Journal of Engineering Science and Technology
Vol. 17, No. 1 (2022) 0257 - 0266

THE EFFECT OF REACTANT MOLAR RATIO TO PERFORMANCE OF H_2SO_4 CATALYST AND PARA-TOLUENE SULFONIC ACID CATALYST IN THE ESTERIFICATION OF PALM FATTY ACID DISTILLATE INTO BIODIESEL

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Abstract

This study aims to compare the use of H_2SO_4 and *para*-toluene sulfonic acid (PTSA) catalysts in converting palm fatty acid distillate (PFAD) into biodiesel. The raw material in this study is PFAD consisting of $CH_3(CH_2)_6COOH$ (Caprylic acid) and $CH_3(CH_2)_8COOH$ (Capric acid), esterified with methanol, and this is affected by the reactant molar ratio, the amount of catalyst, as well as reaction time. Furthermore, the methanol-PFAD mole ratio used are 5:1, 6:1, 7:1, 8:1, 9:1, while the catalyst concentrations PFAD are varied from 5%, 10%, 15%, 20%, as well as 25%, and the reaction is carried out for 120 minutes. In this study, the acid value is a very important parameter for determining the conversion of PFAD to biodiesel, where the initial and final acid values are used to measure the conversion of PFAD to biodiesel. According to the results, H_2SO_4 has better catalytic activity than PTSA for each molar ratio and catalyst concentration. The lowest acid value is achieved when the molar ratio of methanol and PFAD is 9:1, the catalyst concentration is 25%, and a reaction time of 120 minutes. Acid values obtained using H_2SO_4 and PTSA catalysts are 3.10 mg KOH/g and 5.82 mg KOH/g, respectively. An acid value of 3.10 mg KOH/g indicates that around 99.08% of PFAD is converted into biodiesel, and an acid value of 5.82 mg KOH/g indicates that 98.27% of PFAD is converted into biodiesel. This study also examined the effect of mixing H_2SO_4 and PTSA as a catalyst with a ratio of 1:1, and the acid value obtained from this mixing is 5.1 mg KOH/g or 98.48% of PFAD is converted into biodiesel. The catalyst mixing is carried out at a molar ratio of methanol and PFAD of 9:1, catalyst concentration of 25%, and reaction time of 120 minutes. Thus, from the economic and technical point of view, a mixture of H_2SO_4 and PTSA is a suitable catalyst for producing biodiesel from PFAD.

Keywords: Acid value, Biodiesel, H_2SO_4, PFAD, PTSA.

1. Introduction

Biodiesel is a renewable and environmentally friendly fuel because it is made from vegetable and animal oils [1-4]. The raw materials for biodiesel production from plants are abundant, such as palm oil, castor oil, corn oil, soybean oil, coconut oil, cottonseed oil, used cooking oil, etc. [1, 2]. Currently, these oil sources are not all suitable for large scale biodiesel production. However, palm oil is a suitable raw material for large scale biodiesel production without affecting the need for food due to abundance and cheapness [5].

Biodiesel is also obtained using various methods, including transesterification, interesterification, esterification, pyrolysis, and enzymatic processes [6-8]. Catalysts play an important role in biodiesel production, whether heterogeneous or homogeneous [9-14]. H_2SO_4 as a homogeneous catalyst is the catalyst most widely used in biodiesel production because it can catalyse reactions to produce high yields [6, 9, 10, 15-17]. From a technical point of view, H_2SO_4 is an excellent catalyst in the biodiesel industry, but economically, this catalyst has disadvantages due to high costs. Several researchers have utilized cheaper catalysts, for instance, *para*-toluene sulfonic acid (PTSA), to overcome this problem [6, 11, 17].

PTSA is a strong organic acid compound that is non-oxidizing, solid, colourless, easily soluble in water, alcohol, organic solutions, and the price is very low compared to H_2SO_4. Furthermore, PTSA is often used as an adsorbent in various industries and also as a catalyst in protein manufacture [18, 19]. PTSA and H2SO4 catalysts are strong acids that both containing sulphur compounds.

Based on the case above, this study therefore aims to compare the use of H_2SO_4 catalysts and PTSA catalysts in converting PFAD into biodiesel. Both the performances of these catalysts are studied in the esterification reaction of PFAD into biodiesel so that the two catalysts' operating conditions are obtained, which give comparable results. This esterification reaction is reversible, namely, the reaction between fatty acids and methanol to form methyl esters and water. The reaction is carried out with an excess of methanol so that the reaction always forms methyl esters.

This reaction is carried out with the addition of catalysts, for instance, Amberlyst-15 [19, 20], H_2SO_4 [21, 22], and perchloric acid [23]. The acid value indicates the amounts of fatty acids as reactants that do not convert into methyl esters. The esterification reaction that occurs is shown below.

$$\underset{\text{PFAD}}{\text{RCOOH}} + \underset{\text{Methanol}}{\text{CH}_3\text{OH}} \xleftrightarrow{\text{catalyst}} \underset{\text{Methyl Ester}}{\text{RCOOR}} + \underset{\text{Water}}{\text{H}_2\text{O}} \quad (1)$$

The observed variables are the effect of catalyst levels and the reactant molar ratio to the acid values obtained. This study also reports the reaction time's effect on acid value under the most suitable molar ratio conditions. In this study, the acid value is a very important parameter in determining biodiesel yield because the raw material is PFAD [13, 20, 21]. This is different for cases where triglycerides are used as raw material, the acid value cannot be used to describe the yield of biodiesel obtained. Thus, in this study, the determination of acid value is used to measure PFAD conversion into biodiesel.

2. Materials and Methods

2.1. Materials

The raw material used in this study is PFAD, composed majorly of $CH_3(CH_2)_6COOH$ (caprylic acid) and $CH_3(CH_2)_8COOH$) (capric acid), and obtained from a fatty acid factory in Indonesia. Meanwhile, 96% H_2SO_4 and 99% methanol are procured from Merck Chemicals Ltd, and PTSA monohydrate is obtained from Navdeep Chemicals Pvt Ltd.

Based on the analysis conducted, PFAD as a raw material has characteristics as shown in Tables 1 and 2.

Table 1. Characteristics of PFAD.

Properties	Measurement results	Unit	Test Method
Density	0.904	g/cm^3	ASTM D1298
Colour	0.9R	5¼ in Lovibond	AOCS Cc 13e-92
	7.9Y	5¼ in Lovibond	AOCS Cc 13e-92
Acid Value	336	mg KOH/g	AOCS Te 2a-64
Iodine Value	4.36	g I_2/100g	AOCS TI 2a-64
Sulphur	2.05	ppm	ASTM D5453
C_8 (caprylic acid)	32.147	%	ASTM D6584
C_{10} (capric acid)	64.395	%	ASTM D6584
Water content	0.02	%	ASTM D2705

Table 2. Composition of PFAD using Gas Chromatography.

Retention time (min)	Area (pA*s)	Norm weight (%)	Name
1.665	15.3450	0.0279	C_6
2.576	133825e4	32.1471	C_8
3.712	293880e4	64.3952	C_{10}
5.045	170,6161	0.3498	C_{12}
6.722	40.5968	0.0792	C_{14}
8.535	5.4593	0.0099	C_{16}
10.870	10.2411	0.0193	$C_{18:3}$

2.2. Methods

For this experiment, a 1000 mL beaker glass is placed on a hot plate, and a magnetic stirrer is placed inside. The PFAD is put in the beaker glass and heated on a hot plate at 65 0C and a speed of 300 rpm, while slowly adding a mixture of methanol and catalyst. This experiment is carried out by varying the molar ratio of methanol to PFAD of 5:1, 6:1, 7:1, 8:1, 9:1, and the catalyst concentrations are varied as 5%, 10%, 15%, 20%, 25% to the amount of PFAD. All experiments are carried out for 120 minutes, and the effect of reaction time on acid value is determined for the optimum molar ratio.

Determination of the conversion of PFAD into biodiesel can be calculated using Eq. (2), where the free fatty acid removal shows the amount of PFAD converted into biodiesel [13, 20, 21].

$$\text{Free fatty acid removal } (\%) = \frac{Initial\ acid\ value - Final\ acid\ value}{Initial\ acid\ value}\ x\ 100 \qquad (2)$$

This study also examined the effect of mixing H_2SO_4 and PTSA catalysts with a ratio of 1:1 on the conversion of PFAD into biodiesel, with a molar ratio of methanol and PFAD is 9:1. The catalyst mixture used is about 25%, consisting of 50% H_2SO_4 and 50% PTSA.

3. Results and Discussion

Figure 1 shows the colour comparison of PFAD as raw material, biodiesel products by using H_2SO_4 as a catalyst, and biodiesel products by using PTSA as a catalyst. Biodiesel obtained by using H_2SO_4 catalyst and PTSA catalyst has a darker colour than PFAD. The colour of biodiesel measured based on AOCS Method Cc 13e-92 is 1.6R and 8.0Y (5¼ in Lovibond) if using H_2SO_4 catalyst, and 1.3R and 8.2Y (5¼ in Lovibond) if using PTSA catalyst, while PFAD colour is 0.9R and 7.9Y (5¼ in Lovibond). This result is consistent with the research conducted by Chongkhong et al. [22] who carried out free fatty acid esterification using H_2SO_4 catalyst.

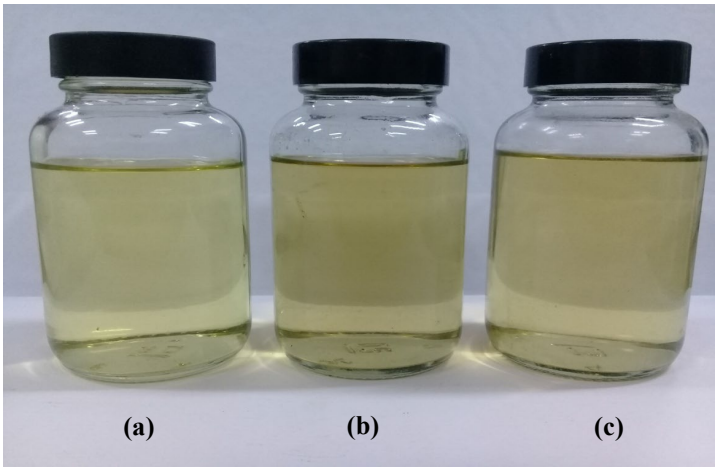

Fig. 1. Colour comparison between PFAD as raw material (a), biodiesel obtained using H_2SO_4 catalyst (b), and biodiesel obtained using PTSA catalyst (c).

Figure 2 shows the effect of reaction time and H_2SO_4 catalyst concentration on acid values on the molar ratio of methanol and PFAD 9:1, while Fig. 3 shows the effect of reaction time and PTSA catalyst concentration on acid values on the molar ratio of methanol and PFAD 9:1. According to the two figures, under the same conditions, the use of the H_2SO_4 catalyst always produces a lower acid value than the use of PTSA catalysts. In both catalysts, for the reaction time interval of 60 minutes to 105 minutes, the acid value decreased significantly for each concentration, but for the reaction time of 105 minutes to 120 minutes, the decrease in acid value is not significant for the two catalysts. Thus, the reaction time and catalyst concentration have a significant impact on reducing acid value [17]. In this study, the acid value obtained is used to determine the conversion of PFAD into biodiesel because the raw material used is a fatty acid (carboxylic acid) which is calculated using Eq. (2) above. In this esterification reaction, the acid value at the end of the reaction describes the fatty acids content that are not converted into biodiesel, meaning that the smaller the acid value indicates that more PFAD is converted into biodiesel.

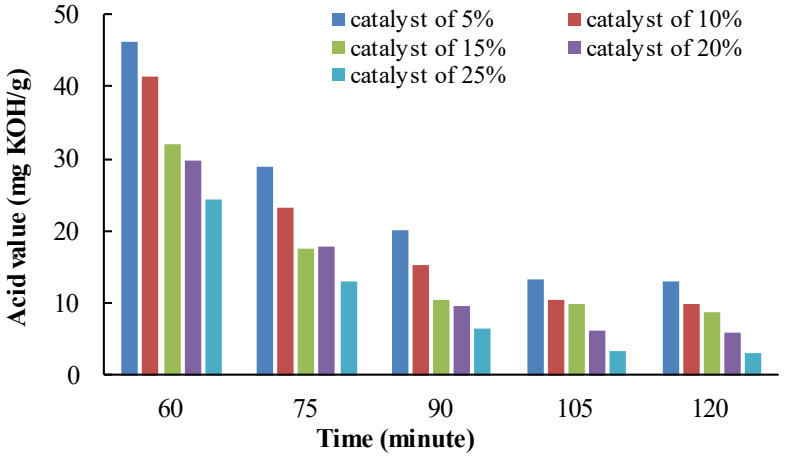

Fig. 2. The effect of time and H_2SO_4 catalyst concentration on acid values in the molar ratio of methanol and PFAD 9:1.

The lowest acid value is obtained with 25% catalyst concentration and 120 minutes reaction time for both catalysts. The acid values obtained using H_2SO_4 catalyst at reaction times of 105 minutes and 120 minutes are 3.47 mg KOH/g and 3.10 mg KOH/g, indicating a 98.97% and 99.08% PFAD conversion, respectively. Meanwhile, the acid values obtained with PTSA catalysts are 5.90 mg KOH/g and 5.82 mg KOH/g, indicating a 98.24% and 98.27% PFAD conversion into biodiesel, respectively. The results achieved are already higher when compared to the results achieved by other researchers who use fatty acids as raw materials or using H_2SO_4 catalysts and PTSA catalysts in producing biodiesel.

These yields are also higher than those of other researchers using other raw materials and other catalysts. Melfi at al [19] and Hykkerud and Marchetti [20] are able to convert oleic acid into biodiesel by 87% and 53% using Amberlyst-15 catalysts, while Marchetti and Errazu are able to convert free fatty acids into biodiesel using H_2SO_4 catalyst up to 96% [21]. Guan et al. [17] reported conversion of 97.1% when using PTSA catalysts for the transesterification of vegetable oil to biodiesel.

Chongkhong et al. [22] could reduce the amount of FFA from 93 wt% to less than 2 wt% at the end of the esterification process by using H_2SO_4 as catalyst. Hayyan et al. [23] used perchloric acid as a catalyst to reach 88% conversion of FFA to fatty acid methyl ester, Kansedo et al. [24] could reach up to 79.6% the yield of palm oil fatty acid methyl esters from palm oil by using montmorillonite KSF as catalyst, and Lokman et al. [25] reached up to 92.3% the yield of methyl ester from palm fatty acid distillate using sulfonated glucose-derived acid catalyst.

Table 3 summarizes the conversion results of PFAD to biodiesel at a molar ratio of 9:1 and a catalyst concentration of 25%. The results obtained using the two catalysts are not much different, and at a reaction time of 120 minutes, the results obtained are better than those obtained by other researchers [17, 19-25].

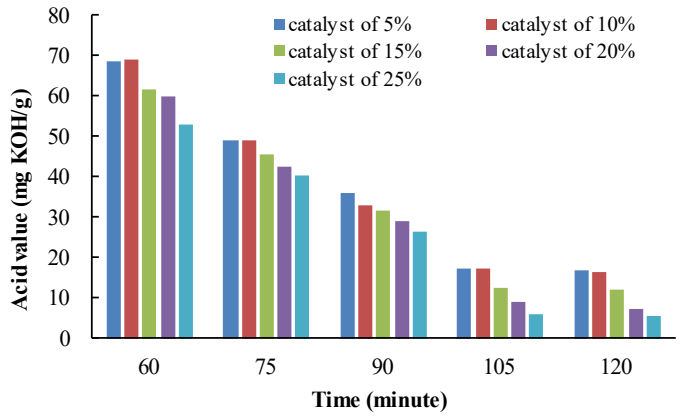

Fig. 3. The effect of time and PTSA catalyst concentration on acid values in the molar ratio of methanol and PFAD 9:1.

Table 3. Conversion of PFAD to biodiesel at molar ratio of methanol to PFAD of 9:1 and 25% catalyst concentration.

Duration of reaction (minute)	Conversion of PFAD into biodiesel (%)	
	Using H_2SO_4 catalyst	Using PTSA catalyst
60	92.77	84.22
75	96.11	88.05
90	98.09	92.18
105	98.97	98.24
120	99.08	98.27

Figure 4 is an example of analysis results using gas chromatography on biodiesel obtained by using the PTSA catalyst of 25%, the molar ratio of methanol and PFAD 9:1, and reaction time of 120 minutes. In Fig. 4, it can be seen that the results are dominated by C_8 and C_{10}.

Figures 5 and 6 show the acid value of biodiesel products as the influence of H_2SO_4 catalyst concentration and PTSA catalyst with a variation of reactant molar ratio and reaction time of 120 minutes. If the acid values in Figs. 5 and 6 are compared at the same molar ratio and catalyst concentration, the acid value obtained by using PTSA catalyst gives comparable results to those obtained by using H_2SO_4 catalyst. Hence, both catalysts have comparable catalytic capabilities in converting PFAD into biodiesel. Furthermore, the molar ratio has a highly significant influence on the acid value produced. The lowest acid value of 3.10 mg KOH/g is achieved when the molar ratio of methanol and PFAD is 9:1, and the catalyst concentration of H_2SO_4 is 25%. Meanwhile, under the same conditions by using PTSA catalysts, the acid value obtained is 5.82 mg KOH/g. The acid value obtained shows that an acid value of 3.10 mg KOH/g means around 99.08% PFAD is converted into biodiesel, and an acid value of 5.82 mg KOH/g means 98.27% PFAD is converted into biodiesel. Thus, a lower acid value indicates a higher conversion rate of PFAD into biodiesel.

Figures 5 and 6 also show the two catalysts are able to obtain an equivalent acid value, but with a different molar ratio of the reactants as well as catalyst concentrations. For instance, the acid value obtained using H_2SO_4 catalyst of 20%

at a 9:1 molar reactant ratio is almost equivalent to the acid value obtained using 25% PTSA at a 9:1 reactant molar ratio, namely 5.92 mg KOH/g and 5.82 mg KOH/g, or the conversion of PFAD into biodiesel from the two catalysts is almost the same, namely 98.24% and 98.27%.

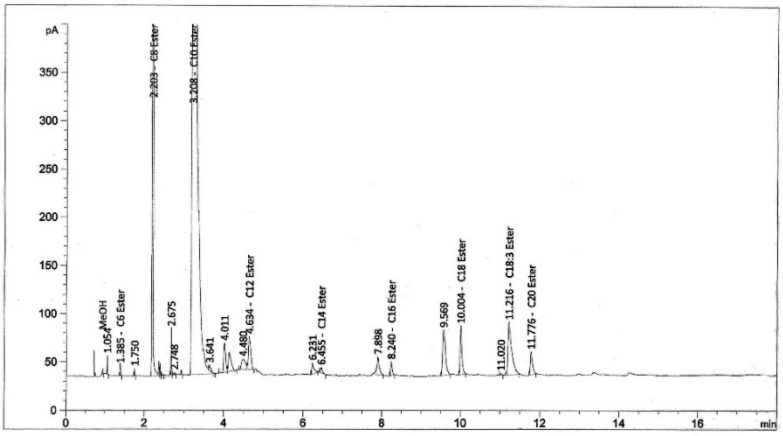

Fig. 4. Gas chromatography analysis of biodiesel using PTSA catalyst of 25%, the molar ratio of methanol and PFAD 9:1, and a reaction time of 120 minutes.

Based on the results obtained using the two catalysts, a mixture of the two catalysts is tested as a catalyst for biodiesel production from PFAD. The amount of catalyst mixture used is about 25% of PFAD, with a ratio of H_2SO_4 and PTSA is 1:1. The molar ratio of methanol and PFAD is 9:1. From this experiment, the results obtained for a reaction time of 120 minutes produces an acid value of 5.1 mg KOH/g or 98.48% PFAD is converted into biodiesel. From an economic and technical point of view, these results provide a great opportunity to use this catalyst mixture in biodiesel production from PFAD.

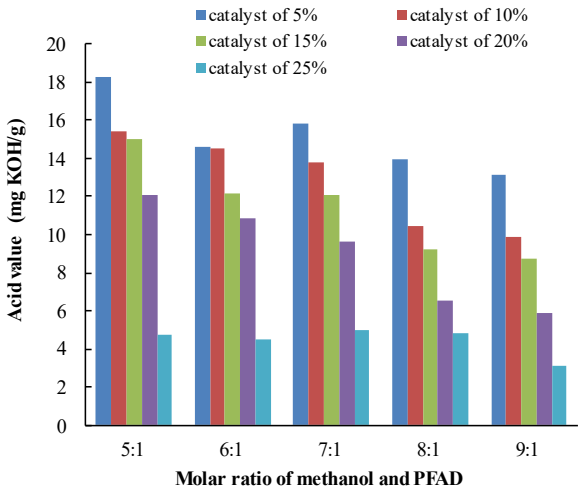

Fig. 5. The effect of the molar ratio of reactants on acid values at various H_2SO_4 catalysts concentrations, and a reaction time of 120 minutes.

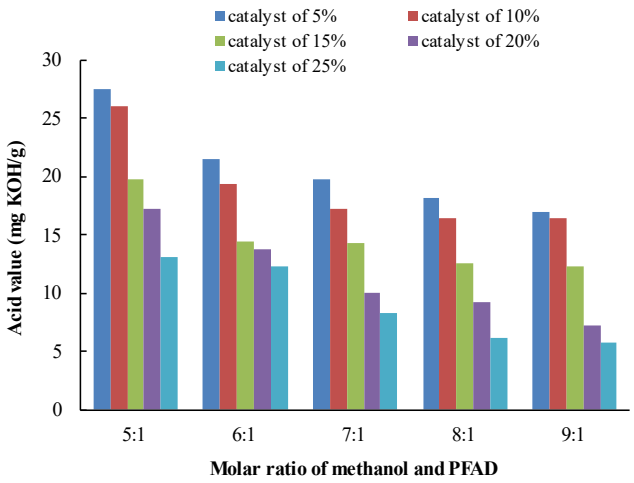

Fig. 6. The effect of the molar ratio of reactants on acid values at various PTSA catalysts concentrations, and a reaction time of 120 minutes.

4. Conclusions

Biodiesel production from PFAD and methanol using H_2SO_4 catalysts and PTSA catalysts can be carried out through esterification reactions, and both catalysts give comparable results. Both catalysts can obtain an equivalent acid value but with different reactant molar ratios or with different catalyst concentrations. The optimum reaction time for the esterification reaction of PFAD with methanol is 120 minutes, and the lowest acid value is obtained with a catalyst concentration of 25% and a molar ratio of methanol and PFAD of 9:1. The lowest acid value obtained is 5.82 mg KOH/g by using the PTSA catalyst and 3.10 mg KOH/g by using the H_2SO_4 catalyst. The use of a mixture of H_2SO_4 and PTSA as a catalyst in a ratio of 1:1 produces an acid value of 5.1 mg KOH/g. This result is achieved with a molar ratio of methanol and PFAD 9:1, catalyst content 25%, and reaction time of 120 minutes, and the acid value of 5.1 mg KOH/g is obtained or 98.48% of PFAD is converted into biodiesel.

Nomenclatures

C_6	$CH_3(CH_2)_4COOH$ (Caproic acid)
C_8	$CH_3(CH_2)_6COOH$ (Caprylic acid)
C_{10}	CH_3 $(CH_2)_8COOH$) (Capric acid)
C_{12}	$CH_3(CH_2)_{10}COOH$ (Lauric acid)
C_{14}	$CH_3(CH_2)_{12}COOH$ (Myristic acid)
C_{16}	$CH_3(CH_2)_{14}COOH$ (Palmitic acid)
$C_{18:3}$	$CH_3CH_2CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_7COOH$ (Linolenic acid)

Abbreviations

AOCS	American Oil Chemists' Society
ASTM	American Society for Testing and Materials

FFA	Free Fatty Acid
PFAD	Palm Fatty Acid Distillate
PTSA	*para*-Toluene Sulfonic Acid

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