THEORETICAL INVESTIGATION OF THERMOGRAVIMETRIC ANALYSIS ON THE DECOMPOSITION OF SOLID-STATE MATERIALS

Dodampola Roshan Dhanushka Kumara

178073D

Thesis submitted in partial fulfillment of the requirements for the degree

Master of Philosophy

Department of Materials Science & Engineering
University of Moratuwa
Sri Lanka

July 2019

DECLARATION

Name of the Supervisor:

I declare that this is my own work and this thesis does not incorporate without

acknowledgement any material previously submitted for a Degree or Diploma in any

other University or Institute of higher learning and to the best of my knowledge and

belief it does not contain any material previously published or written by another

person except where the acknowledgement is made in the text.

I hereby grant to The University of Moratuwa the irrevocable, non-exclusive, and

royalty free license to archive and make accessible my work in whole or in part in all

forms of media, now or hereafter known. I agree that the document mentioned above

may be made available immediately for worldwide access unless an embargo applies.

I retain all other ownership rights to the copyright of my work. I also retain the right

to use in future works (such as articles or books) all or part of my work. I understand

that I am free to register the copyright to my work.

Signature:		Date:
The above candidate has supervision.	carried out research for t	he MPhil thesis under my
Signature of the supervisor:		Date:
Name of the Supervisor:	Dr. D.A.S. Amarasinghe	
Signature of the supervisor: Name of the Supervisor:	Dr. D.Attygalle	Date:
Signature of the supervisor:		Date:

ii

Mr.V.S.C. Weragoda

ACKNOWLEDGEMENT

First and foremost, I would like to thank my supervisor Dr. D.A.S. Amarasinghe, Senior lecturer of the department of materials science and engineering, University of Moratuwa. Starting from the conceptualization of the research to the very end, he had guided me and shaped me to be a good researcher by his eternal optimism and the vast scientific knowledge. He corrected me when I took things too lightly and mentored me not to fall down in hard times throughout this research. Finally, thank you for believing in me and the tremendous support you have given.

My deepest gratitude goes to my second supervisor Dr. Dinesh Attygalle, whose scientific skills and uncompromising quest for excellence are admirable. Without his common-sense, knowledge, perceptiveness and cracking-of-the-whip I would never have finished. Thank you for all the scientific and non-scientific discussions and the guidance given me throughout this time.

Special gratitude goes to Mr. V.S.C. Weragoda, my third supervisor and then, Head of department at materials science and engineering, University of Moratuwa. With all the busy schedules, he had enough time for my research activities. His support was not limited only for the quality of the research but also provided the administrative support throughout the research, including the funding of the research through a research grant. Thank you.

Further, university senate research committee for the financial aid given by grant, SRC/LT/2018/05 is greatly acknowledged.

Furthermore, I would like to thank the research committee, Prof. Sudath Kalingamudali and the former research coordinator and the current head of department Mr. V.Sivahar for reviewing the progress of the research as well for the support given. Also, I greatly appreciate the assistance that I received from all the academic and non-academic staff of Department of Materials Science and Engineering, University of Moratuwa.

I dedicate this thesis to my mother and father whose love and guidance made me the person I am today. Throughout my life you were there by my side loving, caring, punishing and teaching everything. I know you have sacrificed a lot when shaping my future. You are the best parents ever. I am forever in debt. Thank you for everything.

I owe an enormous debt of gratitude to my loving wife Tharaka Perera for the support given. As an electronics and telecommunication engineer, her intuition and the knowledge always uplifted my research work. Her contribution to this research is highly acknowledged. Not only in research aspects, but also as my life partner she was there for all the up and downs in my life. Her love and care always made me special and it helped me to hold on to the achievements in research as well as in life without falling apart at time of difficulty. Throughout this journey, you have sacrificed a lot and thank you for everything.

My sincere gratitude should go to my mother-in-law and father-in-law for the support given during this time, especially for hosting me and my wife. You made the best academic environment for me to continue my research work at home. Thank you for all the support given.

Not to forget my brother and sister who were there in every milestone of my life. Although I was always the stubborn brother, you never let me down. You are the hidden strength of my life. Thank you for helping me to be a better person.

Last, but not least, I want to thank my loving friends, Darshi Egodage, Thisara Sandaruwan, Madhawa Kumarasingha and Uthpala Dilrukshi for their endless support and encouragement throughout this duration.

I would like to thank everybody who was important to the successful realization of this thesis, as well as expressing my apology that I could not mention personally one by one.

Roshan Dodampola

ABSTRACT

Thermogravimetric (TG) analysis and differential thermogravimetric (DTG) analysis are the most commonly used analytical techniques to determine the kinetic behaviour of solid-state chemical reactions through Arrhenius parameters and reaction model, which is called the kinetic triplet of solid-state reactions. There are number of methods proposed in the literature for extracting the kinetic parameters of solid-state reactions from TG & DTG thermograms. However, thermal event separation using curve fitting where overlapped thermal events may be present is mandatory before further TG/DTG analysis. In this study, a better curve fitting procedure and a new model fitting method for kinetic parameter extraction is proposed. Enhanced accuracy of the proposed method is proved by MATLAB® based, simulated DTG signals. Furthermore, a mathematical approach using higher differentials of DTG signal was developed to count the number of thermal events in overlapped DTG peaks.

CONTENTS

Declarationii
Acknowledgementiii
Abstractv
Contentsvi
List of tablesx
List of figuresxi
List of abbreviationsxvi
1. Introduction
1.1. Thermal Analysis
1.1.1. TG/DSC machine and technique
1.1.2. TGA instrumentation
1.2. Reaction kinetics
1.2.1. Solid state reactions9
1.3. Determination of kinetic parameters
1.3.1. Model fitting method
1.3.2. Invariant kinetic parameter methods
1.3.3. Model free method
1.3.4. Determination of reaction model function
1.4. Requirement of a new methodology
1.5. Objectives of the study
1.6. Outline of dissertation
2. Methodology
2.1. DTG Signal generation

	2.2.	Pea	k height and peak position analysis	25
	2.3.	FW	HM analysis	30
	2.4.	Asy	mmetric parameter variation	33
	2.5.	Cur	ve fitting	36
	2.6.	Kin	etic Parameter extraction and analyses	39
3.	. Cha	aract	eristic Properties of DTG Signal	42
	3.1.	DT	G Peak Height	42
	3.1.	.1.	DTG Peak Height Variation	43
	3.2.	Full	l Width at Half Max	49
	3.2.	.1.	FWHM Variation	49
	3.3.	DT	G Peak Position	53
	3.4.	Pea	k Asymmetry	59
	3.4.	.1.	Previous asymmetric parameters	59
	3.4.	.2.	New asymmetric parameter J	59
	3.4.	.3.	Variation of the peak asymmetry parameter- J	60
	3.4.	.4.	Effect of resolution on variation of peak asymmetry	62
4	. Fur	octio	n Selection for Curve Fitting	66
	4.1.	Syn	nmetric functions	66
	4.1.	.1.	Gaussian function	66
	4.1.	.2.	Lorentz function	67
	4.2.	Asy	mmetric functions	68
	4.2.	.1.	Lognormal function	68
	4.2.	.2.	Asymmetric Double Sigmoidal function	69
	4.3.	CO	D Variation	71
	4.3.	.1.	1 st order reactions	72
	13	2	2 nd order reactions	73

	4.3	.3.	A2 reactions	74
	4.3	.4.	D1 reactions	75
	4.3	.5.	P2 reactions	76
	4.3	.6.	R2 reactions	77
	4.4.	Bes	t fitting function	78
5.	De	term	ination of Kinetic Parameters	80
	5.1.	Lin	earized curves for data extracted from fitting	81
	5.2.	The	90% Rule	83
	5.3.	Erro	ors in extracted kinetic parameters	84
	5.4.	Erro	or variation in activation energy by 90% rule	84
	5.4	.1.	E error % variation by 90% rule–1st order reactions	85
	5.4	.2.	E error % variation by 90% rule–2 nd order reactions	86
	5.4	.3.	E error % variation by 90% rule–A2 reactions	87
	5.4	.4.	E error % variation by 90% rule–D1 reactions	88
	5.4	.5.	E error % variation by 90% rule–P2 reactions	89
	5.4	.6.	E error % variation by 90% rule–R2 reactions	90
	5.5.	Det	ermining the best trimming percentage	91
	5.5	.1.	E error bars for height %– Gaussian fit	.93
	5.5	.2.	E error bars for height % – Lorentz fit	95
	5.5	.3.	E error bars for height % – Lognormal fit	97
	5.5	.4.	E error bars for height % – ADS fit	99
6.	Ide	ntifi	cation of Overlapped Peaks	04
	6.1.	Intr	oduction1	04
	6.1	.1.	Resolution - R _s	04
	6.1	.2.	Peak identification using derivatives	105
	6.1	.3.	Critical resolution and shoulder limit	06

	6.1.4.	Statistical theory of peak overlap	107
6	.2. Res	solution of DTG signal	109
	6.2.1.	Resolution variation	109
	6.2.2.	Critical resolution of DTG signal	113
	6.2.3.	Relative height on peak resolution	115
7.	Conclu	sions	116
Ref	erence		118

LIST OF TABLES

Table 1.1: Reaction model functions	12
Table 3.1: Peak height multiplication factors for different mechanisms	48
Table 3.2:FWHM multiplication factors for different mechanisms	52
Table 3.3: Multiplication factors for different mechanisms	57
Table 3.4: Peak position deviation from 1st order reactions	57
Table 3.5: Maximum and minimum J range	62
Table 4.1: COD ranges for fit functions	78
Table 5.1: Activation energy error% range	91
Table 6.1:critical resolutions values for different fixed peaks	114

LIST OF FIGURES

Figure 1.1: Schematic diagram of Modern TGA machine	2
Figure 1.2: schematic diagram of TGA balance	3
Figure 1.3:non-isothermal TGA signal of type T1-1 PVC cable insulation	5
Figure 1.4: isothermal TGA signal of type TI-1 PVC cable insulation at con-	nstant
temperature	5
Figure 1.5: types of rate variations	10
Figure 1.6:DTG signal analysis methods	13
Figure 1.7: Flow chart of improved shape method	17
Figure 2.1:Methodology	21
Figure 2.2: Flow Chart-Signal generation	24
Figure 2.3:Flow Chart- Peak height analysis	27
Figure 2.4:Flow Chart-Peak position analysis	29
Figure 2.5:Flow Chart-FWHM analysis	32
Figure 2.6:Flow Chart-J analysis	35
Figure 2.7:Flow Chart-Curve fitting	38
Figure 2.8:Flow Chart-Arrhenius differential method	40
Figure 2.9:Flow Chart-development of new methodology	41
Figure 3.1:graphical representation of peak height	43
Figure 3.2: DTG Peak height variation-1st order reactions	45
Figure 3.3:DTG Peak height variation-2nd order reactions	45
Figure 3.4:DTG Peak height variation-A2 reactions	45
Figure 3.5:DTG Peak height variation-D1 reactions	46
Figure 3.6:DTG Peak height variation-P2 reactions	46
Figure 3.7:DTG Peak height variation-R2 reactions	46
Figure 3.8:peak height variation of other mechanisms with 1st order reactions	48
Figure 3.9:graphical representation of FWHM	49
Figure 3.10: FWHM variation - 1st order reactions	50
Figure 3.11:FWHM variation - 2nd order reactions	50
Figure 3.12:FWHM variation - A2 reactions	50
Figure 3.13:FWHM variation - D1 reactions	51

Figure 3.14:FWHM variation - P2 reactions	51
Figure 3.15:FWHM variation - R2 reactions	51
Figure 3.16:FWHM variation of other mechanisms with 1st order reactions	52
Figure 3.17:Peak position - 1st order reactions	54
Figure 3.18:Peak position - 2nd order reactions	54
Figure 3.19:Peak position - A2 reactions	54
Figure 3.20:Peak position - D1 reactions	55
Figure 3.21:Peak position - P2 reactions	55
Figure 3.22:Peak position - R2 reactions	55
Figure 3.23:Peak position variation of other mechanisms with 1st order reactions	56
Figure 3.24:Surface fit for peak position variation-1st order reactions	58
Figure 3.25:Graphical representation of asymmetric parameter (J)	60
Figure 3.26: J variation - 1st order reactions	61
Figure 3.27: J variation - 2nd order reactions	61
Figure 3.28:Graphical representation of different peak positions	62
Figure 3.29: J variation- 1st order reactions, Full range.	64
Figure 3.30:J variation-1st order reactions, For 105 <a<2*105 &="" 100kj<e<110kj<="" td=""><td>. 64</td></a<2*105>	. 64
Figure 3.31:J variation-1st order reactions, For 105 <a<2*105 &="" 100kj<e<110kj<="" td=""><td>. 65</td></a<2*105>	. 65
Figure 3.32:J variation- 1st order reactions, Full range	65
Figure 4.1:Gaussian curve	66
Figure 4.2: Gaussian fit-1st order reaction	67
Figure 4.3:Lorentzian curve	67
Figure 4.4:Lorentz fit-1st order reaction	68
Figure 4.5:Lognormal curve	68
Figure 4.6:Lognormal fit-1st order reaction	69
Figure 4.7:ADS curve	69
Figure 4.8:Asymmetric Double Sigmoidal fit-1st order reaction	70
Figure 4.9:COD variation- 1 st order-Gaussian fit	72
Figure 4.10:COD variation- 1 st order-Lorentz fit	72
Figure 4.11:COD variation- 1st order-Lognormal fit	72
Figure 4.12:COD variation- 1st order-ADS fit	72
Figure 4.13:COD variation- 2nd order-Gaussian fit	73

Figure 4.14:COD variation- 2nd order-Lorentz fit
Figure 4.15:COD variation- 2 nd order-Lognormal fit
Figure 4.16:COD variation- 2 nd order-ADS fit
Figure 4.17:COD variation- A2-Gaussian fit
Figure 4.18:COD variation- A2-Lorentz fit
Figure 4.19:COD variation- A2-Lognormal fit
Figure 4.20:COD variation- A2-ADS fit
Figure 4.21:COD variation- D1-Gaussian fit
Figure 4.22:COD variation- D1-Lorentz fit
Figure 4.23:COD variation- D1-Lognormal fit
Figure 4.24:COD variation- D1-ADS fit
Figure 4.25:COD variation- P2-Gaussian fit
Figure 4.26:COD variation- P2-Lorentz fit
Figure 4.27:COD variation- P2-Lognormal fit
Figure 4.28:COD variation- P2-ADS fit
Figure 4.29:COD variation- R2-Gaussian fit
Figure 4.30:COD variation- R2-Lorentz fit
Figure 4.31:COD variation- R2-Lognormal fit
Figure 4.32:COD variation- R2-ADS fit
Figure 5.1:Arrhenius differential method for single peak data
Figure 5.2: Arrhenius differential method for fitted data
Figure 5.3:fiting errors near the tail
Figure 5.4:Graphical representation of the 90% rule
Figure 5.5:Linear regression only for 90%
Figure 5.6:E error % variation by 90% rule–1st order reactions-Gaussian fit 85
Figure 5.7:E error % variation by 90% rule–1st order reactions-Lorentz fit 85
Figure 5.8:E error % variation by 90% rule–1st order reactions-Lognormal fit85
Figure 5.9:E error % variation by 90% rule–1st order reactions-ADS fit
Figure 5.10:E error % variation by 90% rule–2nd order reactions-Gaussian fit86
Figure 5.11:E error % variation by 90% rule–2nd order reactions-Lorentz fit 86

Figure 5.12:E error % variation by 90% rule–2nd order reactions-Lognormal fit	86
Figure 5.13:E error % variation by 90% rule–2nd order reactions-ADS fit	86
Figure 5.14:E error % variation by 90% rule–A2 reactions-Gaussian fit	87
Figure 5.15:E error % variation by 90% rule–A2 reactions-Lorentz fit	87
Figure 5.16:E error % variation by 90% rule-A2 reactions-Lognormal fit	87
Figure 5.17:E error % variation by 90% rule–A2 reactions-ADS fit	87
Figure 5.18:E error % variation by 90% rule–D1 reactions-Gaussian fit	88
Figure 5.19:E error % variation by 90% rule–D1 reactions-Lorentz fit	88
Figure 5.20:E error % variation by 90% rule–D1 reactions-Lognormal fit	88
Figure 5.21:E error % variation by 90% rule–D1 reactions-ADS fit	88
Figure 5.22:E error % variation by 90% rule–P2 reactions-Gaussian fit	89
Figure 5.23:E error % variation by 90% rule–P2 reactions-Lorentz fit	89
Figure 5.24:E error % variation by 90% rule–P2 reactions-Lognormal fit	89
Figure 5.25:E error % variation by 90% rule–P2 reactions-ADS fit	89
Figure 5.26:E error % variation by 90% rule–R2 reactions-Gaussian fit	90
Figure 5.27:E error % variation by 90% rule–R2 reactions-Lorentz fit	90
Figure 5.28E error % variation by 90% rule–R2 reactions-Lognormal fit	90
Figure 5.29:E error % variation by 90% rule–R2 reactions-ADS fit	90
Figure 5.30:E error bars for height %- Gaussian fit -1st order reactions	93
Figure 5.31:E error bars for height %– Gaussian fit -2nd order reactions	93
Figure 5.32:E error bars for height %– Gaussian fit -A2 reactions	93
Figure 5.33:E error bars for height %– Gaussian fit -D1 reactions	94
Figure 5.34:E error bars for height %– Gaussian fit -P2 reactions	94
Figure 5.35:E error bars for height %– Gaussian fit -R2 reactions	94
Figure 5.36: E error bars for height % – Lorentz fit-1st order reactions	95
Figure 5.37:E error bars for height % – Lorentz fit-2nd order reactions	95
Figure 5.38:E error bars for height % – Lorentz fit-A2 reactions	95
Figure 5.39:E error bars for height % – Lorentz fit-D1 reactions	96
Figure 5.40:E error bars for height % – Lorentz fit-P2 reactions	96
Figure 5.41:E error bars for height % – Lorentz fit-R2 reactions	96
Figure 5.42:E error bars for height % – Lognormal fit-1st order reactions	97

Figure 5.43:E error bars for height % – Lognormal fit-2nd order reactions	97
Figure 5.44:E error bars for height % – Lognormal fit-A2 reactions	97
Figure 5.45:E error bars for height % – Lognormal fit-D1 reactions	98
Figure 5.46:E error bars for height % – Lognormal fit-P2 reactions	98
Figure 5.47:E error bars for height % – Lognormal fit-R2 reactions	98
Figure 5.48:E error bars for height % – ADS fit-1st order reactions	99
Figure 5.49:E error bars for height % – ADS fit-2nd order reactions	99
Figure 5.50:E error bars for height % – ADS fit-A2 reactions	99
Figure 5.51:E error bars for height % – ADS fit-D1 reactions	100
Figure 5.52:E error bars for height % – ADS fit-P2 reactions	100
Figure 5.53:E error bars for height % – ADS fit-R2 reactions	100
Figure 5.54:10% range of the error bands	102
Figure 6.1:overlapped DTG signal	104
Figure 6.2: derivatives of TG/DTG signal	105
Figure 6.3:Critical resolution at shoulder limit	106
Figure 6.4:Critical resolution variation with relative peak height	109
Figure 6.5:Graphical representation of Peak shift.	110
Figure 6.6:Resolution variation contours 1st order – 1st order reactions	111
Figure 6.7:Resolution variation contours 2nd order – 2nd order reactions	111
Figure 6.8:Resolution variation contours A2-A2 reactions	111
Figure 6.9:Resolution variation contours D1-D1 reactions	112
Figure 6.10:Resolution variation contours P2-P2 reactions	112
Figure 6.11:Resolution variation contours R2-R2 reactions	112
Figure 6.12: shoulder limit variation	113
Figure 6.13:Critical resolution vs relative height	115

LIST OF ABBREVIATIONS

TGA Thermo Gravimetric Analysis

DTG Differential Thermo Gravimetry

DSC Differential scanning calorimetry

COD Coefficient of Determination

ADS Asymmetric Double Sigmoidal

FWHM Full Width at Half Maximum

IKP Invariant Kinetic Parameter

EGA Evolved Gas Analysis