Feasibility of Using Diesel–Palm Fatty Acid Distillate Ethyl Ester–Hydrous Ethanol Blend in an Unmodified Direct Injection Diesel Engine: An Assessment of Stability, Fuel Properties, and Emissions

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ABSTRACT: This research focuses on the feasibility of using diesel–palm fatty acid distillate ethyl ester (PFADE)–ethanol in a direct injection diesel engine without any major modifications. Hydrous ethanol was selected for blending in diesel to produce diesohol. The palm fatty acid distillate (PFAD) and PFADE were directly blended in ethanol and diesel. A comparative study of the phase stability in diesel–PFAD–hydrous ethanol and diesel–PFADE–hydrous ethanol was performed with varied blend proportions. The fuel properties, emissions (CO, CO₂, NOₓ, O₂, exhaust gas temperature), and fuel consumptions of diesel, PFADE, diesel–PFADE–hydrous ethanol were compared to evaluate the feasibilities of these fuel blends in a diesel engine at the engine speeds 1100, 1400, 1700, 2000, and 2300 rpm. At 2300 rpm, the maximum CO₂ emission with 10 wt % hydrous ethanol in the blend was approximately 2%. With regard to fuel consumption, clearly, 20 wt % diesohol gave higher consumption than 10 wt % ethanol at a maximum engine speed of 2300 rpm. The blend D50PE40E10 gave the lowest fuel consumption, while the maximum fuel consumption was with the D10PE70E20 blend. Therefore, both 10 and 20 wt % hydrous ethanol in the diesel fuel are alternatives usable in a diesel engine without modifications.

1. INTRODUCTION

In recent years, reducing the dependence on petroleum fuels has gained importance, especially in the context of transportation. At present, the outbreak of the coronavirus disease 2019 (COVID-19) has spread across the world which has caused oil price volatility because many governments worldwide announced reduction of activities, travel, and transportations to prevent the spread of COVID-19. However, the price and consumption of petroleum oil may spike later. Therefore, alternative fuels and oxygen-containing biofuels, such as biodiesel and diesohol, have been considered renewable energy source candidates for use in diesel engines. They can be blended with diesel or injected directly into cylinders. Moreover, biofuels reduce the environmental impacts of the emitted pollutants, such as CO₂, CO, NOₓ, particulate matter (PM), and hydrocarbons (HCs). Therefore, the use of biofuels will also reduce greenhouse gas emissions. In Thailand, biodiesel is a renewable alternative fuel that can be produced from crude palm oil (CPO) or waste cooking oil. As an environmentally friendly alternative fuel, ethanol can be produced from agricultural crops and wastes such as molasses, cassava, and sugar cane in Thailand. Other advantages of using ethanol in diesohol include increased oxygen content, reduced calorific value, and high latent heat of evaporation. Consequently, adding ethanol into diesel fuel can enable complete combustion and reduce NO emissions when the combustion temperature is decreased. Regarding the barriers to the use of ethanol in diesel engine, Fernando and Hanna reported that the stability of biodiesel–ethanol–diesel blends is appropriate in cold weather, and the quality of the blend is similar to petroleum diesel. Ethanol has a lower calorific value, cetane number, and lubrication ability than biodiesel or diesel. Shahir et al. studied the feasibility of diesel–biodiesel–ethanol/bioethanol in existing compression ignition engines. They reported as disadvantages of using fuel blends (diesel and ethanol/bioethanol) poor miscibility of ethanol/bioethanol in diesel and low-temperature instability. However, there are many studies on the application of ethanol–diesel blends, which focus on fuel properties, effects

Received: April 1, 2020
Accepted: July 24, 2020
Published: August 7, 2020
on combustion, and emission characteristics. Many reports state that as a polar compound ethanol’s solubility in diesel is affected by temperature and water content. Thus, an emulsifier and a co-surfactant should be added into diesel to obtain a homogeneous blend. Shahir et al. recommended that biodiesel could address these problems of solubility in diesel. Thus, a higher ethanol content can be miscible in a fuel blend with biodiesel. However, an excess amount of ethanol in the blend can cause problems with some standards of fuel properties.

The hydrous ethanol or hydrated ethanol has about 5–7 vol % water which will be added into fuel blends in this study. However, the high polarity of water interacts with the polar ethanol molecules. Nonpolar diesel cannot be compatible with 95% purity of hydrous ethanol. Thus, anhydrous ethanol with lower water content than in hydrous ethanol is also less soluble in diesel fuel than hydrous ethanol. Liu et al. evaluated the potential for utilizing ethanol as an effective additive for hydrous ethanol—diesel blends at various temperatures of 5, 15, and 30 °C. They observed that a blend of 90% hydrous ethanol (with 10 vol % water) and the diesel is almost insoluble due to the existence of water. The cosolvent additive of n-hexanol and n-octanol is recommended to be added into the blend of hydrous ethanol—diesel to obtain the acceptable fuel properties and soluble performance. Guareiro et al. studied the phase stability of both binary (diesohol) and ternary (diesel—biodiesel—ethanol) blends with various concentrations of ethanol. They also studied the effects of both anhydrous ethanol (99.5%) and hydrous ethanol (95%). They found that hydrous ethanol was insoluble in diesel fuel and 10% anhydrous ethanol in the diesel fuel had no phase separation after 90 days. However, over 15% anhydrous ethanol in a binary mixture of diesel and ethanol/diesohol caused phase separation within one day. Lapuerta et al. focused on the stability of the blend, the filterability, and the cold flow properties of ethanol—n-butanol—diesel blends, and these blends were tested in the diesel engine. They reported that the cold filter plugging point of diesel—ethanol blends cannot be measured because of the weak miscibility of these blends. Consequently, the drawback in ethanol—diesel fuel blends is that ethanol has limited solubility in diesel fuel over a wide range of temperatures. The surfactant and cosolvent additives should be added in the diesel blends. These major drawbacks in hydrous ethanol—diesel blends are similar to those reported by Shrivastava et al., Chang et al., and Srinivasnaik et al.

In this study, the low-cost byproduct from physical refining of CPO, namely, palm fatty acid distillate (PFAD), was used as the renewable energy source in a diesel engine without any major modifications. As mentioned by several researchers of the main drawbacks in hydrous ethanol—diesel fuel blends, the nonedible grades of PFAD were used as an emulsifier in the fuel blends to study the phase stability. The main problem of using the vegetable oil—diesel blend directly in diesel engine is the high viscosities, due to the compositions of vegetable oil. The chemical and thermal methods were used to reduce the viscosities of vegetable oils. The important part of this study, pure PFAD will be directly converted to PFAD ethyl ester (PFADE) by a single step of the esterification reaction for blending in the hydrous ethanol—diesel blends. Moreover, there are many studies reporting that hydrous ethanol is not recommended to directly blend in diesel. However, the hydrous ethanol (95 vol %) is cheaper than anhydrous ethanol (99.9 vol %). To overcome the limitations of blending hydrous ethanol in diesel, PFAD and PFADE were used as emulsifiers in making the fuel blends. Therefore, this study aims at filling the existing research gap in blending the hydrous ethanol blends in petroleum diesel, PFAD, and PFADE in order to study phase stability, fuel properties, emissions, fuel consumptions, and so forth. To the best of our knowledge, the two fuel blends diesel—PFAD—hydrous ethanol and diesel—PFADE—hydrous ethanol have not been previously reported on, with regard to stability and fuel properties with varied blend portions. Finally, emissions (CO, CO₂, NOₓ, and O₂) from diesel, PFAD, and the various fuel blends of diesel—PFADE—ethanol were compared to assess the feasibility of these fuel blends in unmodified direct injection (DI) diesel engines.

2. RESULTS AND DISCUSSION

2.1. Phase Stability of Diesel—PFAD—Hydrous Ethanol. Phase stability was studied for the three blend components diesel, PFAD, and hydrous ethanol at room temperature (35 °C). The results are represented in ternary phase diagrams. The phase behavior of the diesel—PFAD—hydrous ethanol blend at 35 °C is shown in Figure 1. The phase behavior definitions used in this study are now defined. The physical appearance can be categorized into four types of phase behavior, as shown in Figure 1. In Figure 1a, the clear liquid is a homogeneous phase without suspended crystals or particles. The liquid 2 phases is a double-phase liquid system. Both layers are clear, and no gel or particles are observed, as
shown in Figure 1b. The gel phase is liquid with crystalline inclusions and looks yellow and cloudy, as shown in Figure 1c. The gel phase usually occurs at low temperatures and becomes semi-transparent and disappears relatively quickly when the temperature is increased. The last phase type is the wax phase or the nonflowing phase, which is a light yellow solid wax, as shown in Figure 1d.

After observing the stability of the blends at 35 °C for 2 days, the long-term stability of blends was observed by keeping them for 90 days. The results of phase behavior of diesel–PFAD–hydrous ethanol at 35 °C are shown in Figure 2. The formations of gel and wax phases were more predominant with ethanol concentrations below 30 wt % and PFAD above 60 wt %. After 2 days, some diesel–PFAD–hydrous ethanol proportions: 50–10–40; 40–10–50; and 30–10–60 were split into two clear liquid phases. In this case, adding over 60 wt % PFAD cannot improve the miscibility of diesel and hydrous ethanol because after 2 days the blend had been separated to wax and gel phases. Increasing the hydrous ethanol content from 40 to 80 wt % in the blend improved the miscibility of PFAD and diesel. Finally, the blend proportions in three-component mix of diesel–PFAD–hydrous ethanol should be in the black dot area to guarantee a consistent homogenous fuel blend at 35 °C. Moreover, possibly the high palmitic acid content in PFAD has a stronger effect than hydrous ethanol, resulting in poor emulsion stability. That is because the dominant fatty acid found in PFAD is palmitic acid, which is a saturated long-chain fatty acid with a 16-carbon backbone.24 Therefore, the high content of PFAD is not compatible in a blend with diesel and hydrous ethanol. The long-chain saturated fatty acids in PFAD should be converted to PFADE. Investigations of diesel–PFAD–hydrous ethanol diesoloh blends are discussed in the next section.

2.2. Phase Stability of Diesel–PFAD–Hydrous Ethanol. A disadvantage of PFAD in a blend with diesel–hydrous ethanol is the wax phase that appears with the evaporation of ethanol. Therefore, the storage tank of diesel–PFAD–hydrous ethanol must be tightly closed after completing the mixing process. This fuel blend is difficult for agricultural applications. Thus, PFADE was used instead of PFAD to avoid these problems. This section attempts to analyze the use of PFADE as a potential amphiphile in diesel–hydrous ethanol blends. First, the phase behaviors of diesel–PFADE–hydrous ethanol were considered to identify the conditions of different components, as shown in Figure 3a. The phase behaviors of diesel–PFADE–hydrous ethanol fuel blends were shown in Figure 1a,b. Regarding the phase behavior, a clear liquid single phase in the three-component system was widest with 30–80 wt % PFADE, 10–50 wt % diesel, and 10–60 wt % hydrous ethanol. Two clear liquid phases appeared after 2 days with less than 20 wt % of PFADE, and no phase separation was observed even after 90 days. Increasing the PFADE content will reduce the amount of diesel fuel in the blend. With PFADE, the biodiesel could be effectively used as an emulsifier in the diesel–hydrous ethanol blends or diesoloh.7,13 Similar results are described by Pidol et al.,25 who used a fatty acid methyl ester (FAME) to stabilize a diesel and ethanol blend. The FAME stabilizes the blend by acting as a surface active agent.25 According to the above discussion, seventeen ternary blends (black dots in Figure 3a) were selected for the analysis of the fuel properties, density and viscosity. The viscosities of diesel–PFADE–hydrous ethanol blends D80PE10E10 and D70PE20E10 were 4.13 and 4.17 cSt. Therefore, these blends did not meet the diesel fuel specification requiring a 1.8 to 4.1 cSt viscosity at 40 °C. Thus, the remaining fifteen ternary blends (black dots in Figure 3b) were selected for further study of emissions from diesel–PFADE–hydrous ethanol.

2.3. Emissions from Diesel–PFADE–Hydrous Ethanol. The emissions of CO, CO2, NOx, and O2 were analyzed with a gas analyzer at the engine speeds 1100, 1400, 1700, 2000, and 2300 rpm. Regarding the ternary plots in Figure 3b, the blends with acceptable viscosity and with a single liquid phase had 10–60 wt % hydrous ethanol, 30–70 wt % PFADE, and 10–50 wt % diesel, and these were tested for gas emissions. However, many studies have recommend that less than 20 wt % ethanol should not be used in a diesel engine without engine modifications. For instance, Pidol et al.25 studied the performance and emissions of diesel fuel in advanced low-temperature combustion, for ethanol–biodiesel–diesel blends. They reported that the 20% ethanol–40% biodiesel–40% diesel blend had poor auto-ignition properties compared to the European standard of 44.5 cetane number.23 Wang et al.26 and Banapurmath et al.27 reported that HC, CO, NOx, and NO emissions can be increased by high ethanol content in diesel fuel.26,27 The results show that CO and HC emissions increased significantly by 40 and 50%, respectively, when ethanol was used. Mahmudul et al.28 reported that the fuel blend (75 vol % diesel–5 vol % palm biodiesel–20 vol % ethanol) was tested at a low load and 1200 rpm speed. The blend with ethanol had a shorter ignition delay than the blend without ethanol. For the reasons mentioned above, over 20 wt % ethanol in the fuel was not tested in the DI diesel engine in this study. Therefore, the remaining seven ternary blends of diesel–PFADE–hydrous ethanol were D50PE40E10, D40PE50E10, D30PE60E10, D40PE40E20, D30PE50E20, D20PE60E20, and D10PE70E20, which were investigated for the emissions of CO, CO2, NOx, and O2 gases.

2.3.1. CO Emissions. Carbon monoxide (CO) is a harmful toxic gas. The incomplete combustion of a HC fuel from the lack of oxygen during combustion increases CO emissions. In general, the biodiesel has a higher oxygen content than petroleum diesel, effectively reducing CO emissions.29 Moreover, CO emissions also depend upon the carbon to hydrogen ratio and the temperature in a cylinder during combustion. In
the case of the jatropha oil methyl ester (JOME) and fish oil methyl ester, the carbon to hydrogen ratio is comparatively low and the in-cylinder gas temperature in a diesel engine is higher than with diesel fuel. The formation of CO is decreased by these factors. Sivaramakrishnan studied the emission characteristics of a variable compression multifuel engine run with the Karanja biodiesel–diesel blend. They reported that CO emissions with the blend B25 below those with standard diesel. The CO emissions decreased when the biodiesel content was increased because of additional oxygen from biodiesel in the fuel blend.

Figure 3. Phase behavior of (a) diesel–PFADE–hydrous ethanol, at 35 °C, and (b) acceptable viscosity of liquid-one phase at 40 °C.

Figure 4a shows the CO emissions at the engine speeds 1100, 1400, 1700, 2000, and 2300 rpm with 10 and 20 wt % ethanol in the fuel blend. With 10 wt % ethanol, the highest CO emissions were with the D40PES0E10 blend at 2300 rpm engine speed. At 1700 rpm engine speed, CO emissions with D50PE40E10 were similar to diesel fuel. The CO emissions with diesohol and PFADE are higher than with diesel fuel at all engine speeds. Similar results are described by Banapurmath et al., who reported that the HC and CO emissions with sesamum oil methyl esters, honge oil methyl esters (HOMEs), and JOME slightly exceeded those with diesel fuel, for a DI compression ignition engine. All the esters result in slightly
higher smoke emissions than diesel, and this is attributed to incomplete combustion because of low volatility and high viscosity of the esters. All esters show increased ignition delay and combustion duration relative to diesel fuel. Moreover, all esters give reduced a thermal efficiency and increased smoke, HC, and CO emissions. An engine could be run with the esters tested without any major modifications.16 With 20 wt % ethanol in the fuel, the CO emissions at various speeds with D40PE40E20, D30PE50E20, D20PE60E20, and D10PE70E20 fuel blends are also shown in Figure 4a. The highest CO emissions were with the D30PE50E20 blend at a 2300 rpm engine speed. Comparing the 10 and 20 wt % ethanol-blended fuels, CO emissions from the DI diesel engine were clearly elevated with 20 wt % ethanol. Zhu et al.,31 Lei et al.,32 and Mozfjr et al.,33 and reported that CO and HC emissions increased with the proportion of ethanol in a fuel blend. For example, CO emissions with 10 wt % ethanol were increased by 155.5, 200.3, and 147.8% when 40, 50, and 60 wt % of PFADE were used, respectively. With 20 wt % ethanol, they increased by 238.9, 263.7, 252.4, and 242.4% when 40, 50, 60, and 70 wt % of PFADE were used in a DI diesel engine, respectively.

2.3.2. CO2 Emissions. The CO2 in exhaust gas is an indication of the complete combustion of the fuel in the engine cylinder.34 The CO2 emissions at various engine speeds with diesel–PFADE–hydrous ethanol blends are shown in Figure 4b. With 10 wt % hydrous ethanol in the blend, the CO2 emissions with PFADE are lower than those with diesel fuel at 1100 rpm engine speed. However, D50PE40E10, D40PE50E10, and D30PE60E10 blends emitted more CO2 than diesel fuel at 2000 and 2300 rpm engine speeds. Moreover, D50PE40E10 emitted significantly less than all other cases at 1700 rpm engine speed. The CO2 emissions with the D40PE40E10 blend were the highest at all engine speeds. These higher CO2 emissions are caused by complete combustion because PFADE contains oxygen and facilitates combustion.34 With 20 wt % ethanol in the fuel at 1100 rpm, PFADE and D30PE50E20 blends emitted less CO2 at 14.78 and 9.47%, respectively. The CO2 emissions of the D30PE50E20 blend increased gradually with the engine speed. The maximum CO2 emissions with 10 wt % hydrous ethanol were approximately 2%, while approximately 1.7% of maximum CO2 was emitted when 20 wt % ethanol fuel was tested at 2300 rpm.

2.3.3. NOx Emissions. Nitrogen oxides are detrimental gases from the combustion in diesel engines.35 Generally, the latent heat of evaporation of ethanol is high, which can decrease the gas temperature in the combustion chamber.15,36 Regarding environmental pollution, NOx emissions are the most harmful and affect the environment through the acid rain as well as harm humans.36 Furthermore, CO and NO are the primary pollutants affecting the formation of tropospheric ozone, which
is an important greenhouse gas. Actually, the main objective of using the diesohol blend was to decrease NOx emissions. The NOx emission results with diesohol having 10 wt % ethanol are shown in Figure 4c. The NOx emissions of all blends were significantly below those with diesel fuel at 1400, 1700, 2000, and 2300 rpm engine speeds. At a maximum engine speed of 2300 rpm, PFADE emitted more NOx than diesel fuel because the temperature in the combustion chamber was increased by oxygen in the biodiesel. Similar results are described by Nabi et al., who tested a four-stroke diesel engine with the karanja oil methyl ester and observed that NOx increased by about 15% under high load conditions because of the 12% oxygen content in B100, which resulted in a higher combustion temperature. Another reason for using hydrous ethanol in a diesohol blend, with 5 vol % water content, is that it decreases the combustion temperature. The NOx content with all blends was lower than with diesel fuel at 1400, 1700, 2000, and 2300 rpm engine speeds, for 10 wt % ethanol in the fuel. With 20 wt % ethanol in the fuel, NOx emissions at various speeds are shown in Figure 4c. The NOx emissions with PFADE and all blends are significantly lower than with diesel fuel. Comparing 10 and 20 wt % ethanol cases of fuel, the NOx emission levels with 20 wt % hydrous ethanol are lower than with 10 wt % at 1400, 1700, 2000, and 2300 rpm engine speeds. At the maximum engine speed of 2300 rpm, NOx emissions were decreased by 34.12, 27.64, and 34.11% by PFADE contents of 40, 50, and 60 wt %, respectively, when 10 to 20 wt % ethanol was used. Moreover, the lowest NOx emissions were 30 ppm (for the D50PE40E10 blend) and 20 ppm (for the D40PE40E20 blend) at 2300 rpm engine speed.

2.3.4. O2 Gas. The O2 content in exhaust gas relates to the combustion in the cylinder, specifically the air to fuel ratio. High O2 content in the exhaust gas indicates incomplete combustion. Figure 4d shows the oxygen emission values with 10 and 20 wt % ethanol fuels at different engine speeds. The oxygen emissions with PFADE and all the blends are below those with diesel fuel, due to a more complete combustion especially at the highest engine speed.

2.3.5. Exhaust Gas Temperature. The exhaust gas temperature (EGT) of diesel, PFADE, and diesel–PFADE–ethanol blends varying at the various engine speeds are shown in Figure 4e. For all of the cases, the EGT increased when the engine speeds increased. The EGT of PFADE and diesohol were similar to diesel at a low engine speed of 1100 rpm. Similar results are described by Yahza et al., who tested the exhaust emissions of biodiesel–ethanol–diesel blends with a single-cylinder diesel engine. They reported that the EGT increased with the increase of engine speeds. A low engine speed of 1760 rpm, the EGT of fuel blends appeared to be similar to that of diesel. The EGT, clearly 10 and 20 wt % diesohol, gave a higher temperature than with diesel and PFADE at the engine speed ranges (1400–2300 rpm). Increasing ethanol proportions in fuel blends led to the high temperature of the exhaust gas because of the shortened combustion period of diesohol. The high EGT occurred at 2300 rpm of engine speed for 10 wt % ethanol and increased by 31.6, 43.6, and 35.4% with PFADE contents of 40, 50, and 60 wt %, respectively, when compared to diesel at the same engine speed. The EGTs at 2300 rpm for different fuels of D50PE40E10, D40PE50E10, D30PE60E10 blends, PFADE, and diesel are 149.1, 162.7, 153.4, 129.0, and 113.5 ºC, respectively. With 20 wt % ethanol in the blend, the average EGTs are lower than those with 10 wt % ethanol in the fuel blends at 2300 rpm engine speed. Because, a higher ethanol content in diesohol caused the high-temperature evaporation and the reduction lower heating value (LHV), and cetane number of fuel properties. As a result, the temperature and pressure inside the combustion chamber were reduced because of the increasing ignition delay. Similar results are described by Tan et al., who reported a reduction of the EGT when bioethanol was increased in the diesel–biodiesel–bioethanol blends because of increasing the amount of bioethanol. Increasing ethanol content will decrease the heating value and cetane number of the fuel blends which is a cause of prolonged ignition delay.

2.3.6. Fuel Consumption. The fuel consumption rate is here expressed in kilograms per hour (kg/h). The fuel consumption rates of diesel, PFADE, and different diesohol blends by the diesel engine at different engine speeds are shown in Figure 5.

All the fuel blends had the consumption increase with engine speed. At all engine speeds, petroleum diesel fuel gave lower fuel consumption than PFADE or any of the diesohol blends. The consumption rates of these alternative fuels reflect their heating values that are lower than that of diesel. Similar results are described by Komariah et al., who studied the effects of palm biodiesel blends on fuel consumption in a fire tube boiler. They reported that the specific fuel consumption of biodiesel was slightly higher than that of diesel, at a high engine load. Nagaraju et al. reported on the use of 20% soybean methyl ester mixed with 80% petroleum diesel (B20) in a high speed DI diesel engine. The results showed that specific fuel consumption was higher than with diesel fuel, which was attributed to the LHV of biodiesel and the late release of energy in the expansion stroke.

Comparing 10 and 20 wt % ethanol fuels, the consumption of 20 wt % diesohol was clearly much higher than with 10 wt % ethanol. At a maximum engine speed of 2300 rpm with diesohol blends, the D50PE40E10 blend gave the lowest fuel consumption, while the maximum fuel consumption with 20 wt % ethanol was with the D10PE70E20 blend. With the D30PE60E10 blend, on increasing engine speed from 1700 to 2000 and 2300 rpm, the fuel consumption increased by 26.33 and 71.99%, respectively. Increasing the engine speed from 1700 to 2000 and 2300 rpm result in the consumption of D10PE70E20 increasing by 29.24 and 82.66%, respectively. Moreover, the fuel consumption rates of PFADE and diesohol blends were higher than that of diesel fuel because the LHVs of the PFADE and 10 wt % ethanol blended fuel are below that of diesel fuel, as shown in Table 1. It is concluded that the fuel consumption of PFADE, D50PE40E10, and D30PE50E20 blends was increased by oxygen in the biodiesel. Similar results are described by Nabi et al., who tested a four-stroke diesel engine with the karanja oil methyl ester and observed that NOx increased by about 15% under high load conditions because of the 12% oxygen content in B100, which resulted in a higher combustion temperature. Another reason for using hydrous ethanol in a diesohol blend, with 5 vol % water content, is that it decreases the combustion temperature. The NOx content with all blends was lower than with diesel fuel at 1400, 1700, 2000, and 2300 rpm engine speeds, for 10 wt % ethanol in the fuel. With 20 wt % ethanol in the fuel, NOx emissions at various speeds are shown in Figure 4c. The NOx emissions with PFADE and all blends are significantly lower than with diesel fuel. Comparing 10 and 20 wt % ethanol cases of fuel, the NOx emission levels with 20 wt % hydrous ethanol are lower than with 10 wt % at 1400, 1700, 2000, and 2300 rpm engine speeds. At the maximum engine speed of 2300 rpm, NOx emissions were decreased by 34.12, 27.64, and 34.11% by PFADE contents of 40, 50, and 60 wt %, respectively, when 10 to 20 wt % ethanol was used. Moreover, the lowest NOx emissions were 30 ppm (for the D50PE40E10 blend) and 20 ppm (for the D40PE40E20 blend) at 2300 rpm engine speed.

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2.3.6. Fuel Consumption. The fuel consumption rate is here expressed in kilograms per hour (kg/h). The fuel consumption rates of diesel, PFADE, and various diesohol blends by a diesel engine.
blends were 12.0, 24.2, and 49.25% higher than that of diesel fuel at the 2300 rpm maximum engine speed.

Several studies have reported that biodiesel has slightly lower energy content than petroleum diesel. Similar results are described by Tesfa et al.,\(^5\) who reported that the main reason for higher fuel consumption in an engine running a biodiesel blend is mainly due to the low-heating value of the biodiesel. Moreover, they stated that the heating values of biodiesels are approximately 8–10% lower than that of diesel fuel, which affects fuel consumption and thermal efficiency by 18 and 25%, respectively.\(^5\) Other reasons for high biodiesel fuel consumption are its high density and high viscosity.\(^5,6\) Jaichandar and Annamalai\(^5\) have reported that the poorer heating value of biodiesel must be compensated for with a higher fuel consumption. The specific fuel consumption of biodiesel was higher than that of diesel by approximately 14%.

3. MATERIALS AND METHODS

3.1. Phase stability of diesel–PFADE–hydrous ethanol and diesel–PFADE–hydrous ethanol was studied using diesel B7 (93% diesel with 7% ME) from a petrol station, and the hydrous ethanol (95 vol %) was purchased from P. General Trading Ltd., Part, Bangkok, Thailand. The PFAD was purchased from a large refinery facility performing palm oil extraction in eastern Thailand. In the esterification reaction for producing PFADE, the PFAD, which is a light yellow solid wax at 30 °C, was used as the raw material. The phase transition of PFAD from the wax to liquid form is at 43 °C.\(^6\) All chemical reactants for acid-catalyzed esterification were of commercial grade: 99.9 vol % anhydrous ethanol and 98% H\(_2\)SO\(_4\) were used as purchased from P. General Trading Ltd., Part, Bangkok, Thailand. The properties of raw materials and chemical reactants are summarized in Table 2.

3.2. PFADE Production. In pre-treatment, most free fatty acids (FFAs) in the PFAD was directly converted by acid-catalyzed esterification to ester, by eq 1.54 The esterification reaction for producing PFADE, the PFADE, was carefully considered in terms of the wax phase. Increasing the ethanol content improved the solubility of wax compounds in the ethyl ester production. To avoid wax formation in diesel–PFADE–hydrous ethanol, the wax phase of PFADE was carefully considered. For the final product, the PFADE phase from esterification will solidify to a wax at room temperature (35 °C), but no wax appears if the ethyl ester purity exceeds 85 wt %. Therefore, over 85 wt % ester of biodiesel from PFAD was produced with a single step of esterification and was chosen to study the phase stability. The

### Table 1. Fuel Specifications of Diesel–PFADE–Hydrous Ethanol\(^a\)

| property                         | diesel (D) | PFADE (PE) | hydrous ethanol (E) | diesel–PFADE–hydrous ethanol |
|----------------------------------|------------|------------|---------------------|----------------------------|
| specif gravity at 15.6 °C        | 0.81–0.87  | 0.851      | 0.855               | 0.857                      |
| viscosity at 40 °C (cSt)         | 1.8–4.1    | 5.76       | 3.41                | 3.80                       | 4.00                      |
| pour point (°C)                  | 10 max     | 18         | −3                  | −3                         | 0                         |
| sulphur (wt %)                   | 0.005      | 0.0015     | <0.01               | <0.01                      | <0.01                     |
| copper strip corrosion (°C)      | no. 1      | no. 1a     | room temperature    |                             |                           |
| oxidation stability (h)          | >24        | 7.07       | 7.68                |                            |
| carbon residue (wt %)            | 0.05 max   | <0.1       |                     |                            |
| flash point (°C)                 | 52 min     | 175        | 18                  |                            |
| high heating value (MJ/kg)       | 46.3       | 42.0       | 41.8                | 40.8                       |
| lower heating value (MJ/kg)      | 43.7       | 40.0       | 38.9                | 38.0                       |

\(^a\)50 wt % diesel + 40 wt % PFADE + 10 wt % ethanol blended fuel. D40PE50E10—40 wt % diesel + 50 wt % PFADE + 10 wt % ethanol blended fuel. D30PE60E10—30 wt % diesel + 60 wt % PFADE + 10 wt % ethanol blended fuel.

### Table 2. Properties of Raw Materials and Chemical Reactants

| property                              | for emulsion fuel | for esterification |
|---------------------------------------|-------------------|--------------------|
| higher heating value (MJ/kg)          | 46.3              | 40.2               |
| cloud point (°C)                      | <10\(^b\)         | 14                 |
| pour point (°C)                       | 3.37              | 18                 |
| flash point (°C)                      | 0.05 max          | 175                |
| viscosity at 40 °C (cSt)              | 22               | 18.5               |
| water content (wt %)                  | 5.0 vol %         | 0.1 vol %          |
| copper strip corrosion (°C)           | <0.1              | no. 1a             |
| density at 30 °C (kg/L)               | 0.830             | 0.864              |
| boiling point (°C)                    | 78.15             | 78.50              |
| purity                                | 95 vol %          | 99.9 vol %         |
| ester (wt %)                          | 86.12             | 96\(^d\)           |
| triglyceride (wt %)                   | 1.12              | 1.31\(^e\)         |
| diglyceride (wt %)                    | 2.29              | 2.33\(^e\)         |
| monoglyceride (wt %)                  | 1.00              | 4.79\(^e\)         |
| free fatty acid (wt %)                | 9.47              | 90.61\(^f\)        |
| price (USD/kg)                        | 0.90\(^c\)        | 0.47\(^d\)         |
|                                       | 0.44\(^d\)        | 0.03\(^f\)         |

\(^b\)Refer to Somnuk et al.\(^10\) \(^c\)Department of Energy Business.\(^49\) \(^d\)Bangchak Corporation Public Company Limited.\(^50\) \(^e\)Bank of Thailand.\(^51\) \(^f\)Palm oil analytics.\(^52\) ICIS.\(^53\)
PFAD. Subsequently, this homogenous mixture was immediately mixed with similar mixing. The phases in diesel−hydrous ethanol were kept in glass bottles for long-term stability. After complete blending of fuels, the lids of sample bottles had to be closed immediately to prevent the evaporation of ethanol.

### 3.3. Alternative Fuel Blends

#### 3.3.1. Blending of Diesel−PFAD−Hydrous Ethanol

The PFAD was melted at 50 °C and the liquid was then blended with hydrous ethanol under a 300 rpm stirrer speed for 5 min. Ethanol improves the miscibility of FFA in PFAD. Subsequently, this homogenous mixture was immediately mixed with similar mixing. The phases in diesel−PFAD−hydrous ethanol were observed for the ranges of diesel (10−50 wt %), PFAD (10−90 wt %), and hydrous ethanol (90−10 wt %), and the results are presented in a ternary diagram.

#### 3.3.2. Blending of Diesel−PFAD−Hydrous Ethanol

The dieseloh blend diesel−PFAD−hydrous ethanol was prepared as follows. First, PFAD was mixed with hydrous ethanol under a 300 rpm stirrer speed for 5 min. This homogenous mixture was then immediately blended with diesel using similar mixing. The phases in diesel−PFAD−hydrous ethanol were observed and are also presented in a ternary diagram. The final blends of both diesel−PFAD−hydrous ethanol and diesel−PFAD−hydrous ethanol were kept in glass bottles for observing the physical appearance. The phase behavior was investigated using the ternary diagram. All blend samples were kept motionless for 2 days at 35 °C (room temperature) to observe physical stability. However, all blends were kept motionless at room temperature for 3 months to observe the long-term stability. After complete blending of fuels, the lids of sample bottles had to be closed immediately to prevent the evaporation of ethanol.

### 3.4. Fuel Property Testing

Regarding the properties of raw materials of emulsion fuel and esterification reactions, as listed in Table 2, the higher heating value was determined using a Calorimeter (IKA Calorimeter System C500 control; Germany) according to ASTM D240-09. The cloud point and pour point were measured using a Herzog CPP 97-2 device; Germany (according to ASTM D2500), and using

#### Table 3. Properties of PFADE

| property | method | PFADE | THA<sup>a</sup> | US<sup>b</sup> | EU<sup>c</sup> |
|----------|--------|-------|-----------------|--------------|--------------|
| ester (wt %) | EN 14103 | 85.24 | 96.5 min | 96.5 min |
| linolenic acid ester (wt %) | EN 14103 | 0.00 | 12.0 max | 12.0 max |
| density at 15 °C (kg/m<sup>3</sup>) | ASTM D298 | 870 | 860−900 | 860−900 |
| viscosity at 40 °C (cSt) | ASTM D445 | 5.76 | 3.5−5.0 | 3.5−5.0 |
| flash point (°C) | ASTM D93 | 175 | 120 min | 93 min |
| carbon residue (wt %) | ASTM D4350 | <0.1 | 0.3 max | 0.5 max |
| water and sediment (vol %) | EN ISO 12937 | 0.237 | 0.05 max | 0.05 max |
| total contamination (mg/kg) | EN 12662 | 24 | 24 max |
| copper strip corrosion | ASTM D130 | no. 1a | no. 1 max | no. 3 max |
| acid value (mg KOH/g) | ASTM D6584 | 31.54 | 0.8 max |
| total glycerin (wt %) | ASTM D6584 | 0.45 | 1.5 max |
| free glycerin (wt %) | ASTM D6584 | 0.0 | 0.02 max |
| iodine number (g iodine/100/g) | ASTM D664 | 46.4 | 120 max |
| cetane number | ASTM D613 | 65.4 | 51 min |
| phosphorus (wt %) | ASTM D1407 | <1.952 | 0.001 max |

<sup>a</sup>The standard specification for methyl ester (adopting standard for the methyl ester to the ethyl ester). <sup>b</sup>Refer to Somnuk et al. <sup>c</sup>Sajjadi et al.
Herzog CPP 97-2 device; Germany (according to ASTM D97), respectively. The flash point, viscosity at 40 °C, water content, copper strip corrosion, and density at 30 °C were similarly determined using the analyzer of characteristics and qualities of biodiesel. The compositions of biodiesel were analyzed to assess the characteristics and qualities of esters in relation to both the specifications of commercial-based biodiesel and the biodiesel community, for use in agricultural engines. The compositions in terms of the components, such as ester, linolenic acid ester, MG, DG, TG, free glycerin, and total glycerin, used in commercial biodiesel standards were analyzed using a gas chromatograph–flame ionization detector (GC–FID, GC 6890; Agilent Technologies; USA). The reference method measured a ME, namely, linolenic acid as ester, using EN 14103, and the percentages of MG, DG, TG, reference method measured a ME, namely, linolenic acid ester, using EN 14103, and the percentages of MG, DG, TG, free glycerin, and total glycerin were determined according to EN 14105. The standard specification for ester adopted by the standard for the ME to ethyl ester. The density and viscosity were measured using a hydrometer following the ASTM D1298-12b method, with the Julabo MD-16G Visco Bath (Julabo Labortechnik GmbH; Seelbach; Germany) following the ASTM D445-17a method. The flash point was analyzed using a gravimetric method and a high-temperature furnace at 500 ± 5 °C. The water content was analyzed using a Karl Fischer coulometric titrator (DL39 Karl Fischer; Mettler-Toledo Instrument. Inc.; Greifensee; Switzerland) according to the EN ISO 12937 method. A gravimetric method was used to determine the total contamination under the EN 12662 method. The copper strip corrosion was measured using a Herzog HZ9011 instrument under ASTM D130-04. The acid value was measured by titration according to ASTM D664-09. The iodine value in biodiesel was analyzed by the Wijs method, with GC–FID (GC 6850; Agilent Technologies; USA) according to EN 14111. The ethanol content was determined with the standard test EN 14110. The cetane number was evaluated using a Cetane Rating Unit (Waukesha CFR F5; Waukesha County; Wisconsin; USA) by following the standard test conditions in ASTM D613-18. The phosphorus content was measured using inductively coupled plasma optical emission spectrometry (PerkinElmer) according to EN 14107. The weight percentages of FFA, ME, TG, DG, and MG in the raw material and the biodiesel were analyzed to assess the characteristics and qualities of esters in this study are listed in Table 5. The percentage uncertainty and measurement technique of instrument measurements used in this study are listed in Table 5. The percentage uncertainty of fuel consumption was calculated with the percentage uncertainties of various instruments (a graduated cylinder, a digital stop watch, and a temperature sensor to obtain the measured variable of volume, time, and temperature of fuel in a graduated cylinder, respectively) employed in this experiment. Therefore, the overall experimental uncertainty was determined as ±1.14% by the principle of propagation of errors. The overall experimental uncertainty was computed using the following equation:

\[
\text{the overall experimental uncertainty is}\]

\[
= \text{square root of } [(\text{uncertainty of CO})^2 + (\text{uncertainty of CO})^2 + (\text{uncertainty of NO})^2 + (\text{uncertainty of O}_2)^2 + (\text{uncertainty of speed})^2 + (\text{uncertainty of fuel consumption})^2]
\]

\[
= \text{square root of } [(0.01)^2 + (0.5)^2 + (0.1)^2 + (0.04)^2 + (0.2)^2 + (0.1)^2 + (1)^2] = \pm 1.14\%
\]
The uncertainty of fuel consumption is square root of \[\sqrt{(\text{uncertainty of volume})^2 + (\text{uncertainty of time})^2 + (\text{uncertainty of temperature of fuel})^2}\] , is equal to square root of \[(1)^2 + (0.1)^2 + (0.2)^2\] = ±1%.

### 4. CONCLUSIONS

Diesohol made by mixing hydrous ethanol with diesel and PFADE was studied. The PFADE acted as an emulsifier enabling a homogenous blend. In this study, the stability and fuel properties of various diesohol blends (diesel–PFADE–ethanol and diesel–PFADE–ethanol) were analyzed and compared to some specifications in diesel and biodiesel standards. Moreover, the emissions from diesel–PFADE–ethanol blends were tested over a range of engine speeds in a standard. The emissions from diesel–PFADE–ethanol blends were signiﬁcantly lower than those with pure diesel fuel at the highest engine speed, due to a more complete combustion. Moreover, the NO\textsubscript{x} emissions of biodiesel and diesohol blends were signiﬁcantly lower than those with pure diesel fuel at 1400, 1700, 2000, and 2300 rpm engine speeds because the results of NO\textsubscript{x} emissions with PFADE and all the blends were lower than with diesel fuel at the highest engine speed, due to a more complete combustion. Moreover, the NO\textsubscript{x} emissions of biodiesel and diesohol blends were signiﬁcantly lower than those with pure diesel fuel.

#### 3 The CO emissions with diesohol and PFADE were higher than with diesel fuel at all engine speeds, and the emissions with D50PE4E10 were similar to diesel fuel at 1700 rpm. Moreover, CO emissions of the 10 wt % ethanol blends were higher than those of 20 wt % ethanol blends because ethanol in the blend increases CO and HC emissions. The maximum CO\textsubscript{2} emissions with 10 wt % hydrous ethanol in the blend was approximately 2%, while with a 20 wt % ethanol blend they were approximately 1.7% at the highest engine speed. The NO\textsubscript{x} emissions of biodiesel and diesohol blends were signiﬁcantly lower than those with pure diesel fuel, at 1400, 1700, 2000, and 2300 rpm engine speeds because the 5 vol % water content in hydrous ethanol can reduce the combustion temperature. Furthermore, the NO\textsubscript{x} emissions with 20 wt % hydrous ethanol were lower than with 10 wt %, except for at the lowest engine speed, 1100 rpm. The oxygen emissions with PFADE and all the blends were lower than with diesel fuel at the highest engine speed, due to a more complete combustion. Moreover, the 5 vol % water content in hydrous ethanol can reduce the combustion temperature because the results of NO\textsubscript{x} emissions of biodiesel and diesohol blends were signiﬁcantly lower than those with pure diesel fuel.

#### 4 The fuel consumption consistently increased with engine speed, regardless of which fuel was used. The fuel consumption rates of diesohol and PFADE were higher than that of diesel fuel because of poorer heating values than that of diesel fuel (i.e., lower energy content per volume of fuel). In addition, the consumption with 20 wt % ethanol was higher than that with 10 wt % ethanol.

For further research and development, the environmental impacts emitted pollutants and health effects study to date have focused on the damage caused by HC, smoke, PM of which these pollutants were not analyzed in this study. These may also become an important database for the assessment of other future emissions and applications of fuel blends. Therefore, the storage tank of hydrous ethanol must be carefully kept. Therefore, a self-operated fuel blend operation can be easily applied to the agricultural diesel engine and possible under consideration for the farm communities and rural communities. However, the stable blends were further screened by compliance with diesel fuel standards, leaving only 10 and 20 wt % hydrous ethanol contents for further studies.
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**ACKNOWLEDGMENTS**

This work was supported by the Prince of Songkla University, grants no. ENG6202045S, and by National Research Council of Thailand (NRCT) under Development of Alternative grants no. ENG6202045S, and by National Research Council. This work was supported by the Prince of Songkla University, Hat Yai, Songkhla 90110, Thailand; orcid.org/0000-0002-1771-5120; Email: krit.s@psu.ac.th

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