Mathematical Modeling and Thermodynamic Properties of Drying of Dekoko Seed

Tamirat Redae Gebreslassie, Nedumaran Balasubramanian

Abstract— Investigating mathematical model and drying kinetics of dekoko (*Pisum sativum var. Abyssinicum*) seeds is the crucial factor in modeling and design of various heat and mass transfer process application of heating and cooling systems. Whereas, thermodynamic properties used to estimate the conduction, convection and mass transfer energy requirement during drying process of the product. Drying characteristics of dekoko seed abtained based on two design parameters such as temperature and air flow rate. Drying experiment carried out with temperature at 45, 55 and 65°C and air flow rate at 1.5 and 2.5 ms^{-1}.The resulting data was analysed for nine models and dekoko seed drying follows logarithmic model with high R^2 and minimum RMSE and SSE values. The effective moisture diffusivities of dekoko seed increased from 3.07×10^{-11} m^2 s^{-1} to 5.04×10^{-11} m^{2}s^{-1} at 1.5 ms^{-1} and from 3.47×10^{-11} m^{2}s^{-1} to 6.57×10^{-11} m^{2}s^{-1} at 2.5 ms^{-1} of air flow rate as drying temperature increase from 45°C to 65°C. The enthalpy decreased with increasing temperature where as Gibbs free energy and entropy were increased at the specified temperature. The drying of dekoko seed is a fesible, slow and endothermic process favourable at higher temperature.

Index Terms— Activation energy, Dekoko seed, Effective Moisture Diffusivity, Gibbs Energy, Drying Process.

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1 INTRODUCTION

DEKOKO (*Pisum sativum var. Abyssinicum*) is one of the family Fabacea plants, harvested only in northern Ethiopia of Tigray region with the local name ***Raya***. Economically in the local market, the price of dekoko seed is twice as much as those of the other winter season food legumes. It has a marvelous taste and high protein content provide upto 39% of the total amino acid [1]. The nutritional composition of dekoko seed was reported as 251 g protein, 19 g fat, 31.7 g total sugar, 370 g starch and 370 g neutral detergent fiber per kg. Dekoko contains 7% lysine and 3% Sulphur.

Drying is a complex separation process of unit operation where simultaneous heat and mass transfer takes place, to reduce the undesired water content to a desired level without altering the physical characteristics of the raw material or the finished products to enhance the quality as well as the shelf life of the product. Drying also enhances the stability of product, improve handling, transportation and storage. It is the critical unit operation in chemical and food processing industries to improve the quality of final product and to estimate the energy consumption [2]. For techno economic feasibility studies involving energy consumption, knowledge of drying kinetic charecteristics between the dried product and the transfer of water within the product is important. There are several models suggested for drying nd their thermodynamic properties on various agricultural products. Thin layer drying model for parboiled wheat [3], rough rice [4], [5], effect of drying air parameters for rice drying [6], comparative studies on thin layer for drying of wheat [7] and single layer drying equation for rough rice [8] are kown models.

The objective of this study is to get experimental information for modelling drying process of dekoko seed and its thermodynamic properties and to determine the effective moisture diffusivities at 1.5 and 2.5 ms^{-1} air velocity which has not been found in the literature.

2 MATERIAL AND METHODS

2.1 Tray Dryer Unit

Laboratory conventional tray dryer (Proras) unit, 3.5kW heating element, made of stainless steal of dimension 0.24x0.38x0.038 m consists of an air duct with a transparent section for viewing as shown in Fig. 1. The wet dekoko seed placed on trays were improved its drying process by heated air passes to the duct. The humidity, temperature and air velocity inside the duct can be measured with an anemometer and a combined temperature and humidity sensor at measuring point before and after the particle samples as shown in schematic diagram in Fig. 2. The weight loss sample on the tray being continuously measured by digital electronic balance with accuracy of 0.01 g .

Fig.1. Tray Dryer Unit

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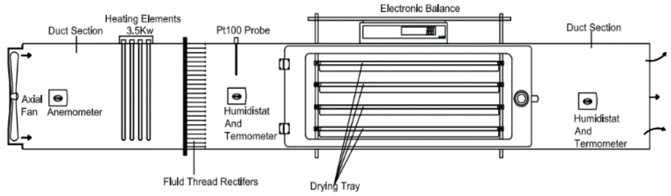

Fig. 2. Tray Dryer Schematic Diagram

2.2 Sample Preparation

The impurities were cleaned by commercial laboratory sieves as the seeds were produced from the local market. To improve the drying process, about 3 kg of dekoko seeds were soaked at temperature 45 °C for 2 h in the water bath. Using 1 mm mesh size sieve, excess water was drained and the samples were kept in a sealed plastic bags to prevent from oxidation and germination. To create uniform moisture distribution, samples were stored in the refrigerator at 5 ± 1 °C for 7 days. The required amount of sample was withdrawn from the refrigerator and reconditioned at the room temperature for 1 h before conducting the experiment.

2.3 Determination of Moisture Content

The amount of water per unit mass of dry dekoko seed after equilibration was determined at the time of experiment in three replications in a circulating air oven at 105 ±2 °C for 24 h [9] with the equation Eq. 1.

$$M_{iX}(db) = \left(\frac{M_{iX} - M_{i+\Delta X}}{M_{iX}}\right) \times 100 \tag{1}$$

Where M_{iX}(db) is the % moisture content on dry basis (kg of water / kg of dry mater), M_{iX} is sample weight before drying and $M_{i+\Delta X}$ is sample weight after drying.

2.4 Matematical Modeling of Drying Kinetics

Mathematical modeling of the drying process is based on set of equations to describe the system as accurately as possible {10], [11]. Modeling interrelates the physical nature of the water content and the product to be dried within the system for improving, designing and operation of the drying system [12]. To determine the moisture ratio of dekoko seed during the drying process, experiments were conducted at 45, 55, and 65 °C of temperature and 1.5 and 2.5 ms^{-1} of air flow rate. The dimentionless moisture ratio (MR) was calculated using Eq. (2) [7], [8], [13].

$$MR = \frac{M_t - M_e}{M_{iX} - M_{te}} \tag{2}$$

Where MR is the moisture ratio, M_t is the moisture content at time t, M_e is the equilibrium moisture content and M_{iX} is the initial moisture content (kg of water/ kg of dry matter).

The validation of various non-linear parametric models was performed using MATLAB R2014a and the goodness of fit of those models were verified and selected based on the statistical parameters of the correlation coefficient (R^2), root mean square error (RSME) and sum squared error (SSE) as given in equation Eq. (3) and Eq. (4) [13], [14].

$$RMSE = \left[\sum_{i=1}^{n}(MR_{pre,i} - MR_{exp,i})^2/N\right]^{1/2} \tag{3}$$

$$SSE = \sum_{i=1}^{n}(MR_{pre,i} - MR_{exp,i})^2/(N - Z) \tag{4}$$

Where $MR_{exp,i}$ and $MR_{pre,i}$ is the ith experimentally observed and predicted moisture rtio respectively, N is the number of observations and Z is the number of constants in the model.

TABLE 1
DRYING MODELS

Sl No - Model Name	Model equation Moisture Ratio (Rx)	Ref.
I - Wang and Sing	$Rx = 1 + at + bt^2$	[8]
II - Lewis (Newton)	$Rx = \exp(-k.t)$	[3]
III - Logarithimic	$Rx = a.\exp(-kt) + c$	[13]
IV -Two exponential terms	$Rx = a.\exp(-kt) + (1-a)\exp(-kat)$	[26]
V - Verma	$Rx = a.\exp(-kt) + (1-a)\exp(-k_1 t)$	[6]
VI- Approximate Diffusion	$Rx = a.\exp(-kt) + (1-a)\exp(-kbt)$	[28]
VII - Two terms	$Rx = a.\exp(-k_1 t) + b.\exp(-k_2 t)$	[23]
VIII - Thompson	$Rx = ((-a - (a^2 + 4bt)^{0.5}./2b)$	[16]
IX - Modified Henderson and Pabis	$Rx = a\exp(-kt) + b\exp(-gt) + c\exp(-ht)$	[5]

2.5 Drying Rate Constant (k) and Effective moisture Diffusivity (D_{eff})

Fock's law of diffusin is commonly used for detrmining the mass transfer diffusion coefficient (D_{eff}) and drying constant (k). For hollow spherical geometry, three dimentional unsteady state mass diffusion of dekoko seed was determined using Eq. (5) with the assumption of the initial moisture content independent of other parameters evaporation of moisture and the equilibrium moisture at the surface. The internal and external heat transfer was due to consuction and convection respectively [15].

Unsteady effective moisture diffusivity (D_{eff}

$$\frac{\partial M}{\partial t} = \frac{\partial}{\partial x}\left(D_{eff}\frac{\partial M}{\partial x}\right) + \frac{\partial}{\partial y}\left(D_{eff}\frac{\partial M}{\partial y}\right) + \frac{\partial}{\partial z}\left(D_{eff}\frac{\partial M}{\partial z}\right) \tag{5}$$

Where D_{eff} is effective moisture diffusion coefficient, m^{2}s^{-1} and M is water content, kg and t is time, s. Time dependent general solution of Eq. (5) and Fig. 3 for radial diffusion of the hollow sphere was developed [11] with boundary condition $r_1 \le r \le r_2$ of the internal surface $r=r_1$ at concentration C_1 and external surface $r=r_2$ at concentration C_2. The total amount of diffusing substances entering or leaving the hollow sphere at time t is given by

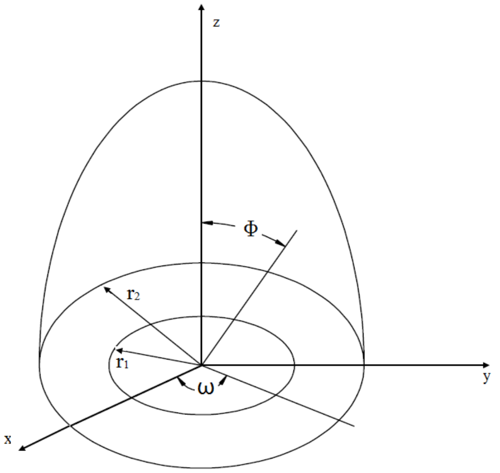

Fig. 3. Geometrical View of hollow sphere

$$MR = \frac{M_t - M_e}{M_{iX} - M_e} = \frac{6}{\pi^2 (r_1^2 + r_1 r_2 + r_2^2)} \sum_{i=1}^{n} \left(\frac{r_2 \cos n\pi - r_1}{n} \right) exp \left(\frac{D_{eff}\, n^2 \pi^2 t}{(r_2 - r_1)^2} \right) \quad (6)$$

Where MR is the dimension less moisture ratio of product, t is the time in s, n is a number of terms, r_2 is equivalent radius in m and pi=3.14159. In limiting to the first term of the equation Eq. (6), it became

$$MR = \frac{M_t - M_e}{M_{iX} - M_e} = \frac{6}{\pi^2} \left(\frac{r_1^2 + r_2^2}{r_1^2 + r_1 r_2 + r_2^2} \right) exp \left(\frac{D_{eff}\, n^2 \pi^2 t}{(r_2 - r_1)^2} \right) \quad (7)$$

For long drying time (MR<0.6), Eq. (6) can be simplified as Eq. (7) by taking the first term of a series solution and taking natural logarithm both side the resulting equation (8) follows:

$$\ln(MR) = ln \left(\frac{6}{\pi^2} \right) - \left(\frac{\pi^2 D_{eff}}{r_2^2} \right) t \quad (8)$$

The effective moisture diffusivity D_{eff} was determined by plotting ln(MR) versus drying time will yield a linear model with slope (U) Eq. (9)

$$U = \left(\frac{\pi^2 D_{eff}}{r_2^2} \right) \quad (9)$$

The equivalent radius r_2 is defined as the radius of the hypothetical sphere having the same or equivalent volume with real particle (dekoko seed). It has been determined by measuring three dimensions of 25 randomly selected seeds using digital caliper with accuracy 0.01 mm and calculated as in Eq. (10)

$$r_2 = \frac{(x \times y \times z)^{1/3}}{2} \quad (10)$$

2.6 Determination of Activation Energy

The temperature dependence of diffusivity was studied by the Arrhenius relationship using Eq. (11) [18]

$$D_{eff} = D_o exp \left(-\frac{E_a}{RT} \right) \quad (11)$$

Where, E_a is the activation energy required for moisture diffusion in kJkmol^{-1}, R is the universal gas constant, 8.314 kJkmol^{-1} K^{-1}, D_o is the pre exponential factor of Arrhenius equation, m^{2}s^{-1}, T is the drying air temperature, K.

The minimum amount of energy required (E_a) to start moisture diffusion or to transport free water molecules from the internal surface of dekoko seed to surrounding was evaluating by plotting ln(D_{eff}) versus absolute temperature T^{-1} from which the slope (-E_a/R) was determined.

2.7 Thermodynamic Properties

Three hermodynamic properties such as entropy, enthalpy and Gibbs free energy were estimated from the experimental data analysis. Enthalpy is the energy required to reduce the amount of water from from its initial state to the desired level, entropy measures the degree of disorder between the moisture content and the product dried and Gibbs free energy is the energy required to transfer water molecules at vapour state to the solid surface [18]. It is positive for enogenous reaction where energy is necessarily to be added from the surrounding and when it become negative for spontaneous process without addition of energy [19]. Eq. (12), Eq. (13), Eq. (14) were used for calculating the entropy, enthalpy and Gibbs free energy for the drying of dekoko seeds respectively as per the methods prescribed [20],[21].

$$\Delta H = E_a - RT \quad (12)$$

$$\Delta S = R \left(\ln k - \ln \frac{k_B}{h_p} - \ln T \right) \quad (13)$$

$$\Delta G = \Delta H - T\Delta S \quad (14)$$

Where, ΔH is enthalpy, J mol^{-1}, ΔS is Entropy, J mol^{-1} K^{-1} and ΔG is Gibbs free energy, J mol^{-1}, k_B is Boltzmann's constant, 1.38×10^{-23} K^{-1}, h_P is Plank's constant, 6.626×10^{-34} Js^{-1}

3 RESULTS AND DISCUSSIONS

3.1 Moisture Content

Analysis of moisture content after stabilization of the sample is essential to keep the initial moisture content at constant equilibrium level in agreement with ASAE standard procedure and found to be 0.59 on dry basis. The equilibrium moisture content of dekoko seeds after exposure at temperature 45, 55 and 65 °C was found as 0.149 without any deviation of drying temperature. The Similar experimental results for initial moistur content on wet basis reported was for persimmon slices 75.2%, [18], for parboiled wheat 44-45% [3] and 30.2% for rapeseed [22].

3.2 Drying Kinetics

As shown in Fig. 4 moistuure ratio of dekoko seed decreases continuously as the drying time increases. As the temperature and air flow rate increases, the drying time and moisture moisture content decreses due to the fact that an increasing the air enthalpy with in the void space of dekoko seed causing the free water molecules evaporates easily. This phenomena agrees other findins for Sultana grapes [23], crop drying [16], Chia seed [24] and for Soybean grain [20]. Suitability of model fpor drying of dekoko seed was based on the best fit of experimental data with nine model equations as shown in Table 2 for 1.5 ms^{-1} and Table 3 for 2.5 ms^{-1} air flow rate. Though all models fit with resonable R^2, logarithmic model is found to be the best suitable model for the dekoko seed drying as shown in Table 4. As shown in Fig. 5, the experimental and predicted data were having high correilation coefficient fotr this system. How ever page and Weibull model, Wand and Singh model and Midilli models fit well for persimmon slices [18], untreated strawberries [13] and rough rice [4] respectively.

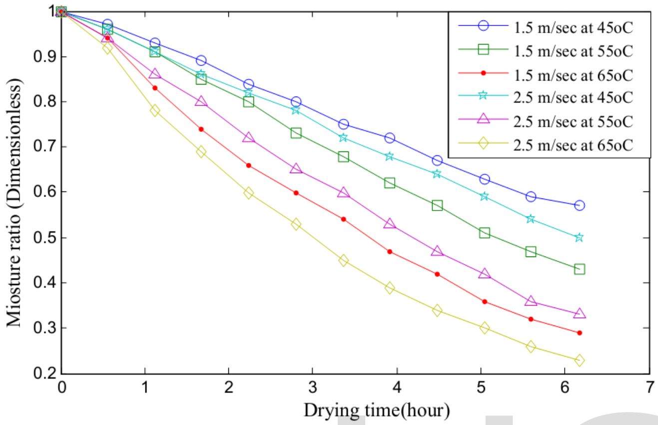

Fig. 4. Moisture Ratio against Drying Time

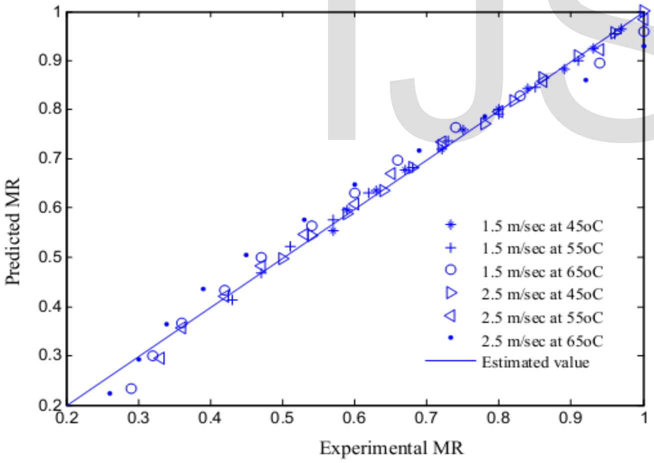

Fig. 5. Comparison of experimental and predicted moisture ratio by logarithimic model

3.3 Effective Moisture Diffusivity

Using Eq. (8) the equivalent radius of dekoko seed was found as 3.09×10^{-3} m. The effective moisture diffusivities of dekoko seed were increased from 3.07×10^{-11} m^2s^{-1} to 5.04×10^{-11} m^2s^{-1} at 1.5 ms^{-1} and from 3.47×10^{-11} m^2s^{-1} to 6.57×10^{-11} m^2s^{-1} at 2.5 ms^{-1} of air flow rate as shown in Fig. 6 as the temperature increase from 45 to 65 °C. This is due to the increase in thermal energy increase the movement of water molecules increase leading to increase in diffusivitySimilar effects were reported for Pistachio nut [24], black tea [26], Persimmon slices [18], [25].

TABLE 2
DRYING CONSTANTS OF LOGARITHIMIC MODEL OF DEKOKO SEEDS

Drying constants	1.5 ms^{-1}			2.5 ms^{-1}		
	45°C	55°C	65°C	45°C	55°C	65°C
a	1.638	1.714	1.303	1.500	1.127	1.067
c	-0.621	-0.6909	-0.2842	-0.482	-0.1122	-0.499
k	0.0522	0.06789	0.1194	0.0663	0.07172	0.2218
R^2	0.9987	0.9982	0.9978	0.9986	0.9988	0.9984

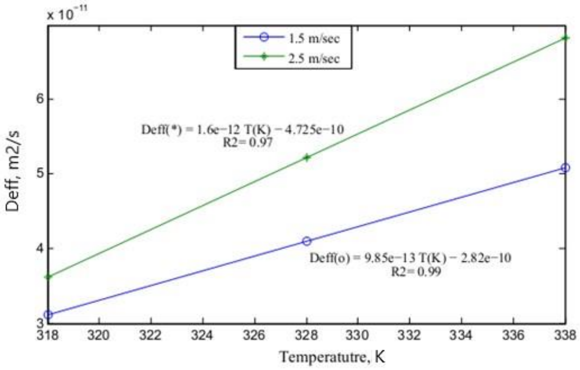

Fig. 6. Effective moisture diffusivity, D_{eff} versus temperature

3.4 Activation Energy

The amount of energy needed for mass diffusion of dekoko seed found as 22.2 $kJmol^{-1}$ and 28.7 $kJmol^{-1}$ at 1.5 ms^{-1} and 2.5 ms^{-1} respectively over the temperature range of 45-65 °C. The relationship between the logarithimic effective moisture diffusivities versus the reciprocal of absolute temperature was presented in Fig. 7. The data was fitted with equation Eq. (11). The D_o increases as the temperature increases from 1.39×10^{-7} to 1.85×10^{-6} m^2s^{-1}. The activation energy also increases from 2673 to 3449 $Jkmol^{-1}$. The diffusivity for other agricultural products varies from 10.676 $kJmol^{-1}$ for Chia seed [24] and 30.79 $kJmol^{-1}$ for pistachio nuts [25].

3.5 Thermodynamic Properties

As shown in Table 7 change in enthalpy, entropy and Gibbs free energy were presented for different temperature and air flow rate. Positive ΔH indicating endothermic process, ΔS negative indicate that the process is feasible and reasonably slow and reversible and positive ΔG indicate that the process is favourable for forward reaction. As the temperature increases the the heat input requirement also reduces since the drying rate increases. Whereas the change intropy decreases at higher temperature and the forward reaction vis-à-vis drying rate increases. Anologus trends were reported for different agricultural products [20], [21], [24], [25]. In general as the air flow rate increases the parameters increases due to increase in moisture carrying capacity of the air.

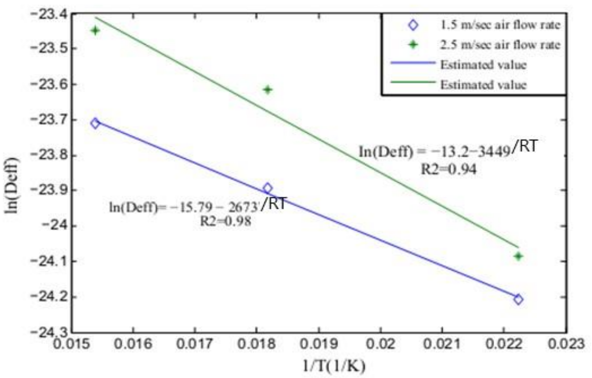

Fig. 7. Arrhenius type relationship between effective moisture diffusivity and reciprocal of absolute temperature

TABLE 3
THERMODYNAMIC PROPERTIES OF DRYING OF DEKOKO SEEDS

Temperature (°C)	ΔH J mol^{-1}	ΔS J mol^{-1} K^{-1}	ΔG J mol^{-1}
1.5 ms^{-1}			
45	19554.9	-269.99	105453.63
55	19471.76	-268.07	107437.93
65	19388.62	-263.62	20008.24
2.5 ms^{-1}			
45	26054.90	-268.01	111321.17
55	25971.76	-267.61	113788.01
65	25888.62	-258.47	113291.53

4 CONCLUSIONS

The experimental investigation of drying of dekoko (*Pisum sativum var. Abyssinicum*) seeds based on the initial moisture ratio of 0.59 to equilibrium moisture ratio of 0.149 follows all established nine models proposed for different agricultural products. Logarithimic model fits well for the drying of dekoko seed. The effective moisture diffusivities described by Arrhenius equation increased as drying temperature and air flow rate 22.2 kJmol^{-1} and 28.7 kJmol^{-1} for 1.5 ms^{-1} and 2.5 ms^{-1} respectively. The change in enthalpy, entropy and Gibbs free energy suggest that the drying of dekoko seed is endothermic, feasible, reasonably slow and favorable in positive direction.

5 ACKNOWLEDGMENTS

Tamirate redae wish to thank gratefully for the financial support provided by Prof Jeong Joong Jeon. We would like to extend our thanks to the all technical staff of chemical engineering and program chair, the dean of school of mechanical chemical and materials engineering, Adama Science and Technology University, Adama, Ethiopia for the support and facilities.

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TABLE 4
EXPERIMENTAL RESULTS OF THIN LAYER DRYING OF DEKOKO SEEDS

Air velocity (V_a)= 1.5 m/sec										
Model	Temp	Model coefficient constants						SSE	R^2	RMSE
I	45	a=-0.0786	b = 0.0013					0.000205	0.9984	0.00988
	55	a= -0.1045	b = 0.0022					0.002692	0.9972	0.01340
	65	a= -0.1406	b = 0.0054					0.001839	0.9979	0.01189
	45	k= 0. 1129						0.01767	0.9852	0.02972
	55	k= 0.1936						0.003731	0.9956	0.01694
II	65	k= 0.2344						0.002547	0.9966	0.01522
III	45	a= 1.6380	c = -0.6217	k = 0.0522				0.001587	0.9987	0.008908
	55	a= 1.7140	c = -0.6909	k = 0.0678				0.001787	0.9982	0.01130
	65	a=1.3030	c = -0.2842	k = 0.1194				0.001959	0.9978	0.01278
VI	45	a= 1.7810	k = 0.1486					0.001605	0.9987	0.008741
	55	a= 1.8280	k = 0.2084					0.000251	0.9997	0.004097
	65	a= 1.7350	k = 0.2424					0.000697	0.9992	0.007324
V	45	a= 10.380	k = 0.1745	k_1 = 0.186				0.001995	0.9984	0.009986
	55	a= -8.7550	k = 0.0360	k_1 = 0.0437				0.003883	0.9960	0.01665
	65	a= -0.2585	k = 0.6509	k_1 = 0.2127				0.000596	0.9993	0.007053
VI	45	a=-5.3060	b= 0.8918	b = 0.8918				0.000575	0.9995	0.005653
	55	a= 1.0210	b= 0.7185	k=0.1923				0.003692	0.9956	0.01832
	65	a= 1.4550	b= 0.5552	k= 0.1854				0.001658	0.9978	0.01357
VII	45	a = 3.940	b= -2.939	k_1= 0.169	k_2 = 0.205			0.001541	0.9988	0.009007
	55	a =1.6760	b= - 0.675	k_1= 0.2022	k_2 = 0.406			0.003883	0.9960	
	65	a= -0.0115	b= 1.052	k_1= 0.1282	k_2= 0.1776			0.005609	0.9937	0.02258
VIII	45	a = -553.2	b =7.392					0.02164	0.9829	0.03210
	55	a = -540.2	b = 8.492					0.020460	0.9790	0.03693
	65	a = -441.5	b = 8.625					0.01000	0.9888	0.02774
IX	45	a = -0.8079	b = -0.002	c = 1.81	g = 42.98	h =0.1491	k= 0.2603	0.001598	0.9987	0.009694
	55	a= 1.5230	b = -0.155	c =-0.3634	g = 0.258	h = 0.3979	k = 0.1926	0.000297	0.9997	0.005204
	65	a = 1.1240	b = 30.34	C= -30.46	g = 1.523	h= 1.521	k = 0.1949	0.000862	0.9990	0.009788
Air velocity (V_a)= 2.5 m/sec										
I	45	a= -0.09137	b= 0.0020					0.001819	0.9985	0.009785
	55	a= -0.1681	b= 0.0085					0.0007822	0.9991	0.008073
	65	a= -0.2071	b= 0.0133					0.00103	0.9986	0.01015
II	45	k= 0.0987						0.021610	0.9829	0.03134
	55	k= 0.1335						0.020440	0.9791	0.03574
	65	k= 0.1684						0.009985	0.9889	0.02671
III	45	a= 1.5	c= -0.4824	k= 0.0662				0.00165	0.9986	0.009573
	55	a= 1.127	c= -0.1122	k= 0.0717				0.00104	0.9988	0.009722
	65	a=1.067	c= -0.0494	k= 0.2218				0.001208	0.9984	0.01159
VI	45	a= 1.77	k= 0.1677					0.000599	0.9995	0.005616
	55	a= 1.61	k= 0.2535					0.0007895	0.9990	0.008111
	65	a= 1.55	k= 0.2942					0.001226	0.9983	0.011070
V	45	a= 9.178	k= 0.1988	k_1= 0.2139				0.0007308	0.9994	0.006372
	55	a= -2.632	k= 0.1254	k_1= 0.1421				0.002167	0.9974	0.01404
	65	a= 1.448	k= 0.1789	k_1= 0.0874				0.00163	0.9978	0.01346
VI	45	a=25.61	b= 0.9613	k= 0.0452				0.006935	0.9945	0.01862
	55	a= 96.21	b= 0.9827	k=0.04235				0.004189	0.9957	0.01730
	65	a= -0.2575	b= 0.3257	k= 0.6527				0.000596	0.9993	0.007053
VII	45	a = -4.389	b= 5.3900	k_1= 0.2241	k_2 = 1961			0.0006035	0.9995	0.005958
	55	a = -0.08056	b= 1.083	k_1= 1.23	k_2 = 0.2135			0.0005726	0.9993	0.007567
	65	a= 7.663	b= -6.666	k_1= 0.12	k_2= 0.107			0.002352	0.9968	0.01715
VIII	45	a = -530.7	b=7.743					0.01769	0.9851	0.03051
	55	a = -277.7	b= 7.334					0.00375	0.9955	0.01768
	65	a = -191	b= 6.694					0.002566	0.9965	0.01602
IX	45	a = 7.822	b= 0.0404	c = -6.814	g = 1.641	h =0.0497	k= 0.05653	0.005944	0.9950	0.01991
	55	a= -0.0117	b=0.1379	c =0.9025	g= 0.1287	h = 0.2147	k = 0.2067	0.002299	0.9973	0.01695
	65	a = -0.2086	b= -1.71	c= 2.934	g = 0.244	h= 0.2537	k = 0.4816	0.001026	0.9986	0.01307