

COMPARISON OF THE ADDITION OF TRIACETIN TO PETROLEUM AND WASTE PLASTIC FUELS

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ABSTRACT

The increasing production capacity of biodiesel every year, the by product in the form of glycerol is increasing and causing the price of glycerol to fall. To increase its value, glycerol can be synthesized into triacetin which can be used as a fuel bio-additive. This study aims to determine the effect of triacetin on the quality of the fuel produced by the pyrolysis of plastic waste and RON 88 gasoline. The research method begins with the synthesis of triacetin from glycerol and acetic acid using Amberlyst 15 wet catalyst in a three-neck flask. The operating temperature was maintained at 100°C with a mixing speed of 290 rpm. Then the triacetin obtained were mixed with fuel from the plastic waste pyrolysis and RON 88 gasoline with a percentage variation of 0 % to 20 % v/v. The best effect was obtained by adding 20 % v/v of triacetin to each fuel. In the plastic waste pyrolysis fuel, the density and viscosity decreased by 0.0046 and 0.093, respectively, and increased calorific value by 160.87. While the RON 88 fuel can increase the mileage by 4.60 % on car engines and 11.11 % on motorcycle engines and can increase the octane number up to 89.

Keywords: bio-additive, fuel, glycerol, octane number, triacetin.

INTRODUCTION

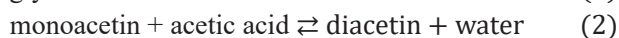
Glycerol is a promising inexpensive feedstock for producing various value-added products. Glycerol can be produced from the biodiesel industry with the amount of product being 10 % of biodiesel. a promising low-cost raw material to produce various value-added products. Glycerol can be produced from the biodiesel industry with the amount of product being 10 % of biodiesel [1]. In 2019, 46.7 billion liters of biodiesel were produced [2] and it is increasing every year [3]. Due to increased biodiesel production, the

availability of glycerol may exceed market demand, causing the price to fall [4]. In addition, crude glycerol still contains components of water and other impurities, causing low economic value. Therefore, glycerol needs to be converted into high-value products. One of the compounds derived from glycerol is triacetin, which is a good bio-additive as an anti-knocking agent [5].

So far, Indonesia still uses imported additives in the form of methyl tertiary butyl ether (MTBE) and ethyl tertiary butyl ether (ETBE) where the production uses the petrochemical route [6]. Triacetin can replace MTBE and ETBE as an additive that is environmentally

friendly, renewable, and less toxic than MTBE and ETBE [7]. This research is focused on studying the effect of triacetin on the quality of fuel. Considering the alternative energy opportunities from biodiesel by-products which are increasing along with the increase in biodiesel production. So, it is hoped that the addition of triacetin as an environmentally friendly bio-additive can improve the quality of fuel.

One way to increase the economic value of glycerol is by acetylation using acetic acid [8]. The acetylation reaction of glycerol with acetic acid will produce acetin (monoacetin, diacetin, and triacetin) which has good commercial significance [9, 10]. Triacetin has potential in the energy sector as an alternative chemical for fuel bio-additives [11]. The combination of biodiesel with 10 % triacetin can improve engine performance in all aspects [12]. The reaction to form triacetin from glycerol is a parallel series reaction with the reaction steps written in Eq. (1 - 3).



The formation of triacetin from glycerol can be accelerated by using various catalysts [13]. High conversion values obtained with short reaction times and low reaction temperatures are a consideration of the selection of homogeneous catalysts [5] such as sulfuric acid [14], phosphoric acid, nitric acid and hydrochloric acid [15]. Unfortunately, these catalyst are difficult to separate from the product [16]. In addition, acidic homogeneous catalysts can corrode equipment, cause adverse effects on the environment, and cannot be recovered [17]. As a consequence, heterogeneous catalysts such as Fe_2O_3 /activated carbon [16], amberlyst-15 [18], Zr-natural zeolite [19], niobic acid supported TPA [20], silica-alumina [21], $\text{Fe}_4(\text{SiW}_{12}\text{O}_{40})_3$ [22], $\text{H}_3\text{PW}_{12}\text{O}_{40}$ [23], and $\text{SO}_4^{2-}/\text{SnO}_2$ [24] are preferred to intensify the reaction.

The use of triacetin as a bio-additive can reduce engine exhaust fumes due to the reduction of carbon molecules in the fuel mixture. Triacetin ($\text{C}_9\text{H}_{14}\text{O}_6$) is a good anti-knocking additive and is easily soluble in biodiesel. Triacetin also has the benefit of suppressing knocking on the engine, increasing engine performance, and reducing emissions [12]. Biodiesel

that uses triacetin as an additive, which is also a cetane number enhancer, has resulted in lower NO emissions to a reasonable extent [25]. In addition, triacetin also functions as an octane booster for gasoline [26], cold flow improver, and viscosity reducer in biodiesel [27].

EXPERIMENTAL

Materials

This study used 98 % glycerol from P&G Chemicals, 98 % sulfuric acid from Chang Cun Petrochemical and amberlyst-15 from The Dow Chemical Company. The fuel that will be used as a sample is RON 88 gasoline and fuel from the pyrolysis of plastic waste. The GC-MS test was carried out to determine the components contained in the fuel from the pyrolysis of plastic waste.

Triacetin synthesis

Glycerol and acetic acid were reacted in a three-neck flask with a ratio of 1:3 using Amberlyst-15 catalyst as much as 3 % by weight of glycerol. The reaction temperature used was 100°C for 120 min with a mixing speed of 120 rpm.

Triacetin blending into fuel

The synthesized triacetin was then mixed into the fuel from the pyrolysis of plastic waste and RON 88 gasoline. The addition of triacetin to the fuel from the pyrolysis of plastic waste was 0 % and 20 % v/v. While mixing with RON 88 fuel as much as 0 %, 10 %, and 20 % v/v. The fuel that has been added with triacetin is then tested including physical tests, namely specific gravity, density, viscosity, flashpoint, and calorific value. In addition, octane number test and engine performance tests were also carried out to determine the effect of adding triacetin in fuel.

RESULTS AND DISCUSSION

GC-MS test results of fuel from pyrolysis of plastic waste

In this study, a GC-MS test was carried out on the fuel from the pyrolysis of plastic waste to determine the constituent compounds. The type of plastic used as the raw material for this pyrolysis is polypropylene (PP). Table 1 shows that the largest component contained in the fuel from the pyrolysis of plastic waste is gas (C1 - C5)

Table 1. Composition of fuel from the pyrolysis of plastic waste.

No	Carbon chain	Type	Content, %
1	$C_1 - C_5$	Gas	39.92
2	$C_6 - C_{11}$	Gasoline	32.24
3	$C_{12} - C_{20}$	Kerosene	21.92
4	$C_{21} - C_{30}$	Solar	0.96
5	$C_{31} - C_{40}$	Heavy Oil	0
6	$> C_{40}$	Residue	4.93

of 39.92 %, then gasoline ($C_6 - C_{11}$) of 32.24 %, and followed by kerosene ($C_{12} - C_{20}$) of 21.92 %.

Effect of triacetin on the physical properties of fuel

The fuel that has been mixed with triacetin is then tested for its physical properties. For the fuel from the pyrolysis of plastic waste, the physical properties tested are specific gravity, density, viscosity, and flash point. Table 2 shows that there is a decrease in the value of each parameter of pure fuel with fuel that has been blended with triacetin as a bio-additive. For example, the specific gravity decreased from 0.79 to 0.78 because of a decrease in density with a value of 0.79 g mL^{-1} in pure fuel to 0.78 g mL^{-1} after the addition of triacetin. Then, the kinematic viscosity decreased from $1.59 \text{ mm}^2 \text{ s}^{-1}$ to $1.49 \text{ mm}^2 \text{ s}^{-1}$.

Density and viscosity are important to fuel properties, as the injection system, pump and injector must deliver a precisely adjusted amount of fuel to produce proper combustion [28]. Density and viscosity, greatly affect spray properties, atomization and combustion processes, engine deposit formation, and engine behaviour in cold weather conditions [29]. The higher the viscosity of the fuel, the thicker it is and the harder it is to flow. On the other hand, the

lower the viscosity, the thinner the fuel, and the easier it flows. If the fuel is too thick, it will be difficult to pump, difficult to ignite the burner, and difficult to flow. Poor atomization will result in the formation of carbon deposits on the burner tips or walls. High viscosity also causes more problems in cold weather because viscosity increases with decreasing temperature [30]. The addition of triacetin bio-additive shows a decrease in the density and viscosity of the fuel so that it can improve the quality of the combustion process in the engine. In addition, triacetin also functions as a cold flow improver in fuel [31].

The addition of the triacetin bio-additive to the fuel also affects the flash point. Table 2 shows the decrease in flash point values from $< 18^\circ\text{C}$ to $< 5^\circ\text{C}$. The flash point of a liquid is defined as the lowest temperature at which a substance generates enough vapor to form a (vapor/air) mixture that can be ignited (piloted ignition). Flashpoint is an important concept in fire investigation and fire protection because it is the lowest temperature at which the risk of fire exists in the presence of liquids [32]. Although it does not have much effect on engine performance, as the flash point decreases, it is necessary to be careful with the liquid because it is easy to ignite [33].

In addition, this study also tested the calorific value of the fuel. The fuel from the pyrolysis of pure plastic waste and which has been added with a percentage of 20 % bio-additive is tested for its calorific value. The calorific value is a number that states the number of calories produced from the combustion process of a certain amount of fuel with oxygen. The calorific value is inversely proportional to the specific gravity (density). The test results showed an increase in calorific value after the addition of triacetin bio-additive marked by a value of $10839.57 \text{ cal g}^{-1}$ on pure fuel and $1100.44 \text{ cal g}^{-1}$ after the addition of triacetin bio-additive. Fig. 1 shows

Table 2. The results of the test of the physical properties of the fuel from the pyrolysis of plastic waste with triacetin 20 % v/v.

No	Type of test	Unit	Pure sample	Sample + 20 % triacetin	Test methodology
1	Specific gravity at 60/60 F	-	0.7937	0.7883	ASTM D 1298
2	Density at 15°C	g cm^{-3}	0.7921	0.7875	ASTM D 1299
3	Kinematic viscosity at 40°C	$\text{mm}^2 \text{ s}^{-1}$	1.59	1.4970	ASTM D 445
4	Flash point PM.c.c	$^\circ\text{C}$	< 18	< 5	ASTM D 93

a comparison of the heating value of several types of fuels such as diesel fuel [34], Alcohol-to-Jet - Synthetic Paraffinic Kerosene (ATJ-SPK), Alcohol-to-Jet - Synthetic Kerosene with Aromatic (ATJ-SKA), and green diesel as a comparison of research results [35]. The comparison results indicate that the heating value of the fuel from the pyrolysis of plastic waste with the addition of 20 % triacetin gives a higher calorific value than other fuels.

The effect of triacetin on engine performance

In the analysis of the running engine test, two vehicle engines were used, namely the Daihatsu Zebra 1300 cm³ 1993 car and the Supra Fit 100 cm³ 2007 motorcycle to determine the amount of fuel consumption. Table 3 shows the results of the analysis of the running engine test on a Daihatsu Zebra Car 1300 cm³. The test was carried out at a distance of 1000 m. The data from this test showed that the two samples of the tested fuel from the pyrolysis of plastic waste could not run the vehicle engine, but the engine could start. This is because the high kerosene fraction is quite high, namely 21.92 %, causing a small evaporation rate and no combustion occurring in the engine.

In the RON 88 gasoline sample tested, the engine can run normally without any obstacles. However, each sample has a difference in volume consumption in the 1000 m mileage. The results of the analysis in Table 8 show that the average volume consumption of the highest sample oil is in the RON 88 gasoline sample with 10 % triacetin, which is 70.67 cm³ per 1000 m², while the lowest yield occurs in the premium with 20 % triacetin, which is 64.47 cm³ per 1000 m². The value of the increase in performance on the Daihatsu Zebra

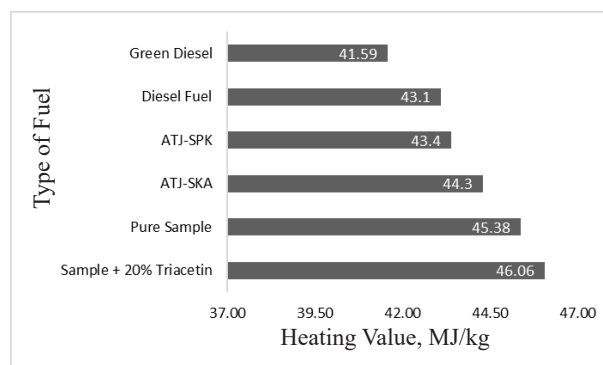


Fig. 1. Comparison of the heating value of various fuels.

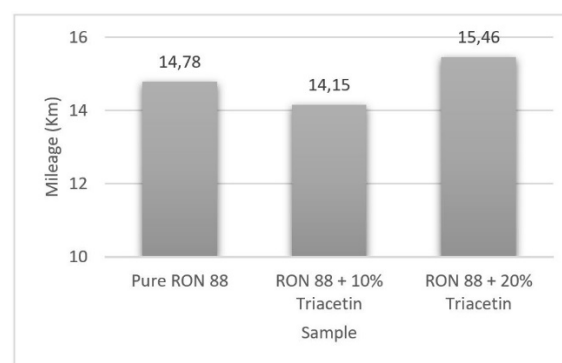


Fig. 2. Effect of the addition of triacetin on vehicle mileage on a Daihatsu Zebra 1300 cm³ 1993 car.

1300 cm³ 1993 engine per liter of fuel after adding triacetin is presented in Fig. 2. The latter shows that the addition of 10 % triacetin decreased the mileage from 14.78 km on pure RON 88 to 14.15 km with a percentage decrease of 4.25 %. Then after the addition of the next 10 % triacetin, a distance of 15.46 km was obtained with an increase of 9.28 %. From these results,

Table 3. The results of the performance test of the running engine on fuel with the addition of triacetin in the Daihatsu Zebra 1300 cm³ 1993 car.

No	Sample	Distance, m	Volume, cm ³	Description
1	Pure fuel from the pyrolysis of plastic waste	1000	0.00	The engine turns on stationary, but the car can't run
2	Fuel from the pyrolysis of plastic waste + 20 % triacetin	1000	0.00	The engine turns on stationary, but the car can't run
3	Pure RON 88	1000	67.67	Engine running normally
4	RON 88 + 10 % triacetin	1000	70.67	Engine running normally
5	RON 88 + 20 % triacetin	1000	64.67	Engine running normally

Table 4. The results of the performance test of the running engine using fuel with the addition of triacetin on the Supra Fit motorcycle 100 cm³ 2007 motorcycle.

No	Sample	Distance, m	Volume, cm ³	Description
1	Pure fuel from the pyrolysis of plastic waste	500	0.00	The engine can't start
2	Fuel from the pyrolysis of plastic waste + 20 % triacetin	500	0.00	The engine can't start
3	Pure RON 88	500	9.33	Engine running normally
4	RON 88 + 10 % triacetin	500	8.83	Engine running normally
5	RON 88 + 20 % triacetin	500	8.33	Engine running normally

the average value of the increase in car engine performance for every 10 % addition of triacetin is 2.52 %.

While the results of the analysis of the running engine test on the Honda Supra Fit 100 cm³ 2007 motorcycle can be seen in Table 4. Table 4 shows that for the motorcycle engine, the fuel sample from the pyrolysis of plastic waste cannot even start the engine. This is due to the high-density value, so that combustion is difficult to occur in the motor engine. Generally, fuel for motor vehicles has a density value between 715 - 770 kg m⁻³ [36]. While the fuel sample has a density of more than 770 kg m⁻³. Meanwhile, in the pure RON 88 sample, RON 88 + 10 % triacetin and RON 88 + 20 % triacetin the engine can start and run normally with the volume value for 500 m in a row is 9.33 cm³, 8.83 cm³, and 8.33 cm³.

The effect of the addition of triacetin to fuel on the mileage of the Supra Fit 100 cm³ 2007 motorcycle engine per litter of fuel is presented in Fig. 3. Fig. 3 shows that the addition of 10 % triacetin has increased the mileage from 53.59 km on pure RON 88 to 56.62 km with a percentage increase of 5.66 %. Then after the addition of the next 10 % triacetin, a distance of 60.02 km was obtained with an increase in value of 6.00 %. From these results, the average value of the increase in motorcycle engine performance for every 10 % addition of triacetin is 5.83 %.

From the results of engine performance tests in both car engines and motorcycle engines, fuel added with triacetin has better performance results, marked by a tendency to decrease fuel consumption. The best results occur in premium fuels with 20 % triacetin, with a consumption value that is more efficient than others.

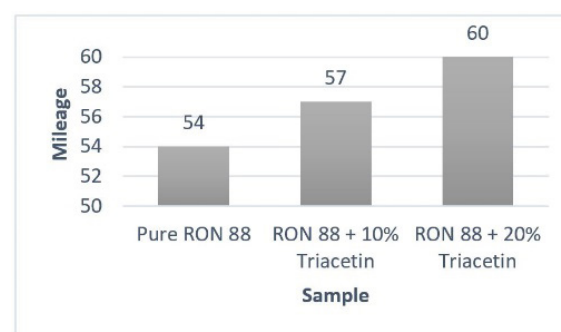


Fig. 3. The effect of adding triacetin on vehicle mileage on Supra Fit 100 cm³ 2007 motorcycle.

The effect of triacetin on the octane number of gasoline

Octane number is a measure of the tendency of the air-fuel mixture to resist self-ignition. The presence of self-ignition will cause a decrease in engine efficiency and increase engine wear [37]. Fuels with a higher-octane number can be run at higher compression ratios without causing detonation or engine knocking [38]. The octane number is determined using a test machine (CFR engine) and compared with a mixture of trimethyl-pentane (isooctane) with n-heptane which has an anti-knock capacity like the sample. For example, a fuel having an octane number of 90, has a similar anti-knock behaviour provided by a mixture containing 90 % isooctane and 10 % n-heptane fuel by volume. [39].

The octane number test was carried out on samples of pure RON 88, RON 88 with 10 % triacetin and RON 88 with 20 % triacetin. The results of the octane number

test of each sample can be seen in Fig. 4. Fig. 4 shows an increase in the octane number from the addition of triacetin to RON 88 gasoline. Pure RON 88 has an octane number of 87.4 while RON 88 with the addition of 10 % triacetin obtained an octane number of 88.1 with an increase of 0.7. Then after the addition of 20 % triacetin obtained an octane number of 89 with an increase of 1.6. From the data in Fig. 5, the average increase in octane number for every 10 % addition of triacetin is 0.8.

From these results, the addition of 20 % triacetin to gasoline can increase the octane number of RON 88 to 90. The higher the octane number of the fuel, the better the quality due to the increased quality of the combustion process in the engine, thereby reducing the possibility of knocking processes. From these results, triacetin is an octane booster and a good anti-knocking agent which is indicated by the increase in the octane number of the fuel after it is added.

CONCLUSIONS

Triacetin as a fuel bio-additive has a good effect on fuel from the pyrolysis of plastic waste, which is characterized by a decrease in specific gravity by 0.0054, a decrease in density by 0.0046, and a decrease in viscosity by 0.093, as well as an increase in the heating value of 160.87 MJ kg⁻¹. In the engine performance test of fuel from the pyrolysis of plastic waste, it cannot run, due to the high kerosene fraction, causing a small evaporation rate and resulting in no combustion in the engine. The results of the engine performance test of the RON 88 gasoline running both on car engines and motorcycle engines, the best results were obtained with the addition of 20 % triacetin. Whereas the RON 88 with the addition of 20 % triacetin, with a volume of 1 L can run the Daihatsu Zebra 1300 cm³ 1997 car engine as far as 15.4631 km with an average performance increase of 2.52 % for every 10 % addition of triacetin and on the Honda Supra Fit 100 cm³ 2007 obtained a distance of 60.02 km with an average value of 5.83 % increase in performance. The addition of triacetin to gasoline can increase the octane number, the results of the tests show that the average increase in the octane number for every 10 % addition of triacetin is 0.8. The best results were obtained at the percentage of 20 % triacetin with a value of 89.

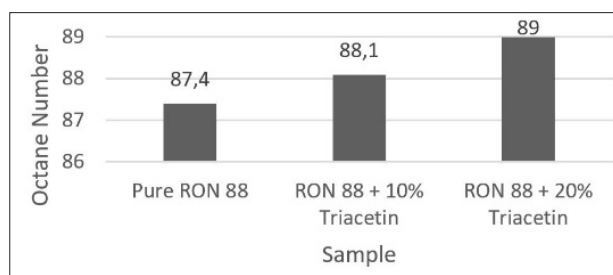


Fig. 4. The effect of adding triacetin on the octane number of RON 88 gasoline.

Authors' contributions: Z.M.: *Conceptualization, Design of the research, Project management and funding acquisition*; Z.L.: *Experimental work*; A.S.: *Experimental work*; A.M.: *Editing of the manuscript*; E.A.: *Review, Writing, Editing*.

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