

UNIVERSITI TEK NOLOGI MARA

**DESULFURIZATION
OF HETEROCYCLIC SULFUR IN
JAMBI COAL USING POTASSIUM
CARBONATE-ETHYLENE GLYCOL
DEEP EUTECTIC SOLVENT**

**SYARIFAH NURSYIMI AZLINA
BINTI SYED ISMAIL**

Thesis submitted in fulfilment
of the requirements for the degree of
Doctor of Philosophy
(Science)

Faculty of Applied Sciences

October 2025

ABSTRACT

Coal combustion releases SO₂, contributing to environmental pollution. Therefore, effective desulfurization is essential to break the strong C-S bonds in heterocyclic sulfur coal. This study is unique because desulfurization was conducted on solid coal with its complex and heterogeneous structure. Most previous studies have focused on liquid fuels, in which C-S bonds are easier to break compared to those in solid coal. Potassium carbonate-ethylene glycol (PC-EG) as Deep Eutectic Solvent (DES) is used as a replacement for volatile and flammable organic solvents. Physicochemical analysis showed that molar ratios of 1:8, 1:12, 1:16, and 1:19 reached eutectic points and remained in liquid form, as confirmed by DSC and phase diagram analysis. FTIR analysis confirmed the presence of H-bonding, but the interaction reduced as molar ratio increased. Increasing molar ratios and temperatures decreased viscosity, pH, and density while increased ionic conductivity. Thermal analysis showed that the mixtures remained stable between 110-160 °C. The findings indicate the optimal use of PC-EG at suitable molar ratios and temperatures to improve desulfurization performance. Then, Jambi coal was pretreated with PC-EG mixtures under various molar ratios, temperatures, and time. RSM-CCD was employed to minimize the number of experimental runs while identifying optimal parameters. The optimal parameters were identified as 1:16 molar ratio, 40 °C temperature, and 60 min extraction time, achieving 65.77% heterocyclic sulfur removal. ANOVA analysis revealed that extraction time had the greatest impact, followed by molar ratio and temperature. The findings suggest that other DESs can perform similarly to DES-16 with sufficient processing time. Viscosity and ionic conductivity also play important roles in desulfurization performance. Ultimate analysis indicated a reduction in carbon (57.43%), hydrogen (4.67%), nitrogen (0.74%), and total sulfur (1.28%) after desulfurization. The reduction in sulfur content was consistent with the findings from FTIR and XPS analyses. However, oxygen (35.89%) content increased due to the formation of sulfoxides and sulfones. Proximate analysis demonstrates lower volatile matter (VM) (40.12%) and ash contents (5.73%) with higher fixed carbon (FC) (54.15%). The VM and FC contents produce higher fuel ratio (1.35), indicating more efficient combustion, longer burning time, reduced smoke, and increased calorific value (CV). However, CV (20.90 MJ/kg) decreased due to decrease in carbon and sulfur content. TG analysis revealed slower weight loss, indicating improved thermal stability and structural integrity of treated coal. GCMS analysis of the model sulfur compounds confirmed the extraction and transformation of heterocyclic sulfur during desulfurization. The reaction mechanism was elucidated, highlighting the interactions between carboxylate ions in PC-EG and the sulfur species. The experiments were conducted on a small scale under controlled laboratory conditions, which do not accurately represent the high-temperature environments of industrial coal desulfurization. This limitation may affect the applicability of the findings to large-scale or industrial desulfurization processes. Additionally, the study did not assess solvent reusability, highlighting another limitation of the research at this scale.

ACKNOWLEDGEMENT

Bismillahir Rahmanir Rahim,

I am deeply grateful to Allah SWT for His countless blessings and for granting me the strength and opportunity to pursue and complete the challenging yet profoundly rewarding journey of my PhD.

I would like to express my sincere gratitude to my supervisor, Professor Ts. Dr. Mohd Azlan bin Mohd Ishak, for giving me the opportunity to conduct research under his supervision. I sincerely appreciate his valuable ideas and support during my doctoral studies. My heartfelt thanks also go to my co-supervisor, Professor Kehormat Dr. Haji Khudzir bin Haji Ismail, for his continuous guidance, consistent support and dedication to encouraging my progress throughout my PhD studies. Their combined mentorship has played a crucial role in shaping my enriching PhD journey. Thank you both for believing in me and for your constant motivation.

My appreciation also goes to my co-supervisors, Associate Professor Ir. Dr. Azil Bahari Alias and Dr. Razi Ahmad, for their support and for granting me access to the instrumentation at their research centre. My gratitude also goes to Universiti Teknologi MARA (UiTM) Perlis and UiTM Shah Alam and the administrative and laboratory staff, especially Puan Norliana Ali, for their support in providing facilities and assistance during my laboratory work.

Special thanks to my Ketua Pusat Pengajian (KPP), Dr. Nur Nasulhah Kasim, for providing support and a flexible working environment that greatly facilitated completing this thesis. I also extend my heartfelt appreciation to my fellow teammates, Associate Professor Dr. Wan Izhan Nawawi Wan Ismail, Miss Asnida Yanti Ani, Mr. Mohd Fauzi Abdullah and Dr. Siti Nurlia Ali, for their invaluable support in enhancing my understanding of research methodologies and the complex instruments used in my coal-related studies. Thank you to my lovely friends in the Faculty of Applied Sciences, Mrs. Rohayu Ramli, Dr. Rizana Yusof, Mrs. Hanani Yazid, and many others, for their constant encouragement and meaningful support throughout this journey.

I would like to express my heartfelt gratitude to my beloved parents for their unconditional love and prayers, which made my PhD journey easier. I am also deeply thankful to my siblings for shouldering the responsibility of caring for our parents, allowing me the opportunity and confidence to navigate this challenging path successfully. Lastly, I express my deepest gratitude to my husband for his love, understanding, prayers, and continuing support for me to successfully navigate and complete this challenging journey. Alhamdulillah.

TABLE OF CONTENTS

	Page
CONFIRMATION BY PANEL OF EXAMINERS	ii
AUTHOR'S DECLARATION	iii
ABSTRACT	iv
ACKNOWLEDGEMENT	v
TABLE OF CONTENTS	vi
LIST OF TABLES	xii
LIST OF FIGURES	xiv
LIST OF SYMBOLS	xvii
LIST OF ABBREVIATIONS	xviii
LIST OF NOMENCLATURE	xxi
CHAPTER 1 INTRODUCTION	1
1.1 Research Background	1
1.2 Problem Statement	3
1.3 Research Objectives	5
1.4 Scope and Limitations	6
1.5 Significance of Study	7
1.6 Thesis Outline	9
CHAPTER 2 LITERATURE REVIEW	11
2.1 Coal and Its Classification by Rank	11
2.2 Physicochemical Properties of Coal	12
2.2.1 Ultimate Analysis	13
2.2.2 Proximate Analysis	14
2.2.3 Calorific or Heating Value	16
2.3 Types of Sulfur in Coal	17
2.3.1 Inorganic Sulfur in Coal	17
2.3.2 Organic Sulfur in Coal	18
2.4 Coal Desulfurization: Knowledge Gaps and Research Opportunities	18

CHAPTER 1

INTRODUCTION

This chapter presents the background and rationale for investigating coal desulfurization using a potassium carbonate-ethylene glycol (PC-EG) as a Deep Eutectic Solvent. The problem statement establishes the scope of the study and clearly outlines the specific research objectives. The chapter also emphasizes the significance and relevance of the study, highlighting its potential effect on coal desulfurization technologies.

1.1 Research Background

The primary challenge in coal desulfurization is the effective removal of sulfur-containing compounds, especially those in heterocyclic forms [1]. Heterocyclic sulfur compounds, such as benzothiophene, are strongly bonded to the coal macromolecular structure, resulting in significant challenges for extraction [2]. During combustion, sulfur in coal is released as sulfur dioxide (SO₂), which then reacts with water and oxygen in the atmosphere to form acid rain. This phenomenon has harmful effects on the environment [1, 3]. Moreover, high concentration of aromatic compounds reduces fuel quality, highlighting the need to separate heteroaromatic chemicals from aliphatic components [2].

Traditional hydrodesulfurization (HDS) methods are effective in removing sulfur from aliphatic hydrocarbons. However, the removal of heterocyclic sulfur such as thiophene, benzothiophene, and their derivatives remains challenging due to steric hindrance. Furthermore, the HDS process operates under high temperatures and pressures, which can lead to the breakdown of coal macromolecular structure and increase operational costs. To address these limitations, combining extraction with oxidative desulfurization (EODS) has been identified as a cost-effective alternative to traditional HDS [4]. EODS operates under mild conditions and employs environmentally friendly extractants and catalysts to remove aromatic sulfur compounds [5]. However, one drawback of the EODS method is its reliance on organic solvents, which raise concerns regarding safety and environmental impact. These issues have driven the search for greener alternatives, such as Deep Eutectic Solvents (DESS)