ZINC BORATE PRODUCTION IN A BATCH REACTOR

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

DENİZ GÜRHAN

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
CHEMICAL ENGINEERING

DECEMBER 2005

Approval of the Graduate School of Natural and Applied Sciences

Prof. Dr. Canan ÖZGEN
Director

I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

Prof. Dr. Nurcan BAÇ
Head of Department

This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science

Prof. Dr. Saim ÖZKAR
Co-Supervisor

Prof. Dr. İnci EROĞLU
Supervisor

Examining Committee Members

Prof. Dr. Nurcan BAÇ	(METU, CHE)	
Prof. Dr. İnci EROĞLU	(METU, CHE)	
Prof. Dr. Saim ÖZKAR	(METU, CHE)	
Assoc. Prof. Göknur BAYRAM	(METU, CHE)	
Prof. Dr. Zeki AKTAŞ	(Ankara Uni, CHE)	

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name, Last Name : Deniz GÜRHAN

Signature :

ABSTRACT

ZINC BORATE PRODUCTION IN A BATCH REACTOR

Gürhan, Deniz
M.S., Department of Chemical Engineering
Supervisor : Prof. Dr. İnci Eroğlu
Co-Supervisor: Prof. Dr. Saim Özkar

December 2005, 113 pages

Zinc borate is a flame retardant additive used in polymers, wood applications and textile products. There are different types of zinc borate having different chemical composition and structure. In this study, the production of zinc borate that had the molecular formula of $2ZnO.3B_2O_3.3,5H_2O$ was studied.

The aim of this study was to investigate the effects of reaction parameters on the properties of zinc borate that had been synthesized by the reaction of boric acid and zinc oxide at the existence of the seed crystals and to determine the optimum experimental conditions for zinc borate production reaction. Reaction kinetics was also investigated to find a suitable kinetics model.

The effect of boric acid to zinc oxide ratio -H_3BO_3:ZnO ratio- (3:1, 3.5:1, 5:1 and 7:1), the particle size of zinc oxide (10μm and 25μm), stirring rate (275 rpm, 400 rpm, 800 rpm and 1600 rpm), temperature (75°, 85° and 95°) and size of seed crystals (10μm and smaller size) on reaction rate, reaction completion time, composition and particle size distribution of zinc borate were investigated.

Experiments were performed in a continuously stirring, temperature controlled batch reactor with a volume of 1.5L. During the experiments samples were taken to be analyzed in regular time intervals. The analyses of the samples gave the concentration change of zinc oxide and boron oxide in the solid as well as the conversion of zinc oxide to zinc borate with respect to time and the rate of reaction was calculated. The products were also analyzed for particle size distribution.

The experimental results showed that the reaction rate increased with the increasing H_3BO_3:ZnO ratio, particle size of zinc oxide, stirring rate and temperature. Concomitantly reaction completion time was also decreased by increasing H_3BO_3:ZnO ratio, stirring rate and temperature.

The particle size of final product, zinc borate, decreased with increasing stirring rate and size of zinc borate used as seed and increased with increasing particle size of zinc oxide used as reactant. The average particle sizes of the final product zinc borates synthesized at the end of the experiments were ranged between 4.3 μm and 16.6 μm.

The zinc borate production reaction was mainly fitted the unreacted core model for the case of diffusion through product layer controls.

Keywords : Zinc borate, boric acid, reaction kinetics, flame retardancy.

ÖZ

KESİKLİ SİSTEMDE ÇİNKO BORAT ÜRETİMİ

Gürhan, Deniz
Y. Lisans, Kimya Mühendisliği Bölümü
Tez Yöneticisi : Prof. Dr. İnci Eroğlu
Ortak Tez Yöneticisi: Prof. Dr. Saim Özkar

Aralık 2005, 113 sayfa

Çinko borat polimerlerde, ahşap uygulamalarda ve tekstil ürünlerinde kullanılan alev geciktirici bir katkı malzemesidir. Değişik kimyasal yapılı çinko borat bileşikleri mevcuttur. Bu araştırmada $2ZnO.3B_2O_3.3,5H_2O$ formüllü çinko borat üretimi araştırıldı.

Yapılan bu çalışmanın amacı, deney koşullarının borik asitle çinko oksidin aşı kristali varlığındaki reaksiyonundan elde edilen çinko borat ürününün özelliklerine etkilerinin araştırılması ve çinko borat üretim reaksiyonu için en uygun deney koşullarının belirlenmesidir. Ayrıca uygun bir kinetik model bulmak için reaksiyon kinetiği de incelenmiştir.

Borik asidin çinko okside oranının -H_3BO_3:ZnO oranı- (3:1, 3.5:1, 5:1 ve 7:1), çinko oksit tane boyutunun (10µm ve 25µm), karıştırma hızının (275 dev/dak, 400 dev/dak, 800 dev/dak ve 1600 dev/dak), sıcaklığın (75°, 85° ve 95°) ve aşı kristallerinin tane boyutunun (10µm ve daha küçük tane boyutlu) reaksiyon hızına, reaksiyon tamamlanma süresine, oluşan çinko borat ürününün kompozisyonuna ve tane boyut dağılımına etkileri araştırıldı.

Deneyler sürekli karıştırılan 1.5 litrelik kesikli cam bir reaktörde sıcaklık kontrollü olarak gerçekleştirildi. Deneyler sırasında analiz yapılmak üzere düzenli aralıklarda numuneler alındı. Yapılan analizler sonucunda deney sırasında borik asit ve çinko oksitin zamana göre değişimleri ve çinko oksidin zamana göre çinko borata dönüşümü ve reaksiyon hızı hesaplandı. Son ürünlerde ayrıca parça boyut dağılım analizleri yapıldı.

Bulgular, reaksiyon hızının artan H_3BO_3:ZnO oranı, çinko oksit tane boyutu, karıştırma hızı ve sıcaklık ile arttığını göstermektedir. H_3BO_3:ZnO oranı, karıştırma hızı ve sıcaklık arttırıldığında ise reaksiyon tamamlanma süresi azalmaktadır.

Oluşan çinko borat ürününün tane boyutunun artan karıştırma hızı ve aşı kristallerinin tane boyutu ile azaldığı ve artan çinko oksit hammadde tane boyutu ile arttığı bulundu. Yapılan deneylerde son ürün tane boyutlarının 4.3µm ile 16.6 µm arasında değiştiği görüldü.

Çinko borat üretim reaksiyonunun kinetiği genel olarak, büzüşen çekirdek modelindeki ürün tabakasına difüzyonun kontrol ettiği duruma uydu.

Anahtar kelimeler : Çinko borat, borik asit, reaksiyon kinetiği, alev geciktiricilik.

To My Family,

ACKNOWLEDGMENTS

I am deeply grateful to Prof. Dr. İnci Eroğlu for her valuable guidance, helpful suggestions, continuous encouragement, support and humanity throughout my graduate study. Her support made everything better and easier. She is the one I want to take advise at every stage of my life.

I would like to express my sincere appreciations to Prof: Dr. Saim Özkar for his advices, support, discussions and creative ideas that contributed greatly to my study.

I am grateful to Prof. Dr. Nusret Bulutçu for his great help for the analysis, his valuable advices and suggestions in my study.

My special thanks go to Dr. Gaye Çakal, Anıl Erdoğdu, Ela Eroğlu and Serdar Erkan for their great helps and valuable support during my study.

I would like to express my gratitude to my friends Hande Kaya, Sezen Soyer, Aslı Sayar, Nazar İleri, Hakan Önder Olcay, Ebru Erünal and Mehmet Özgür Seydibeyoğlu for their great friendship and motivation during my study.

I wish to thank my friends Mustafa Öztürk and Gürhan Taşkaya for their great friendship, support and encouragements throughout the study.

I would also like to thank to Ms. Kerime Güney for her great help in the analysis and her great support.

This study was supported by METU BAP2004-07-02-00-98.

TABLE OF CONTENTS

PLAGIARISM.. iii

ABSTRACT iv

ÖZ vi

ACKNOWLEDGEMENT ix

TABLE OF CONTENTS x

LIST OF TABLES xiii

LIST OF FIGURES xv

LIST OF SYMBOLS AND ABBREVIATIONS xx

CHAPTER

1. INTRODUCTION 1

2. LITERATURE SURVEY 5

2.1. Concept of Flame Retardancy……….. 5

2.2. Zinc Borate Properties and Usage 8

2.3. Zinc Borate as a Flame Retardant 13

2.4. Zinc Borate Sythesis……………………… 15

3. EXPERIMENTAL 17

3.1. Materials Used.. 17

3.2. Experimental Set-up 17

3.3. Experimental Procedures…………... 19

3.4. Analysis Procedures……………………................................... 22

3.4.1. Determination of Zinc Oxide in Solid Sample…………… 22

3.4.2. Determination of Boric Acid in Solid Sample.................. 23

3.4.3. Determination of Boric Acid in Liquid 24

3.5. Determination of Crystal Size Distribution.............................. 25

3.6. Crystal Image Analysis. 26

3.7. TG/DTA Analysis……... 26

3.8. Scope of the Experiments…... 26

4. RESULTS AND DISCUSSION 30

4.1. Product Characterization….. 32

4.1.1. XRD Results………………. 32

4.1.2. TG/DTA Results…………….. 36

4.1.3. Analytical Results………………….. 39

4.2. Effects of Experimental Parameters to Zinc Oxide Conversion……………………………………………………… 42

4.2.1. Effect of Stirring Rate…………… 41

4.2.2. Effect of Reactants Ratio…………………………... 44

4.2.3. Effect of Temperature…… 47

4.2.4. Effect of Seed………………….. 49

4.2.5. Effect of Size of Zinc Oxide Particle.............................. 50

4.2.6. Effect of Size of Zinc Borate Seed………………….. 53

4.3. Particle Size Distribution Analysis 55

4.3.1. Effect of Stirring Rate…………… 55

4.3.2. Effect of Reactants Ratio…………………………... 56

4.3.3. Effect of Temperature…… 57

4.3.4. Effect of Size of Zinc Oxide Particle.............................. 59

4.3.5. Effect of Size of Zinc Borate Seed………………….. 60

4.4. Reaction Kinetics……………………… 62

4.4.1. The Case of Chemical Reaction Controls...................... 63

4.4.2. The Case of Diffusion Through Product Layer Controls. 67

4.4.3. Calculation of Activation Energy…………………………. 77

5. CONCLUSIONS AND RECOMMENDATIONS............................... 81

REFERENCES 86

APPENDICES

A. Raw Data of Experiments …….. 88

B. Liquid Analysis…………………………… 95

C. Crystal Image Analysis 98

D. Properties of Raw Materials Used 101

D.1. Properties of Boric Acid 101

D.2. Properties of Zinc Oxide... 102

D.3. Properties of Zinc Borate 104

E. Reproducibility 107

F. Sample Calculation…… 109

LIST OF TABLES

TABLE

1.1. Major uses of boron minerals, borates and boron compounds……… 2

2.1. Consumption of flame retardants by type and region based on 2001 values.. 7

2.2. Zinc borate usage in different polymers and its benefits.................... 9

3.1. Performed Experiments 29

4.1. The analytical analysis of the final products and the chemical formula for all the performed experiments.. 40

4.2. Comparison of the final products with the commercially taken zinc borate........................... 50

4.3 Average particle sizes of final zinc borate products and commercial zinc borate.. 61

4.4 Summary of values of model parameters for selected experiments.... 76

A.1 The change of ZnO and B_2O_3 contents in the samples collected during Experiment2 (800rpm stirring rate, 95°C temperature, 10µm ZnO, H_3BO_3:ZnO ratio of 5:1, $C_{b(initial)}$ = 3.96 mol/lt)…………………… 88

A.2 The change of ZnO and B_2O_3 contents in the samples collected during Experiment3 (1000rpm stirring rate, 95°C temperature, 10µm ZnO, H_3BO_3:ZnO ratio of 7:1, $C_{b(initial)}$ = 4.91 mol/lt) ………………….. 88

A.3 The change of ZnO and B_2O_3 contents in the samples collected during Experiment4 (1600rpm stirring rate, 95°C temperature, 25µm ZnO, H_3BO_3:ZnO ratio of 5:1, $C_{b(initial)}$ = 5.12 mol/lt) …………………... 89

A.4 The change of ZnO and B_2O_3 contents in the samples collected during Experiment5 (1600rpm stirring rate, 95°C temperature, 10µm ZnO, H_3BO_3:ZnO ratio of 7:1, $C_{b(initial)}$ = 4.99 mol/lt) …………………... 89

A.5 The change of ZnO and B_2O_3 contents in the samples collected during Experiment6 (1600rpm stirring rate, 95°C temperature, 10µm ZnO, H_3BO_3:ZnO ratio of 5:1, $C_{b(initial)}$ = 4.0 mol/lt) ……………………. 90

A.6 The change of ZnO and B_2O_3 contents in the samples collected during Experiment7 (1600rpm stirring rate, 95°C temperature, 10µm ZnO, H_3BO_3:ZnO ratio of 3.5:1, $C_{b(initial)}$ = 4.92 mol/lt) ………………… 90

A.7 The change of ZnO and B_2O_3 contents in the samples collected during Experiment8 (1600rpm stirring rate, 95°C temperature, 25µm ZnO, H_3BO_3:ZnO ratio of 3.5:1, $C_{b(initial)}$ = 4.87 mol/lt) ………………… 90
A.8 The change of ZnO and B_2O_3 contents in the samples collected during Experiment9 (1600rpm stirring rate, 75°C temperature, 25µm ZnO, H_3BO_3:ZnO ratio of 5:1, $C_{b(initial)}$ = 3.32 mol/lt) ………………… 91
A.9 The change of ZnO and B_2O_3 contents in the samples collected during Experiment10 (1600rpm stirring rate, 85°C temperature, 25µm ZnO, H_3BO_3:ZnO ratio of 5:1, $C_{b(initial)}$ = 4.31 mol/lt) ………….. 91
A.10 The change of ZnO and B_2O_3 contents in the samples collected during Experiment11 (1600rpm stirring rate, 95°C temperature, 25µm ZnO, H_3BO_3:ZnO ratio of 5:1, nano size zinc borate used as seed, $C_{b(initial)}$ = 5.23 mol/lt) ……………………………………………… 92
A.11 The change of ZnO and B_2O_3 contents in the samples collected during Experiment12 (400rpm stirring rate, 95°C temperature, 10µm ZnO, H_3BO_3:ZnO ratio of 5:1, $C_{b(initial)}$ = 5.12 mol/lt) ………………….. 92
A.12 The change of ZnO and B_2O_3 contents in the samples collected during Experiment13 (1600rpm stirring rate, 80°C temperature, 25µm ZnO, H_3BO_3:ZnO ratio of 5:1, $C_{b(initial)}$ = 5.12 mol/lt) ………….. 93
A.13 The change of ZnO and B_2O_3 contents in the samples collected during Experiment14 (1600rpm stirring rate, 95°C temperature, 10µm ZnO, H_3BO_3:ZnO ratio of 3:1, $C_{b(initial)}$ = 5.16 mol/lt) ………….. 93
A.14 The change of ZnO and B_2O_3 contents in the samples collected during Experiment15 (275rpm stirring rate, 95°C temperature, 10µm ZnO, H_3BO_3:ZnO ratio of 5:1, $C_{b(initial)}$ = 5.12 mol/lt) ……………………………………………………………………………………… 94
D.1 Some physical and chemical properties of boric acid(H_3BO_3)………………………………………………………………………… 101
D.2 Some physical and chemical properties of zinc oxide(ZnO)………… 103
D.3 Some physical and chemical properties of zinc borate($2ZnO.3B_2O_3.3,5H_2O$) ……………………………………………..... 105
D.4 Particle size distribution graph of zinc borate obtained from Borax Morarji Limited, Bombay with smaller particle size……………………. 106
F.1 Summary of the calculation of zinc oxide conversion………………… 111

LIST OF FIGURES

FIGURE

3.1. The schematic representation of experimental set-up 20

3.2. The picture of the experimental set-up... 21

4.1. The X-ray pattern of zinc borate used as seed during the experiments…………………….. 32

4.2. The X-ray pattern of final product obtained in Experiment 3 (1000rpm stirring rate, 7:1mole ratio, 95ºC temperature, 25µm zinc oxide) …………………………………………………………….. 33

4.3. The X-ray pattern of final product obtained in Experiment 6 (1600rpm stirring rate, 5:1mole ratio, 95ºC temperature, 25µm zinc oxide) …………………………………………………………….. 33

4.4. The X-ray pattern of final product obtained in Experiment 7 (1600rpm stirring rate, 3,5:1mole ratio, 95ºC temperature, 25µm zinc oxide) …………………………………………………………….. 34

4.5. The X-ray pattern of final product obtained in Experiment 8 (1600rpm stirring rate, 3.5:1mole ratio, 95ºC temperature, 10µm zinc oxide) …………………………………………………………….. 34

4.6 The X-ray pattern of final product obtained in Experiment 9 (1600rpm stirring rate, 5:1mole ratio, 75ºC temperature, 10µm zinc oxide) …………………………………………………………….. 35

4.7 The X-ray pattern of final product obtained in Experiment 10 (1600rpm stirring rate, 5:1mole ratio, 85ºC temperature, 10µm zinc oxide) …………………………………………………………….. 35

4.8 TGA data of zinc borate supplied by Chengdu Chemphys Chemical Industry Co. Ltd, China…………………………………… 36

4.9 The TG/DTA pattern of Experiment 1 (800rpm stirring rate, 5:1mole ratio, 95ºC temperature, 10µm zinc oxide)……………… 37

4.10 The TG/DTA pattern of Experiment 4 (1600rpm stirring rate, 5:1mole ratio, 95ºC temperature, 25µm zinc oxide) ……………… 37

4.11 The TG/DTA pattern of Experiment 8 (1600rpm stirring rate, 3.5:1mole ratio, 95ºC temperature, 25µm zinc oxide) …………… 38

4.12 The TG/DTA pattern of Experiment 9 (1600rpm stirring rate, 5:1mole ratio, 75ºC temperature, 25µm zinc oxide) ……………… 38

4.13 The TG/DTA pattern of Experiment 10 (1600rpm stirring rate, 5:1mole ratio, 85ºC temperature, 25µm zinc oxide……………….. 39

4.14 ZnO conversion vs time graph to observe the effect of stirring rate (Temperature (95ºC), initial reactants ratio (H_3BO_3:ZnO ratio of 5:1) and type of zinc oxide particles (average particle size of 10µm) were constant) ………………………………………………… 42

4.15 ZnO% vs time graph to observe the effect of stirring rate (Temperature (95ºC), initial reactants ratio (H_3BO_3:ZnO ratio of 5:1) and type of zinc oxide particles (average particle size of 10µm) were constant) ………………………………………………… 43

4.16 B_2O_3% vs time graph to observe the effect of stirring rate (Temperature (95ºC), initial reactants ratio (H_3BO_3:ZnO ratio of 5:1) and type of zinc oxide particles (average particle size of 10µm) were constant) ………………………………………………… 43

4.17 ZnO conversion vs time graph to observe the effect of reactants ratio(Temperature (95ºC), stirring rate(1600rpm) and type of zinc oxide particles (average particle size of 10µm) were constant)….. 45

4.18 ZnO% vs time graph to observe the effect of reactants ratio(Temperature (95ºC), stirring rate(1600rpm) and type of zinc oxide particles (average particle size of 10µm) were constant)….. 46

4.19 B_2O_3% vs time graph to observe the effect of reactants ratio(Temperature (95ºC), stirring rate(1600rpm) and type of zinc oxide particles (average particle size of 10µm) were constant)….. 46

4.20 ZnO conversion vs time graph to observe the effect of temperature(initial reactants ratio (H_3BO_3:ZnO ratio of 5:1), stirring rate(1600rpm) and type of zinc oxide particles (average particle size of 25µm) were constant)……………………………… 48

4.21 ZnO% vs time graph to observe the effect of temperature(initial reactants ratio (H_3BO_3:ZnO ratio of 5:1), stirring rate(1600rpm) and type of zinc oxide particles (average particle size of 25µm) were constant) ……………………………………………………… 48

4.22 B_2O_3% vs time graph to observe the effect of temperature (initial reactants ratio (H_3BO_3:ZnO ratio of 5:1), stirring rate(1600rpm) and type of zinc oxide particles (average particle size of 25 µm) were constant) ……………………………………………………… 49

4.23 ZnO conversion vs time graph to observe the effect of zinc oxide particle size(Temperature (95ºC), initial reactants ratio (H3BO3:ZnO ratio of 3,5:1) and stirring rate(1600rpm) were constant) ……………………………………………………… 51

4.24 ZnO% vs time graph to observe the effect of zinc oxide particle size(Temperature (95ºC), initial reactants ratio (H3BO3:ZnO ratio of 3,5:1) and stirring rate(1600rpm) were constant)……………… 52

4.25 B_2O_3% vs time graph to observe the effect of zinc oxide particle size(Temperature (95ºC), initial reactants ratio (H3BO3:ZnO ratio of 3,5:1) and stirring rate(1600rpm) were constant)……………… 52

4.26 ZnO conversion vs time graph to observe the effect of zinc borate particle size(Temperature (95ºC), initial reactants ratio (H3BO3:ZnO ratio of 5:1), stirring rate(1600rpm) and type of zinc oxide particles (average particle size of 25µm) were constant)…. 53

4.27 ZnO% vs time graph to observe the effect of zinc borate particle size(Temperature (95ºC), initial reactants ratio (H3BO3:ZnO ratio of 5:1), stirring rate(1600rpm) and type of zinc oxide particles (average particle size of 25µm) were constant) …………………… 54

4.28 B_2O_3% vs time graph to observe the effect of zinc borate particle size(Temperature (95ºC), initial reactants ratio (H3BO3:ZnO ratio of 5:1), stirring rate(1600rpm) and type of zinc oxide particles (average particle size of 25µm) were constant) …………………… 54

4.29 Particle size distribution graph to observe the effect of stirring rate (Temperature (95ºC), initial reactants ratio (H_3BO_3:ZnO ratio of 5:1) and type of zinc oxide particles (average particle size of 10µm) were constant) ……………………………………………… 56

4.30 Particle size distribution graph to observe the effect of reactants ratio(Temperature (95ºC), stirring rate(1600rpm) and type of zinc oxide particles (average particle size of 10µm) were constant)….. 57

4.31 Particle size distribution graph to observe the effect of temperature(initial reactants ratio (H_3BO_3:ZnO ratio of 5:1), stirring rate(1600rpm) and type of zinc oxide particles (average particle size of 25µm) were constant) …………………………… 58

4.32 Particle size distribution graph to observe the effect of zinc oxide particle size(Temperature (95ºC), initial reactants ratio (H_3BO_3:ZnO ratio of 3,5:1) and stirring rate(1600rpm) were constant) …………………………………………………………….. 59

4.33 Particle size distribution graph to observe the effect of zinc borate particle size(Temperature (95ºC), initial reactants ratio (H_3BO_3:ZnO ratio of 5:1), stirring rate(1600rpm) and type of zinc oxide particles (average particle size of 25µm) were constant)….. 60

4.34 The plot of Equation 4.16 for Experiment 8 (1600rpm stirring rate, 95°C temperature, 25µm ZnO, H_3BO_3:ZnO ratio of 3.5:1)….. 66

4.35 The plot of Equation 4.16 for the Experiment 7 (1600rpm stirring rate, 95°C temperature, 10µm ZnO, H_3BO_3:ZnO ratio of 3.5:1)….. 67

4.36 The plot of Equation 4.16 for the Experiment 4 (1600rpm stirring rate, 95°C temperature, 25µm ZnO, H_3BO_3:ZnO ratio of 5:1)……. 68

4.37 The plot of Equation 4.16 for the Experiment 7 (1600rpm stirring rate, 85°C temperature, 25µm ZnO, H_3BO_3:ZnO ratio of 5:1) …… 68

4.38 The plot of Equation 4.16 for the Experiment 9 (1600rpm stirring rate, 75°C temperature, 25µm ZnO, H_3BO_3:ZnO ratio of 5:1) …… 69

4.39 The plot of Equation 4.30 for Experiment 4(1600rpm stirring rate, 95°C temperature, 25µm ZnO, H_3BO_3:ZnO ratio of 5:1) ………… 73

4.40 The plot of Equation 4.30 for Experiment 10(1600rpm stirring rate, 85°C temperature, 25µm ZnO, H_3BO_3:ZnO ratio of 5:1) …… 73

4.41 The plot of Equation 4.30 for Experiment 9(1600rpm stirring rate, 75°C temperature, 25µm ZnO, H_3BO_3:ZnO ratio of 5:1) ………… 74

4.42 The plot of Equation 4.30 for Experiment 7(1600rpm stirring rate, 95°C temperature, 25µm ZnO, H_3BO_3:ZnO ratio of 3.5:1) 75

4.43 Boric acid concentration versus time graph of Experiment 9 (temperature of 75°C, Stirring rate of 1600rpm, H3BO3:ZnO ratio of 5:1, ZnO size of 0,6µm) ………………………………………… 78

4.44 Boric acid concentration versus time graph of Experiment 10 (temperature of 85°C, Stirring rate of 1600rpm, H3BO3:ZnO ratio of 5:1, ZnO size of 0,6µm) ………………………………………… 78

4.45 Boric acid concentration versus time graph of Experiment 4 (temperature of 95°C, Stirring rate of 1600rpm, H3BO3:ZnO ratio of 5:1, ZnO size of 0,6µm) ………………………………………….. 79

4.46 The graph of Equation 4.34 for three different temperatures(75°C, 85°C and 95°C) …………………………….. 80

B.1 The change of B_2O_3 concentration in the liquid phase for different temperatures((initial reactants ratio (H_3BO_3:ZnO ratio of 5:1), stirring rate(1600rpm) and type of zinc oxide particles (average particle size of 25µm) were constant) …………………………… 95

B.2 The change of B_2O_3 concentration in the liquid phase for different ZnO's(Temperature (95ºC), initial reactants ratio (H_3BO_3:ZnO ratio of 3,5:1) and stirring rate(1600rpm) were constant)………… 96

B.3 The change of B_2O_3 concentration in the liquid phase for different stirring rates(Temperature (95ºC), initial reactants ratio (H_3BO_3:ZnO ratio of 5:1) and type of zinc oxide particles (average particle size of 10µm) were constant) …………………… 96

B.4 The change of B_2O_3 concentration in the liquid phase for different H_3BO_3:ZnO ratios. (Temperature (95ºC), stirring rate(1600rpm) and type of zinc oxide particles (average particle size of 10µm) were constant) ……………………………………………………… 97

B.5 The change of B_2O_3 concentration in the liquid phase for different zinc borates. (Temperature (95ºC), initial reactants ratio (H_3BO_3:ZnO ratio of 5:1), stirring rate(1600rpm) and type of zinc oxide particles (average particle size of 25µm) were constant)….. 97

C.1 Image of product zinc borate obtained at Experiment 4 (temperature of 95ºC, stirring rate of 1600rpm, H_3BO_3:ZnO ratio of 5:1, ZnO size of 25µm) …………………………………………. 98

C.2 Image of product zinc borate obtained at Experiment 5 (temperature of 95ºC, stirring rate of 1600rpm, H_3BO_3:ZnO ratio of 7:1, ZnO size of 10µm) …………………………………………. 99

C.3 Image of product zinc borate obtained at Experiment 6 (temperature of 95ºC, stirring rate of 1600rpm, H_3BO_3:ZnO ratio of 5:1, ZnO size of 10µm) …………………………………………… 99

C.4 Image of product zinc borate obtained at Experiment 7 (temperature of 95ºC, stirring rate of 1600rpm, H_3BO_3:ZnO ratio of 3.5:1, ZnO size of 10µm) ………………………………………… 100

C.5 Image of product zinc borate obtained at Experiment 8 (temperature of 95ºC, stirring rate of 1600rpm, H_3BO_3:ZnO ratio of 5:1, ZnO size of 25µm) …………………………………………… 100

D.1 The solubility of boric acid with temperature in terms of B_2O_3……. 102

D.2 Particle size distribution graph of zinc oxide obtained from Kartal Oksit Limited, Ankara, Turkey with an average particle size of 10μm……………………………………………………………………… 103

D.3 Particle size distribution graph of zinc oxide obtained from MKS Limited, İstanbul, Turkey with an average particle size of 25μm… 104

D.4 Particle size distribution graph of zinc borate obtained from Great Lakes Co, USA with an average particle size of 10μm…………… 105

E.1 The change of ZnO content with respect to time in the solid (H_3BO_3:ZnO ratio (5:1), stirring rate (1600rpm), average particle size of zinc oxide (25 μm) and temperature (95°C) were constant) ……………………………………………………………….. 108

E.2 The change of B_2O_3 content with respect to time in the solid (H_3BO_3:ZnO ratio (5:1), stirring rate (1600rpm), average particle size of zinc oxide (25 μm) and temperature (95°C) were constant) ……………………………………………………………….. 108

LIST OF SYMBOLS

a	The weight of ZnO in the sample resulting from the addition of 1 ml of 0.05M EDTA. The value of the “a” is 0.004069 g/l.
A	Arrhenius constant
a_p	Particle fluid interfacial area (cm^2cm^{-3})
b	The ratio of reaction coefficient of zinc oxide to reaction coefficient of boric acid
c_{Bo}	Initial concentration of boric acid (kmol m^{-3})
c_{Bt}	Concentration of boric acid at time t (kmol m^{-3})
dc_{Bt} / dt	Rate of decomposition of boric acid (kmol m^{-3} s^{-1})
d_{pin}	Initial diameter of particle size of zinc oxide (m)
d_{pt}	Diameter of particle size of zinc oxide at time t (m)
dN_B/dt	Rate of diffusion of boric acid to the reaction surface
D_e	Effective diffusion coefficient of reactant B
E_a	The activation energy (J mol^{-1})
f(x)	Function dependent of conversion
F_{NaOH}	Factor of the NaOH solution
g(x)	Function dependent of conversion
k_r	Rate constant (cm s^{-1})
$k_r^{'}$	Constant, $k_r / 6d_{pin}$ (s^{-1})
m	Relative molecular mass of zinc oxide (81.37)
n	Amount of sample (g)
N_{NaOH}	Normality of NaOH solution (0.5 N)
ρ_A	Density of zinc oxide

P_{B2O3}	The weight percentage of B_2O_3 in the taken sample
P_{ZnO}	The weight percentage of ZnO in the taken sample
Q_B	Flux of B through surface of any radius r
Q_{Bc}	Flux of B to the reaction surface
Q_{Bs}	Flux of B through exterior surface of particle(inward +, outward -)
r	Radius of product layer and unreacted core at any time
r_c	Radius of unreacted core
R	The gas constant (8,314J/mol-K)
R'	Radius of product layer and unreacted core during the constant flux
τ	Space time
t	Time (s)
t_{lag}	Time for formation of product layer and constant flux
T	The absolute temperature (K)
v	Volume of boric acid solution (m^3)
V_{EDTA}	The amount of EDTA added to observe the color change of the indicator (ml)
V_{NaOH}	Volume of NaOH required for titration after adding the mannitol to the solution (ml)
w	Mass of zinc oxide (kg)
w_{in}	Initial mass of zinc oxide (kg)
w_t	Mass of zinc oxide at time t (kg)
x	Fractional conversion of zinc oxide at time t
ρ	Density (kg m^{-3})

CHAPTER 1

INTRODUCTION

In the world, Turkey, USA and Russia have large reserves for boron mines. In terms of total reserve basis, Turkey has a share of 64 %, the other important country USA has 9 %. Total world boron reserves on the basis of B_2O_3 content are 363 million tons proven. 522 million tones probable and possible, and as a total of 885 million tons. With a share of 64 %, Turkey has a total boron reserves of 563 million tons on the basis of B_2O_3 content.

Boron minerals can be used in some sectors in the industry as crude minerals. In general, their applications after refining and end-products are wider than crude ones. Boron minerals, borates and compounds have a very wide range of applications. Table 1.1 illustrates the major uses of boron minerals, borates and boron compounds.

Zinc borate is a boron based inorganic material that is used mainly as flame retardant additive. It is also used to protect wood products aboveground from insect and fungal attacks and used as antibacterial material in some applications (Roskill, 2002).

Table 1.1 Major uses of boron minerals, borates and boron compounds. (Roskill, 2002)

USAGE AREA	MAJOR USES
Agriculture	-Essential micronutrient for all plant
Detergents and Soaps	-Act as pH buffer -Soften the washing water -Enhance the solubility of other ingredients -Act as a gentle but powerful bleaching agent
Ceramic Glazes and Enamel Frits	-Provide good fluxing properties -Provide a good base for dissolving coloring agents
Insulation Fiberglass	-Reduce the temperature at which fibers are formed -Improve the durability of the glass fibers -Reduce the viscosity of the molten glass
Timber Preservation	- Prevent and control the spread of bacteria - Inhibit corrosion - Act as flame retardant
Flame Retardants	- Enhance the performance of alumina trihydrate - Effective as flame retardants
Nuclear Power Stations	- Absorb thermal neutrons - Used to control nuclear reaction - Used in nuclear shielding.
Cosmetics and Medicine	- Neutralize fatty acid - Act as emulsifiers in certain creams - Give mild antiseptic properties
Metallurgy	- Used as cover fluxes - Dissolve and remove unwanted metal oxides as slag
Other	-Glass -Optical fibers -Magnets -Adhesives -Photography

There are different zinc borates with different chemical compositions and structures. In this study the one with the formula of $2ZnO.3B_2O_3.3,5H_2O$ which was also the most used zinc borate commercially was studied. This compound has the unusual property of retaining its water of hydration at temperatures up to 290°C. This thermal stability makes it attractive as a fire retardant additive for plastics and rubbers that require high processing temperatures (Shete 2004). It is widespreadly produced by reaction of zinc oxide and boric acid in proper temperature and mixing conditions. The reaction can be described as follows;

$$6B(OH)_{3(aq)} + 2ZnO_{(s)} \longrightarrow (2ZnO.3B_2O_3.3,5H_2O) + 5.5H_2O_{(l)} \quad (1.1)$$

Almost all the studies in the published literature were about the usage of zinc borate in different polymer and wood systems and related fire tests.(Agrawal, 1991; Basfar, 2002; Tsunoda, 2002; Garba, 1999; Bourbigot, 1999; Pi, 2003; Ning, 2000). There were only few references about the synthesis of zinc borate with the molecular formula of $2ZnO.3B_2O_3.3,5H_2O$ (Shete, 2004; Nies, 1970; Dong, 1998).

When it is used as an additive, the size of zinc borate becomes important. The size of zinc borate can be decreased by grinding. However, this is quite energy consuming technology. It is our idea to produce smaller zinc borate crystals by optimizing the experimental conditions. Therefore, objective of this study was to present a comprehensive set of experiments to see the effects of experimental parameters (boric acid to zinc oxide ratio, the particle size of zinc oxide used, stirring rate, temperature and usage of seed crystals) on the product specifications, conversion of zinc oxide and the composition change of zinc borate during the production reaction. In this study the effects of experimental parameters to the final zinc borate particle size were also investigated.

Another aim of this study was to determine optimum reaction parameters for zinc borate production reaction considering minimum reaction completion time and minimum possible final zinc borate particle size. A recent study (Shete, 2004) has reported quite longer reaction completion time since zinc borate has not been used as seed at the beginning of reaction. In the present study it was hypothesized that the presence of adequate amount of seed crystals would decrease the reaction completion time.

This study also focused on modeling of zinc borate production reaction based on the experimental data collected.

All the results were compared with the literature and the studies performed so far.

The present study was a detailed study has been done so far in terms of characterization of the product and reaction kinetics modeling.

Considering that Turkey has the largest boron reserves in the world and zinc borate is one of boron based material that would be possibly produced in Turkey in a near future, this study would be a good reference for scaling up the zinc borate production reaction. This study would also be a basis for future improvements for zinc borate production technologies.

CHAPTER 2

LITERATURE SURVEY

2.1 CONCEPT OF FLAME RETARDANCY

Because plastics are synthetic organic materials with high carbon, and often high hydrogen contents, they are combustible. For various applications in the building, electrical transportation, mining and other industries plastics have to fulfill flame retardancy requirements laid down in mandatory regulations and voluntary specifications.

An ideal flame retardant should be easy to incorporate in and be compatible with the plastic (i.e. not bleed out) and not alter its mechanical properties. Furthermore, it should be colorless, exhibit good light stability and be resistant to aging and hydrolysis. It should also be matched to the decomposition temperature of the polymer, i.e. its effect must begin below the decomposition temperature of the plastic and continue over the whole range of its decomposition. It must not cause corrosion, must be temperature resistant, effective in small amounts, odorless and without harmful physiological effects. It must also emit only low levels of smoke and toxic gases and finally be cheap as possible (Gachter, 1993).

In the room containing the flame retarded products there was :

a) 15 times more available escape time;
b) Only 25% of the heat released;

c) 50% less material consumed by the fire;
d) One third of the toxic gases (expressed at CO equivalents) released;
e) Little difference in the production of smoke (European Flame Retardant Association Web site : http://www.cefic-efra.org/, March 2004).

There are many different flame retardants, and these work in a number of different ways. Some flame retardants are effective on their own, other products are used mainly or only as “synergists”, acting to increase the effect of other types of flame retardant.

The major classes of flame-retardant chemicals are the halogenated organics, the halogenated or non-halogenated phosphorus based esters, the antimony trioxide and alumina trihydrate. Together they account for about 90% of the flame retardants in commerce today. Other compounds of commercial importance are magnesium hydroxide, ammonium phosphates, melamine and various borates and molybdates primarily as smoke suppressants (Edenbaum, 1992).

Consumption of flame retardants by type and region based on 2001 values is given in Table 2.1.

To understand how flame retardants work it is first necessary to see how materials burn. Combustion is defined as a succession of physical and chemical processes whereby substances of sufficiently high caloric potential in reaction with oxygen and with the emission of light and heat form less energetic products: water, carbon dioxide and carbon monoxide. With a given energy supply the rate of temperature increase of the material depends on its specific heat, its density, thermal conductivity, latent heat and its heat of evaporation.

Table 2.1 : Consumption of flame retardants by type and region based on 2001 values (thousands of metric tones) (European Flame Retardant Association Web site : http://www.cefic-efra.org/, March 2004)

	USA	Western Europe	Japan	Other Asia	Quantity (Total)	Value (millUS$)
Brominated compounds	60	42	47	9	239	774
Organophosphorus compounds	58	83	26	>19	186	465
Chlorinated compounds	17	51	5	25	98	108
Alumina Trihydrate	285	168	40	>9	502	219
Antimony Oxides	30	25	14	30	99	265
Other*	43	39	11	Na	> 93	140
Total	493	408	143	>173	1217	
Total (mill US$)	627	556	373	> 415		1971

The reaction of combustible gases with oxygen is an exothermic reaction which, at a given energy supply, exceeds the endothermic pyrolysis reaction and initiates flame propagation. The reaction taking place can be described in very simplified way as follows;

$$RH \longrightarrow R^{*} + H^{*} \tag{2.1}$$

$$H^{*} + O_2 \longrightarrow HO^{*} + O^{*} \tag{2.2}$$

$$HO^{*} + CO \longrightarrow CO_2 + H^{*} \tag{2.3}$$

A flame retardant should inhibit or even suppress the combustion process. Depending on their nature, flame retardants can act chemically and/or physically in the solid, liquid or gas phase. They interfere with combustion during a particular stage of this process e.g. during heating, decomposition, ignition or flame spread (Gachter, 1993).

---

* Zinc Borate, magnesium hydroxide, melamines and molybdates

2.2 ZINC BORATE PROPERTIES AND USAGE

Zinc Borate is a boron-based fire retardant with a chemical composition of **$xZnO.yB_2O_3.zH_2O$** The most commonly used grade has following structure **$2ZnO.3B_2O_3.3{,}5H_2O$.** There are different types of zinc borate.

$ZnO.B_2O_3.H_2O$
$ZnO.3B_2O_3.7\text{-}7{,}5H_2O$
$2ZnO.3B_2O_3.9H_2O$
$3ZnO.2B_2O_3.5H_2O$
$ZnO.B_2O_3.2H_2O$
$4ZnO.B_2O_3.H_2O$
$2ZnO.3B_2O_3$

Zinc borate $2ZnO{\cdot}3B_2O_3{\cdot}7H_2O$ is formed when borax is added to aqueous solutions of soluble zinc salts at temperatures below about 70°C. An x-ray structure determination has indicated that this compound is orthorhombic and has a zinc triborate monohydrate structure, $Zn[B_3O_3(OH)_5]{\cdot}H_2O$ (Nies 1964). Zinc borates $2ZnO{\cdot}3B_2O_3{\cdot}7H_2O$ and $ZnO{\cdot}B_2O_3{\cdot}2H_2O$ lose water of hydration when heated from 130 to 250°C (Woods, 1975).

Zinc Borate can be used as a fire retardant in PVC, polyolefins, elastomers, polyamides, epoxy resins. In halogen-containing systems, it is also used in conjunction with antimony oxide, while in halogen-free systems, it is normally used in conjunction with alumina trihydrate, magnesium hydroxide, or red phosphorus. In some particular application Zinc Borate can be used alone.

Zinc Borate acts through :

a) zinc halide or zinc oxyhalide that accelerate the decomposition of halogen sources and promote char formation.
b) by the B_2O_3 moiety released, a low melting glass, that can stabilize the char. B_2O_3 released can also promote the formation of ceramic formation in systems containing ATH or magnesium hydroxide.
c) the endothermic, stepwise release of water that can promote the formation of foamy char.

Table 2.2 shows the usage of zinc borate in different polymers and the benefits of its usage (Special Chemistry Web Site : http://www.specialchem.com/, October 2004).

Table 2.2 Zinc borate usage in different polymers and its benefits

Polymer	Benefits
PVC	♦ Smoke suppressant ♦ Flame retardant ♦ Synergist of antimony oxide ♦ Lowers total fire retardant cost ♦ Char promoter
Polyolefins	♦ Smoke suppressant/char promoter ♦ Afterglow suppressant ♦ Improves elongation properties ♦ Anti-arcing agent
Polyamides	♦ Anti-tracking agent ♦ Synergist of halogen sources ♦ Afterglow suppressant ♦ Used in both halogen containing and halogen-free nylons
Elastomers	♦ Smoke suppressant ♦ Afterglow suppressant ♦ Char promoter ♦ Anti-arcing and antitracking agent
Epoxy resin	♦ Smoke suppressant ♦ Char promoter ♦ Partial or complete replacement of antimony oxide

Zinc borate is of special commercial importance. It has been a workhorse among all of the known zinc borates. Its water of hydration is retained up to about 290 °C. It is noted for the following attributes.

a) Synergist of halogen sources
b) Can either partially or completely replace antimony oxide
c) Can function as a smoke suppressant
d) Can function as an afterglow suppressant
e) Can promote char formation and prevent dripping in most polymers
f) Can function as an anti-tracking agent
g) Its refractive index is similar to that of most polymers, which results in the retention of considerable translucency and allows the use of low pigment loading.

Recent research at Borax and published literature reported the following newly discovered benefits with the use of zinc borate:

a) Reduces rate of heat release in PVC and engineering plastics
b) Improves aged elongation property of polyolefins
c) Improves thermal stability of bromine/antimony oxide systems
d) Improves corrosion resistance of processing equipment
e) Improves laser marking quality
f) Promotes ceramic formation with aluminum trihydrate
g) Can function as an flame retardant in certain halogen-free systems (European Flame Retardant Association Web site : http://www.cefic-efra.org/, November 2004).

Agrawal and coworkers (1991) studied zinc borate complex as flame retardant filler. Water- insoluble complexes have been prepared by reaction of boric acid, pentaerythritol and metal salts i.e., acetates of zinc, cadmium, mercury, copper, nickel, cobalt and manganese. The composition of these complexes has been established by determining the metal content and by elemental analysis and structural aspects have been studied by far-IR spectra. The heat-resistance data indicated that the zinc borate complex is better than other metal-borate complexes. The effect of 10-60 parts of zinc borate complex on novel unsaturated polyester-7(II) in respect of gel time, exotherm peak temperature, tensile strength, % elongation, nitroglycerine absorption and flame retardance has been studied. The burning rate and oxygen index data coupled with data on gel time, exotherm peak temperature, nitroglycerine absorption and mechanical properties suggested that zinc borate complex was a potential flame retardant filler for unsaturated polyesters.

Basfar (2002) studied flammability of radiation cross-linked low density polyethylene as an insulating material for wire and cable. He investigated the influence of various combinations of aluminum trihydroxide and zinc borate as flame retardant fillers. He concluded that the usage of zinc borate with amounts of 4-8phr in a mixture of 40 phr LDPE, 60 phr EVA and10 phr aluminum trihydroxide ($Al(OH)_3$) was applicable. With zinc borate usage the mechanical properties (tensile strength, elongation) and flammability characteristics were improved.

Tsunoda and coworkers (2002) studied the effects of zinc borate on the properties of medium density fiberboard (mdf). He examined the resistance of medium density fiberboards treated with zinc borate to fungal and termite attack. It was concluded that zinc borates contents of above 1.00 percent boric acid equivalent protected medium density fiberboards from both decay ant termite attack without significant loss in mechanical or physical properties. It was also stated that the very low solubility of zinc borate was definitely beneficial for the treatment of wood composites aboveground where such composites were protected from weather.

Garba (1999) studied the effect of zinc borate as flame retardant formulation on some tropical woods. It was concluded that zinc borate in the presence of hydrogen chloride functioned effectively as a flame retardant for all the woods considered especially when used in the vapor phase, and in the condensed phase and/or in dehydration process. Incorporation of acidified (with HCl) zinc borate into the materials reduces flame propagation rate, after-glow time and flame temperature. On the other hand, this treatment increases add-on, LOI and char-formation.

Bourbigot and coworkers (1999) investigated the recent advances in the use of zinc borates in flame retardancy of ethylene-vinyl acetate (EVA). The aim of this study was to study the effect of zinc borates in halogen free EVA based formulations in terms of fire performances and of chemistry. In this work zinc borates were used as synergistic agents in EVA-ATH and EVA-$Mg(OH)_2$ flame retardant formulations and smoke suppressants. It was demonstrated that zinc borates ($2ZnO.3B_2O_3.3,5H_2O$, $4ZnO.B_2O_3.H_2O$) are useful synergistic agents in EVA-ATH and EVA-$Mg(OH)_2$ formulations and they act as smoke suppressant. Moreover, the solid state NMR spectra of the residues collected from the cone calorimeter experiments allows to propose a mechanism for the mode of action of these FR systems. It was demonstrated that the decomposition of ATH to Al_2O_3 during the heating of the polymer leads to an increase of the ignition time. The formation of Al_2O_3 in situ from ATH during the combustion of the polymer reduces flammability significantly. Concurrently zinc borate transformed and it was proposed that the zinc borates aided in developing a more vitreous protective residual layer, which reduces the combustion rate.

Pi and coworkers (2002) studied the effects of zinc borate (ZB) and aluminum trihydrate (ATH) on the flame retardant and mechanical properties of PVC. It was concluded that the incorporation of a small amount of zinc borate and zinc borate-ATH could greatly increase the limiting oxygen index of PVC and suppressed the release of aromatic compounds during the burning of PVC. It was also concluded that the mechanochemical modification of zinc borate and zinc borate –ATH could decrease their particle sizes and distribution and enhanced the interfacial interaction of PVC/ZB and PVC/ZB-ATH, causing a great increase in the impact and yield strengths and elongation at break of PVC/ZB and PVC/ZB-ATH.

Ning and coworkers (2000) also studied the effects of zinc borate (ZB), aluminum trihydrate (ATH) and their mixture on the flame retardant and smoke suppressant properties of poly vinyl chloride (PVC) as well as their mechanism for flame retardancy and smoke suppression were studied through the limiting oxygen index (LOI) test, smoke density test, TGA, GC-MS and SEM. The results showed that incorporation of a small amount of ZB, ATH and their mixture could greatly increase the LOI of PVC and reduce the smoke density of PVC during combustion. The mixture of ZB with ATH has a good synergistic effect on the flame retardance and smoke suppression of PVC. TGA and GC-MS analyses results showed that incorporation of small amount of ZB, ATH and their mixture greatly promoted char formation of PVC and decreased the amount of hazardous gases such as benzene and toluene released in PVC during combustion.

2.3 ZINC BORATE AS A FLAME RETARDANT

Yang and coworkers (1999) studied the flame retardancy behavior of zinc borate. According to the study, zinc borates as flame retardant additives in multicomponent flame retardant systems were generally believed to behave in the flame retardancy process mainly as follows:

(1) zinc borate (hydrates) dehydrates endothermically and the hydrate water vaporizes, absorbs heat and dilutes oxygen and gaseous flammable components;
(2) zinc borate at a sufficiently high temperature can melt to produce a glassy layer insulating the flammable surface; and
(3) zinc borate changes the decomposition route of some flammable substances, inhibiting the formation of flammable gases.

In this study the effect of boron chloride formation from zinc borate in burning PVC was elucidated:

Boron halides had low boiling points; during the burning process of PVC with added zinc borate hydrate, the boron that was lost mainly by vaporization in the form of boron chloride.

It has been suggested that hydrogen chloride may be formed mainly because of the presence of boron halide. Two reactions were studied by thermodynamic analysis and using literature data:

$$B_2O_3 + 6HX \longrightarrow 2BX_3 + 3H_2O \qquad (2.4)$$

$$2ZnO.3B_2O_3.3{,}5H_2O + 22HX \longrightarrow 2ZnX_2 + 6BX_3 + 14{,}5H_2O \qquad (2.5)$$

According to the performed experiments following results have been derived:

(1) from the thermodynamic data, boron chloride and water could strongly interact with each other, therefore there was no boron chloride formed;

(2) there was a possibility that there was no chemical reaction between zinc borate and hydrogen chloride (including the formation of zinc chloride);

(3) another possibility was that the gaseous reactants in the gas solid reaction had difficulty penetrating the inside of the solid reactants which might have resulted in some chemical reaction occurring at high temperature to form zinc chloride and boron anhydrate.

(4) Based on the experiments. Reaction (2.5) was impossible; that was boron chloride could not be obtained from the reaction of boric acid and hydrogen chloride.

2.4 ZINC BORATE SYNTHESIS

Nies and coworkers (1970) investigated different methods to produce zinc borate. In the first example a solution was prepared containing borax pentahydrate, boric acid and water. A second solution with zinc oxide, sulfuric acid, and water was also prepared. A seed of zinc borate with chemical formula of $2ZnO.3B_2O_3.9H_2O$ was added. The mixtures were stirred and filtrated. The formula of the zinc borate obtained was $2{,}06ZnO.3B_2O_3.3{,}59H_2O$.

In the second example, a solution containing borax, boric acid and water was prepared. A second solution containing zinc chloride and water was also prepared. The solutions were mixed and seeded with the crystal ($2{,}06ZnO.3B_2O_3.3{,}59H_2O$) obtained from previous example. The mixture was stirred and filtered. The analysis of the resulting zinc borate was $2{,}07ZnO.3B_2O_3.3{,}71H_2O$.

In the third example, boric acid added to water. Previously prepared crystals of $2ZnO.3B_2O_3.3{,}5H_2O$ were added as seed. A mixture of boric acid and zinc oxide was then added. The mixture was stirred, filtrated, washed and dried. The formula of the zinc borate obtained was $2,07ZnO.3B_2O_3.3,66H_2O$.

Dong and coworkers (1998) studied to synthesize nanometer zinc borate using ethanol supercritical fluid drying technique. To prepare nanometer zinc borate; zinc nitrate was added to borax aqueous solution with stirring. After filtering, and washing with distilled water and ethyl alcohol the precipitate was added to ethyl alcohol and stirred into a slurry. The slurry was added to enough absolute ethyl alcohol in an autoclave. The ethanol and the nitrogen along with the remaining alcohol was removed very slowly. It was possible to synthesize nanometer zinc borate with a particle size of 20-50nm.

Shete and coworkers (2004) presented a comprehensive set of experimental results on the influence of process variables on the size distribution of a product made in a batch heterogeneous reaction. In this work, the effect of speed of agitation, mean initial particle size of zinc oxide, temperature, boric acid concentration in the solution on conversion of zinc oxide and mean particle size of zinc borate were investigated. The controlling mechanism, mixing effects and reaction kinetics were also studied.

As could be seen from the contents of the works in literature, there was a lack of a study that focused on the characterization of the zinc borate product at the end of the experiments, observing the effects of the experimental parameters on reaction rate and final zinc borate product size and reducing the reaction completion time.

CHAPTER 3

EXPERIMENTAL

3.1. MATERIALS USED

Boric acid (H_3BO_3, with purity of 99.9% by weight), zinc oxide (ZnO), zinc borate ($2ZnO.3B_2O_3.3{,}5H_2O$) and distilled water were used to produce zinc borate.

The boric acid (H_3BO_3) was provided from Emet Boric Acid Plant, Kutahya, Turkey. The zinc oxide (ZnO) was supplied by two suppliers. The one with 10 µm particle size was provided by MKS Limited, İstanbul, Turkey and the ZnO having particle size of 25 µm was provided from Kartal Oksit Limited, Ankara, Turkey. The zinc borate ($2ZnO.3B_2O_3.3{,}5H_2O$) again was obtained from two suppliers. The one with average particle size of 10 µm was supplied from Great Lakes, USA and the other with particle size of 2 µm was from Borax Morarji Limited, Bombay. The fourth reactant the distilled water was obtained by distilling the tap water by the use of a water distillation apparatus (Nüve NS 108) at METU Boric Acid Research Laboratory. All the other chemicals used in the analysis were purchased in reagent grade from Merck and J.T Baker.

3.2. EXPERIMENTAL SET-UP

Experimental set-up consisted of a reactor with a volume of 1.5 L, a mechanical stirrer, a heating jacket, a pH meter, a thermocouple, a temperature control unit and a vacuum pump. The schematic representation and picture of the experimental set-up were given in Figure 3.1 and Figure 3.2, respectively.

The batch reactor was made up of borosilicate glass. Inside diameter of the reactor and height of the reactor was 12 cm and 30 cm, respectively. The top section of the reactor was covered by a flexyglass plate. The top section of the reactor has four entrances. At the center, stirrer was placed. One of the other entrances was for placing thermocouple which was connected to the temperature control unit. The third entrance was used for putting reactants in the reactor and placing the pH electrode inside the reactor. The samples were withdrawn from the last entrance of the reactor.

A mechanical stirrer (Heidolph RZR 2041) was used to mix the slurry in the reactor. The mixing rate of the stirrer could be seen on the monitor of the stirrer.

The reaction temperature was controlled by a temperature controller unit. This unit consisted of a thermocouple, a temperature controller and heating jacket. The batch reactor was placed in a heating jacket and the thermocouple connected the temperature controller was put into the reactor. The reaction temperature was kept constant at desired temperature during each experiment by adjusting a set point on the temperature controller. The reaction temperature could be seen on the display of temperature controller. A 50 ml syringe attached to a glass pipe was used to withdrawn the sample from the reactor.

The products, zinc borate and the water are separated by use of vacuum filtration. This unit consists of a vacuum pump (KNF NO22, Germany) connected to a flask and a funnel was placed on top of flask. Filter paper (Blue band filter paper) was placed on the funnel and solid particles were collected on the filter paper, whereas the solution was collected in the flask.

3.3. EXPERIMENTAL PROCEDURES

Firstly, the boric acid solution was prepared and put in the reactor. All the boric acid used in the experiment was dissolved in water. Solution was prepared considering the saturation value of boric acid at the performed experiment temperature. The mechanical stirrer was started to operate at the desired stirring rate. The temperature control unit was adjusted to the reaction temperature and kept constant. After the boric acid solution reached to desired temperature in the reactor, the zinc oxide, at stoichometric ratio or in excess, was added slowly into the reactor. Lastly small amounts of zinc borate (about 1.5% of the used boric acid in the solution) acting as seed in the reaction was added. The time for adding the seed was considered as the starting time of the reaction. The samples were withdrawn by 50 ml syringe attached to a glass pipe. Then, samples were filtered immediately by using filter and then finally washed with hot water to remove the excess boric acid stacked to the surface.

Solid particles and liquid were collected on filter paper and flask, respectively. The liquid sample was taken from the flask by the help of micropipettes (Finpipette, Thermo Labsystems) and analyzed for boric acid concentration. The filtrates were washed with hot water to remove the excess boric acid and analyzed for change of boric acid and zinc oxide percents with respect to time and size distribution analysis.

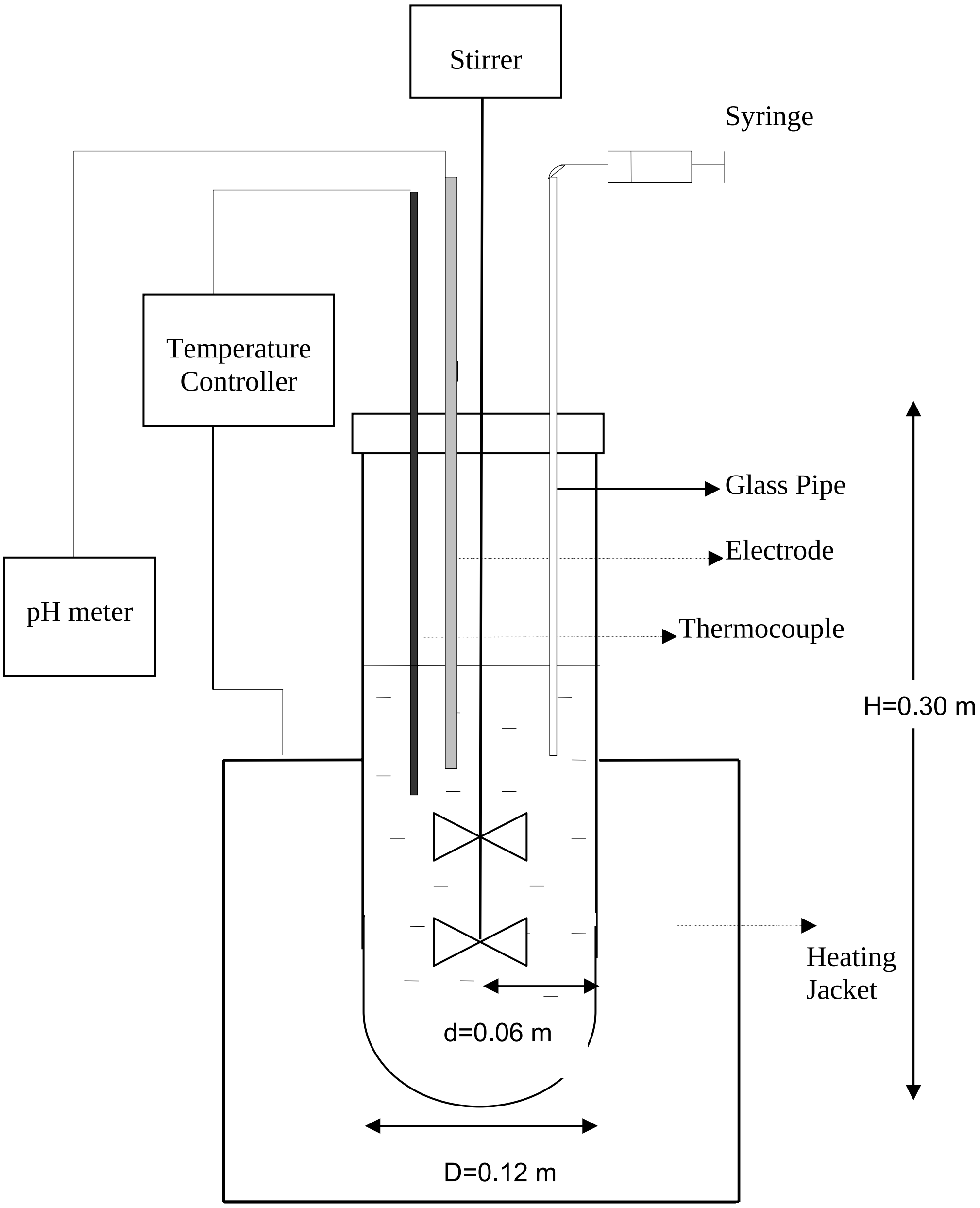


Figure 3.1. The schematic representation of the experimental set-up

Figure 3.2. The picture of the experimental set-up

3.4. ANALYSIS PROCEDURES

The samples taken from the reactor were filtered immediately. In the liquid phase, boric acid amount was determined. In the solid phase zinc oxide and boric acid amounts were determined and size distribution analysis was performed. The crystal images were analyzed by using light microscope.

The analysis techniques used for determination of the quantity of zinc oxide and boric acid in the solid sample was modified by Prof.Dr. Nusret Bulutcu (Istanbul Technical University, Chemical Engineering Department) on the basis of basic boric acid and zinc oxide analysis.

3.4.1. Determination of Zinc Oxide in solid sample

Preparation of Ammonia Buffer Solution: The solution was prepared by dissolving 33.75 grams of ammonium chlororide in 460 ml of ammonia solution.

Preparation of 0.05M EDTA : The solution was prepared by dissolving 18.613 grams of A.R Disodium dihydrogen ehtylenediaminetetra – acetate dehydrate, accurately weighed in distilled water and dilute to 1 litre in a standard volumetric flask with distilled water (Shete, 2004).

Preparation of Erichrome Black T Indicator : The indicator was prepared by dissolving 0.2 grams of the dyestuff in 15 ml of triethanolamine and 5 ml of absolute ethanol (Shete, 2004).

This analysis was applied to the solid part of the taken sample. 0.2-0.3 gram of the sample weighted and dissolved by using 1 ml of hydrochloric acid (with purity of 37%). 15-20 ml of ammonia buffer solution was added to hold the pH around 9.5. The final solution was titrated with 0.05M EDTA solution by adding few drops of Erichrome Black T indicator. Titration was performed with the help of micropipettes (Finpipette, Thermo Labsystems) and continued until the color changed from the purple to blue. The volume of EDTA used in the titration step was recorded. Zinc oxide percentage in the solid phase was calculated from the Equation 3.1 (Wilson, 1992):

$$P_{ZnO} = V_{EDTA} \,.\, (a) / n \qquad 3.1$$

where P_{ZnO}, V_{EDTA} and “n” are the weight percentage of ZnO in the taken sample, volume of the EDTA used and amount of sample, respectively.

In Equation 3.1, the constant “a” is the weight of ZnO in the sample resulting from the addition of 1 ml of 0.05M EDTA. The value of the “a” is 0.004069 g/l. It was calculated from the basic EDTA analyses principles.

Volume of EDTA used(ml) **X** Molarity of EDTA (0.05M EDTA used through the study) **X** Atomic weight of the metal ion (Zn^{+2} ions detected in the analyses but since it was in the form of ZnO for simplicity the atomic weight of ZnO was taken, 81.37) **=** Weight of metal complex. (Wilson, 1992)

3.4.2. Determination of Boric Acid in Solid Sample

The determination of boric acid in the solid sample was performed as follows: 0.2-0.3 gram solid sample was weighed and dissolved with 1 ml of hydrochloric acid (with purity of 37%). Before titration begins, necessary EDTA solution should be added to prevent any mistakes that could be caused by the existence of Zn ions. The amount of EDTA necessary for the titration of the sample in order to calculate the ZnO% percent added previously and to avoid any mistake an additional amount of approximately 10ml was added to the sample. After EDTA addition, the solution was titrated with 1 N NaOH (obtained from E.Merck) until a pH of 7 was obtained. At this step a titrator (Schott, TitroLine easy) involving a magnetic stirrer and pH-meter was used to get accurate results. After reaching the pH of 7, 10-15 gram mannitol was added to the solution. Finally, solution was again titrated with 1 N NaOH until the pH of the solution becomes 7. The volume of NaOH used in the second titration step was recorded. Boric acid percentage in the liquid phase was calculated from Equation 3.2 (Erdoğdu, 2004).

$$
\begin{aligned}
P_{B2O3} &= (V_{NaOH} * F_{NaOH} * 0.1) / n * (69.6202/2) * (100/1000) \\
&= 0.348101 * (V_{NaOH} * F_{NaOH}) / n \qquad 3.2
\end{aligned}
$$

where P_{B2O3}, V_{NaOH}, F_{NaOH} and “n” are the weight percentage of B_2O_3 in the taken sample, volume of the NaOH used, factor of NaOH solution and amount of sample, respectively.

3.4.3. Determination of Boric Acid in Liquid

Two-three drops of methyl red indicator were added to the filtrate. Then H_2SO_4 , (1:3 by vol.) was added to the solution until the color of the solution was pink. The solution was titrated with 6 N NaOH until the color is changed from pink to yellow. H_2SO_4 was added until the color of the solution turns to pink again. The solution was titrated with 1 N NaOH until a pH of 4.5 was obtained. At this step a titrator (Schott, TitroLine easy) involving a magnetic stirrer and pH-meter was used to get accurate results. Phenolphatelyn indicator and 2-3 g mannitol (obtained from E.Merck) were added to the solution. Finally, solution was titrated with 1N

NaOH until the pH of the solution becomes 8.5. The volume of NaOH used in the second titration step (pH between 4.5-8.5) was recorded. Boric acid concentration in the liquid phase was calculated from the Equation 3.3 (Çakal, 2004).

$$c_{Bt} = V_{NaOH}\, F_{NaOH}\, N_{NaOH} / V_{sample} \qquad 3.3$$

where c_{Bt}, V_{NaOH}, F_{NaOH}, N_{NaOH} and V_{sample} are the concentration of boric acid solution at the sample taken time, the volume of the NaOH used, factor of the NaOH, normality of NaOH, and the volume of the sample, respectively.

3.5. DETERMINATION OF CRYSTAL SIZE DISTRIBUTION

Sample taken from the reactor was filtered. The cake was washed with a large volume of water.

The particle size distributions of the solid samples were determined by a particle size analyzer (Malvern Instruments, Mastersizer 2000), in Ankara University, Chemical Engineering Department; İstanbul Technical University, Chemical Engineering Department and The Central Laboratory, Middle East Technical University utilizing the principle of laser ensemble light scattering. This instrument can detect the particle range of 0.02-2000 μm. The analysis was done by using wet dispersion method with a repeatability of +/- 0.5%. Tap water was used as dispersant in the analysis.

In the analysis, some amount of solid was taken from the sample bottles and put into beaker filled with water. This beaker was put on its place in the analyzer. Solid was continued to be added until the laser obscuration value on the computer reaches 14-15%. Then the analyzer was ready to give the crystal size distribution of the sample. The analysis was repeated for several times to see if the same result was obtained or not. The resulting graph could be achieved and the volume weighted mean of the curve could be obtained from the computer program.

3.6. CRYSTAL IMAGE ANALYSIS

The cake was analyzed for crystal structure of solid particles. A small amount of solid sample was taken and put on the glass. A drop of water was added because it was not possible to analyze the dry filtrate. Then, the samples were analyzed. Morphology of gypsum crystals was obtained by a light microscope connecting to online to a computer by a Pro Series, high performance CCD Camera. Images were seen live in monitor by Image Pro Plus 3.0 software. Views of solid samples were snapped and saved into the computer. The magnification bar was added on each picture of the crystals views.

3.7. TG/DTA ANALYSIS

TG/DTA analysis of the final products of some selected samples were performed by the “Setaram Labsys Simultaneous Thermogravimetrik Analyser and Diferential Thermal Analyser” device existed in METU Central Laboratory.

3.8. SCOPE OF THE EXPERIMENTS

Five sets of experiments were performed during the study. The effect of boric acid on zinc oxide ratio, the particle size of zinc oxide, stirring rate, temperature and size of seed crystals on reaction rate and particle size distribution of zinc borate were investigated.

In the first set of the experiments the effect of reactants ratio were investigated. The other parameters such as temperature (95°C), stirring rate (1600 rpm), type of zinc oxide (average size of 10 μm) and the seed (average size of 10 μm) were kept constant. Four different mole ratio of boric acid to zinc oxide (H_3BO_3:ZnO) were used. The mole ratio of the reactants changed from the stoichometric ratio (3:1) to the excess of boric acid, 3.5:1, 5:1 and 7:1.

In the second set of the experiments the effect of zinc oxide particle size on the reaction rate was investigated. The other parameters such as temperature (95°C), stirring rate (1600 rpm), reactants ratio (3.5:1) and the type of the seed (average size of 10 μm) were kept constant. Two different size of zinc oxide particle were used in the experiments. One with the average size of 10 μm and the other is approximately 25 μm.

In the third set of the experiments, it was aimed to investigate the effect of stirring rate. Other reaction parameters that were temperature (95°C), reactants ratio (5:1 and 7:1), type of zinc oxide (average size of 10 μm) and the seed (average size of 10 μm) were kept constant. The stirring rate was changed as 275 rpm, 400 rpm, 800 rpm and 1600 rpm.

In the fourth set of experiments the temperature effect on the reaction was observed. Other reaction parameters that are reactants ratio (5:1), stirring rate (1600 rpm), type of zinc oxide (average size of 25 μm) and the seed (average size of 10μm) were kept constant. The temperatures of 75°C, 80°C, 85°C and 95°C were tried.

In the fifth set of the experiments the effect of seed on the reaction rate was observed. Firstly two experiment with same experimental conditions (temperature at 95°C, mole ratio of 5:1, stirring rate of 800 rpm, zinc oxide with an average particle size of 10 μm) were performed but one without using seed. Then different size of zinc borate seeds were compared by keeping constant other variables (temperature at 95°C, mole ratio of 5:1, stirring rate of 1600 rpm, zinc oxide with an average particle size of 10 μm). One seed had an average particle size of 10 μm and the other was 2 μm.

All performed experiments and their conditions were summarized in Table 3.1.

Table 3.1. Performed experiments

Experiment number	Stirring Rate (rpm)	H_3BO_3/ZnO ratio	Size of seed (µm)	Temperature (°C)	Size of zinc oxide (µm)
Run 1	**800**	**5:1**	**-**	**95**	**10**
Run 2	**800**	**5:1**	**10**	**95**	**10**
Run 3	**1000**	**7:1**	**10**	**95**	**10**
Run 4	**1600**	**5:1**	**10**	**95**	**25**
Run 5	**1600**	**7:1**	**10**	**95**	**10**
Run 6	**1600**	**5:1**	**10**	**95**	**10**
Run 7	**1600**	**3.5:1**	**10**	**95**	**10**
Run 8	**1600**	**3.5:1**	**10**	**95**	**25**
Run 9	**1600**	**5:1**	**10**	**75**	**25**
Run 10	**1600**	**5:1**	**10**	**85**	**25**
Run 11	**1600**	**5:1**	**2**	**95**	**25**
Run 12	**400**	**5:1**	**10**	**95**	**10**
Run 13	**1600**	**5:1**	**10**	**80**	**25**
Run 14	**1600**	**3:1**	**10**	**95**	**10**
Run 15	**275**	**5:1**	**10**	**95**	**10**

CHAPTER 4

RESULTS AND DISCUSSION

The collected experimental data was classified into three categories; characterization of the final zinc borate products, factors affecting the conversion of zinc oxide and percentage change of boric acid and zinc oxide in the solid sample and the kinetic model according to the data obtained during the experiments.

In product characterization part, the performed XRD and TG/DTA analysis of some selected experiments were shown to determine whether zinc borate could be synthesized successfully.

In the following part, it was possible to see the effects of experimental conditions (stirring rate, reactants ratio, temperature, usage of seed, zinc oxide particle size) to the conversion of zinc oxide and the percentage change of zinc oxide and boric acid during the performed experiments.

In the particle size distribution part, the effects of experimental parameters (stirring rate, reactants ratio, temperature, usage of seed, zinc oxide particle size) on the size of final zinc borate products were observed.

In the kinetics model part, the activation energy was calculated and a kinetic model was proposed based on the experimental data collected.

In these parts the results were compared with the ones obtained from the literature.

The raw data of the performed experiments was given in Appendix A. In the raw data one could find when the samples were taken during the experiments, the analytical analysis results of the samples (amount of EDTA used during titration and amount of zinc oxide present according to used EDTA; amount of NaOH used during titration and boron oxide present according to used NaOH) and the percentage of ZnO and B_2O_3 at the analyzed samples.

The liquid analyses of the experiments were given in Appendix B. The changes of B_2O_3 content in the liquid with respect to time were given in the graphs. The experiments were classified and drawn together in the same graph according to stirring rate, temperature, mole ratio and size of zinc oxide particles.

The crystal image analyses of some selected experiments were given in Appendix C. One could measure the individual crystal size of final zinc borate particles with the help of these images.

Physical and chemical properties of boric acid, zinc oxide and zinc borate, solubility data of boric acid, particle size distributions of the two zinc oxides (average particle size of 10 μm and 25 μm) used as reactant in the experiments and particle size distributions of the two zinc borates (average particle size of 10μm and smaller particle size) used as seed in the experiments were given in Appendix D.

To check the reproducibility of the experimental set up and analysis used during the study, two experiments with the same experimental conditions were performed. The results and comparison were given in Appendix E.

A sample calculation was made for the zinc oxide conversion calculations, determination of the activation energy and reaction modeling in Appendix F.

4.1. PRODUCT CHARACTERIZATION

4.1.1. XRD RESULTS

To determine whether zinc borate has been synthesized successfully at the end of the experiments XRD patterns of the final products were compared with the one of commercially taken zinc borate.

The XRD graphs of different products and the one of the commercially taken zinc borate used as seed were shown in Figure 4.1 to Figure 4.7.

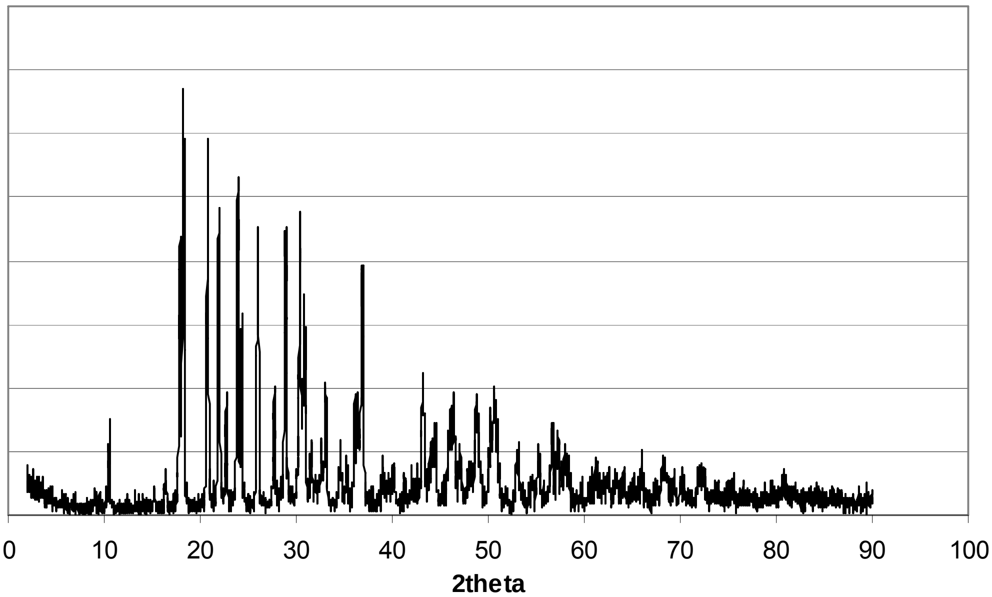


Figure 4.1: The X-ray pattern of zinc borate used as seed during the experiments.

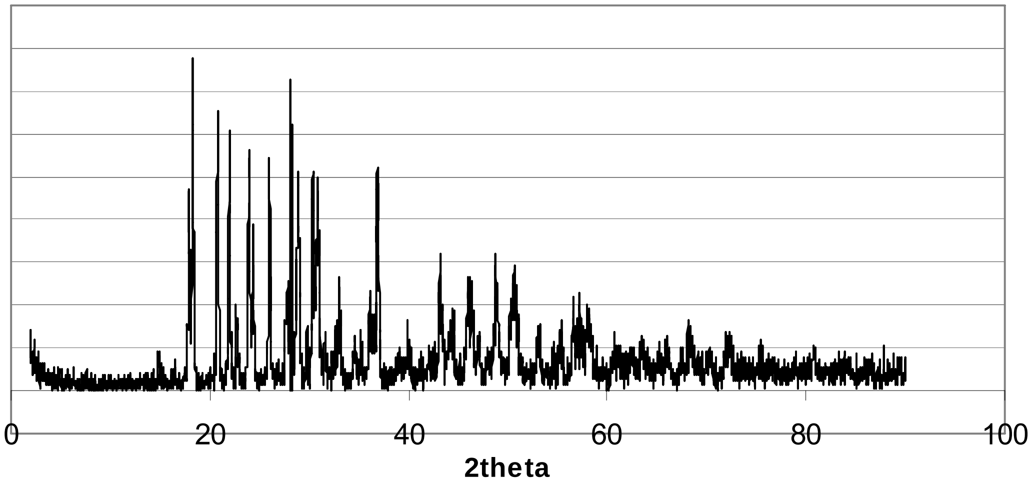


Figure 4.2 : The X-ray pattern of final product obtained in Experiment 3 (1000rpm stirring rate, 7:1mole ratio, 95ºC temperature, 10µm zinc oxide)

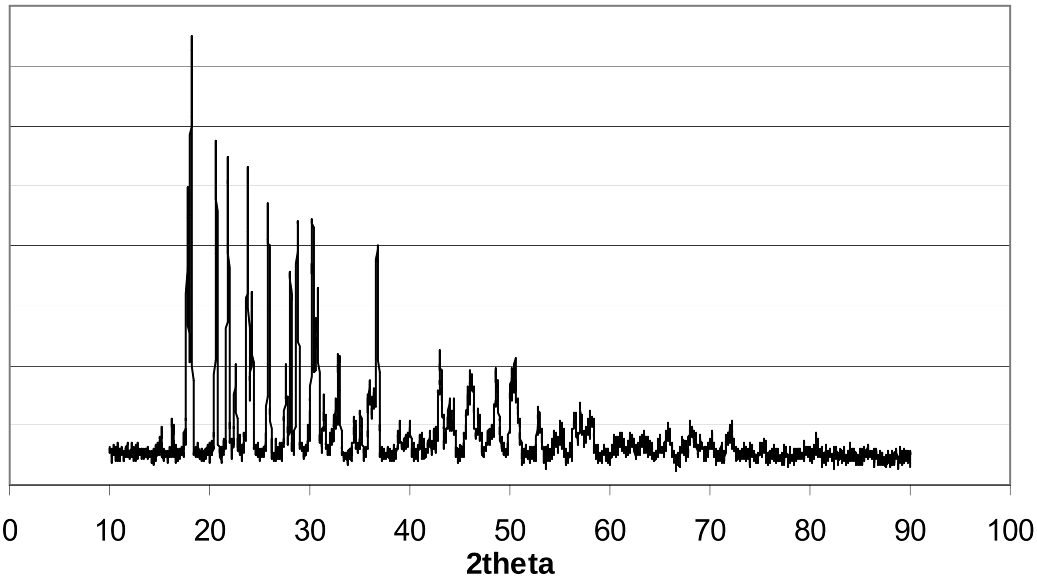


Figure 4.3 : The X-ray pattern of final product obtained in Experiment 6 (1600rpm stirring rate, 5:1mole ratio, 95ºC temperature, 10µm zinc oxide)

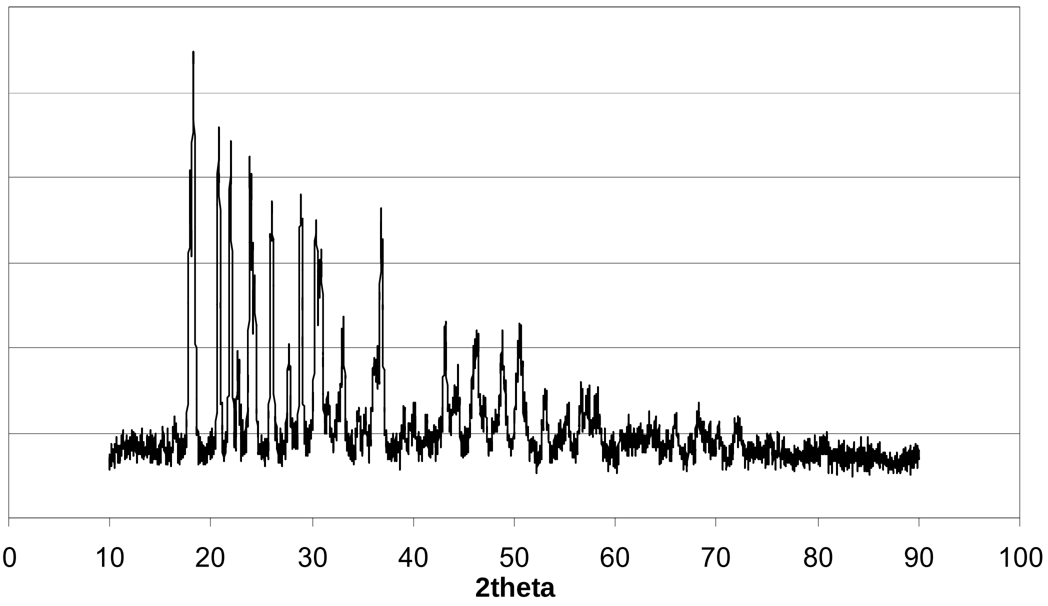


Figure 4.4 : The X-ray pattern of final product obtained in Experiment 7 (1600rpm stirring rate, 3,5:1mole ratio, 95ºC temperature, 10µm zinc oxide)

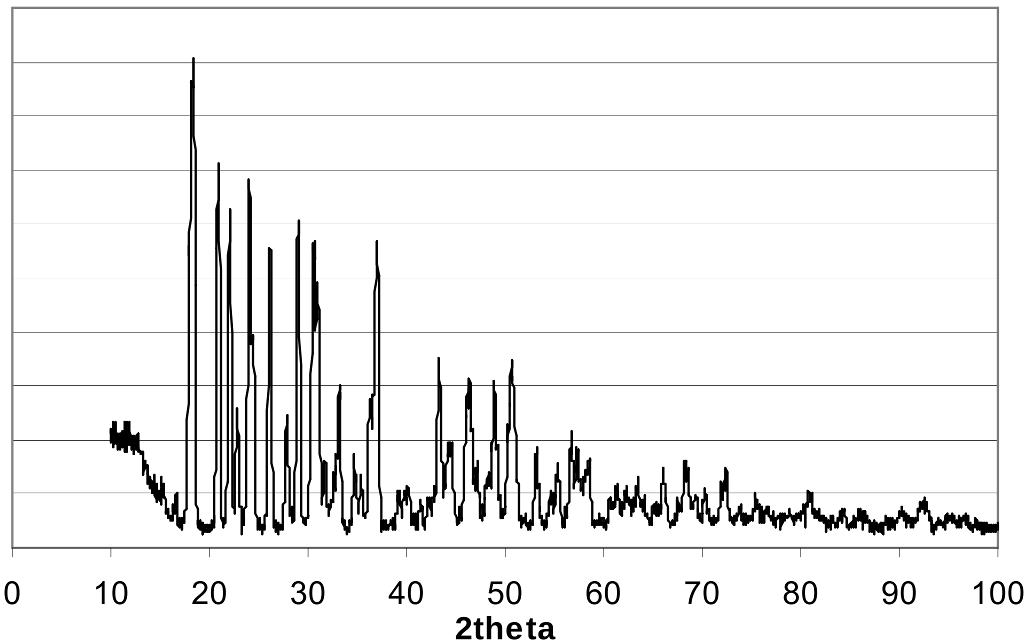


Figure 4.5 : The X-ray pattern of final product obtained in Experiment 8 (1600rpm stirring rate, 3.5:1mole ratio, 95ºC temperature, 25µm zinc oxide)

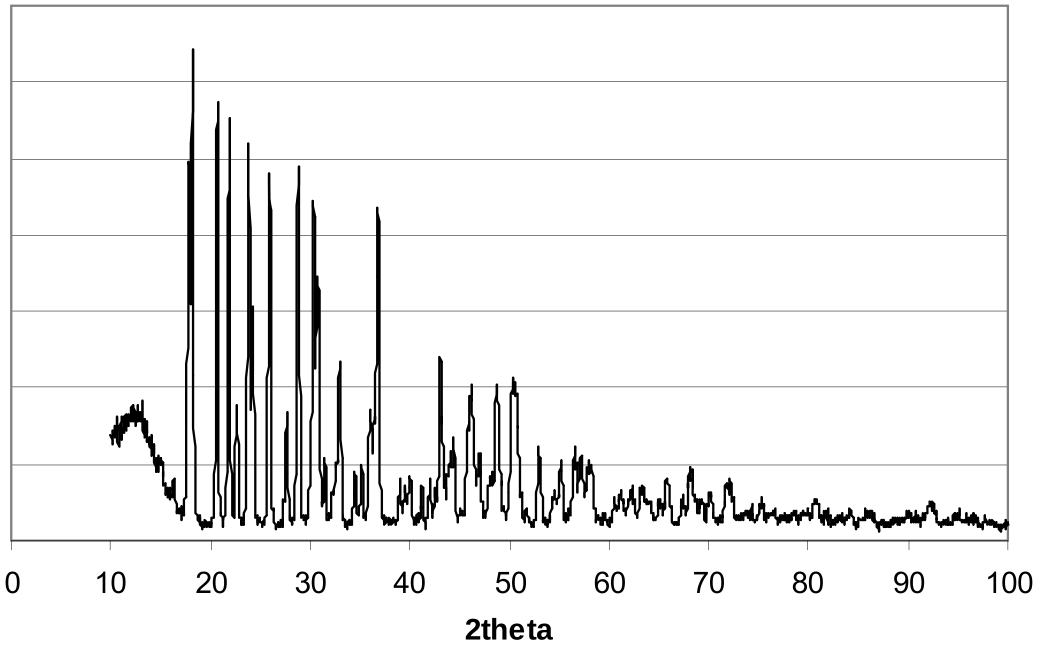


Figure 4.6 : The X-ray pattern of final product obtained in Experiment 9 (1600rpm stirring rate, 5:1mole ratio, 75ºC temperature, 25µm zinc oxide)

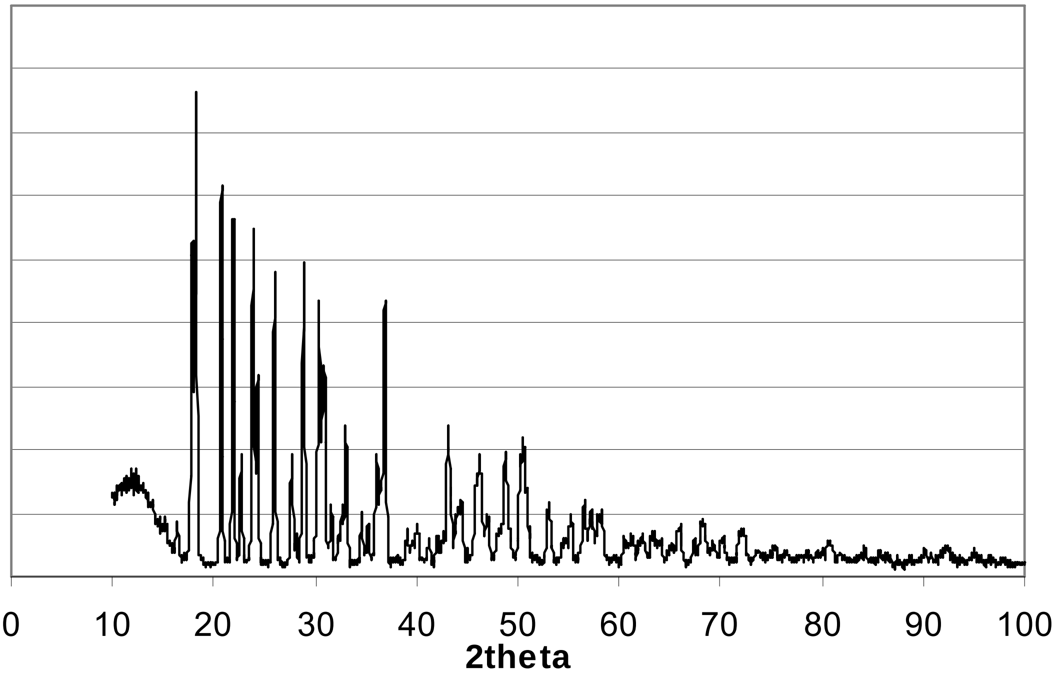


Figure 4.7 : The X-ray pattern of final product obtained in Experiment 10 (1600rpm stirring rate, 5:1mole ratio, 85ºC temperature, 25µm zinc oxide)

The comparison of the results of final zinc borate products of the performed experiments and the commercially taken zinc borate showed that zinc borate was synthesized successfully. The peaks of the seed and the selected experiments were consistent with each other. The same peaks were observed at the same “2theta” values.

4.1.2. TG/DTA RESULTS

To determine whether the obtained zinc borates at the end of the experiments were able to hold its crystal water in its structure to the desired temperature, TG/DTA analysis were performed and compared with the one obtained from the manufacturing company (supplied by Chengdu Chemphys Chemical Industry Co. Ltd, China). In the literature, it was indicated that zinc borate could keep its crystal water up to 290ºC (Shete, 2004). The results were shown from Figure 4.8 to Figure 4.13.

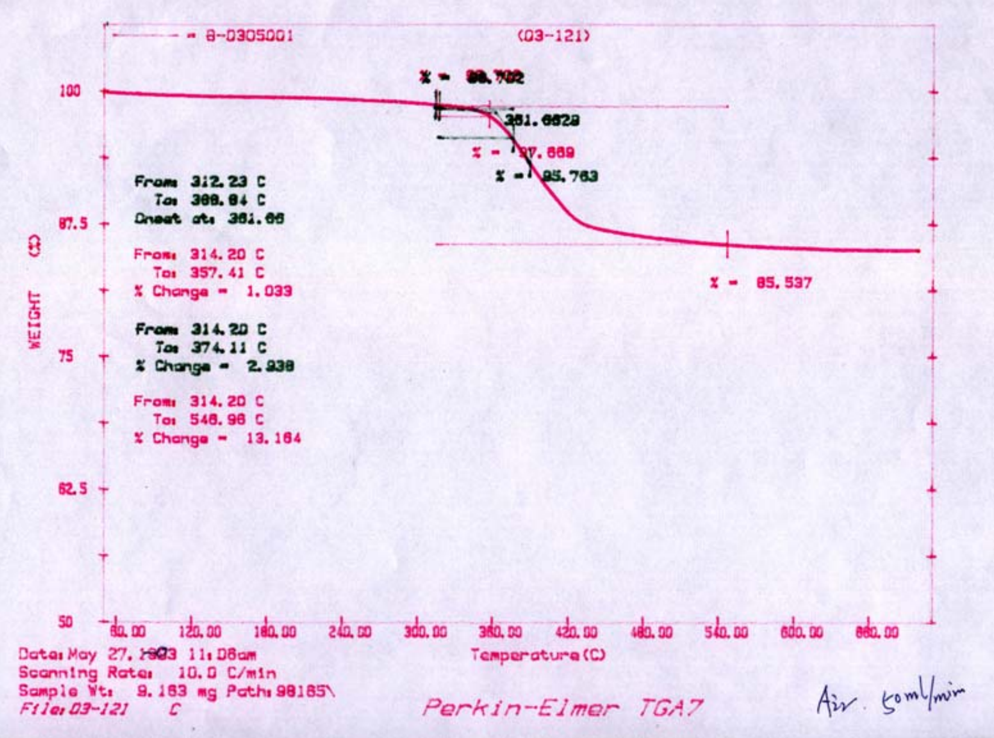


Figure 4.8 : TGA data of zinc borate supplied by Chengdu Chemphys Chemical Industry Co. Ltd, China

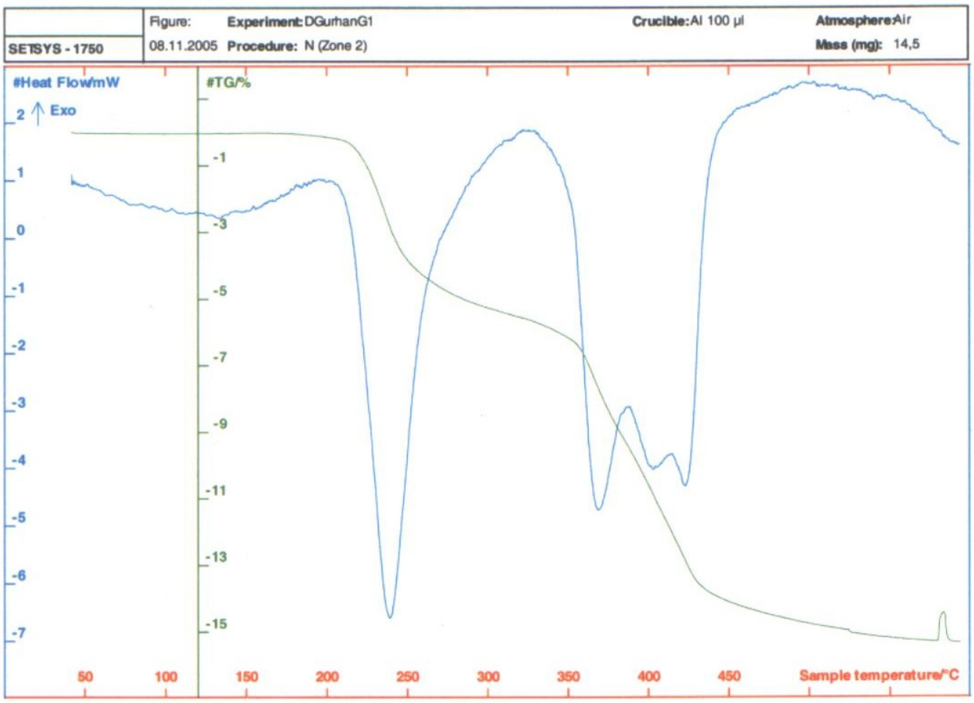


Figure 4.9 : The TG/DTA pattern of Experiment 1 (800rpm stirring rate, 5:1mole ratio, 95ºC temperature, 10µm zinc oxide, with the absence of the seed)

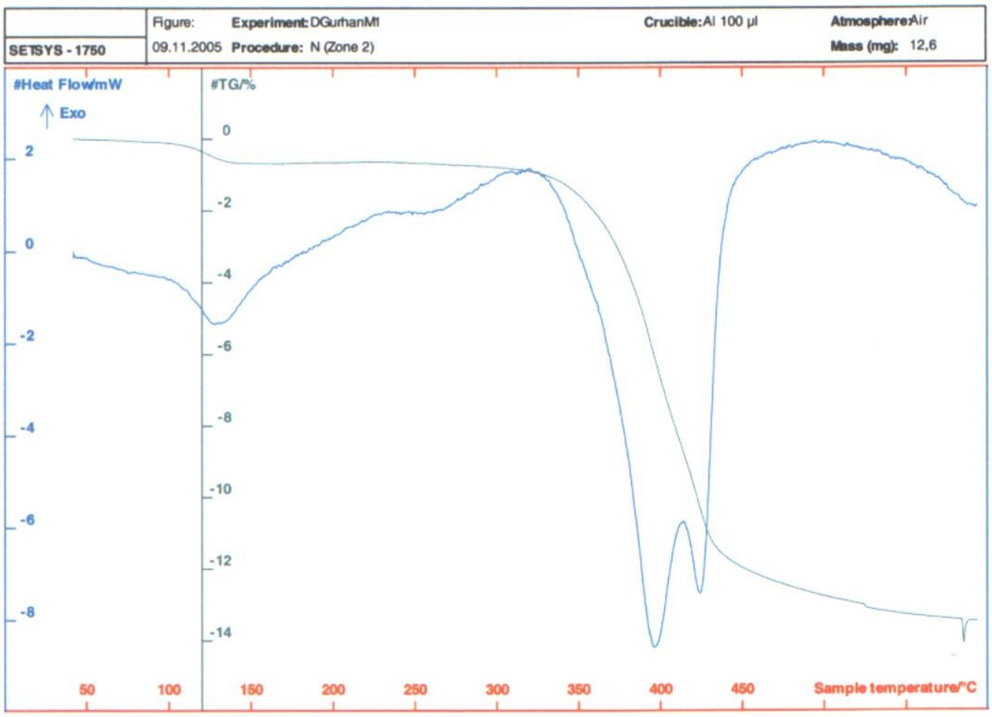


Figure 4.10 : The TG/DTA pattern of Experiment 4 (1600rpm stirring rate, 5:1mole ratio, 95ºC temperature, 25µm zinc oxide)

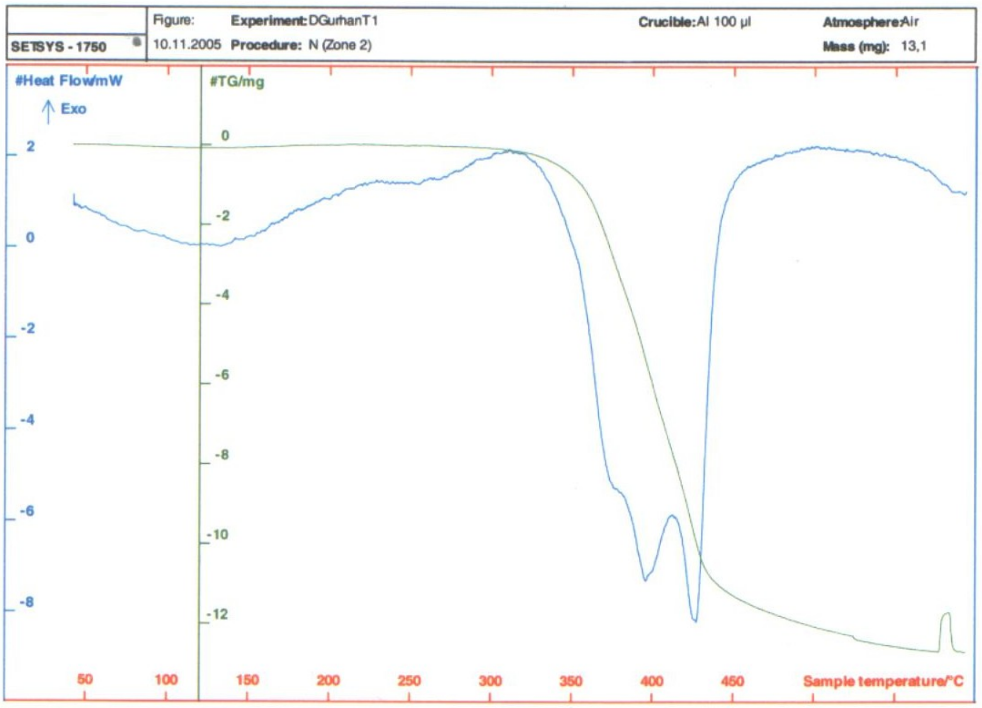


Figure 4.11 : The TG/DTA pattern of Experiment 8 (1600rpm stirring rate, 3.5:1mole ratio, 95ºC temperature, 25µm zinc oxide)

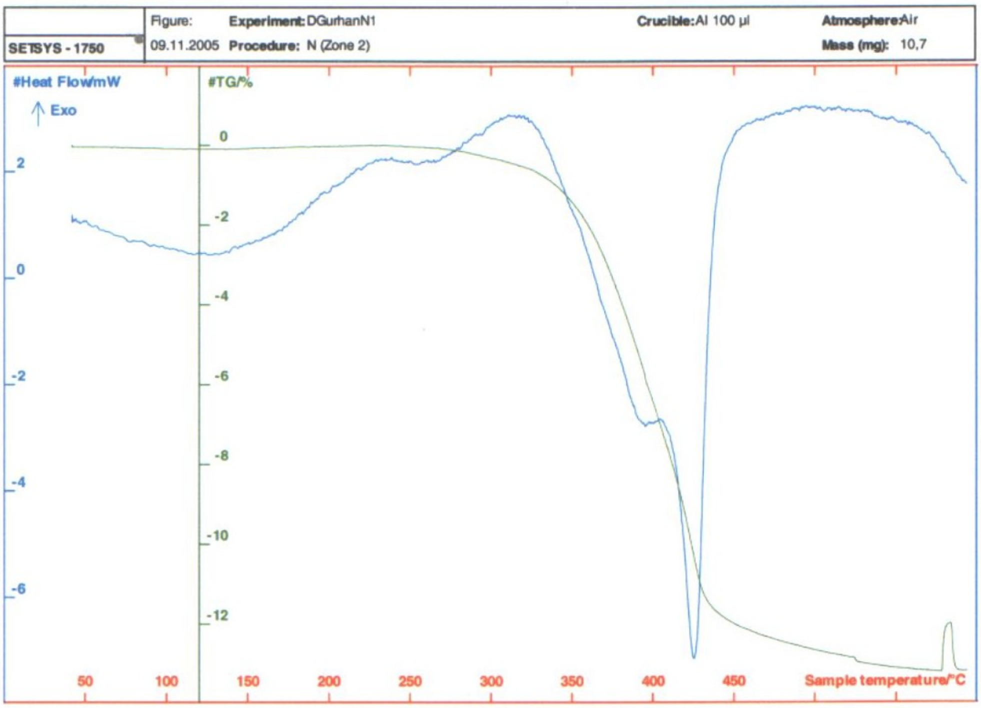


Figure 4.12 : The TG/DTA pattern of Experiment 9 (1600rpm stirring rate, 5:1mole ratio, 75ºC temperature, 25µm zinc oxide)

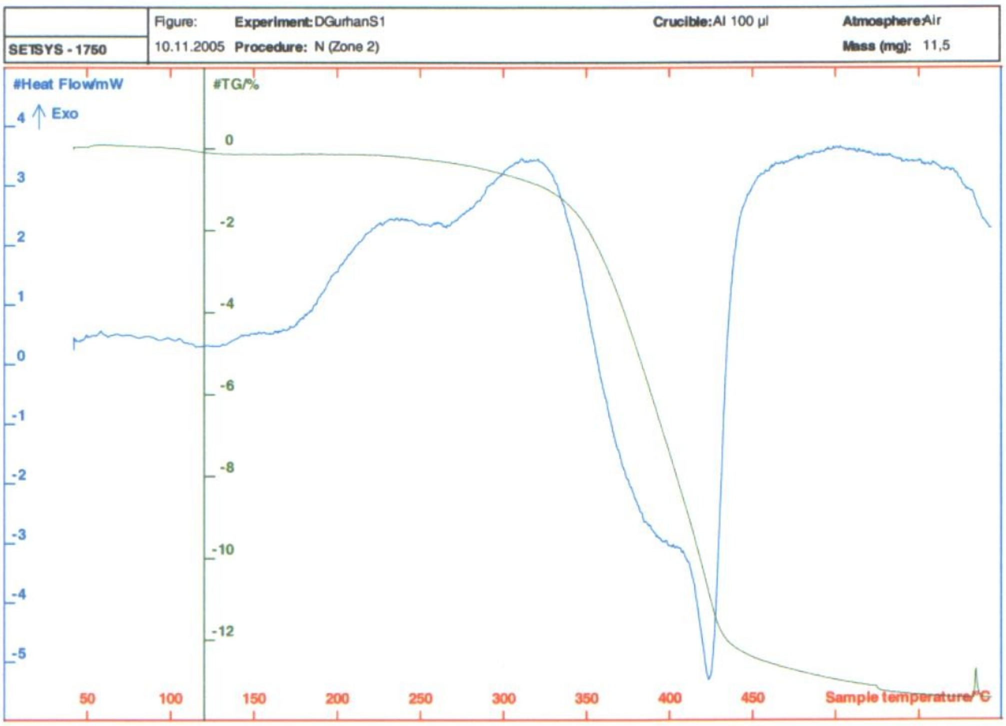


Figure 4.13 : The TG/DTA pattern of Experiment 10 (1600rpm stirring rate, 5:1mole ratio, 85ºC temperature, 25µm zinc oxide)

The TG/DTA patterns of the experimental products and the TG/DTA pattern of the zinc borate obtained from the manufacturing firms showed that zinc borate was synthesized successfully except the Experiment 1 which was performed at the absence of the seed. The y-axis of the TG/DTA graphs gave the amount of water loss in the product in other words the amount of water (by weight percent) in the product. The water content by TG/DTA analysis was given in Table 4.1.

4.1.3. ANALYTICAL RESULTS

The ZnO and B_2O_3 contents of the final product, zinc borates were determined by analysis explained in Part 3.4 and compared with the one taken commercially. The results were summarized in Table 4.1.

Table 4.1: The analytical results of the final products and the chemical formula for all the performed experiments

Run number	**ZnO%**	**B_2O_3%**	**H_2O%[*]**	**H_2O% (from TG/DTA graph)**	**Chemical formula (based on the analytical results)**
Seed	**37.6**	**46.9**	**15.5**	**14.3**	**$2,06ZnO.\ 3B_2O_3.\ 3,83H_2O$**
Run 1	**41.8**	**40.0**	**18.2**	**15.2**	**$2,68ZnO.\ 3B_2O_3.\ 5,28H_2O$**
Run 2	**37.1**	**48.0**	**14.9**	**-**	**$2,08ZnO.\ 3B_2O_3.\ 3,46H_2O$**
Run 3	**37**	**49.2**	**13.8**	**-**	**$2,11ZnO.\ 3B_2O_3.\ 2,85H_2O$**
Run 4	**37.8**	**47.0**	**15.2**	**13.6**	**$2,12ZnO.\ 3B_2O_3.\ 3,51H_2O$**
Run 5	**36.8**	**47.0**	**16.2**	**-**	**$2,12ZnO.\ 3B_2O_3.\ 3,55H_2O$**
Run 6	**39.0**	**48.1**	**12.9**	**-**	**$2,11ZnO.\ 3B_2O_3.\ 3,43H_2O$**
Run 7	**38.3**	**47.0**	**14.7**	**-**	**$2,13ZnO.\ 3B_2O_3.\ 3,52H_2O$**
Run 8	**40.0**	**48.2**	**11.8**	**12.8**	**$2,33ZnO.\ 3B_2O_3.\ 3,20H_2O$**
Run 9	**38.8**	**46.5**	**14.7**	**13.2**	**$2,17ZnO.\ 3B_2O_3.\ 3,50H_2O$**
Run 10	**38.0**	**46.7**	**15.3**	**13.4**	**$2,18ZnO.\ 3B_2O_3.\ 3,19H_2O$**
Run 11	**39.2**	**46.5**	**14.3**	**-**	**$2,06ZnO.\ 3B_2O_3.\ 3,45H_2O$**
Run 12	**39.2**	**46.3**	**14.5**	**-**	**$2,21ZnO.\ 3B_2O_3.\ 3,55H_2O$**
Run 13	**39.7**	**43.8**	**16.5**	**-**	**$2,40ZnO.\ 3B_2O_3.\ 4H_2O$**
Run 14	**43.3**	**44.7**	**12.0**	**-**	**$2,48ZnO.\ 3B_2O_3.\ 3,11H_2O$**
Run[†] 15	**39.7**	**45.9**	**14.4**	**-**	**$2,19ZnO.\ 3B_2O_3.\ 3,44H_2O$**

---

[*] The percentage of water was calculated from the difference of ZnO and B_2O_3 contents considering complete conversion of ZnO

4.2. EFFECTS OF EXPERIMENTAL PARAMETERS ON ZINC OXIDE CONVERSION

4.2.1. Effect of Stirring Rate

To observe the effect of stirring rate on the reaction rate, different stirring rates at constant conditions were studied. Temperature (95ºC), initial reactants ratio (H_3BO_3:ZnO ratio of 5:1) and type of zinc oxide particles (average particle size of 10μm) were kept constant.

The ZnO conversion in the solid was given in Figure 4.14. The change of ZnO content with respect to time and B_2O_3 content with respect to time were shown in Figure 4.15 and Figure 4.16 respectively.

After performing the analytical analysis to the samples taken at every half an hour it was observed that reaction completed at nearly same times for different stirring rates above 400 rpm. The stirring rate was changed as 275rpm (Exp 15), 400rpm (Exp 12), 800rpm (Exp 2) and 1600rpm (Exp 6). The analytical results showed that it was possible to get higher reaction rates for high stirring rates (800 rpm and 1600 rpm) but with decreasing stirring rates (275 rpm and 400 rpm) ZnO conversion with respect to time decreased. At low stirring rates (275 rpm and 400 rpm) more time was required to convert all zinc oxide to the zinc borate. There was nearly no difference in terms of conversion for the stirring rates 800 rpm and 1600 rpm. Reaction completion time also decreased with the increasing stirring rate.

It was concluded that stirring rate had no effect on reaction rate and reaction completion time after a value (it was seen that this value was 800 rpm). The change of reaction rate with changing stirring rate showed that the internal diffusion had a negligible effect on overall reaction rate for high stirring rates. On the other hand at low stirring rates mass transfer coefficient decreased and affected the overall rate.

Shete and coworkers (2004) also examined the effect of stirring rate to the zinc oxide conversion. It was concluded that as the speed was increased conversion also increased. Thus higher conversion was achieved with the increase in speed of agitation in a shorter time. However at higher speeds the speed of agitation has no effect on conversion.

In terms of effect of stirring rate on reaction rate and reaction completion time, similar results were found in this study compared to the study performed by Shete et.al (2004).

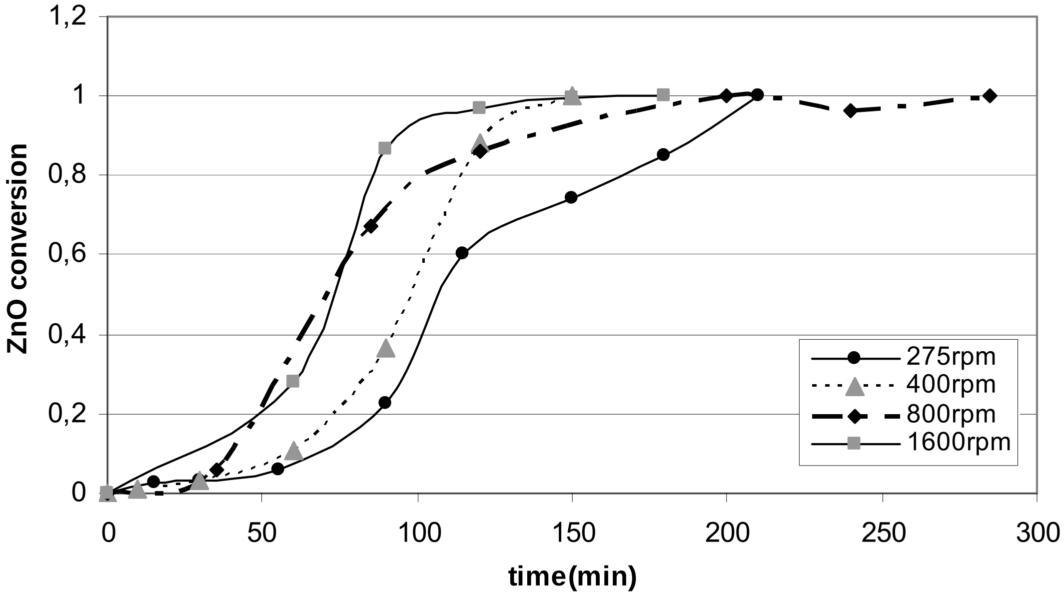


Figure 4.14 : ZnO conversion vs time graph to observe the effect of stirring rate (Temperature (95ºC), initial reactants ratio (H_3BO_3:ZnO ratio of 5:1) and type of zinc oxide particles (average particle size of 10µm) were constant)

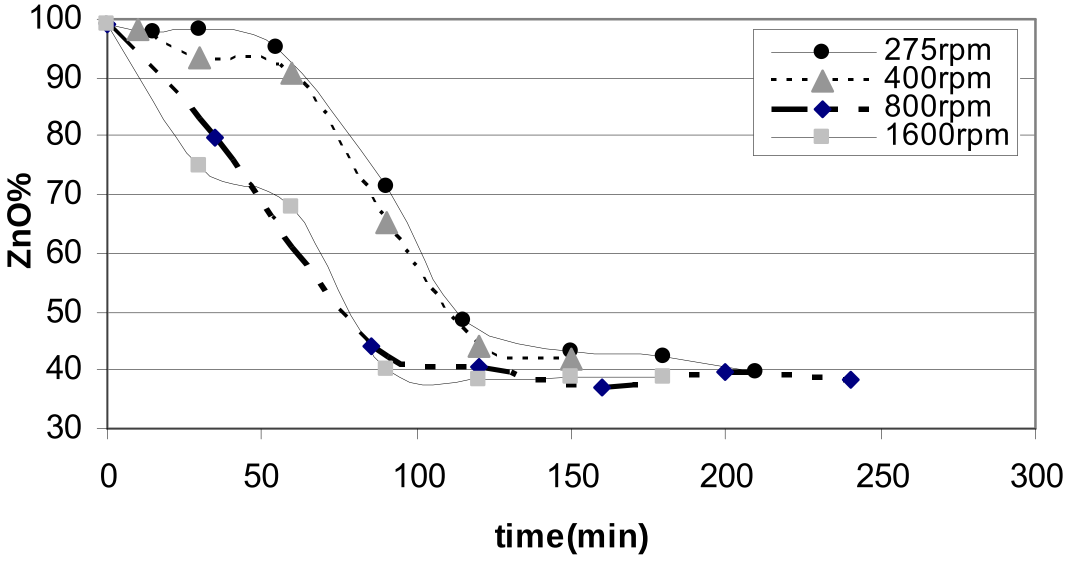


Figure 4.15 : ZnO% in the solid vs time graph to observe the effect of stirring rate (Temperature (95ºC), initial reactants ratio (H_3BO_3:ZnO ratio of 5:1) and type of zinc oxide particles (average particle size of 10µm) were constant)

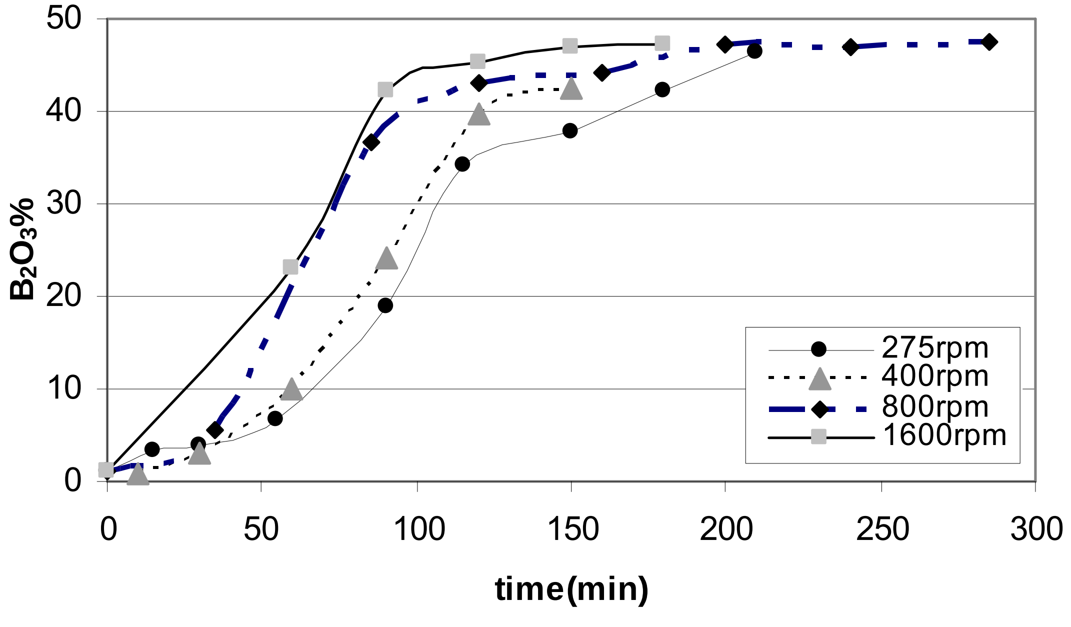


Figure 4.16 : B_2O_3% in the solid vs time graph to observe the effect of stirring rate (Temperature (95ºC), initial reactants ratio (H_3BO_3:ZnO ratio of 5:1) and type of zinc oxide particles (average particle size of 10µm) were constant)

4.2.2. Effect of Reactants Ratio

The effect of reactants ratio – the ratio of boric acid to the zinc oxide at the beginning of the reaction – was performed by changing the reactants ratio at constant temperature (95ºC), stirring rate (1600rpm), and zinc oxide with a particle size of 10μm. Reactants ratio was changed from the stoichometric ratio(3:1) to the excess of boric acid. H_3BO_3:ZnO ratios of 3:1, 3,5:1, 5:1, 7:1 were studied.

The zinc oxide conversion with respect to time was given in Figure 4.17. This comparison with respect to change in ZnO% content and B_2O_3% content with time were shown in Figure 4.18 and Figure 4.19.

It was observed that reaction rate increased with increasing H_3BO_3:ZnO ratio. The analytical results showed that the rate of reaction increased very slightly with the high H_3BO_3:ZnO ratio(7:1). Reaction completion time decreased slightly with the increasing H_3BO_3:ZnO ratio. The reactions completed for mole ratios of 3,5:1(Exp7), 5:1(Exp6) and 7:1(Exp5) after 3 hours, 2,5 hours and 1,5 hours respectively but it was not possible to synthesize zinc borate with the stoichometric mole ratio of 3:1 (Exp 14). The solution analyses of the experiment 14 showed that there was still boric acid in the solution which should be consumed completely at the end of the reaction in order to consume all zinc oxide used in the reaction. These results showed that boric acid should be used in excess to convert all zinc oxide to zinc borate.

As could be seen from the figures the negligible change of reaction rate for different reactants ratio (H_3BO_3:ZnO) showed that the zinc borate production reaction could be accepted as zero order that the rate independent of the concentration of the reactants.

Shete and coworkers (2004) also examined the effect of boric acid concentration to the zinc oxide conversion. Three different boric acid to zinc oxide ratios were used (3:1, 4:1 and 5:1). It was concluded that conversion of zinc oxide increased with increase in concentration of boric acid since. An additional quantity of boric acid formed a layer around the zinc borate particles. The problem solved by washing the zinc borate particles continuously with hot water for some time.

In terms of the effect of reactants ratio on the reaction rate and reaction completion time different results were obtained in this study compared to the study performed by Shete and coworkers (2004). In present study, different from the study of Shete et.al (2004), by changing reactants ratio no effects on the reaction rate and reaction completion time was observed.

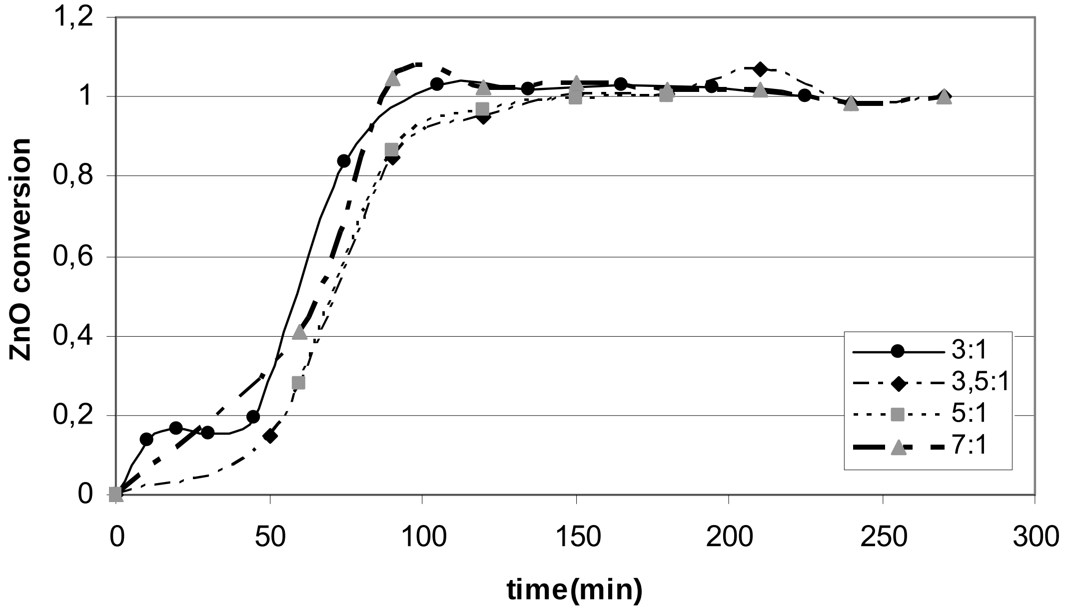


Figure 4.17 : ZnO conversion vs time graph to observe the effect of reactants ratio(Temperature (95°C), stirring rate(1600rpm) and type of zinc oxide particles (average particle size of 10µm) were constant)

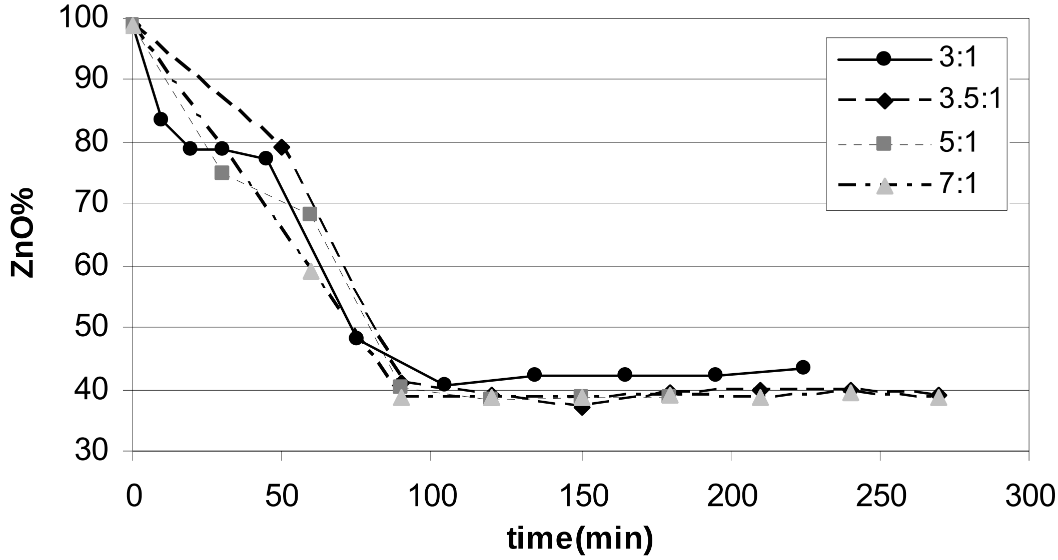


Figure 4.18 : ZnO% in the solid vs time graph to observe the effect of reactants ratio(Temperature (95ºC), stirring rate(1600rpm) and type of zinc oxide particles (average particle size of 10μm) were constant)

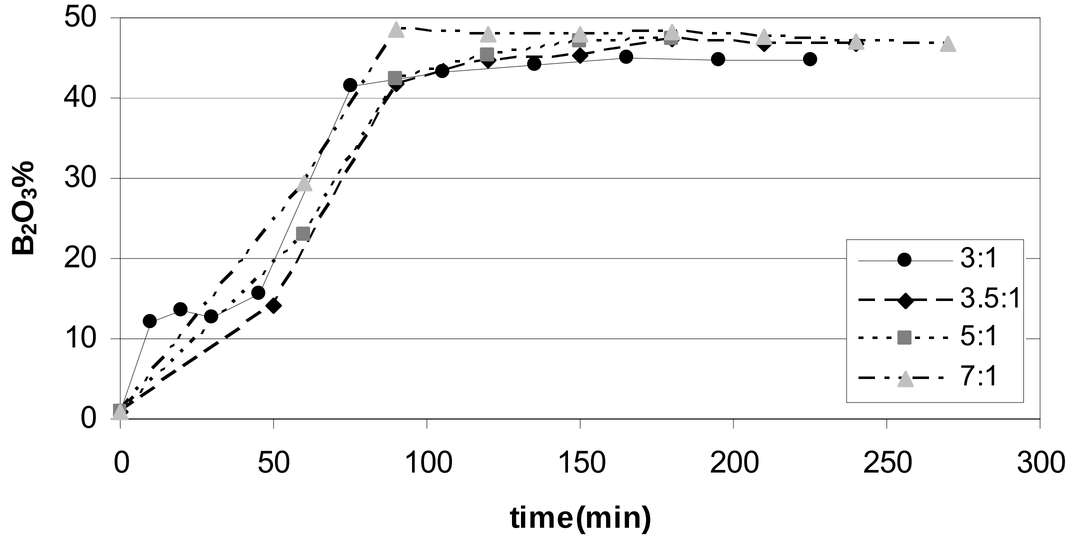


Figure 4.19 : B_2O_3% in the solid vs time graph to observe the effect of reactants ratio(Temperature (95ºC), stirring rate(1600rpm) and type of zinc oxide particles (average particle size of 10μm) were constant)

4.2.3. Effect of temperature

To search the effect of temperature on the reaction rate different temperatures were examined with constant stirring rate and reactants ratio. At 5:1 of H_3BO_3:ZnO ratio 1600rpm stirring rate and 25 µm particle size of ZnO. The reactions were performed at temperatures 75°C, 80°C, 85°C and 95°C.

The zinc oxide conversion in the solid with respect to time is given in Figure 4.20. The comparison with respect to ZnO% and B_2O_3% content with time was shown in Figure 4.21 and Figure 4.22.

It was observed that the reaction completed later for lower temperature – at 75°C(Exp 9) and 80°C (Exp 13) -. There were nearly no difference at 85°C(Exp 10) and 95°C(Exp 4). At the experiment performed at 75°C and 85°C, the reaction completed after 4 hours from the beginning, this time became 1,5 hours for the temperatures of 85°C and 95°C. The analytical results performed to the samples showed that the reaction rate increased with the increasing temperature. The reaction rate was high for the temperatures 85°C and 95°C while reaction rate decreased for the lower temperatures (75°C and 80°C).

Shete and coworkers (2004) also studied to see the effect of temperature on reaction rate and zinc oxide conversion. Three different temperatures were studied (90^{O}C, 100 ^{O}C and 110 ^{O}C). It was seen that as temperature increased the rate of reaction increased sharply.

In terms of the effect of temperature on the reaction rate and reaction completion time similar results were found in this study compared the study performed by Shete and coworkers (2004).

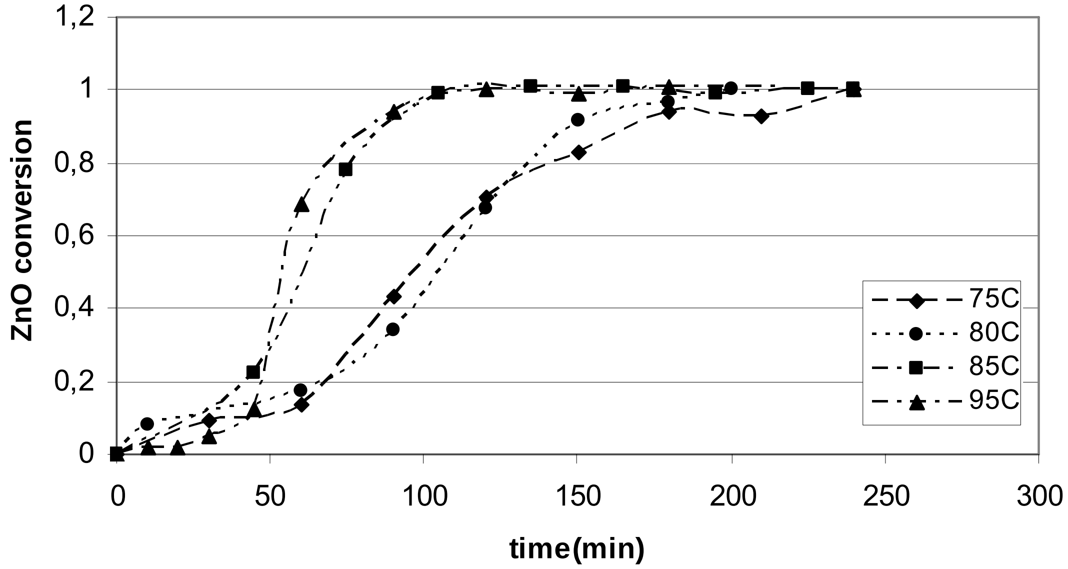


Figure 4.20 : ZnO conversion vs time graph to observe the effect of temperature(initial reactants ratio (H_3BO_3:ZnO ratio of 5:1), stirring rate(1600rpm) and type of zinc oxide particles (average particle size of 25µm) were constant)

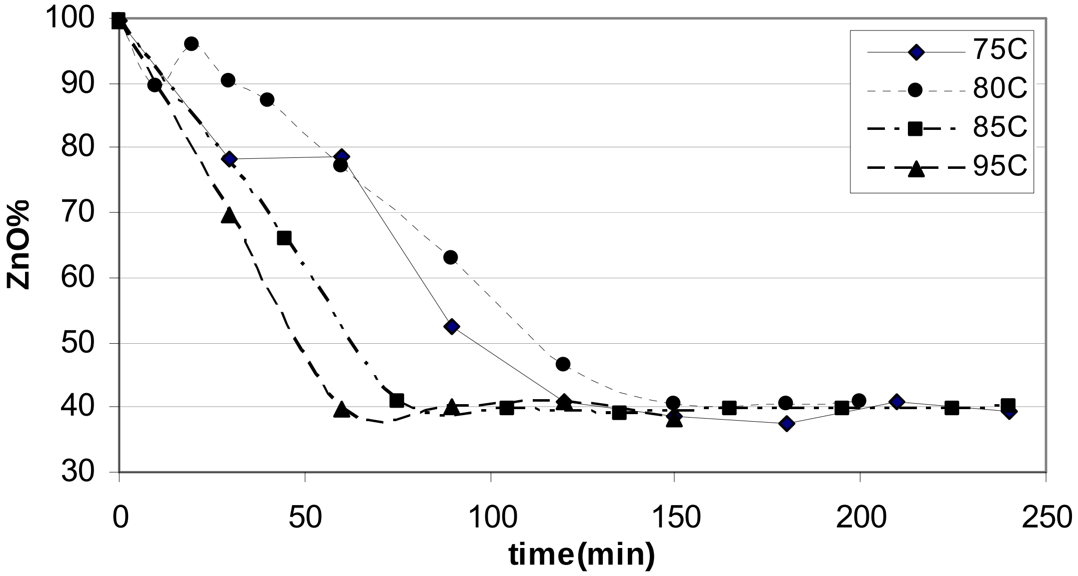


Figure 4.21 : ZnO% in the solid vs time graph to observe the effect of temperature(initial reactants ratio (H_3BO_3:ZnO ratio of 5:1), stirring rate(1600rpm) and type of zinc oxide particles (average particle size of 25µm) were constant)

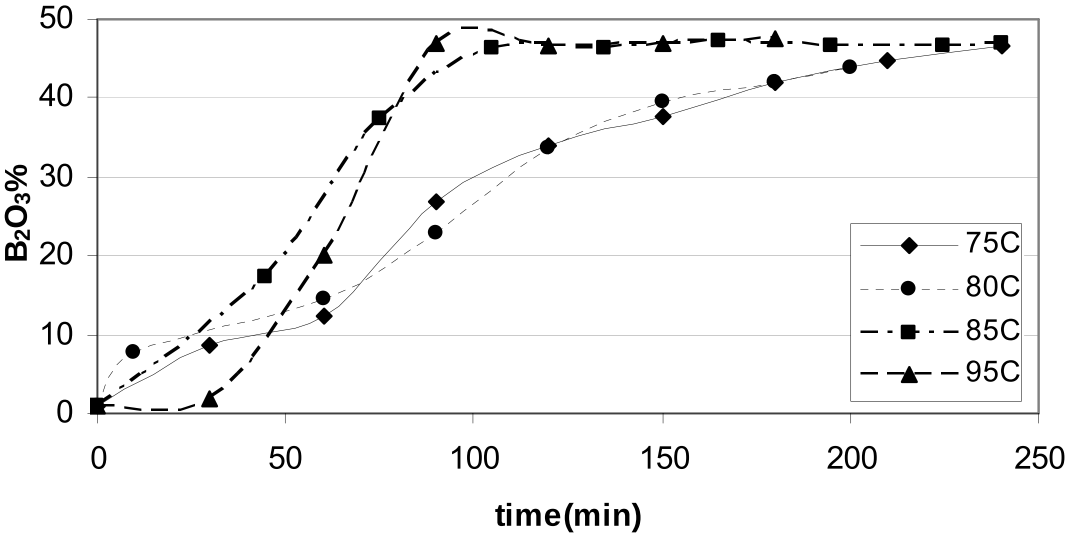


Figure 4.22: $B_2O_3\%$ in the solid vs time graph to observe the effect of temperature (initial reactants ratio (H_3BO_3:ZnO ratio of 5:1), stirring rate(1600rpm) and type of zinc oxide particles (average particle size of 25 μm) were constant)

4.2.4. Effect of seed

To examine whether the reaction run in the absence of seed zinc borate, two different experiments were performed with the same experimental conditions – same temperature (95°C), reactants ratio (H_3BO_3:ZnO ratio of 5:1) and stirring rate (800 rpm) – one with seed (Exp 2) and the other was in the absence of seed (Exp1).

Based on the analytical results of the final products, it was seen that zinc borate could not be synthesized without using zinc borate as seed. The composition of the final product of the experiment performed in the absence of the seed did not match the commercially taken zinc borate compositions. The composition of final products of two experiments and the commercially taken one were shown in Table 4.2.

Table 4.2 : Comparison of the final products with the commercially taken zinc borate

Source	***ZnO%***	***B_2O_3%***
Seed zinc borate	37.6	47.0
Experiment with seed (Exp9)	37.1	48
Experiment without seed (Exp8)	41.8	40

These experimets showed that it was not possible to produce zinc borate in the absence of zinc borate seed.

4.2.5. Effect of size of zinc oxide particle

Zinc oxides with different particles sizes were used to see its effects on the reaction rate. Temperature (95°C), stirring rate (1600 rpm), reactants ratio (H_3BO_3:ZnO ratio of 3,5:1) were kept constant but different zinc oxide particles were used with particle size of 10µm and 25 µm.

The zinc oxide conversion in solid with respect to time is given in Figure 4.23. The comparison in terms of ZnO and B_2O_3 content with respect to time was shown in Figure 4.24 and Figure 4.25.

The results of the analytical analyses performed to the samples showed that surprisingly reaction rate increased slightly with the increasing zinc oxide particle size. A difference could be seen by looking the conversion graphs while the experiment performed with the larger particle size of zinc oxide gave the full conversion at early stages. There was nearly no difference at the reaction completion time. The reaction performed with ZnO having particle size of 10 µm (Exp 7) and the reaction performed with ZnO having particle size of 25 μm (Exp 8) completed after 1,5 hours from the beginning of the reaction.

Shete and coworkers (2004) also studied the effect of mean initial particle size of zinc oxide on the zinc oxide conversion, three different mean particle sizes of zinc oxide were used. The time needed for conversion of zinc oxide was longer with increase in mean particle size of zinc oxide.

In terms of the effect of size of zinc oxide particles on the reaction rate and reaction completion time different results were obtained from the study of Shete and coworkers (2004). In this study to increase the size of zinc oxide particles decreased the reaction completion time while Shete et.al (2004) found that reaction completion time was increased by increasing the size of zinc oxide particles.

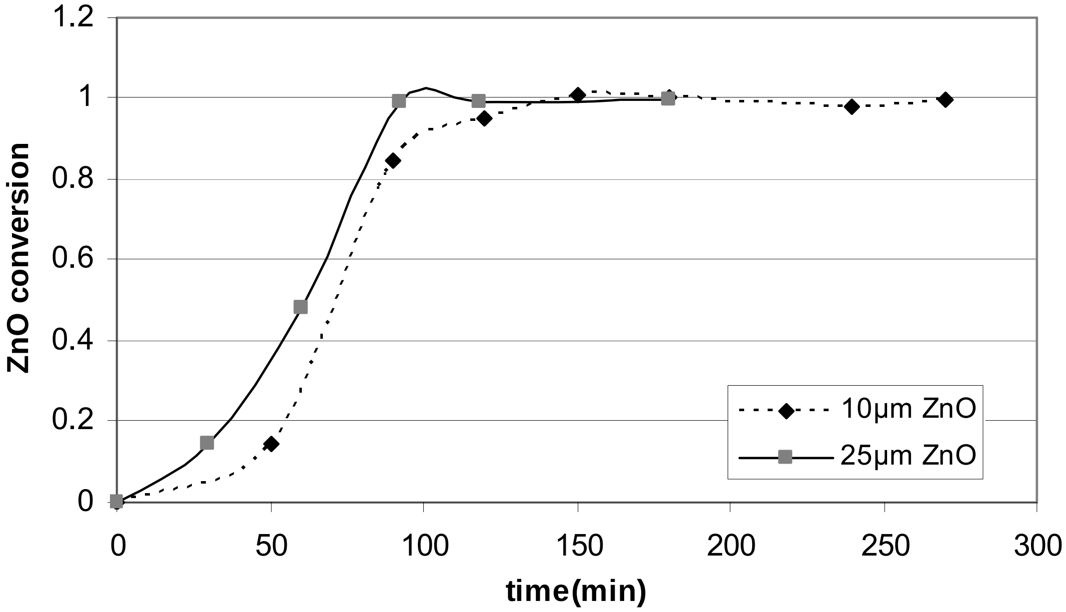


Figure 4.23 : ZnO conversion vs time graph to observe the effect of zinc oxide particle size(Temperature (95ºC), initial reactants ratio ($H3BO3$:ZnO ratio of 3,5:1) and stirring rate(1600rpm) were constant)

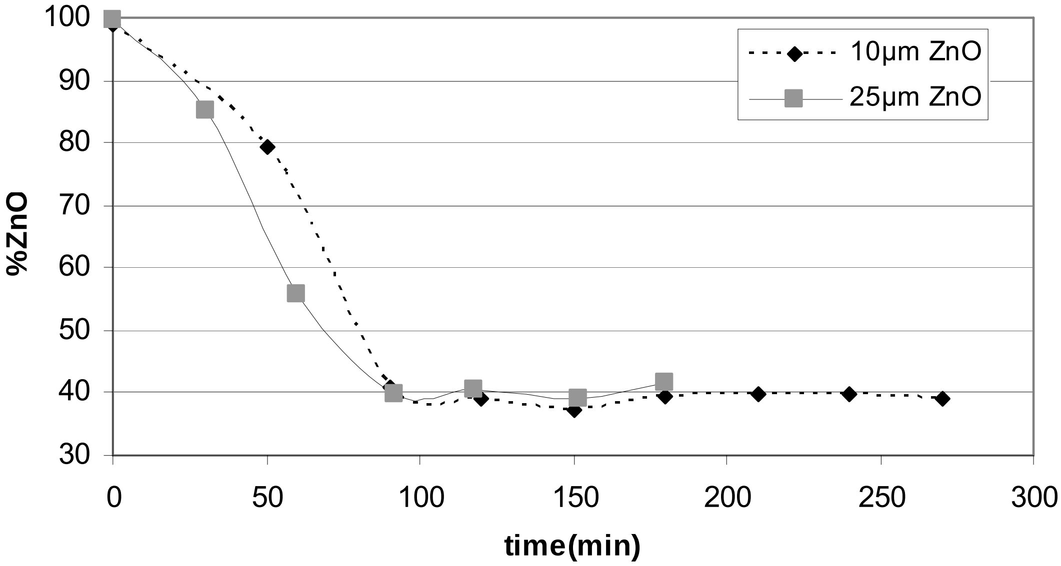


Figure 4.24 : ZnO% in the solid vs time graph to observe the effect of zinc oxide particle size(Temperature (95ºC), initial reactants ratio (H3BO3:ZnO ratio of 3,5:1) and stirring rate(1600rpm) were constant)

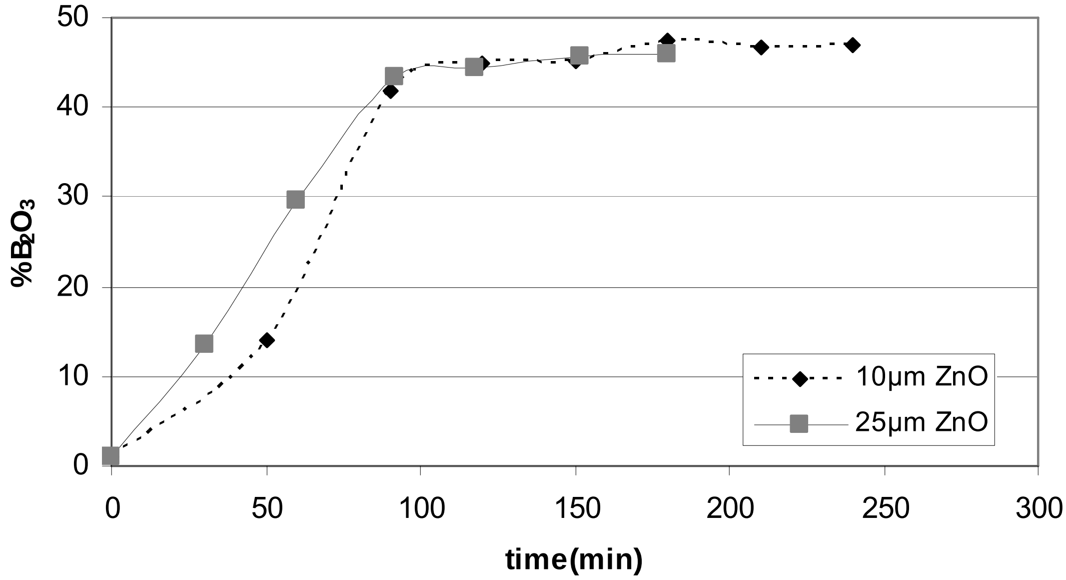


Figure 4.25: B_2O_3% in the solid vs time graph to observe the effect of zinc oxide particle size(Temperature (95ºC), initial reactants ratio (H3BO3:ZnO ratio of 3,5:1) and stirring rate(1600rpm) were constant)

4.2.6. Effect of size of zinc borate seed

To observe the effect of size of zinc borate seed on the reaction rate different size of zinc borate seeds were used with constant experimental conditions (at 1600 rpm stirring rate, H_3BO_3:ZnO ratio of 5:1, 95°C temperature and 10 µm particle size of ZnO). Two different sizes of zinc borates (10 µm and 2 µm) were used.

The zinc oxide conversion in the solid with respect to time was given in Figure 4.26. The comparison with respect to ZnO% and B_2O_3% content with time was shown in Figure 4.27 and Figure 4.28.

At the end of the experiments, it was seen that there was no difference at the completion time for both experiments performed with 10 µm seed (Exp 4) and 2 µm seed (Exp 11). On the other side the reaction rate changed for different size of zinc borate seeds.

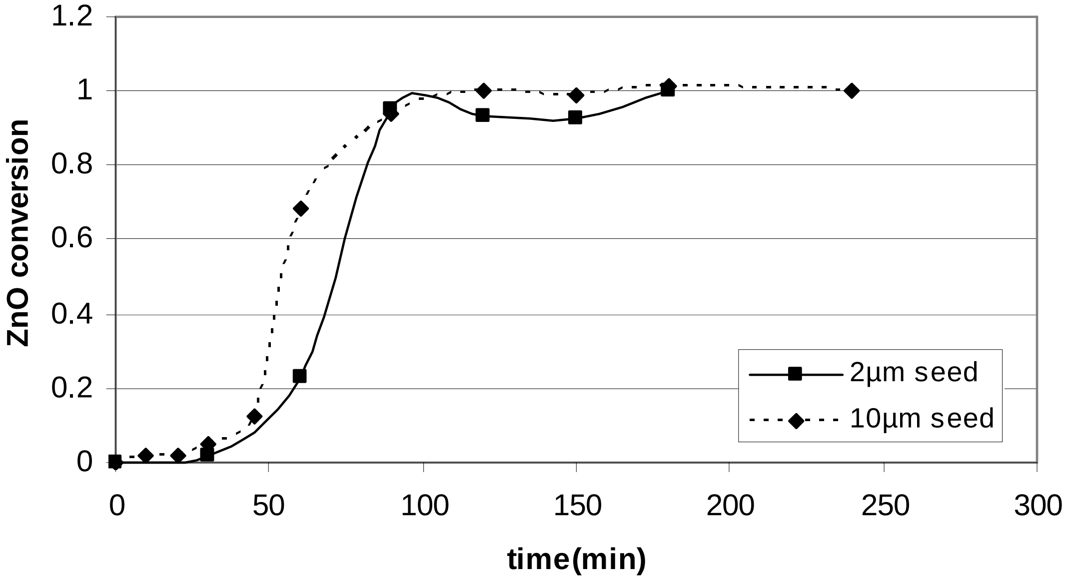


Figure 4.26 : ZnO conversion vs time graph to observe the effect of zinc borate particle size(Temperature (95ºC), initial reactants ratio (H_3BO_3:ZnO ratio of 5:1), stirring rate(1600rpm) and type of zinc oxide particles (average particle size of 25µm) were constant)

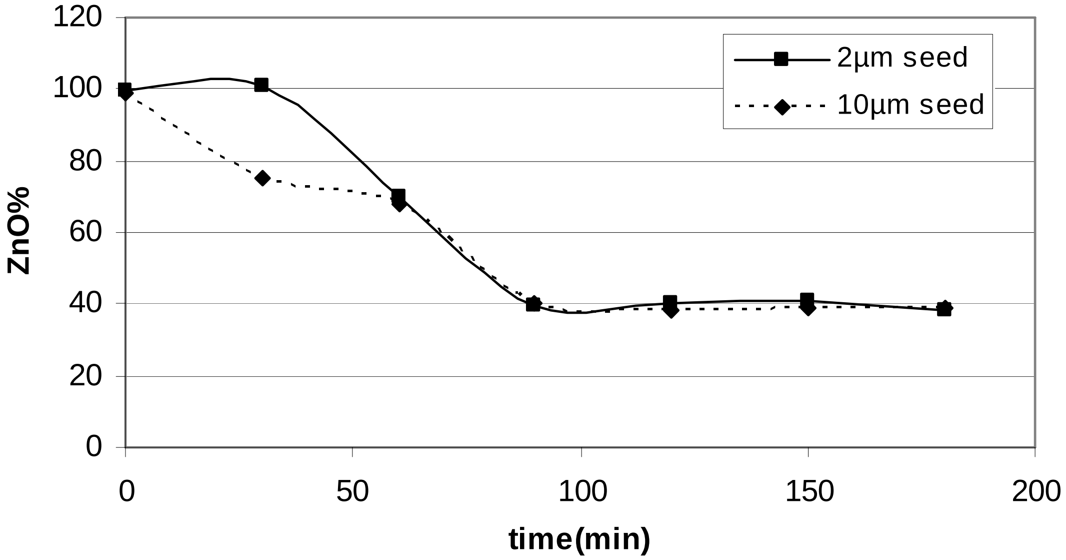


Figure 4.27 : ZnO% in the solid vs time graph to observe the effect of zinc borate particle size(Temperature (95ºC), initial reactants ratio (H3BO3:ZnO ratio of 5:1), stirring rate(1600rpm) and type of zinc oxide particles (average particle size of 25µm) were constant)

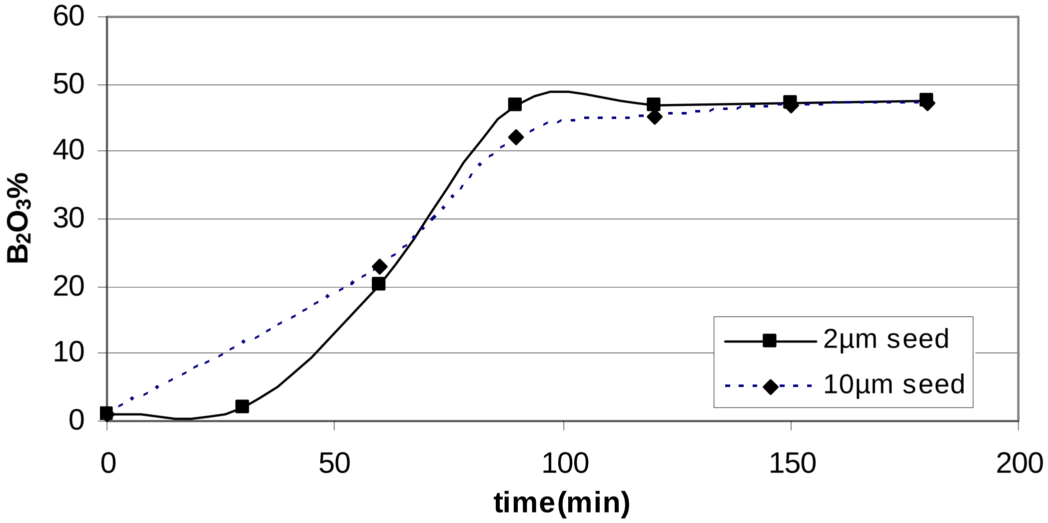


Figure 4.28 : B_2O_3% in the solid vs time graph to observe the effect of zinc borate particle size(Temperature (95ºC), initial reactants ratio (H3BO3:ZnO ratio of 5:1), stirring rate(1600rpm) and type of zinc oxide particles (average particle size of 25µm) were constant)

4.3. PARTICLE SIZE DISTRIBUTION ANALYSIS

To see the effect of experimental parameters on the effect of particle size distribution of the final product, particle size distribution analysis of the experiments carried out at different conditions were performed.

Effect of stirring rate, reactants ratio (H_3BO_3:ZnO), temperature, size of zinc oxide particles and the size of zinc borate used as seed were examined.

The average particle sizes of the final zinc borate products and the one obtained commercially were summarized in Table 4.3.

4.3.1. Effect of stirring rate

To observe the effect of stirring rate on the particle size distribution of final product zinc borate, different stirring rates at constant conditions were studied. Temperature (95ºC), initial reactants ratio (H_3BO_3:ZnO ratio of 5:1) and type of zinc oxide particles (average particle size of 10μm) were kept constant. The comparison of the particle size distributions of the experiments were given in Figure 4.29.

The stirring rate was changed as 275 rpm (Exp 15), 400 rpm (Exp 12), 800 rpm (Exp 2) and 1600 rpm (Exp 6). After performing the particle size analysis to the final zinc borate product, it was observed that at higher stirring rates average particle size of zinc borate decreased. On the other hand no change was observed above the stirring rate of 800 rpm.

Shete and coworkers (2004) also studied the effect of stirring rate on the particle size of final zinc borate product. They concluded that mean particle size of zinc borate decreased with increase in speed of agitation. The results of Shete et.al (2004) were consistent with the ones obtained in this study.

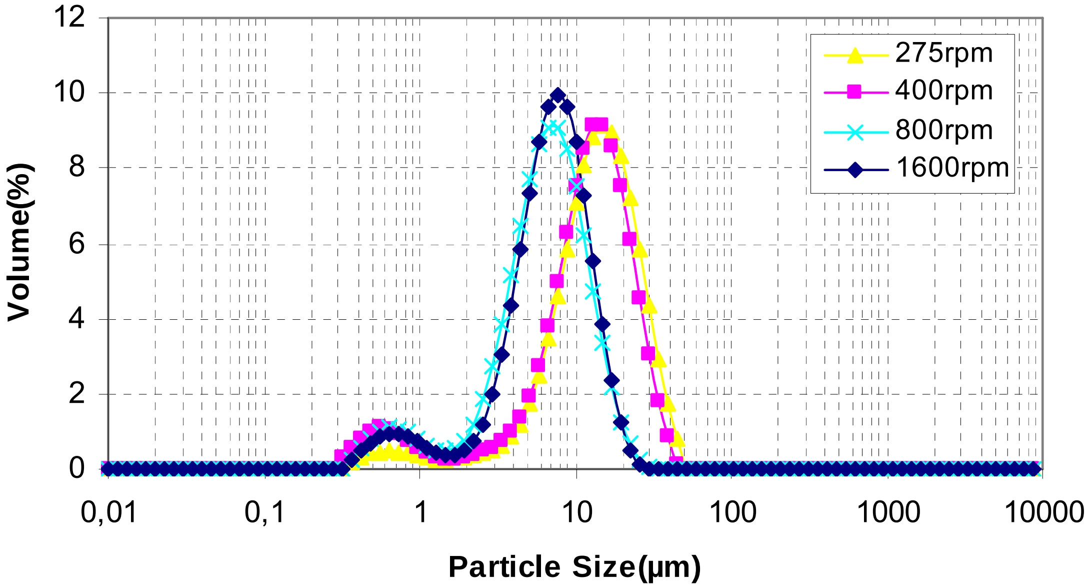


Figure 4.29 : Particle size distribution graph to observe the effect of stirring rate (Temperature (95ºC), initial reactants ratio (H_3BO_3:ZnO ratio of 5:1) and type of zinc oxide particles (average particle size of 10µm) were constant)

4.3.2. Effect of Reactants Ratio

To see the effect of different mole ratios of H_3BO_3:ZnO on the particle size distribution, the experiments with constant temperature and stirring rate with different H_3BO_3:ZnO ratio were compared. The comparison was shown in Figure 4.30.

Four different H_3BO_3:ZnO ratios were studied. The ratios of 3:1 (Exp 14), 3,5:1 (Exp 7), 5:1 (Exp 6) and 7:1 (Exp5) were examined keeping temperature (95ºC), stirring rate (1600 rpm) and particle size of zinc oxide (average particle size of 10 µm) constant. It was seen that the there were nearly no difference for different H_3BO_3:ZnO ratios.

Shete and coworkers (2004) found different results for this study. They concluded that the size of zinc borate particles increased with an increase in quantity of boric acid. This was because an additional quantity of boric acid forms a layer around the zinc borate particles. Different from the results of the study of Shete et.al (2004), no changes were observed in this study since the products were washed with hot water to remove the boric acid layer stuck to the surface.

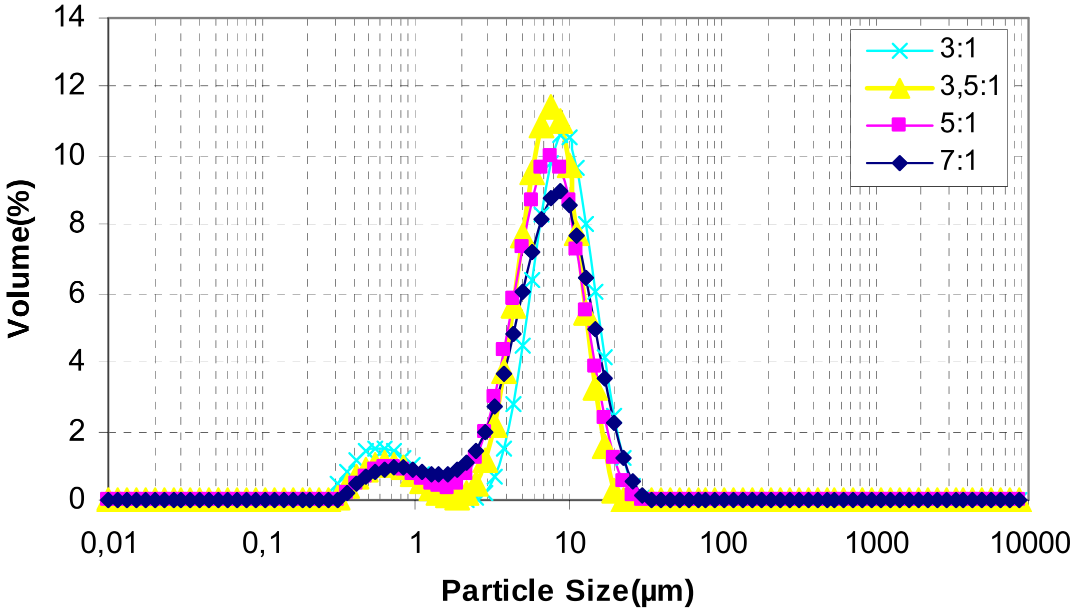


Figure 4.30: Particle size distribution graph to observe the effect of reactants ratio(Temperature (95ºC), stirring rate(1600rpm) and type of zinc oxide particles (average particle size of 10µm) were constant)

4.3.3. Effect of temperature

To observe the effect of temperature on the particle size distribution, different temperatures were examined with constant stirring rate and reactants ratio. The reactions were performed at temperatures 75°C, 80°C, 85°C and 95°C at 5:1 of H_3BO_3:ZnO ratio, 1600 rpm stirring rate and 25 μm particle size of ZnO. The comparison of particle size distributions for different temperatures was given in Figure 4.31.

The effect of temperature to the final zinc borate product particle size was interesting. The smallest average particle size of zinc borate was obtained at temperatures 75°C (Exp 9) and 85°C (Exp 10) while at 80°C (Exp 13) largest average particle size was obtained.

Shete and coworkers (2004) concluded that there was an approximately linear decrease in particle size of zinc borate with increase in temperature. Different from the results of the study of Shete et.al (2004), no relationship was obtained between temperature and average particle size of zinc borate.

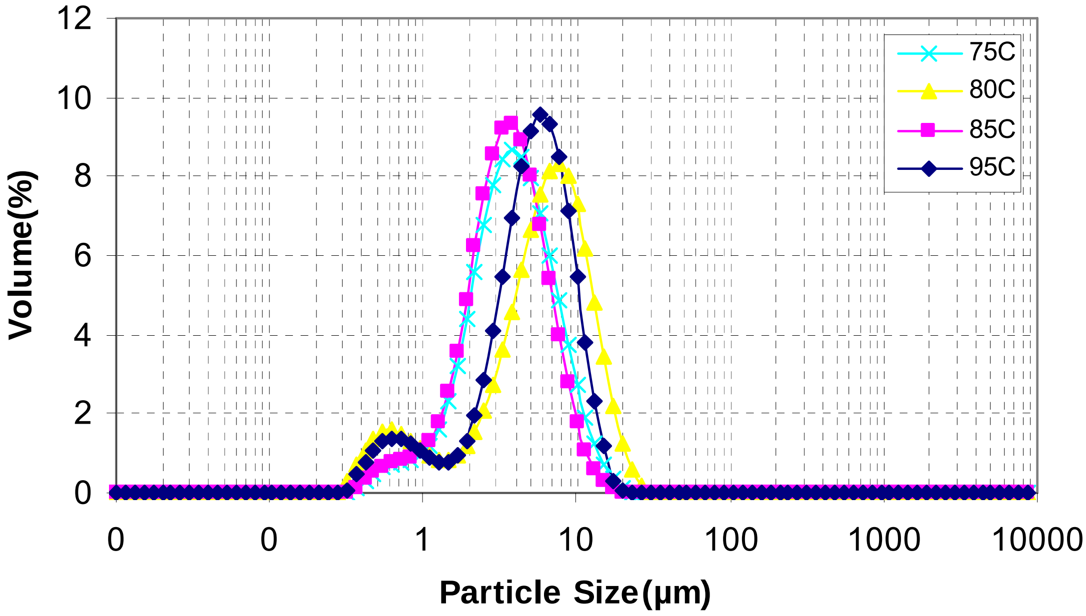


Figure 4.31 : Particle size distribution graph to observe the effect of temperature(initial reactants ratio (H_3BO_3:ZnO ratio of 5:1), stirring rate(1600rpm) and type of zinc oxide particles (average particle size of 25μm) were constant)

4.3.4. Effect of size of zinc oxide particle

In order to see the effect of ZnO particle size on the average particle size of final zinc borate product two experiments were performed with same experimental conditions (temperature(95°C), stirring rate(1600rpm), reactants ratio (H_3BO_3:ZnO ratio of 3,5:1)) but with different ZnO particles. One with 10μm (Exp7) and the other was 25μm (Exp 8) average particle size. The comparison was shown in Figure 4.32.

The comparison showed that as zinc oxide particle size decreased, the particle size of final zinc borate product decreased slightly.

Similar the results of the present study, Shete and coworkers (2004) also concluded that the mean particle size of zinc borate was higher for higher mean initial particle size of zinc oxide.

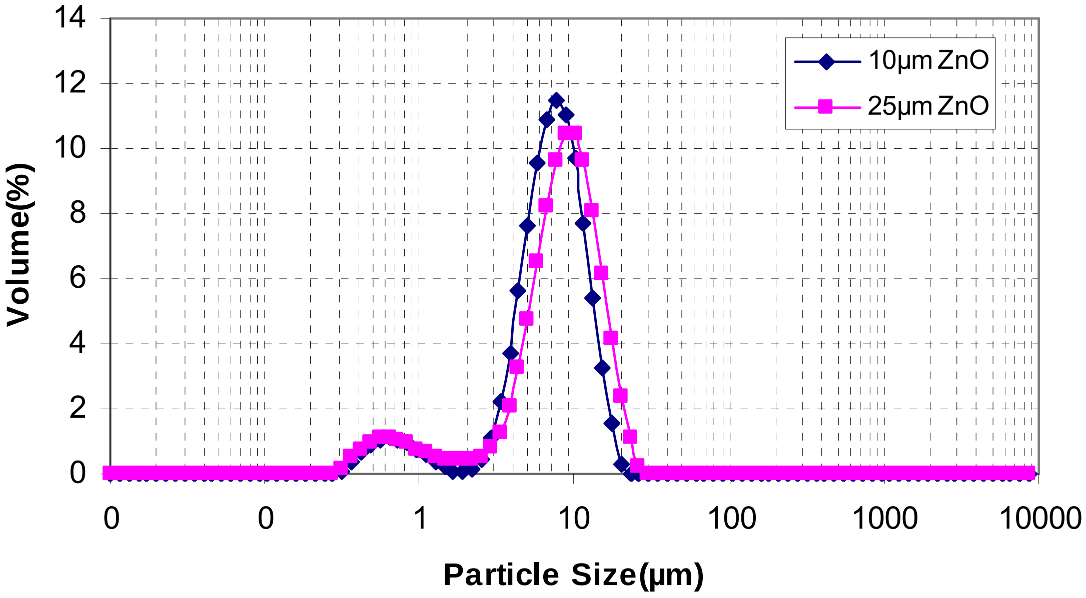


Figure 4.32: Particle size distribution graph to observe the effect of zinc oxide particle size(Temperature (95ºC), initial reactants ratio (H_3BO_3:ZnO ratio of 3,5:1) and stirring rate(1600rpm) were constant)

4.3.5. Effect of size of zinc borate seed

To observe the effect of size of zinc borate seed on the particle size of final product zinc borate, different size of zinc borate seeds were used with constant stirring rate, reactants ratio and temperature. At H_3BO_3:ZnO ratio of 5:1, stirring rate of 1600 rpm, ZnO particle size of 25 μm and temperature of 95°C, two different size of zinc borates were used. One experiment was performed with the seed of 10 μm average particle size (Exp4) and the other experiment was performed with the seed of 2 μm average particle size (Exp11).

The effect of using different zinc borate seed on the particle size of final product zinc borate was interesting. The higher particle size of zinc borate seed gave smaller particle size of final zinc borate product. The comparison was shown in Figure 4.33.

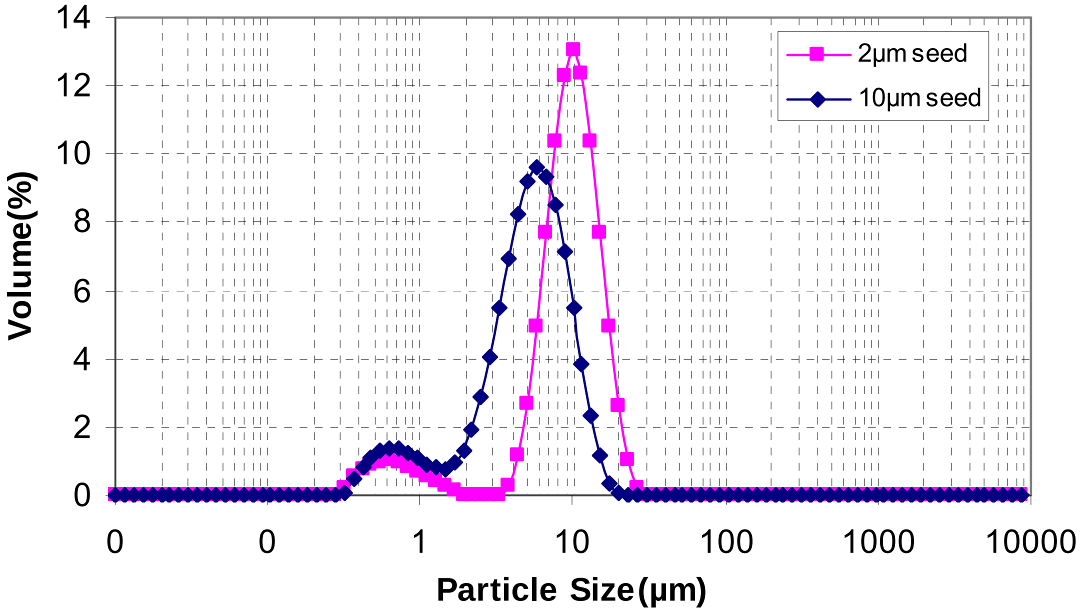


Figure 4.33 : Particle size distribution graph to observe the effect of zinc borate particle size(Temperature (95ºC), initial reactants ratio (H_3BO_3:ZnO ratio of 5:1), stirring rate(1600rpm) and type of zinc oxide particles (average particle size of 25μm) were constant)

Table 4.3 : Average particle sizes of final zinc borate products and commercial zinc borate

Experiment number	**Experimental Conditions**	**Average Particle Size (µm)**
Zinc borate	**-**	10.2
Run 1	**-**	-
Run 2	800rpm stirring rate, 95°C temperature, 10µm ZnO, H_3BO_3:ZnO ratio of 5:1, $C_{b(initial)}$ = 3.96 mol/lt	7.7
Run 3	1000rpm stirring rate, 95°C temperature, 10µm ZnO, H_3BO_3:ZnO ratio of 7:1, $C_{b(initial)}$ = 4.91 mol/lt	16.1
Run 4	1600rpm stirring rate, 95°C temperature, 25µm ZnO, H_3BO_3:ZnO ratio of 5:1, $C_{b(initial)}$ = 5.12 mol/lt	6.0
Run 5	1600rpm stirring rate, 95°C temperature, 10µm ZnO, H_3BO_3:ZnO ratio of 7:1, $C_{b(initial)}$ = 4.99 mol/lt	8.8
Run 6	1600rpm stirring rate, 95°C temperature, 10µm ZnO, H_3BO_3:ZnO ratio of 5:1, $C_{b(initial)}$ = 4.0 mol/lt	8.2
Run 7	1600rpm stirring rate, 95°C temperature, 10µm ZnO, H_3BO_3:ZnO ratio of 3.5:1,$C_{b(initial)}$ = 4.92 mol/lt)	8.0
Run 8	1600rpm stirring rate, 95°C temperature, 25µm ZnO, H_3BO_3:ZnO ratio of 3.5:1,$C_{b(initial)}$ = 4.87 mol/lt	9.5
Run 9	1600rpm stirring rate, 75°C temperature, 25µm ZnO, H_3BO_3:ZnO ratio of 5:1, $C_{b(initial)}$ = 3.32 mol/lt	4.8
Run 10	1600rpm stirring rate, 85°C temperature, 25µm ZnO, H_3BO_3:ZnO ratio of 5:1, $C_{b(initial)}$ = 3.32 mol/lt	4.3
Run 11	1600rpm stirring rate, 95°C temperature, 25µm ZnO, H_3BO_3:ZnO ratio of 5:1, 2µm seed, $C_{b(initial)}$ = 5.23 mol/lt)	12.7
Run 12	400rpm stirring rate, 95°C temperature, 10µm ZnO, H_3BO_3:ZnO ratio of 5:1, $C_{b(initial)}$ = 5.12 mol/lt	14.5
Run 13	1600rpm stirring rate, 80°C temperature, 25µm ZnO, H_3BO_3:ZnO ratio of 5:1, $C_{b(initial)}$ = 5.12 mol/lt	7.4
Run 14	1600rpm stirring rate, 95°C temperature, 10µm ZnO, H_3BO_3:ZnO ratio of 3:1, $C_{b(initial)}$ = 5.16 mol/lt)	9.6
Run 15	275rpm stirring rate, 95°C temperature, 10µm ZnO, H_3BO_3:ZnO ratio of 5:1, $C_{b(initial)}$ = 5.12 mol/lt	16.6

4.4. REACTION KINETICS

Through the studies performed in “Reaction Kinetics” part some assumptions were made

1) Both zinc oxide particles and zinc borate particles were assumed to be spherical

2) Zinc oxide particles were assumed to be insoluble in water

3) Boric acid ions in boric acid solution react with zinc oxide particles on the surface of the latter (Shete, 2004).

Zinc borate production reaction is a heterogeneous reaction with an insoluble product. Zinc borate (in solid form) was formed with the reaction of zinc oxide (in solid form) and boric acid (in aqueous form).

In general for the non-catalytic reaction of particles with surrounding fluid it is considered two simple idealized models, the progressive conversion model and the shrinking unreacted core model (Levenspiel, 1999).

Shete and coworkers (2004) suggested the unreacted core model with these following steps;

Step 1: Diffusion of borate ions from the bulk of the boric acid solution to the surface of zinc oxide particles (physical).

Step 2: Penetration and diffusion of borate ions through the blanket of ash layer covering the unreacted core to the surface of unreacted core of zinc oxide (physical).

Step 3: Reaction of borate ions with zinc oxide particles at reaction surface (chemical).

Step 4: Formation of zinc borate and diffusion of co-product water molecule through the ash layer covering the unreacted core back to the bulk phase (physical).

Step 5 (possibility): Peeling of zinc borate layer due to shear/collisions, etc.

4.4.1. The case of chemical reaction controls

Since stirring rate had no effect on reaction rate after a value (it was seen in this study that this value was 800 rpm) the effect of mass transfer on the rate of zinc borate production reaction was negligible.

The reaction was assumed to be kinetically controlled and first order surface reaction;

The general rate expression for a first order surface reaction was (Shete, 2004);

$$\frac{dc_{Bt}}{dt} = k_r a_p c_{Bt} \tag{4.1}$$

$$a_p = 6/d_{pt} \tag{4.2}$$

where d_{pt} was diameter of zinc oxide particle at time t (which was unknown quantity). This could be eliminated with the help of zinc oxide and fractional conversion of zinc oxide.

The weight of zinc oxide was given by,

$$w = \frac{\pi}{6} d_{pt}^{3} \rho N \tag{4.3}$$

The fractional conversion of zinc oxide in terms of weight of zinc oxide could be expressed as;

$$x = \frac{\text{weightofzincoxidereacted}}{\text{initialweight}} \tag{4.4}$$

$$x = \frac{(w_{in} - w_{t})}{w_{in}} \tag{4.5}$$

Inserting Equation 4.3 into Equation 4.5,

$$x = \frac{(d_{pin}^{3} - d_{pt}^{3})}{d_{pin}^{3}} \tag{4.6}$$

$$d_{pt} = d_{pin}(1-x)^{1/3} \tag{4.7}$$

Inserting Equation 4.7 into Equation 4.1,

$$\frac{dc_{Bt}}{dt} = k_{r} \frac{6}{d_{pin}(1-x)^{1/3}} c_{Bt} \tag{4.8}$$

Redefining the concentration of boric acid at time t with the change of zinc oxide depending on the stoichometric ratios;

$$c_{Bt} = c_{Bo} - \frac{3(w_{in} - w_t)}{mv} \tag{4.9}$$

Where,

$$w_t = w_{in}(1 - x) \tag{4.10}$$

Inserting Equation 4.10 into Equation 4.9

$$c_{Bt} = c_{Bo} - \frac{3(w_{in} - (1 - x)w_{in})}{mv} \tag{4.11}$$

$$c_{Bt} = c_{Bo} - \frac{3w_{in}x}{mv} \tag{4.12}$$

Inserting Equation 4.12 into Equation 4.7,

$$\frac{dc_{Bt}}{dt} = k_r \frac{6}{d_{pin}}(1 - x)^{-1/3}(c_{Bo} - \frac{3w_{in}x}{mv}) \tag{4.13}$$

$$\frac{dc_{Bt}}{dt} = k_r^{'} f(x) \tag{4.14}$$

Where,

$$k_r^{'} = k_r \frac{6}{d_{pin}} \tag{4.15}$$

and

$$f(x) = (1 - x)^{-1/3}(c_{Bo} - \frac{3w_{in}x}{mv}) \tag{4.16}$$

The terms in Equation 4.14 could be obtained from the experimental data. Experiment 8 was chosen for this study since it was the experiment that zinc borate was synthesized successfully with nearly stoichometric ratio of the reactants (H_3BO_3:ZnO ratio of 3.5:1). The plots of Equation 4.14 for Experiment 8 was given in Figure 4.34.

The nearly straight line of the plot supported that the reaction was first order with respect to boric acid.

The slope of the line gave the value of $k_r^{'}$. Since the initial zinc oxide particle size was known Experiment 8(which was 25µm), reaction rate constant was calculated as 1.77 X 10^{-5} cm s^{-1}.

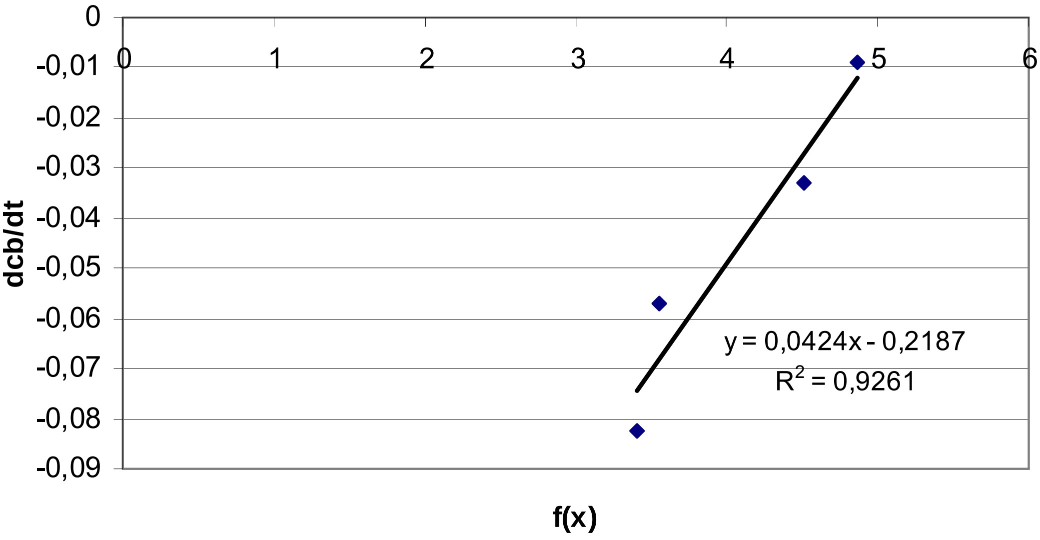


Figure 4.34 : The plot of Equation 4.16 for Experiment 8 (1600rpm stirring rate, 95°C temperature, 25µm ZnO, H_3BO_3:ZnO ratio of 3.5:1)

The other experiment performed at nearly stoichometric ratio (H_3BO_3:ZnO ratio of 3.5:1) the plot of Equation 4.14 gave nearly straight line. On the other hand the slope was negative which was not applicable according to Equation 4.15. the plot of Equation 4.14 for Experiment 7 was given in Figure 4.35. For the experiments performed at the excess of boric acid the plot of Equation 4.14 did not give the straight line. The plot of Equation 4.14 for the Experiment 4, Experiment 9 and Experiment 10 were given in Figure 4.36, Figure 4.37 and Figure 4.38 respectively.

Different from the studies on modeling of zinc borate production reaction, an alternative model should be found to express the behaviour of this reaction at different conditions.

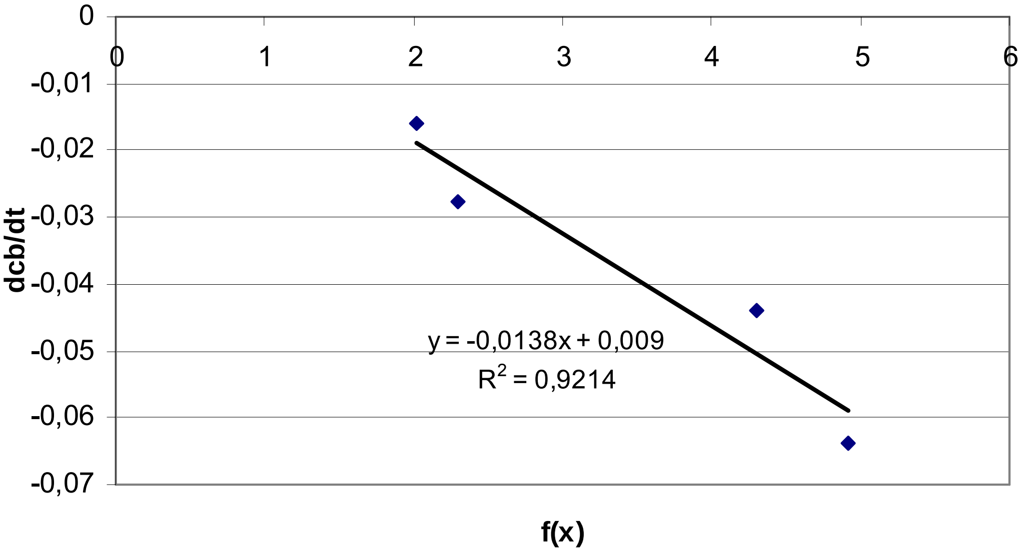


Figure 4.35: The plot of Equation 4.16 for the Experiment 7 (1600rpm stirring rate, 95°C temperature, 10μm ZnO, H_3BO_3:ZnO ratio of 3.5:1)

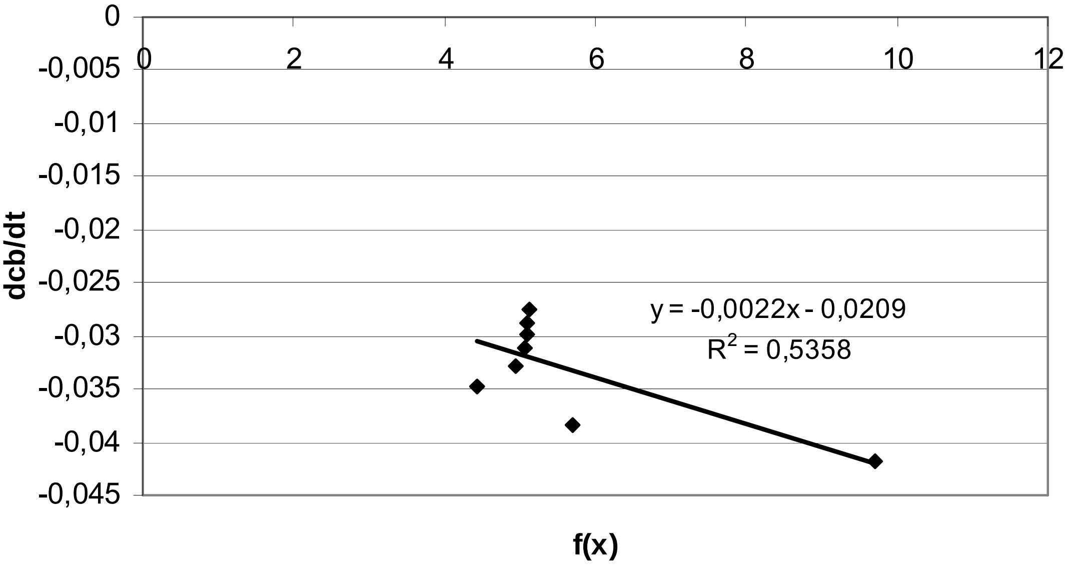


Figure 4.36 : The plot of Equation 4.16 for Experiment 4(1600rpm stirring rate, 95°C temperature, 25µm ZnO, H_3BO_3:ZnO ratio of 5:1)

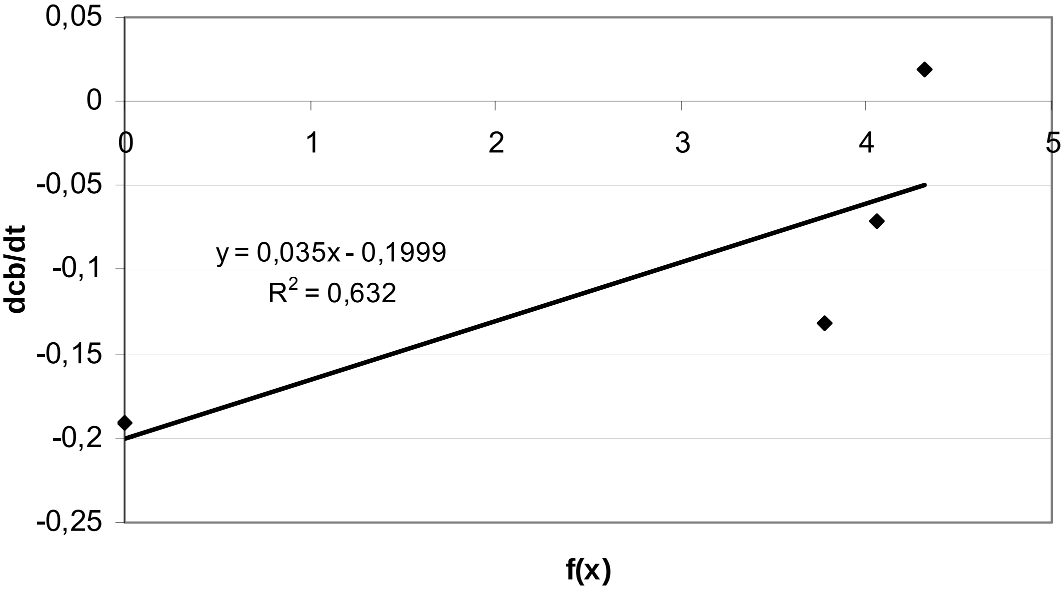


Figure 4.37 : The plot of Equation 4.16 for Experiment 10(1600rpm stirring rate, 85°C temperature, 25µm ZnO, H_3BO_3:ZnO ratio of 5:1)

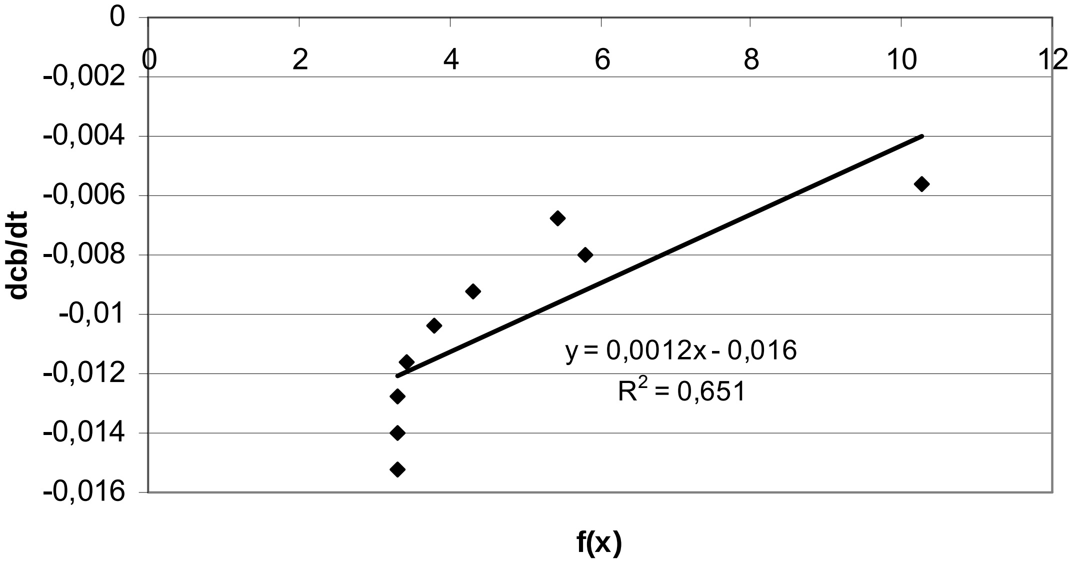


Figure 4.38 : The plot of Equation 4.16 for Experiment 9(1600rpm stirring rate, 75°C temperature, 25μm ZnO, H_3BO_3:ZnO ratio of 5:1)

4.4.2. The case of diffusion through product layer controls

The inconsistency of the chemical reaction controlling model for the higher initial ratios of boric acid to zinc oxide made it necessary to develop another model for the high boric acid to zinc oxide ratios.

According to the unreacted core model there was a case of constant flux. In case of constant flux through the product layer the resistance to diffusion through the product layer controls the rate of reaction (Levenspiel, 1999).

If the case was adapted to zinc borate production reaction, both reactant borate ions and the boundary of the unreacted core move inward toward the center of the zinc oxide particle. For this case it was assumed that the concentration gradient of borate ions in the ash layer at any time, the unreacted core was stationary.

Different from the classical model, there was a lag time in this reaction (t_{lag}). An extra time was necessary for the formation of the product layer and for the stabilizing the flux constant.

Thus the rate of reaction at any instant was given by its rate of diffusion to the reaction surface, or

$$-\frac{dN_B}{dt} = 4\pi r^2 Q_B = 4\pi R'^2 Q_{Bs} = 4\pi r_c^2 Q_{Bc} = \text{constant} \qquad (4.17)$$

For convenience, let the flux of B (boric acid) within the ash layer be expressed by Fick's law for equimolar counterdiffusion, through other forms of this diffusion equation would give the same result. Then, noting that both Q_B and dC_{Bt}/dr were positive, then

$$Q_B = D_e \frac{dC_{Bt}}{dr} \qquad (4.18)$$

where D_e was the effective diffusion coefficient of the reactant in the product layer. Often it was difficult to assign a value beforehand to this quantity because the property of the ash could be very sensitive to small amounts of impurities in the solid and to small variations in the particle's environment. Combining Equation 4.17 and 4.18;

$$-\frac{dN_B}{dt} = 4\pi r^2 D_e \frac{dC_{Bt}}{dt} = \text{cons}\tan t \qquad (4.19)$$

Integrating across the ash layer form R' to r_c;

$$-\frac{dN_B}{dt}\int_{R'}^{r_c} \frac{dr}{r^2} = 4\pi D_e \int_{C_{Bo}}^{0} dC_{Bt} \qquad (4.20)$$

or

$$-\frac{dN_B}{dt}\left(\frac{1}{r_c}-\frac{1}{R'}\right)=4\pi D_e C_{Bo} \tag{4.21}$$

For a given size of unreacted core, dN_B/dt was constant, however as the core shrinked the product layer became thicker, lowering the rate of diffusion of the reactant. Consequently integration of Equation 4.20 with respect to time and other variables should yield the required relationship. But the equation contained three variables t, N_B and r_c one of which had to be eliminated or written in terms of other variables before integration could be performed. As with film diffusion N_B could be eliminated by writing in terms of r_c. This relation was given by,

$$-dN_A=-bdN_B=-\rho_A dV=-\rho_A d\left(\frac{4}{3}\pi r_c^3\right)=-4\pi\rho r_c^2 dr_c \tag{4.22}$$

Replacing Eqn 4.22 in Eqn 4.21, separating variables and integrating. We obtain,

$$-\rho_A\int_{r_c=R'}^{r_c}\left(\frac{1}{r_c}-\frac{1}{R'}\right)r_c^2 dr_c=bD_e C_{Bo}\int_{t_{lag}}^{t}dt \tag{4.23}$$

or, $$t-t_{lag}=\frac{\rho_A R'^2}{6bD_e C_{Bo}}\left[1-3\left(\frac{r_c}{R'}\right)^2+2\left(\frac{r_c}{R'}\right)^3\right] \tag{4.24}$$

For the complete conversion of particle $r_c=0$ and the time required was,

$$\tau=\frac{\rho_A R'^2}{6bD_e C_{Bo}} \tag{4.25}$$

The progression of reaction in terms of the time required for complete conversion was found by dividing Equation 4.24 by Equation 4.25, or

$$\frac{t'}{\tau} = 1 - 3\left(\frac{r_C}{R'}\right)^2 + 2\left(\frac{r_C}{R'}\right)^3 \tag{4.26}$$

where,

$$t' = t - t_{lag} \tag{4.27}$$

$$1 - x = \left(\frac{\text{volumeofunreactedcore}}{\text{totalvolumeofparticles}}\right) = \frac{\frac{4}{3}\pi r_c^3}{\frac{4}{3}\pi R'^3} = \left(\frac{r_c}{R'}\right)^3 \tag{4.28}$$

using the above relation Equation 4.26 became,

$$\frac{t'}{\tau} = 1 - 3(1-x)^{2/3} + 2(1-x) \tag{4.29}$$

Redefining Equation 4.29,

$$t' = \tau g(x) \tag{4.30}$$

where

$$g(x) = 1 - 3(1-x)^{2/3} + 2(1-x) \tag{4.31}$$

Since t’ and g(x) were known in Equation 4.30, τ could be calculated by drawing the t’ graph with respect to g(x). The plot of Equation 4.30 for the Experiment 4, Experiment 10 and Experiment 9 were given in Figure 4.39, Figure 4.40 and Figure 4.41 respectively.

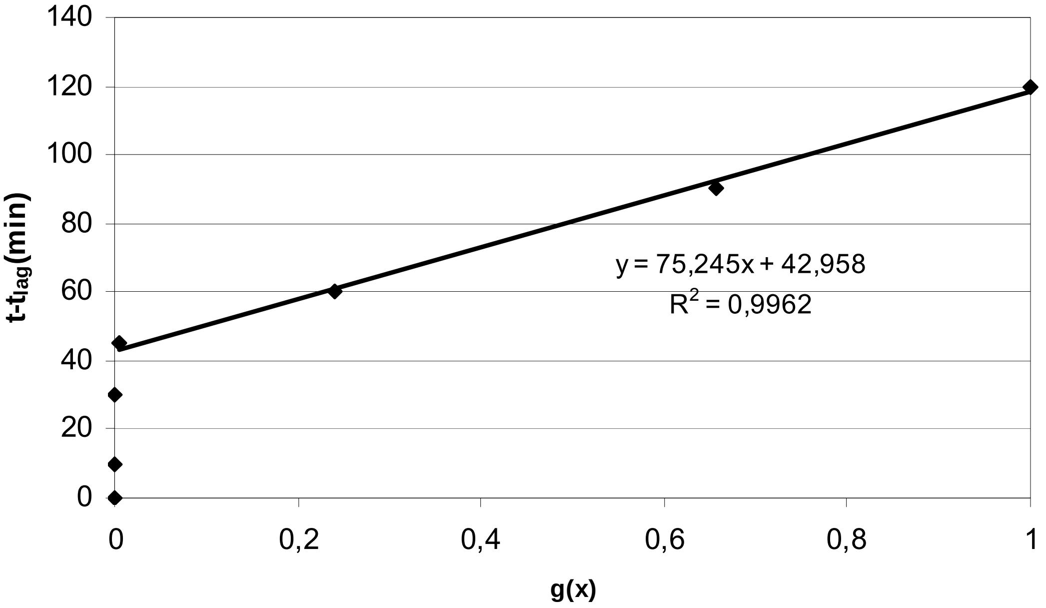


Figure 4.39 : The plot of Equation 4.30 for Experiment 4(1600rpm stirring rate, 95°C temperature, 25µm ZnO, H_3BO_3:ZnO ratio of 5:1)

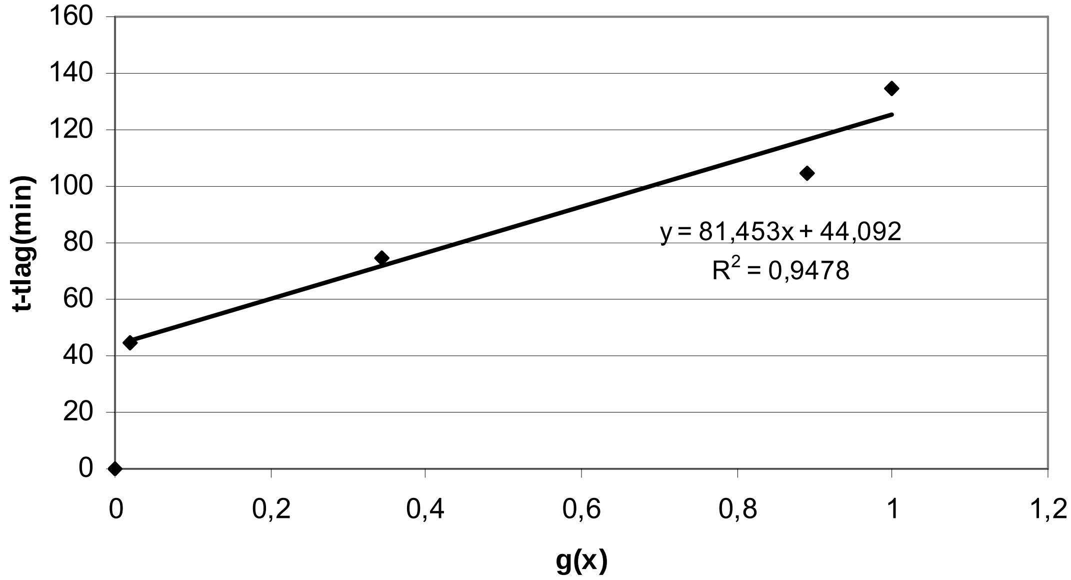


Figure 4.40 : The plot of Equation 4.30 for Experiment 10(1600rpm stirring rate, 85°C temperature, 25µm ZnO, H_3BO_3:ZnO ratio of 5:1)

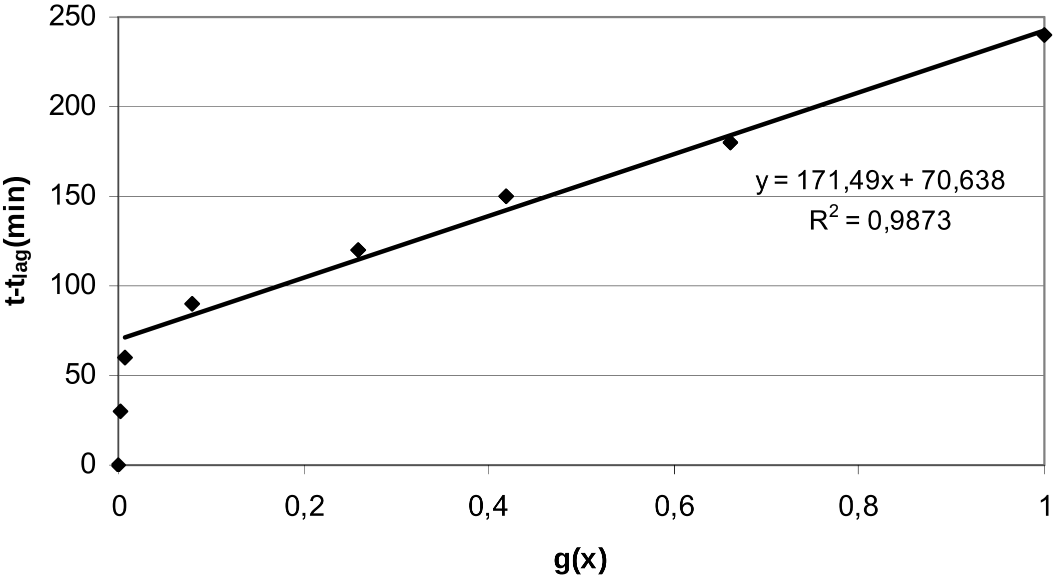


Figure 4.41 : The plot of Equation 4.30 for Experiment 9(1600rpm stirring rate, 75°C temperature, 25µm ZnO, H_3BO_3:ZnO ratio of 5:1)

As could be seen from the above figures, the interception at the y-axis gave us the lag time values. The lag time for the temperatures of 75°C, 85°C and 95°C were 71min, 44min and 43min respectively. Lag time increased as temperature decreased. These results showed that at lower temperatures more time was necessary to form a product layer which allowed constant flux during the reaction.

The values of the slopes at the above figures gave the space times according to Equation 4.30. The value of the space times for temperatures 75°C, 85°C and 95°C were 172min, 81min, 75min respectively. According to these results it was obvious that space times decreased as temperature increased. In other words reaction completion time decreased as temperature increased which was consistent with the results of Section 4.2.3.

Experiment 7 which was performed nearly at stoichometric ratio (H_3BO_3:ZnO ratio of 3.5:1) and did not fit with the previous case also gave satisfactory results for this case. The lag time and space time were calculated as 48min and 102min respectively. The plot of Equation 4.30 for Experiment 7 was given in Figure 4.42.

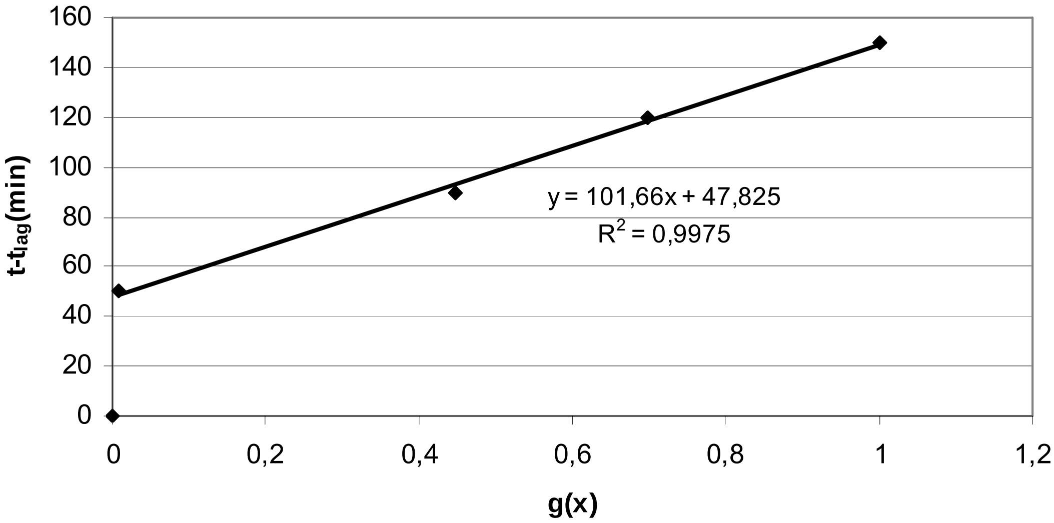


Figure 4.42 : The plot of Equation 4.30 for Experiment 7(1600rpm stirring rate, 95°C temperature, 10μm ZnO, H_3BO_3:ZnO ratio of 3.5:1)

According to Equation 4.25, D_e value could be calculated with some assumptions. Through calculations R’ was taken constant and equal to the initial radius of zinc oxide particle. The other important assumption was that the concentration of boric acid in the liquid (C_{Bo}) was taken constant. The value was accepted as the initial concentration value of the solution.

Based on these assumptions the calculated diffusion coefficient (D_e) values, precalculated lag time(t_{lag}) and space time (τ) values according to temperature (T) and concentration of boric acid (C_{Bo}) were summarized in Table 4.4.

Table 4.4 : Summary of values of model parameters for selected experiments

Run number	**Experimental conditions**	**t_{lag}(min)**	**τ (min)**	**D_e(cm^2s^{-1})**
4	1600rpm stirring rate, 95°C temperature, 25µm ZnO, H_3BO_3:ZnO ratio of 5:1, C_{Bo} = 5.12 mol/lt	43	75	3.1×10^{-13}
9	1600rpm stirring rate, 75°C temperature, 25µm ZnO, H_3BO_3:ZnO ratio of 5:1, C_{Bo} = 3.32 mol/lt	71	172	2.1×10^{-13}
10	1600rpm stirring rate, 85°C temperature, 25µm ZnO, H_3BO_3:ZnO ratio of 5:1, C_{Bo} = 4.31 mol/lt	44	81	3.4×10^{-13}
7	1600rpm stirring rate, 95°C temperature, 10µm ZnO, H_3BO_3:ZnO ratio of 3.5:1, C_{Bo} = 4.92 mol/lt	48	102	3.8×10^{-14}

As could be seen from Table 4.4, the diffusion coefficients were very small. According to the range D_e falled, diffusion could be accepted to be happened in solid phase (Fogler, 1999). This kind of diffusivity was called “Configurational diffusion” which was the case of diffusion happened in solid matrix. The radii of pores were so small that it behaved as non-porous solid.

There were actually no relations between the D_e values in terms of concentration or temperature. The mechanism of diffusion of gases, liquids and solids in solids was extremely complicated and generalized theories were not available (Incropera, 2000).

4.4.3. Calculation of activation energy

To calculate activation energy of zinc borate production reaction from boric acid and zinc oxide the Arrhenius Equation was used (Brown, 1997). In activation energy calculation, diffusion through product layer controlling case was accepted. Since flux through the product layer was constant neither boric acid nor zinc oxide should appear on the reaction rate equation so the reaction could be taken as zero order.

$$k_r = Ae^{-Ea/RT} \qquad (4.32)$$

where $$k_r = -\frac{dC_{bt}}{dt} \qquad (4.33)$$

where k_r is the rate constant, C_{bt} is the concentration of boric acid in mol/lt, *Ea* is the activation energy, *R* is the gas constant (8,314 J/mol-K) and *T* is the absolute temperature. The term A is constant, or nearly so, as temperature is varied taking the natural log of both sides of Equation 4.32, we have;

$$\ln k_r = -\frac{Ea}{RT} + \ln A \qquad (4.34)$$

Equation 4.34 has the form of straight line; it predicts that a graph of lnk versus 1/T will be a line with a slope equal to –Ea/R and a y-intercept equal to lnA. To predict Ea from the Equation 4.34 the results of experiments performed at three different temperatures (75°C, 85°C and 95°C) were used. The boric acid concentration (in the solution) versus time graph of experiments performed at 75°C (Experiment 9), 85°C (Experiment 10) and 95°C (Experiment 4) were given in Figure 4.43, Figure 4.44 and Figure 4.45, respectively.

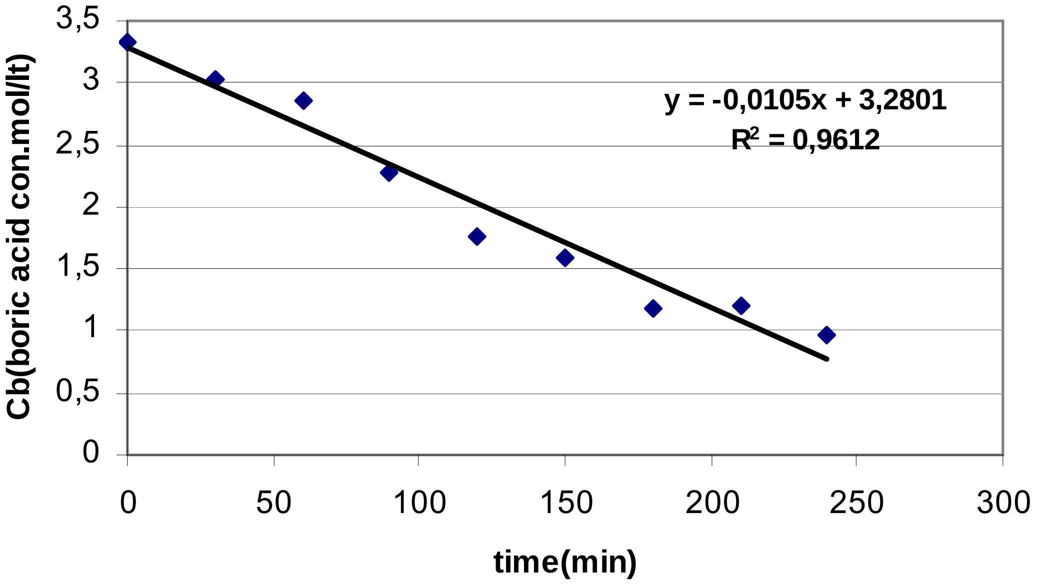


Figure 4.43 : Boric acid concentration versus time graph of Experiment 9 (temperature of 75°C, Stirring rate of 1600rpm, H3BO3:ZnO ratio of 5:1, ZnO size of 0,6µm)

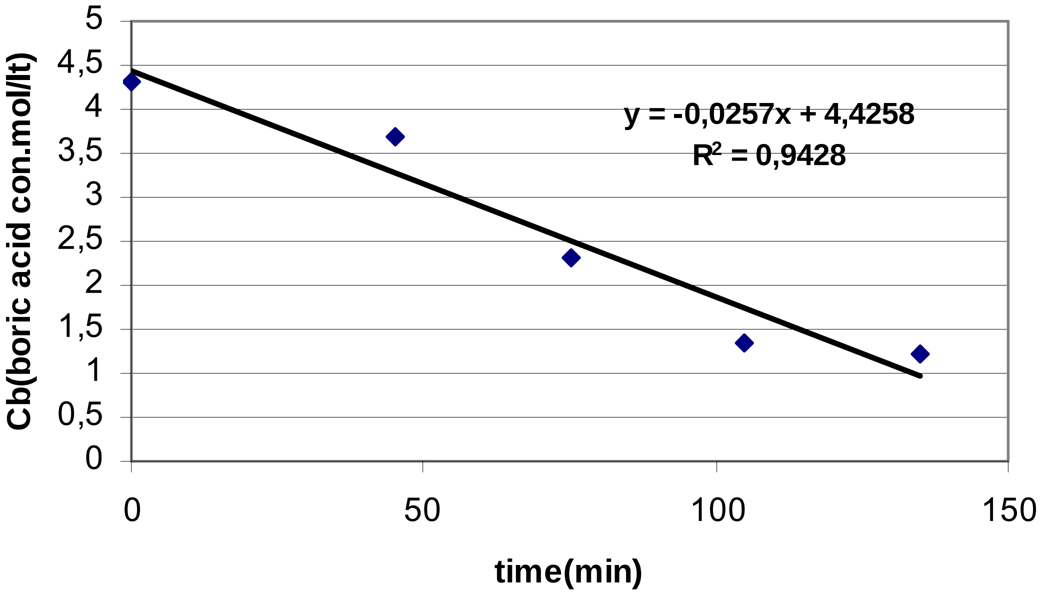


Figure 4.44 : Boric acid concentration versus time graph of Experiment 10 (temperature of 85°C, Stirring rate of 1600rpm, H3BO3:ZnO ratio of 5:1, ZnO size of 0,6µm)

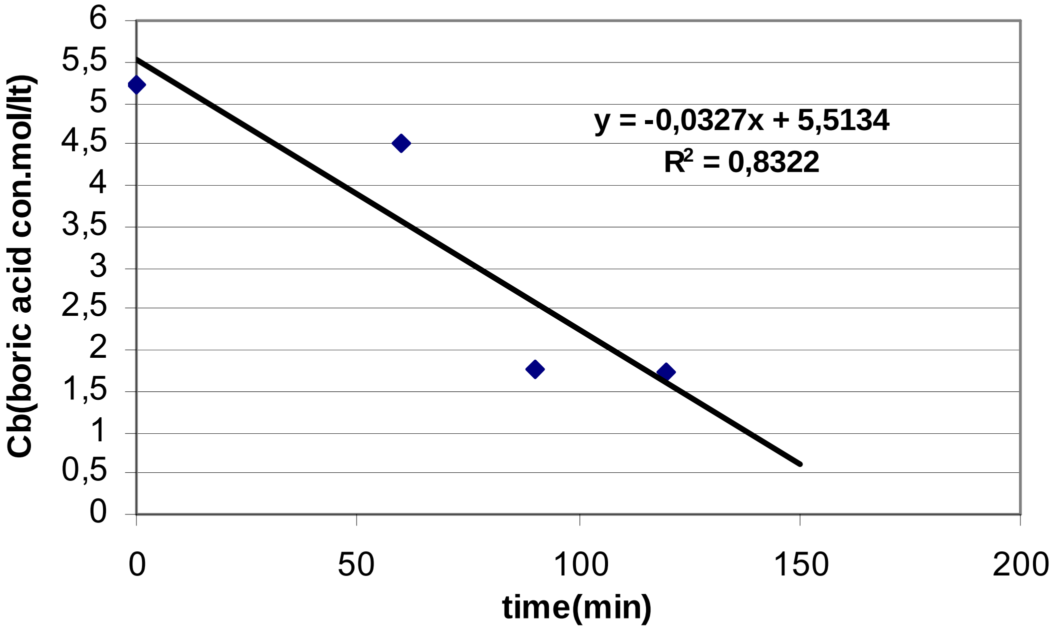


Figure 4.45 : Boric acid concentration versus time graph of Experiment 4 (temperature of 95°C, Stirring rate of 1600rpm, H3BO3:ZnO ratio of 5:1, ZnO size of 0,6μm)

From the slopes of these figures and the temperatures, it was possible to draw Equation 4.34 on a graph for three different temperatures.

By using Figure 4.46, it was possible to estimate activation energy from the slope of the line. The straight line obtained in Figure 4.46 corrected the assumption of zero order reaction made at the beginning of the calculations.

Using the slope of the line (-7311,1), the numerical value of *R* constant (8,314J/mol-K) and Equation 4.34, the activation energy was calculated as 60784,5 J.mol^{-1}.

The value of 6,1X10^{4} J.mol^{-1} was was consistent with the literature (Shete, 2003).

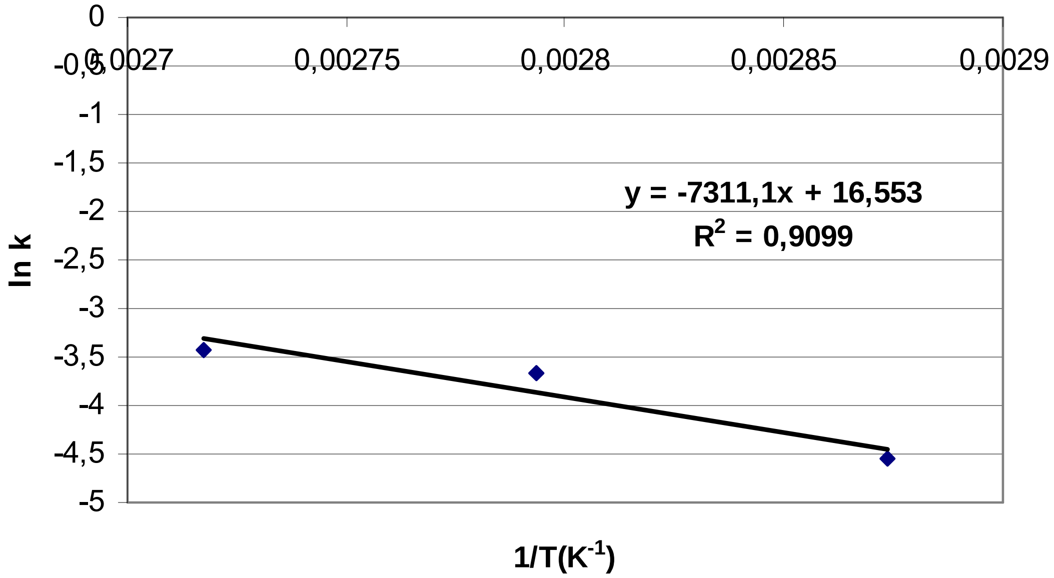


Figure 4.46 : The graph of Equation 4.34 for three different temperatures(75°C, 85°C and 95°C)

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

Zinc borate is a flame retardant additive that can be used in polymers, wood and textile products. It is mostly produced from the reaction between boric acid and zinc oxide under proper conditions (temperature, stirring rate and reactants ratio).

In this study it was aimed to investigate the effects of reaction parameters (temperature, stirring rate, reactants ratio, size of zinc oxide particles and the role of zinc borate as seed) on the zinc borate production reaction rate and the particle size of the final zinc borate product.

Five sets of experiments were performed during the study. The effect of boric acid to zinc oxide ratio (H_3BO_3:ZnO ratio), the particle size of zinc oxide, stirring rate, temperature and size of seed crystals on reaction rate, reaction completion time and particle size distribution of zinc borate were investigated. Activation energy of the reaction was calculated and reaction kinetics was studied. During the experiments samples were taken to be analyzed. The analyses showed the change of zinc oxide and boron oxide in the solid and conversion of zinc oxide with respect to time and rate of reaction was estimated. The final products were also analyzed for particle size distribution.

In the first set of the experiments the effect of reactants ratio on the reaction rate and reaction completion time were observed. The other parameters such as temperature (95°C), stirring rate (1600 rpm), type of zinc oxide (average size of 25 μm) and the seed (average size of 10 μm) were kept constant. Four different mole ratio of boric acid to zinc oxide (H_3BO_3:ZnO) were used. The mole ratio of the reactants changed from the stoichometric ratio (3:1) to the excess of boric acid, 3.5:1, 5:1 and 7:1. The analytical analysis showed that the rate of reaction increased very slightly with the high H_3BO_3:ZnO ratio(7:1). Reaction completion time decreased slightly with the increasing H_3BO_3:ZnO ratio. It was possible to convert all the zinc oxide to the zinc borate for the ratios of 3.5:1, 5:1 and 7:1 but all zinc oxide could not be converted to zinc borate in the stoichometric ratio of 3:1. The B_2O_3 analysis of the liquid showed that there was still boric acid that should be consumed completely in the solution at the end of the experiment. The changing H_3BO_3:ZnO ratios did not affect the particle size of final zinc borate product. There were nearly no difference in the particle size distribution curves for different reactants ratio. According to these results excess boric acid should be used in the zinc borate production reaction in order to convert all the zinc oxide in the reaction and to get a high reaction rate. The results for the effect of reactants ratio was different from the literature. They found that reaction completion time decreased and particle size of zinc borate product increased by increasing reactants ratio (H_3BO_3:ZnO ratio).

In the second set of the experiments, the effect of the size of zinc oxide particles on the reaction rate and reaction completion time was observed. The other parameters such as temperature (95°C), stirring rate (1600 rpm), reactants ratio (3.5:1) and the type of the seed (average size of 10 μm) were kept constant. Two different sizes of zinc oxide particles were used in the experiments. One with the average size of 10 μm and the other was approximately 25 μm. The results of the analytical analyses performed to the samples showed that surprisingly reaction rate increased slightly with the increasing zinc oxide particle size. A small difference could be seen by looking the conversion graphs while the experiment performed with the larger particle size of zinc oxide gave the full conversion at early stages. There was nearly no difference at the reaction completion time. The effect of the zinc oxide particle size to the final zinc borate particle size was investigated. With the decreasing zinc oxide particle size the particle size of final zinc borate product decreased slightly. According to these results the particle size of zinc oxide did not have a considerable effect on the reaction rate and final size of zinc borate. The obtained results in present study was different from the literature. They found that reaction completion time and particle size of zinc borate product decreased by decreasing the zinc oxide particle size.

In the third set of the experiments, it was aimed to investigate the effect of stirring rate. Other reaction parameters that were temperature (95°C), reactants ratio (5:1 and 7:1), type of zinc oxide (average size of 25 μm) and the seed (average size of 10 μm) were kept constant. The stirring rate was changed as 275 rpm, 400 rpm, 800 rpm and 1600 rpm. The analytical results showed that it was possible to get higher reaction rates for high stirring rates (800rpm and 1600rpm) but with decreasing stirring rates (275 rpm and 400 rpm) ZnO conversion with respect to time decreased. At low stirring rates (275 rpm and 400 rpm) more time was required to convert all zinc oxide to the zinc borate. There was nearly no difference in terms of conversion for the stirring rates 800rpm and 1600rpm. Reaction completion time also decreased with the increasing stirring rate. The change in stirring rates also affected the final zinc borate particle size. With the increasing stirring rate the particle size of zinc borate decreased. According to the results to use high stirring rates had beneficial effects on reaction rate and particle size (high reaction rate and smaller particle size) but after a limit increasing stirring rate had no effect on both reaction rate and particle size of final zinc borate product. The obtained results were consistent with the literature.

In the fourth set of experiments the temperature effect on the reaction was observed. Other reaction parameters that are reactants ratio (5:1), stirring rate (1600rpm), type of zinc oxide (average size of 10 μm) and the seed (average size of 10μm) were kept constant. Four different temperatures (75°C, 80°C, 85°C and 95°C) were tried. The analytical results performed to the samples showed that the reaction rate increased with the increasing temperature. The reaction rate was high for the temperatures 85°C and 95°C while reaction rate decreased for the lower temperatures (75°C and 80°C). Reaction completion time was shorter for the temperatures of 85°C and 95°C. The effect of temperature to the final zinc borate product particle size was interesting. The smallest average particle size of zinc borate was obtained at temperatures 75°C and 85°C while at 80°C largest average particle size was obtained. The results related with the reaction rate and reaction completion time were consistent with the literature. On the other hand different from the previous study no relation was found between temperature and particle size of zinc borate.

In the fifth set of the experiments the effect of seed on the reaction rate was observed. Firstly two experiment with same experimental conditions (temperature at 95°C, mole ratio of 5:1, stirring rate of 800rpm, zinc oxide with an average particle size of 25 μm) were performed but one without using seed. The analytical analysis showed that it was not possible to synthesize zinc borate in the absence of the seed. The composition of the final product was different from the commercially taken zinc borate for the experiment performed in the absence of the zinc borate seed. According to these results zinc borate should be used as seed at the beginning of zinc borate production reaction.

Different size of zinc borate seeds were also compared by keeping other variables constant (temperature at 95°C, mole ratio of 5:1, stirring rate of 1600 rpm, zinc oxide with an average particle size of 10 μm). One seed had an average particle size of 10 μm and the other had 2μm. The results of analytical analyses showed that the size of zinc borate seed had no effect on reaction rate and completion time of the reaction. The effect of using different zinc borate seed on the particle size of final product zinc borate was interesting. The larger particle size of zinc borate seed gave smaller particle size of final zinc borate product. According to these results large particle size of zinc borate should be used as seed to get small particle size of zinc borate at the end of the zinc borate production reaction.

Considering the lower completion time, high reaction rate and lower particle size of zinc borate product optimum experimental conditions for producing zinc borate could be summarized as follows : H_3BO_3:ZnO ratio of 5:1, ZnO particle size of 10 μm, stirring rate of 800 rpm, temperature of 85°C and zinc borate particle size of 10 μm as seed.

Zinc borate production reaction was fitted with the unreacted core model. Different from the literature, reaction mainly was consistent with the case of diffusion through product layer controls. Different from the classical form of the model, lag time was observed for this reaction. Lag time was necessary to form the product layer which allowed to constant flux during the reaction. It was seen that lag time and space time increased with decreasing temperature. The small values of calculated diffusion coefficients showed that diffusion happened in solid phase.

The activation energy of the zinc borate production reaction was calculated as 61 $kJ.mol^{-1}$ by using Arrhenius equation. This value was consistent with the one obtained in literature.

REFERENCES

Agrawal J.P, Gupta D.C, Khare Y, Satpute R.S, “Zinc borate complex as flame retardant filler”, Journal of Applied Polymer Science, Vol.43, pp.373-377, 1991

Basfar A.A, “Flammability of radiation cross-linked low density polyetylene as an insulating material for wire and cable”, Radiation Physics and Chemistry, Vol,63, pp.505-508, 2002

Bourbigot S, Bras M.L, Leeuwendal R, Shen K.K, Schubert D, “Recent advances in the use of zinc borates in flame retardancy of EVA”, Polymer Degradation and Stability, Vol.64, pp.419-425, 1999

Brown T.L, LeMay H.E, Bursten B.E, “Chemistry, The Central Science”, New Jersey, Prentice Hall, 7th edition, 1997

Çakal G.O.Y, “Dynamic Behavior of Continuous Flow Stirred Slurry Reactors in Boric Acid Production”, Ph. D Thesis, Middle East Technical University, Ankara, Turkey, 2004

Dong J.X, Hu Z.S, “The study of antiwear and friction-reducing properties of the lubricant additive, nanometer zinc borate, Tribology International, Vol.31, No.5, pp.219-223, 1998

Edenbaum J, “Plastics Additives and modifiers handbook”, New York, Van Nostrand Reinhold, 1992

Erdoğdu A., M.Sc. Thesis, Middle East Technical University, Ankara, Turkey, 2004

Fogler H.S, “Elements of Chemical Reaction Engineering”, New Jersey, Prentice Hall, 4th edition, 1999

Gachter R, Muller H, “Plastics additive handbook”, Munich; New York:Hanser, 4th edition, 1993

Garba B, “Effects of zinc borate as flame retardant formulation on some tropical woods”, Polymer Degradation and Stability, Vol.64, pp.517-522, 1999

Incropera F.P, DeWitt D.P, “Fundamentals of Heat and Mass Transfer”, New York, John Wiley and Sons. Inc., 4th edition, 2000

Levenspiel O., ”Chemical Reaction Engineering”, New York, John Wiley&Sons, 3rd edition, 1999

Nies N. P., Campbell G. W., in R. M. Adams, ed., Boron, Metallo-Boron Compounds, and Boranes, New York, Interscience Publishers, 1964, pp. 192–194

Nies N.P, Beach L, Hulbert R.W, “Zinc borate and low hydration method for preparing the same”, US patent no: 3,549,316, 1970

Ning Y, Guo S, “Flame-retardant and smoke-suppressant properties of zinc borate and aluminium trihydrate filled rigid PVC”, Journal of Applied Polymer Science,Vol.77, pp.3119-3127, 2000

Pi H, Guo S, Ning Y, “Mechanochemical improvement of the flame-retardant and mechanical properties of zinc borate and zinc borate-aluminium trihydrate- filled poly(vinyl chloride)”, Journal of Applied Polymer Science,Vol.89, pp.753-762, 2003

Shete A.V, Sawant S.B, Pangarkar V.G, “Kinetics of fluid-solid reaction with an insoluable product:zinc borate by the reaction of boric acid and zinc oxide”, Journal of Chemical Technology and Biotechnology, Vol.79, pp.526-532, 2004

Tsunoda K, Watanabe H, Fukuda K, Hagio K, “Effects of zinc borate on the properties of medium density fiberboard”, Forest Products Journal, Vol.52, No.11/12, pp.62-65, 2002

Wilson C.L, Wilson D.W, “Comprehensive Analytical Chemistry”, Amsterdam, New York Elsevier Publications, 1992

Woods W. G., in V. M. Bhatnager, ed., Advances in Fire Retardants, Part 2, Technomic, Pa., 1973, 120–153; J. P. Neumeyer, P. A. Koenig, and N. B. Knoepfler, U.S. Agric. Res. Serv., South Reg., ARS-S-64, 70 (1975).

Yang Y, Shi X, Zhao R, “Flame retardant behaviour of zinc borate”, Journal of Fire Sciences, Vol.17, pp.355-361, 1999.

APPENDIX A

RAW DATA OF EXPERIMENTS

Table A.1 The change of ZnO and B_2O_3 contents in the samples collected during Experiment2 (800rpm stirring rate, 95°C temperature, 10µm ZnO, H_3BO_3:ZnO ratio of 5:1, $C_{b(initial)}$ = 3.96 mol/lt)

Sample taken time (min)	Weight of sample (gr)	Amount of EDTA used (ml)	Amount of ZnO in the sample (gr)	%ZnO in the sample	Amount of NaOH used (ml)	Amount of B_2O_3 in the sample (gr)	%B_2O_3 in the sample	H_3BO_3 con. in the liquid (mol/l)
35	0.205	40.2	0.164	79.8	0.328	0.011	5.58	-
85	0.205	22.2	0.090	44.1	2.16	0.075	36.7	-
120	0.205	20.4	0.083	40.5	2.53	0.088	43.0	1.81
160	0.205	24.0	0.097	47.6	2.61	0.091	44.2	1.71
200	0.205	18.6	0.076	37.0	2.78	0.097	47.3	1.46
240	0.205	20.0	0.081	39.7	2.77	0.097	47.1	1.62
285	0.205	19.4	0.079	38.4	2.79	0.097	47.4	1.37

Table A.2 The change of ZnO and B_2O_3 contents in the samples collected during Experiment3 (1000rpm stirring rate, 95°C temperature, 10µm ZnO, H_3BO_3:ZnO ratio of 7:1, $C_{b(initial)}$ = 4.91 mol/lt)

Sample taken time(min)	Weight of sample (gr)	Amount of EDTA used(ml)	Amount of ZnO in the sample(gr)	%ZnO in the sample	Amount of NaOH used(ml)	Amount of B_2O_3 in the sample(gr)	%B_2O_3 in the sample
30	0.205	-	-	-	-	-	-
50	0.205	41.0	0.167	81.4	1.26	0.044	0.916
90	0.205	20.2	0.082	40.0	0.643	0.022	0.950
120	0.205	19.9	0.081	39.5	2.77	0.096	4.14
140	0.205	20.0	0.081	39.7	2.83	0.098	4.21
170	0.205	20.3	0.083	40.3	2.83	0.099	4.16
200	0.205	20.2	0.082	40.1	2.86	0.100	4.22
230	0.205	20.0	0.082	39.8	2.85	0.099	4.23

Table A.3 The change of ZnO and B_2O_3 contents in the samples collected during Experiment4 (1600rpm stirring rate, 95°C temperature, 25µm ZnO, H_3BO_3:ZnO ratio of 5:1, $C_{b(initial)}$ = 5.12 mol/lt)

Sample taken time (min)	Weight of sample (gr)	Amount of EDTA used (ml)	Amount of ZnO in the sample (gr)	%ZnO in the sample	Amount of NaOH used (ml)	Amount of B_2O_3 in the sample (gr)	%B_2O_3 in the sample	H_3BO_3 con. in the liquid (mol/l)
10	0.205	49.6	0.202	98.5	0.131	0,005	2.16	4.02
20	0.205	49.6	0.202	98.4	0.110	0.004	1.80	4.00
30	0.205	47.0	0.191	93.3	0.339	0.012	5.58	3.75
45	0.205	46.0	0.187	91.4	0.822	0.029	13.5	3.48
60	0.205	22.9	0.093	45.4	2.21	0.077	36.4	3.09
90	0.205	20.2	0.082	40.2	2.69	0.094	45.7	1.62
120	0.205	19.5	0.079	38.6	2.76	0.096	46.9	1.61
150	0.205	19.8	0.081	39.4	2.78	0.097	47.2	1.61
180	0.205	19.4	0.079	38.6	2.78	0.097	47.3	-
240	0.205	19.5	0.080	38.8	2.77	0.096	47.0	-

Table A.4 The change of ZnO and B_2O_3 contents in the samples collected during Experiment5 (1600rpm stirring rate, 95°C temperature, 10µm ZnO, H_3BO_3:ZnO ratio of 7:1, $C_{b(initial)}$ = 4.99 mol/lt)

Sample taken time(min)	Weight of sample (gr)	Amount of EDTA used (ml)	Amount of ZnO in the sample (gr)	%ZnO in the sample	Amount of NaOH used (ml)	Amount of B_2O_3 in the sample (gr)	%B_2O_3 in the sample
60	0.205	29.7	0.121	58.9	1.73	0.060	29.3
90	0.205	19.4	0.079	38.5	2.86	0.099	48.5
120	0.205	19.5	0.080	38.8	2.82	0.098	48.0
150	0.205	19.4	0.079	38.5	2.83	0.098	48.0
180	0.205	19.7	0.080	39.1	2.84	0.099	48.2
210	0.205	19.5	0.079	38.8	2.81	0.098	47.7
240	0.205	19.9	0.081	39.5	2.77	0.096	47.1
270	0.205	19.5	0.080	38.8	2.76	0.096	46.9

Table A.5 The change of ZnO and B_2O_3 contents in the samples collected during Experiment6 (1600rpm stirring rate, 95°C temperature, 10µm ZnO, H_3BO_3:ZnO ratio of 5:1, $C_{b(initial)}$ = 4.0 mol/lt)

Sample taken time(min)	Weight of sample (gr)	Amount of EDTA used (ml)	Amount of ZnO in the sample(gr)	%ZnO in the sample	Amount of NaOH used (ml)	Amount of B_2O_3 in the sample(gr)	%B_2O_3 in the sample
60	0.205	34.2	0.139	67.9	1.36	0.047	23.0
90	0.205	20.2	0.082	40.1	2.49	0.087	42.2
120	0.205	19.3	0.079	38.3	2.66	0.093	45.2
150	0.205	19.5	0.079	38.7	2.77	0.096	47.0
180	0.205	19.5	0.080	38.8	2.78	0.097	47.2

Table A.6 The change of ZnO and B_2O_3 contents in the samples collected during Experiment7 (1600rpm stirring rate, 95°C temperature, 10µm ZnO, H_3BO_3:ZnO ratio of 3.5:1, $C_{b(initial)}$ = 4.92 mol/lt)

Sample taken time(min)	Weight of sample (gr)	Amount of EDTA used (ml)	Amount of ZnO in the sample (gr)	%ZnO in the sample	Amount of NaOH used (ml)	Amount of B_2O_3 in the sample (gr)	%B_2O_3 in the sample	H_3BO_3 con. in the liquid (mol/l)
50	0.205	40.0	0.163	79.3	0.831	0.029	14.1	2.51
90	0.205	20.7	0.084	41.0	2.46	0.086	41.7	1.04
120	0.205	19.7	0.080	39.2	2.64	0.092	44.8	0.756
150	0.205	18.8	0.076	37.3	2.66	0.093	45.2	0.826
180	0.205	19.8	0.081	39.3	2.80	0.097	47.5	-
210	0.205	20.1	0.082	39.8	3.02	0.105	51.3	-
240	0.205	20.0	0.081	39.6	2.76	0.096	46.8	0.803
270	0.205	19.6	0.080	39.0	2.76	0.096	46.8	0.838

Table A.7 The change of ZnO and B_2O_3 contents in the samples collected during Experiment8 (1600rpm stirring rate, 95°C temperature, 25µm ZnO, H_3BO_3:ZnO ratio of 3.5:1, $C_{b(initial)}$ = 4.87 mol/lt)

Sample taken time(min)	Weight of sample (gr)	Amount of EDTA used (ml)	Amount of ZnO in the sample (gr)	%ZnO in the sample	Amount of NaOH used (ml)	Amount of B_2O_3 in the sample (gr)	%B_2O_3 in the sample	H_3BO_3 con. in the liquid (mol/l)
30	0.205	42.9	0.175	85.2	0.793	0.028	13.5	-
60	0.205	28.0	0.114	55.6	1.74	0.061	29.6	3.04
90	0.205	20.0	0.081	39.7	2.56	0.089	43.5	1.00
120	0.205	20.5	0.083	40.7	2.62	0.091	44.5	0.778
150	0.205	19.8	0.080	39.2	2.69	0.094	45.6	0.696
180	0.205	20.9	0.085	41.6	2.70	0.094	45.8	0.712

Table A.8 The change of ZnO and B_2O_3 contents in the samples collected during Experiment9 (1600rpm stirring rate, 75°C temperature, 25µm ZnO, H_3BO_3:ZnO ratio of 5:1, $C_{b(initial)}$ = 3.32 mol/lt)

Sample taken time (min)	Weight of sample (gr)	Amount of EDTA used (ml)	Amount of ZnO in the sample (gr)	%ZnO in the sample	Amount of NaOH used (ml)	Amount of B_2O_3 in the sample (gr)	%B_2O_3 in the sample	H_3BO_3 con. in the liquid (mol/l)
30	0.205	39.5	0.161	78.3	0.503	0.018	8.54	3.02
60	0.205	39.5	0.161	78.5	0.731	0.025	12.4	2.87
90	0.205	26.4	0.107	52.3	1.59	0.055	26.9	2.29
120	0.205	20.6	0.084	40.8	2.00	0.070	34.0	1.76
150	0.205	19.4	0.079	38.5	2.22	0.077	37.8	1.59
180	0.205	19.0	0.077	37.7	2.46	0.086	41.8	1.19
210	0.205	20.6	0.084	40.9	2.64	0.092	44.8	1.21
240	0.205	19.9	0.081	39.4	2.74	0.095	46.6	0.976

Table A.9 The change of ZnO and B_2O_3 contents in the samples collected during Experiment10 (1600rpm stirring rate, 85°C temperature, 25µm ZnO, H_3BO_3:ZnO ratio of 5:1, $C_{b(initial)}$ = 4.31 mol/lt)

Sample taken time (min)	Weight of sample (gr)	Amount of EDTA used (ml)	Amount of ZnO in the sample (gr)	%ZnO in the sample	Amount of NaOH used (ml)	Amount of B_2O_3 in the sample (gr)	%B_2O_3 in the sample	H_3BO_3 con. in the liquid (mol/l
45	0.205	33.1	0.135	65.8	1.02	0.036	17.4	3.70
75	0.205	20.5	0.084	40.8	2.20	0.076	37.3	2.31
105	0.205	20.0	0.081	39.7	2.73	0.095	46.3	1.35
135	0.205	19.7	0.080	39.1	2.74	0.095	46.4	1.21
165	0.205	20.0	0.082	39.8	2.79	0.097	47.3	-
195	0.205	20.1	0.082	39.9	2.74	0.095	46.6	-
225	0.205	20.0	0.081	39.6	2.75	0.096	46.7	-
240	0.205	20.2	0.082	40.0	2.77	0.096	47.1	-

Table A.10 The change of ZnO and B_2O_3 contents in the samples collected during Experiment11 (1600rpm stirring rate, 95°C temperature, 25µm ZnO, H_3BO_3:ZnO ratio of 5:1, 2µm seed, $C_{b(initial)}$ = 5.23 mol/lt)

Sample taken time (min)	Weight of sample (gr)	Amount of EDTA used (ml)	Amount of ZnO in the sample (gr)	%ZnO in the sample	Amount of NaOH used (ml)	Amount of B_2O_3 in the sample (gr)	%B_2O_3 in the sample	H_3BO_3 con. in the liquid (mol/l
30	0.205	50.9	0.207	97.1	0.116	0.004	1.96	5.21
60	0.205	35.1	0.143	69.7	1.19	0.041	20.1	4.52
90	0.205	19.9	0.081	39.5	2.76	0.096	46.8	1.75
120	0.205	20.2	0.082	40.2	2.75	0.096	46.8	1.72
150	0.205	20.5	0.084	40.7	2.77	0.096	47.0	-
180	0.205	19.2	0.078	38.2	2.81	0.098	47.7	1.68

Table A.11 The change of ZnO and B_2O_3 contents in the samples collected during Experiment12 (400rpm stirring rate, 95°C temperature, 10µm ZnO, H_3BO_3:ZnO ratio of 5:1, $C_{b(initial)}$ = 5.12 mol/lt)

Sample taken time (min)	Weight of sample (gr)	Amount of EDTA used (ml)	Amount of ZnO in the sample (gr)	%ZnO in the sample	Amount of NaOH used (ml)	Amount of B_2O_3 in the sample (gr)	%B_2O_3 in the sample	H_3BO_3 con. in the liquid (mol/l
15	0.205	48.6	0.198	0.964	0.174	0.006	2.95	3.80
30	0.205	47.3	0.193	0.940	0.332	0.012	5.64	3.60
50	0.205	29.7	0.121	0.590	1.58	0.055	26.9	3.25
90	0.205	21.2	0.086	0.421	2.39	0.083	40.5	1.90
120	0.205	20.2	0.082	0.401	2.68	0.093	45.5	1.46
160	0.205	19.9	0.081	0.395	2.74	0.095	46.5	1.45
180	0.205	20.0	0.081	0.397	2.76	0.096	46.9	1.26
240	0.205	20.0	0.082	0.398	2.72	0.095	46.1	1.27

Table A.12 The change of ZnO and B_2O_3 contents in the samples collected during Experiment13 (1600rpm stirring rate, 80°C temperature, 25µm ZnO, H_3BO_3:ZnO ratio of 5:1, $C_{b(initial)}$ = 5.12 mol/lt)

Sample taken time (min)	Weight of sample (gr)	Amount of EDTA used (ml)	Amount of ZnO in the sample (gr)	%ZnO in the sample	Amount of NaOH used (ml)	Amount of B_2O_3 in the sample (gr)	%B_2O_3 in the sample	H_3BO_3 con. in the liquid (mol/l
10	0.205	45.2	0.184	89.7	0.454	0.016	7.71	2.77
20	0.205	48.2	0.196	95.7	-	-	-	2.40
30	0.205	45.5	0.185	90.3	-	-	-	2.04
40	0.205	44.0	0.179	87.3	-	-	-	1.88
60	0.205	38.9	0.158	77.2	0.850	0.030	14.4	2.59
90	0.205	31.7	0.129	63.0	1.34	0.047	22.8	2.38
120	0.205	23.4	0.095	46.5	1.98	0.069	33.6	2.11
150	0.205	20.3	0.083	40.3	2.32	0.081	39.4	1.54
180	0.205	20.4	0.083	40.6	2.47	0.086	42.0	1.35
200	0.205	20.7	0.084	41.0	2.58	0.090	43.9	1.24

Table A.13 The change of ZnO and B_2O_3 contents in the samples collected during Experiment14 (1600rpm stirring rate, 95°C temperature, 10µm ZnO, H_3BO_3:ZnO ratio of 3:1, $C_{b(initial)}$ = 5.16 mol/lt)

Sample taken time (min)	Weight of sample (gr)	Amount of EDTA used (ml)	Amount of ZnO in the sample (gr)	%ZnO in the sample	Amount of NaOH used (ml)	Amount of B_2O_3 in the sample (gr)	%B_2O_3 in the sample	H_3BO_3 con. in the liquid (mol/l
10	0.205	42.1	0.171	83.6	0.730	0.025	12.0	3.13
20	0.205	39.7	0.162	78.8	0.826	0.028	13.6	3.65
30	0.205	39.7	0.162	78.8	0.766	0.026	12.6	3.32
45	0.205	38.9	0.158	77.1	0.945	0.032	15.5	3.48
75	0.205	24.1	0.098	47.9	2.52	0.085	41.4	0.901
105	0.205	20.5	0.083	40.7	2.63	0.089	43.3	0.539
135	0.205	21.2	0.086	42.1	2.69	0.091	44.2	0.492
165	0.205	21.2	0.086	42.1	2.73	0.092	44.9	0.463
195	0.205	21.3	0.087	42.3	2.72	0.092	44.8	0.388
225	0.205	21.8	0.089	43.3	2.72	0.092	44.7	0.398

Table A.14 The change of ZnO and B_2O_3 contents in the samples collected during Experiment15 (275rpm stirring rate, 95°C temperature, 10µm ZnO, H_3BO_3:ZnO ratio of 5:1, $C_{b(initial)}$ = 5.12 mol/lt)

Sample taken time (min)	Weight of sample (gr)	Amount of EDTA used (ml)	Amount of ZnO in the sample (gr)	%ZnO in the sample	Amount of NaOH used (ml)	Amount of B_2O_3 in the sample (gr)	%B_2O_3 in the sample	H_3BO_3 con. in the liquid (mol/l
15	0.205	49.2	0.200	97.7	0.204	0.007	3.35	4.23
30	0.205	49.6	0.202	98.4	0.235	0.008	3.87	3.39
55	0.205	47.8	0.195	94.9	0.409	0.014	6.73	3.48
90	0.205	36.1	0.147	71.6	1.14	0.039	18.8	3.39
115	0.205	24.4	0.099	48.3	2.08	0.070	34.2	2.97
150	0.205	21.9	0.089	43.4	2.29	0.077	37.7	2.34
180	0.205	21.4	0.087	42.5	2.57	0.087	42.4	1.94
210	0.205	20.0	0.081	39.7	2.83	0.095	46.5	1.60

APPENDIX B

LIQUID ANALYSIS

Since all the boric acid was in water initially, the boric acid analysis in the liquid would be helpful to understand the consumption of boric acid throughout the reaction. The comparison of the boric acid concentration change with respect to time in the liquid phase for different temperatures, stirring rates, reactants ratio (H_3BO_3:ZnO), different size of zinc oxide and zinc borate were given in Figure B.1 to Figure B.5.

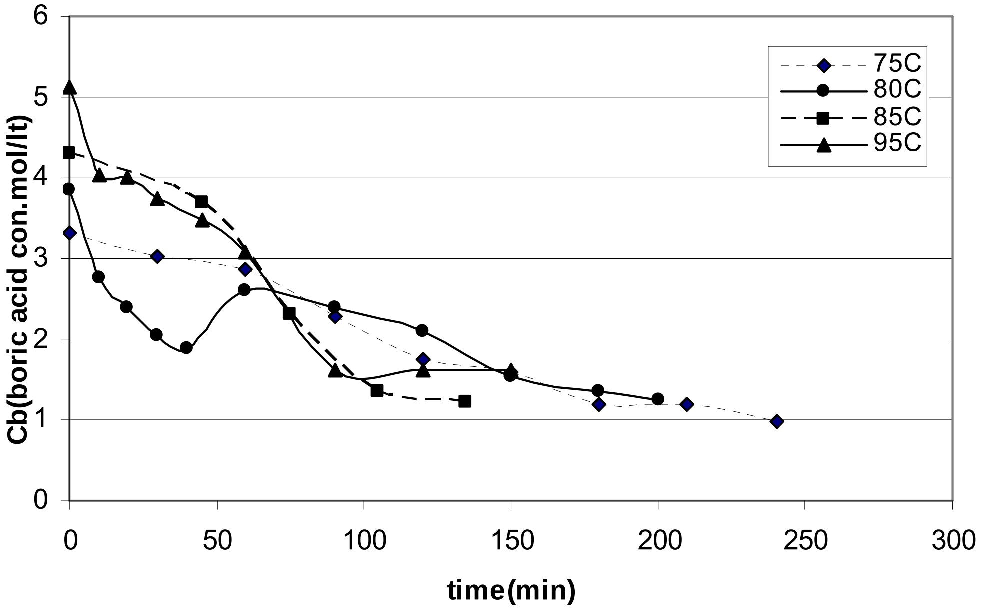


Figure B.1: The change of B_2O_3 concentration in the liquid phase for different temperatures((initial reactants ratio (H_3BO_3:ZnO ratio of 5:1), stirring rate(1600rpm) and type of zinc oxide particles (average particle size of 25μm) were constant)

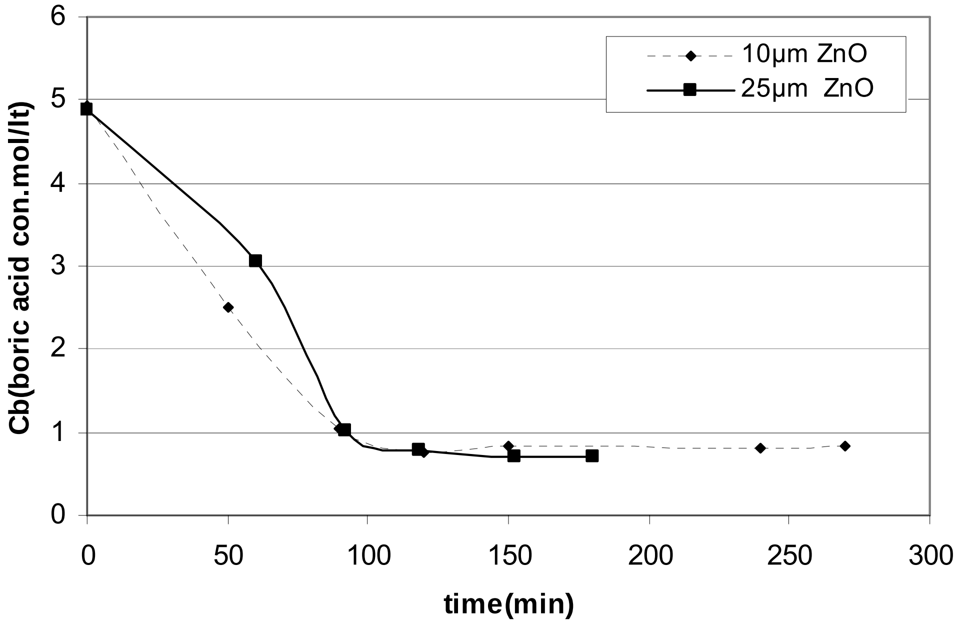


Figure B.2 : The change of B_2O_3 concentration in the liquid phase for different ZnO's(Temperature (95ºC), initial reactants ratio (H_3BO_3:ZnO ratio of 3,5:1) and stirring rate(1600rpm) were constant)

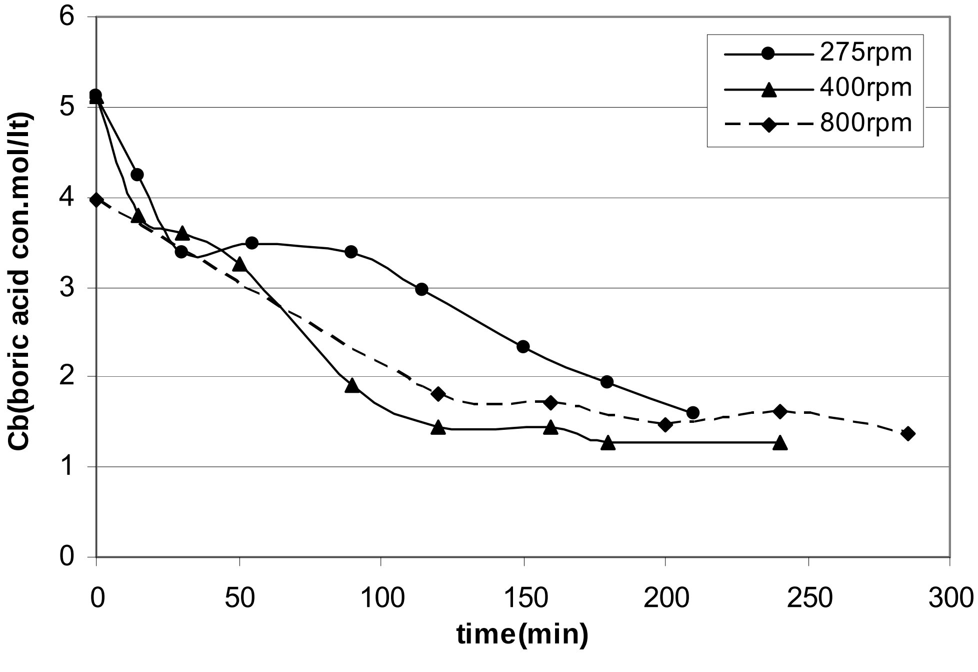


Figure B.3 : The change of B_2O_3 concentration in the liquid phase for different stirring rates(Temperature (95ºC), initial reactants ratio (H_3BO_3:ZnO ratio of 5:1) and type of zinc oxide particles (average particle size of 10µm) were constant)

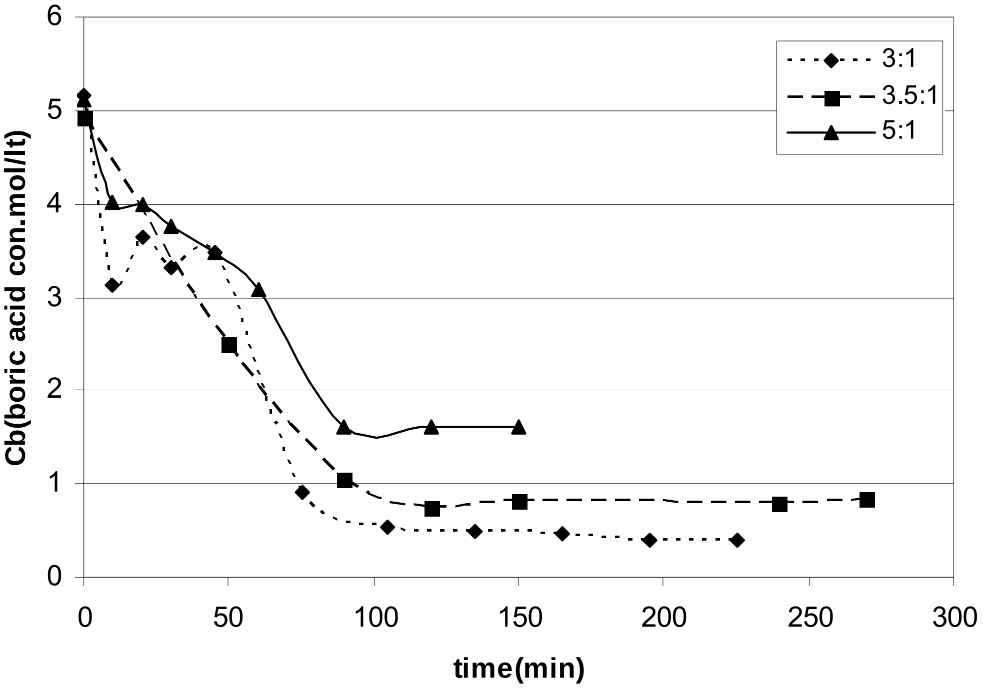


Figure B.4 : The change of B_2O_3 concentration in the liquid phase for different H_3BO_3:ZnO ratios. (Temperature (95ºC), stirring rate(1600rpm) and type of zinc oxide particles (average particle size of 10µm) were constant)

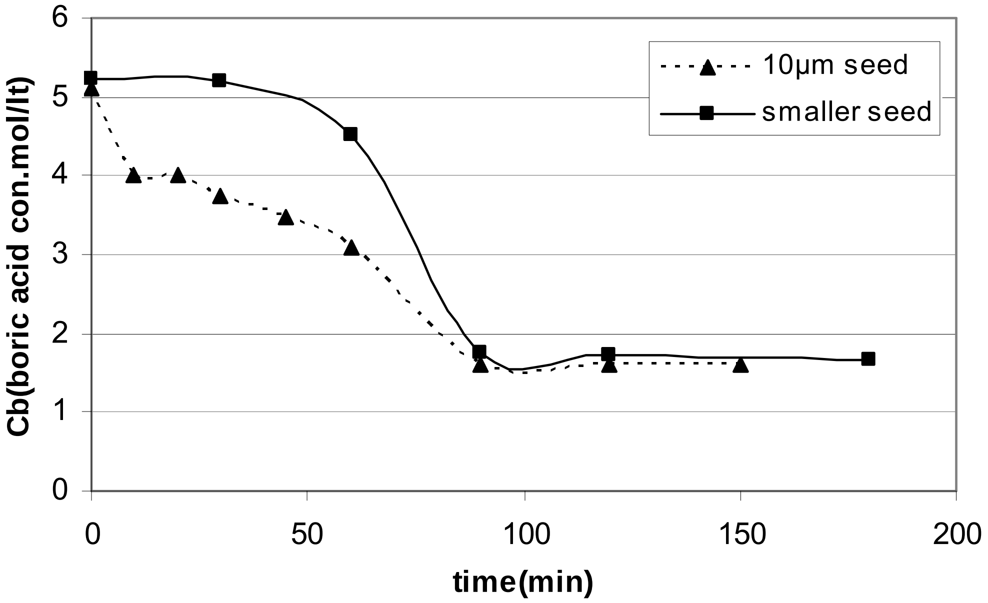


Figure B.5 : The change of B_2O_3 concentration in the liquid phase for different zinc borates. (Temperature (95ºC), initial reactants ratio (H_3BO_3:ZnO ratio of 5:1), stirring rate(1600rpm) and type of zinc oxide particles (average particle size of 25µm) were constant)

APPENDIX C

CRYSTAL IMAGES ANALYSIS

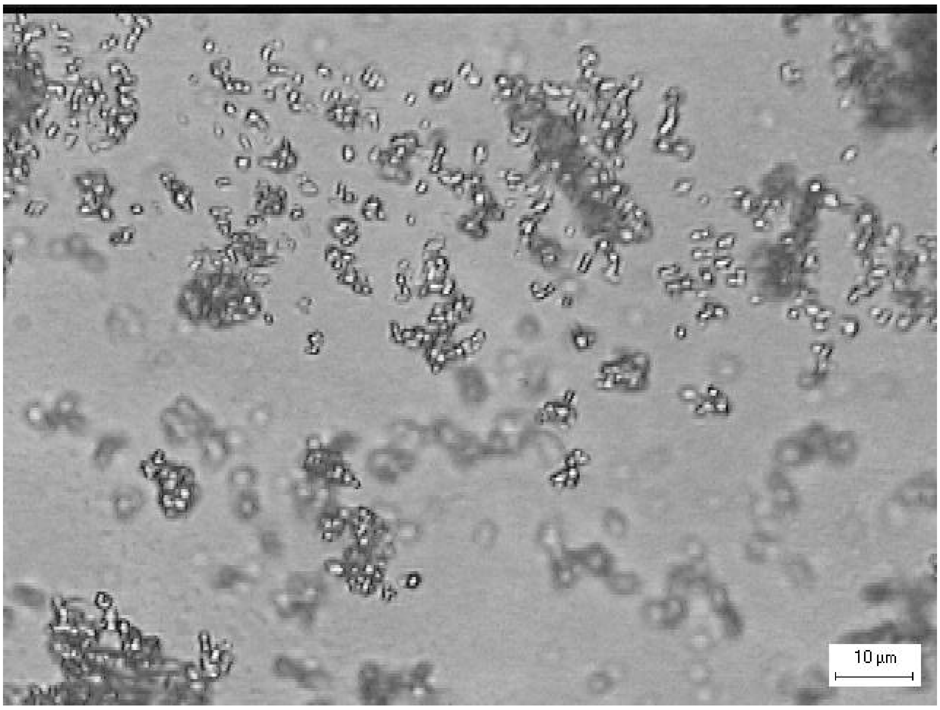


Figure C.1 : Image of product zinc borate obtained at Experiment 4 (temperature of 95ºC, stirring rate of 1600rpm, H_3BO_3:ZnO ratio of 5:1, ZnO size of 25µm)

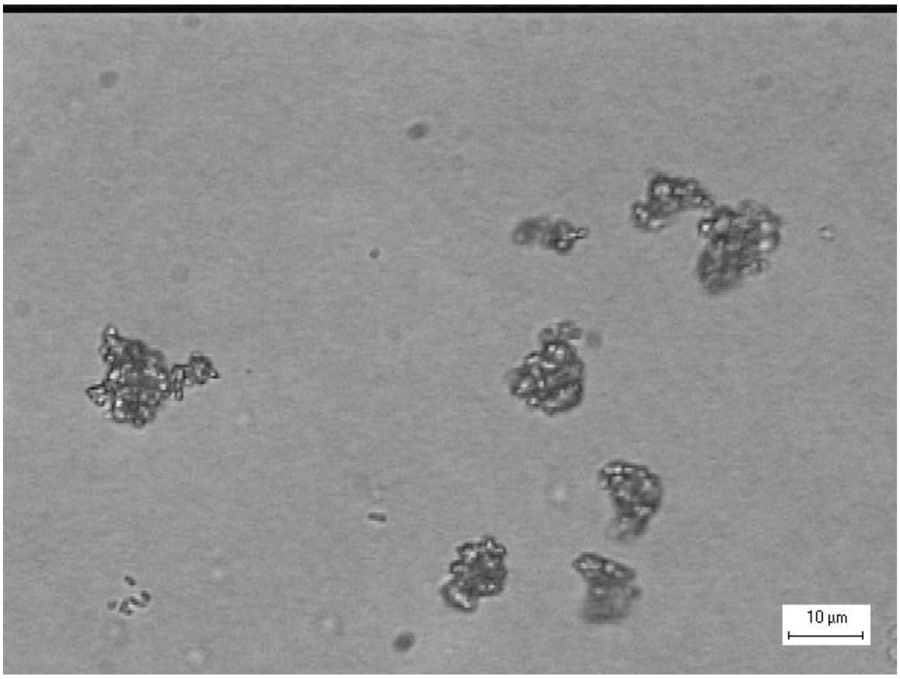


Figure C.2 : Image of product zinc borate obtained at Experiment 5 (temperature of 95ºC, stirring rate of 1600rpm, H_3BO_3:ZnO ratio of 7:1, ZnO size of 10µm)

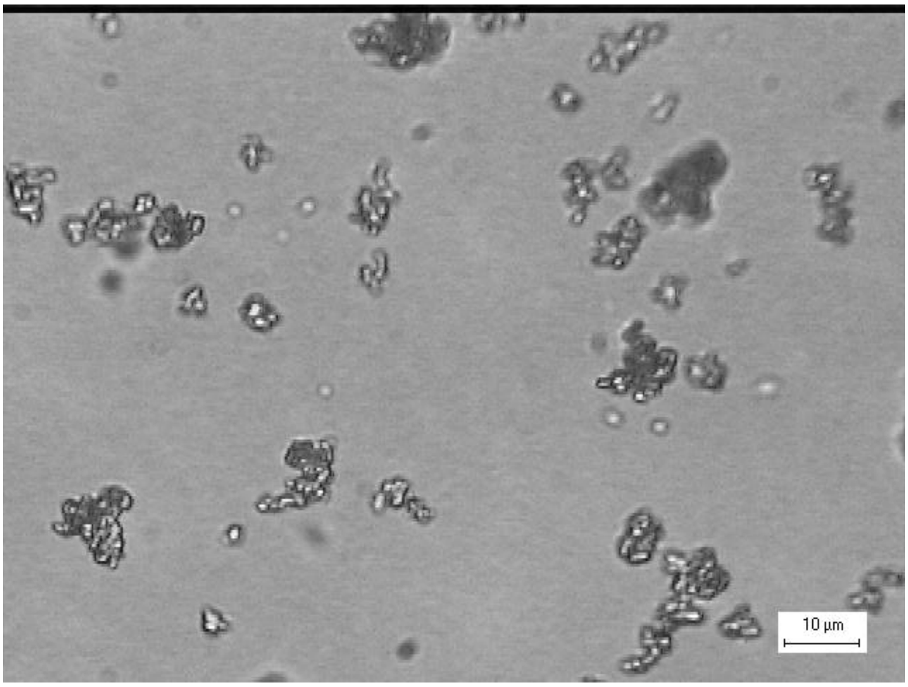


Figure C.3 : Image of product zinc borate obtained at Experiment 6 (temperature of 95ºC, stirring rate of 1600rpm, H_3BO_3:ZnO ratio of 5:1, ZnO size of 10µm)

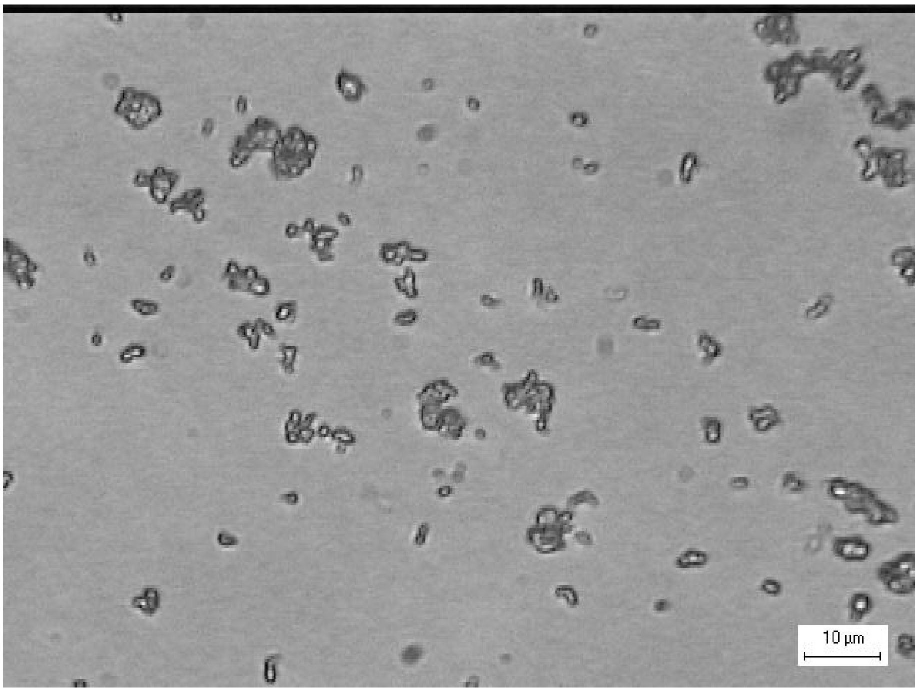


Figure C.4 : Image of product zinc borate obtained at Experiment 7 (temperature of 95ºC, stirring rate of 1600rpm, H_3BO_3:ZnO ratio of 3.5:1, ZnO size of 10µm)

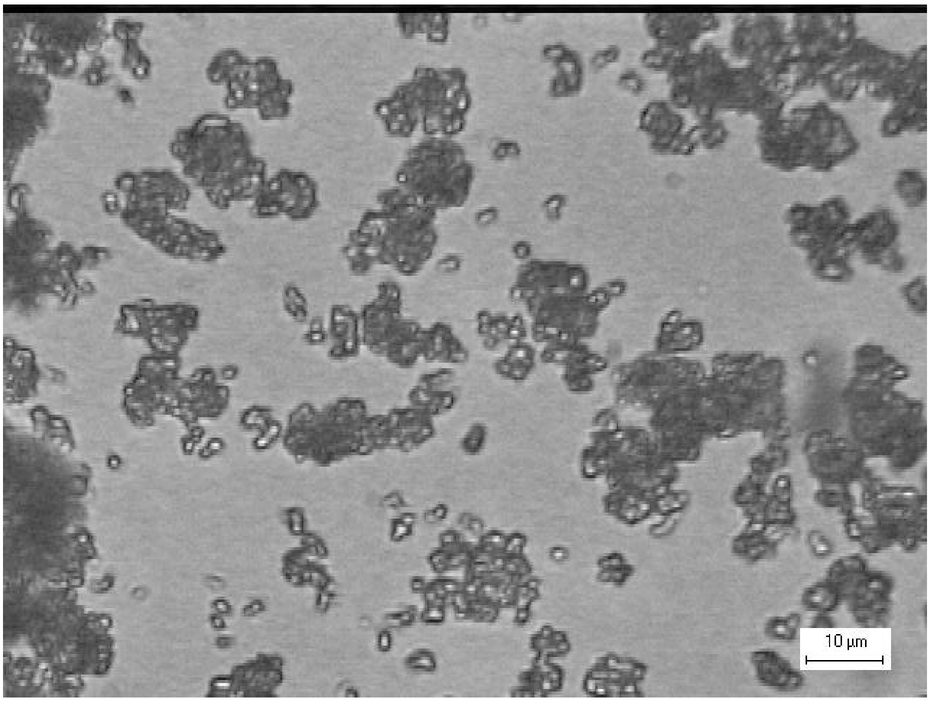


Figure C.5 : Image of product zinc borate obtained at Experiment 8 (temperature of 95ºC, stirring rate of 1600rpm, H_3BO_3:ZnO ratio of 5:1, ZnO size of 25µm)

APPENDIX D

PROPERTIES OF RAW MATERIALS USED

D.1. PROPERTIES OF BORIC ACID

The boric acid (H_3BO_3, with purity of 99.9% by weight) was provided from Emet Boric Acid Plant, Kütahya, Turkey.

Some physical and chemical properties of boric acid were listed in Table D.1; the solubility table of boric acid for different temperatures was given in Figure D.1.

Table D.1 : Some physical and chemical properties of boric acid(H_3BO_3)

Vapour Pressure (mm Hg)	2.6 (at 20°C)
Bulk Density	780-815 kg/m^3
Density	1.435
Solubility in water	4.7% (at 25°C), 27.5% (at 100°C)
pH	6.1 (0.1% solution); 5.1(1.0 % solution); 3.7 (4.7% solution) at 20°C
Molecular Weight	61.83
Melting Point	171°C
Boiling Point	Decomposes
Appearance	White granules
Odor	Odorless

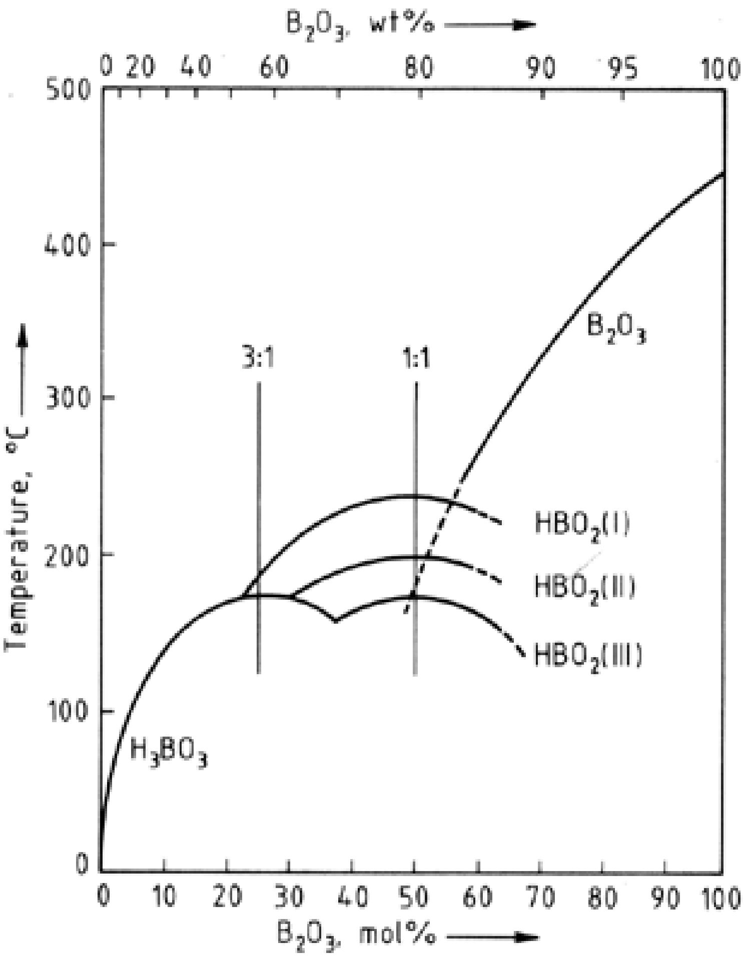


Figure D.1 : The solubility of boric acid with temperature in terms of B_2O_3 (Kirk-Othmer Encyclopedia of Chemical Technology, Wiley Inter Science Web SİtehttP : www.mrw.interscience.wiley.com/, December 2004)

D.2. PROPERTIES OF ZINC OXIDE

The zinc oxide (ZnO) was supplied by two suppliers. The one with 25 μm particle size was provided by MKS Limited, İstanbul, Turkey and the ZnO having particle size of 10 μm was provided from Kartal Oksit Limited, Ankara, Turkey.

Some physical and chemical properties of zinc oxide were given in Table D.2. The particle size distribution curves for the two different sizes of zinc oxides were given in Figure D.2 and Figure D.3.

Table D.2 : Some physical and chemical properties of zinc oxide(ZnO)

Vapour Pressure (mm Hg)	NA
Density	5.606
Solubility in water	Insoluable
Molecular Weight	81.37
Melting Point	1975°C
Boiling Point	NA
Appearance	White to yellowish powder
Odor	Odorless

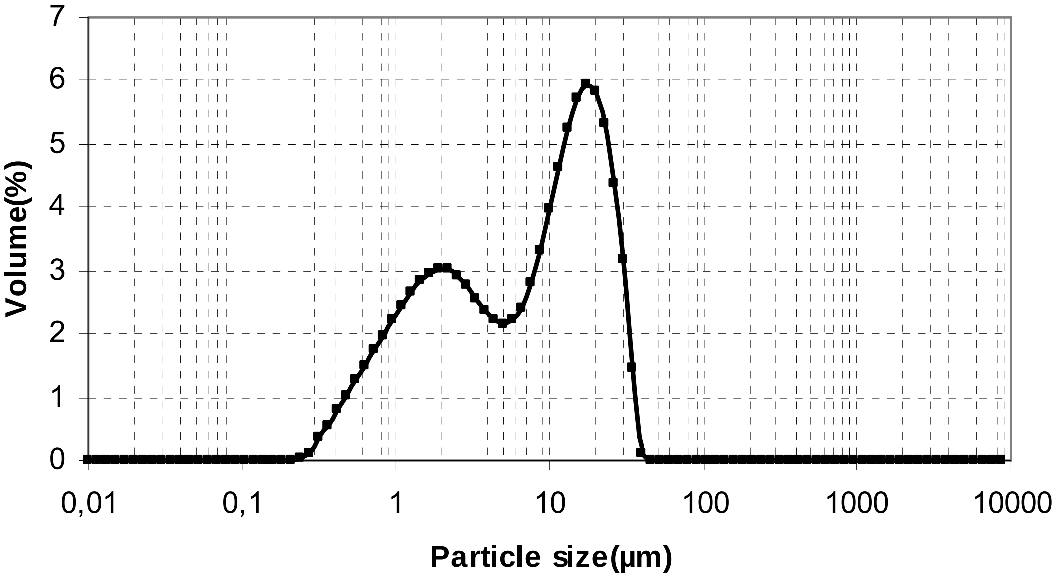


Figure D.2 : Particle size distribution graph of zinc oxide obtained from Kartal Oksit Limited, Ankara, Turkey with an average particle size of 10µm

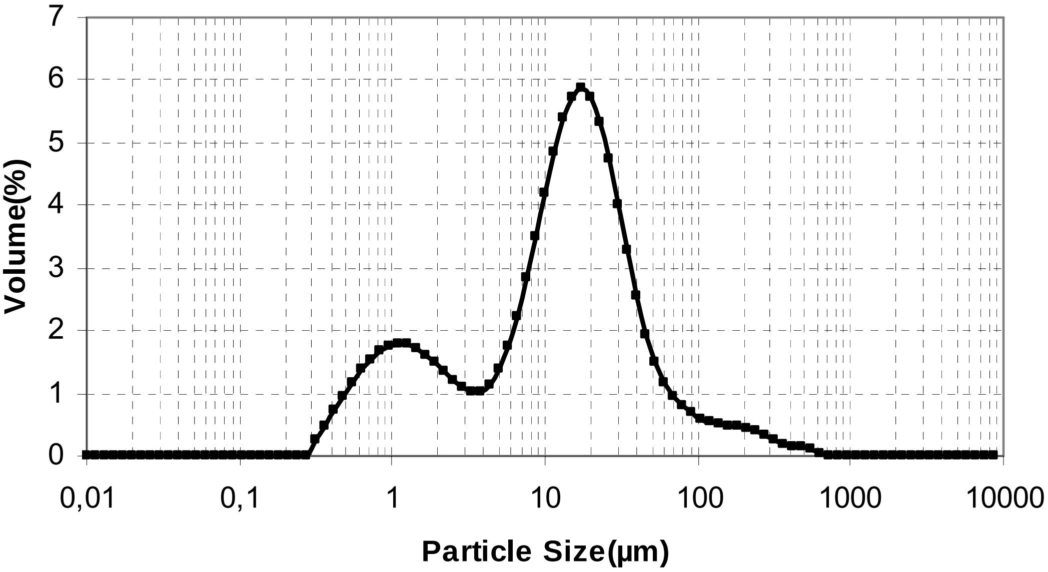


Figure D.3 : Particle size distribution graph of zinc oxide obtained from MKS Limited, İstanbul, Turkey with an average particle size of 25µm

D.3. PROPERTIES OF ZINC BORATE

The zinc borate ($2ZnO.3B_2O_3.3,5H_2O$) again was obtained from two suppliers. The one with average particle size of 10 µm was supplied from Great Lakes, USA and the one with particle size of 2µm was from Borax Morarji Limited, Bombay.

Some physical and chemical properties of zinc borate were given in Table D.3. The particle size distribution curves for the two different sizes of zinc borates were given in Figure D.4 and Table D.4.

Table D.3 : Some physical and chemical properties of zinc borate($2ZnO.3B_2O_3.3,5H_2O$)

Vapour Pressure (mm Hg)	Negligible
Bulk Density	NA
Density	2.68
Solubility in water	0.1g/100ml
Molecular Weight	434.69
Melting Point	NA
Boiling Point	NA
Decomposition Point	>500°C
Appearance	White powder
Odor	Odorless

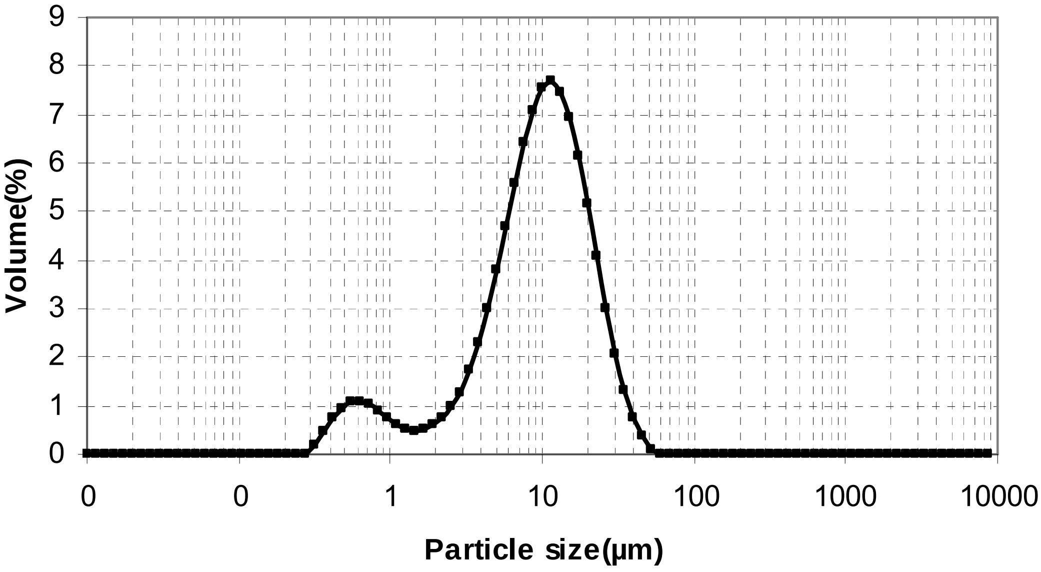
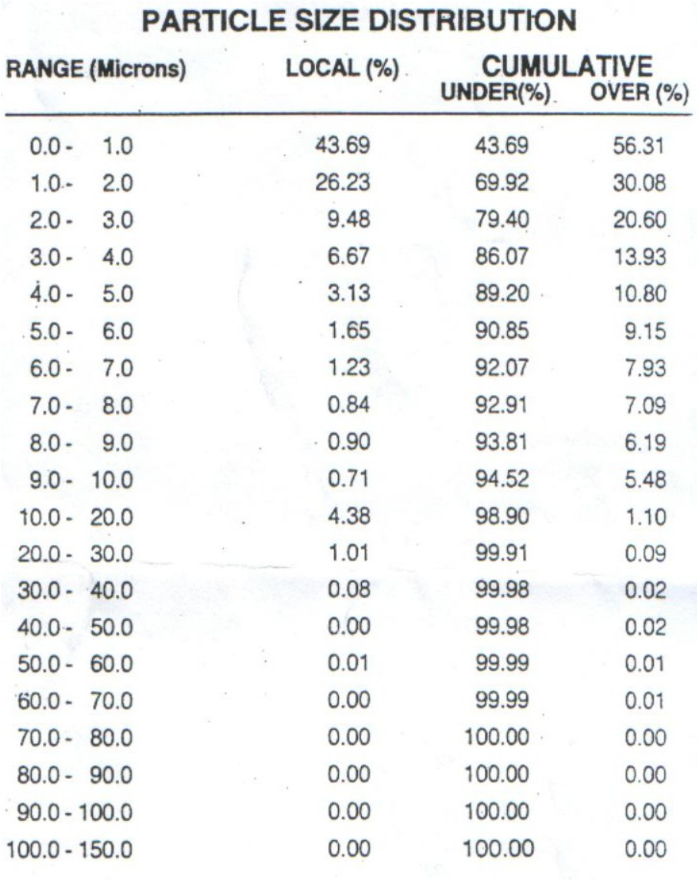


Figure D.4 : Particle size distribution graph of zinc borate obtained from Great Lakes Co, USA with an average particle size of 10µm

Table D.4 : Particle size distribution graph of zinc borate obtained from Borax Morarji Limited, Bombay with particle size of 2µm



PARTICLE SIZE DISTRIBUTION

RANGE (Microns)	LOCAL (%)	CUMULATIVE UNDER(%)	CUMULATIVE OVER (%)
0.0 - 1.0	43.69	43.69	56.31
1.0 - 2.0	26.23	69.92	30.08
2.0 - 3.0	9.48	79.40	20.60
3.0 - 4.0	6.67	86.07	13.93
4.0 - 5.0	3.13	89.20	10.80
5.0 - 6.0	1.65	90.85	9.15
6.0 - 7.0	1.23	92.07	7.93
7.0 - 8.0	0.84	92.91	7.09
8.0 - 9.0	0.90	93.81	6.19
9.0 - 10.0	0.71	94.52	5.48
10.0 - 20.0	4.38	98.90	1.10
20.0 - 30.0	1.01	99.91	0.09
30.0 - 40.0	0.08	99.98	0.02
40.0 - 50.0	0.00	99.98	0.02
50.0 - 60.0	0.01	99.99	0.01
60.0 - 70.0	0.00	99.99	0.01
70.0 - 80.0	0.00	100.00	0.00
80.0 - 90.0	0.00	100.00	0.00
90.0 - 100.0	0.00	100.00	0.00
100.0 - 150.0	0.00	100.00	0.00

APPENDIX E

REPRODUCIBILITY

To check the reliability of the experimental set up and the analytical analysis used during the study, two experiments were performed by keeping all the experimental conditions constant.

Two experiments performed with same experimental conditions (H_3BO_3:ZnO ratio (5:1), stirring rate (1600 rpm), average particle size of zinc oxide (25 µm) and temperature (95°C) were constant). Samples were collected at the same times and analyzed with the same analytical procedures (described in Section 3.4). The collected results after the analysis were compared.

Based on the analysis performed the change of ZnO and B_2O_3 contents in the solid samples with respect to time were given in Figures E.1 and E.2.

As could be seen from the figures, the errors could be neglected. These results showed that the reproducibility of the experimental set up and the analysis methods used during the study were satisfactory.

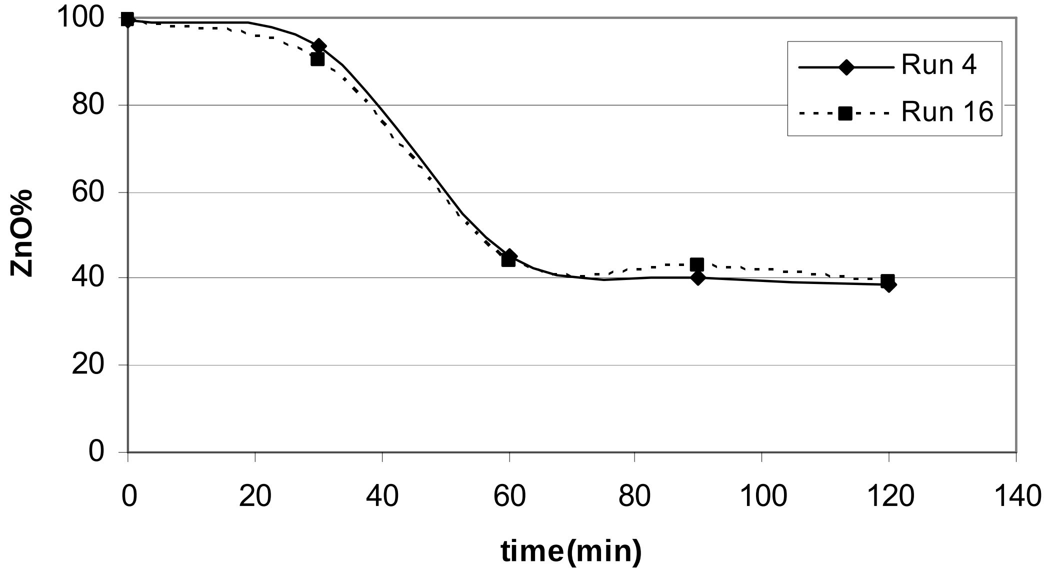


Figure E.1 : The change of ZnO content with respect to time in the solid (H_3BO_3:ZnO ratio (5:1), stirring rate (1600rpm), average particle size of zinc oxide (25 µm) and temperature (95°C) were constant)

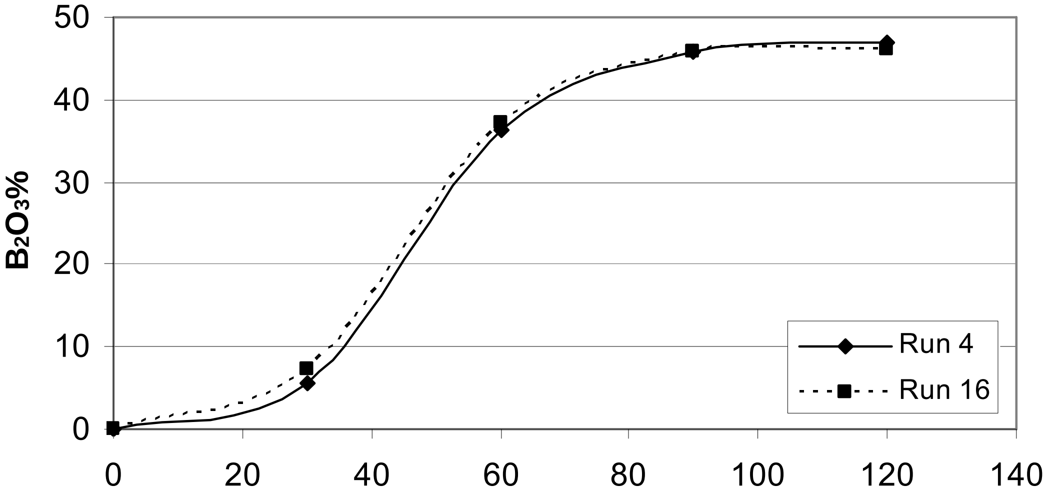


Figure E.2 : The change of B_2O_3 content with respect to time in the solid (H_3BO_3:ZnO ratio (5:1), stirring rate (1600rpm), average particle size of zinc oxide (25 µm) and temperature (95°C) were constant)

APPENDIX F

SAMPLE CALCULATION

In this section there is a sample calculation about the calculation of conversion of zinc oxide.

Zinc oxide and boron oxide analysis were performed to the every solid sample taken during the experiments. In the solid sample since all the boric acid used in the experiments were in aqueous form and the samples were washed with hot water to remove the boric acid stuck to the surface, initially all the solid was zinc oxide. After the reaction initiated and zinc borate began to form in solid phase, boron oxide existed in the structure of zinc borate ($2ZnO.3\boldsymbol{B_2O_3}.3,5H_2O$) started to appear in solid analysis. In other words, the appearance of the boron oxide (B_2O_3) in the solid samples analysis resulted from its existence in zinc borate structure.

By applying this situation the zinc oxide conversion with respect to time could be calculated. Since all the boron oxide detected in the solid analysis was in the form of zinc borate, a relevant ratio of zinc oxide should also appear in formed zinc borate structure ($2\boldsymbol{ZnO}.3B_2O_3.3,5H_2O$) based on the existence of boron oxide. This relevant ratio gave the converted zinc oxide in the sample.

A sample calculation was made, based on the logic expressed, on the analysis results of Experiment 10. Raw data of the experiments was taken from Appendix A.

Table A.9 The change of ZnO and B_2O_3 contents in the samples collected during Experiment10 (1600rpm stirring rate, 85°C temperature, 25µm ZnO, H_3BO_3:ZnO ratio of 5:1, $C_{b(initial)}$ = 4.31 mol/lt)

Sample taken time (min)	Weight of sample (gr)	Amount of EDTA used (ml)	**Amount of ZnO in the sample (gr)**	%ZnO in the sample	Amount of NaOH used (ml)	**Amount of B_2O_3 in the sample (gr)**	%B_2O_3 in the sample	H_3BO_3 con. in the liquid (mol/l
45	0.205	33.1	**0.135**	65.8	1.02	**0.036**	17.4	3.70
75	0.205	20.5	**0.084**	40.8	2.20	**0.076**	37.3	2.31
105	0.205	20.0	**0.081**	39.7	2.73	**0.095**	46.3	1.35
135	0.205	19.7	**0.080**	39.1	2.74	**0.095**	46.4	1.21
165	0.205	20.0	**0.082**	39.8	2.79	**0.097**	47.3	-
195	0.205	20.1	**0.082**	39.9	2.74	**0.095**	46.6	-
225	0.205	20.0	**0.081**	39.6	2.75	**0.096**	46.7	-
240	0.205	20.2	**0.082**	40.0	2.77	**0.096**	47.1	-

In the table above, the amount of ZnO and B_2O_3 contents in the samples were summarized. The results came to nearly constant values after the 165th minute. At this stage all the used zinc oxide was converted to zinc borate and because of this reason no changes observed. So the composition of the final product was known. If the result of the last analyses was taken, the final product contained 47.1% B_2O_3, 40.0% ZnO and 12.9% H_2O (by difference).

Based on the logic expressed above, all the boron oxide calculated at the end of analysis were in the form of zinc borate and a corresponding ratio of zinc oxide should also appear in the zinc borate structure. The corresponding ratio was calculated from the final composition of the zinc borate product (the ratio of the boron oxide content (47.1) to the zinc oxide content (40.0)).

The corresponding ratio was : $\frac{47.1}{40.0} = 1.18$

This ratio would be kept constant in the formed zinc borate product structure and gave us the amount of zinc oxide in the zinc borate. In other words since the total zinc oxide content was known, this calculation would give the zinc oxide conversion. The calculation was summarized in Table F.1:

Table F.1 : Summary of the calculation of zinc oxide conversion

Sample taken time (min)	Weight of sample (gr)	Amount of ZnO in the sample (gr)	Amount of B_2O_3 in the sample (gr)	The amount of ZnO in zinc borate product structure	Conversion (The amount of ZnO in zinc borate product structure/ Amount of ZnO in the sample
45	0,205	0,135	0,036	0,030	0,225
75	0,205	0,084	0,076	0,065	0,778
105	0,205	0,081	0,095	0,081	0,991
135	0,205	0,080	0,095	0,081	1,01
165	0,205	0,082	0,097	0,082	1,01
195	0,205	0,082	0,095	0,081	0,99
225	0,205	0,081	0,096	0,081	1,00
240	0,205	0,082	0,096	0,082	1,00

Alternative way for calculation of zinc oxide conversion;

There was an alternative method for the calculation of zinc oxide conversion. Some of the equations used in part 4.4.2 would be used again in this alternative zinc oxide conversion calculation

Redefining the concentration of boric acid at time t with the change of zinc oxide depending on the stoichometric ratios;

$$c_{Bt} = c_{Bo} - \frac{3(w_{in} - w_t)}{mv} \qquad (4.9)$$

where,

$$w_t = w_{in}(1-x) \tag{4.10}$$

Inserting Equation 4.10 into Equation 4.9

$$c_{Bt} = c_{Bo} - \frac{3(w_{in} - (1-x)w_{in})}{mv} \tag{4.11}$$

$$c_{Bt} = c_{Bo} - \frac{3w_{in}x}{mv} \tag{4.12}$$

All the terms in Equation 4.12 was known (w_{in} = 53g, m = 81.37, v = 0.750L, c_{Bt}, c_{Bo} and x terms were available in Table A.9 and Table G.1). so the conversion could be calculated for every sample.

For the sample taken at t = 45min, x = 0.234
t = 75min, x = 0.768
t = 105min, x = 1.14
t = 135min, x = 1.19

As could be seen from the calculations the conversion values of 45th minute and 75th minute were close previous calculated conversion values (they were 0.225 and 0.778 respectively) but other two values were bigger than "1" which was impossible in terms of conversion.

The reason for this difference was the usage of excess boric acid during the experiments. Since the unreacted boric acid stuck to the surface of the solid formed during the experiment, an unreacted quantity of boric acid left the boric acid solution and came to its solid form. So larger amount of boric acid left the solution and came to solid form on the surface of the product. These amount of boric acid that was unreacted was responsible for this difference. So the first calculation procedure of zinc oxide was correct and gave the correct values.
