), emulsion fuels had higher CO₂ than diesel at all loads except for the 80 Nm case. The excess oxygenated additives contained in the emulsion fuels promoted the transformation of CO to CO₂ [45]. The ratios of oxygen to carbon for GDE10 and SDE10 were higher than other emulsion fuels. Therefore, GDE10 and SDE10 had access to sufficient oxygenated additives for the further oxidation of CO to CO₂, which resulted in higher CO₂ emission than ADE10 and HDE10. However, a high concentration of OH radical concentration in HDE10 was found to promote the conversion of C to CO [49]. The low energy density and the evaporation of water decreased the flame temperature and thus there was insufficient energy available for the conversion of CO to CO₂ [47].

3.3.3. NO_x emissions

Thermal NO_x formation was closely related to the content of oxygenated additives [42,50]. Fig. 8(a) shows that NO_x emissions of all tested fuels were increased with the increase of the engine load from 15 Nm to 70 Nm. At a load of 80 Nm, the NO_x emissions of all fuels were increased. This may be because the insufficient oxygen in fuel-rich zones inhibited NO_x formation at high loads. When compared with diesel, ADE10 and HDE10 generally had less NO_x emissions, whereas GDE10 and SDE10 had more NOx emissions. As shown in Table 3, GDE10 and SDE10 had higher oxygen content than other emulsion fuels and diesel. The sufficient oxygenated additives in GDE10 and SDE10 improved premixed combustion, and as a result thermal NO_x was more likely to form [51]. Although ADE10 and HDE10 contained more oxygen than diesel, the local oxygen concentrations could decrease due to the existence of water [52]. In addition, Chen et al. [1] found that with shorter combustion duration, the emulsion fuels cut down the duration of high temperature and thus inhibited NO_x formation.



Fig. 7. CO₂ emissions of diesel and emulsions at different loads.



Fig. 8. NO_x emissions of diesel and emulsions at different loads.

3.3.4. Smoke opacity

As seen in Fig. 9(a), the smoke opacity was increased with an increase in engine load for all of the tested fuels. Fig. 9(b) shows that the emulsion fuels had less smoke emissions than diesel and the effectiveness of the emulsion fuels was in the following order: HDE10 > ADE10 > SDE10 > GDE10. The formation of soot could be increased by high temperature, oxygen-poor and polycyclic aromatic hydrocarbons (PAH) [50]. The evaporation of water decreased the flame temperature of the emulsion fuels, which resulted in less smoke formation. More oxygenated additives contained in emulsions reduced soot formation by improving post-flame oxidation of the soot [1]. The lower carbon content of emulsion fuels made it less likely to produce soot [39]. In addition, the C-O bond contained in the emulsions could also remove carbon from the reaction pathway to soot [53]. For HDE10, the components, such as methanol, were found to improve premixed combustion, which can inhibit soot formation in the diffusive combustion phase [54]. In addition to the improved mixing of air and fuels caused by microexplosion, the better distribution of OH radicals in the HDE10 further decreased smoke formation through the oxidation of black carbon particles and soot precursors [47,55]. Alcohol, such as methanol and acetol in HDE10, could provide OH radicals to convert hydrogen atoms to molecular hydrogen [56]. The reduced hydrogen atoms would slow the growth of soot and the propagation of aromatic rings [57]. Although HDE10 had a higher carbon content than other emulsions, the fractions of carbon derived from the oxygenated additives would not participate in soot formation [58]. For SDE10 and GDE10, the higher viscosity induced poor atomization and produced larger fuel droplets in the combustion chamber. The smaller surface area with larger droplets made combustion less complete, which increased smoke emissions [48]. Counteracted by the negative impacts of increased viscosity on smoke emissions, SDE10 and GDE10 did not result in greater soot emissions reduction when compared to HDE10.



Fig. 9. Smoke opacity of diesel and emulsions at different loads.

4. Conclusions

Emulsification was used to blend synthetic bio-oil or its fractions and diesel with Span 80 as the surfactant. The added synthetic bio-oil and its fractions reduced the heating value of emulsions due to the higher contents of water and oxygenated additives. As a result, emulsion fuels increased BSFC and BSEC compared with diesel. The brake power and exhaust gas temperature did not experience an obvious reduction due to the more complete combustion caused by micro-explosions.

All emulsion fuels reduced CO and smoke emissions while increasing CO₂ emissions compared to diesel at almost every load. HDE10 had the lowest CO and smoke emissions. Higher NO_x emissions with SDE10 and GDE10 compared to other emulsions and diesel indicated that sugars accelerate NO_x formation. Compared with other emulsion fuels, HDE10 favored clean combustion due to the higher OH radical concentration and lower viscosity. Based on engine performance and emissions, this study indicates that not all bio-oil components are appropriate for use as fuel in diesel engines. The emissions improvement caused by OH radicals and the emissions deterioration induced by sugars offer guidance on emissions reduction via fuel composition optimization.

Bio-oil compositions rely mainly on feedstock and process conditions, and therefore, the expected bio-oil containing desirable components for diesel engine operation could be produced through selecting bio-oil feedstock and controlling process parameters. This study shows that bio-oil with a high content of hydroxyl radicals is more suitable for use in the diesel engine, whereas bio-oil with sugars was not suitable. The results provide insights into the production of bio-oil which is desirable for diesel engines. More research should be conducted to investigate the combustion characterizations, such as ignition delay and in-cylinder pressure.

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