

UNIVERSITI TEKNOLOGI MARA

**CHEMICAL DESULPHURISATION OF LOW
RANK MAE MOH COAL VIA MIXTURES OF
HYDROGEN PEROXIDE AND
HYDROCHLORIC ACID SOLUTION,
A MILD OXIDISING TREATMENT**

AZIL BAHARI ALIAS

Thesis submitted in fulfilment of the requirements
for the degree of
Master of Science

Faculty of Applied Sciences

November 2004

ACKNOWLEDGEMENTS

The present research work would not have been achieved without the trust and financial support from the University Technology MARA on behalf of Malaysia Ministry of Science, Technology and Environment (MOSTE). For these reasons, I profoundly thank them for supporting me during my studies.

I also wish to express my gratitude to my supervisors, Prof Madya Dr. Hj. Khudzir Hj. Ismail for his encouragement, supervision and valuable suggestions throughout this investigation and whom I personally admire in all senses, Mr. Mohd. Azlan Mohd. Ishak for his impeccable direction and help concerning the experimental work and Prof Madya Dr. Rahman Mohammad for his illuminating advice which in several occasions helped me out. Also not forgotten to all the members of Fossilised Biomass Energy Group Research (FBEGR), University Technology MARA, Perlis Branch for their help and support throughout the research.

I also wish to acknowledge my parents whom I admire the most and my wife and son for their continuous supports which was vital throughout the completion of the thesis.

TABLE OF CONTENTS

	Page
Acknowledgments.	iii
List of Tables.	vii
List of Figures.	ix
List of Appendices.	xvi
Glossary.	xvii
Abstract.	xviii
1.0 Introduction.	1
1.1 Coal as an Alternative Energy.	1
1.2 Importance of Pre-Combustion Technique.	5
1.3 Scopes and Objectives of Research.	6
2.0 Literature Review.	9
2.1 Coal Formation and Classification.	9
2.2 Origin of Sulphur Forms in Coal.	16
2.3 Chemical Reactions of Sulphur-Containing Functional Groups in Coal.	19
2.4 Chemical Desulphurisation Techniques.	23
2.4.1 Chemical Desulphurisation using Mild Oxidising Agents.	24
2.4.2 Chemical Desulphurisation using Mild Reducing Agents.	27
2.4.3 Chemical Desulphurisation using Strong Bases.	28
2.4.4 Chemical Desulphurisation using Strong Organic Bases.	30
2.5 Kinetic Analysis on Coal Desulphurisation Process.	31
3.0 Materials and Methods.	32
3.1 Chemicals and Materials.	32
3.1.1 Acidic Chromous Chloride Solution.	32
3.1.2 Hydrogen Peroxide, H ₂ O ₂ .	32
3.1.3 Hydrochloric Acid, HCl.	33
3.1.4 Nitric Acid, HNO ₃ .	33
3.1.5 Sulphuric Acid, H ₂ SO ₄ .	34
3.1.6 Potassium Permanganate, KMnO ₄ .	34
3.1.7 Barium Chloride 2-hydrate, BaCl ₂ .2H ₂ O.	34
3.1.8 Ethanol.	35
3.2 Coal Preparation and Coal Assays.	35
3.3 Sulphur Assays, The American Society of Testing & Materials (ASTM D2492)	35
3.3.1 Sulphate Sulphur Determination.	37
3.3.2 Pyritic Sulphur Determination.	37
3.4 Chemical Desulphurisation.	40
3.4.1 Chromous Chloride, CrCl ₂ Method.	40
3.4.1.1 Preparation of Acidic Chromous Chloride Reagent.	40

ABSTRACT

Combustion of coals to produce energy has created environmental problems such as sulphur, which is converted to SO_2 and SO_3 gases and the ash product. In order to produce a "clean coal", the pre-treatment processes of sulphur removal from coal have to be effective to remove sulphur and ash without severe effects on the coal microstructure and calorific value. In this study, a mild oxidising treatment of H_2O_2 and HCl mixtures has been identified to remove sulphur and ash from low rank Mae Moh III coal (MM3). The optimum conditions achieved were 30ml 6% (O_2 content) peroxide : 70ml 0.1N HCl (reagent volume mixed ratio) with leaching temperature and time of 50°C and 8 hours, respectively. Under these conditions, *c.a.* 53%, 88%, 100%, 37% and 72% of sulphur_{total}, sulphur_{pyrite}, sulphur_{sulphate}, sulphur_{organic} and ash were removed with 31% of coal dissolution were achieved, respectively. Preliminary study of desulphurisation at elevated pressure was also carried out under the optimal conditions. The results indicated that, sulphur_{organic} removal of fresh and pyrite-free coals were further increased to 30 and 40%, respectively. Different protic acids mixed with peroxide (H_2SO_4 and HNO_3), coal and single-reagent treatment (unmixed reagent) were also applied under the optimal conditions. The results showed that, mixtures of H_2O_2 : HCl gave higher sulphur_{total} removal. Furthermore, it was found that no synergistic effect was contributed by single-reagent treatment on the desulphurisation of MM3. The mild oxidising treatments slightly affected the coal microstructure as revealed by Scanning Electron Microscope – Energy Dispersive X-ray. Likewise, the calorific value of the treated coal samples was not affected as analyzed by bomb calorimeter. A kinetic analysis on pyritic removal reaction of MM3 was found to correlate well with a second-order rate equation that gave activation energy of $61.4 \times 10^6 \text{ J kmol}^{-1}$.

CHAPTER 1

INTRODUCTION

1.1 Coal as an Alternative Energy.

Coal plays a key role as a primary source of organic chemical feedstocks in the world till the 1950's and maintained its large share as a primary source of energy in the 20th century. Further, Krevelen [1] reported that the history of production and consumption of coal prove that this energy has been widely used especially in industrial area. Based on the 1998 world's consumption level, the demonstrated coal reserves are enough for consumption for over 215 years, whereby oil and natural gas reserves are only enough for at least 39 and 63 years, respectively [2]. Thus, coal may become more important as an energy source in the 21st century.

Figure 1.1 shows the production of fossil fuels since the industrial revolution. This figure clearly illustrates the tremendous evolution in the coal mining industry especially during the previous century. After 1910, the growth in coal production decreased considerably. The apparent relative decrease in the coal consumption after 1910 can be attributed to the increasing demand for petroleum and natural gas. After 1945, the production capacity of coal has stepped up from 20 million tons in 1900 to about 3250 million tons in 1990. The main factor responsible for this increase was the improved efficiency of the coal-consuming technical processes. Today, about 3-5 times as much useful energy is obtained from 1 ton of coal than was the case 50 years ago [1]. Figure 1.1 also proves that the development of coal production matched by that of natural gas and mineral oil in the future.