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Mathematical Modeling of Degree of Thermal Oxidation of Edible Oil as a Function of Induction Temperature for Various Fixed Induction Time

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Abstract- This study was conducted for the Modeling of Degree of Thermal Oxidation of Blended Refined Edible Oil (80% sunflower and 20% Soya bean Oil) in respect to Induction Temperature at various different fixed Induction Times. In this, different models have been developed for Peroxide Value of edible oil for different fixed time (0-120) minutes, within the Temperature range of 120 – 200 ^{0}C with interval of 5 ^{0}C and graphs (with R^2) have been plotted using Microsoft EXCEL.

Index Terms- Peroxide value, Induction time, Induction temperature, MS Excel.

I. 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 temperature of edible oil which would lead to the least amount of oxidation as well as the induction or exposure time of the oil to the high temperature for the same desirable requirement of minimizing the oxidation of edible oil during processing using edible oils as a heating medium.

Mathematical models can enable the optimization of frying time and temperature to reduce the rancidity of frying oils. In light of above considerations the study was conducted in order to attain the following objectives

1) To determine the relationship of the Thermal oxidation as function of temperature and induction time of the frying oil.
2) To develop a mathematical model for optimization of time and temperature for minimum rancidity or thermal oxidation of edible oil use in the frying or cooking process.

The chemistry of oxidation at high temperatures is very complex since both thermal and oxidative reactions are involved. During the deep fat frying a number of chemical reactions takes place – hydrolysis, oxidation, thermal decomposition and polymerization. The chemical mechanism of thermal oxidation is principally the same as the autoxidation mechanism, but the thermal oxidation rate is faster than the autoxidation rate. Oxidative stability is very important factor in oil quality especially for these used for frying because of the high temperature applied. Frying oil must have high oxidative stability during use. On the other hand, the presence of natural substances such as tocopherols, oryzanol, sterol fraction, squalene etc., enhances their stability at higher temperatures. Since many factors affect the rate of deterioration of fats used for deep-fat frying, no single procedure will be reliable under all conditions. With prolonged heating time the accumulation of deterioration products leads to organoleptic failures and a decrease of the nutritive value. Deep-fat frying decreases the unsaturated fatty acids and increases polar material. Many methods have been used for determination of fat deterioration during frying. They include methods for assessment of peroxide value, iodine value dienes, fatty acids, polar components etc.

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.

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II. MATERIALS AND METHODS

Oil was purchased from the market as refined blended oil (80% sunflower oil and 20% soyabean oil) of composition as shown in Table I.

TABLE I Approx. Composition of Oil.

Contents	Qty. per 100g
Energy	900
Carbohydrate (g)	0
Protein (g)	0
Fat (g)	100
- Saturated fatty acids (g)	10
- Monounsaturated fatty acid (g)	26
- Polyunsaturated fatty acid (g)	64
- Omega-6 [n-6] (g)	63
- Omega-3 [n-3] (g)	1
- Trans fatty acid (g)	0
Total Essential fatty acids (g)	53
Cholesterol (mg)	0
Vitamin E (mg/I.U*)	50/50
Moisture (g)	0.987
Peroxide value (meq) at 28 ^{0}C	19.8
AntiOxidant TBHQ (mg)	12

1 Preparation of samples

The oil was first heated on hot plate in 500 ml beaker filled to 290ml, to reach the required temperature and then incubated in hot baking oven to maintain the temperature of the oil for required time intervals.

2 Sample Collection

2.1 Firstly, Samples (30 ml) were collected in the brown color bottle within the temperature range of 120-200 ^{0}C with interval of 10 ^{0}C for 0-120 minutes of induction time with the interval of 20 minute. And so the number of sample was 9*7=63. And there peroxide values were measured.

2.2 Secondly, Samples (30 ml) were collected in the brown color bottle within the temperature range of 125-195 ^{0}C with the interval of 10 ^{0}C for 0-60 minutes of induction time with the interval of 15 minute. And so the number of sample was 8*5=40. And there peroxide values were measured.

As such total number of samples collected was (63+40)=103.

*Assumptions

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

b) No mixing or agitation.

III. MEASUREMENT OF OXIDATION

3.1 Peroxide Value (PV) Analytical method.

3.1.1 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.

3.1.2 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.

<u>Generation of hydroperoxides:</u>

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

<u>Generation of iodine:</u>

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

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

<u>Titration step:</u>

I_2 (purple) + $2\ Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2\ NaI$ (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)

3.1.4 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.

3.1.5 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)

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

IV. GRAPHICAL ANALYSIS

The experimental data obtain using the previous procedures were analyzed by plotting Graph and developing Models for various observations for 17 different temperatures within the range of 120-200 ^{0}C with interval of 5 ^{0}C.

V. RESULT

Below are the different graphs plotted for peroxide value (meq/kg) verses induction temperature (^{0}C) for different fixed time (minutes) and the developed Models (where y is peroxide value and x is temperature in ^{0}C).

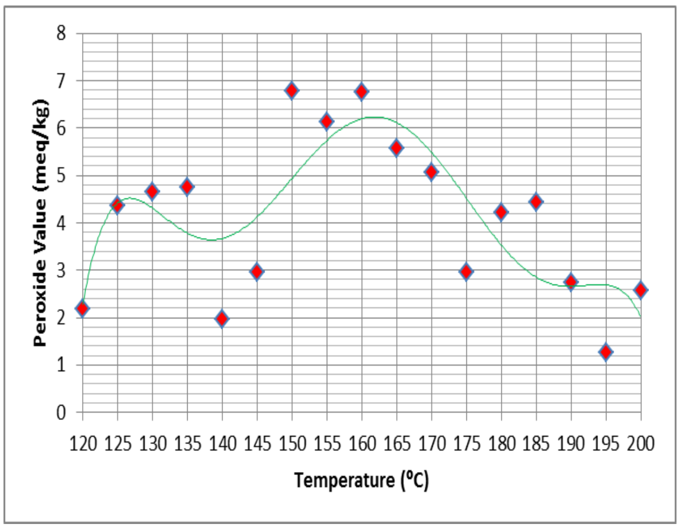

Figure 1. Peroxide value(meq/kg) Vs Induction Temperature (^{0}C) for 0 minute.

Developed Model I

$y = -5E\text{-}09x^6 + 5E\text{-}06x^5 - 0.002x^4 + 0.4367x^3 - 52.021x^2 + 3281x - 85603$

$R^2 = 0.6169$

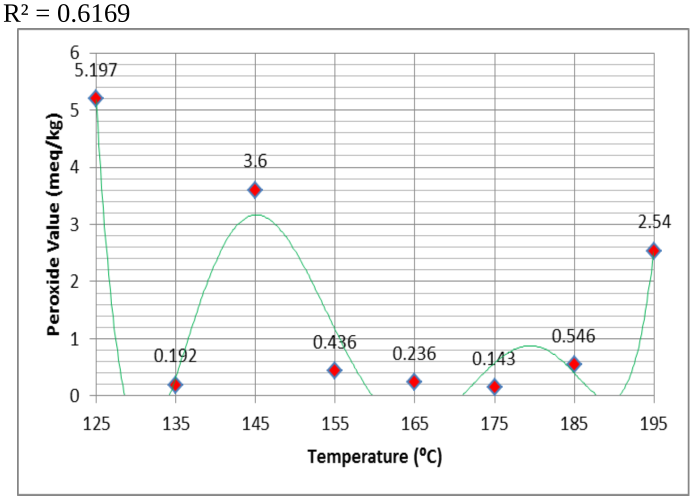

Figure 2. Peroxide value(meq/kg) Vs Induction Temperature (^{0}C) for 15 minute.

Developed Model II

$y = 2E\text{-}08x^6 - 2E\text{-}05x^5 + 0.0094x^4 - 2.0021x^3 + 239.94x^2 - 15263x + 402615$

$R^2 = 0.9445$

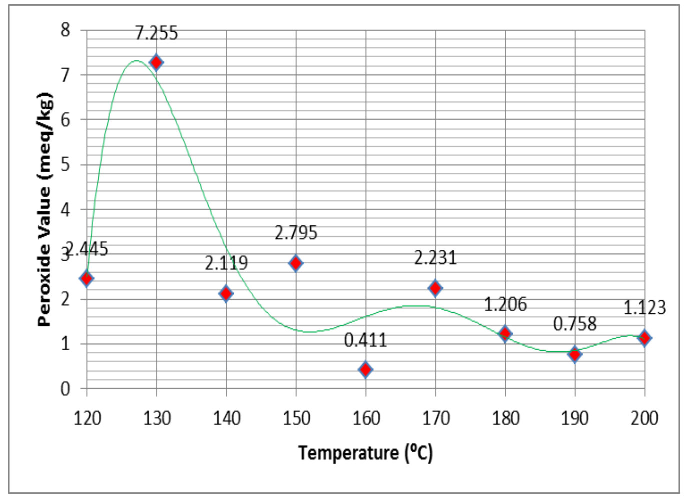

Figure 3. Peroxide value(meq/kg) Vs Induction Temperature (^{0}C) for 20 minute.

Developed Model II

$y = -0.0048x^6 + 0.1628x^5 - 2.1795x^4 + 14.574x^3 - 50.234x^2 + 81.023x - 40.841$

$R^2 = 0.8497$

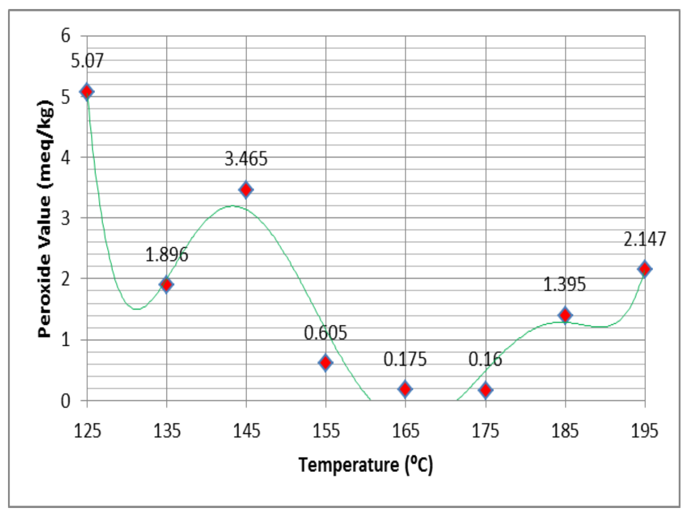

Figure 4. Peroxide value(meq/kg) Vs Induction Temperature (^{0}C) for 30 minute.

Developed Model IV

$y = 0.0135x^6 - 0.3883x^5 + 4.3828x^4 - 24.539x^3 + 70.627x^2 - 97.717x + 52.674$

$R^2 = 0.9589$

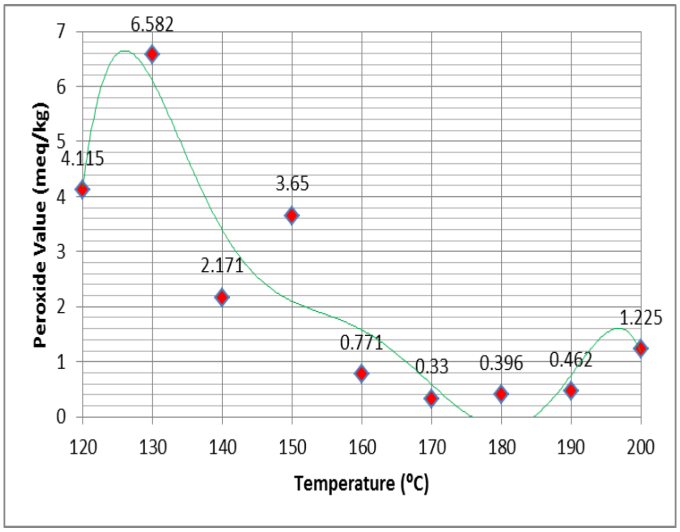

Figure 5. Peroxide value(meq/kg) Vs Induction Temperature (^{0}C) for 40 minute.

Developed Model V

$y = -0.0049x^6 + 0.1542x^5 - 1.8991x^4 + 11.699x^3 - 37.418x^2 + 56.288x - 24.628$

$R^2 = 0.8599$

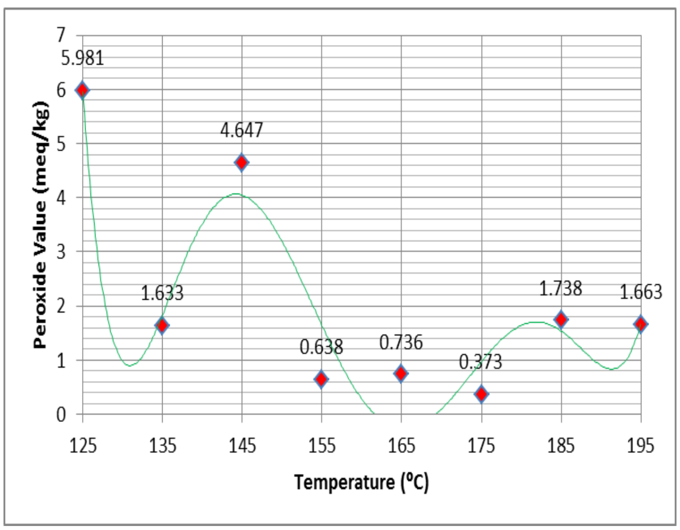

Figure 6. Peroxide value(meq/kg) Vs Induction Temperature (^{0}C) for 45 minute.

Developed Model VI

$y = 0.0202x^6 - 0.5789x^5 + 6.5237x^4 - 36.508x^3 + 105.14x^2 - 145.15x + 76.515$

$R^2 = 0.9031$

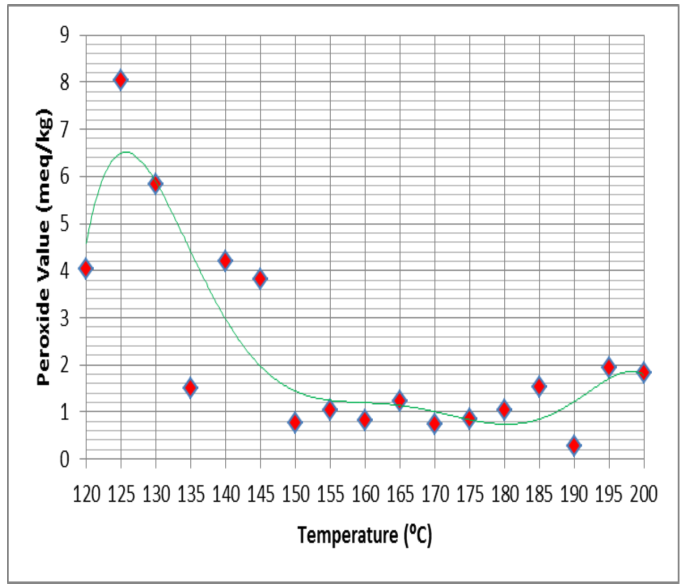

Figure 7. Peroxide value(meq/kg) Vs Induction Temperature (^{0}C) for 60 minute.

Developed Model VII

y = -3E-09x6 + 3E-06x5 - 0.0013x4 + 0.2835x3 - 34.385x2 + 2210.5x - 58815

$R^2 = 0.7527$

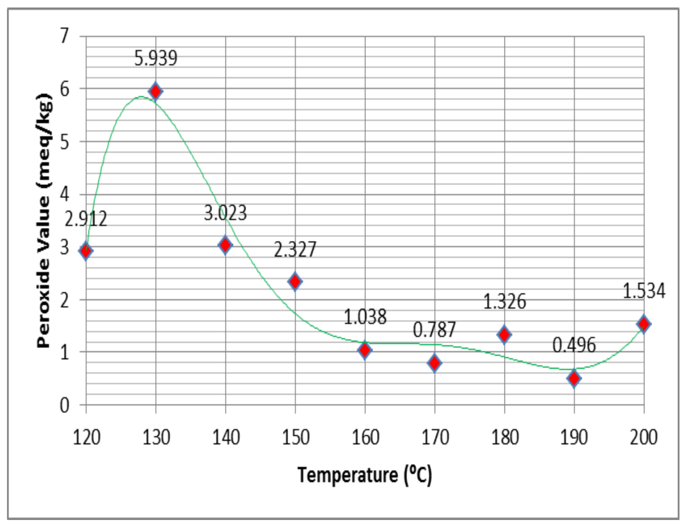

Figure 8. Peroxide value(meq/kg) Vs Induction Temperature (^{0}C) for 80 minute.

Developed Model VIII

$y = -0.0013x^6 + 0.0485x^5 - 0.7329x^4 + 5.4942x^3 - 21.098x^2 + 37.174x - 17.936$

$R^2 = 0.9539$

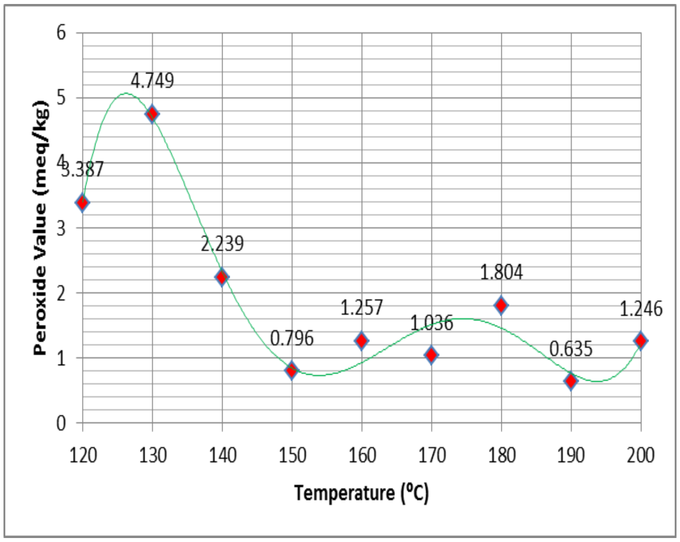

Figure 9. Peroxide value(meq/kg) Vs Induction Temperature (^{0}C) for 100 minute.

Developed Model IX

$$y = -0.0007x^6 + 0.0323x^5 - 0.552x^4 + 4.4181x^3 - 17.248x^2 + 29.435x - 12.688$$

$R^2 = 0.9676$

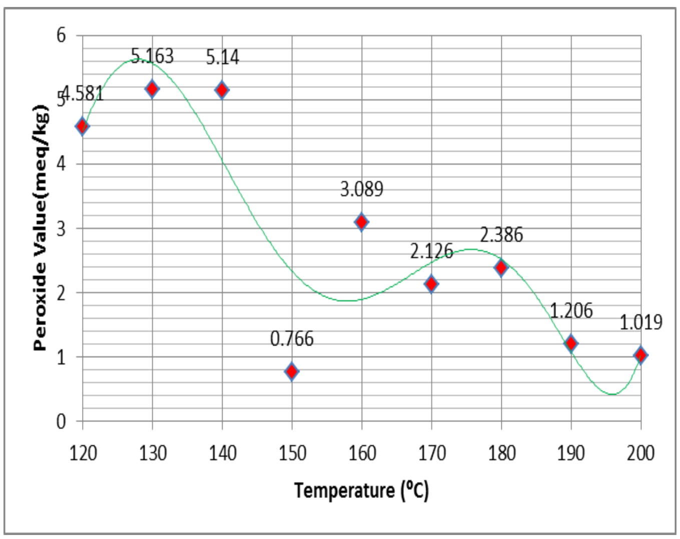

Figure 10. Peroxide value(meq/kg) Vs Induction Temperature (^{0}C) for 120 minute.

Developed Model X

$$y = 0.0019x^6 - 0.048x^5 + 0.4153x^4 - 1.3153x^3 - 0.0233x^2 + 5.4557x + 0.034$$

$R^2 = 0.7829$

VI. DISCUSSION

Most of the Models developed are of higher order polynomial, mainly of fourth, fifth or sixth order and R^2 for some of them are close to 1.0, except for models X, VII and I. Model I for 0 minute induction time is not so fit for prediction with R^2=0.6169. Rest of the suggested models are best fit to the plotted graph and one can easily determine or predict the values of peroxide at different temperature of induction for fixed Induction time.

VII. CONCLUSION

The models developed are to best fit the curve plotted (PV vs time) and helpful in determination of the temperature of heating for minimum peroxide value of oil for fixed time of cook.

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