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Application of Pineapple Skin Waste as a Source of Biosolvent for Use as Wax Inhibitor

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Abstract

Wax paraffin deposition is a problem faced in the pipeline for petroleum industries that they blockage the partial or full inside the pipe, which will decrease the production rate. One of the treatments is to use the preventive methods called wax inhibitors which are expected to inhibit the crystallization of paraffin wax, and bio-solvent is included. Hydrolysis and fermentation technique are used to produced bio-solvent. Hydrolysis aims to break lignin and hemicellulose, damage the crystal structure, and increase the porosity of the material. At the same time, the occurrence of pentose changes and some glucose into ethanol is present in the fermentation process. Then, purified by the distillation process to obtain bio solvent products that are applied with waxy crude oil can reduce the pour point value of crude oil. From the hydrolysis process with five variations of acid percentage, the amount of reducing sugars increase. By increasing temperature from 50 ° C to 100 ° C, the reducing sugars continues to increase until it reaches the optimal point of 18.2 ° Brix. The amount of inoculant also affects the level of bio-solvent where the optimum results using inoculants are 0.015 g/ml., which produces 6% levels of bioethanol. The high ethanol content of 2% had a density value of 0.979 g/mL. The best °API at 5% is 13.901, and the average value is about 13.0945, where the best viscosity values for ethanol content of 6% are 0.814. Bioethanol testing using waxy crude oil is carried out with the bioethanol content of 6%. The addition of the ethanol contents only decreased the pour point 2-3°C. At sample, #LGK19 experienced a 3°C drop in pour point from 45°C to 42°C. Therefore, it can be concluded that bioethanol used as a solvent can potentially inhibit paraffin deposition.

INTRODUCTION

Paraffin wax deposition is a phenomenon that disturbs the activities of the petroleum industry (Hal[illegible]n et al., 2011). Paraffin consists of a mixture of hydrocarbons formed from a linear chain consisting of 20 to 40 carbon atoms, alkanes with branched, and cyclic chains (Taraneh et al., 2008). Paraffin contained in the well can cause a decrease in production rates and must be treated immediately (Afdhol et al., 2020; Ardiansyah et al., 2019; Hidayat & Abdurrahman, 2018). Thus, Problems regarding crystallization and precipitation of paraffin wax during the production and transportation of crude oil will cost billion-dollar annually (Yang et al., 2015). At a lower temperature, crystallization of waxes creates a problem in the crude oil pipeline that waxes crystalize as an interlocking network of fine sheets, and it will cause the blockage of the pipeline because the waxes trap oil in the cage. Paraffin deposition that can occur in hydrocarbon flow lines has a high-risk potential in oil production because of partial blockage of pipelines Paraffin hydrocarbon liquids, including crude oil and condensate, form a paraffin solid phase when the temperature drops below the liquid cloud point. Cast points are indicators of temperature where oil will solidify into a gel. At the pour point, the fluid still flows under gravity; at the next lower measurement

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temperature (lower than 3 °C), the fluid has already formed a gel and does not flow. In the ambient temperature, where the fluid is at or below the temperature of the pour point, special pouring strategies are needed to maintain fluid flow capability. Therefore, the ambient temperature condition can be analyzed in general, which the analysis is conservative, and the extreme 100-year minimum seabed temperature is used along the pipeline route (Yuan et al., 2012).

The wax problems have been widely treated using chemical additives. The use of wax dispersants can modify the size and shape of wax crystals which alter their growth and surface properties to reduce the affinity of crystal interlocking and forming their dimensional network thereby lower pour point and viscosity. The most widely used wax dissolvers are polymers, they often possess highly polar functional groups in which the polarity is similar to surfactant characters, and it will be considered as the basic prerequisite for dispersant. Polar nitrogen-containing polymers can be applied as a wax dispersant and flow improvers. Besides it, Biosolvent can prevent the hydrocarbon chain longer because bioethanol comes from the reduced sugar content from biomass that is a result of pretreatment., hydrolysis and fermentation processes. Because of the nature of biosolvent which can prevent wax deposition, it can be used as a solvent.

Examples of effective organic solvents include benzene-, carbon disulfide, chlorinated hydrocarbons-, xylene- and toluene-based chemicals. For example, when trichloroethylene-xylene (TEX) was added to Nigerian crude oil in a ratio of 0.01 to 0.1 wt %, TEX was able to depress WAT, reduce the total wax deposition from 0.050 g/g to 0.0015 g/g (at 0.1 wt %), and further increase the wax deposition inhibition performance by adding a corrosion inhibitor (Bello et al., 2006).

There are two methods to overcome these problems, which are divided into prevention and preventive methods (Khaibullina, 2016). The first one is a preventive method which injects the wax inhibitor (Abdurrahman et al., 2018; Al-Yaari, 2011). This wax inhibitor can inhibit the formation of paraffin deposits that solvents can be used as a wax inhibitor.

According to the Indonesian Central Statistics Agency in 2017, pineapple production in 2017 reached 1,795,986 tons and ranked 4th after the production of bananas, mangoes and oranges. Meanwhile, pineapple waste comes from 21.73-24.48% of pineapple production. This figure is relatively large if the waste material is disposed of in a landfill and leads to unhygienic conditions (Bhandari et al., 2013). This work adopted the pineapple skin waste as bio solvent that the use of waste as a new product is a good solution because it is easy to be applied, which the price is relatively cheap and efficient (Bhandari et al., 2013; Yuliusman, Afdhol, & Sanal, 2018). Organic waste processes have been widely applied as bio-solvent such as: palm shells (Yuliusman, Nasruddin, Afdhol, Amiliana, et al., 2017), tea waste (Afdhol, Lubis, et al., 2019), coffee grounds (Yuliusman, Nasruddin, Afdhol, Haris, et al., 2017), risk husk and corn cob waste (Afdhol, Hidayat, et al., 2019), and inorganic waste from plastic waste (Yuliusman, Afdhol, Sanal, et al., 2018).

The purpose of this work is to convert pineapple peels into bioethanol products as a solvent. Therefore, it can identify bioethanol content and a feasibility study for the use as a solvent. An application of bioethanol as a wax inhibitor is to reduce the wax content paraffin in crude oil (Afdhol, Abdurrahman, et al., 2019). In addition, the pineapple is easily obtained, and the selection of pineapple skin waste as bio solvent because of its content which is rich in glucose fiber that makes this waste to be a potential raw material for bio solvent production (Table 1). The sugar contained in waste material can be fermented and has the potential to hydrolyze cellulose and hemicellulose (Conesa et al., 2016).

Table 1. Pineapple skin waste composition

	Component	
	Overall Waste (%)	Skin (%)
Cellulose	19,4	14,0
Hemi-cellulose	22,4	20,2
Lignin	4,7	1,5
Ash	0,7	0,6
CSM	53,4	64,8
Total sugar	11,7	-
Protein	4,4	4,1
Digestion	63,2	64,3

Therefore, this pineapple skin waste can be used as a biosolvent product as a solvent to prevent the occurrence of paraffin deposition and also minimize pollution environment.

METHODOLOGY

Pretreatment

Pineapple skin waste is carried out by physical treatment to reduce the size of the skin, and it is blending between the pineapple skin with a 1:2 aquadest ratio, then separating the pineapple skin pulp and pineapple skin extract. After separation, the hydrolysis process is conducted. Acid preparation for the hydrolysis process is sulfuric acid (H_2SO_4) and anaerobic bacterial preparation for the fermentation process is yeast saccharomyces.

Acid Diluent

Apply acid diluent in the acidification chamber with sulfuric acid concentration of 96% and aquadest. The acid dilution process is conducted by the equation:

$$V1 \; x \; M1 = V2 \; x \; M2 \qquad (1)$$

Lignocellulosic Biomass Hydrolysis

this process aims to break lignin bonds, eliminate lignin and hemicellulose content, damage the crystal structure of cellulose, and increase the porosity of materials (Sun & Cheng, 2002). By entering the prepared pineapple skin waste into a 500 cc Erlenmeyer and adding sulfuric acid (H_2SO_4) with a variable acid concentration of 5%, 10%, 15%, 20%, and 25%. The hydrolysis process is carried out in an oven with temperature variations of 50 °C, 60 °C, 70 °C, 80 °C, 90 °C, 100 °C, 110 °C, 120 °C, 130 °C, 140 °C, and 150 °C for 180 minutes.

Test for Reducing of Sugar Using a Portable Refractometer HT113ATC

Sterilize the device using aquadest and drops of prism refractometer with liquid that has been prepared in the hydrolysis process, then read the results of °Brix on the tool with the help of sunlight for more optimal results.

pH Adjustment

pH around 3.5-4.0 was maintained during hydrolysis and 5.0-6.5 during fermentation. If the pH becomes basic, concentrated HCl is added, and if the acid is added NaOH drop by drop to keep the pH at that range.

Fermentation

Fermentation can convert pentose and some hexose sugars into ethanol, which is a process that has been continually improving, especially with genetic adoption. When the sample has been carried out the process of hydrolysis and pH adjustment, the next step is the fermentation process where the sampel is added yeast with variables 0.005 g/ml, 0.01 g/ml, 0.015 g/ml, 0.02 g/ml, and 0.025 g/ml. All of the samples are tightly closed so that there is no air entered and fermented for 72 hours at room temperature.

Distillation

Distillation uses an alcohol distillation unit at 78.4 ° C (Thangavelu et al., 2019).

Alcohol Content Test

Table 2 shows the common properties of Alcohol.

Table 2. Specification of Alcohol

Properties	Value
Molecular Weight g/mol	46.1
Cold Point °C	-114.1
Boiling Point °C	78.32
Density g/ml	0.7983
Viscosity, cp	1.17

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1. Density Testing with Pycnometer

Considering an empty picnometer and weighing a pycnometer that already contains the sample. Density can be calculated by the equation:

$$\rho = \frac{m}{v} \quad (2)$$

2. Viscosity Testing

This test uses an oswald viscimeter by inserting a 10 ml biosolvent sample into the instrument and starting the test by opening the lid (ball valve) and measuring with a stopwatch to set it to the flash limit. Calculate about 3-5 times of test and measure the average. Then calculate the viscosity of the sample using the equation:

$$\mu = 0.4994 \times t \quad (3)$$

3. Specific Gravity (SG) Testing

Specific Gravity (SG) is determined using the density of water and density of the sample by the equation:

$$SG = \frac{\text{density of solution (wort)}}{\text{density of water}} \quad (4)$$

RESULT AND DISCUSSION

Effect of Hydrolysis with Sulfuric Acid Concentration (H_2SO_4) and Temperature on Reducing Sugar

1. Variation of Sulfuric Acid Concentration (H_2SO_4)

Acid concentration of 5% has a reducing sugar of 5.5 °Brix, and for 10%, 15%, 20%, and 25% have a reducing sugar of 8.8 °Brix, 13.3 °Brix, 16 °Brix, and 18.2 °Brix. Thus, the higher the level of acid concentration, the higher the reducing sugar. High reducing sugar will produce tremendeous levels of ethanol as well (Winarni & Maulidina, 2018), which it can be seen in Figure 1. But acid concentrations which are too high have several disadvantages such as equipment corrosion, long reaction times, and expensive costs (Talebnia et al., 2010).

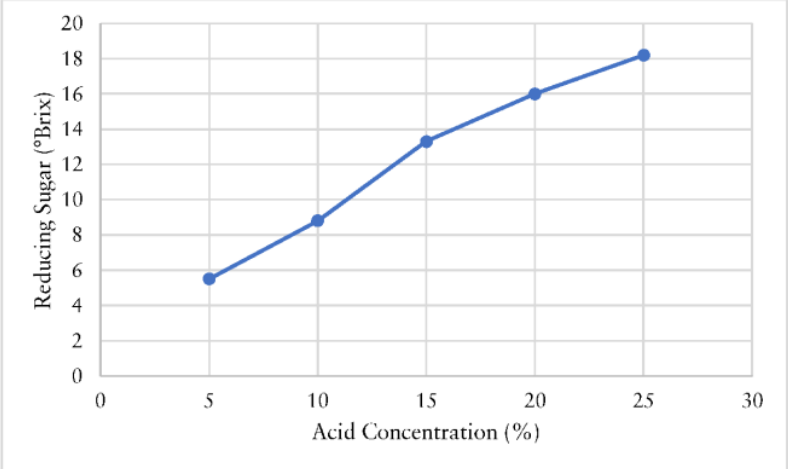

Figure 1. Reducing sugar test for varied acid concentration

2. Temperatur Variations

Temperature is a key factor in the hydrolysis process. In this study, there were 11 variations in temperature, from 50 °C, 60 °C, 70 °C to 150 °C. The higher the temperature, the higher the reducing sugar content in a sample. The elevated temperature is marked by the more intense color after the hydrolysis sample and can be seen as shown in Figure 2.

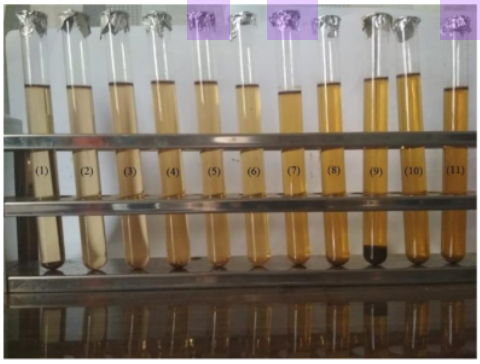

Figure 2. Hydrolysis results at a temperature of (1) 50°C (2) 60°C (3) 70°C (4) 80°C (5) 90°C (6) 100°C (7) 110°C (8) 120°C (9) 130°C (10) 140°C (11) 150°C

However, there is an optimum temperature condition where when hydrolysis passes the optimum temperature, the reduction of sugar content in the sample will also decrease further and can be seen in Figure 3. The graphic reading shows that the optimum temperature is 100 °C. At temperatures of 50 °C to 100 °C, the results of the reducing sugar test keep increasing. But after a temperature reached 100 °C, the result of the reduced sugar test decreases. This occurs because of the presence of glucose in the sample which breaks into charcoal. However, water as a hydrolyzing agent remains in the liquid phase at the optimum temperature. Therefore, good contact occurs which allows the reaction to going well (Osvaldo et al., 2012).

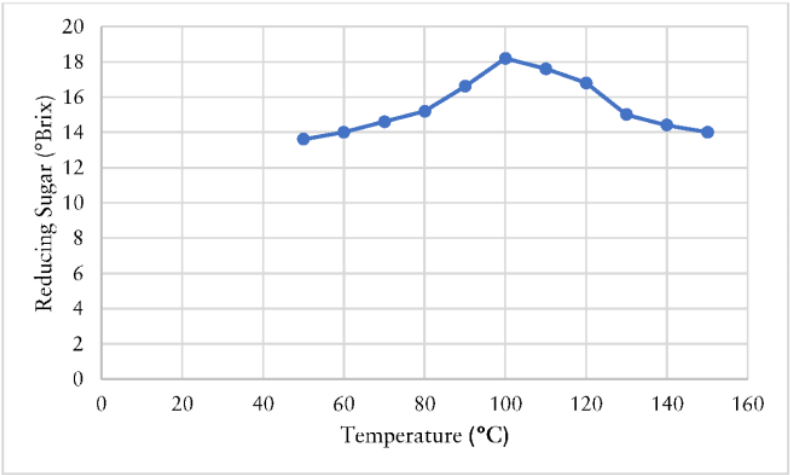

Figure 3. Reduction sugar test at elevated temperature

Effect of Fermentation with Variation of Inoculant Amounts on Biosolvent Content

It can be seen from Figure 4 that the difference in the amount of inoculants affects ethanol levels later, biosolvent levels decrease with increasing inoculant concentration after reaching its optimum point, from the inoculant number 0.005 g/ml to 0.01 g/ml the ethanol content could increase from 2% to 4%, then it would be added the inoculant. Therefore. the amount of inoculant became 0.015 g/ml and the ethanol content still increased to 6%, but when added more inoculant, 0.02 g/ml and 0.025 g/ml, ethanol content decreases by 4%.

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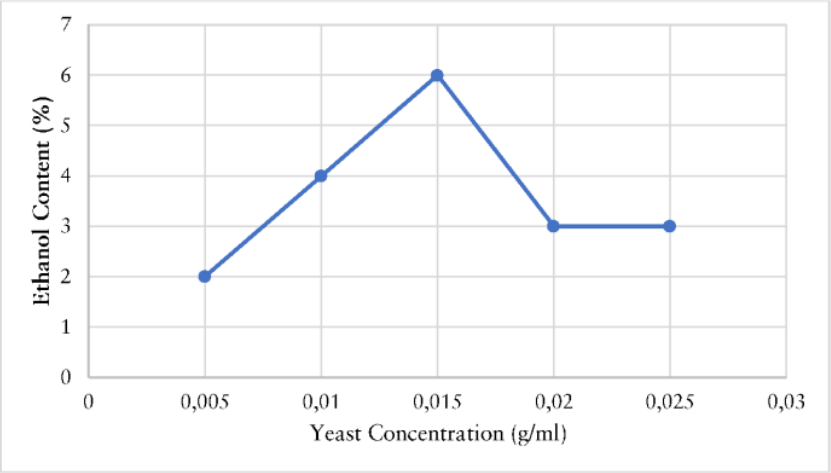

Figure 4. Biosolvent content (%) vs. varied inoculant amount

Density, Specific Gravity (SG), and Viscosity

In the Figure 5, the higher the ethanol content, the lower the density value of ethanol. Therefore, it has an inverse relationship. The ethanol content of 2%, 3%, 4%, and 6% had a density value of 0.979 g/ml, 0.978 g/ml, 0.975 g/ml, and 0.97 g/ml. Thus, the average ethanol content of 2%, 3%, 4%, and 6% ethanol is 0.975. The higher the ethanol content, the higher the SG value. Because the density is directly proportional to SG. The average SG of ethanol 2%, 3%, 4%, and 6% was 0.9785.

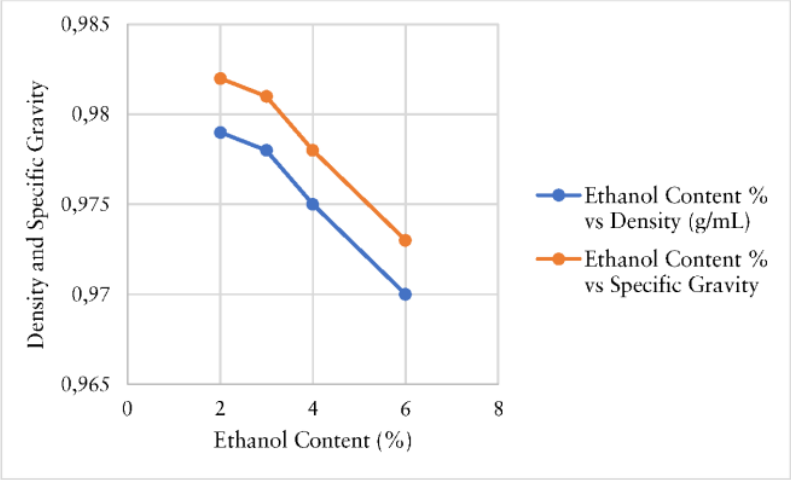

Figure 5. Effect of varied biosolvent content on density and specific gravity

Besides it, the °API values are directly proportional to specific gravity, which the higher the ethanol content, the higher the °API values. Figure 6 shows the ethanol contents for 2%,3%,4%, and 6% that had each °API around 12.583, 12.728, 13.166, and 13.901, and the average value is about 13.0945. The flash point and fire point values show the same thing as the ethanol properties, which the higher the bioethanol content, the more the flash point and fire point values. The ethanol content of 2%, 3%, 4%, and 6% had flash point values of 48 °C, 37 °C, 34 °C, and 33 °C, Meanwhile the fire point values are 64 °C, 63 °C, 61 °C, and 61 °C. Therefore, Figure 7 shows the average value of the flash point and fire point of 2%, 3%, 4%, and 6% ethanol content are 38 and 62.25.

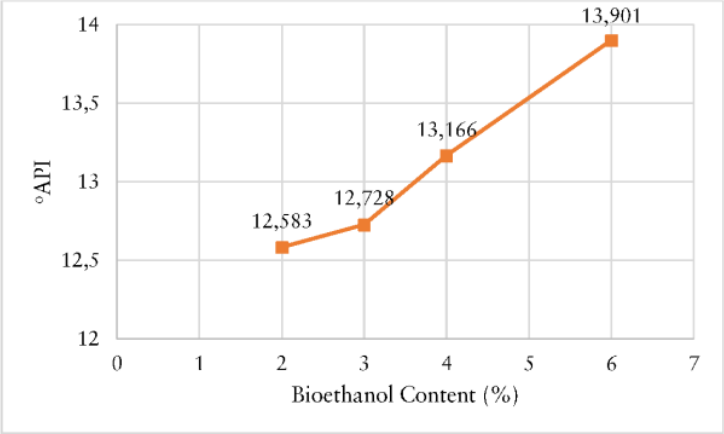

Figure 6. Effect of varied bioethanol content on °API

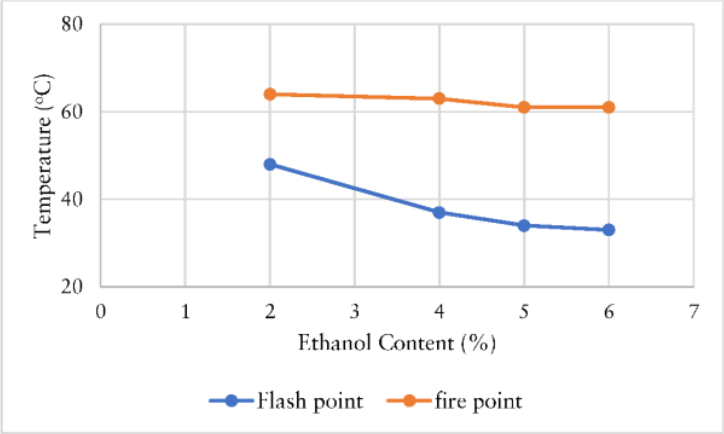

Figure 7. Effect of varied bioethanol content on flash and fire point

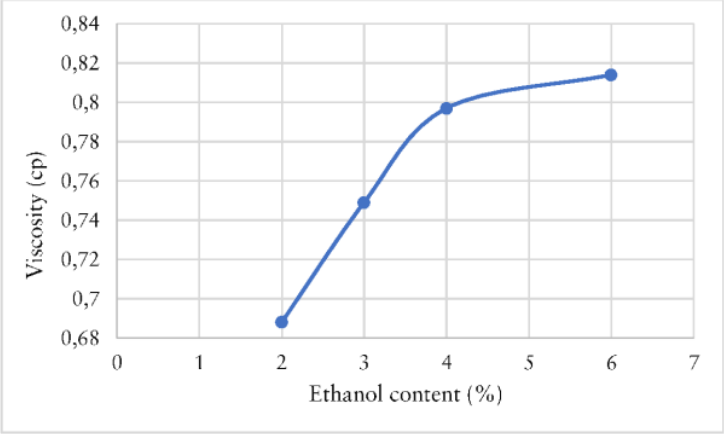

Figure 8. Effect of varied bioethanol content on viscosity

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The higher the ethanol content, the more the viscosity (Figure 8). Therefore, it can be concluded that the relationship between ethanol content and viscosity is directly proportional, where the viscosity values for ethanol content of 2%, 3%, 4%, and 6% are 0.688, 0.749, 0.797, and 0.814. Thus, the average value of viscosity at ethanol content of 2%, 3%, 4%, and 6% is 0.762.

Mixing Methanol with Waxy Crude Oil

Bioethanol testing using waxy crude oil is conducted with the optimum bioethanol content is 6%. The crude oil is obtained from wells at PT SPR Langgak containing the wax, which are LGK25, LGK19, and LGK03. Table 3 shows the change on pour point when adding bioethanol into waxy crude oil.

Table 3. The aftereffect on pour point when adding bioethanol into the waxy crude oil

Well	Without Ethanol (°C)	Mixing Ratio of Waxy Crude Oil + Ethanol (°C)					
		5%	10%	15%	20%	50%	100%
#LGK25	44	44	44	43	43	42	42
#LGK19	45	44	43	43	43	42	42
#LGK03	47	47	46	46	46	46	46

Figure 9 shows the pour point value for each waxy crude oil in which the trends are not significantly declined where to pour point is the temperature below which the liquid loses the flow's characteristics. The addition of the ethanol contents around 5%, 10%, 15%, 20%, 50% and 100% only decreased the pour point 2-3 °C.

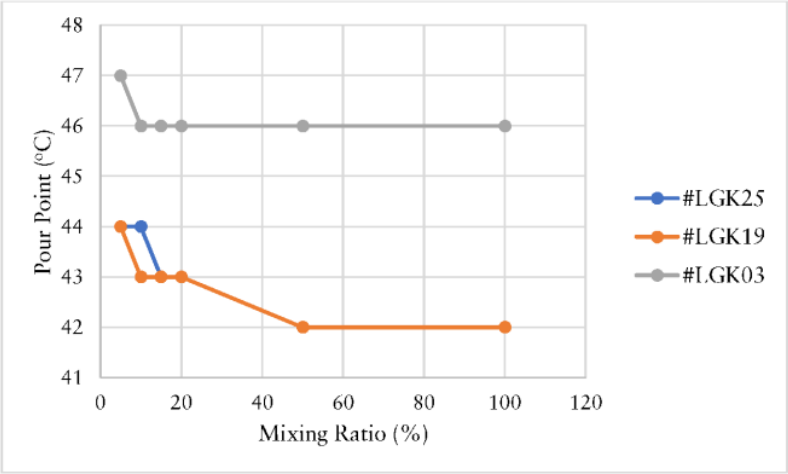

Figure 9. The difference on pour point after adding varied bioethanol concentration

Mixing bioethanol with waxy crude oil can reduce the pour point value by 1 °C to 3 °C. #LGK25 well experienced a 2 °C drop in pour point from 45 °C to 43 °C, #LGK19 experienced a 3 °C drop in pour point from 45 °C to 42 °C, and #LGK03 well oil experienced a 1 °C drop in pour point from 47 ° C to 46 ° C. However, the recommended bioethanol dosage is not higher than 400 ppm (400,000 mg in 1,000,000 ml) because it is not economically recommended.

CONCLUSION

The wax deposition is the most common flow assurance problem endured by petroleum industries, especially during the production and transportation of crude oil. This study carried out the waste of pineapple skin through 4 stage procedures to become a bio solvent, pretreatment by decreasing sample size, hydrolysis with a sulfuric acid catalyst, fermentation with Saccharomyces, and distillation with a temperature of 78.4 °C with the fermentation of 450 ml samples producing ethanol by ± 50 ml. The optimum reducing sugar in this study is 18.2 °Brix with a temperature of 100 °C and 25% sulfuric acid with content 6% alcohol at the amount of inoculant 0.015 g/ml The ethanol high content of 2% had a density value of 0.979 g/ml. The best °API at 5% is 13.901, and the average value is about 13.0945.

Where the best viscosity values for ethanol content of 6% are 0.814. Bioethanol testing using waxy crude oil is conducted with the optimum bioethanol content is 6%. The addition of the ethanol contents only decreased the pour point 2-3°C. at sample #LGK19 experienced a 3°C drop in pour point from 45°C to 42°C. Therefore, it can be concluded that bieotanol used as a solvent can potentially inhibit paraffin deposition.

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