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

Ravi Shankar

Department of Food Process Engineering, Vaugh School of Agriculture Engineering and Technology,
Sam HigginBottom Institute of Agriculture, Technology and Sciences-Deemed University,
P.O Naini, Allahabad, U.P-211007, India

ABSTRACT: This is about relating the thermal induction time range from 0-40 minutes for Rape seed 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 RAPE SEED OIL COMPOSITION.

Table 1. [19]Composition of Refined Rape Seed Oil used.

Component	Oil Type
	rapeseed
Main fatty acids (% of peak area)	
Palmitic	2
Stearic	2
C_{20}–C_{22} saturated	2
Monoenoic	49
Dienoic	34
Trienoic	8
Eicosenoic	1.5
Trans-unsaturated	0.5
Peroxide value (meq/kg)	0.58
Acid value (mg/g)	0.07
Conjugated dienes (% m/m)	0.4
Polar compounds (% m/m)	0.8
Tocopherols (mg/kg)	
Tocopherol α	294
Tocopherol β+γ	392
Tocopherol δ	12
Total tocopherols	698

2.2 PREPARATION OF SAMPLES (REFERENCE [19])

2.3 SAMPLE COLLECTION (REFERENCE [19])

*Assumptions

a) Surface area exposed to atmosphere is constant or same.

b) 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:

$R\text{-}H + O_2 \longrightarrow ROOH$ (Reaction I)

Generation of iodine:

$KI + CH_3COOH \longrightarrow HI + CH_3COO^-K^+$ (Reaction II)

$ROOH + 2\,HI \longrightarrow ROH + H_2O + I_2$ + starch indicator (Reaction III)

Titration step:

I_2(purple)$+2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2\,NaI$ (colorless) (Reaction IV)

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:

$O_2^{2-} + 2I^- + 4H^+ \longrightarrow I_2 + 2H_2O$ (Reaction V)

$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$ (Reaction VI)

2.4.1.4 PROCEDURE

i) Approx. 3.0g of the sample was transfered, 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 shaked 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, $y = \beta 0 + \sum \beta_i x_i + \sum \beta_{ii} x^2{}_i$, where y is the response, xi is the uncoded independent variable (factor), and $\beta 0$, β_i, β_{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)

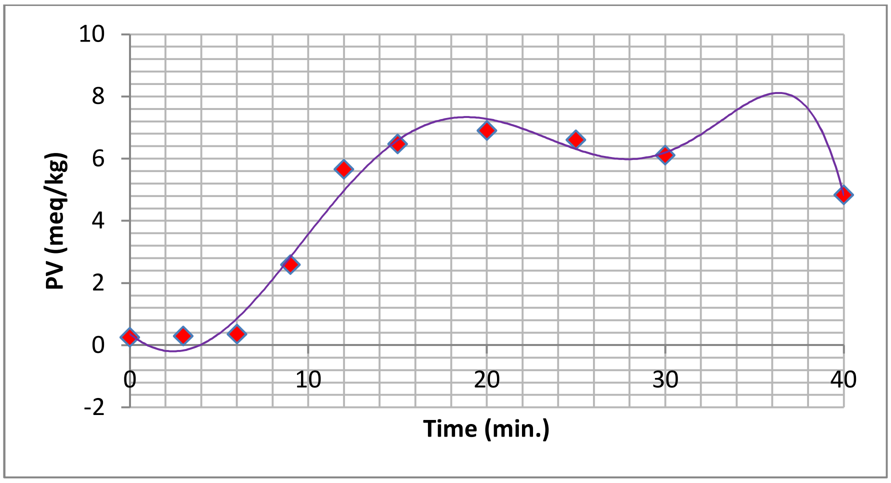

Fig 1. Graph plotted on M S Excel peroxide value Vs Induction Time during Microwave cooking of oil.

Model 1 equation:

$y = -2E\text{-}07x^6 + 2E\text{-}05x^5 - 0.0006x^4 + 0.003x^3 + 0.0889x^2 - 0.4552x + 0.361$
$R^2 = 0.9826$

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

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	2.12	0.5014	0.4391	0.0117	71.47	
Quadratic	1.12	0.8775	0.8425	0.7492	18.14	Suggested
Cubic	1.21	0.8791	0.8187	-1.2737	164.43	
Quartic	0.77	0.9587	0.9257	-6.1478	516.91	Suggested
Fifth	0.62	0.9787	0.9520	-3.9871	360.65	
Sixth	0.65	0.9826	0.9479	-669.0200	48453.88	

"Model Summary Statistics": Focus on the model maximizing the "Adjusted R-Squared" and the "Predicted R-Squared".

Table 3. showing P-Value for fit summary

Summary (detailed tables shown below)

Source	Sequential p-value	Lack of Fit p-value	Adjusted R-Squared	Predicted R-Squared	
Linear	0.0219		0.4391	0.0117	
Quadratic	0.0024		0.8425	0.7492	Suggested
Cubic	0.7864		0.8187	-1.2737	
Quartic	0.0267		0.9257	-6.1478	Suggested
Fifth	0.1250		0.9520	-3.9871	
Sixth	0.4695		0.9479	-669.0200	

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	160.44	1	160.44			
Linear vs Mean	36.26	1	36.26	8.05	0.0219	
Quadratic vs Li	27.20	1	27.20	21.49	0.0024	Suggested
Cubic vs Quad	0.12	1	0.12	0.080	0.7864	
Quartic vs Cub	5.76	1	5.76	9.64	0.0267	Suggested
Fifth vs Quartic	1.44	1	1.44	3.75	0.1250	
Sixth vs Fifth	0.29	1	0.29	0.68	0.4695	
Residual	1.26	3	0.42			
Total	232.76	10	23.28			

"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 Quadratic 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	63.46	2	31.73	25.07	0.0006	significant
A-Time	*28.94*	*1*	*28.94*	*22.87*	*0.0020*	
A^2	*27.20*	*1*	*27.20*	*21.49*	*0.0024*	
Residual	8.86	7	1.27			
Cor Total	72.32	9				

The Model F-value of 25.07 implies the model is significant. There is only a 0.06% chance that an F-value this large could occur due to noise.

Table 6. ANOVA analysis table.

Std. Dev.	1.12	R-Squared	0.8775
Mean	4.01	Adj R-Squared	0.8425
C.V. %	28.08	Pred R-Square	0.7492
PRESS	18.14	Adeq Precisior	12.732

The "Pred R-Squared" of 0.7492 is in reasonable agreement with the "Adj R-Squared" of 0.8425; i.e. the difference is less than 0.2.

Model 2 Fifth degree equation from the Design Expert Software 8.0

Final Equation in Terms of Actual Factors:

PV =
-0.99221
+0.60056 * Time
-0.011471 * $Time^2$

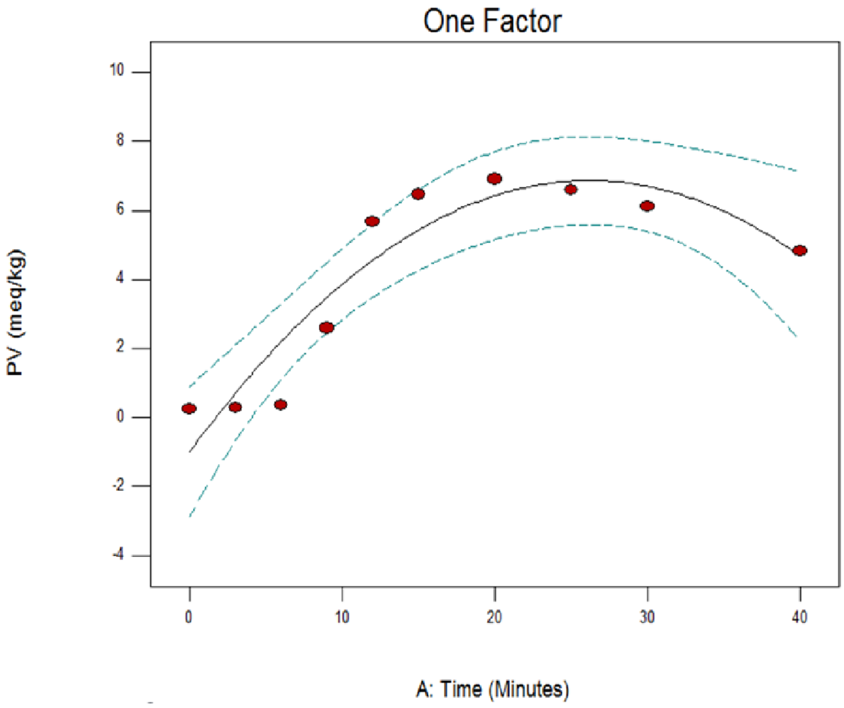

Fig 2. Graph Peroxide value Vs Induction Time by Software for Quadratic Model

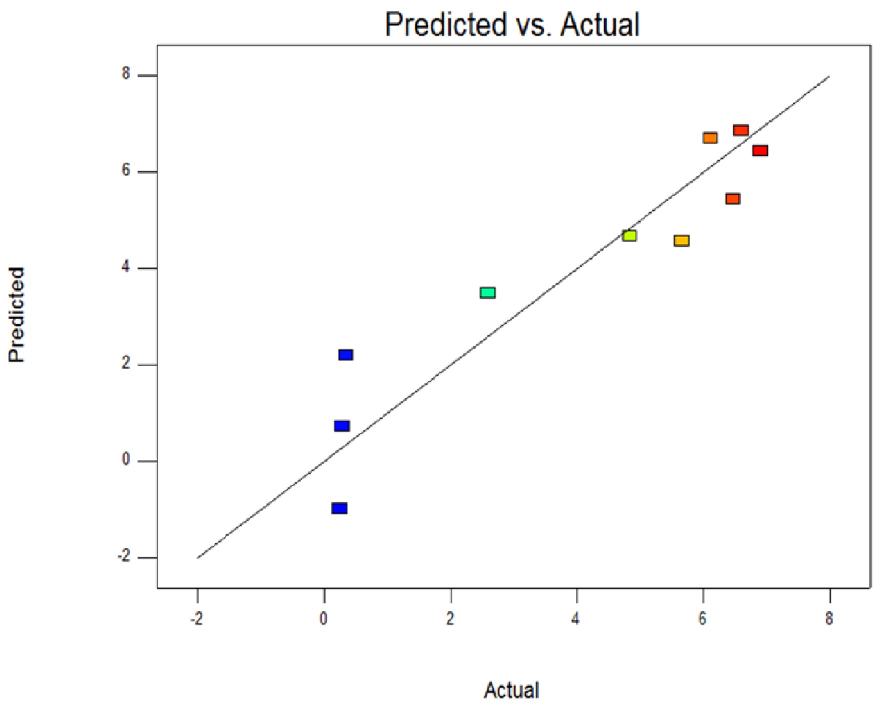

Fig 3. Graph Predicted Vs Actual values of Oxidation for model 2

Table 7. ANOVA for Response Surface Quadratic model

Response 1 PV

ANOVA for Response Surface Quadratic 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	97.93	2	48.96	18.87	0.0015	significant
A-Time	*30.15*	*1*	*30.15*	*11.62*	*0.0113*	
A^2	*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 Precisior	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 2 Quadratic Equation by Design Expert Software 8.0

Final Equation in Terms of Actual Factors:

PV =

-0.017681

+0.80836 * Time

-0.016592 * $Time^2$

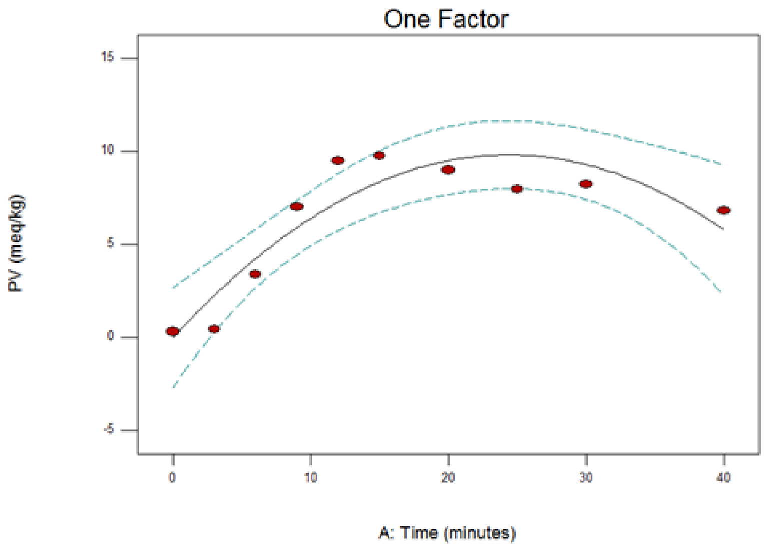

Fig 4. Graph Peroxide value Vs Induction Time by Software for Quadratic Model

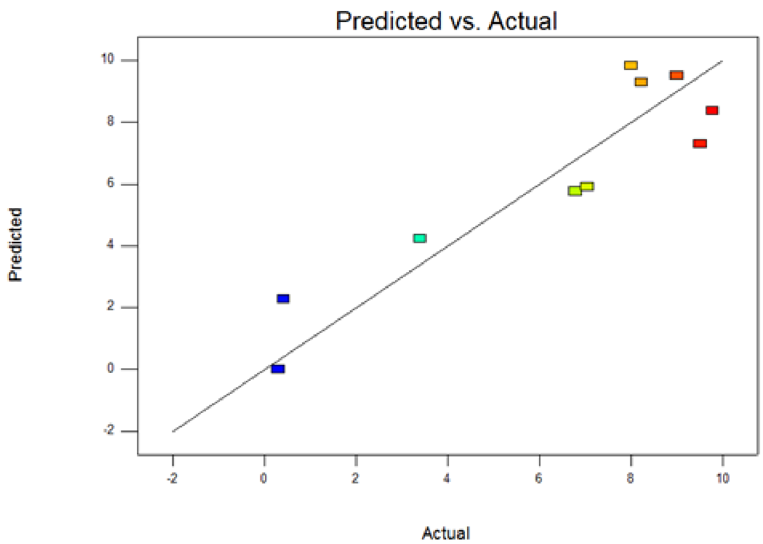

Fig 5. Graph Predicted Vs Actual values of Oxidation for model 2

4 CONCLUSION

We can see there are three equations or model developed which are significant as there R^2>=0.8775 for relationship between peroxide value and Microwave heating time duration.

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AUTHOR’S BIOGRAPHY

RAVI SHANKAR- AMIMI, AMIAEI, AMIE, Pursuing M.Tech (4th sem) in Food Technology (Food Process Engineering), Department of Food Process Engineering, Vaugh School of Agriculture Engineering and Technology, SHIATS-Deemed University, P.O-Naini, Allahabad, U.P-211007, India. B.E in Food Technology, SLIET, Sangrur, (P.T.U) Punjab, India.

CORRESPONDENCE AUTHOR’S ADDRESS

Ravi Shankar

Duplex no. 40, Dev Villa, Post Office Road, Mango, Jamshedpur, Jharkhand-831001