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Comparison of glycerol ketals, glycerol acetates and branched alcohol-derived fatty esters as cold-flow improvers for palm biodiesel

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HIGHLIGHTS

- ▶ Best cold-flow improvers were 2-butyl esters of palm oil.
- ▶ Pour and cloud points were decreased about 6 °C.
- ▶ DSC analyses showed that additives decrease crystallization points of biodiesel.
- ▶ Particle size analyses showed that the additives act by decreasing crystal sizes.
- ▶ 2-Butyl esters of palm oil did not have detrimental impact on fuel properties.

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ABSTRACT

Comparative results on the evaluation of cold-flow improvers for palm biodiesel, of the type glycerol ketals, glycerol acetates and branched alcohol-derived fatty esters, are presented. Glycerol ketals were obtained through the reaction of glycerol with acetone catalyzed by *p*-toluene sulfonic acid. Glycerol acetates were obtained through the reaction of glycerol with acetic acid catalyzed by *p*-toluene sulfonic acid. Branched alcohol-derived fatty esters were obtained through the esterification of palm-derived fatty acids with branched alcohols, catalyzed by sulfuric acid. These additives were mixed with palm biodiesel at levels of 1%, 3%, 5% and 10% and the effects on pour and cloud points were measured. Crystallization points of pure and additivated palm biodiesel were determined by differential scanning calorimetry (DSC). Effects of additives on the crystallization process were analyzed by measuring the size of crystals formed upon cooling. The best cold-flow improvers were 2-butyl esters of palm oil; upon addition of 5% of this additive the pour and cloud points were reduced about 6 °C. DSC analyses accurately showed that the additives decrease decrystallization points of biodiesel. Particle size analyses by dynamic light scattering showed that the additives act by decreasing crystal sizes; besides, this technique proved to be an easy and accurate way to determine the cold-flow behavior of biodiesel. Addition of 2-butyl esters of palm oil did not have any detrimental impact on the fuel properties of palm biodiesel.

1. Introduction

Biodiesel, which is a relatively clean-burning, renewable fuel produced from animal and vegetable oils, is used to replace a portion of the diesel fuel consumed worldwide. Biodiesel has three large advantages over regular petroleum diesel [1]. First, it is not a petroleum-based fuel, therefore, it reduces the dependency on petroleum. Second, biodiesel is produced domestically, which means that using biodiesel will create jobs and contribute to local economies. The third major advantage of biodiesel is that it is cleaner than conventional diesel; biodiesel produces significantly less harmful emissions than regular petroleum diesel when burned in a combustion engine [1]. Compared to petroleum-based diesel, biodiesel reduces emissions of carbon monoxide (by approximately 50%), carbon dioxide (by 78% on a net lifecycle basis), aromatic hydrocarbon (56% reduction of benzofluoranthene, 71% reduction of benzopyrenes), sulfur oxides (completely eliminates emissions of SO_x because biodiesel does not contain sulfur), particulate (by as much as 65% of small particles of solid combustion products); besides, biodiesel is non-flammable (has a flash point generally higher than of 160 °C), biodegradable (it is fully degraded in a waterway environment within approximately 28 days, just like sugar) and non-toxic. However, biodiesel emits higher levels of nitrogen oxides (NO_x); pure biodiesel emits up to 13% more NO_x than conventional diesel. From an engine point of view, most of biodiesels have higher cetane number than conventional diesel, both biodiesel and mineral diesel have similar energy and power

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content, biodiesel has better lubricant characteristics enabling a reduction in wear and extended efficiency for injectors.

Biodiesel also has some performance disadvantages. The performance of biodiesel in cold conditions is markedly worse than that of petroleum diesel. At low temperatures, diesel fuel forms wax crystals, which can clog fuel lines and filters in a vehicle's fuel system [2,3]. The cloud point (CP) is the temperature at which a sample of the fuel starts to appear cloudy, indicating that wax crystals (ca. 0.5 mm size) have begun to form. As the temperature is decreased, crystals continuing precipitating and gradually growth reaching sizes of ca. 0.5–1 mm, then they begun to agglomerate and the system is not anymore liquid. The pour point (PP) is the temperature below which the fuel will not flow [4]. The cloud and pour points for biodiesel are higher than those for petroleum diesel. While the CP and PP of petroleum diesel are ca. −15 °C and −27 °C, respectively, the corresponding values for biodiesel are about 15–25 °C higher [2,4]. Vehicles running on biodiesel blends may therefore exhibit more drivability problems at less severe winter temperatures than do vehicles running on petroleum diesel. The solvent property of biodiesel can cause other fuel-system problems. Biodiesel may be incompatible with the seals used in the fuel systems of older vehicles and machinery, necessitating the replacement of those parts if biodiesel blends are used. Petroleum diesel forms deposits in vehicular fuel systems, and because biodiesel can loosen those deposits, they can migrate and clog fuel lines and filters. Another disadvantage of biodiesel is that it tends to reduce fuel economy. Energy efficiency is the percentage of the fuel's thermal energy that is delivered as engine output, and biodiesel has shown no significant effect on the energy efficiency of any test engine. Volumetric efficiency, a measure that is more familiar to most vehicle users, usually is expressed as miles traveled per gallon of fuel (or kilometers per liter of fuel). The energy content per gallon of biodiesel is approximately 11% lower than that of petroleum diesel. Composition of fatty raw materials used for biodiesel production has a huge effect on fuel properties. Table 1 shows that biodiesel from animal fats and palm oil, which have the highest levels of saturated fatty acids, have the highest CP and PP. Palm oil is the main biodiesel raw material used in tropical countries. Therefore, poor cold-flow properties of this biodiesel are a critical issue that needs to be solved, because room temperatures lower than CP and PP can be easily reached in regions located at high altitudes.

Several strategies have been reported to improve cold-flow properties of biodiesel, amongst the most important are: (i) blending with petroleum diesel [2,11–14], (ii) winterization to reduce the amount of saturated fatty esters [6,15–18], (iii) use of additives to reduce intramolecular associations and, therefore, to decrease crystallization temperatures [3,4,6,10,19–31] and (iv) blending of biodiesels from different sources [14,32,40]. The third strategy, i.e., use of additives, has been the most widely investigated, especially with additives derived from glycerol. Melero et al. [41] investigated the influence of oxygenated compounds derived from glycerol on the quality parameters (European standard EN 14214) of soybean biodiesel. The glycerol-derived oxygenated compounds studied were: a mixture of tert-butylated glycerol (5 wt.% mono-tert-butyl glycerol, 55 wt.% di-tert-butyl glycerol, 38 wt.% tri-tert-butyl glycerol), a glycerol ketal (2,2-dimethyl-4-hydroxymethyl-1,3-dioxolane 98 wt.%), tri-acetyl glycerol and a mixture of glycerol esters (6 wt.% mono-acetyl glycerol, 45 wt.% di-acetyl glycerol, 47 wt.% tri-acetyl glycerol). The best performance as a biodiesel component was achieved by the mixture of tert-butylated glycerol obtained from the etherification of glycerol with isobutylene. Unfortunately, isobutylene availability in refineries is usually very limited and mainly addressed to the production of ETBE and alkylates. García et al. [42] investigated a new ketal derived from glycerin (2,2-dimethyl-1,3-dioxolan-4-yl methyl acetate) as a biodiesel fuel component. The biodiesel used was a commercial European soybean-based biodiesel. They found that this additive not only improves biodiesel viscosity but also meets the requirements established by diesel and biodiesel fuels by the European and American Standards (EN 14214 and ASTM D6751, respectively) for other important parameters, such as flash point and oxidation stability, which have not been studied before with previous ketals. Although the new obtained ketal does not improve cold properties as much as triacetin, it does not exert a negative effect either.

This manuscript presents the comparative results on the evaluation of cold-flow improvers for palm biodiesel of the type glycerol ketals, glycerol triacetate and branched alcohol-derived fatty esters. These additives were mixed with palm biodiesel at levels of 1%, 3%, 5% and 10% and their effects on pour and cloud points as well as on crystallization temperatures and crystal sizes were measured. The comparative effect of these additives on the cold-flow properties of palm biodiesel, the most popular in tropical countries, has not been previously reported. In addition, particle size analyses (by dynamic light scattering) were carried out to investigate the effect of the additives on the crystallization process of palm biodiesel; this technique has not been previously used for this kind of study. It has been reported that some additives improve the cold-flow properties of biodiesel but negatively affect other properties required by international standards [41,42]. Amongst these properties, flash point, oxidation stability and viscosity have been the most affected. Therefore, these properties were evaluated for the best cold-flow improver found in this work.

Table 1
Cold-flow properties of biodiesel from different sources.

Oil/alcohol	Viscosity (cP)	Cloud point (°C)	Pour point (°C)	Refs.
Canola/methanol	4.23	−3	−4	[5]
Canola/ethanol	–	−1	−6	[2]
Soy/methanol	4.01	0	−2	[6]
Soy/ethanol	4.41	1	−4	[2]
Soy/butanol	–	−3	−7	
Soy/isopropanol	–	−9	−12	
Sunflower/methanol	4.30	−1	−3	
Sunflower/ethanol	–	−1	−5	
Rapeseed/methanol	3.85	−2	−9	
Rapeseed/ethanol	–	−2	−15	
Palm/methanol	3.94	16	12	[7,8]
Palm/ethanol	–	8	6	[2]
Cotton/methanol	–	6	0	[5]
Beef tallow/methanol	4.9	17	15	[9]
Lard/methanol	4.9	11	12	[10]