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Effect of monopalmitic content and temperature on precipitation rate in biodiesel-petroleum diesel blends

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Abstract The need for cleaner fuel increases alongside the necessity of reducing greenhouse gas emissions. Biodiesel is considered as one of best options for cleaner energy. However, it has disadvantages due to lower stability, lesser cold flow properties (CFP), and higher viscosity, which are mainly caused by fatty acid type and content. These works investigate CFP of various biodiesel blends B20 & B30, with the objective on how the monopalmytic as one of the saturated monoglycerides (SMG) content and Temperatures affect the precipitation rate. A set of 100ml separatory funnels containing various samples were put in refrigerators in controlled-temperature, i.e.15°C; 20°C; and room temperature. The rate of precipitation was observed every day for 2 weeks using 0.8µm membrane filter. Results indicated precipitation rate of B30 was higher than that of B20. As it was expected, the precipitate was taken at the same temperature, 20°C, resulting in B30 had more precipitate in the end (37.6 mg) compared to B20 (22.2 mg). The closer to cloud point also indicates the higher rate of precipitation as 4th day B20 at 15°C (25.4 mg) compared 4th day B20 at 20°C (19.3 mg). The change of crystal from less stable α-phase to more stable, less soluble β-phase is also proven to significantly affect the rate of precipitation.

1 Introduction

Biodiesel is a fast growing renewable energy that can be produced from animal and plant oil, as well as from oil waste such as cooking oil waste through esterification process (Altaie et al. 2016). The transesterification process transforms the fatty acid in oil into fatty acid methyl ester (FAME). The main composition of biodiesel itself are methyl ester consists of a different type; oleic, linoleic, palmitic. The properties of biodiesel largely depend on its

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composition, and it mostly because of the oil sources. Fatty acid composition affects the cold flow properties (CFP) significantly. Biodiesel freezing point increases as atom carbon in the chain of carbon increases and decreases as double bond increased. Biodiesel that comes from saturated fatty acid has higher Cloud point (CP) and Pour point (PP). Thus Biodiesel from vegetable oil have CP and PP lower from animal oil [1]

Transesterification of triglycerides with alcohol produces alkyl esters (biodiesel) and glycerol. This reaction happened through series of transformation from triacylglycerol to diacylglycerol and monoacylglycerol to eventually become glycerol. In each step, methyl ester is made. In normal optimum condition yield of conversion very high, so that trace from triacylglycerol is very low, however this trace even in very minimum amount affect the biodiesel properties significantly [1]

Biodiesel has its own distinct advantages as it is more safety-renewable energy, nontoxic and better performance on a car than petroleum diesel, and has a lubricant effect [2]. However, until now only 20% biodiesel-80% Petroleum diesel blend (B20) has been allowed to be used in the car without modification. This is due to Cold Flow Properties (CFP) that causes precipitation to form at not just below cloud point (CP) temperature but also above CP [3]. This precipitate leads to the fuel filter and dispenser filter to eventually clogged. This made blend range that allowed only 5-20% as ruled in ASTM D9675.

The precipitation normally occurs because of following condition: (1) blending biodiesel with petroleum diesel, (2) Transesterification with branched-chain alcohol, (3) Winterization, (4) Chemical additives, (5) Fatty acid modification [4]. Winterization is the most common reason for precipitation. Mainly because of the temperature can go down below cloud point, however The precipitation also occurs above cloud point due to a huge gap between cloud point and final melting point. This happens on high saturated monoglycerides contain between 0.2-0.3%wt [5]

The formation of precipitate starts with a trace of monoglycerides that unsaturated become a cloud, or change in solution color into milky. At this point it will form metastable crystal. The next step crystal become polymorf and increases in number, bigger in size, and more stable. This stable crystal then creates precipitation in the bottom of the container [6].

This study focused on the precipitation occurs at temperatures above cloud point. The aim of this experiment is to know how the rate of precipitation happened during unstable period and stable period. Monopalmitic is chosen as variation as it affects the CFP significantly [7], and it is abundant in palm-oil feedstock.

2 Materials and Methods

2.1 Characterization of Biodiesel and Petroleum diesel

Biodiesel that was used are palmitic oil bought from Indonesia. The petroleum diesel was bought from Indonesia. The composition profile of this biodiesel and petroleum diesel was characterized by using Gas Chromatography/Mass Spectrometry.

Biodiesel was added volumetrically to petroleum diesel to obtain B20 and B30. To modify the monopalmitic content, a certain mass of monopalmitic is added to change the monopalmitic contain from around 0.4% to 0.6% and 0.8%. Magnetic stirer was used to homogenize the solution at 55°C and speed of 1000 rpm. Characterisation for biodiesel and petroleum diesel were done on the following ASTM properties: density, kinematic viscosity, cloud point, water and sediment, fame contain, acid number, oxidation stability, aromatic contain, monoglyceride contain, total glycerol, free glycerol.

In order to increase monopalmitic contain, standard equation for concentration are used as below:

$$m_a = \frac{C \times V \times \rho}{x} \quad (1)$$

m_a = mass of monopalmitic to add (g)
C = Concentration to increase (wt/wt%)
V = Volume of B100 (ml)
P = Density (g/ml)

2.2 Beaker Test

Biodiesel blend consist of B20, B30, and Monopalmitic variation were observed every day for the first week and on 10th and 14th day for the 2nd week. This biodiesel was stored under controlled-refrigerator at temperature of 15°C, 20°C, and room temperature. Room temperature was ranging between 28-30°C. The sample then was taken each day to undergo vacuum filtration with membrane filter pores 0,8µ. This method is a modification from Cold Soak Filter Test (CSFT) from ASTM D7501. The standard method from ASTM is for determination of fuel filter blocking potential of biodiesel. The initial method controled biodiesel around 4,5°C for 16 hour then filtered using vacuum filter 0,7µm. This work changed the temperature to observe how the biodiesel perform under various temperature that is higher than cloud point.

3 Results and discussion

3.1 Characterization result

Parameters that influence the performance of biodiesel have been analyzed . Tthe cloud point (CPs of B30 was higher than B20. Table 1 shows basic characterization as ruled in ASTM, for the petroleum diesel and biodiesel used in this experiment. Table 2 shows that Monopalmitic and Stearic as monoglycerides that dominant in the sample. As the precipitate contained low Monooleic, it was considered that monooleic has minimum effect on the precipitation.

Table 1 Parameter Analysis for Biodiesel and Petroleum Diesel

Paramater	Units	Petroleum diesel	Biodiesel
Density at 15C	kg/m3	842.5	856.8
Kinematic Viscosity	mm2/s	3.35	4.51
Cloud Point	°C	1.7	n.a
Water and Sedimen	% (wt)	n.a	0
Fame Contain	% (wt)	n.a	99.5
Acid Number	mg KOH/g	n.a	0.34
Oxidation stability	minutes	n.a	601.5
Aromatic Contain	% (wt)	2.54	n.a
Monoglyceride contain	% (wt)	n.a	0.4
Total Glycerol	% (wt)	n.a	0.1

Free Glycerol	% (wt)	n.a	0.003

n.a. = data not available

Table 2 Monoglycerides percentage contain

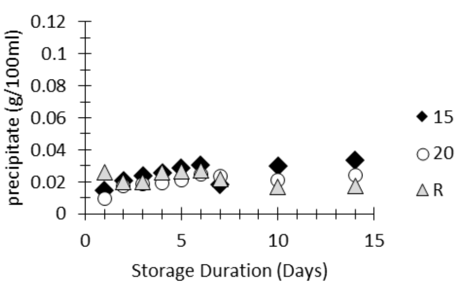
Monoglyceride	Mass Percentage
Monopalmitic	0.357
Monooleic	0.183
Monostearic	0.391

Table 3 Paramater Analysis on Biodiesel Blend

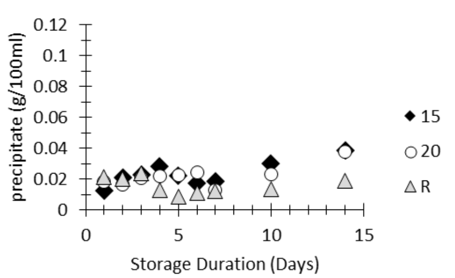
Parameter	Unit	Result		Petroleum diesel standard	Methods
		B20	B30		
Density at 15	kg/m3	841.1	849.1	815-870	ASTM D4052
Kinematic Viscosity	Mm2/s	3.75	3.82	2-4.5	ASTM D445
Cloud Point	°C	4.3	4.7	18 (Max)	ASTM D5773
Water	% (wt)	208.11	210.31	500 (Max)	ASTM D6304
Sediment	% (wt)	0	0	0.01 (Max)	ASTM D473
Fame Contain	% (vol)	19.9	29.9	20	ASTM D7806
Acid Number	mg KOH/g	0.089	0.101	0.6	ASTM D664
Oxidation stability	Hour	36.87	36.59	35 (Min)	EN 15751

3.2 Baker test result

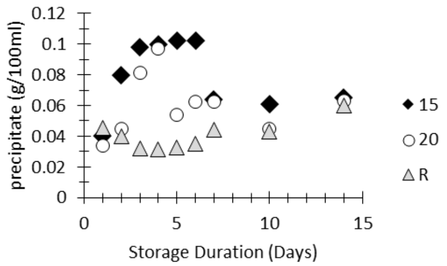
Biodiesel sample was put in separator dunnel then vacuum –filtered on daily schedule . the results were put in g/100ml. Standard monopalmitin contain from biodiesel are around 0,4%. The result shown are for the initial monopalmitin contain and after modification



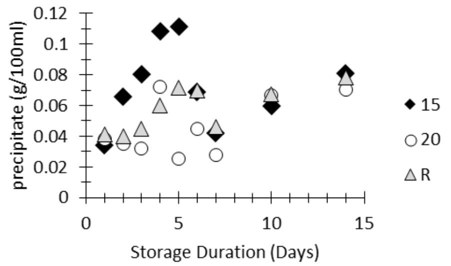
(a)



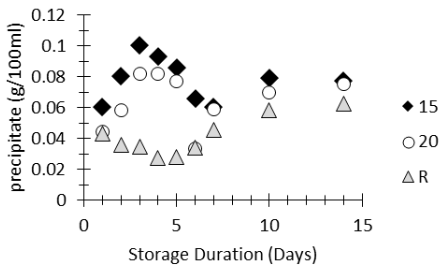
(b)



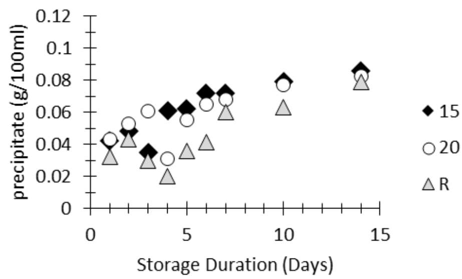
(c)



(d)



(e)



(f)

Fig. 1. The change of formation precipitate at :(a) B20, (b) B30, (c) B20 0,6% Monopalmitic, (d) B30 0,6% Monopalmitic, (e) B20 0,8% Monopalmitic, (f) B30 0,8% Monopalmitic

Between 5th – 7th days at downeard fluctuation of precipitation weight

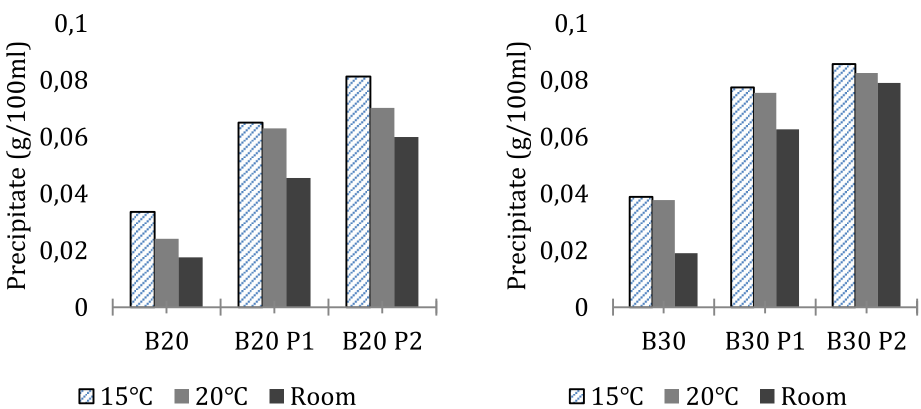


Fig. 2. Precipitate at the end of 14th day

and precipitation rate. This due to changes in the crystal stability.Differential scanning calorimetry can further explain that in biodiesel, at early start in a cooling process, metastable α-phase will change into its final form more stable but less soluble β-phase. This β-phase also has higher final melting points (FMT), which much effect the precipitate at the last day [8].

Moreover Chupka also found that at low concentration of monopalmitic,, all of the precipitate dissolved during the transformation process. Thus the decreasing of precipitate also affected by this.

Fig 1. Also explain how the change in temperature affect the rate of precipitation. B20 which stored at 15°C has higher rate at α-phase (0.003g/100ml/day) compared to B20 stored at 20°C (0.0026g/100ml/day). This due to the closer to cloud point (CP), in this experiment between 4-5°C.

Adding more monopalmitic increase the CP, as CP affect the precipitation rate, thus if we compare the precipitation rate at α-phase at the same temperature 15°C, B20 has lower precipitation (0.003g/100ml/day) compared to B20 0.8% Monopalmitic (0.0137g/100ml/day). Same result for B30 (0.0049g/100ml/day) compared to B30 0.8% Monopalmitic (0.0237g/100ml/day)

Moreover Monopalmitic has reverse micelles structure, this helps rate precipitation to increase as it can lower nucleation energy from monoglyceride. Monopalmitic can then assumed to work like catalyst (Dunn, 2009)

Fig. 5 shows the increae in Monopalmitate precipitate significantly. Adding 0,2% saturated monopalmitate increase almost 0.05 mg/100 of prexipitation. The B30 and B20 blends show less The B20 and B20 blends show less significant increase compared to the B20 0.4% Monopalmitic and B20 0.6% Monopalmitic.

4 Conclusion

This CFP study examined the effect of monopalmytic as one of the saturated monoglycerides (SMG) content and temperatures on the precipitation of biodiesel occurred even above cloud point in significant amount. The closer to cloud point the more precipitation produced. After several days, during the 5-7 days the amount of recipitation in the filter decresed, with the concentration on biodiesel-petroleum diesel blend.

5 Acknowledgment

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