STUDIES ON OLIVE OIL AND RATE OF PHOTO/CATALYTIC CLEAVAGE OF UNSATURATED FATTY ESTER CONTENT

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Abstract Oils are not just sources of condensed energy and flavours but also rich sources of fat soluble vitamins and essential fatty acids. These underscore studies in their oxidative stability and shelf-life. Olive oil of *Olea europaea* fruits was extracted and subjected to iodine value test, after catalysis using 0.4g TiO_2 and 2.0g H_2O_2, photoxidation and photocatalysis using UV and the catalysts above. A strong positive linear relationship exists between the iodine value and time under all reaction conditions. The reaction rates were not linear for any of the given conditions but reduced reaction rates were observed. The reaction rates were well correlated with time under the given conditions having shown correlation coefficient values, r, close to +1.

Keywords: olive oil, photocatalysed, correlation coefficient, shelf life

INTRODUCTION

The increasing demand and consumption of high-quality vegetable oils has spurred the interest of researchers in probing methods that ensure their oxidative stability and extend shelf-life. Vegetable oil forms a vital part of human diet, providing a concentrated source of energy and essential nutrients (Fakarurhobo, 2009). They are amongst the crucial areas of concern and research in terms of human nutrition as they act as carriers of fat-soluble vitamins like Vitamin A, D, E and K, provide unique textures and flavours to food and are rich source of essential fatty acids such as linolenic and linoleic acid (Mengistie *et al*., 2018).

Oils, like most organic materials are composed of carbon, hydrogen and oxygen in definite proportions. These elements combine naturally to form aliphatic chains known as fatty acids. Three of these chains esterified with glycerol form a molecule known as a triglyceride—Fatty Acid Ester (NEODA, 2019). The triglycerides are the main constituents of vegetable oils (Bruice, 2007). Olive oil is a vegetable oil that is pressed from olives, the fruit of the olive tree (Ayton *et al.*, 2012). It is believed to be associated with a relatively long life in good health. Olive oil is considered to be resistant to oxidation in comparison with other vegetable oils due to its low content of polyunsaturated fatty acids and the presence of natural antioxidants (Velasco *et al.*, 2002 and Ayton *et al.*, 2012).

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Vegetable oils are sensitive to photochemical reactions. These reactions only occur when initiated by the absorption of light energy from the ultraviolet, visible or infrared region of the electromagnetic spectrum (Mondal, 2018). It is one of the major reactions responsible for the degradation of unsaturated fatty esters (Choe *et al.*, 2006).When vegetable oils are exposed to long term UV radiation, peroxides are primarily formed. They rearrange to alcohols, aldehydes, ketones, carboxylic acids etc. These secondary products are key agents responsible for flavour deterioration, increase in toxicity and decline in the nutritional quality of the irradiated vegetable oil (Maduelosi *et al*., 2012). Light in this way can be used to monitor photo degradation of olive oil by determining the rate of the photochemical reaction.

The rate of reaction provides basic information required to deduce the individual reactions that reactants undergo in order to make products (Ball, 2011). It can be seen as the speed at which the reaction proceeds leading to the formation of products. For a photochemical reaction, the rate not only depends on the composition and temperature (Atkins *et al*., 2006) but also on the intensity of the light absorbed by the reacting molecules, the presence of oxygen, the degree of unsaturation and the presence of pigments called chlorophyll (Fekarurhobo, 2009). The rates of chemical reactions are obtained from measurements of concentration as a function of time (Silbey *et al.*, 2005 and Chang, 2014). It can be expressed mathematically as:

$$\text{Rate} = \frac{change\ in\ amount}{change\ in\ time} = \frac{\Delta(amount)}{\Delta(time)}$$

If the rate of the reaction is low, it implies that the speed at which the reaction proceeds is slow and vice versa. This work studies the rate of photochemical reactions of olive oil bearing in mind the need to adjust storage conditions while devising measures to preserve the nutritional quality, consequently extending the shelf life of olive oil.

MATERIALS AND METHODS

Sample Collection

Extra virgin olive oil (obtained from the fruit of *Olea europaea*) was purchased from a supermarket in Benin-City, Edo State, Nigeria.

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Determination of iodine value of olive oil (Wij's method)

The iodine value of the olive oil was determined by Wij's method (Ogundiran *et al*., 2012). 1.0g of the oil sample was weighed and dissolved in 20ml of carbon tetrachloride (CCl_4) in a 500ml conical flask. The oil solution formed was mixed with 25ml of Wij's solution. The flask containing the solution was stoppered with a glass stopper and shaken. The flask was allowed to stand in the dark for 30 minutes with occasional shaking. After which, 20ml of 10%w/v potassium iodide (KI) and 100ml of distilled water was added to the oil solution. The liberated iodine solution was then titrated with 0.1M sodium thiosulphate solution until the yellow colour almost disappeared, then 12ml of 1% starch solution was added as indicator and the titration continued until the purple colour disappeared. This was noted as the end point. A blank test was also carried out using the Wij's method but, in the absence of the oil. The iodine value was calculated as follows:

$$\text{Iodine value} = \frac{(V_1 - V_2) \times M \times 12.69}{W}$$

Where;

V_1 (ml) = volume of sodium thiosulphate used for the blank test

V_2 (ml) = volume of sodium thiosulphate used for the oil

W (g) = Weight of the sample of oil

M (mol/dm^3) = Molarity of standard sodium thiosulphate solution

Photo-oxidation of the Olive oil Sample

The ultraviolet lamp was set up with a magnetic stirrer placed beneath it. 20g of olive oil sample was weighed into a 100ml beaker which was placed on top of the magnetic stirrer and was exposed to Ultraviolet (UV) light for 1,3,6,9 and 12 hours. At the various time intervals, 1g of the oil sample was weighed and the iodine value was determined using Wij's method.

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Catalytic oxidation of the Olive oil sample

20g of the oil sample was weighed in a 100ml beaker, 0.4g of TiO_2 and 2g of H_2O_2 was added to the oil and properly stirred. The oil solution was left to stand at room temperature in the dark for 1, 3, 6, 9 and 12 hours respectively. At the various time intervals, 1g of the oil sample was weighed and the iodine value was determined using Wij's method.

Photocatalytic oxidation of the Olive oil Sample

20g of the oil sample was weighed in a 100ml beaker, 0.4g of TiO_2 and 2g of H_2O_2 was added to the oil and properly stirred. The ultraviolet lamp was set up with a magnetic stirrer placed beneath it. The beaker containing the mixture of oil/TiO_2 and H_2O_2 was placed on top of the magnetic stirrer and was exposed to UV light for 1,3,6,9 and 12 hours. At the various time intervals, 1g of the oil sample was weighed and the iodine value was determined using Wij's method.

RESULTS AND DISCUSSION

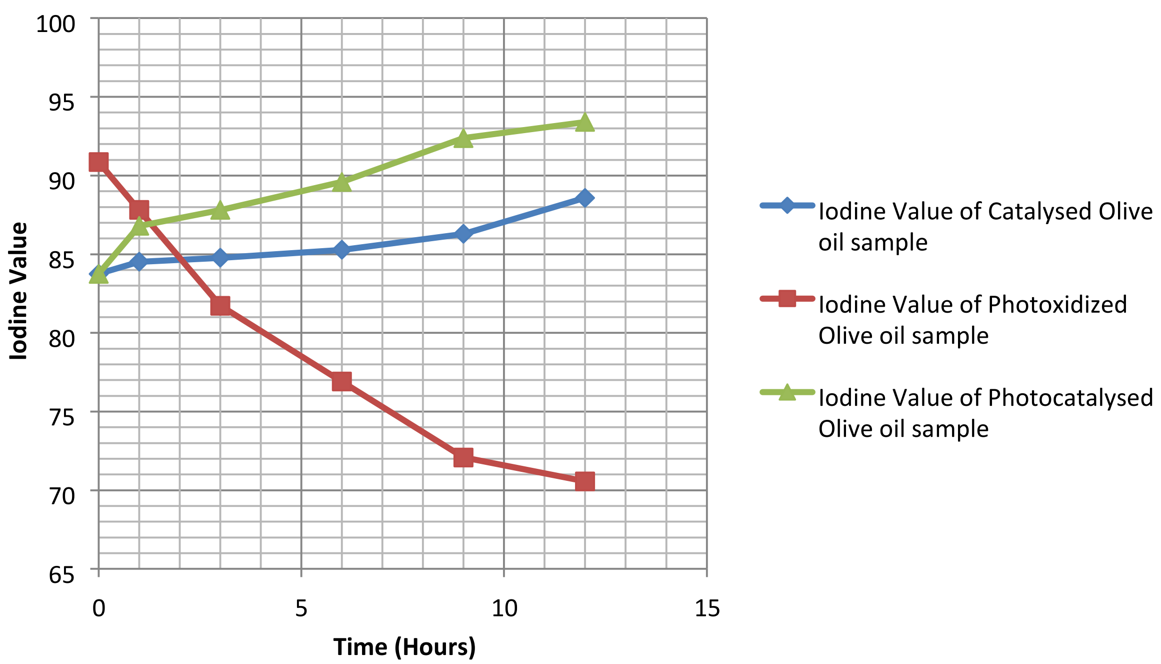

Figure 1: Graph of iodine value against time showing the catalysed, photoxidized & photocatalysed reactions of the olive oil sample

The correlation values of catalysed (TiO_2 /H_2O_2) and Photocatalysed (UV + TiO_2 /H_2O_2) olive oil samples were 0.956 and 0.971 respectively. This implies that a strong positive linear relationship exists between the iodine value and time. As described by (Gogtay *et al*., 2017) the iodine value and time increased simultaneously. That is, the iodine value increased with time as the reaction progressed. This result suggests that the catalysed reactions might have led to rearrangement of bonds leading to production of new compounds with increased unsaturation. While the correlation between iodine value and time of photoxidized olive oil sample was -0.973, showing that a strong positive linear relationship exists between the iodine value and time as well. The correlation values are close to +1, indicating that cleavage of unsaturated fatty esters occurred on the olive oil sample as the reaction progressed.

Table 1: Results showing the rate of reaction of olive oil under different conditions

Reaction Time	**Catalytic conditions and Rate values**		
	TiO_2 /H_2O_2 h^{-1}	**UV h^{-1}**	**UV + TiO_2 /H_2O_2 h^{-1}**
0	0.75	3.10	2.45
1	0.34	2.36	0.95
3	0.20	1.61	0.58
6	0.25	1.43	0.72
9	0.50	1.00	0.60
12	1.07	0.25	0.33
Average Rate	0.40	1.69	0.80

The catalysed and photocatalysed samples of olive oil show irregularities in their rates of reactions. The reaction rate for the catalysed olive oil decreased within the first three hours from $0.75h^{-1}$ to $0.20h^{-1}$ and increased after the third hour up to the twelfth hour from $0.20h^{-1}$ to $1.07h^{-1}$. That of the photocatalysed olive oil sample decreased within the first three hours from $2.45h^{-1}$ to $0.58h^{-1}$, increased at the sixth hour ($0.72h^{-1}$) and decreased thereafter up to the twelfth hour. These irregularities in the reaction rates could be attributed to the composition of the mixture (Atkins *et al*., 2006) that is, the presence of catalyst/oxidants (TiO_2/H_2O_2), or as a result of variation in the degree of unsaturation of the cleaved products formed within the reacting mixture (Fekarhurobo, 2009).

The rate of reaction for the photoxidized olive oil decreased progressively from an initial rate of 3.10 h^{-1} to 0.25 h^{-1} at the twelfth hour as shown in Table 1 above. This implies that the speed of the reaction decreased as the unsaturated fatty esters in the olive oil were cleaved to saturated fatty compounds. In

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other words, as the reaction progressed and saturated products were formed, the rate at which cleavage occurred with time in the reacting mixture decreased. This indicates that as more of the reacting species underwent cleavage, there existed a decrease in the concentration of unsaturated fatty esters in the reacting mixture resulting to a slower rate of reaction (Ball, 2011). Ultimately, when all unsaturated fatty esters of the sample of olive oil are cleaved to saturated compounds the rate of reaction will become 0. From Table 1, the average rate of the reaction when the sample of olive oil was exposed to only ultraviolet light of 300watts is 1.69h^{-1}; it is lower for the photocatalysed (0.80h^{-1}) and catalysed (0.40h^{-1}) reaction. The results also show that significant cleavage occurred right from the first hour of exposure of the olive oil sample to ultraviolet light. This implies that, when pure olive oil samples are exposed to ultraviolet light, the rate at which cleavage occurs per hour is higher compared to when a catalyst is used to effect cleavage.

CONCLUSION

Rancidity in oils is attributable to impurities that elicit oxidative processes; this has the effect of forming odorous and undesirable products, thus rendering oils unfit for consumption. From the forgoing experiments and results, exposure to ultraviolet light is a greater culprit than material impurities which could constitute catalysts or reactive sights for the oxidative deterioration of oils. The correlation values of the catalysed, photocatalysed and photoxidized reactions which are 0.956, 0.971 and 0.973 respectively are close to +1 which indicates a strong positive correlation between the reactions with time. It follows that the degree of oxidation is a function of time of exposure/contact between the oil and the oxidizing agent. Olive oil and hence vegetable oils need to be protected from sunlight to conserve nutritional value and extend shelf-life.

REFERENCES

Atkins, P. and De Paula, J., (2006). Physical Chemistry. 8th ed. Oxford University Press, Britain. pp 794-796

Ayton, J., Mailer, R.J. and Graham, K., (2012). The Effect of Storage Conditions on Extra

Ball, D.W., (2011). Physical Chemistry. Quebecor world, USA. pp 681-683

Bruice, P.Y., (2007). Organic Chemistry. 5th ed. Peason Education Inc., New Jersey. pp 1165- 1167

***p* - ISSN: 2536 – 6866**
***e* - ISSN: 2659 - 1529**

Chang, R., (2014). Physical Chemistry for the Chemical Sciences. Marquis Book Printing, Canada. pp 671-672

Choe, E. and Min, D.B., (2006). Mechanisms and Factors for Edible oil Oxidation. *Comprehensive Reviews in Food Science and Safety*. 5; 169-186.

Fekarurhobo, G.K., Obomanu, F.G. and Maduelosi, J., (2009). Effects of Short-Term Exposure to Sunlight on the Quality of Some Edible Vegetable Oils. *Research Journal of Applied Sciences.* 4(5); 152-156.

Gogtay, N.J. and Thatte, U.M., (2017). Principles of Correlation Analysis. *Journal of the Associaiton of Physicians of India*, 65: 78-81.

Maduelosi, N.J., Obomau, F.G. and Fekarurhobo, G.K., (2012). Dye-Sensitized Photo- Oxidation of Some Vegetable oils. *Journal of Emerging Trends in Engineering and Applied Sciences,* 3(5): 740-742.

Mengistie, T., Alemu, A. and Mekonnen, A., (2018). Comparison of Physicochemical Properties of Edible Vegetable oils commercially available in Bahir Sa, Ethiopia. *Chemistry International*, 4(2): 130-135

Mondal, S., (2018). Photochemical Reactions. Retrieved on the 6th of December, 2019 from www.researchgate.net

National Edible Oil Distribution Association, (2019). Chemistry of Oils and Fats. Retrieved on the 4th of December, 2019 from www.neoda.org.uk.

Ogundiran, M.B. and Adeniyi, S.O., (2012). Determination of Fat Contents, Iodine Values, Tarace and Toxic Metals in Commonly Consumed Frozen Fish in Nigeria. *American Journal of Food Technology*, 7(1): 34-42

Silbey, R.J., Alberty, A.R.and Bawendi, M.G., (2005). Physical Chemistry. 4th ed. John Wiley & Sons Inc., New Jersey. pp 642-644

Velasco, J. and Dobarganes, C., (2002). Oxidative Stability of Virgin Olive oil. *European Journal Lipid Sci. Technology*, 104: 661-676

Virgin Olive Oil Quality. Australia: Rural Industries Research and Development Corporation. pp 1-4