

## Mathematical Modeling of Degree of Thermal Oxidation of Edible Oil (Sun Flower) as a Function of Induction Time at Fixed Induced Power During Microwave Heating

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**ABSTRACT:** This is about relating the thermal induction time range from 0-40 minutes for sunflower oil (refined) of definite composition with the change in the thermal oxidation by the models developed by using M S Excel and Statistical Software, Design Expert Software 8.0 with there  $R^2$ . And through analysis of prepared model data with their plotted graph.

**KEYWORDS:** Thermal Oxidation, Peroxide value, Design Expert Software 8.0, M S Excel, Microwave Oven, Modeling.

### 1 INTRODUCTION

Thermal oxidation of edible oil is an important determination of the quality of edible oil. During processing of food stuffs involving the use of edible oils such as blended oil as a heat transfer medium, the oil owing to high temperature undergoes thermal oxidation over a period of time. Due to the thermal oxidation of edible oils, they become unfit for further use after a period of time. Hence proper control of processing condition is a desirable requirement in order to delay the onset of thermal oxidation of edible oil.

Mathematical modeling is an effective way of representing a particular process. It can help us to understand and explore the relationship between the process parameters. Mathematical modeling can help to understand and quantitative behavior of a system. Mathematical models are useful representation of the complete system which is based on visualizations. Mathematical modeling is an important method of translating problems from real life systems to conformable and manageable mathematical expressions whose analytical consideration determines an insight and orientation for solving a problem and provides us with a technique for better development of the system. Mathematical models in the field of oxidation of edible oils can enable the determination of time of cook of edible oil which would lead to the least amount of oxidation of edible oil during processing using edible oils as a heating medium.

Mathematical models can enable the optimization of frying time at fixed power to reduce the rancidity of frying oils. In light of above considerations the study was conducted in order to attain the following objective

- 1) To determine the relationship of the Thermal oxidation as function of Induction time of the frying oil at fixed power during microwave cooking

Heating is an important part of many food processing operations. Many desirable changes, as well as undesirable reactions, occur in vegetable oils when they are heated at elevated temperature. However, during heating, vegetable oils are very sensitive and susceptible to quality changes, caused by chemical instability, that are dependent on both chemical composition and environmental factors. Lipid oxidation is one of the major deleterious reactions during heating that

markedly affects the quality of vegetable oils. This chemical reaction is of primary concern to many researchers in the field of fats and oils. The extensive studies on lipid oxidation have spurred a vast array of findings in the field of fats and oils processing. Today, it is well known that this deleterious reaction leads to the formation of various oxidation products, which may result in the oil and fat products becoming unfit for human consumption. Compositional and/or environmental effects on lipid oxidation can be expressed by a mathematical relationship. However, this relationship applies only to several simple food systems and reactions. More often, oxidative reactions of vegetable oils are more complex and unique in their behavior, and the appropriate model must be derived individually for each product and oil system. Temperature is one of the main environmental factors that influence the rate of quality loss. The dependence on temperature of most reactions in foods can be expressed more precisely by the Arrhenius model.

Shahidi and Spurvey (1996) stated that Autoxidation of oils and the decomposition of hydroperoxides increase as the temperature increases. Velasco and Dobarganes (2002) stated that the formation of autoxidation products during the induction period is slow at low temperature. The concentration of the hydroperoxides increases until the advanced stages of oxidation. Marquez-Ruiz *et al.* (1996) suggested that The content of polymerized compounds increases significantly at the end of the induction period of autoxidation. Yang and Min (1994); Rahmani and Saari Csallani (1998) suggested that temperature has little effect on oil oxidation due to the low activation energy of 0 to 6 kcal/mole. Sattar *et al.* (1976) stated that light is much more important than temperature in oil oxidation.

## 2. MATERIALS AND METHODS

### 2.1 Edible Sunflower Oil composition.

**Table 1.** <sup>19</sup>Composition of Refined Sunflower used.

Component	<i>Oil Type</i>
	sunflower
<b>Main fatty acids (% of peak area)</b>	
Palmitic	4
Stearic	3
C <sub>20</sub> -C <sub>22</sub> saturated	1
Monoenoic	34
Dienoic	57
Trienoic	trace
Eicosenoic	-
Trans-unsaturated	0.8
Peroxide value (meq/kg)	0.2
Acid value (mg/g)	0.06
Conjugated dienes (% m/m)	0.6
Polar compounds (% m/m)	0.4
<b>Tocopherols (mg/kg)</b>	
Tocopherol α	373
Tocopherol β+γ	34
Tocopherol δ	14
Total tocopherols	418

2.2 Preparation of samples (reference [19])

2.3 Sample Collection (reference [19])

\*Assumptions

- Surface area exposed to atmosphere is constant or same.
- No mixing or agitation.

2.4 MEASUREMENT OF OXIDATION

2.4.1 Peroxide Value (PV) Analytical method.

2.4.1.1 Purpose and Scope

This method describes the determination of peroxides values for vegetable oils and fats. The peroxide value is a parameter specifying the content of oxygen as peroxide, especially hydro peroxides in a substance. The peroxide value is a measure of the oxidation present.

2.4.1.2 Principle

The sample treated in the solution with a mixture of acetic acid and a suitable organic solvent and then with a solution of potassium iodide. The liberated iodine is titrated with a standard solution of sodium thiosulphate.

Peroxides and similar products which oxidize potassium iodide under the conditions of the test will contribute to the peroxide value. Variations in procedure may affect the results. Peroxide values are expressed either in milliequivalents of peroxide/kg or millimoles of peroxide/l.

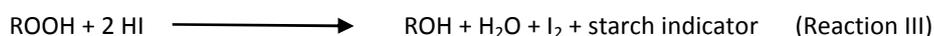
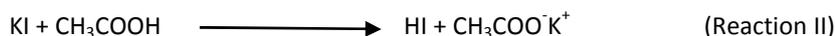
Reaction scheme:

The peroxide value is determined by measuring the iodine liberated from potassium iodide by a peroxide, using sodium thiosulphate solution as the titrant. In the presence of acetic acid, the reaction scheme for hydroperoxides is as follows.

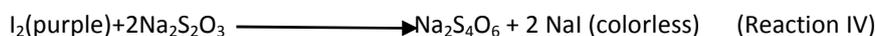
Generation of hydroperoxides:



Generation of iodine:



Titration step:



Reaction of peroxides of the structures R-O-O-R' and

R-CH-O-O-CH-R' follows an analogous pathway. Whilst cyclic peroxides do not react quantitatively under the conditions described here.

Alternatively, the ion reaction is of more of general applicability:



#### 2.4.1.4 Procedure

- i) Approx. 3.0g of the sample was transferred, accurately weighed, into a 250 ml conical flask.
- ii) 25 ml of the appropriate solvent mixture (glacial acetic acid: chloroform, 1:2) and 1 ml saturated potassium iodide solution freshly prepared was added.
- iii) Was Allowed to react for 60 sec. and shaking thoroughly during this period. Then 35 ml of distilled water was added.
- iv) Then was titrated with 0.001 N sodium thiosulphate solution using 0.5 ml 1%starch solution as indicator.
- v) During the titration shaken until the blue color disappeared.
- vi) Blank titration was carried under the same conditions.

#### 2.4.1.5 Calculations

S=titration of sample.

B=titration of blank.

SW=weight of sample taken.(gm)

N=normality of sodium thiosulphate used.(0.001)

PV=peroxide value (meq/kg)

$$PV = (S-B) * N * 1000 / SW$$

#### 2.5 Graphical Analysis

The experimental data obtain using the previous procedures were analyzed by plotting Graph and developing Models for various observations for different time.

#### 2.6 Statistical Analysis

The experimental data obtain using the previous procedures were analyzed by the response surface regression procedure using the following higher-order polynomial equations: like,  $y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2$ , where  $y$  is the response,  $x_i$  is the uncoded independent variable (factor), and  $\beta_0, \beta_i, \beta_{ii}$  are intercept, linear and quadratic respectively. Design Expert software package 8.0 was used for regression analysis, analysis of variance (ANOVA) and developing of models of different forms by transformation (linear and of higher order) based on above mentioned principles of forming a functions. Confirmatory experiments were carried out to validate the equations using the combinations of independent variable which were not part of the original experimental design but were within the experimental region. Various models were compared for the best fit summary and there  $R^2$  values were compared to choose the best appropriated model for particular data design and selected runs.

### 3 RESULT AND DISCUSSION

3.1 Below is the graphical trend of peroxide value with respect to time of heating and the drawn trend line by M S-Excel and the equation developed with it R-Square. (data reference 19)

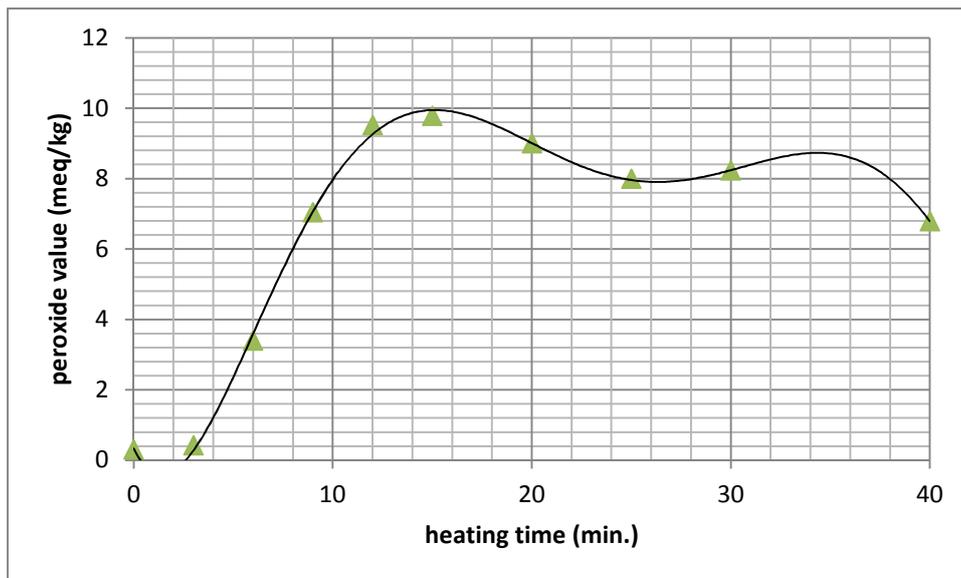


Fig 1. Graph plotted on M S Excel peroxide value Vs Induction Time during Microwave cooking of oil.

Model 1 equation:

$$y = 2E-07x^6 - 3E-05x^5 + 0.0017x^4 - 0.0447x^3 + 0.4925x^2 - 1.1387x + 0.3323$$

where x is time of induction of oil in minutes, and y is the peroxide value at specified induction time

$$R^2 = 0.9986$$

3.2 The results from Statistical Analysis using Expert Design Software we get

Table 2. Model fit Summary

Model Summary Statistics						
Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	
Linear	3.06	0.3534	0.2726	-0.1958	138.82	
<u>Quadratic</u>	<u>1.61</u>	<u>0.8436</u>	<u>0.7989</u>	<u>0.3600</u>	<u>74.29</u>	<u>Suggested</u>
Cubic	1.37	0.9025	0.8537	0.4740	61.07	
Quartic	1.32	0.9255	0.8659	-18.9449	2315.34	
<u>Fifth</u>	<u>0.32</u>	<u>0.9966</u>	<u>0.9923</u>	<u>-7.8785</u>	<u>1030.69</u>	<u>Suggested</u>
Sixth	0.23	0.9986	0.9959	-12.3528	1550.09	

Table 3. showing P-Value for fit summary

Response	1	PV	Transform:	None	
Summary (detailed tables shown below)					
Source	Sequential p-value	Lack of Fit p-value	Adjusted R-Squared	Predicted R-Squared	
Linear	0.0699		0.2726	-0.1958	
<u>Quadratic</u>	<u>0.0023</u>		<u>0.7989</u>	<u>0.3600</u>	<u>Suggested</u>
Cubic	0.1056		0.8537	0.4740	
Quartic	0.2688		0.8659	-18.9449	
<u>Fifth</u>	<u>0.0008</u>		<u>0.9923</u>	<u>-7.8785</u>	<u>Suggested</u>
Sixth	0.1225		0.9959	-12.3528	

Table 4. Showing Sequential Model Sum of Square

Sequential Model Sum of Squares [Type I]						
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Mean vs Total	390.13	1	390.13			
Linear vs Mean	41.02	1	41.02	4.37	0.0699	
<u>Quadratic vs L</u>	<u>56.90</u>	<u>1</u>	<u>56.90</u>	<u>21.93</u>	<u>0.0023</u>	<u>Suggested</u>
Cubic vs Quad	6.84	1	6.84	3.62	0.1056	
Quartic vs Cub	2.67	1	2.67	1.55	0.2688	
<u>Fifth vs Quartic</u>	<u>8.25</u>	<u>1</u>	<u>8.25</u>	<u>83.06</u>	<u>0.0008</u>	<u>Suggested</u>
Sixth vs Fifth	0.24	1	0.24	4.55	0.1225	
Residual	0.16	3	0.053			
Total	506.21	10	50.62			

\*Sequential Model Sum of Squares [Type I]\*: Select the highest order polynomial where the additional terms are significant and the model is not aliased.

Table 5. showing ANOVA for Response surface Fifth Model

Response	1	PV				
ANOVA for Response Surface Fifth model						
Analysis of variance table [Partial sum of squares - Type III]						
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	115.69	5	23.14	232.92	< 0.0001	significant
A-Time	7.92	1	7.92	79.71	0.0009	
A <sup>2</sup>	0.57	1	0.57	5.78	0.0741	
A <sup>3</sup>	10.70	1	10.70	107.72	0.0005	
A <sup>4</sup>	0.14	1	0.14	1.38	0.3052	
A <sup>5</sup>	8.25	1	8.25	83.06	0.0008	
Residual	0.40	4	0.099			
Cor Total	116.09	9				

The Model F-value of 232.92 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise.

Table 6. ANOVA analysis table.

Std. Dev.	0.32	R-Squared	0.9966
Mean	6.25	Adj R-Squared	0.9923
C.V. %	5.05	Pred R-Square	-7.8785
PRESS	1030.69	Adeq Precisor	40.434

A negative "Pred R-Squared" implies that the overall mean is a better predictor of your response than the current model.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 40.434 indicates an adequate signal. This model can be used to navigate the design space.

### Model 2 Fifth degree equation from the Design Expert Software 8.0

#### Final Equation in Terms of Actual Factors:

$$\begin{aligned}
 PV = & \\
 & +0.24316 \\
 & -0.74793 * \text{Time} \\
 & +0.35607 * \text{Time}^2 \\
 & -0.028012 * \text{Time}^3 \\
 & +8.27271\text{E-}004 * \text{Time}^4 \\
 & -8.38166\text{E-}006 * \text{Time}^5
 \end{aligned}$$

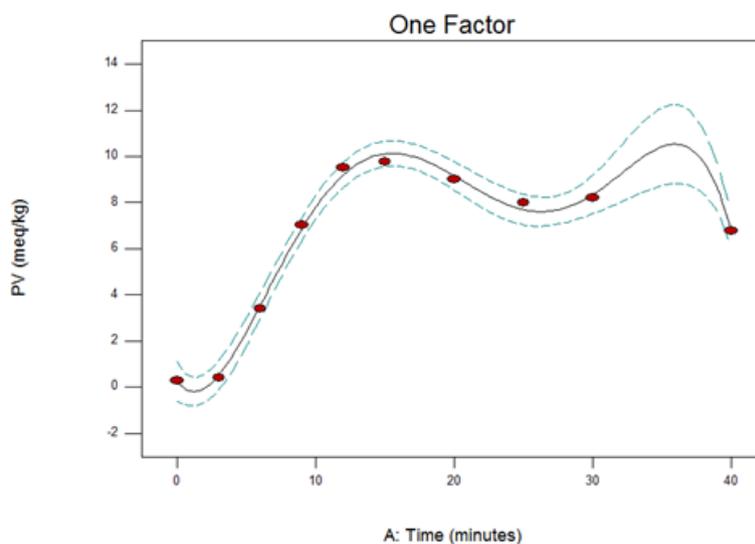


Fig 2. Graph Peroxide value Vs Induction Time by Software for Fifth Model

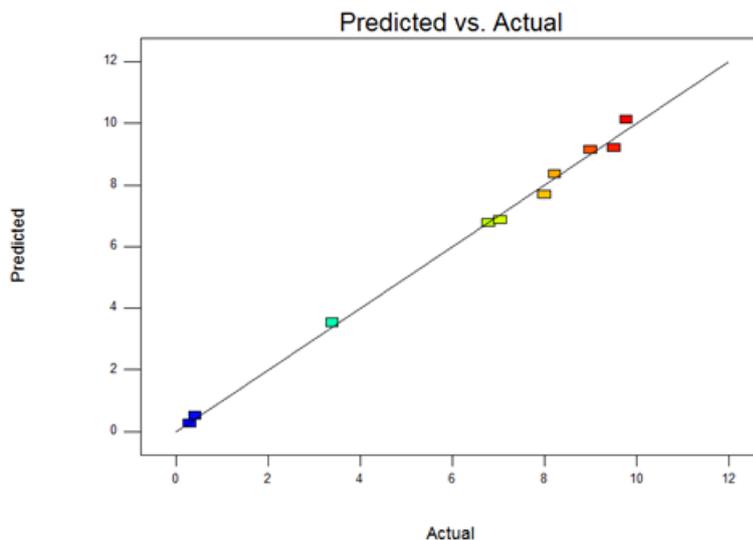


Fig 3. Graph Predicted Vs Actual values of Oxidation for model 2

Table 7. ANOVA for Response Surface Quadratic model

Source	Sum of Squares	df	Mean Square	F Value	p-value	
Model	97.93	2	48.96	18.87	0.0015	significant
A-Time	30.15	1	30.15	11.62	0.0113	
A <sup>2</sup>	56.90	1	56.90	21.93	0.0023	
Residual	18.16	7	2.59			
Cor Total	116.09	9				

The Model F-value of 18.87 implies the model is significant. There is only a 0.15% chance that an F-value this large could occur due to noise.

Table 8. ANOVA Analysis Table for Quadratic Model

Std. Dev.	1.61	R-Squared	0.8436
Mean	6.25	Adj R-Squared	0.7989
C.V. %	25.79	Pred R-Square	0.3600
PRESS	74.29	Adeq Precisor	11.152

The "Pred R-Squared" of 0.3600 is not as close to the "Adj R-Squared" of 0.7989 as one might normally expect; i.e. the difference is more than 0.2. This may indicate a large block effect

Model 3 Quadratic Equation by Design Expert Software 8.0

Final Equation in Terms of Actual Factors:

$$PV = -0.017681 + 0.80836 * Time - 0.016592 * Time^2$$

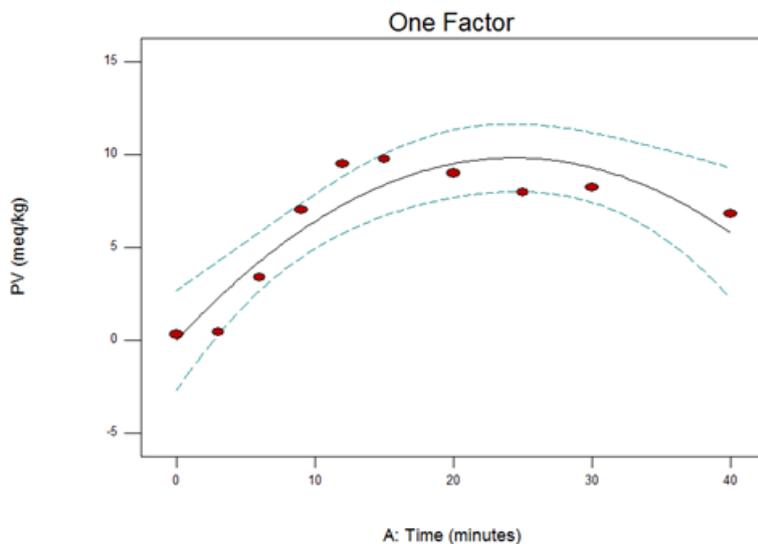


Fig 4. Graph Peroxide value Vs Induction Time by Software for Quadratic Model

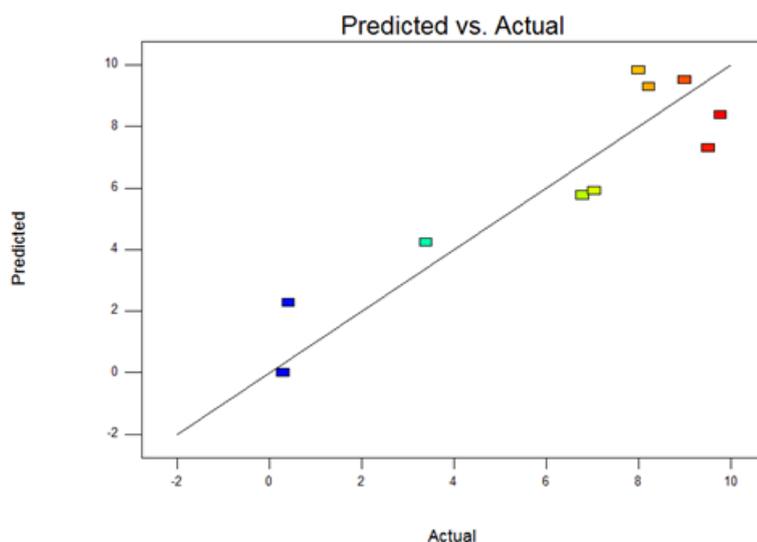


Fig 5. Graph Predicted Vs Actual values of Oxidation for model 3

#### **4 CONCLUSION**

We can see there are three equations or model developed which are significant as there  $R^2 \geq 0.80$  for relationship between peroxide value and Microwave heating time duration.

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