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Mathematical Modeling of Degree of Thermal Oxidation of Lard 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 Lard 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 or fat 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 or fat.

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 Fat can enable the determination of time of cook of edible Fat 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 fat. 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 Lard 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 fat 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 lard. 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 lard 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.

2 MATERIALS AND METHODS

2.1 EDIBLE LARD COMPOSITION.

Table 1. [19]Composition of Lard used.

Component	Pork lard
Main fatty acids (% of peak area)	
Palmitic	28
Stearic	11
C_{20}–C_{22} saturated	1
Monoenoic	52
Dienoic	6
Trienoic	trace
Eicosenoic	–
Trans-unsaturated	trace
Peroxide value (meq/kg)	1.2
Acid value (mg/g)	0.6
Conjugated dienes (% m/m)	trace
Polar compounds (% m/m)	1.2
Tocopherols (mg/kg)	
Tocopherol α	5
Tocopherol β+γ	—
Tocopherol δ	—
Total tocopherols	5

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)

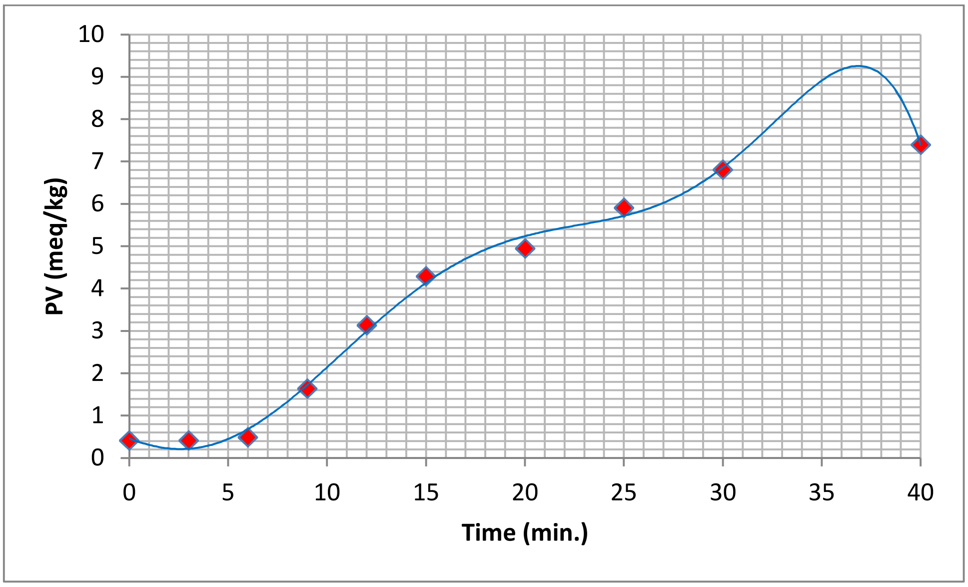

Fig 1. Graph plotted on M S Excel peroxide value Vs Induction Time during Microwave cooking of Lard.

Model 1 equation:

$y = -1E-07x^6 + 1E-05x^5 - 0.0005x^4 + 0.0047x^3 + 0.0206x^2 - 0.1726x + 0.4587$
$R^2 = 0.9962$

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

Summary (detailed tables shown below)

Source	Sequential p-value	Lack of Fit p-value	Adjusted R-Squared	Predicted R-Squared	
Linear	< 0.0001		0.9246	0.8624	
Quadratic	0.0443		0.9535	0.8840	Suggested
Cubic	0.1181		0.9651	0.7004	
Quartic	0.0688		0.9798	-1.1211	
Fifth	0.1174		0.9873	-1.7514	
Sixth	0.3145		0.9886	-230.8472	

Table 3. showing P-Value for fit summary

Sequential Model Sum of Squares [Type I]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Mean vs Total	125.39	1	125.39			
Linear vs Mean	61.92	1	61.92	111.29	< 0.0001	
Quadratic vs Linear	2.05	1	2.05	5.99	0.0443	Suggested
Cubic vs Quad	0.86	1	0.86	3.33	0.1181	
Quartic vs Cub	0.80	1	0.80	5.34	0.0688	
Fifth vs Quartic	0.37	1	0.37	3.96	0.1174	
Sixth vs Fifth	0.12	1	0.12	1.45	0.3145	
Residual	0.25	3	0.084			
Total	191.76	10	19.18			

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	125.39	1	125.39			
Linear vs Mean	61.92	1	61.92	111.29	< 0.0001	
Quadratic vs Linear	2.05	1	2.05	5.99	0.0443	Suggested
Cubic vs Quad	0.86	1	0.86	3.33	0.1181	
Quartic vs Cub	0.80	1	0.80	5.34	0.0688	
Fifth vs Quartic	0.37	1	0.37	3.96	0.1174	
Sixth vs Fifth	0.12	1	0.12	1.45	0.3145	
Residual	0.25	3	0.084			
Total	191.76	10	19.18			

Table 5. Model Summary Statistics

Model Summary Statistics

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	
Linear	0.75	0.9329	0.9246	0.8624	9.13	
Quadratic	0.59	0.9639	0.9535	0.8840	7.70	Suggested
Cubic	0.51	0.9767	0.9651	0.7004	19.88	
Quartic	0.39	0.9888	0.9798	-1.1211	140.79	
Fifth	0.31	0.9944	0.9873	-1.7514	182.63	
Sixth	0.29	0.9962	0.9886	-230.8472	15388.84	

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

Table 6. showing 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	63.98	2	31.99	93.34	< 0.0001	significant
A-Time	*58.54*	*1*	*58.54*	*170.82*	*< 0.0001*	
A^2	*2.05*	*1*	*2.05*	*5.99*	*0.0443*	
Residual	2.40	7	0.34			
Cor Total	66.37	9				

The Model F-value of 93.34 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise.

Table 7. ANOVA analysis table.

Std. Dev.	0.59	R-Squared	0.9639
Mean	3.54	Adj R-Squared	0.9535
C.V. %	16.53	Pred R-Square	0.8840
PRESS	7.70	Adeq Precisior	25.148

The "Pred R-Squared" of 0.8840 is in reasonable agreement with the "Adj R-Squared" of 0.9535; 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:

$$PV = -0.43436 + 0.32764 * Time - 3.15126E-003 * Time^2$$

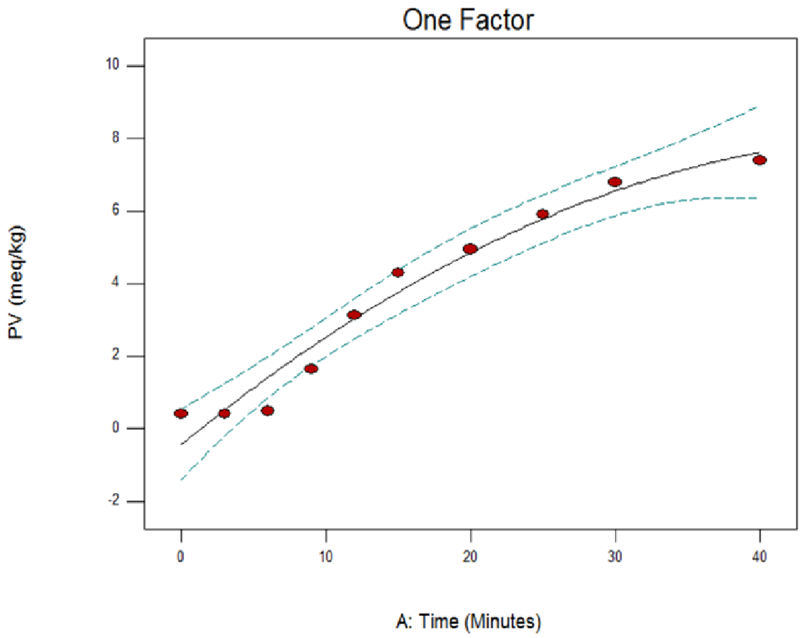

Fig 2. Graph Peroxide value Vs Induction Time by Software for Quadratic Model

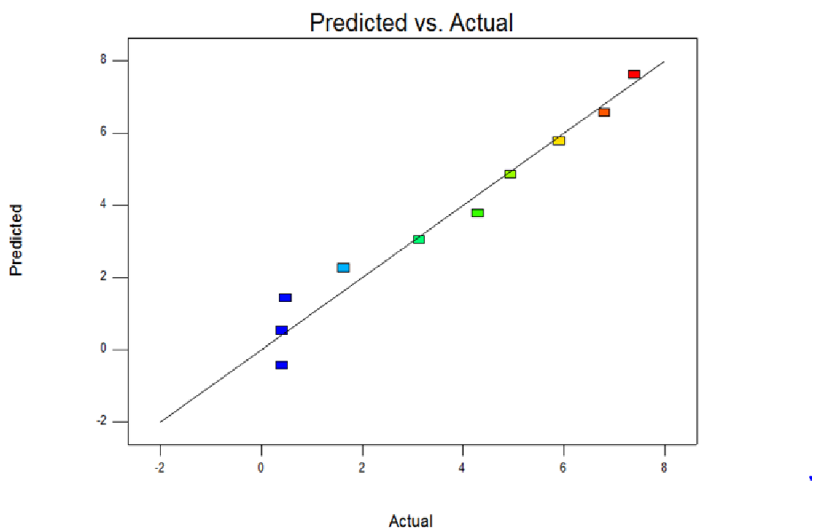

Fig 3. Graph Predicted Vs Actual values of Oxidation for model 2

4 CONCLUSION

We can see there are two equations or models developed which are significant as there R^2 >=0.9639 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.