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Study on Characteristics of Ricinoleic Acid as a Phase Change Material

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Abstract. Today the use of fatty acids as heat storage substance is growing. The use of several types of fatty acids such as oleic acid, palmitic acid, and stearic acid as heat storage materials has been studied. But, ricinoleic acid from castor oil has not been studied yet. This study was conducted to ascertain the characteristics of ricinoleic acid as a heat storage material. Methyl ricinoleic was obtained through transesterification of castor oil by methanol with sodium methoxide catalyst. Methyl ricinoleic was then hydrolyzed using sodium hydroxide in ethanol to produce ricinoleic acid. Ricinoleic acid was identified by FTIR (Fourier Transform Infrared Spectrophotometer) test standard ASTM E 1252-07 and its chemical composition was determined by Gas Chromatography-Mass Spectrometry (GC-MS). The identification of the type, amount, and environment of hydrogen in the compound was determined by Nuclear Magnetic Resonance (NMR). The analysis on characteristics, that is, transition and melting temperatures of material was performed by DSC (Differential Scanning Calorimetry) test standard ASTM D 3419-08. Based on the results of FTIR, GC-MS, ^{1}H-NMR, dan ^{13}C-NMR tests, the spectra that were obtained indicated that the test substances were methyl and ricinoleic acid 70.349%. The results of DSC tests indicate that the characteristics of ricinoleic acid absorbed and released latent heat at the temperature from 8.58^{o}C and absorbed sensible heat at the temperature from -7.17^{o}C to 8.58^{o}C.

Introduction

Currently the energy needs in the industrial and building sectors is getting increased. As a result, the impact on the environment is increasing as well. On the other hand, the world is running out of energy supply which will eventually run out. Therefore, an important step is required to develop more efficient technology that is environmentally friendly.

Some research in the field of energy conservation has been carried out in order to obtain such a technology. Thermal energy storage in the form of sensible heat and latent heat becomes important aspect of energy conservation [1]. One of the rapid technological developments is latent heat utilization applications. Latent heat storage is one of the most efficient ways to store thermal energy [2]. To take advantage of latent heat, heat storage materials are required. The process of heat storage takes place during phase change process. There are four kinds of phase changes; they are solid-gas, liquid-gas, solid-solid, and solid-liquid. The processes of sublimation (solid-gas) and evaporation (liquid-gas) are followed by a large volume change of materials, so that it is impractical for latent heat storage. On the other hand, solid-solid phase transformations are accompanied by small density changes, but the transformation has a low latent heat. Therefore, the heat storage process widely used is the one that takes place at solid-liquid phase change. The material used as a latent heat storage medium is known as phase change material (PCM).

In the last 20 years more than 150 kinds of PCM technologies have been made and about 45 out of them with both organic and inorganic materials have already been available commercially [4]. Latent heat storage using a PCM is an effective way to store thermal energy. The advantage of this method is that it has a high energy storage density and its storage process goes through isothermal method [5,6]. PCM is also suitable for different applications such as heating and cooling rooms [7].

Some inorganic materials used as PCM, among others, are calcium chloride hexhydrate and calcium chloride tetrahydrate, while organic materials, among others, are paraffin, lauric acid, and palmitic acid. Lauric acid is produced from coconut oil fatty acids, whereas palmitic acid is from palm oil fatty acids. The use of fatty acids as PCM allows storing large thermal energy in a small density [8]. PCM and organic materials have advantages, among others, they freeze quickly, or without supercooling; their composition is unchangeable; and they are not hazardous [9]. Meanwhile, research on the characteristics of ricinoleic acid from castor oil as PCM has not been previously conducted.

Fatty acid from castor oil contains ricinoleic acid 89.5%, linoleic acid 4.2%, Oleic acid 3.0%, steareat acid 1.0%, palmitic acid 1.0%, dehydroxystearat acid 0.7%, linoleneat acid 0.3%, and eikosanoat acid 0.3% [10]. The composition implies that ricinoleic acid is much more dominant than other fatty acids of castor oil. In addition, ricinoleic acid is not corrosive to container materials, is eco-friendly, and available in markets. Based on these properties, ricinoleic acid has a potential to be used as a PCM.

One of the types of natural materials in Indonesia used as a PCM, is Micro [11]. In addition to micro, a natural material that meets these criteria is ricinoleic acid produced from castor oil plant (Ricinus communis Linn). Ricinoleic acid has the chemical formula (12 (R)-hydroxy-9z-octadecenoic acid) with the molecular formula C18H34O3 [11]. However, research on its use as a PCM natural material has never been held. Therefore, it is very important to do research related to its use as a PCM. This study was conducted to determine the characteristics of ricinoleic acid as a phase change material.

Material and Method

The substances used in the study were castor oil, sodium metal, anhydrous methanol, potassium hydroxide, diethyl ether, hydrochloric acid, ethanol, sulfuric acid, sodium sulfate anhydrous, and universal indicator produced by PT Kimia Farma.

Methyl ricinoleic was obtained through a transesterification reaction of castor oil by methanol with the catalyst sodium methoxide. Methyl ricinoleic was then hydrolyzed using sodium hydroxide in ethanol to produce ricinoleic acid [13]. Ricinoleic acid was identified by using Fourier Transform Infrared Spectrophotometer (FTIR) Shimandzu IR Prestige-21 with the test standard ASTM E 1252-07. And the chemical composition of the substance was determined by Gas Chromatography-Mass Spectrometry (GC-MS) Agilent Type 7890 A.

Identification of hydrogen type, amount of hydrogen, and hydrogen environment in the compound was determined by Nuclear Magnetic Resonance (NMR) JEOL Type JNM-ECA 500. The analysis on the characteristics of transition and melting temperatures of the materials were performed by Differential Scanning Calorimetry (DSC) with the test standard ASTM D 3419-08. The testing was carried out using 15-20 mg of ricinoleic acid with heating and cooling treatment at the temperatures of -30°C - 80°C with a heating and cooling rate 5°C/min.

Results and Discussion

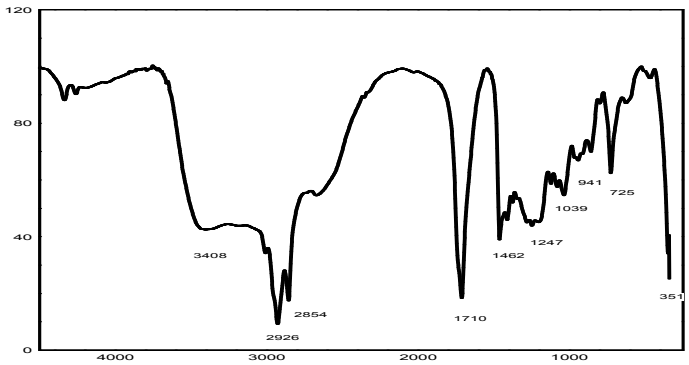
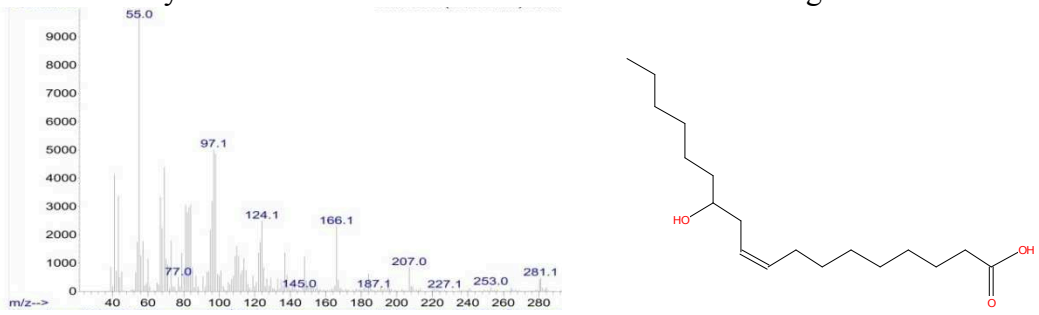


Figure 1 Spectra of results of FTIR test on ricinoleic acid

The FTIR test on ricinoleic acid that resulted in spectra 3408 cm^{-1} indicated a functional group O-H stretch. This functional group indicates the acidic nature of substance and existed in the first carbon chain. Spectra 2926 cm^{-1} and 2854 cm^{-1} were aliphatic C-H functional groups. The C-H functional groups were located at C9 and C10 of carbon double bonds (unsaturated). The functional groups also indicated a double bond of cis like the nature of fatty acids in general [14]. Spectra 1710 cm^{-1} was the functional group C = O stretch. As the functional groups O-H, the functional groups C=O were also attached to first chain and indicated an acid nature. Spectra 1462 $^{cm-1}$ was functional group CH2 and CH3. The functional group CH2 was attached to each saturated carbon chain while CH3 was to carbon chain C18. Spectra 1247 cm^{-1} to 1039 cm^{-1} were C-O functional groups. The first C-O functional group was strongly alleged the hydroxyl group at C12 chain. The hydroxyl group is the hallmark of ricinoleic acid [12]. The second CO functional group was alleged to derive from solvent. Spectra 941 cm^{-1} was the functional group of aliphatic NO; spectra 725 cm^{-1} was the functional group CH; and spectra 351 cm^{-1} was suspected of impurities. The last three functional groups were suspected of components of solvents and impurities. Ricinoleic acid samples were then tested by GC-MS and the results obtained are shown in Figure 2.



(a) (b)

Figure 2 Spectra of results of GC-MS test (a) Structural formula of Ricinoleic acid (b)

GC-MS tests brought about methyl composition and ricinoleic acid 70.349% and the remaining was of other fatty acid and impurities. Next, ^{1}H-NMR dan ^{13}C-NMR tests were conducted to identify the kinds, amount, and environment of hydrogen in ricinoleic acid compound. The results are shown in the following Figure 3.

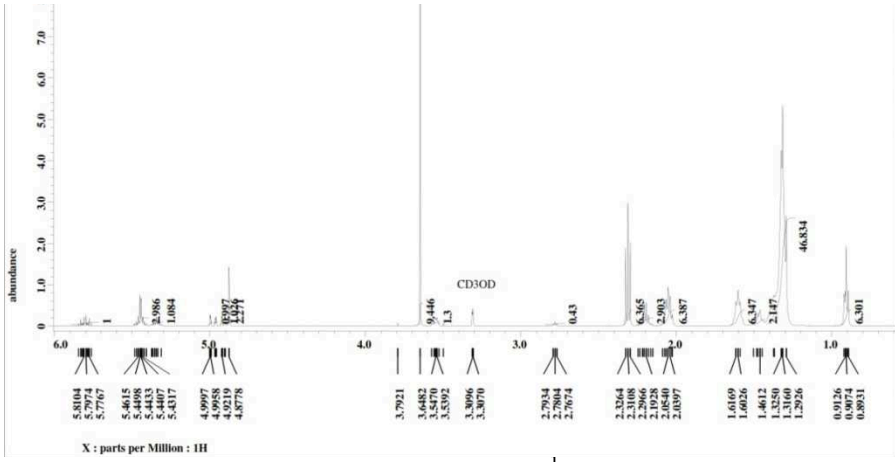


Figure 3 Spectra of results of ^{1}H- NMR test

Data ^{1}H-NMR: ($CDCl_3$, 125 MHz), δ (ppm); 0,893191 (18-H, 3H, t); 1,2926 (CH2, 16H, m); 1,4612 (13-H, 2H, m); 1,6026 (3-H, 2H, m); 2,0397 (8-H, 2H, m); 2,1928 (-OH, 1H, s); 2,2966 (11-OH, 2H, t); 2,7674 (2-H, 2H, t); 3,5392(12-H, 1H, m); 4,8778 (-OCH3, 3H, s); 5,4317 (9-H, 1H, m); 5,7767 (10-H, 1H, m).

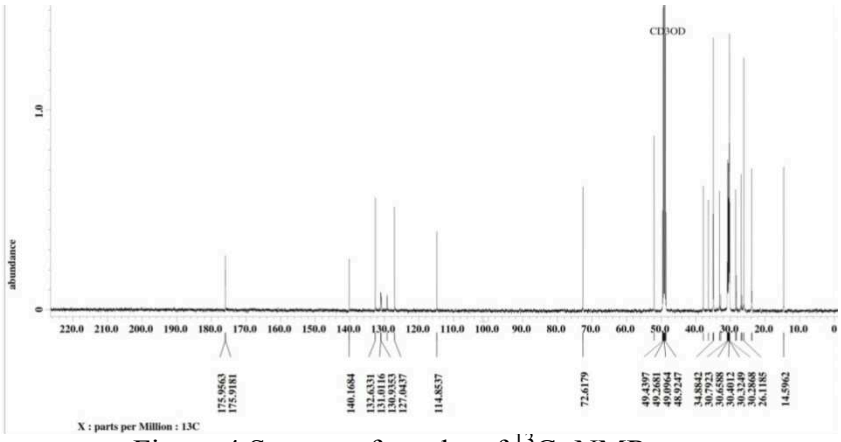


Figure 4 Spectra of results of ^{13}C- NMR test

Data ^{13}C-NMR ($CDCl_3$, 125 MHz), δ (ppm); 175,9563 (C=O); 140,1684 (C-10); 132,6331 (C-9); 127,0437 (C-1); 72,6179 (C-12); 30,7923 (O-CH3); 30,6588 (C-13); 30,3249 (C-2); 26,1185 (C-17); 14,5962 (C-18). The results of 1H-NMR and 13C-NMR tests indicated that the number of hydrogen and carbon atoms and their positions strongly justified the results of FTRIR and GC-MS tests.

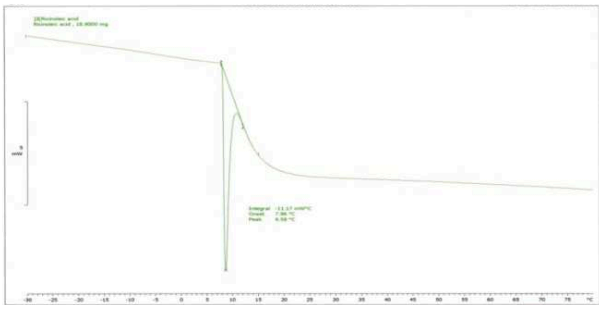


Figure 5 Temperature characteristics of ricinoleic acid

The DSC tests on ricinoleic acid resulted in heat absorbance characteristics with a melting temperature 8.58^{o}C, onset temperature -6.01^{o}C, crystallization temperature -7.17^{o}C, and heat fusion 3.35^{o}C. A crystallization taking place below a melting temperature implied that in the process of ricinoleic acid crystallization a supercooling happened despite its small size. This was in line with what Mehling [9] stated, that is, the crystallization of ricinoleic acid generally do not occur, or the supercooling is too small.

Conclusion

On the basis of the results of FTIR, GC-MS, ^{1}H-NMR, and ^{13}C-NMR tests, a spectra w was obtained, which indicated that the tested substances were methyl and ricinoleic acid 70.349%. The DSC test results indicated a characteristic that ricinoleic acid absorbed and released latent heat at the temperature 8.58^{o}C and absorbed sensible heat at the temperature from -7.17^{o}C to 8.58^{o}C

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