

**CHLORINATION OF NITRIDED MALAYSIAN ILMENITE
CONCENTRATE REDUCED WITH POLYPROPYLENE AND COAL**

by

NAJWA BINTI IBRAHIM

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TABLES OF CONTENTS

	Page
ACKNOWLEDGEMENT	ii
TABLES OF CONTENTS	iii
LIST OF TABLES	vi
LIST OF FIGURES	ix
LIST OF SYMBOLS	xii
LIST OF ABBREVIATION	xiv
ABSTRAK	xvi
ABSTRACT	xvii
CHAPTER ONE: INTRODUCTION	
1.1 Research background	1
1.2 Objectives	3
1.3 Problem statement	4
1.4 Research Scopes	5
1.5 Thesis outline	6
CHAPTER TWO: LITERATURE REVIEW	
2.1 Overview	9
2.2 Titanium Applications	12
2.3 Ilmenite Ores	16
2.4 Research Background Malaysian Ilmenite Ores	18
2.5 Synthesis of $\text{TiO}_x\text{C}_y\text{N}_z$ From Ilmenite	21
2.5.1 Effect of Reducing Agent (waste plastics + coal)	24
2.5.2 Effect of Temperature	25
2.5.3 Effect of C:O molar ratio	26
2.6 The Leaching of Ilmenite	28
2.7 Production of TiCl_4 by chlorination process	31
2.7.2 Effect of Parameters in chlorination	35
2.8 Design of Experiment	37

CHAPTER THREE: METHODOLOGY

3.1	Introduction	39
3.2	Experimental Flowchart	41
3.3	Optimization of the sample for CTRN and Chlorination	44
3.4	Sample preparation and mixing	48
3.4.1	Oxidation test	50
3.4.2	Flowrate Calibration of Gases	52
3.4.3	Calibration of Furnace Temperature	53
3.5	Carbothermal Reduction and Nitridation (CTRN)	55
3.5.1	Extent of Reduction (X_o)	56
3.5.2	Extent of Nitridation (X_N)	57
3.6	Aeration Leaching	58
3.7	Chlorination of Nitrided Malaysian Ilmenite	60
3.8	Sample Characterization	63
3.8.1	CHNS Analysis	64
3.8.2	X-Ray Diffraction (XRD)	65
3.8.3	X-ray Fluorescence (XRF)	68
3.8.4	Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)	68
3.8.5	Thermal Gravimetric Analysis TGA	69

CHAPTER FOUR: RESULTS AND DISCUSSION

4.1	Introduction	71
4.2	Raw Sample Characterization and properties studies	71
4.2.1	Elemental Analysis by XRF	72
4.2.2	Phase Identification of Ilmenite by X-ray Diffraction Analysis	73
4.2.3	Morphology Analysis by Scanning Electron Microscopy (SEM)	74
4.2.4	Thermal Gravimetric Analysis (TGA) of Carbon Sources and Elemental Analysis of PP and MB coal	76
4.2.5	Carbon Analysis by Oxidation Test	79
4.3	Carbothermal Reduction and Nitridation (CTRN)	81
4.3.1	Introduction	81
4.3.2	Statistical Analysis of Responses	81
4.3.3	Phase Development in Reduction of Ilmenite	92

4.3.4	Effect of Reduction Time on Phase Development	98
4.3.5	Effect of Temperature on Phase Development	100
4.3.6	Effect of C:O Molar Ratio on Phase Development	101
4.3.7	Morphological Analysis of Reduction Sample	106
4.3.8	Elemental analysis by CHNS	111
4.4	Leaching of reduced ilmenite by Becher Process	123
4.4.1	XRD analysis	125
4.4.2	SEM/EDX image	127
4.5	Chlorination of nitrated Malaysian ilmenites concentrate	129
4.5.1	Statistical Analysis of Response	130
4.5.2	Production of $TiCl_4$ by chlorination of nitrated ilmenite	138
4.5.3	Morphology image of chlorinated sample by SEM/EDX	152

CHAPTER FIVE: CONCLUSION AND RECOMENDATIONS 154

REFERENCES 156

APPENDICES

Appendix A: CALCULATIONS

Appendix B: ICP CALIBRATION CURVE

Appendix C: SOLUBILITY DATA SERIES OF $TiCl_4$ AND HCl

Appendix D: CALCULATIONS OF IODINE 0.05N PROVED BY
BIO SYNERGY BERHAD

Appendix E: Temperature profile data for furnace temperature

Appendix F: Chlorine Production rate

Appendix G: Factorial Design

Appendix H (a): ICSD Number of Osbornite (TiN)

Appendix H (b): ICSD number of Fe

Appendix H (c) : ICSD number of Ti_3O_5

Appendix H (d) : ICSD number of $TiCl_3$

Appendix H (e) : ICSD number of TiO_2

LIST OF PUBLICATIONS

LIST OF TABLES

	Page
Table 2.1 Chemical analysis of various ilmenite ores composition from all over the world. (Kathori 1974)	10
Table 2.2 The properties of ilmenites concentrates ((Force, 1991)	18
Table 2.3 The concentration of REE in soils and sediments samples in	20
Table 3.1 Materials and Chemicals used in CTRN, aeration leaching and chlorination process	40
Table 3.2 Experimental code and levels of factors in the Full Factorial Design (FFD) for CTRN	45
Table 3.3 Design of Experiment for CTRN of Malaysian ilmenite	46
Table 3.4 The parameters for chlorination process	47
Table 3.5 Full Factorial Design for chlorination	48
Table 4.1 Element existed in raw ilmenite analyzed by XRF	72
Table 4.2 ICSD for existed in raw ilmenite phases	74
Table 4.3 EDX analysis of raw ilmenite	75
Table 4.4 Carbon, Hydrogen, Nitrogen and Sulfur analysis by elemental analyzer	76
Table 4.5 Thermal treatment of oxidation at 850 °C for 6 hours	80
Table 4.6 Statistical design and result for responses in CTRN process	83
Table 4.7 Analysis of ANOVA for regression model (a) Extent of reduction, X_O , (b) Extent of Nitridation, X_N , (A= C:O molar ratio (unitless), B=PP:MB coal ratio (unitless), C= Soaking time (hrs), D= Temperature (°C)	84
Table 4.8 Statistical parameters for X_O and X_N responses	85
Table 4.9 Summary of Weighted R profile, R_{wp} and Goodness of Fit, GoF	97

Table 4.10	X_O and X_N of C3PP25 at 1250 °C at the different soaking time (C: Ored=3 and PP: MB =25:75)	99
Table 4.11	Summary of Carbon and Nitrogen content in reduced ilmenite by CHNS analysis	112
Table 4.12	Summary of the extent of reduction for CTRN under an H_2 - N_2 gas atmosphere	114
Table 4.13	The X_N for CTRN under an H_2 - N_2 atmosphere	121
Table 4.14	Summary of $TiO_xC_yN_z$ stoichiometry from the calculations	123
Table 4.15	The weight loss (X) and extent of chlorination, X_{Ti}	130
Table 4.16	Analysis of ANOVA for regression model (a) Weight loss, (%), (b) Extent of chlorination, X_{Ti} , (A= N_2 flowrate (cc/min), B=Temperature (°C), C= Soaking time (min),	131
Table 4.17	Statistical parameter for weight loss and X_{Ti}	133
Table 4.18	The comparison of elemental distribution of synthesized $TiCl_4$ product with commercial $TiCl_4$	140
Table 4.19	Percentage of Ti extracted calculated from ICP	141

LIST OF FIGURES

		Page
Figure 2.1	The standard process in the production of TiO ₂ pigment and Ti metal, (Kang and Okabe, 2013)	14
Figure 2.2	Pigments and Polishing Compounds: Titanium dioxide powder is carefully processed to remove impurities and classified by particle size (Force, 1991)	16
Figure 2.3	Extent of reduction in N ₂ gas atmosphere of synthetic rutile, titania, HYT170 and primary ilmenite by Rezan et al.(2012)	23
Figure 2.4	Schematic of TiCl ₄ purification (left) and the Kroll process (right) (Sibum et al., 2002).	32
Figure 3.1	The flowchart of Chlorination of Nitrided Malaysian Ilmenite concentrates for TiCl ₄ production	43
Figure 3.2	PP melting point scans by TGA, (TGADSC Mettler Toledo)	49
Figure 3.3	The close-up soap bubble ring movement for gas calibration	53
Figure 3.4	Schematic diagram for furnace temperature calibration	54
Figure 3.5	Temperature profile for carbothermal and nitridation process	54
Figure 3.6	Schematic furnace for CTRN of ilmenite	55
Figure 3.7	Isothermal heating rate profile of CTRN of ilmenite.	56
Figure 3.8	Schematic diagram of the aeration leaching (Becher) process for iron removal	59
Figure 3.9	The experimental setup for chlorination of TiO _x C _y N _z	61
Figure 3.10	Perkin Elmer 2400 Series II for CHN analysis	65
Figure 3.11	Heating profile of TGA analysis of PP and Mukah coAL	70
Figure 4.1	XRD phases analysis of raw Ilmenite	73

Figure 4.2	Morphology image of raw ilmenite	75
Figure 4.3	TGA analysis for a different mixture of ilmenite with PP and Mukah coal at different C:O ratio	77
Figure 4.4	Thermogravimetric curve of the pyrolysis of experimental samples C7PP25 (75% of PP + 25% of coal) and C7PP100 (100% of PP)	78
Figure 4.5	Predicted vs Actual graph for the extent of reduction, X_O (%)	87
Figure 4.6	Predicted vs Actual graph for the extent of nitridation, X_N (%)	87
Figure 4.7	Perturbation plotted for extent of reduction, X_O (%), (A= C:O molar ratio (unitless), B=PP:MB coal ratio (unitless), C= Soaking time (hrs), D= Temperature ($^{\circ}\text{C}$))	88
Figure 4.8	Partial pressure of CO at various temperature	89
Figure 4.9	Perturbation plotted for extent of nitridation, X_N (%), (A= C:O molar ratio (unitless), B=PP:MB coal ratio (unitless), C= Soaking time (hrs), D= Temperature ($^{\circ}\text{C}$))	90
Figure 4.10	3D plotted for extent of reduction, X_O (%)	91
Figure 4.11	3D plotted for extent of nitridation, X_N (%)	91
Figure 4.12	The summary of the formation Fe and $\text{TiO}_x\text{C}_y\text{N}_z$ from FeTiO_3	95
Figure 4.13	Predominance diagram for Ti-O-N system of CTRN process	96
Figure 4.14	Comparison XRD for (a) unreduced ilmenite with CTRN at 1250°C (b) for 1 hour (C3PP253) and (c) for 3 hours (C3PP254)	98
Figure 4.15	Comparison XRD analysis at different temperature for (a) unreduced ilmenite, with CTRN at 3 hours (b) reduced at 1150°C , (c) reduced at 1250°C . The fixed conditions were C: Ored=7 and PP: MB = 100:0	100

Figure 4.16	Comparison of XRD analysis at different C: Ored molar ratio. The fixed conditions were PP: MB = 100:0, CTRN at 1250 °C for 1 hour. (a) unreduced ilmenite , (b) C:Ored = 3 and (c) C:Ored = 7	101
Figure 4.17	SEM/EDX analysis of sample reduced at a reduced highest molar ratio of C: Ored =7 in H ₂ -N ₂ gas at 1250 °C for 3 hours. a) sample C7PP1004, EDX analysis for b) spot 1, c) spot 2	104
Figure 4.18	Weight loss (%) by TGA analysis for sample C7PP100 in Ar atmosphere with a heating rate of 10 °C/min.	106
Figure 4.19	FESEM images of raw and reduced ilmenite (1250°C for 3 hrs in H ₂ -N ₂) by reductants composed of MB coal and PP with various PP wt. %, b) 75 wt. % MB coal- 25 wt. % PP, c) 40 wt. % MB coal- 60 wt. % PP, d) 100 wt. % PP	107
Figure 4.20	SEM/EDX analysis for C7PP100 reduced at 1250°C for 3 hrs in H ₂ -N ₂ , a) Morphological image of reduced sample b) EDX analysis at Ti rich zone, c) EDX analysis at Fe rich zone	109
Figure 4.21	SEM images of the formation of spherical metallic Fe grains and TiO _x C _y N _z during CTRN.	110
Figure 4.22	Effect of reaction extent on the equilibrium CO ₂ molar ratio in titanium oxycarbide at T = 1600 °C, P = 1 atm (Cao et al., 2015)	115
Figure 4.23	Kinetic plots for reduction using chemical reaction mechanism at a different temperature	117
Figure 4.24	Arrhenius plot for reduction of ilmenite under an H ₂ -N ₂ atmosphere	119
Figure 4.25	Pourbix diagram of Fe-Ti-OH at 70 °C	124
Figure 4.26	The comparison XRD graph plotted after reduction of ilmenite (before leaching process) and after Becher process (after leached Fe metallic)	126
Figure 4.27	The morphological image and EDX analysis of reduced and leached sample. (a) SEM image of reduced sample (C:Ored = 3, PP:MB coal= 100%), (b) SEM image of leached sample (leached for 8 hours at 70 °C, (c) EDX analysis of reduced sample, (d) EDX analysis of leached sample	128

Figure 4.28	Predicted vs actual graph for X (%), $R^2 = 0.999$	134
Figure 4.29	Predicted vs actual graph for X_{Ti} (%), $R^2 = 0.991$	134
Figure 4.30	A perturbation plot for X, wt. % with respect to 3 factors. (A= N ₂ flowrate (mL/min), B=Temperature (°C), C= Soaking time (min),	135
Figure 4.31	A perturbation plot for X_{Ti} (%) with respect to 3 factors. (A= N ₂ flowrate (mL/min), B=Temperature (°C), C= Soaking time (min),	136
Figure 4. 32	The Cl ₂ and N ₂ gas flow rate (mL/min) versus chlorination time (min)	137
Figure 4.33	The plotted data of solubility TiCl ₄ and HCl from J. Hala (1989)	139
Figure 4.34	XRD comparison of chlorination at different time. Figure (a) unchlorinated sample(b) chlorinated sample for 30, N6 ($X_{Ti} = 69.92\%$) and-(c) chlorinated samples for 60 minutes, N3 ($X_{Ti} = 88.7\%$) at constant temperature 400°C and 200 cc/min	143
Figure 4.35	XRD analysis at 60 minutes for different temperatures of 300-400 °C with N ₂ flowrate of 200 cc/min.	144
Figure 4.36	Kinetic curve effect of temperature on TiCl ₄ production	145
Figure 4.37	Plot of $1 - (1 - X)^{1/3}$ vs time at various temperatures	147
Figure 4.38	Plot of $1 - 2/3X - (1 - X)^{2/3}$ vs time at various temperatures	147
Figure 4.39	Plotted graph of the values of $1 - (1 - X)^{1/3} + B (1 - 2/3X - (1 - X)^{2/3})$ at various temperatures	149
Figure 4.40	Arrhenius plot for TiN chlorination by a gas mixture of Cl ₂ -N ₂ .	150
Figure 4.41	a) The morphological image with EDX analysis for highest X_{Ti} (88.70%) b) the morphology image of lowest X_{Ti} (56.63 %)	151
Figure 4.42	SEM/EDX analysis of residues obtained from chlorination at 400 °C with 60 min and N ₂ flowrate 200 mL/min	152

LIST OF SYMBOLS

°C	Percentage
%	Carbon, Hydrogen , Nitrogen and Sulphur analysis of PP and Mukah coals (carbon sources)
±	Plus-minus
µm	micrometre
cm	centimetre
g	gram
kJ	kilojoule
J	Joule
θ	Theta - Angle of incidence
L	Litre
ml	Millilitre
min	minutes
W _f	Weight final of sample
W _i	Weight initial of sample
K	Kelvin
atm	atmosphere
O _i	Oxygen initial content
O _f	Oxygen final content
ΔG°	Delta G°
Wt	weight
hrs	hour
ppm	Part per million

\AA	angstrom
λ	Wavelength
X	Weight loss
X_N	Extent of nitridation
X_O	Extent of reduction
X_{Ti}	The extent of chlorination or percentage of titanium extraction
R_{wp}	Weighted profile factor
GoF	Goodness of Fit

LIST OF ABBREVIATION

AQ-2	Anthraquinone-2-sulfonic acid sodium salt monohydrate
CHNS	Carbon Hydrogen Nitrogen Sulphur
CTRN	Carbothermal reduction and nitridation
DOE	Design of Experiment
EDX	Energy-dispersive X-ray Spectroscopy
Fe	Iron
Fe ₂ O ₃	Hematite
Fe ₃ O ₄	Magnetite
Fe ₂ TiO ₅	Pseudobrookite
FeTiO ₃	Ilmenite
FTIR	Scanning Electron Microscope
H ₂	Hydrogen gas
H ₂ SO ₄	Sulphuric acid
HCl	Hydrochloric acid
ICP	Inductively Coupled Plasma
KMnO ₄	Potassium permanganate
P ₂ O ₅	Phosphorus pentoxide
PP	Polypropylene
N ₂	Nitrogen gas
NH ₄ Cl	Ammonium chloride
MB	Mukah Balingan coal
SEM-EDX	Scanning electron microscope-energy dispersive x-ray
TGA	Thermal gravimetric analysis

Ti	Titanium
TiC	Titanium Carbide
TiCl ₄	Titanium Tetrachloride
TiN	Titanium Nitride
TiO ₂	Titanium Dioxide / rutile
TiO _x C _y N _z	Titanium Oxycarbonitride
UV-Vis	Ultraviolet–visible spectroscopy
XRD	X-ray Diffraction
XRF	X-ray Fluorescence
-γFe ₂ O ₃	Magnetite

PENGLORINAN KONSENTRAT ILMENIT NITRIDA MALAYSIA OLEH PROSES PENURUNAN BERSAMA POLIPROPILENA DAN ARANG

ABSTRAK

Penghasilan $\text{TiO}_x\text{C}_y\text{N}_z$ daripada ilmenit Malaysia dan pengklorinan pada suhu rendah untuk menghasilkan TiCl_4 telah diteliti dalam projek ini. Objektifnya adalah untuk meningkatkan teknologi alternatif bagimenghasilkan TiCl_4 . Kesan terhadap masa CTRN, ratio karbon kepada oksigen dan penambahan plastik PP kedalam arang bagi pembentukan Fe dan $\text{TiO}_x\text{C}_y\text{N}_z$ daripada ilmenit telah dikaji. Reka bentuk Eksperimen (DOE) telah ditugaskan untuk mereka bentuk parameter dalam proses CTRN Proses CTRN telah dilakukan pada suhu 1150 dan 1250 °C di bawah atmosfera $\text{H}_2\text{-N}_2$ untuk 60 dan 180 min. Campuran ratio karbon kepada oksigen bermula dari ratio 3.0 dan 7.0. Peratus X_o and X_N meningkat apabila kandungan PP kepada arang meningkat daripada 25 wt. %, 60 wt. % and 100 wt. %. Analisis SEM/EDX menunjukkan produk disintesis oleh 60 wt. % and 100 wt. % mempunyai mikrostruktur yang unik iaitu zarah Fe sfera. Zarah Fe sfera ini boleh dipisahkan dengan mudah daripada fasa $\text{TiO}_x\text{C}_y\text{N}_z$. Peratus X_O and X_N yang paling tinggi masing-masing adalah 93.15% dan 93.85% bagi C7PP1004. Selepas proses CTRN, pembuangan Fe dilakukan selama 8 jam dengan larut lesap jenis Becher pada 70 °C dengan kehadiran NH_4Cl dan 0.1 wt. % AQ-2 sebagai pemangkin yang efektif. Sekali lagi DOE digunakan dalam pengklorinan untuk merancang percubaan experiment. Mekanisma pengklorinan nitrida ilmenit telah dikaji pada 300 – 400. Peratus X_{Ti} daripada $\text{TiO}_x\text{C}_y\text{N}_z$ pada 300 C ialah 84.00% dan pada 400 C ialah 88.70 dalam masa 60 minit. Ketulenan TiCl_4 adalah 97% adalah dihasilkan daripada nitrida ilmenit Malaysia. Oleh itu, projek ini menunjukkan proses CTRN, proses larut lesap

dan proses pengklorinan boleh menjadi kaedah menghasilkan TiCl_4 daripada ilmenite Malaysia.

**CHLORINATION OF NITRIDED MALAYSIAN ILMENITE
CONCENTRATE REDUCED WITH POLYPROPYLENE AND COAL**

ABSTRACT

The production of Titanium Oxycarbonitride ($\text{TiO}_x\text{C}_y\text{N}_z$) from Malaysian ilmenite and its chlorination at low temperatures for production of Titanium Tetrachloride (TiCl_4) was studied in this project. The objective was to improve an alternative technology for production of TiCl_4 . The effects of carbothermal reduction and nitridation (CTRN) on parameters of time, carbon to oxygen molar ratio ($\text{C}:\text{O}_{\text{red}}$) and the addition of waste PP plastic into coal (PP:MB coal) on the formation of Fe and $\text{TiO}_x\text{C}_y\text{N}_z$ from ilmenite were investigated. Design of Experiments (DOE) was assigned to design the parameters in CTRN process. The CTRN process was done at temperature of 1150 and 1250 °C under $\text{H}_2\text{-N}_2$ atmosphere for 60 and 180 min. A mixture of $\text{C}:\text{O}_{\text{red}}$ molar ratio ranging from 3.0 and 7.0 ratios. The extent of reduction (X_{O}) and the extent of nitridation (X_{N}) was increasing as increase PP:MB coal content from 25 wt. %, 60 wt. % and 100 wt. %. SEM/EDX analyses showed that the product synthesized by 60 wt. % and 100 wt. % PP had a unique microstructure in which is spherical Fe particles. This spherical Fe can be easily separated from $\text{TiO}_x\text{C}_y\text{N}_z$ phase. The highest X_{O} and X_{N} were 93.15% and 93.85%; respectively for C7PP1004. After CTRN process, Fe removal was carried out for 8 hours by an aeration leaching Becher type process at 70 °C in the presence of NH_4Cl and 0.1 wt. % AQ-2 as the effective catalysts. Again DOE was used in chlorination to design the experiment run. The parameters for chlorination were time (30 min and 60

min), temperature (300 °C and 400 °C) and N₂ gas flowrate (200 mL/min and 400 mL/min). The X_{Ti} moderately increased with increasing the temperature and decreasing flow rate of N₂ gas from 200 mL/ min to 400 mL/min. The highest weight loss and X_{Ti} of TiO_xC_yN_z at 300 °C and 400 °C were 84.0% and 88.7 % in 60 minutes, respectively. The TiCl₄ with the purity of about 97% was eventually produced from Malaysian ilmenite. Therefore, project demonstrated that the process of CTRN, leaching process and chlorination process could be a feasible method in production of TiCl₄.

CHAPTER ONE

INTRODUCTION

1.1 Research background

Titanium is a metallic element commonly known as Ti in the periodic table. Titanium is silver in colour and has a lustrous appearance (Ewald et al., 2006). It is known to be highly resistant to corrosion due to their stable passive layer, and it is chemically inert (Schmutz et al., 2008). Although Ti on its own has many uses, Ti compound such as TiO_2 , TiN, and TiC are also useful in various industries. For example, TiC is used in the groundwork of ceramic materials, which are regularly used in machine steel materials with high cutting speed (Ghidiu et al., 2014). Generally, Ti metal can be alloyed with aluminium (Al) and Fe, among other metals, to form durable and lightweight alloys for most engineering and construction industries. Derived Ti compounds mentioned above are also economically in demand. Concerning TiO_2 pigment, mainly used by paint, paper and cosmetics industry for its high index of refraction (2.55-2.733) and light-scattering ability (El-Sherbiny et al., 2014). On the other hand, the composition of TiN and TiC are known to have a hardness equivalent of 9 to corundum in the Mohs Scale (Tabor, 2000). This makes the latter excellent for manufacturing and machining industries.

Geological occurrences of Ti comes in various minerals, such as Anatase, Brookite, Ilmenite, Leucosene, Perovskite, Rutile and Sphene. However, given the amount of Titanium in these minerals, only Ilmenite and Rutile are considered to be economically viable to be mined. According to the Mineral Commodity Summary

(Ober, 2018), Asia countries were listed for Rutile world production but not listed for Ilmenite world production. Although not listed, production of Ilmenite in Malaysia does exist. Ilmenite is obtained in the form of tin mining run-off, commonly known to the locals as "Amang" (Zulfahmi et al., 2012, Kiong and Hoe, 2003). Large tin mining plants in Perak and Selangor are setting these "Amang" aside for any potential refining ore beneficiation process. An alternative to "Amang", Ilmenite in Malaysia can be found in alluvial and hard rock deposits. Such deposits are located in Langkawi (Begum et al., 2016, Hassan, 1987) and also Terengganu (Yeap, 1977). However, traditional mining appears not to be lucrative due to the exhaustion of high-grade reserves and low ilmenite prices, According to US Geological survey the estimated value of titanium mineral concentrates consumed in the United States in 2017 was \$561 million (Ober, 2018). Now, with the improvement in mineral processing, ilmenite reserves in Malaysia has a bright future as it may be used for producing Ti metallic products.

This research was conducted to investigate the production of TiCl_4 from $\text{TiO}_x\text{C}_y\text{N}_z$ in Malaysian ilmenite supplied by Chee Ng Minerals Sdn. Bhd from Kampar, Perak. Ilmenite ore was a major raw material for titania pigment and titanium metal production. The general chemical composition of ilmenite is iron titanium oxide, FeTiO_3 . Ilmenite concentrates can be nitrided to $\text{TiO}_x\text{C}_y\text{N}_z$ in the H_2 - N_2 gas mixture at 1200 °f (Rezan et al., 2011). This project aimss to convert Malaysian ilmenite to $\text{TiO}_x\text{C}_y\text{N}_z$ by CTRN with different blends of coal with waste PP. The goal of using PP was used as reductant agent to replace coal as primary reductant agent due to the higher cost of coal. After CTRN, the product sample was leached for 8 hours of leaching time and 0.1 wt. % of catalyst Anthraquinone-2-sulfonic acid sodium salt monohydrate (AQ-2) to enhance metallic iron removal as a

retarded agent in the chlorination process. The leached samples then were chlorinated in a horizontal furnace to produce TiCl_4 at a low temperature of 400 °C

The project analyzes all the relevant kinetic data by a statistical DOE. Therefore, the study of CTRN and chlorination was undertaken with the aim to develop further understanding mechanisms of Malaysian ilmenite into $\text{TiO}_x\text{C}_y\text{N}_z$ and TiCl_4 as intermediary products in the Ti metal production cycle. The project studied Malaysian ilmenite ores which are the primary ore of Ti. The usage of titanium metals is limited because of its high production cost. Production of titania white pigments and titanium metal includes processing of titanium minerals to TiCl_4 . The commercial chlorination process in the production of Ti metal or TiO_2 pigment requires 800-1100 °C. However, the chlorination of $\text{TiO}_x\text{C}_y\text{N}_z$ produced from ilmenite can be implemented at 200-350 °C (Ahmadi, 2017). Low-temperature chlorination can improve the efficiency of production of TiCl_4 . This makes chlorination of $\text{Ti}(\text{O}_x\text{C}_y\text{N}_z)$ an attractive technology in processing of titanium minerals (Li et al., 2012).

1.2 Objectives

There were 3 objectives for this project. The objectives were listed below:

- i. To investigate the effect of CTRN with PP as a new innovative reductant.
- ii. To study the efficiency of iron removal in nitrated Malaysian ilmenite by aeration leaching process in NH_4Cl solution
- iii. To improve the production TiCl_4 from Malaysian Ilmenite after CTRN by chlorination process at lower temperature

- iv. To determine the most significant factors in the CTRN process and chlorination process by Design of Experiment (DOE)

1.3 Problem statement

Due to the high production cost of TiO_2 white pigments and Ti metal, the usage of titanium was limited. This also includes the processing of Ti minerals to titanium tetrachloride (TiCl_4) production. The commercial chlorination process in the production of Ti metal or TiO_2 pigment requires a temperature range of 800 °C to 1100 °C for the reaction to be favourable (Noubactep, 2009). By producing $\text{TiO}_x\text{C}_y\text{N}_z$ via CTRN of ilmenite in the $\text{H}_2\text{-N}_2$ gas atmosphere, it will allow the production of TiCl_4 . However, the existence of metallic Fe after CTRN with $\text{TiO}_x\text{C}_y\text{N}_z$ will affect the formation of TiCl_4 . Therefore aeration leaching method called Becher process was used to remove the metallic Fe in nitrated ilmenite to increase the efficiency of the TiCl_4 production from $\text{TiO}_x\text{C}_y\text{N}_z$. TiCl_4 can be produced by chlorination at a lower temperature in the range of 200 °C to 350 °C. Titanium metal can now be produced from TiCl_4 by pure magnesium metal reduction at a lower cost due to low-temperature synthesis of TiCl_4 . In the lower temperature of chlorination, impurities will not chlorinate or chlorinate very slowly (Adipuri, 2011). This permits selective chlorination of $\text{TiO}_x\text{C}_y\text{N}_z$, decreases chlorine gas consumption and waste generation, and makes the whole technology of ilmenite processing more efficient and environmentally friendly. The low temperature of chlorination will lower the cost of production of Ti metal.

1.4 Research Scopes

Currently, an innovative method used for production of hydrogenated titanium (TiH_2) sponge by reacting TiCl_4 and liquid Mg under an H_2 atmosphere. The cost of this process is considerably lower (20%) than the cost of dominant Ti sponge production by Mg reduction through the Kroll process (Duz et al., 2013; Duz et al., 2017). However, literature survey shows that it could be lowered by using the chlorination of $\text{TiO}_x\text{C}_y\text{N}_z$ at lower temperature (200-500 °C) (Adipuri et al., 2008; Adipuri et al., 2009). In this study, the preparation of $\text{TiO}_x\text{C}_y\text{N}_z$ by CTRN of ilmenite followed by Fe removal through the aeration leaching process and continue with chlorination can be done at low temperature.

The CTRN process is newly developed for the synthesis of TiO_xC_y and/or $\text{TiO}_x\text{C}_y\text{N}_z$ from FeTiO_3 and has been well studied at different atmospheres (Ar, CO, CH_4 , N_2 and $\text{H}_2\text{-N}_2$) (Dewan et al., 2010; Rezan et al., 2012b; Rezan et al., 2012c). In the synthesis of $\text{TiO}_x\text{C}_y\text{N}_z$ by CTRN process of FeTiO_3 , graphite has typically been used as the main reductant in the 50 vol.% $\text{H}_2\text{-N}_2$ gas mixture (Rezan et al., 2011; Rezan et al., 2012a). However, the use of waste plastics as a source of carbon in CTRN of ilmenite, in literature only addressed for polyethylene terephthalate (PET) that had been done by Ahmadi (2017). Unfortunately PET only contains about 62.5% C compared to PP which contains about 85% of C. PP is the most common plastics going into landfills, are widely used in packaging applications and are encountered on a daily basis (Reis et al., 2011). Thus, ecological options for recycling waste plastics are strongly required for economic and environmental

In this research, ilmenite from Malaysia was converted to metallic Fe and $\text{TiO}_x\text{C}_y\text{N}_z$ in the first stage, then after Fe removal, chlorination process at low temperature was performed to synthesize pure TiCl_4 from $\text{TiO}_x\text{C}_y\text{N}_z$. No detailed

investigations were found on CTRN of the ilmenite concentrate from Malaysia particularly with utilization of PP as an alternative reductant and its effect on the morphology of nitrated ilmenite. The effect of utilization of waste plastics on the extent of CTRN as well as its effect on microstructure of nitride ilmenite needs more investigation.

The research investigated the processing of $\text{TiO}_x\text{C}_y\text{N}_z$ from the ilmenite concentrate recovered from tin tailing of tin-ore processing plants in Malaysia by CTRN and chlorination. The effect of CTRN parameters ($\text{C}:\text{O}_{\text{red}}$ molar ratio, PP:MB coal ratio, temperature and time) on the formation of Fe and $\text{TiO}_x\text{C}_y\text{N}_z$ phases in CTRN and production of TiCl_4 in low-temperature chlorination process were investigated in this research.

1.5 Thesis outline

This thesis was organized into five chapters:

- i. Chapter 1 is the introduction of this study. The general idea of the recent work was presented with a synopsis of the research background. The problem statement was highlighted, and the related info regarding the research area were given details. Furthermore, the research objectives were listed.
- ii. Chapter 2 is the literature review. This section consists of a short introduction of Ti metal and its application in the industrial world. Then, the most common Ti mineral, which is the ilmenite was further described with focus on Malaysian ilmenite. A literature review on the synthesizing ilmenite ores by addition of waste polymer to $\text{TiO}_x\text{C}_y\text{N}_z$ with importance on using CTRN was also presented. Also, the most important parameter for production of