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Eco-Friendly Chitosan-Based Biodiesel Heterogeneous Catalyst Support Membrane

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Abstract

A chitosan-polyvinyl pyrrolidone K-30 (Cs-PVP.K30) membrane was prepared as a heterogeneous catalyst supporting membrane in the transesterification process in the production of biodiesel from palm oil and methanol through the blend reaction between chitosan (Cs) and polyvinyl pyrrolidone K-30 polymer (PVP K-30). Several membranes were characterized by their physicochemical and catalytic properties. Based on physicochemical data, it was found that including the carbonyl group from PVP K-30 into the chitosan framework correlated with an increase in porosity, hydrophilicity, water absorption, and the degree of swelling of the membrane. The results of the analysis using Fourier Transmittance Infra-red (FTIR) showed the spectra of carbonyl (-C=O) and hydroxyl (-OH) groups at wavenumbers 1648 cm^{-1} and 3363 cm^{-1}, which shows that the reaction of chitosan alloy with PVP K-30 has been successfully carried out. The catalytic site of the Cs-PVP K30-NaOH membrane in the biodiesel production process was studied under several conversion conditions. It was found that the conversion of biodiesel reached 93.90% with a reaction time of 90 minutes, a temperature of 65°C, and an oil/methanol mole ratio of 1:7.

1. Introduction

Biodiesel is one of the alternative diesel fuels produced from renewable resources through a transesterification reaction that converts vegetable oils, animal fats, and alcohol into fatty acid esters and glycerin with the help of a catalyst [1]. Biodiesel is more environmentally friendly than diesel fuel due to its high cetane number, low sulfur content, and high oxygen content is biodegradable and non-toxic [2].

Currently, biodiesel can be produced by adding a catalyst for oil esterification. Three catalysts can be used: homogeneous catalysts, enzymes, and heterogeneous. Homogeneous catalysts such as KOH, NaOH, CH_3OK, H_2SO_4, H_3PO_4, and HCl in biodiesel production are very sensitive to free fatty acids (FFA), difficult to recycle, high operating costs, and corrosive [2]. Enzyme catalysts are very difficult to handle and expensive, the reaction rate is slow, and enzyme deactivation often occurs [3]. Several heterogeneous catalysts have been used to produce biodiesel, such as Cs-CC, with a yield of 98.40% [4], ACM with a yield of 99.25% [2], and $[(CH_2COOH)_2IM]$ HSO_4@H-UiO-66 with 93.82% yield [5]. Heterogeneous catalysts provide many advantages because they can be easily separated from their products by filtration, regenerated, reused, environmentally friendly, cheaper, and non-corrosive [6].

Several researchers have explored using natural materials as a base catalyst for supporting catalysts in the biodiesel production process [7]. Ease of obtaining, availability, and ability to be degraded are interesting considerations for researchers. Chitosan is one of the natural materials being developed to catalyze the biodiesel process [8]. Chitosan is attractive for use as a catalyst because of the reactivity of its two groups (-OH and $-NH_2$) which are easily modified with other compounds or functional groups according to the intended use. However, unmodified chitosan has several drawbacks, such as being easily damaged, unstable, low stability in acid solutions, and low hydrophilicity [9]. Modifications on chitosan were made to overcome these deficiencies, either through blending or crosslinking with other compounds.

Several studies have developed modifications to chitosan including chitosan-guanidine [10], chitosan-sulphosuccinate [2], chitosan-sulfate [11], and chitosan-citric acid [4]. Chitosan is mixed with other hydrophilic polymers to increase the mechanical strength lost in the wet state. Polyvinyl pyrrolidone K-30 (PVP K-30) is a hydrophilic, compatible, and fairly well-dispersed synthetic polymer in the chitosan matrix when doped into it [12]. In addition, PVP K-30 is a water-soluble polymer that has beneficial effects on absorption, viscosity, solubility, condensation, and is able to form homogeneous mixtures with chitosan. PVP K-30 can form hydrogen bonds with chitosan through the formation of bonds between the amino and hydroxyl groups of chitosan and the carbonyl groups of PVP K-30 [13]. By studying the above, in this research, a series of Cs-PVP. The K30 membranes will be made to support NaOH which will be used as a heterogeneous catalyst in biodiesel production.

2. Methods

2.1. Tools and Materials

The tools used during this study were standard laboratory tools (Pyrex and Herma), magnetic stirrers, hotplates (Biomega), ovens (Kirin), pH meters, Petri dishes (Sterilplan), analytical balances (OHAUS), ultrasonic baths. Homogenizer, shaker, thickness meter (Mitutoyo), microscope (RaxVision), Gas Chromatography-Mass Spectrophotometer/GC-MS (Shimadzu GCMS-QP2010 SE), FTIR (FTIR PerkinElmer Frontier). The materials used during this study were chitosan (MW 40,000 g/mol, Surindo Biotek Cirebon), PVP K-30 (MW 36,000 g/mol, BASF Pharma), CH_3COOH (MW 60,052 g/mol, Merck), NaOH (MW 39.997 g/mol; Merck), distilled water (MW 18.0153 g/mol), methanol (MW 32.04 g/mol, Merck), ethanol (MW 46.07 g/mol, Merck), Na_2SO_4 (MW 142.04 g/mol, Merck), phenolphthalein (MW 318.32 g/mol, Merck), KOH (MW 56.1 g/mol, Merck), palm oil (palm oil, MW 849.5 g/mol, FILM).

2.2. Preparation of 1.5% Chitosan Solution

A 1.5 g Chitosan powder is dissolved in 100 mL of 1% acetic acid in a 100 mL beaker glass by stirring using a stirrer for 24 hours at room temperature.

2.3. Fabrication of K-30 Chitosan-Polyvinyl Pyrrolidone Membrane

Cs-PVP membrane (v/v) was made in 5 variations (4:1, 3:2, 1:1, 2:3, and 1:4). First, 1.5 g of PVP K-30 was dissolved in 100 mL of distilled water and stirred for 1 hour at 55°C until a homogeneous mixture was obtained. Then, chitosan solution was added and stirred for ± 2 hours at 55°C until homogeneous. The solution was placed in an ultrasonic bath homogenizer for 20 minutes at 55°C. The resulting Cs-PVP solution was printed using a petri dish (d = 5 cm) and dried in an oven for ± 12 hours at 40°C. The printed membrane was immersed in 2 M NaOH, 10 mL for ± 12 hours, and air-dried at room temperature. After drying, all membranes were measured for weight and thickness; the results are shown in Table 1.

2.4. Membrane Characterization

2.4.1. Fourier Transform Infra-Red (FTIR)

Chitosan membrane and Cs-PVP.K30 were tested using an FTIR spectrophotometer to determine the success of the reaction. The FTIR spectra were recorded at room temperature in the range of 4000–500 cm^{-1}.

2.4.2. Microscope Test

Cs-PVP K-30 membranes were analyzed using a microscope (RaxVision) to determine the surface appearance of Cs-PVP K-30 and Cs-PVP K-30-NaOH membranes used as catalysts for biodiesel production using 4.5 times magnification.

2.4.3. Membrane Thickness and Weight Test

The thickness of the membrane was determined using a thickness meter (Mitutoyo). Five different locations were used to retrieve information on membrane thickness. The membrane weight of each synthetic composition was determined using an Ohaus analytical balance. For each membrane, measurements of thickness and weight were taken five times.

2.4.4. Swelling Degree Test

The degree of swelling was determined by soaking the synthesized membrane in 10 mL of distilled water for 24 hours.

2.4.5. Porosity Test

The porosity of the membrane was tested by immersing the membrane in 10 mL of distilled water for 24 hours, then drying it quickly using a tissue so that the percent porosity value of the membrane was obtained.

2.4.6. Water Absorption Test

The membranes synthesized from chitosan and Cs-PVP were weighed on an analytical balance in a dry or 0 hours condition, then soaked in 10 mL of water at room temperature for 6 hours, where weight was measured every hour by wiping quickly and weighing.

2.4.7. pH Resistance Test

Each membrane sample was weighed to obtain the initial dry weight of the membrane and then soaked with 10 mL of a solution with a variety of pH 3, 5, 7, 9, and 11 for 24 hours, in which the pH was adjusted using acetic acid and sodium hydroxide. Then the membrane was dried and weighed to obtain the final dry weight.

2.4.8. Hydrophilicity Test

The hydrophilicity of the membrane was tested using sessile drops, which involved dropping a drop of water on the surface of the synthesized membrane and then taking an image of the membrane that had been dripped with a drop of water.

2.4.9. Biodegradation Test

The membrane was tested on the biodegradation test by embedding all the membrane samples in compost for 15 weeks. The membrane is weighed using an analytical balance. Then the membrane was buried with compost and given humid conditions (watering) every week after measurement, as well as insect worms, to adjust the composition of the earth's soil environment.

2.5. Biodiesel Applications

2.5.1. Synthesis of Biodiesel

30 mL of palm oil as a Free Fatty Acid (FFA) source was added to 10 mL of methanol as an agent to produce Fatty Acid Methyl Ester (FAME/biodiesel). When the mixture reached the desired temperature, a 1.5% Cs-PVP membrane with a diameter of about 5 cm, a weight of between 40 and 75 mg, and a thickness of between 6.7 and 7.6 10-2 mm was added. The membrane was then allowed to react for a predetermined amount of time. Biodiesel conversion in this study used the pycnometer method and was calculated using Equation (1).

$$Biodiesel\ conversion\ (\%) = \frac{weight\ of\ biodiesel\ yield\ (g)}{weight\ of\ oil\ (g)} \times 100 \quad (1)$$

2.5.2. Density Test

The density test was performed using a clean and dry pycnometer and then weighed carefully.

2.5.3. Acid Number Test

The acid number was determined by weighing 1 g of the sample and mixing it with 5 mL of 96% ethanol. The solution was added to five drops of phenolphthalein indicator and titrated with 0.1 N KOH, then stopped when the solution turned pink. This process took 30 seconds [14]. Furthermore, the acid number can be known by entering the data into Equation (2) [15].

$$Acid\ number = \frac{mL\ KOH \times N\ KOH \times Mr\ KOH}{W\ sample} \quad (2)$$

Where mL KOH is the volume of KOH for titration (mL), N KOH is the normality of KOH (0.1 N), Mr KOH is the molecular mass of KOH (56.11 g/mol), and W sample is the weight of the sample weighed (g).

2.5.4. Water Content Test

The water content was measured by heating ± 5 g of the sample in a pre-weighed porcelain cup. Oven heating was carried out at ± 150°C for 15 minutes after weighing the cold cup. After five minutes of reheating, the cup was weighed until the weight remained constant. Suppose the second weighing was 0.003 g less than the first; heated again to constant weight. The amount of water in an oil is the number of components that evaporate (SNI 01-5009.12-2001). Moisture content was calculated using Equation (3).

$$Water\ content\ (\%) = \frac{W_1 - W_2}{W_1 - W} \times 100 \quad (3)$$

Where W is the weight of the empty cup (g), W_1 is the weight of the cup and oil sample (g), and W_2 is the weight of the cup and oil sample after heating (g).

2.5.5. GC-MS

The results of the biodiesel catalyst of chitosan membrane and Cs-PVP K-30-NaOH were analyzed using GC-MS (Shimadzu GCMS-QP2010 SE, Integrated Laboratory, UNDIP) to determine the levels of methyl esters in the biodiesel samples.

3. Results and Discussion

3.1. Membrane Characterization

3.1.1. Functional groups analysis

The success of the modification between chitosan and PVP K-30 can be assessed from the functional groups' suitability, as shown in Figure 2. FTIR analysis of chitosan (Cs) revealed that the absorptions at 3361 cm^{-1} and 2920 cm^{-1} are assigned to -OH and -CH strains, respectively. The -NH twin group was seen at absorptions of 1645 cm^{-1} and 1587 cm^{-1}. The presence of a CO group is shown in the absorption in the area of 1057 cm^{-1}. Compared to the FTIR spectrum of PVP K-30, the absorption at 2949 cm^{-1} indicates -CH stretching vibrations. Meanwhile, the absorptions at 1648 cm^{-1} and 1283 cm^{-1} correspond to the stretching vibrations of C=O and typical absorption of - CN groups. The presence of peaks at 1587 cm^{-1} and 1283 cm^{-1} in Cs-PVP K-30 explains the homogeneous mixing between chitosan and PVP K-30. These results follow the research of Kumar *et al.* [13]. Both -OH and C=O functional groups showed possible hydrogen bond interactions [16]. Figure 1 shows the reaction mechanism in which chitosan, a hydrogen donor, forms hydrogen bonds with the carbonyl group of PVP K-30. Therefore, hydrogen bonding interactions can occur in a mixture of chitosan and PVP K-30 [13].

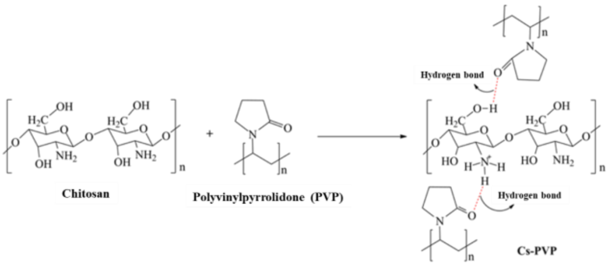

Figure 1. Reaction mechanism between chitosan and PVP K-30

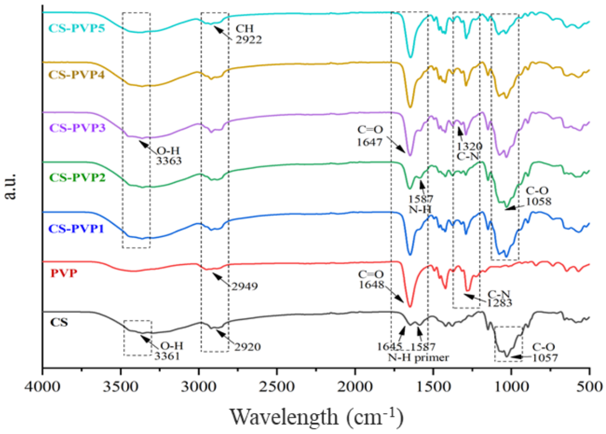

Figure 2. FTIR spectra of Cs, PVP K-30, and Cs-PVP K-30 membranes

3.1.2. Morphology

Figure 3 shows a general view of how the membrane appears in the surface section. Based on the results, chitosan in a membrane has a smooth and porous surface. PVP K-30 cannot form a membrane because PVP K-30 has a lower molecular weight than chitosan and only acts as an additive.

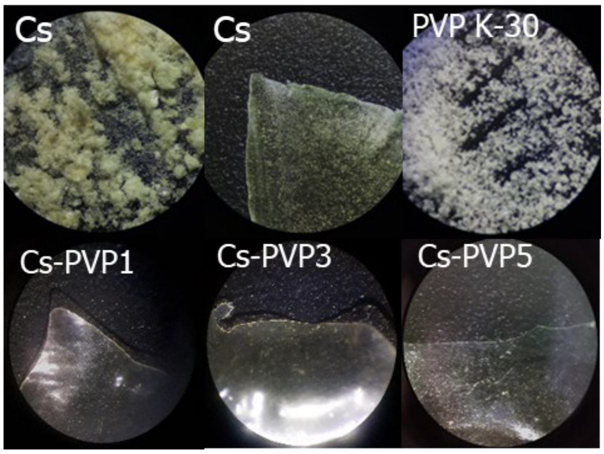

Figure 3. Microscopy images of Cs solid and membrane, PVP K-30, and Cs-PVP

3.1.3. Membrane Thickness and Weight

Membranes have different weights and thicknesses, which indicate the mass content of substances from the membrane. The more mass content will increase the weight and thickness of the membrane [17]. The increase in mass and the number of monomers from PVP K-30 and chitosan makes the membrane bulky. The results of measuring the thickness and weight of the synthesized membrane can be seen in Table 1.

Table 1. Measurement of the weight and thickness of the synthesized membrane

membrane	Before catalysis		After catalysis	
	Weight (mg)	Thickness ($\times 10^{-2}$ mm)	Weight (mg)	Thickness ($\times 10^{-2}$ mm)
Cs	74.98	7.62	74.50	7.58
Cs-PVP. K30.1	70.48	7.50	68.00	7.30
Cs-PVP. K30.2	57.94	7.30	55.20	7.20
Cs-PVP. K30.3	53.66	7.10	51.00	6.90
Cs-PVP. K30.4	48.54	6.70	47.50	6.50
Cs-PVP. K30.5	42.44	5.94	40.50	5.70

Table 1 demonstrates that increasing chitosan concentrations in membranes result in thicker blending membranes. A difference in the mass of compounds in the membrane per unit area of the membrane led to this result. The heavy catalytic process did not significantly affect the results of the membrane before and after the process. This phenomenon reveals how the membrane can be recovered after being utilized.

3.1.4. Swelling Degree of Membrane

The swelling degree test of a membrane is essential to determine the amount of substance or material the membrane can absorb. The membrane can diffuse the permeate phase in the membrane pores as the volume rises. The swelling degree test of the membrane was done by measuring the diameter of the membrane before and after water immersion [18].

Table 2 shows that the percentage degree of the swelling has increased with an increasing volume ratio of PVP K-30. This result showed that the PVP K-30 had hydrophilic properties, which might enhance the inner membrane's ability to absorb water and fill the holes, increasing the membrane's expansion. Water is always produced at the end of the reaction in the biodiesel production process, interfering with the yield. By utilizing membranes that can absorb water, it is envisaged that biodiesel synthesis can function more efficiently.

Table 2. The value of the swelling degree of membrane porosity

Membrane Type	Swelling Degree (%)	Porosity (%)
Cs	131	62.6
Cs-PVP. K30.1	134	73.0
Cs-PVP. K30.2	135	101.4
Cs-PVP. K30.3	138	170.0
Cs-PVP. K30.4	145	173.0
Cs-PVP. K30.5	148	265.0

3.1.5. Porosity

Membrane porosity was tested to determine the amount of empty (porous) space in the membrane. The performance of the membrane might improve with more available space. The data in Table 2 concludes that adding PVP K-30 to chitosan increased the membrane porosity. The presence of hydrophilic PVP K-30 resulted in an interaction between the solvent (water molecule) and the membrane which resulted in the rapid diffusion of the solvent across the membrane and provided a larger pore size. A hydrophilic –OH group causes the membrane to be more hydrophilic, so the phase inversion process in dilute acid solvents facilitates the increase in membrane porosity [19].

3.1.6. Biodegradation

Biodegradation is the ability of matter to decompose into CO_2, H_2O, methane, inorganic compounds (mineralization), and biomass [20]. Biodegradation is subjective because it is a natural process that can occur very slowly, from months to hundreds of years, depending on the individual material and disposal environment [21]. Biodegradation tests on chitosan and Cs-PVP membranes were carried out using the soil burial test method by burying the membranes into the soil for 15 weeks. The result of the reduction in membrane area can be seen in Table 3.

Table 3. Reduction in membrane weight during biodegradation

Membrane Type	Weight loss per week (%)													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
CS	0	13	29	29	32	32	37	41	48	51	67	71	82	88
Cs-PVP1	0	23	38	49	75	88	89	91	93	94	97	98	100	100
Cs-PVP2	0	21	40	43	83	94	97	98	98	99	100	100	100	100
Cs-PVP3	0	21	44	48	99	99	100	100	100	100	100	100	100	100
Cs-PVP4	0	27	41	48	53	100	100	100	100	100	100	100	100	100
Cs-PVP5	0	27	67	68	85	100	100	100	100	100	100	100	100	100

Based on the activity of removing the membrane, it was discovered that the degradation rate increased with increasing PVP K-30 mass. The Cs-PVP membrane is hydrophilic, and it contains elements of carbon (C), oxygen (O), hydrogen (H), and nitrogen (N), which cause the membrane to decompose in the presence of microorganisms. Overall, the chitosan and Cs-PVP membrane samples can be degraded by soil microbes, allowing them to be used as membrane candidates while not contributing to the earth's residual environmental pollution.

3.2. Biodiesel Applications

3.2.1. Biodiesel Synthesis

The biodiesel synthesis was performed to determine the amount of biodiesel conversion results produced in each treatment under the previously determined optimum conditions. In biodiesel production, the Cs-PVP K-30 membrane was immersed in NaOH solution to form a Cs-PVP K-30-NaOH membrane. The membrane acts as a support for the base catalyst, ensuring that the catalytic process runs smoothly. This research studied three critical factors in biodiesel synthesis: time, temperature, and the molar ratio [2].

Table 4. Biodiesel conversion results

Sample	Biodiesel conversion (%)
Without catalyst	41.610%
NaOH catalyst	89.24%
chitosan film	89.17%
Cs-PVP1	92.98%
Cs-PVP2	92.52%
Cs-PVP3	90.86%
Cs-PVP4	93.90%
Cs-PVP5	93.15%

Based on the optimal time data, it was found that the largest conversion occurred at 90 minutes with a value of 89.71%. Hence, 90 minutes was the optimum reaction time. The optimum temperature is obtained at 65°C with a conversion of 93.35%. This result follows the results of [4], so the optimum temperature in biodiesel manufacture is 65°C. The molar ratio at 1:21 only resulted in a conversion of 5.86%. This was because the amount of methanol was too large, resulting in saponification and very little biodiesel. Then there was a significant increase in conversion at a molar ratio of 1:7, which was 94.53%. So the molar ratio used in biodiesel synthesis was 1:7. Furthermore, biodiesel synthesis was carried out in three treatments: 1) without catalyst, 2) chitosan-NaOH film, and 3) Cs-PVP K-30-NaOH catalyst. The results of the biodiesel conversion in the three treatments can be seen in Table 4.

Based on these data, it shows that the best biodiesel conversion was in the Cs-PVP4 composition. Based on porosity data, this membrane type had the highest porosity value among other types of membranes. The membrane's porosity will synergize with the area of the membrane that can contact and support NaOH to become a catalyst in the biodiesel process, increasing biodiesel conversion. The biodiesel synthesis process can occur without a catalyst; however, the reaction will occur very slowly and requires high temperatures (> 250°C), as shown in Table 5. This result is inseparable from the thickness, weight, swelling, and porosity data which show that the Cs-PVP has the best value.

Table 5. Comparison of biodiesel conversion with different catalysts

Catalyst	Reaction Conditions	Conversion	Reference
ACM	70°C; 1:22,53; 120 minutes	99.25%	[2]
$[(CH_2COOH)_2IM]HSO_4$@H-UiO-66	80°C; 1:10,3; 300 minutes	93.82%	[5]
SO_4	65°C; 1:6; 180 minutes	42.21%	AP. Purnamasari, 2013
chitosan	65°C ; 1:7 ; 90 minutes	89.17%	In this study
Cs-PVP4	65°C ; 1:7 ; 90 minutes	93.90%	In this study
HZ/1.0/60	100°C; 1:45 ; 420 minutes	83.00%	Vieira et al., 2015
Cs-CC	70°C; 1:3; 75 minutes	98.40%	[4]
CaO	65°C; 1:15; 150 minutes	86.00%	Hariono, 2016
KOH/Zeolite	28°C; 1:7; 180 minutes	93.00%	Fereidooni et al., 2017

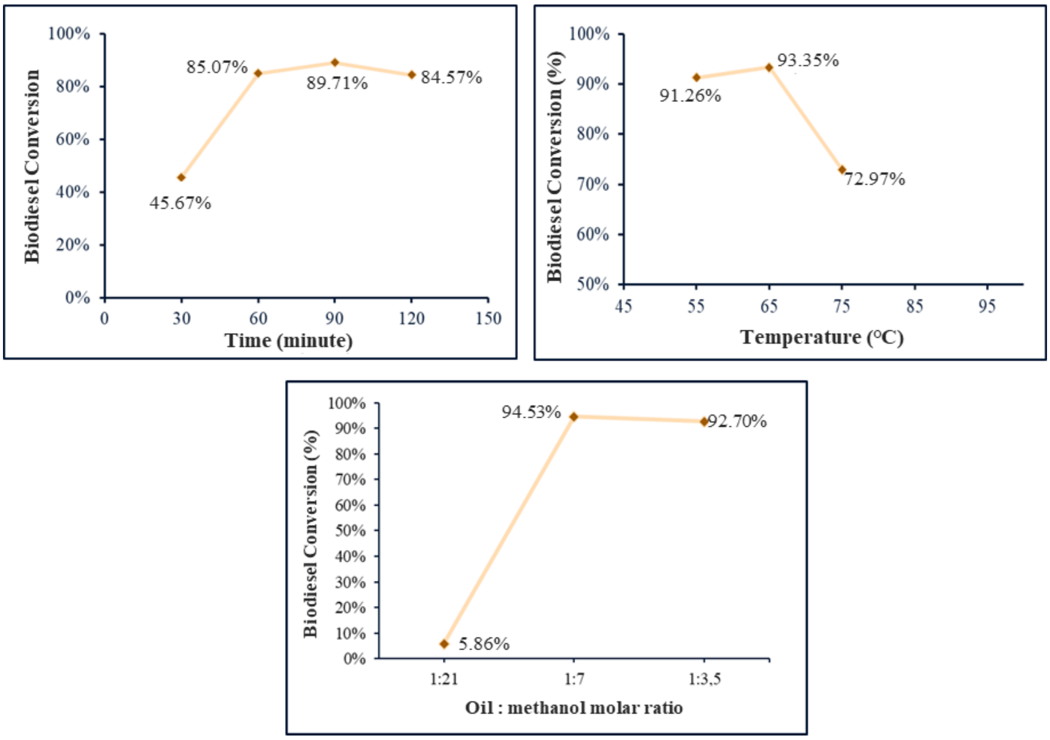

Figure 4. Biodiesel production used three factors: optimal time, temperature, oil: MeOH molar ratio

3.2.2. Density

One of the characteristics of biodiesel based on the Indonesian National Standards (SNI) for biodegradation is density. The density value based on SNI biodiesel is 0.85-0.89 g/mL at 40°C. The density values obtained from the biodiesel samples can be seen in Table 6. The density values are affected by the number of triglycerides contained in the biodiesel. Density is related to the heating value and power a diesel engine produces. Low density will result in a high heating value. The data showed that biodiesel using chitosan and Cs-PVP catalysts meets the 2015 SNI biodiesel quality standard requirements.

Table 6. Physicochemical characterization of biodiesel

Sample	Density (g/mL)	Acid Number (mgKOH/g)	Water content (%)
Oil	0.92	0.59	0.14%
Without Catalyst	0.87	0.78	0.08%
NaOH catalyst	0.86	0.59	0.06%
Chitosan Catalyst	0.88	0.54	0.02%
Cs-PVP1	0.88	0.23	0.04%
Cs-PVP2	0.87	0.20	0.08%
Cs-PVP3	0.87	0.19	0.58%
Cs-PVP4	0.88	0.18	0.69%
Cs-PVP5	0.87	0.17	0.65%

3.2.3. Acid Number

High-quality oils contain only small amounts of free fatty acids, with most of the fatty acids bound as esters or triglycerides [22]. The acid number measures the free fatty acid content in the biodiesel sample. The acid number also indicates the milligrams of 0.1 N KOH required to neutralize the free fatty acids in a 1 g biodiesel sample. According to SNI, the average maximum biodiesel acid number is 0.8 mg KOH/g. In Table 5, the acid number value of the biodiesel sample with or without a catalyst meets SNI standards and does not exceed the maximum value. The amount of acid number influences the quality of biodiesel. The higher the acid number, the lower the quality of biodiesel.

3.2.4. Water content

Moisture content is one of the indicators used to evaluate biodiesel quality. The better the quality, the lower the moisture content of the biodiesel sample. As a result, hydrolysis reactions are less likely to produce more free fatty acids and unpleasant odors [22]. The water content shows the percentage of water contained in the biodiesel sample. According to SNI, the condition for the value of water content for good biodiesel is a maximum of 0.05. The water content values obtained in Table 6 show that the biodiesel samples' average water content is still very high. This result is due to the water content of the biodiesel sample. Because of its high water content, biodiesel is more susceptible to microbial growth, which can contaminate biodiesel, corrode engines, and cause hydrolysis reactions. The higher the value of biodiesel's water content, the more vulnerable it is to damage [22].

3.3. Transesterification Reaction

Transesterification is a reaction between vegetable oil (triglycerides) and alcohol to produce methyl esters and glycerol as a by-product, as shown in Figure 5. The transesterification process also uses a catalyst in the reaction. The process still occurs properly without a catalyst; however, the transesterification procedure would require considerable time [23].

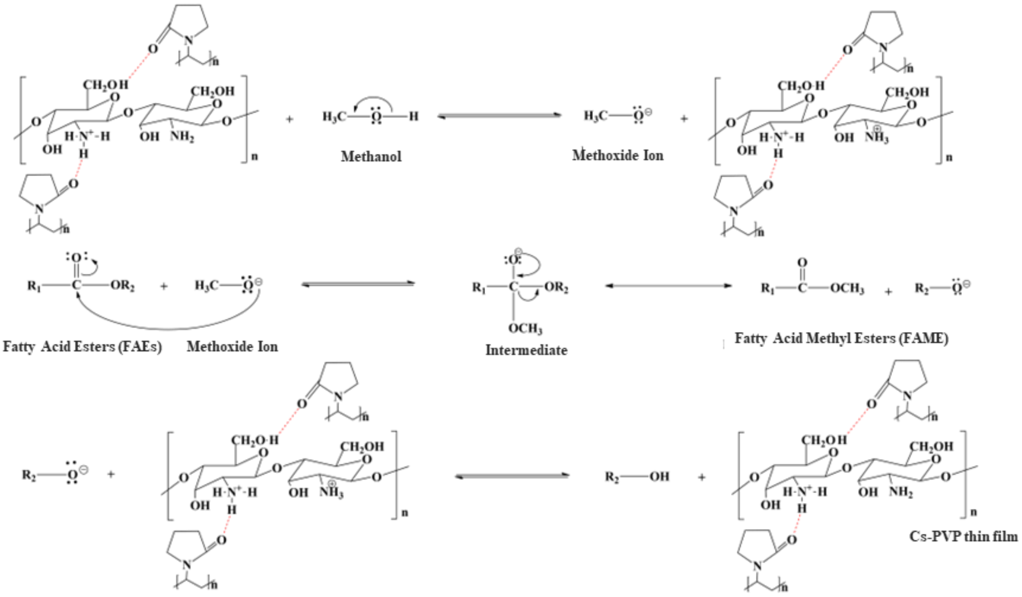

Figure 5. Biodiesel transesterification using Cs.PVP.K30-NaOH

Figure 5 shows the predicted mechanism of the base-catalyzed Cs-PVP K-30-NaOH transesterification reaction starting with a methoxide ion attack. The triglyceride carbonyl carbon atom generates intermediates, which are then eliminated (the acyl group is terminated), followed by the formation of methyl esters and glyceride ions. The base catalyst will first react with methanol to form a methoxide ion, which will then be converted into a nucleophile reagent. A nucleophilic reaction occurs when an ester is formed under alkaline conditions with methoxide ions. A nucleophilic reaction occurs when esters react with methoxide ions under alkaline conditions. Finally, methyl ester and glycerol are obtained.

3.4. GC-MS

Biodiesel is a mixture of long-chain fatty acid esters with some carbon atoms in long chains ranging from 14 to 22 [24]. Analysis was done using GC-MS to identify the materials that made up the methyl ester produced in this study. The analysis results can be shown in Figure 6, with the percentages of several methyl ester components listed in Table 7. The peaks obtained in the GC-MS analysis can be used to explain what methyl esters are formed. Based on the library search, fragmentation of methyl ester compounds in GC-MS showed that peak 1 was methyl hexadecanoate, peak 2 was methyl cis-9 octadecanoate, and peak 3 was octadecanoic acid.

Based on the results of GC-MS analysis, the mass spectra of the methyl ester compound with a retention time of 41.71 minutes with a composition of 32.41% can be seen in Figure 7. The fragmentation of the compound by Mc Lafferty rearrangement is described in Figure 8. The mass spectrum of the fragmentation of methyl hexadecanoic is written as m/z = 270 for the molecular ion $C_{17}H_{34}O_2$ produced from methyl hexadecanoic when irradiated with an energy of 70 eV. The molecular ion $C_{17}H_{34}O_2$ undergoes fragmentation by releasing the C_3H_7 radical and produces fragments of m/z=227 originating from $C_{14}H_{27}O_2$. At the same time, the lowest peak is located at m/z=74, originating from $C_3H_6O_2$ formed because this ion is stabilized by the presence of McLafferty rearrangement. Subsequent cleavage with the release of the $C_{13}H_{27}$ radical produces a peak with m/z=87.

Table 7. Biodiesel methyl ester based on GCMS analysis

Retention Time (minutes)	Compound	Composition (%)
41.71	Methyl hexadecenoate	32.41
45.90	Methyl cis-9 octadecanoate	52.86
46.25	Methyl octadecanoate	3.67

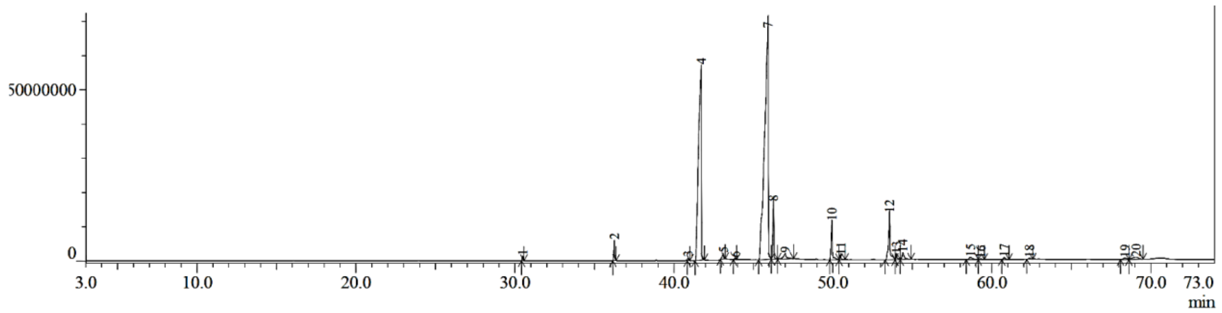

Figure 6. GC-MS of biodiesel samples

The results of the GC-MS analysis indicated that the methyl cis-9-octadecanoic compound had a retention time of 45.90 minutes with a composition of 52.86%, as seen in Figure 9. The fragmentation of the compound by Mc Lafferty rearrangement is described in Figure 10. The mass spectrum of methyl cis-9 octadecanoic is written with m/z=296, which comes from the molecular ion $C_{19}H_{36}O_2^+$ formed when exposed to an energy of 70 eV. The molecular ion $C_{19}H_{36}O_2^+$ releases the $C_3H_6O_2$ radical. It produces a fragment with m/z=222 originating from $C_{16}H_{30}$, which then releases the CH_3 radical, forming a peak m/z=207 originating from $C_{15}H_{27}^+$. The m/z=180 peak originating from $C_{13}H_{24}$, which underwent fragmentation by releasing CH_2 radicals, produced a peak of m/z=166. The molecular ion $C_{19}H_{36}O_2^+$ can also undergo fragmentation by releasing CH_3OH and producing a peak in m/z=264 originating from $C_{18}H_{32}O^+$. The peak with m/z=111 originating from $C_7H_{11}O^+$ releases CH_2 radicals and yields m/z=97 originating from $C_6H_9O^+$, while the lower peak comes from $C_4H_7^+$ with m/z=55.

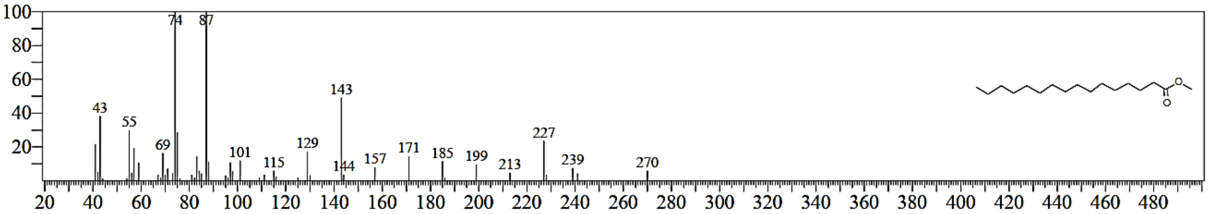

Figure 7. Mass spectrum of methyl hexadecanoate

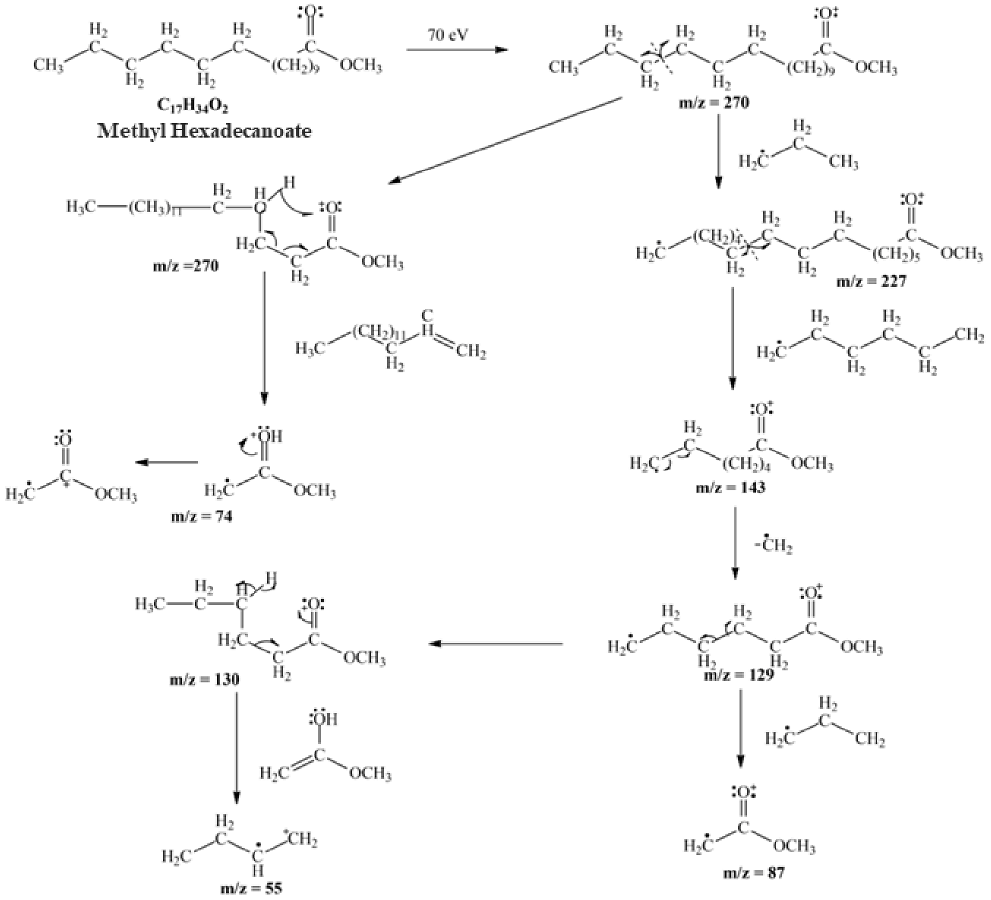

Figure 8. Methyl hexadecanoate fragmentation pattern

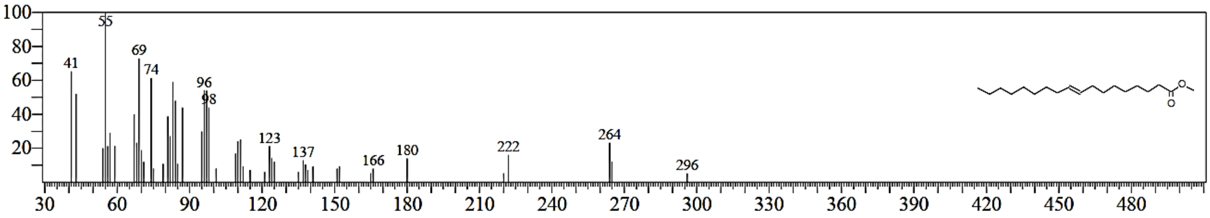

Figure 9. Mass spectrum of methyl cis-9-octadecanoate

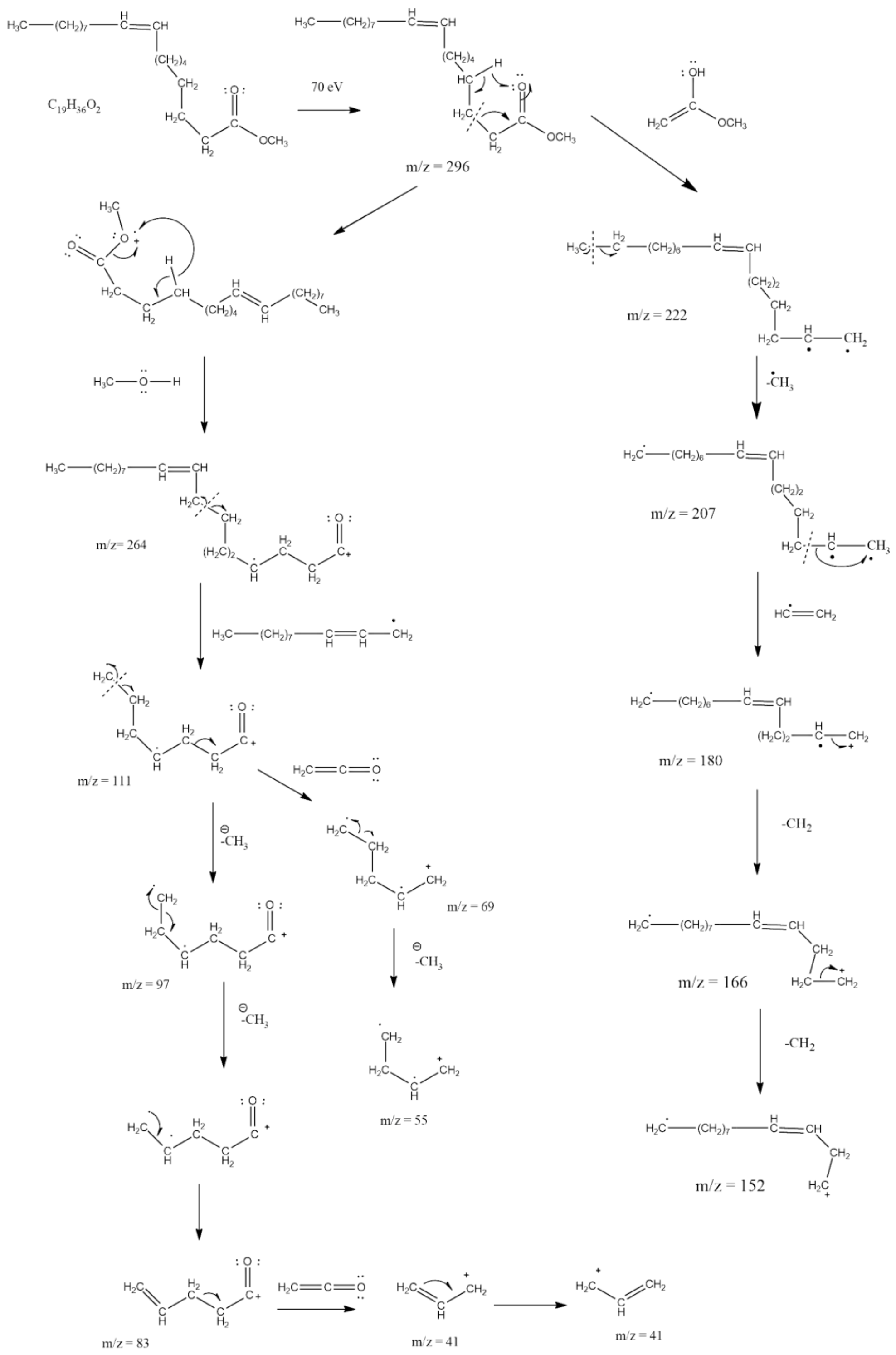

Figure 10. Fragmentation pattern of cis-9-octadecanoate methyl

Based on the results of GC-MS analysis, the mass spectra of the methyl octadecanoic compound with a retention time of 46.25 minutes with a composition of 3.67% can be seen in Figure 11. The fragmentation of the compound by Mc Lafferty rearrangement is described in Figure 12. The mass spectrum of methyl octadecanoate is written with m/z=298, which comes from the molecular ion $C_{19}H_{38}O_2^+$ produced from methyl octadecanoate. The molecular ion $C_{19}H_{38}O_2^+$ undergoes radical fragmentation by releasing the C_3H_7 radical and produces a fragment of m/z=225 originating from $C_{16}H_{31}O_2^+$. The peak m/z=129, which comes from $C_7H_{13}O_2^{+,}$ is generated from $C_{16}H_{31}O_2^+$, which releases C_5H_{10}. The molecular ion $C_7H_{13}O_2^+$ undergoes McLafferty rearrangement by releasing $C_3H_6O_2$, producing a peak in m/z=55 originating from C_4H_7. In contrast, the peak m/z=87 originates from $C_4H_7O_2^+$, which originates from the $C_{19}H_{38}O_2^+$ fragment, which releases the radical $C_{15}H_{31}$. The lower peak is located at m/z=74, originating from $C_3H_6O_2^+$, taking its shape due to a McLafferty rearrangement.

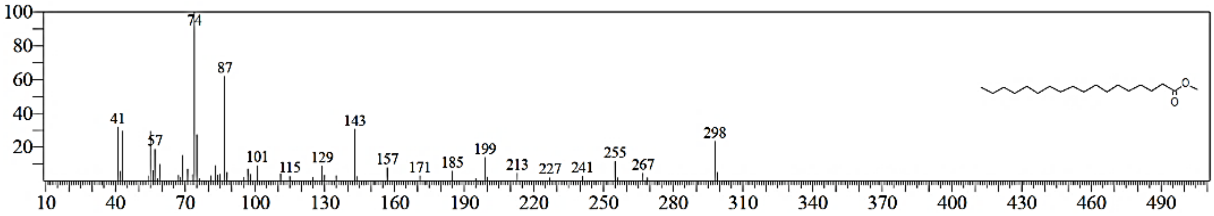

Figure 11. Mass spectrum of methyl octadecanoate

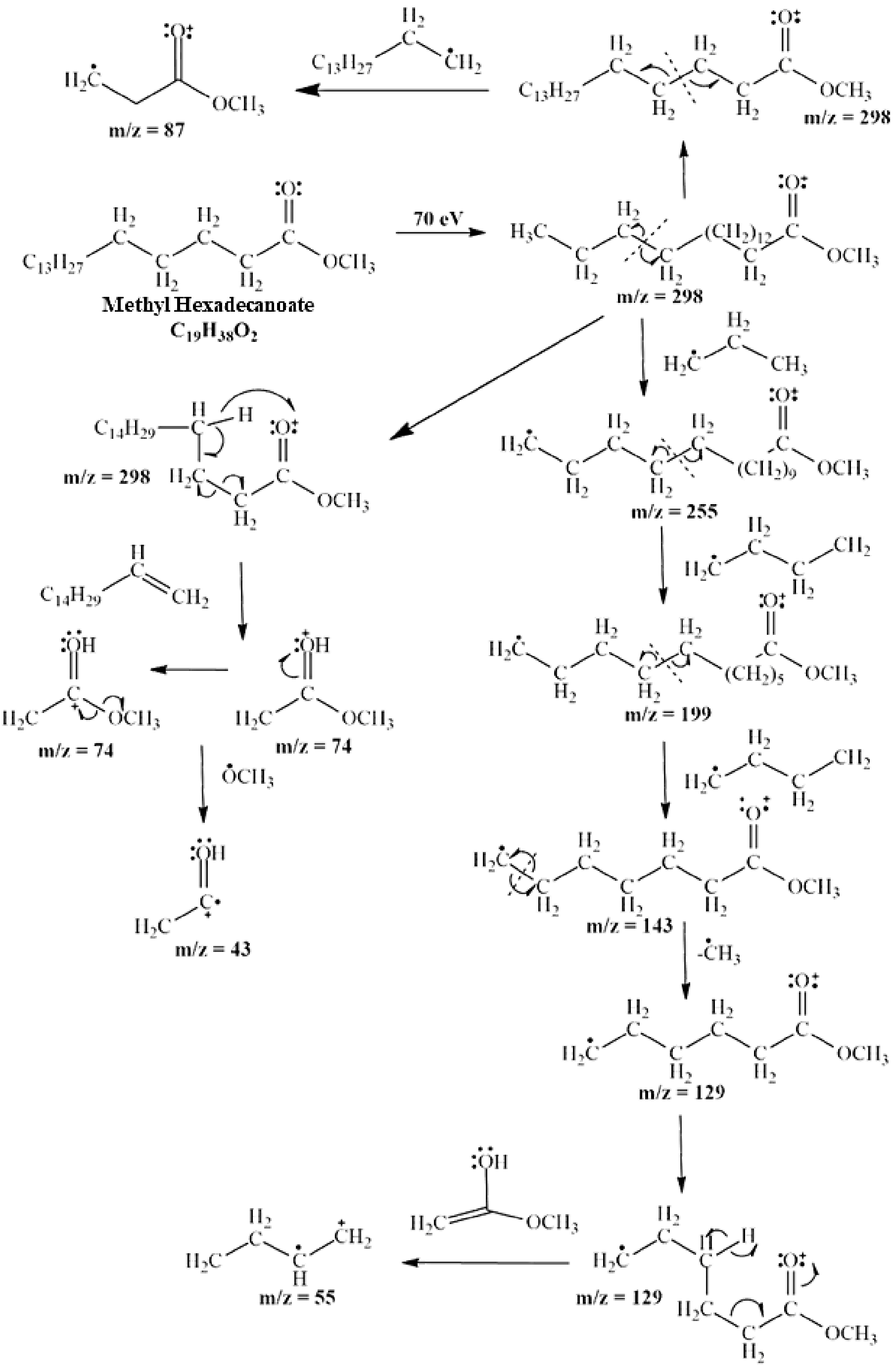

Figure 12. Methyl octadecanoate fragmentation pattern

4. Conclusion

Modification of Cs-PVP.K30 has been successful, and the best characterization of the chitosan-polyvinylpyrrolidone K-30 (Cs-PVP) membrane was obtained on the Cs-PVP5 membrane. This membrane showed a swelling degree of 148.37%, a porosity of 265.04%, and persisted at neutral or alkaline pH conditions. Then, the catalytic process in the optimal transesterification reaction takes place at a maximum time (t_{max}) of 90 minutes, a maximum temperature (T_{max}) of 65°C, and a molar ratio of 1:7 ($oil_{(l)}$: $MeOH_{a(aq)}$). Therefore, the best membrane conversion result obtained was Cs-PVP-NaOH of 93.90%.

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