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Short Communication

Improvement of the cold flow characteristics of biodiesel containing dissolved polymer wastes using acetone

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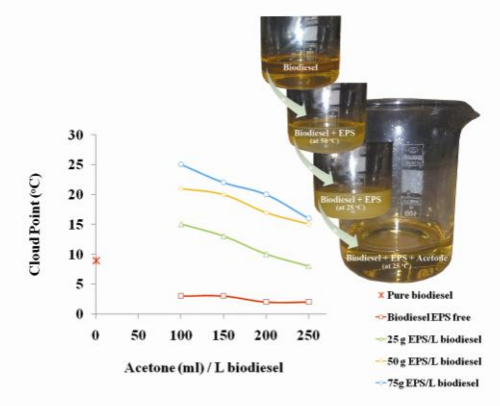
HIGHLIGHTS

- Investigating the unique biosolvent features of biodiesel.
- Biodiesel; a unique bio-solvent to recycle the waste polymers e.g. EPS.
- Investigating various solvents to stabilize biodiesel-polymer fuel blend.
- Improving cold flow characteristic of biodiesel-polymer fuel blend using acetone.

GRAPHICAL ABSTRACT



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ABSTRACT

Due to the fast fossil fuel depletion and at the same time global warming phenomenon anticipated for the next coming years, the necessity of developing alternative fuels e.g. biofuels (i.e. bioethanol, biodiesel, biogas and etc.) has turned into an important concern. Recently, the application of the bio-solvency properties of biodiesel for recycling waste polymers has been highlighted. However, the impact of polymer dissolution on cold flow characteristics of biodiesel was never investigated. The present study was set to explore the impact of different solvents in stabilizing biodiesel-polymer solution. Among them, acetone was proved to be the best fuel stabilizer. Subsequently, cold flow characteristic i.e. cloud point, of the biodiesel-polymer-acetone fuel was found to have improved (decreased) due to the inclusion of acetone. Finally, flash point analysis of the fuel blends containing acetone was done to ensured high safety of the fuel blend by dramatically increasing the flash point values of biodiesel-polymer fuel blends.

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1. Introduction

Today, there is an intense need for renewable, pollutant-free sources of energy (Shirazi et al., 2013). Increasing concerns about environmental pollutions, the soaring price of petroleum products together with the depletion of fossil fuels have led to considerable research to identify alternative fuel sources (Mohammadi et al., 2012a). It is well documented that biodiesel is superior to conventional diesel in terms of its sulphur content, aromatic content, flash point and lubricity improving properties. More specifically, biodiesel is essentially sulphur free and non-aromatic while conventional diesel can contain up to 500 ppm SO_2 and 20–40 wt% aromatic compounds (Phan and Phan, 2008). Biodiesel is defined as the mono-alkyl esters of long-chain fatty acids derived from renewable feedstock, and is mainly synthesized by transesterification of triglycerides with short chain alcohols i.e. methanol and ethanol (Guo et al., 2009; Cerenoch et al., 2009; Joshi et al., 2011).

The triglycerides used for biodiesel production are usually fats or oils with significant amounts of saturated fatty compounds and therefore, display higher cloud points (Bhale et al., 2009; Joshi et al., 2011). While most of the properties of biodiesel are comparable to those of petroleum based diesel fuel, improvement of its low temperature flow characteristic still remains one of the major challenges limiting its widespread use (Bhale et al., 2009; Chastek et al., 2011). In previous studies, in order to address this challenge, various strategies have been proposed, such as winterization, blending with fossil diesel fuel, and usage of additives (Echim et al., 2012). The cloud point is defined as the temperature at which a liquid fatty material becomes cloudy due to the formation of crystals and solidification of saturates. Crystallization of the saturated fatty acid methyl ester (FAME) components of biodiesel during cold seasons causes operability problems as solidified material clog fuel lines and filters (Bhale et al., 2009).

During recent years, different biodiesel additives have been introduced in order to improve fuel properties mainly cold flow characteristics and flash point value. For instance, Guo et al. (2009) found out that ethanol inclusion could effectively adjust the volatility and flash point value of biodiesel (Guo et al., 2009). In a more recent investigation, Joshi et al. (2011) reported that ethyl levulinate as a potential bio-based diluent for biodiesel improved the cold flow properties. They also revealed that flash point value decreased with increasing contents of ethyl levulinate (Joshi et al., 2011). Boshui et al. (2010) evaluated the influence of three cold flow improvers i.e. olefin-ester copolymers (OECP), ethylene vinyl acetate copolymer (EACP) and polymethyl acrylate (PMA), on the cold flow properties of a soybean biodiesel. These researchers argued that the ability of the used cold improvers differed in improving the cold flow properties of soybean biodiesel and that the inclusion of OECP at the rate of 0.03% led to the most significant improvement (Boshui et al. 2010).

On the other hand, biodiesel has been recently used as a bio-solvent for recycling waste polymers such expanded polystyrene (EPS); an amorphous and linear polymer, which is composed of 98% air by weight (Kumar et al., 2009; Mohammadi et al., 2012a; Mohammadi et al., 2012b), polystyrene (PS) (Kuzhiyil and Kong, 2009), and polyethylene (PE) (Zhang et al., 2010). However, the impact of the dissolution of such waste materials on clod flow characteristics of biodiesel has yet to be investigated.

Therefore, the present study was set to evaluate the stabilizing effect of various solvents on biodiesel-waste EPS solution and moreover, the impact of the best fuel stabilizer on cloud point value of the fuel blend was also investigated.

2. Materials and methods

2.1. Materials

Biodiesel was produced in a reactor from waste cooking oil methyl ester along with methanol in a basic environment (KOH) through the transesterification reaction as depicted in Fig. 1. The physical parameters of diesel and biodiesel fuels used are listed in Table 1. All solvents were purchased from Merck (Germany). EPS waste (M_n=91000) with the density of 17 kg/m^3 was obtained from Tabriz Petrochemical Company (T.P.C).

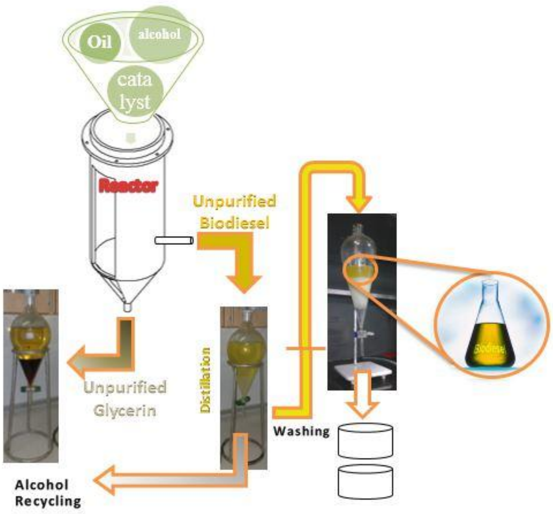

Fig. 1. Biodiesel production process

2.2. Apparatus

The methyl esters profile was determined according to the D6751standard using an Agilent 6890N GC (Agilent Technologies, USA), equipped with an on-column injection system, a flame ionization detector and a DB-WAX capillary column (30 m×0.25 mm×0.25μm). Flash point was determined by a continuously closed cup flash point (CCCFP) Tester using the Grabner FLPH Miniflash Tester (Grabner, Austria). Cloud point test which characterized the low temperature operability of biodiesel fuels was measured in accordance with the ASTM D2500 standard.

Table 1
Physical properties of diesel and biodiesel fuels.

Properties	Unit	Diesel	Biodiesel	Standard
Flash point	℃	56	176	ASTM D93
Kinematic viscosity @ 40℃	mm^2/s	2.92	4.73	ASTM D445
Density	g/cm^3	0.82	0.88	ASTM D941
Cetane Number	-	40	48	ASTM D 613
Cloud point	℃	-6	9	ASTM D2500
Gross heating Value	MJ/kg	137.64	127.05	ASTM D240

2.3. EPS dissolution and fuel stabilization

EPS was dissolved in biodiesel by heat treatment as previously described by Mohammadi et al. (2012a,b). Briefly, biodiesel was heated to 50℃ and then EPS was added to 1 L of heated biodiesel at three levels of 25, 50 and 75 g. As the dissolution process was reversible and the dissolved polymers precipitated especially by decreasing the temperature, therefore, in a preliminary experiment different solvents were used as co-solvent in order to stabilize the fuel. The co-solvents used included cyclohexane, xylene, toluene, tetrahydrofuran, benzene, methyl ethyl ketone, acetone, pyridine, dimethyl formamide, methanol and ethanol. Subsequently, cold flow characteristic i.e. cloud point of the biodiesel-polymer fuel blend containing the best stabilizer at different levels (ml/1 L biodiesel) was measured. Finally, flash point analysis of the fuel blends containing the best stabilizer was also investigated in order to evaluate the safety of the fuel blends.

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3. Results and discussions

Chromatographic analysis showed that the major unsaturated fatty acids in the WCO were linoleic acid (52.4%), and oleic acid (C-18:2) (22.4 %), as listed in Table 2. Among the different solvents used (i.e. including cyclohexane, xylene, toluene, tetrahydrofuran, benzene, methyl ethyl ketone, acetone, pyridine and dimethyl formamide, methanol and ethanol), acetone was found to have the best stabilizing effect. Benzene, toluene, xylene and acetone were shown to possess good stabilizing effects, however, the first three were excluded from the experiment due to their harmful effect on human health and environment. Fig. 2, illustrates the fuel blend production (EPS dissolution in biodiesel) and acetone-aided stabilization procedure. As could be observed, biodiesel turned tarnished upon the addition of EPS and this cloudy state was intensified after cooling to ambient temperature (Figure 2a, b and c). The biodiesel-EPS blend was then completely cleared by addition of acetone (d).

Table 2
The fatty acid methyl ester (FAME) profile of the biodiesel produced from waste cooking oil (WCO)

Methyl ester	FAME chain	%
Methyl palmitate	$R^* - (CH_2)_{14} - CH_3$	11.6
Methyl stearate	$R - (CH_2)_7 - CH = CH - (CH_2)_7 - CH_3$	5.5
Methyl oleate	$R - (CH_2)_{16} - CH_3$	22.4
Methyl oleate	$R - (CH_2)_5 - CH = CH - (CH_2)_8 - CH_3$	1.9
Methyl linoleate	$R - (CH_2)_7 - CH = CH - CH_2 - CH = (CH_2)_4 - CH_3$	52.4
Methyl linolenate	$R - (CH_2)_7 - (CH = CH - CH_2)_3 - CH_3$	6.2

*R= $COOCH_3$

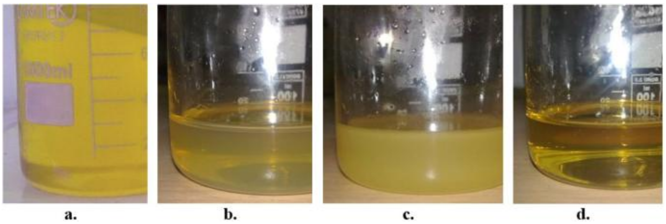

Fig. 2. Biodiesel-EPS blend fuel production and acetone-aided stabilization procedures, a: neat biodiesel, b: EPS-Biodiesel mixture at 50℃, c: EPS-Biodiesel mixture at ambient temperature (25℃) and, d: Biodiesel-EPS-acetone fuel blend

Subsequently, cloud point of the biodiesel-polymer-acetone fuel was also analyzed. Poor cold flow properties may result in fuel line and pump blockage, ultimately leading to fuel starvation (Giakoumis, 2013). These problems are particularly enhanced during cold starting particularly at low ambient temperatures and should be addressed either through physical or chemical treatments. Cloud point value of the neat WCO biodiesel used in this study was measured at 9 ºC. As presented in Fig. 3, addition of 100 ml acetone in 1 litter EPS-free biodiesel decreased the cloud point value to 3ºC. Higher values of acetone had no significant impact on cloud point values of EPS-free biodiesel. On the other hand, cloud point values increased proportional to the EPS content. This could be regarded as a drawback to energy recovery from polymer wastes through their dissolution in biodiesel. However, the addition of acetone had a positive influence on the cloud point values of biodiesel-EPS solutions and in part compensated for the disadvantage of EPS addition. As shown in Fig. 3, at the EPS level of 25 g /L biodiesel, by increasing the inclusion rate of acetone from 100 ml/L biodiesel to 150, 200 and 250 ml/L biodiesel, the cloud point value decreased from 15 to13, 10 and 8 ºC, respectively. Similar trends were observed at the higher EPS levels of 50 and 75 g /L biodiesel.

The improvement observed could be explained by the fact that cold flow improving additives such as acetone in this study can decrease the size, or inhibit the formation, of the wax crystallites formed upon cooling the fuel, and thus lower the temperature at which wax plugging becomes a problem (Giakoumis, 2013). Misra and Murthya (2011) also stressed that treatment with chemical additives is the most convenient and economical way of improving the low temperature properties of diesel fuels. They argued that the chemical additives generally referred to as pour point depressants, flow improvers or wax modifiers promote the formation of small (10–100mm) needle shaped crystals. These crystals experience significantly reduced growth and agglomeration rates as temperature decreases below cloud point. On the other hand, although most of these crystals are caught in fuel filters, the cake layer formed on the filter surface is considerably more permeable to fuel flow and therefore the magnitude of their deteriorating impact on cold flow properties of biodiesel is much less (Misra and Murthy, 2011).

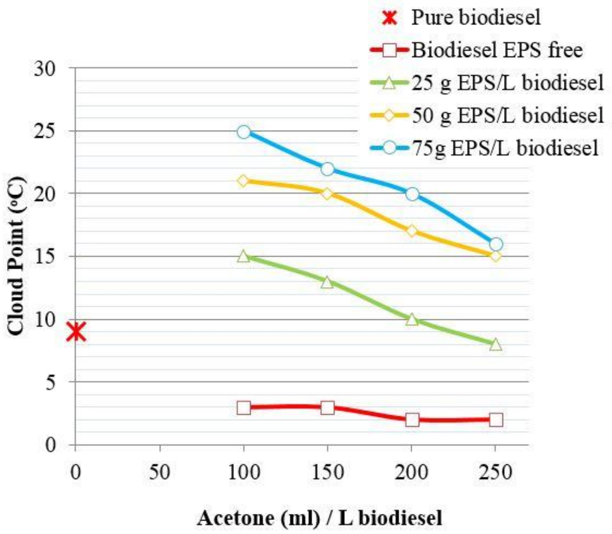

Fig. 3. Cloud point values vs. acetone content at different levels of EPS dissolved in 1L biodiesel

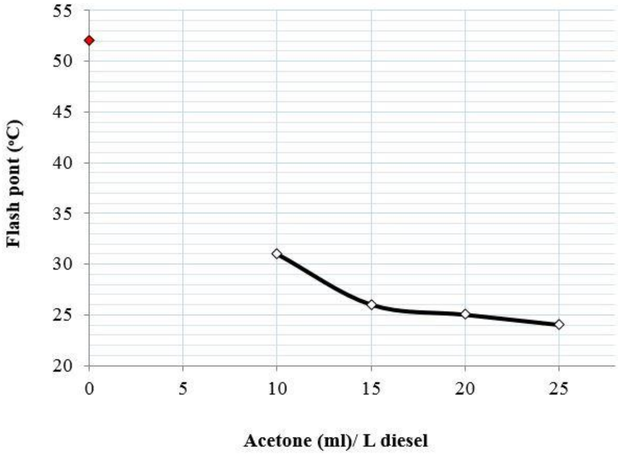

Fig. 4. Flash point values vs. acetone content in diesel fuel

Despite of good performance of acetone as fuel stabilizer and cold flow improver, it is a flammable solvent with a flash point value of as low as -17ºC, and could potentially deteriorate the safe-storage criterion of the fuel; therefore, the effect of acetone inclusion on EPS-biodiesel was also investigated by assessing the flash point value of the EPS-biodiesel-acetone blends. As presented in Fig. 4, flash point value of the petroleum-derived diesel decreased by increasing the acetone content. Moreover, the addition of EPS at all acetone levels also led to dramatic increases in flash point values. But interestingly, increasing the acetone inclusion rate in EPS-free biodiesel fuel and EPS-biodiesel fuel blends caused the flash point values to climb up (Fig. 5). The repetition of all the experiments with industrial grade acetone produced the same results as well. Most probably, a chemical reaction must have taken place between acetone and biodiesel. This is probably the only justification since when scrutinizing the observed changes in the flash point curve of the EPS-free biodiesel caused by the addition of increasing concentrations of acetone in comparison with the other curves i.e. those of the different EPS contents (25, 50 and 75 g/L biodiesel), a constant trend is observed. Therefore, the unexpected results obtained herein could only be associated to the occurrence of a chemical reaction between biodiesel and acetone which led to an increase in flash point value. But the flash point values started decreased by increasing the acetone content more than 200 ml/L biodiesel. This could be ascribed to overshadowing of the chemical phenomenon by the physical impact of extra acetone.

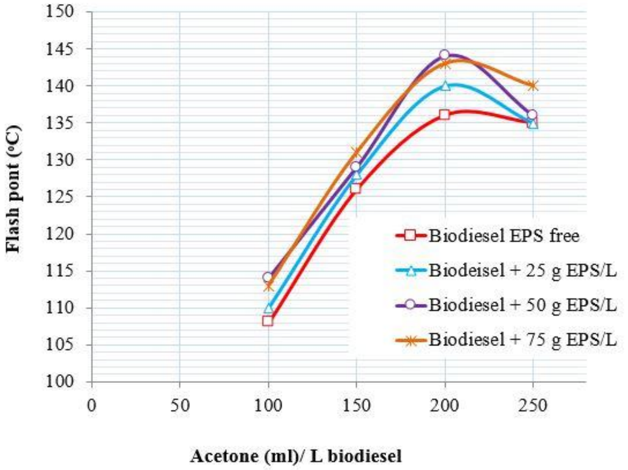

Fig. 5. Flash point values vs. acetone content at different levels of EPS dissolved in 1L biodiesel

4. Conclusions

In this study some co-solvents were utilized as fuel stabilizer to achieve energy recovery from EPS wastes through dissolution in biodiesel and to simultaneously improve biodiesel-EPS cold flow properties. Among all the solvents tested in the present study, acetone was found to have possessed the best stabilization effect when recycling EPS waste by dissolution in biodiesel. Moreover, acetone addition largely compensated for the deteriorating impact of polymer dissolution on cloud point value of the fuel. It also improved the flash point criterion and consequently fuel safety.

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