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Synthesis Of Epoxidized Oleic Acid- Based Palm Oil by Peracid Mechanism

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Abstract. Commercial epoxides available in the market are mainly petroleum and animal based which are non-environmental friendly and often non-halal. Oleic acid (C18:1) derived from palm kernel oil contains the unsaturation double bond (C=C) in its long alkyl chain makes it an attractive fatty acid for the production of eco-friendly epoxide. The epoxidation of oleic acid was carried out by using in situ generated performic acid (HCOOOH) to produce epoxidized oleic acid. Performic acid was formed by mixing formic acid (as oxygen carrier) and hydrogen peroxide (as oxygen donor). The results indicated that optimum conditions occurred at moderate agitation speed 300 rpm and by using 30% hydrogren peroxide. Sulfuric acid was found to be the most efficient catalyst. It was found that a maximum relative conversion to oxirane (RCO) achieved was 87.61 % at optimal condition.

1. Introduction

Palm oil is one of the vegetable oil that exist in the industry and it is widely used in the development of polymeric materials [1]. The growth of vegetable oil in the demand has increased compared to petroleum-based polymer. This is because vegetable oil is eco-friendly and low cost as well as the petroleum has given an environmental pollution concern and increasing in cost [2]. So, the vegetable oil becomes an alternative in the production of epoxide. In the epoxidation of vegetable oil reaction, oxirane ring-opening or known as epoxide ring degradation will occurs [3]. The oxirane ring-opening will reduce the yield and in order to gain high yield and high peroxide values of epoxidized vegetable, the opening need to be minimized [4]. Moreover, palm oil containing low in unsaturated double bond contents and this will limit synthesis and oxirane cleavage reaction of EPO[2]. The commercial production of palm oil is quite high compared to other vegetable oil and thus make the study of synthesis and oxirane cleavage of palm oil more practical and economical [5].

Oleic acid or also known as cis-9-octadecenoic acid has good characteristics such as have low melting point which is 13.4 ℃, boiling point is 360 ℃, colourless to pale yellow, crystalline form and long chain of carboxylic acid [6]. While, in term of composition, oleic acid from palm oil and palm kernel oil is 39.2% and 15.4% respectively. This value shows that oleic acid contained in palm oil is higher than palm kernel oil which is the ratios between these two is about 18:1. So, the potential to obtain oleic acid as a material that will be used in epoxidation is not complicated [7]. Normally the usage of palm oil is often for edible purposes while palm kernel oil is used for non-edible purposes such as making soaps and detergents [8].

Oleic acid was chosen in this study because it is one of the organic chemical raw material and can produce epoxidized of oleic acid after epoxidation. There are many applications of oleic acid such as plastic plasticizer, as production of azelaic acid by oxidation, raw material for manufacture carbon paper, manufacture of soap and as an analysis reagents and solvents [9] [10]. The epoxidized of rapeseed oil is highly commercial importance as a plasticizer and stabilizer for plastics, lubricants, and an intermediate for the synthesis of surfactants. Previous studies were focused on epoxidation of vegetable oils (complete triglyceride) [11],[12],[13]. The present study however focuses on the epoxidation of fatty acid, a smaller molecule as compared to a triglyceride molecule. The objective of the present study is to investigate the optimum reaction conditions with respect to the yield of epoxidized oleic acid.

2. Methodology

Crude oleic acid, formic acid and sulfuric acid catalyst were added simultaneously into the reactor. The mixture was stirred continuously at fixed speed and the mixture was gradually heated to the desired temperature. The reaction time for each experiment was 50 minutes and it was recorded at the beginning of the introduction of hydrogen peroxide. Hydrogen peroxide was added drop by drop. Sampling for analysis was done by withdrawing approximately 5ml of reaction mixture for every 5 minutes. The samples were quenched and cooled for 2 minutes before being analyzed using oxirane oxygen content (OOC) analytical method. The OOCexp value was determined by direct method using hydrobromic acid (HBr) solution in glacial acetic acid (AOCS Cd 9-57). The percentage of conversion can be calculated based on the theoretical OOC and the iodine value was determined according to Wijs method.

3. Results and Discussion

3.1 Effect of Aqueous Hydrogen Peroxide Concentration on the Rate of Reaction

In this study, hydrogen peroxide serves as the oxygen donor, which contributes active oxygen to the formic acid in order to form performic acid. According to Oftring et al., [14] any hydrogen peroxide aqueous solutions that contains 10 - 55% of hydrogen peroxide by weight can be used to form peracid solution. Therefore, experiments to study the effect of hydrogen peroxide concentration were carried out using hydrogen peroxide at a concentration of 30 and 35% in aqueous solution. The effect of aqueous hydrogen peroxide concentration on the percentage relative conversion to oxirane (RCO) for oleic acid epoxidation with performic acid at 75 °C reaction temperature and 1:1 formic acid to hydrogen peroxide mole ratio is presented in Figure 1. It was found that hydrogen peroxide concentration of 30% had a positive effect on the rate of epoxidation, achieving higher RCO of around 87.61%. A concentration of 35% resulted in a lower rate of epoxidation and lower RCO which renders it unsuitable for use in this study which focussed on improving the reaction rate and epoxide yield. Hence, the hydrogen peroxide with a concentration of 30% in aqueous solution was chosen for all subsequent reactions.
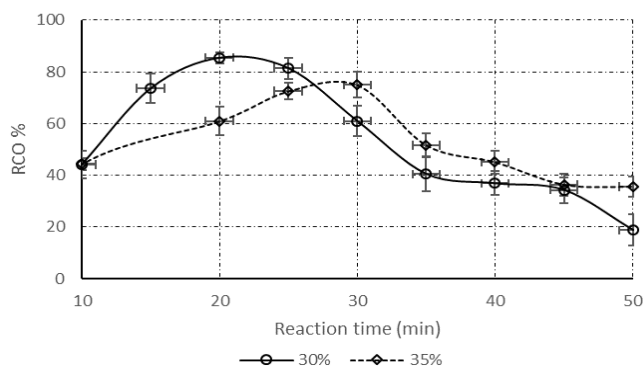
Figure 1. Effect of Hydrogen Peroxide Concentration on the Percentage Relative Conversion to Oxirane.

3.2. Effect of Oxygen Carrier on the Rate of Reaction

Two types of oxygen carrier (peracid) investigated were in situ peracetic and performic acids. Their influences on the epoxidation of oleic acid are shown in Figure 2. It shall be noted that epoxidation can be carried out using either formic acid or acetic acid [15]. It can be seen from Figure 2 that the maximum yield of epoxide was achieved when formic acid was used as the oxygen carrier compared to acetic acid. It is likely that the high epoxide yield obtained was due to the immediate reaction between the performic acid formed with the C=C double bonds in the oleic acid chain as well as minimization of oxirane ring degradation. According to Jalil et al [16] formic acid has the ability to minimize oxirane ring-opening by preventing the deprotonation of performic acid.

Furthermore, it can be observed that the time taken to produce maximum yield of epoxides was reduced when formic acid was used as the oxygen carrier. Nevertheless, should the in situ performic acid concentration becomes too high, it will contribute to a strong acidic condition which causes severe loss of epoxide by ring opening route. In this case, a use of inert solvents such as heptanes and toluene was suggested [17] and the addition of acid-neutralizing compounds was recommended during the epoxidation process in order to maintain a pH value of 3 – 6 [18]. Selection of oxygen carrier does not only affect the rate of conversion to oxirane, but also the stability of oxirane produced
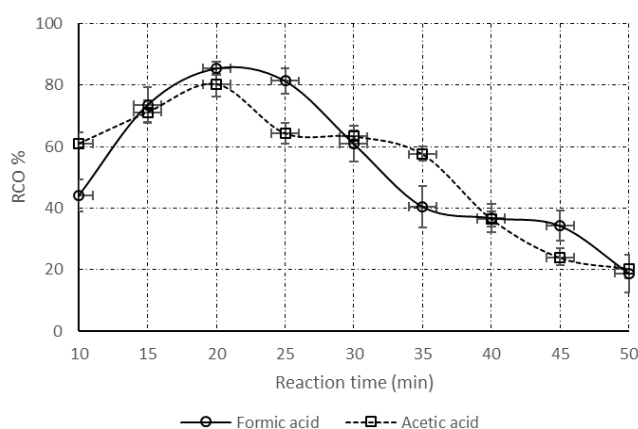

Figure 2. Effect of Oxygen Carrier on the Percentage of Relative Conversion to Oxirane.

3.3. Effect of Catalyst Loading on the Rate of Reaction

The effect of catalyst loading (sulphuric acid concentration) on the percentage of relative conversion (RCO) to oxirane for oleic acid epoxidation was also investigated in this study. The catalyst function is to lower the activation energy and increases the rate of reaction, which indirectly decreases operational cost resulting from prolonged reaction. In this study, the sulphuric acid concentration was varied from 0.2 to 1.0 g and the results are illustrated in Figure 3. Clearly, the rate of epoxidation reaction increases with an increase in sulphuric acid loading. It is also apparent that high RCO (~88%) was achieved at a shorter reaction time using 0.2g sulphuric acid. Increasing the catalyst loading to 0.6 and 1.0g resulted in higher epoxidation rate but lower RCO at around 70%. This result is noteworthy when compared to the findings of Campanella et al., [19] who investigated the epoxidation of fatty acid methyl esters by in situ performic acid without the addition of catalyst. The results of Campanella et al., [20] showed a conversion to oxirane of 83.5% at 40 °C was only achieved after a reaction time of 600 minutes.

In contrast, the maximum conversion to oxirane was attained within 25 minutes at 55 °C in this study. It is believed that the extra hydrogen ions from the external acid catalyst contributed to the increase in an oxirane ring formation. The high RCO obtained from the addition of 0.2 g of sulphuric acid may be attributed to the hygroscopic nature of the sulphuric acid [21]. Since the formation of performic acid is a reversible process, the performic acid acts as the substrate which is responsible for subsequent epoxidation, along with oleic acid. The hygroscopic nature of the sulphuric acid results in the absorption of water causes equilibrium constant (K_{eq}) was maintained. As a result, higher amount of performic acid was produced which in turn leads to a higher RCO, in accordance to the Le Chatelier principle [22]. However, the performic acid begins to decompose once the equilibrium balance favouring performic acid formation is not met, thus decreases the performic acid concentration and concurrently increases the water content in the reacting liquid system [8]. The rapid increment of water minimizes the hygroscopic effect of the sulphuric acid on the water molecules. A sulphuric acid concentration of 0.6 and 1.0 g results in a high acidic condition which causes premature rupture of the oxirane rings and thus decreases the RCO. Under both conditions, the hygroscopic effect of the sulphuric acid is minimum compared to the degradation of oxirane rings caused by the high acidity of the reaction medium.
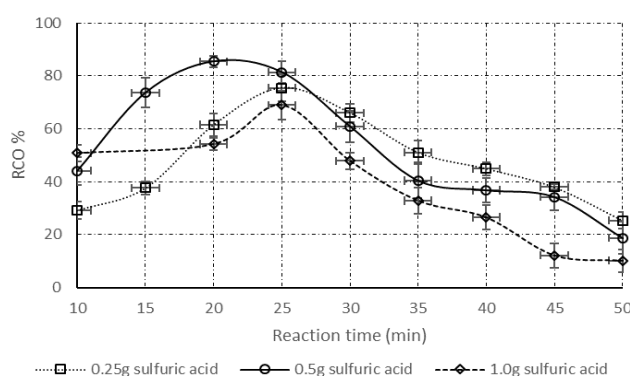

Figure 3. Effect of Catalyst Loading (Sulphuric Acid Concentration) on the Relative Conversion to Oxirane.

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4. Conclusions

In this study, crude oleic acid derived from palm oil has been epoxidized using in situ formed performic acid (HCOOOH) in order to produce epoxidized oleic acid. Epoxidized vegetable oils have gained great importance in recent years due to the fact that they are derived from renewable and sustainable resources and therefore perceived as environmental friendly. In this study, crude oleic acid derived from palm oil has been epoxidized using in situ formed performic acid (HCOOOH) in order to produce epoxidized oleic acid. A good conversion to oxirane was observed at 300 rpm stirring speed as well as 30%(wt/wt) aqueous hydrogen peroxide concentration, 0.2g of sulphuric acid catalyst and formic acid as an oxygen carrier were used.

Acknowledgements

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