



Research article

The miscibility of hydrogenated bio-oil with diesel and its applicability test in diesel engine: A surrogate (ethylene glycol) study



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ABSTRACT

In this work, the miscibility of hydrogenated biomass-pyrolysis-oil with diesel and its applicability in diesel engine has been tested by using its surrogate-ethylene glycol. The miscibility of ethylene glycol and 1,3-propylene glycol with diesel has been tested, finding that only 10% vol ethylene glycol could be mixed with diesel and 1,3-propylene glycol is immiscible with diesel. In order to make a direct comparison, 10% ethanol-90% diesel, 10% ethylene-90% diesel, and 10% ethyl acetate-90% diesel blends have been tested in a diesel engine under the same operation conditions. The engine performance of ethylene glycol is comparable to ethanol and ethyl acetate. There is no significant difference in brake specific fuel consumption and exhaust gas temperature for blends. The three oxygenated compounds all have lower CO emissions than diesel. Besides, ethylene glycol and ethyl acetate could reduce the NO_x emission. All the three fuels have reported the reduction of soot emission. This work offers the possibility that ethylene glycol (hydrogenated bio-oil) could be used as a useful additive (up to 10% vol) in diesel.

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1. Introduction

With the depletion of fossil fuels, applications of bio-fuels in internal combustion engines are receiving increasing attention [1]. The first-generation bio-fuels, biodiesel and bioethanol lead to the problem of food versus fuel [2]. Under this condition, researches and applications on the second-generation bio-fuels, which are made from lignocellulosic biomass, woody crops, and agricultural residues, flourished after 2000 [3–5].

Bio-oils from fast pyrolysis of lignocellulosic biomass show different characteristics from conventional fossil oils, like high water content, high density, acidic, and low heating value. What's more, bio-oils are highly polar and contain a large amount of oxygen (about 35–40 wt% in dry basis), resulting that bio-oils are not soluble in fossil fuels [6]. However, considering their potential to replace or partly replace fossil fuels, the applications of bio-oil from fast pyrolysis of biomass are the focus of intense studies [7].

Normally, bio-oils are injected into engines with diesel by dual-injection system or blended and emulsified with diesel before injection. Though some researchers have reported the applicability of raw bio-oil in internal combustion engine, severe problems also appeared when running raw bio-oil, such as its poor ignition characteristics [8–10], and causing severe corrosions and blockages on injectors [11–13]. In order to deal with these problems, catalytic hydrogenation

and esterification have been used to upgrade raw biomass pyrolysis oil. Though there are some reports on the catalytic hydrogenation and esterification process of pyrolysis oil [14], few of them covered the application of upgraded biomass pyrolysis oil in internal combustion engines. Pelaez-Samaniego et al. prepared bio-oil rich in esters from sugarcane trash pyrolysis oil, suggesting that it was technically feasible to use blends of carboxylic acids esters derived from the biomass bio-oil with gasoline in conventional Otto engines [15]. Bert Van de Beld et al. treated pine wood pyrolysis oil with mild hydrogenation and reactive distillation (with butanol) to get bio-oil, after 40 h fueling with upgraded pyrolysis oil in diesel engine, they reported that no notable effect on flue gas emissions and fuel consumption [16]. Wildschut et al. hydrotreated beech wood pyrolysis oil in an autoclave with catalysts and tested the received bio-oil in a 5 kW engine, finding that smooth engine operation was successful when hydrotreated pyrolysis oil was used, while engine operation was not successful when crude pyrolysis oil was used [17].

Bio-oil catalytic hydrogenation has been regarded as a potential routes for production of second generation bio-fuels in the future [14]. Table 1 lists the main product distribution of catalytic hydrogenated aqueous biomass pyrolysis oil referred from Vispute et al.'s work [18]. From Table 1, it could be concluded that the main products after hydrogenation were polyols (ethylene glycol and propylene glycol), and the distribution of ethylene glycol and propylene glycol took up more than 50% after high temperature hydrogenation process.

Compared with surrogates for other popular bio-fuels, such as ethanol for bio-ethanol, and ethyl acetate for bio-diesel, few studies have

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Table 1
Product distribution of catalytic hydrogenated aqueous biomass pyrolysis oil.

	Low temperature hydrogenation ^a		High temperature hydrogenation ^b	
	mmol carbon L-1	Percentage (%)	(mmol carbon L-1)	Percentage (%)
Acetic acid	203.2	9.38	104.9	6.30
Levogluconan	341.8	15.79	0	0.00
Methanol	49.1	2.27	56.8	3.41
Ethanol	19.7	0.91	47.9	2.88
1-Propanol	9.7	0.45	42.5	2.55
Ethylene glycol	498	23.00	465.1	27.95
Propylene glycol	236.1	10.90	400.8	24.08
Cyclohexanol	124.6	5.75	51.3	3.08
1,2-Butanediol	32.1	1.48	137.4	8.26
1,4-Butanediol	54.2	2.50	68.6	4.12
butyrolactone	103	4.76	110.6	6.65
Glycerol	0	0.00	48.8	2.93
1,2-cyclohexanediol	106.9	4.94	107.7	6.47
Sorbitol	386.9	17.87	21.8	1.31

^a Low temperature hydrogenation, 5% wt Ru/C catalyst, temperature 398 K (125 °C).

^b High temperature hydrogenation, after low temperature hydrogenation, continue using 5% wt Pt/C catalyst, 523 K (250 °C).

been reported about the combustion and emission characteristics of glycols. In this article, ethylene glycol, ethanol, and ethyl acetate were chose as the surrogates for a direct comparison on performance and emission characteristics in a diesel engine. Brake specific fuel consumption, exhaust gas temperature, CO, NO, NO₂, soot (smoke opacity) emissions were compared based on fuel types and operating conditions.

2. Experimental procedure and specifications

Ethanol, ethylene glycol, and ethyl acetate used in this study were purchased from Sigma Chemical Co. and used directly without any further treatment. The commercial 0# diesel was purchased from PetroChina (Nanjing). The properties of diesel, ethanol, ethylene glycol, ethyl acetate and the blends were listed in Table 2. Compared to ethanol and ethyl acetate, ethylene glycol has a lower LHV (lower heating value) but a higher density. Besides, boiling point and viscosity of ethylene glycol are much higher than ethanol and ethyl acetate. For the blends, there is no big difference observed for low heating value and density. The high boiling point lead to a higher T10 for 90% diesel/10% ethylene glycol blend. Adding 10% of blends to diesel will decrease the cetane number of diesel a bit, changing from 56 to around 50.

To study the miscibility of polyols in diesel, diesel, ethanol/ethylene glycol/1,3-propylene glycol, ethyl acetate were mixed into a homogeneous mixture by a magnetic stirrer at room temperature 25 °C (As ethyl acetate is miscible with diesel and ethanol, it was used to improve the miscibility of polyols with diesel). Each component (ethanol/

ethylene glycol/1,3-propylene glycol) was varied from 0% to 100% by volume with 10% increment. After agitation, all of the blends were kept motionless for 24 h at 25 °C to observe the physical stabilities. Finally, phase grams were used to depict the results of three-component systems [19,20].

Standard 0# diesel, ethanol (10% vol)-diesel (90% vol), ethylene glycol (10% vol)-diesel (90% vol), ethyl acetate (10% vol)-diesel (90% vol) blends were prepared for engine testing. A one-cylinder, 4-cycle, direct injected, water-cooled Changchai R170 diesel engine was used in this study. Specifications of the engine were shown in Table 3. Loads were applied by using a hydraulic dynamometer provided by Xiangyi Co., Changsha, China. A MRU VARIO PLUS gas analyzer was used to measure the exhaust temperature (type K thermocouple) and exhaust gas emissions of CO, NO, and NO₂ (electrochemical sensors). A NANHUA NHT-6 opacimeter was used to measure the exhaust gas opacity. The analyzers were calibrated routinely by fresh air before every run of experiments. The diesel engine was controlled by an engine control system provided by Xiangyi Co., Changsha, China. A simplified representation of the experimental setup was illustrated as Fig. 1. The engine ran between no load and 90% load conditions. 2.7 kW (rated output) which corresponded to 90% of maximum output of the engine was achieved as the maximum engine load. All the tests had been repeated to check the reproducibility of the experiments and the average values had been used for following analysis.

3. Results and discussions

3.1. The miscibility of polyols in diesel

The miscibility of bio-oil with diesel is a big problem to the use of bio-oil [6]. Therefore, emulsification for bio-oil/diesel mixture is necessary [21]. In order to remove the influence of emulsifiers/additives, and to make a direct comparison between ethanol, polyols, and ethyl acetate, direct blends of these fuels with diesel were used. Under this condition, the miscibility of polyols should be checked firstly. Seen from Table 1, ethylene glycol and propylene glycol take up the main fraction in hydrogenated bio-oil, so the miscibility of ethylene glycol, and 1,3-propylene glycol has been tested here.

Fig. 2 showed the miscibility of ethylene glycol with diesel at room temperature (25 °C). Seen from Fig. 2, only 10% vol ethylene glycol could be mixed with diesel, and 90% vol ethylene glycol could be mixed with 10% vol ethyl acetate. What's more, adding ethyl acetate didn't improve the miscibility of ethylene glycol with diesel. This made a big difference to the miscibility of ethanol [20]. For ethanol at the same room temperature, 10% vol and above 80% vol ethanol could be mixed with diesel, and ethanol was miscible with ethyl acetate, with the help of ethyl acetate, ethanol, ethyl acetate, and diesel could be mixed with any ratio (Fig. 3).

Table 2
Properties of diesel, ethanol, ethylene glycol, ethyl acetate and the blends.

	0# diesel	Ethanol ^a	Ethylene glycol ^a	Ethyl acetate ^a	90% diesel/10% ethanol	90% diesel/10% ethylene glycol	90% diesel/10% ethyl acetate
Low heating value ^b /MJ kg ⁻¹	44.1	28.6	17.47	23.90	43.63	43.23	43.31
Density ^c (20 °C)/g cm ⁻³	0.8341	0.790	1.1132	0.902	0.8293	0.8415	0.8333
Boiling point ^d /°C	T10 = 223 T50 = 266 T90 = 311	78	197	77	T10 = 172 T50 = 269.5 T90 = 323	T10 = 231 T50 = 270 T90 = 327	T10 = 119.5 T50 = 268.5 T90 = 334
Flash point/°C	63	13	115	7.2	–	–	–
Viscosity ^e (40 °C)/mm ² s ⁻¹	4.462	1.1	10.2	0.45	4.414	6.387	3.112
Cetane number ^f	56.1	6	–	–	51.1	50.8	48.1
Oxygen content (% mass)	–	34.78	51.61	36.36	–	–	–

^a The properties of ethanol, ethylene glycol and ethyl acetate are from Wikipedia.

^b The low heating value of 0# diesel and the blends are measured by GB 384–1981.

^c The density of 0# diesel and the blends are measured by SH/T 0604–2000.

^d The boiling point of 0# diesel and the blends are measured by GB/T 6536–2010.

^e The viscosity of 0# diesel and the blends are measured by GB/T 265–1988 (2004).

^f The cetane number of 0# diesel and the blends are measured by GB/T 0694–2000.

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