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UNSATURATION DEGREE OF DATED PALM KERNEL OIL AND ITS POTENTIAL AS PRECURSOR FOR EPOXIDATION

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Abstract:

Vegetable oils are triglycerides derived from plants and made up of chains of fatty acids that it can be saturated or unsaturated depending on the number of carbon-carbon double bonds. This research work was aimed to characterized the palm-based oil (fresh palm kernel oil (PKO), dated PKO, oleic acid, fresh palm olein and dated palm olein) on characterizations and to investigate feasibility of dated PKO as precursor for epoxidation and compare its performance with fresh PKO. The epoxidation reaction was completed with formic acid (HCOOH) as oxygen carrier and hydrogen peroxide (H2O2) as oxygen donor with 90 minutes of reaction time by using a mol ratio of PKO:HCOOH:H2O2 at 1:1:1. The optimum percentage of relative conversion oxirane (%RCO) for fresh PKO and dated PKO was 3.4% and 3.0% respectively was recorded at 50 minutes of reaction time. The ageing of the PKO does not effects the the time of PKO to epoxidized. The iodine value (IV) for fresh and dated PKO was 13.642 g I2/100g and 12.373 g I2/100g was recorded the lowest compared to other oils. Thus, the result of these studies indicate that the dated PKO may be a precursor for epoxidation process due to its performance. In order to further expand this study, it is suggested to investigate additional value-added capabilities after ring opening, as epoxides were very active compounds.

***Keywords*:**

Epoxidation, Unsaturation Degree, Palm Kernel Oil, Iodine Value

Introduction:

The oil palm tree has flourished and has steadily grown into a profitable agricultural crop for the production of palm oil in these countries [1]. In the modern era, oil palm plantations will occupy an area of roughly 3.37 million hectares of Malaysian land. In 2015, oil palm plantations in Malaysia were estimated to have occupied a land area of unprecedented 5.64 million hectares [1]. Fresh fruit bundles (FFBs) of the oil palm tree contain two types of oil which is palm oil (PO) extracted from the fruit pulp (mesocarp) and palm kernel oil (PKO) extracted from the seed or kernel. PKO is removed from the kernel or palm fruit seed by mechanical screw pressing or by means of solvent extraction [1].

The kernel oil contains a wide variety of fatty acids that are found as acyl groups in the triacylglycerols of the oil. This palm kernel oil is an impressive source of saturated fatty acids but also includes monounsaturated and polyunsaturated fatty acids [2]. PKO is known to be lauric oil because lauric acid is the main fatty acid in its composition at around 50 per cent. **Error! Reference source not found.** shows the fatty acid composition of palm oil and palm kernel oil [3].

Table 0.1 Fatty acid composition of palm oil and palm kernel oil [3]

Fatty Acid	Palm Oil (PO)	Palm Kernel Oil (PKO)
Caproic acid	-	0.2
Caprylic acid	-	3.3
Capric acid	-	3.5
Lauric acid	0.2	47.8
Myristic acid	1.1	16.3
Palmitic acid	44.0	8.5
Stearic acid	4.5	2.4
Oleic acid	39.2	15.4
Linoleic acid	10.1	2.4
Linolenic acid	0.4	-
Arachidic acid	0.1	0.1

The carbon-carbon double bond of unsaturated fatty acids in palm kernel oil (namely oleic acid and linoleic acid) can be epoxidized in order to produce epoxy functional group or better known as epoxide or oxirane [4]. Epoxidized vegetable oils have been used in a variety of uses such as plasticizers, polyols, lubricants, resins, composites and coatings [5]. Epoxide is a cyclic ether of three ring atoms. It is also known as epoxy ring or oxirane ring. This ring is roughly characterized by a symmetrical triangle, which makes it highly strained and more reactive than other ethers [4].

Fats and oils are inexhaustible assets that can chemically or enzymatically be treated to create materials that can regularly become a replacement for materials derived from petroleum [4]. One of the major reactions that can be used to boost the efficiency of these fats and oils is epoxidation [4]. Epoxidation increases the polarity and consistency of vegetable oils and enhances their compatibility with polymers [6].

Epoxidation of fatty acids is a carbon-carbon double bond reaction with activated oxygen, which results in the incorporation of an oxygen atom, turning the initial double bond into a three-part epoxy ring [6]. Epoxidized vegetable oils can also be used as plasticizers/stabilizers in the polymer industry [6]. Epoxidation of long chain olefins, and unsaturated fatty acid, for example, soybean oil and other plant oils was doned on an industrial scale [7].

Various methods have been developed for the epoxidation of vegetable oils such as homogenous catalytic system by percarbocylic acid, Heterogeneous catalytic system by acidic ion exchange resins (AIERs), Chemoenzymatic epoxidation, and other metal-catalyzed heterogeneous systems as the oxidant and bio-based catalyst [8]. The epoxidation with percarboxylic acids will be the method used for *in-situ*

epoxidation in this research. Epoxidation is a chemical reaction that converts carbon–carbon double bonds into oxirans (epoxides) using a number of oxidizing agents [8].

Due to the high strain of epoxy ring from epoxidation, it is susceptible to various parameter changes. Therefore using the suitable reaction conditions is paramount in the epoxidation in order to achieve high conversion to epoxide and good stability of epoxy ring. The conditions usually used to maximize the epoxidation of vegetable oil are the temperature of the reaction, the mole ratio of the oxygen donor, the mole ratio of the oxygen carrier, and also the type of catalyst used [4].

The research aims to determine the degree of unsaturation of dated palm kernel oil. Iodine value (IV) is the method to determine the degree of unsaturation of the palm kernel oil. Degree of unsaturation is important to identify the different between edible oil such as fresh palm kernel oil and dated palm kernel oil. Previous research said that the unsaturation increase and saturation decrease as dated palm kernel oil become discoloured and fungal-damaged [9]. Microorganisms are known to cause chemical characteristics that lead to deterioration in quality of oils [10]. Once in a while the fungus increases the amount of unsaturated fatty acids in the mouldy seeds which also cause iodine number to increase [11]. Thus, increase the iodine number will increase the unsaturation degree of palm kernel oil.

Research Methodology:

Figure 1 Illustrates the process flow for Iodine Value (IV) determination. IV was determine through titration methods known as wijs methode. 0.2 g of sample was dissolved with 15 ml of cyclohexane-glacial acetic acid mixture and 25 ml of the Wijs solution. The conical flask was then stored in a dark storage for 60 minutes. After 60 minutes, the conical flask was quickly removed from the dark storage and the reaction was quenched by adding 20 ml of KI solution with 100 ml of water. The sample was titrated with 0.1 N sodium thiosulfate under agitation until yellow colour almost disappeared. Then, add 2 ml of starch indicator and continued titration until blue colour disappeared.

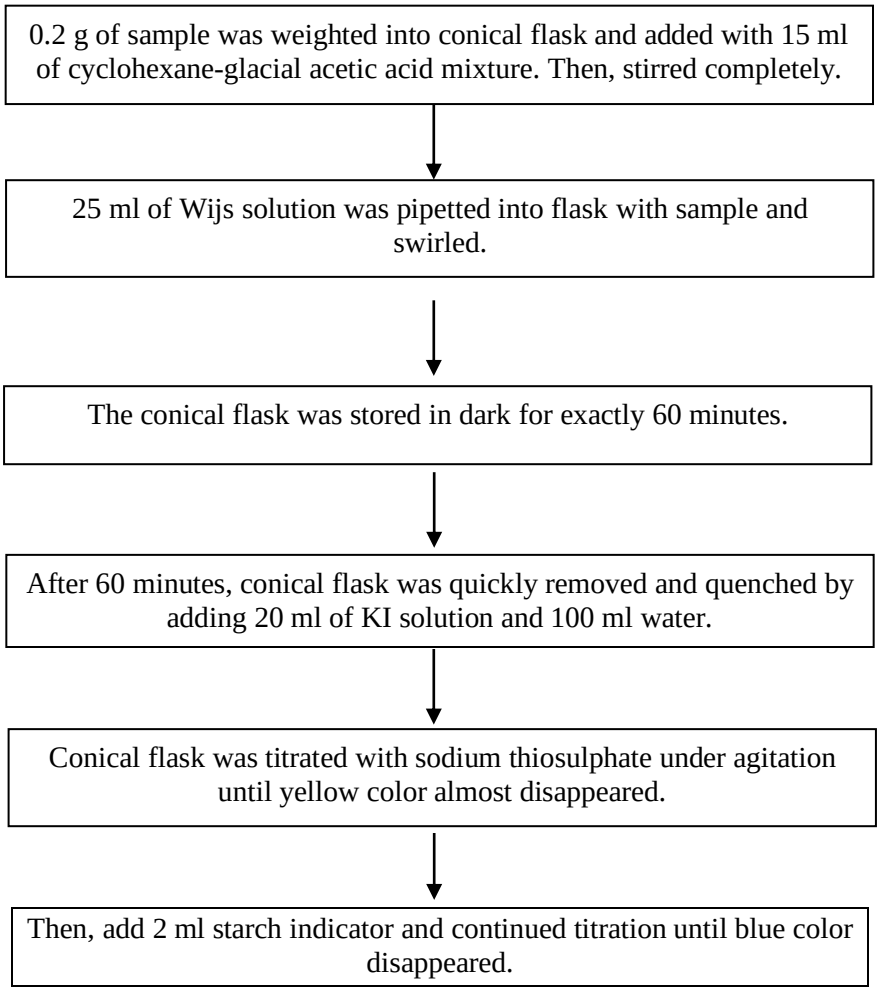

Figure 1 Process Flow of Iodine Value Determination.

Figure 2 Illustrates the process flow for epoxidation. The epoxidation was carried out in 400 ml of beaker with overhead stirrer. 250 g of sample, 33.4 g of formic acid and 0.5 g of sulpjuric acid was added simultaneously into the beaker. The mixture of reactants was stirred by overhead stirrer with agitation speed at 500 rpm. Hydrogen peroxide was added at constant flow rate of 4 ml/min using dropper by maintaining the temperature of sample around 40 to 50 °C. 5 ml of sample was taken every 10 minutes using syringe into the sampling bottle. A small amount of sodium sulphate was added immediately into the sample bottle to quench the reaction. Sample taken in sampling bottle was allowed to cool down for 20 minutes.

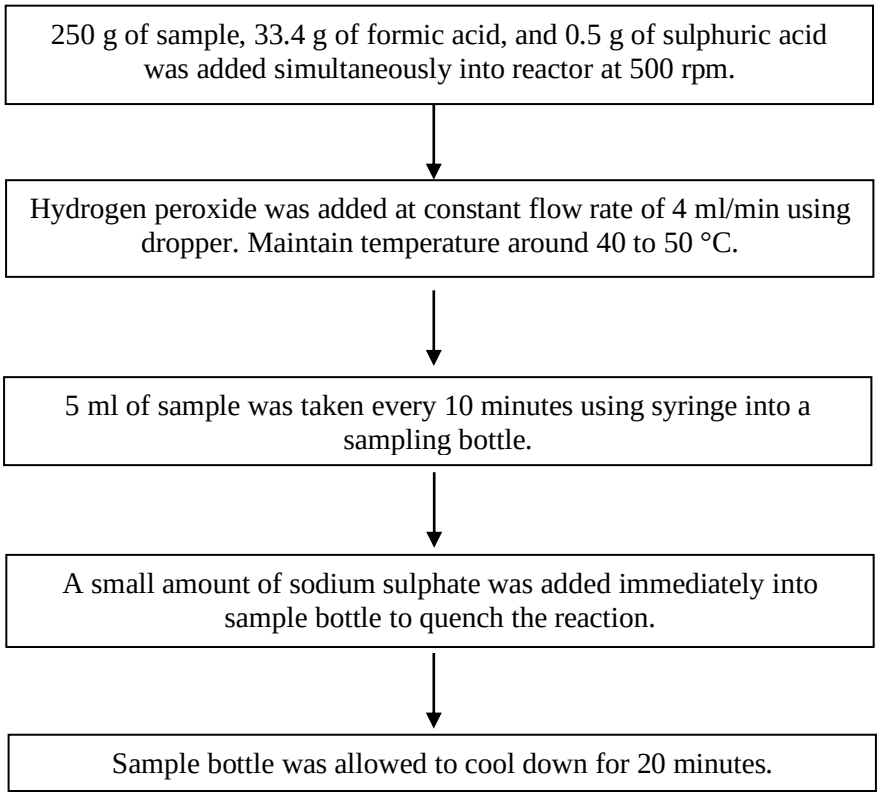

Figure 2 Process Flow of Epoxidation.

Figure 3 Illustrate the process flow for Oxirane Oxygen Content (OOC) Analysis. 0.4 g of sample was weighted into conical flask. Sample was dissolved in 10 ml of acetic acid followed by 5 drops of crystal violet solution. The solution was titrated under agitation with standardized hydrogen bromide solution until bluish green

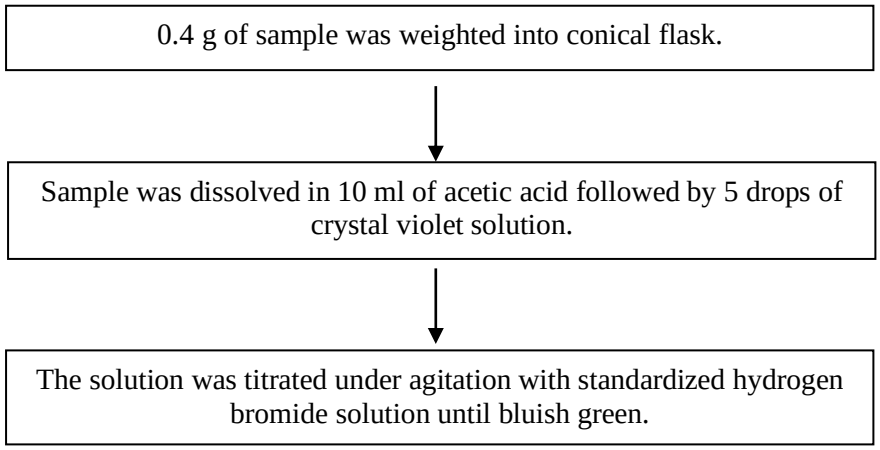

Figure 3 Process Flow of OOC Analysis.

Results:

Table 1 Physicochemical properties of raw materials

Property	**Fresh PKO**	**Date PKO**	**Oleic Acid (analytical grade)**	**Fresh palm olein**	**Date palm olein**
Physical appearance (at room T)	White semi-solid	White semi-solid	Clear liquid	Clear liquid	Clear liquid
Iodine value, g I_2/100 g (AOCS Official Method Cd Id-92)	13.642	12.373	16.180	17.633	15.863
Density (g/cm^3)	0.851	0.877	0.890	0.881	0.883

Fresh PKO and Dated PKO in form of white semi-solid because there is a precipitation occur. While the other oil have clear liquid appearance because they are purified oil. Iodine value offered insight into the reactivity and degree of unsaturation of fatty acids. The iodine value was a calculation of the number of double carbon bonds. A higher iodine value has resulted in a more reactive and less stable fatty acid content. From

, oleic acid, fresh palm olein and dated palm olein have record a high iodine value which is 16.180 g I_2/100 g, 17.633 g I_2/100 g and 15.863 g I_2/100 g because they are pure unsaturated. From a theoretical point of view, the higher iodine value means a higher chance of iodine ions being bound to the unsaturated carbon chain.

The iodine value of fresh PKO is 13.642 g I_2/100 g and dated PKO is 12.373 g I_2/100 g which is mean the lowest compare to the others sample because they are made of the mixture of saturated and unsaturated fatty acid composition. Dated PKO shows the lower iodine value than fresh PKO due to the consumption of double bonds during the reaction take place [12]. The difference between palm kernel oil and olein oil are due to the fatty acid content [1].

Next, density for all of the material were quite the same because there is no reaction occur on raw materials. However, this is also a significant indicator of the substance. The density of a substance plays a vital role not only in consumer protection, commerce, safety and health, taxes, but also in research and development. It should be remembered that the density increases the molecular weight of the material, which influences its viscosity and the capacity of the substance to flow.

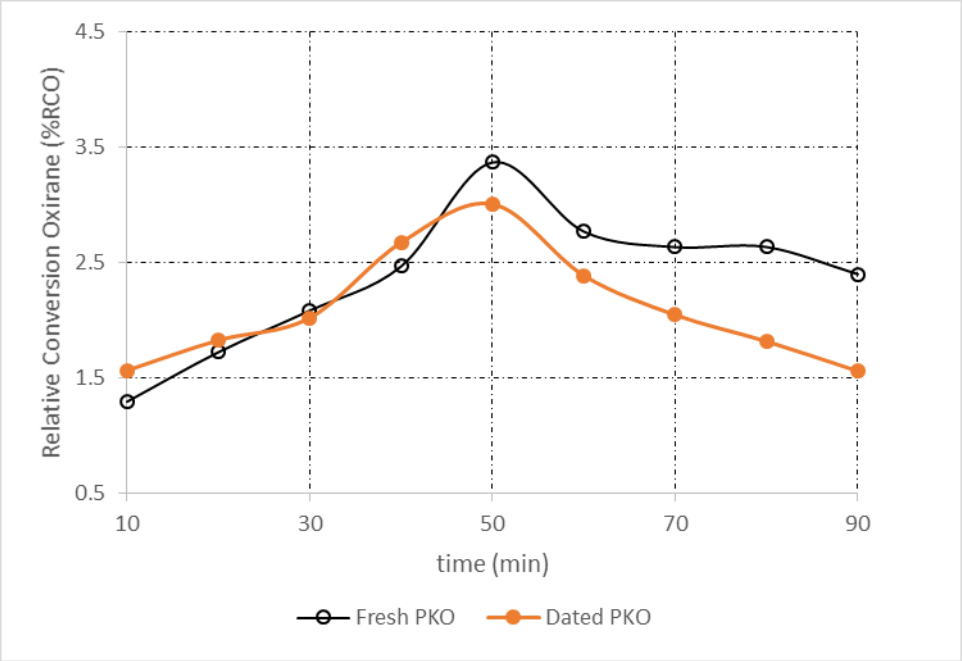

Figure 4 Epoxidation of palm kernel oil

In this experiment, the reaction was carried out at 40° C with agitaion speed 500 rpm. Mol ratio of PKO:HCOOH:H_2O_2 (1:1:1) was used for both fresh and dated PKO which prolonged for 90 minutes. Formic acid functions as an autocatalyst in the forming of an oxiran ring. **Error! Reference source not found.** show the epoxidation of fresh and dated palm kernel oil. For the first 20 minutes of the experiment, it has been seen that the oxirane content of dated PKO is higher than that of fresh PKO. After 50 minutes, the graph of oxirane for both PKO starts to decrease due to the degradation or opening of the ring.

The maximum of oxirane value for fresh PKO is 3.4 %RCO while dated PKO is 3.0 %RCO. The more the oxirane value the more of yield of epoxide because oxirane oxygen content indicates the percentage content of epoxide group. Both palm kernel oils had reached the optimal or optimum oxirane content at the same time taken which is at 50 minutes of the experiment. Thus, the ageing of the palm kernel oil does not influence the time for the percentage content of epoxide.

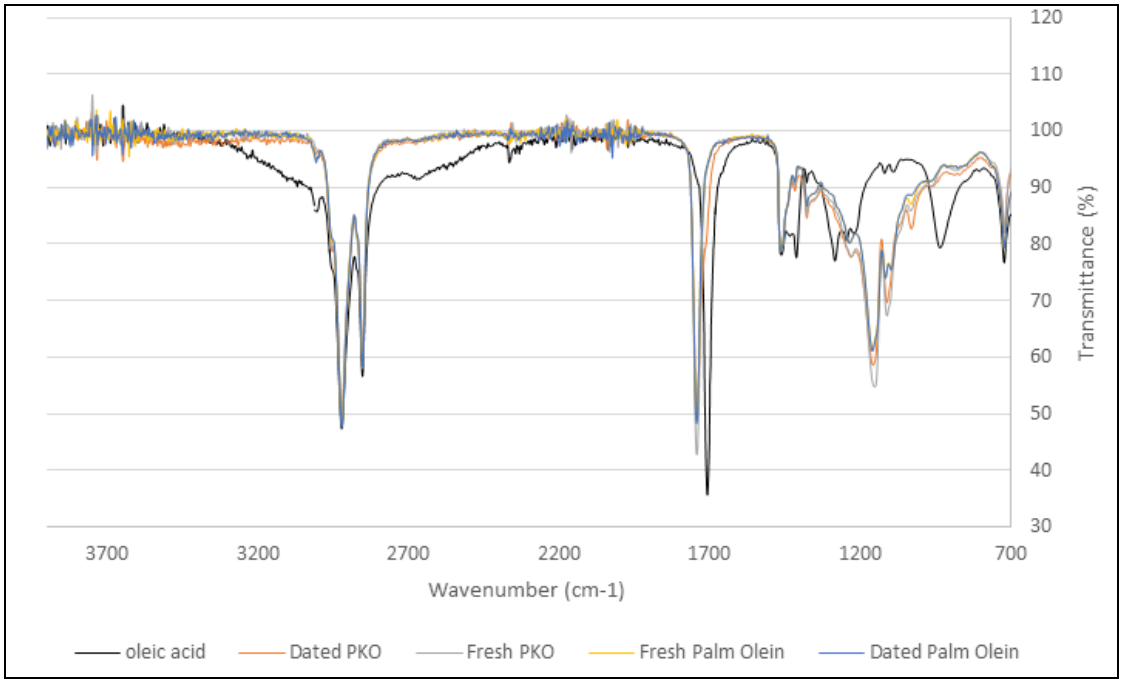

Figure 5 Comparison FTIR Spectra between all types of oil

Table 2 Functional group detected in FTIR Spectra

Functional group	FTIR
C=0 stretching	1700
C=H stretching (CH_2)	2800
C=H stretching (CH_3)	2950
C=C stretching	3000

FTIR test was applied to the fresh and dated PKO, oleic acid, fresh and dated palm olein in order to identify the present of functional group in the substance. FTIR spectroscopy can be used to determine the molecular composition of the compounds from the absorption bands typical of particular functional groups which are presented as peak spectra [1]. **Error! Reference source not found.** lists the major functional groups foundt in the oil sample used. **Error! Reference source not found.** shown a representive set of infrared spectrum between the raw material in the range of 700 to 3700 cm^{-1}. Based on **Error! Reference source not found.**, overtone streaching vibration peak of C=O for ester was detected at wavenumber 1700 cm^{-1}. At wavenumber 2800 cm^{-1}, C=H streching (CH_2) was appearred while streching vibration peak of C=H (CH_3) aslo being detected at wavenumber 2950 cm^{-1}. Besides, all the substances also had carbon carbon double bond (C=C) streching as recorded in FTIR spectra. This is due to the esterified carbonyl function [1]. It thus demonstrates that all form of oil was appropriate for the epoxidation process.

Conclusion:

In this study, Fresh and dated palm kernel oils was used as raw material for epoxidation with a presence of formic acid as catalyst by using overhead stirrer with 500 rpm about 90 min. Iodine value, density and FTIR were the method used for the oil characterization including on the other oils such as fresh palm olein, dated palm olein and Oleic acid. Experiment for epoxidation has recorded the highest percentage of RCO which is 3.4 % for fresh PKO while dated PKO is at 3.0 %. Both fresh PKO and dated PKO had achieved optimum oxirane value at 50 minutes of the process experiment.

Oleic acid, fresh palm olein and dated palm olein with 16.180 g I_2/100 g, 17.633 g I_2/100 g and 15.863 g I_2/100 g were the highest iodine value compared to the fresh and dated palm kernel oils with 13.642 g I_2/100 g and 12.373 g I_2/100 g respectively. Different edible oils such as dated and fresh PKO, oleic acid, dated and fresh palm olein have various iodine levels according to differing degrees of unsaturation due to the existence of different numbers of double bonds in the carbon atom series [13].

The density of the oil sample does not indicate any difference such as fresh PKO with 0.851 g/cm^3, dated PKO with 0.877 g/cm^3, oleic acid with 0.890 g/cm^3, fresh palm olein with 0.881 g/cm^3 and dated palm olein with 0.883 g/cm^3. FTIR spectra have shown the major functional group presence in the palm-based oil and the important one is carbon carbon double bonds at wavenumber 3000 cm^{-1}. This oil samples are preferred for epoxidation reactions.