Palm olein ozonation as a renewable resourse: spectroscopic analysis for monitoring the degree of saturation

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Abstract: The manufacturing of organic compounds by environmentally-friendly methods has been intensively reexamined in recent years. Several excellent methods have been devised to produce organic compounds from renewable resources. The ozonation is one of the high active oxidation methods which lead to production of organic compounds by the breaking of double bonds. Palm olein as a renewable source is subjected to the ozonation process to break the double bond which leads to the formation of two carbonyl groups as well described by Criegee mechanism. The monitoring of the degree of saturation was obtained by the Fourier transform infrared spectroscopy (FTIR) by observing the change in function groups as a result of ozone consumption and heat of reaction. The reaction time was 2 hrs at different temperatures and without any solvent or participating catalyst. The complete cleavage of a double bond occurred at 150 °C temperature of reaction.

1. Introduction
Palm Olein (Palm Oil fractionation product) considers one of the most important used oils for industrial application in Malaysia as it has huge amounts of fatty acids i.e. Saturated and unsaturated fatty acids[1]. The Unsaturated fatty acids are subjected to a variety of reactions with several compounds to form a wide range of products[2]. These reactions may involve either the carboxyl group or the carbon–carbon double bond in an unsaturated fatty acid [3, 4]. The oxidation of unsaturated fatty acids results in partial or complete cleavage of the carbon–carbon double bond[5, 6]. One of the most active oxidation methods is the Ozonolysis; the process by which ozone (O₃) reacts with alkenes to break the double bond and form two carbonyl groups which could be monitored simply by Spectroscopic analysis.

A number of works was done by some researchers on the monitoring of the degree of saturation by using a Spectroscopic analysis. Nestor, at.el, was investigate the degree of saturation for the sunflower oil and sunflower methyl esters by using FT-IR and H1NMR [7, 8], the study had monitored the consumption of ozone by the unsaturated fatty acids and the changes in the functional groups. Other work was investigated by N. Vlachos and his colleagues [9], their work was used FT-IR spectroscopy to monitor the oxidation process of corn oil samples undergone during heating or/and exposure to ultraviolet radiation. In our work, the ozonation of palm olein was performed under different temperature. All the experiment was conducted without using a catalyst and participating solvent. The degree of saturation for palm olein was monitored throughout the change in function groups by the Fourier transform infrared spectroscopy (FTIR).
2. Materials and Methods

2.1 Materials
Palm Olein (Fractionated palm oil) as starting material was purchased from LAMSOON Company (Malaysia). IR spectra were obtained on a Thermo Scientific, Nicolet 6700 FT-IR spectrometer. The gas bubbling reactor was fabricated by Dura Glass (Malaysia). Ozone was generated by use of an AC series ozone generator from IN (USA).

2.2 Methods
Oxygen gas at a flow rate of 1 L/min and pressure of 0.03 MPa was fed into the electric ozone generator to generate ozone gas which was directed as fine bubbles into the reactor containing Palm Olein. The reaction temperature was maintained at 50, 80, 120, 150 °C for time of 2hr with vigorous stirring. Unreacted ozone was decomposed before emission of gas to atmosphere.

3. Results and discussion
The Ozonolysis reaction proceeds by the three-step Criegee mechanism [4] which includes, first, the formation of a primary ozonide (PO), second, the decomposition of the PO to aldehydes (or ketones) and carbonyl oxides (or Criegee intermediates, CI) [4], then, finally, recombination of the carbonyl oxide and the aldehyde (or ketone) to form secondary ozonide (SO). The suggested mechanism of this study which described in scheme 1 explores the mechanism of the reaction regarding to the high percentage content of unsaturated fatty acid (Oleic Acid 45% approximately) [5] which may influence by the attack of ozone according to the ozonation process. This mechanism observes the breakage of the double bond, Cycloaddition and Retro Cycloaddition to form the aldehyde and the carboxylic group; otherwise the hydrogen peroxide was subjected to the reaction for further oxidation and obtaining the final products i.e. Azelaic acid and Pelargonic acid after the extraction and drying [10].
The major changes in the functional groups found in palm olein and ozonized samples were analyzed by FTIR. Figure 1 shows the IR spectra of palm olein, while the figures 2, 3, 4 and 5 show the ozonized samples at 50, 80, 120, 150 °C respectively with increasing amounts of consumed ozone and increasing the heat of reaction. One characteristic band of palm olein at 3006.0 cm$^{-1}$ due to the presence of C=C bond, this bond reduced with increasing amounts of ozone consumed and increasing the temperature of reaction. At the 50 and 80 °C reaction temperatures, there is no change observed for the double bond as shown in figure 2, 3 respectively, while its starts slightly decreasing with increasing of the temperature i.e. 120 °C as shown in figure 4.

Figure 1. The suggested mechanism of the reaction.
Fig. 1 Palm Olein before Ozonation

Fig. 2 Palm Olein at 50°C of Ozonation

Fig. 3 Palm Olein at 80°C of Ozonation

Fig. 4 Palm Olein at 120°C of Ozonation
After the increasing of reaction temperature to 150 °C, the double bond was disappeared as a result of completely ozone consumption and by reacting with the double bond at high temperature as illustrated at figure 5.

4. Conclusion
Ozonolysis of Palm olein was performed at different temperatures without a solvent and participating catalyst. The reaction was performed with very fine gas bubble size. The contact time between gas and liquid was increased by vigorous stirring; at the same time the temperature of reaction was increased as well to enhance reaction of ozone with the double bond of unsaturated fatty acids in Palm olein. The Fourier transforms infrared spectroscopy (FTIR) results illustrate clearly the change in function group and the completely cleavage of the double bond at 150 °C temperature and 2hr time of the reaction.

ACKNOWLEDGEMENTS
The authors would like to extend their appreciation to the University Kebangsaan Malaysia, and to the CRIM for research grant UKM-KK-02-FRGS0196-2010.

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