JURNAL PENDIDIKAN KIMIA (JPKIM)
ISSN: 2085-3653| e-ISSN: 2549-3116

J. Pendidik. Kim 2023, 15(2), 155 - 162
DOI 10.24114/jpkim.v15i2.43668

Research Article

The effect of methanol flow rate and repeated use on amberlyst catalyst characteristics in palm fatty acid distillate (PFAD) esterification reaction

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Received 17 February 2023 ♦ **Revised** 30 August 2023 ♦ **Accepted** 31 August 2023

Citation: Wardana, D., Eddiyanto, E., Nurfajriani, N., & Gea, S. (2023). The effect of methanol flow rate and repeated use on amberlyst catalyst characteristics in palm fatty acid distillate (PFAD) esterification reaction. Jurnal Pendidikan Kimia (JPKIM), 15(2), 155–162. https://doi.org/10.24114/jpkim.v15i2.43668

Keywords

Amberlist
Biodiesel
Esterification
PFAD

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Abstract

Palm fatty acid distillate (PFAD) is a waste from cooking oil which is rich in free fatty acids (FFA). The high FFA content in PFAD allows PFAD to be processed into a renewable and economically valuable energy source, namely biodiesel through an esterification process using methanol with the help of an amberlyst catalyst. This study aims to see how the effect of variations in flow rates on the conversion of PFAD to biodiesel which takes place in a continuous reactor and to see the effect of repeated use of catalysts at optimum conditions on the conversion rate. The results showed that the optimum conditions were obtained with a methanol flow rate of 2 ml/minute. The flow rate of methanol above 2 ml/minute actually inhibits the reaction process. The repeated use of the catalyst reduces the availability of active sites and increases the presence of impurities and reduces the thermal stability of the catalyst at high temperatures.

Introduction

Along with the times, the need for renewable energy will increase. This is because the existence of fossil fuels has a very long time to be renewed, and if it is used continuously for quite a long time then its availability will be depleted. Currently, one solution that has been taken is to substitute it with biofuels, one of which is biodiesel from the fatty acid esterification process (Burmana, 2020).

One of the raw materials that can be used to produce biodiesel is palm fatty acid distillate (PFAD). This is because PFAD is a waste from the cooking oil refining process which is high in free fatty acids (Kurniawan et al. 2020). In the process, from the cooking oil refining process, 5-6% PFAD will be obtained (Chongkong et al. 2007).

In the industrial world, the use of heterogeneous catalysts is preferred compared to homogeneous catalysts, this is because the use of homogeneous catalysts can cause corrosion in production equipment. The use of heterogeneous catalysts can anticipate this, apart from that heterogeneous catalysts also have the advantage of being easy to separate and can be used repeatedly (Hutagaol et al 2020).

One of the heterogeneous catalysts that can be used in the PFAD esterification process to produce biodiesel is the amberlyst catalyst. Amberlyst is a highly polymerized hydrocarbon compound with the presence of cross-links (cross-linking) in the compound molecule, this makes it difficult to dissolve. This catalyst has the availability of ion groups which during the catalytic process will be exchanged with reactants (Lestari et al. 2000). Amberlyst is an effective catalyst in the fatty acid esterification process and in the oil transesterification process (Xia, 2012). In this catalyst, the catalytic process starts from the process of reactant diffusion to the surface of the catalyst. Furthermore, the adsorption and diffusion processes of the reactants occur on the surface of the catalyst. The reaction process occurs in the adsorption layer and forms a product. After that, the product desorption process occurs from the surface of the catalyst and the product exits gradually back to the fluid phase (Chorkendorf and Niemanstverdiet, 2003). The amberlyst mechanism in the PFAD catalytic process to produce biodiesel is shown in Fig.-1.

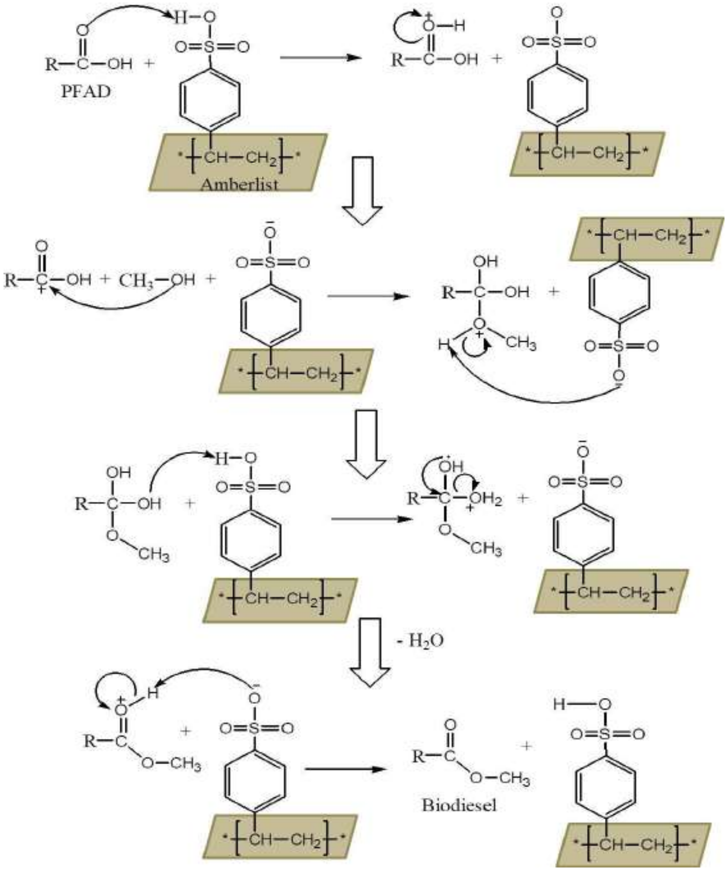

Fig.-1. Amberlyst Catalyst Reaction Mechanism on PFAD Esterification

However, this catalyst still has a weakness, namely a decrease in catalytic activity if used repeatedly. One of the causes is a decrease in the presence of active sites, or the presence of impurities that can poison the active sites and close the pores of the catalyst thereby inhibiting the ion exchange process (Argyle and Bartholomew, 2015). This is important to study so that the efficiency of repeated use of amberlyst catalysts can be determined.

Apart from being related to the choice of catalyst, another important thing that is important to study is how the ratio of methanol to PFAD affects the rate of biodiesel conversion. It is important to know the optimum conditions for producing biodiesel with high yields. Giving methanol in less amount will make the reaction rate run slowly so that the resulting yield will be very low. However, if methanol is given in excessive amounts it will actually be able to deactivate the catalyst so that it will reduce the number of products (Tshizanga, 2015).

Based on some of the above, this research empowers PFAD as a renewable energy source, where the esterification process is carried out using an amberlyst catalyst. The process takes place in a continuous reactor. In the process, the reactant in the form of methanol is added continuously to the reactor in a constant amount during the esterification process (Khan et al. 2016). In this study, process optimization was carried out including variations in the methanol ratio with PFAD (which was modeled through the flow rate velocity). In addition, a test process of using the catalyst repeatedly at optimum conditions was carried out to see how it affects the characteristics of the catalyst.

Method

Tools and Materials

The tools used in this study were laboratory glassware, heating mantles, magnetic bars, thermometers, silicone hoses of various sizes, condensers, peristaltic pumps, schlenk flasks, electric burettes, Fourier Transform Infrared (FTIR, Agilent Technologies), Thermogravimetry Analyzer (Hitachi STA7300) and an electric burette

(Metrohm). While the materials used included PFAD, amberlyst catalyst, methanol (Merck, Germany), standardized 0.1 N and 0.5 N ethanolic KOH, isopropyl alcohol, nitrogen gas, phenolphthalein indicator, and demineralized water.

Esterification Process

The schematic of the reactor in the esterification process is shown in Fig.-2. The conditions of the reactor in the esterification process are as follows: the evaporation temperature of methanol in flask 1 (90°C), esterification reaction temperature in flask 2 (115oC), stirring speed (500 rpm), reaction time (3.5 hours), PFAD weight (500 grams), amberlyst catalyst (8% of PFAD weight) and methanol flow rates in various peristaltic pumps (1 ml/minute, 2ml/minute, 3ml/minute). After the reactor is running, samples are taken every 30 minutes and acid value and FTIR analysis is carried out. After the optimum conditions were found, repeated use of the amberlyst catalyst was carried out under these conditions and characterization was carried out which included FTIR and TGA tests.

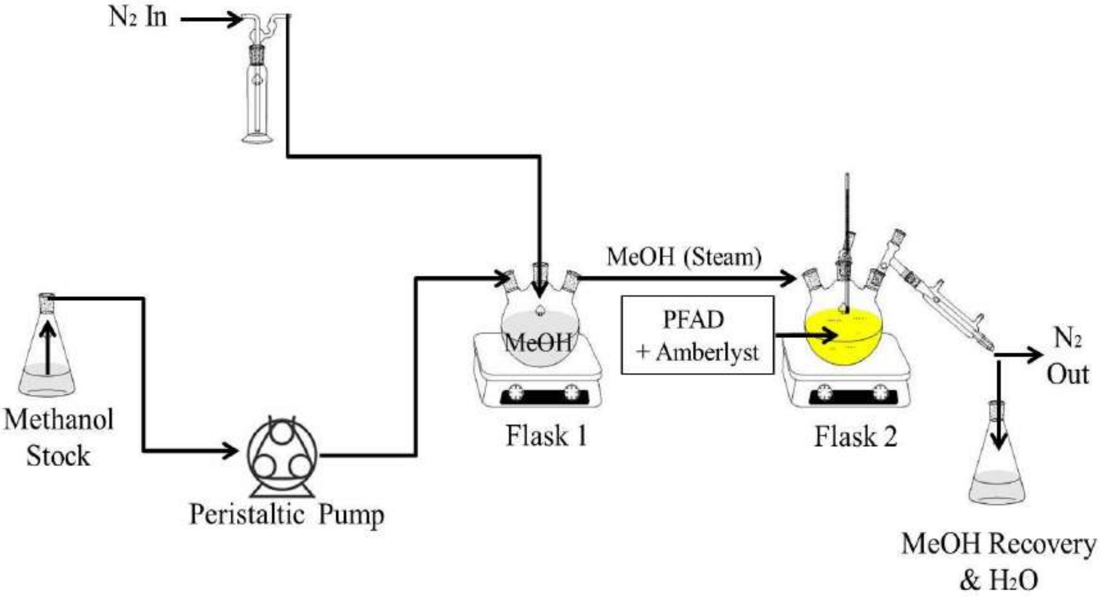

Fig.-2. Reactor Circuit

Determination of Acid Value and Conversion Rate

Every 30 minutes, samples were taken, then weighed as much as 5 grams and dissolved in 50 ml of isopropyl alcohol. After that, it was titrated with standardized KOH until the color changed. The formula for determining the value of the acid value (AOCS, 2017):

$$\text{Acid Values (mgKOH/g)}=\frac{H\times N\times 56.11}{W}$$

V = KOH volume (ml), N = KOH normality, W = sample weight (grams), 56.1 = KOH molecular weight

While the conversion rate every 30 minutes is calculated by comparing the initial acid value of PFAD with the acid value during the sampling process. The formula for determining the conversion rate (Melfi et al. 2020):

$$\text{Conversion (\%)} = \frac{\text{Initial Acid Value - Acid Value at a Specific Time}}{\text{Initial Acid Value}}\times 100\%$$

Results and Discussion

After the esterification process was carried out for 3.5 hours at various methanol flow rates (1 ml/minute, 2 ml/minute, and 3 ml/minute) and analysis of changes in acid value, the data were obtained as shown in Table 1.

Table 2. PFAD to FAME Conversion Rate Based on Decreasing Acid Value at Variations of Flow Rates

Reaction Time [minutes]	Flow Rate 1ml/min		Flow Rate 2ml/min		Flow Rate 3ml/min	
	Acid Value [mg KOH/g]	Conv. Rate [%]	Acid Value [mg KOH/g]	Conv. Rate [%]	Acid Value [mg KOH/g]	Conv. Rate [%]
0	209.09	0	209.09	0	209.09	0
30	158.22	24.33	136.23	34.85	114.56	45.21
60	105.84	49.38	86.77	58.50	62.38	70.17
90	65.34	68.75	32.71	84.36	27.98	86.62
120	28.84	86.21	9.57	95.42	4.22	97.98
150	11.23	94.63	1.73	99.17	2.25	98.92
180	5.98	97.14	0.44	99.79	1.72	99.18
210	2.49	98.81	0.29	99.86	1.34	99.36

There was a decrease in acid value every time interval of 30 minutes. The longer the reaction time, the value of the acid value will decrease. This is because there has been a reaction between the fatty acids and methanol which produces methyl ester compounds, this increase in the ester content causes a decrease in the acid value (Abidin et al. 2012). The changes in acid number values per 30 minutes are shown in Fig.-3.

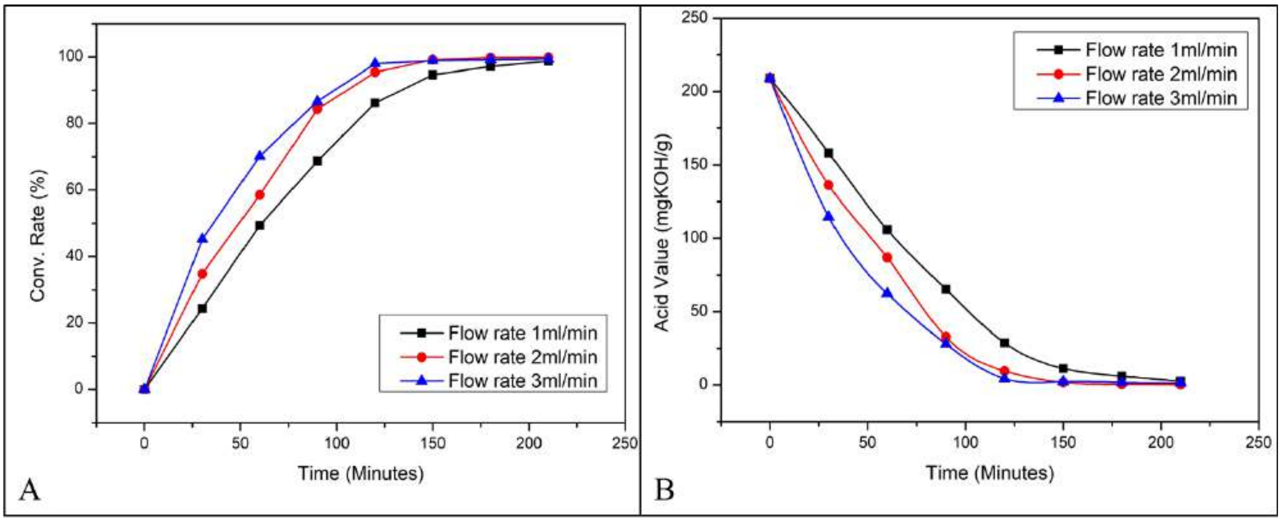

Fig.-3. A. Change in Acid Value; dan B. Conversion Rate

The speed of the methanol flow rate affects the biodiesel conversion rate. The methanol flow rate of 1 ml/minute produces the lowest conversion rate. This is because if this is caused the faster the slower the flow rate of methanol, the lower the concentration will be in the reaction process. The lower the concentration, the fewer reactant molecules will be available, and will reduce the possibility of collisions with PFAD molecules which will result in a decrease in the speed of the reaction rate (Haryono, 2019).

At a methanol flow rate of 30 ml/minute, it can be seen that up to 90 minutes the conversion rate is the fastest. However, after 90 minutes the reaction tends to be constant and the difference in decreasing acid value is no longer high, in fact it is lower than the methanol flow rate of 2 ml/minute. This is due to the fact that too much methanol is given not only to speed up the reaction process for biodiesel formation but also to accelerate the process of forming a by-product, namely water. Because the water produced so quickly causes some of the water to be unable to be removed directly from the reactor and is retained for a certain period during the reaction process which ultimately leads the reaction to be reversible and slows down the conversion rate (Pasaribu and Rustamaji, 2012). Water retained on the surface and pores of the catalyst is able to prevent the reactants from reaching the active site of the catalyst which plays a role during the reaction process (Boz et al. 2014) moreover, water is polar while PFAD is non-polar. FTIR spectra of Amberlist in methanol flow rate variation. This was confirmed by FTIR spectra of amberlite as shown in the Fig.-4.

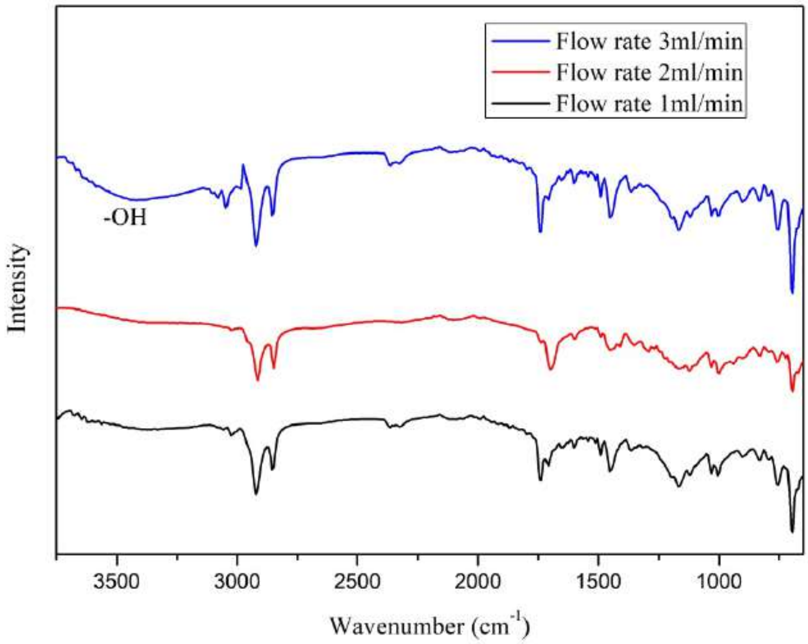

Fig.-4. FTIR Spectra of Amberlist in Methanol Flow Rate Variation

The FTIR analysis results show that at a methanol flow rate of 3ml/minute, there is a broad absorption at wave number (3500-3400cm-1) at a methanol flow rate of 3 ml/minute which probably comes from the –OH group on the water molecule (Mistry, 2009).

Optimum conditions were found at the methanol flow rate of 2ml/minute, this was because there was no significant difference in the conversion rate when compared to the methanol flow rate of 3ml/minute and even at the end of the reaction, the conversion rate obtained was slightly above it even though using a higher amount of methanol. a little. After the optimum conditions for the reaction have been found, repeated use of the catalyst is carried out, the results of the FTIR analysis are listed below Fig.-5.

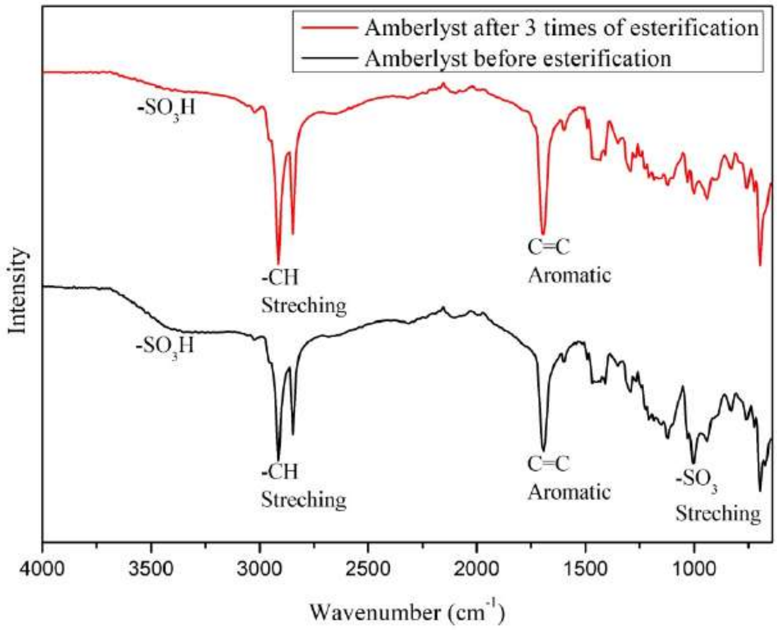

Fig.-5. FTIR Spectra of Amberlyst Before and After Being Used Three Times

The results of the FTIR analysis of all analytes indicated that there was absorption at wave number 2914 cm-1 as a stretching vibration of –CH from the polystyrene chain making up the Amberlyst (Mistry). Then it can be seen that there is absorption at wave numbers 1600-1700 (cm-1) as a stretching vibration of aromatic C=C from the presence of a benzene ring (Pujiastuti et al. 2010). The existence of the active site -SO3H was confirmed by the appearance of absorption with weak intensity at wave number 3500-3400 cm-1 (Gutch et al. 2007) where after 3 times esterification process, the intensity of this absorption seemed to decrease. In addition, there is absorption at around wave number 1100-1000 cm-1 as a stretching vibration from the presence of the –SO3H group, where after 3 uses, the intensity of this absorption decreases, which means there is a decrease in the presence of active sites (Pujiastuti et al. 2010). In addition to functional group analysis, another characterization that was carried out was thermal decomposition analysis, as stated in Fig.-6.

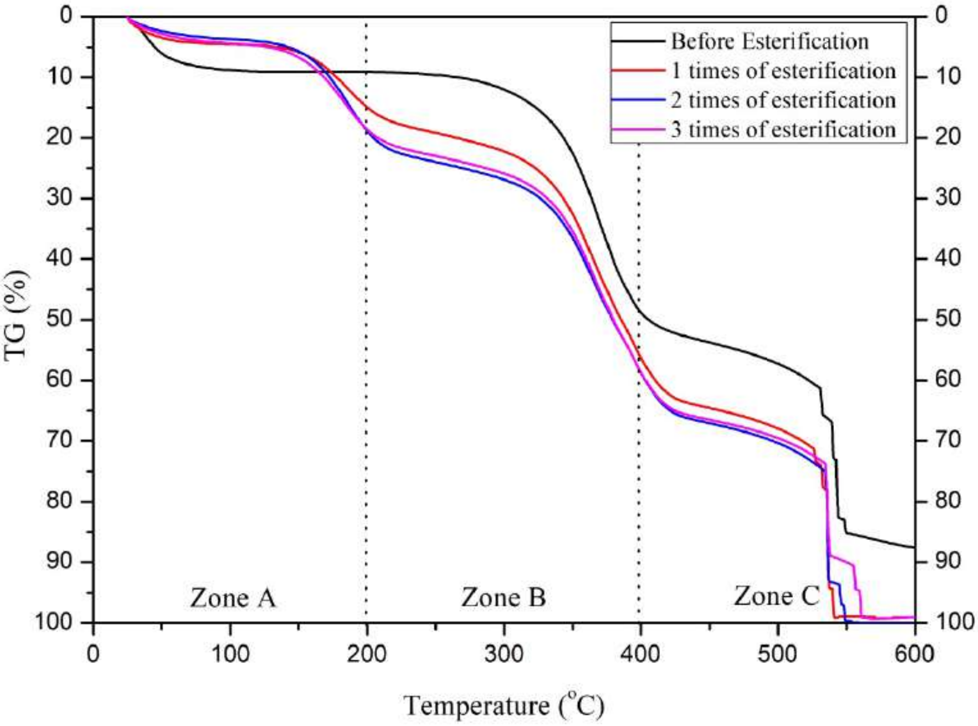

Fig.-6. Amberlyst TGA curve after 3 uses

Fig.-6 shows the temperature at which amberlyst undergoes decomposition, if observed the decomposition temperature of amberlyst can be divided into 3 zones. First, decomposition occurs with a decrease in mass weight <10% below 200°C which is probably the weight of the presence of water in the polymer matrix (Rabil et al. 2020) or the presence of volatile compounds (Han et al. 2019). Furthermore, it was seen that there was a significant decrease in mass, which was around 50% in the temperature range of 200°C-400°C which is probably caused by the polystyrene chain and the presence of sulfonic acid groups which are starting to depolymerize. Then the greatest mass shrinkage occurs above the temperature of 400°C, where at this stage the Divinylbenzene (DVB) matrix begins to degrade (Ciopec et al. 2013). Before the esterification process it was seen that the reduction in mass weight (decomposition) of the amberlyst catalyst was slower, but after the first esterification process it was seen that the decomposition rate had changed. In zone A (0-100°C) the rate of decomposition slowed but was followed by a significant increase in zone B (200-400°C) day Zone C (400-600°C). Furthermore, on the second use the decomposition rate increased, although not significantly, and slightly slowed down on the third use. This shows that after the esterification process the amberlyst catalyst is no longer in a pure state (Sudrajat et al. 2015). This is due to deposits of alkyl compounds originating from PFAD which are retained from the surface or pores of the catalyst. Where the biggest deposit is in the second use, but in the third use there is a slight decrease. When compared with before use it is clear that there is a difference where before using the catalyst weight loss was only close to 90% but after use the weight loss changed to close to 100%. This shows that the reaction process has an impact in the form of a decrease in thermal stability) on the polymer structure making up the amberlyst at high temperatures (Noshadi et al. 2013).

Conclusion

The speed of the methanol flow rate in the PFAD esterification process has an influence on the decrease in the acid value and conversion rate. Optimum results were obtained at a conversion rate of 2 ml/minute. The methanol flow rate that was too slow, namely 1 ml/minute, also slowed down the conversion rate, but the methanol flow rate that was too high, namely 3ml/minute, did not provide a significant increase, on the contrary, it actually slowed down the conversion rate at the end of the reaction. The repeated use of the catalyst has an effect on the availability of active sites, where after 3 repeated uses it can be seen that the presence of active sites has decreased which is confirmed by a decrease in intensity at wave numbers 3500-3400cm-1 from the –SO3H group. The results of the TGA analysis show that after the repeated esterification process the catalyst contains impurities attached to the catalyst. This is shown from the increase in decomposition temperature after using a catalyst.

Conflict of Interests

The author (s) declares that there is no conflict of interest in this research and manuscript.

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