

Optimization Studies of Coal Organic Sulfur Removal using Potassium Carbonate and Ethylene Glycol as a Deep Eutectic Solvent

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Combustion of coal emits sulfur dioxide gas into the atmosphere. When reacting with water vapour, this gas produces sulfuric acid, also known as acid rain, causing environmental destruction, and endangering human health. One option to address these issues is to remove the sulfur from coal before combustion. Physical and chemical pre-treatments using oxidizing or reducing agents easily remove inorganic sulfur from coal, namely pyrite and sulfate sulfur. However, organic sulfur is hard to remove unless a particular reagent is applied to break the carbon-sulfur bonds to release the sulfur from the coal matrix. This study reports the utilization of a mixture of potassium carbonate and ethylene glycol (K₂CO₃:EG) under sonication to extract organic sulfur from coal. The ultrasonic shockwave separates sulfur from the coal's macromolecular structure by breaking the chemical connections that hold sulfur to coal. CCD-RSM experimental design was presented to overcome traditional methods that make finding the optimal standard difficult and time-consuming. The effects of molar ratio, temperature, and extraction time on the removal of organic sulfur in coal were investigated, and sonicating coal at 40 °C for 60 minutes with 1:16 K₂CO₃:EG was found to be the ideal parameter. The changes to the thiophene and organic sulfate FTIR peaks may serve as a preliminary measure of the effectiveness of K₂CO₃:EG in coal desulfurization. This research shows that solvent-pre-treated coal may be safe and environmentally advantageous, two goals of the 2030 Agenda for Sustainable Development.

Keywords: Coal desulfurization; potassium carbonate; ethylene glycol; Deep Eutectic Solvent; Response Surface Methodology

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In 2019, fossil fuels generated 63% of total global power generation, with coal accounting for 36% of total power output by energy source [1]. Coal is used in the iron, steel, cement, and chemical industries in addition to energy production. Desulfurizing the electric power sector is necessary due to several air quality issues, such as the emission of pollutants that impact human health and affect the atmosphere and climate change [2]. The direct combustion of high-sulfur coal produces sulfur dioxide pollutants in the atmosphere [3] and results in acid rain [4]. It is well known that acid rain causes metals to corrode, which may destroy ecological infrastructure, cause breathing problems in humans and animals [5, 6] and cause severe organ damage [2] in addition to killing crops and reducing the ozone layer.

Coal contains both organic and inorganic sulfur. Inorganic sulfur in coal is mostly pyrite and sulfate [7], while organic sulfur is composed of thiophene, mercaptan, sulfoether, sulfone, and sulfoxide [8]. Chemical bonds between organic sulfur compounds

like dibenzothiophene (DBT) and the coal matrix make them difficult to remove [9]. Even if complete desulfurization is achievable, the working conditions are incredibly harsh, which makes the desulfurization process more expensive [2].

Hydrodesulfurization (HDS) is the most used oil refining desulfurization technique. It is based on chemical reactions when sulfur compounds and hydrogen are mixed with a catalyst. Due to the high temperatures and pressures required, HDS does not effectively remove heterocyclic sulfur compounds, such as thiophenes, but it successfully removes aliphatic sulfur compounds. Extraction desulfurization (EDS) is the most promising alternative to HDS since it is a straightforward technique, uses less energy, has a low temperature and pressure, and has no influence on product quality. However, volatile and flammable organic solvents used as extraction solvents in EDS should be replaced with more environmentally friendly and safe solvents [10].

Over the last 20 years, green processes have attracted much attention to reduce the use of dangerous and toxic chemicals and increase awareness of environmental problems. Solvents are a vital field of research in green chemistry due to the hazardous and flammable nature of most conventional chemicals. A newly developed class of solvents called ionic liquids (ILs) has drawn the interest of scientists from a wide range of disciplines since the early 2000s [2]. A solvent composed of the ILs 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) and N-methyl pyrrolidinone (NMP) was used to extract organic precursor chemicals from direct coal liquefaction residue (DCLR), and the findings indicated that the mixed solvent was effective at extracting the organic components but inert to inorganic chemicals. The total sulfur was reduced from 4.97% to 0.44% [11].

Pre-treated lignite and thermal bituminous coal using low-cost choline amino acid-alkali ILs decreased aliphatic carbon, carbonyl groups, and sulfur compared to untreated coal. This result showed that the mixture of ILs was significant for coal pre-treatment [12]. Suguwara et al. [12], found that imidazolyl ILs with alkyl sulfate anion at 100–200 °C for one hour effectively extracted sulfur compounds from coal's 1-methylnaphthalene soluble fraction. It was discovered that [Mmim][MESO4] eliminated 44% of benzothio-*phene*, 26% of 1,2-ethyldithiol, 13% of phenylmercaptan, and 4% of diethyl disulfide. Additionally, multi-step extraction could be able to remove additional sulfur. However, the high-temperature treatment will change the combustible organic part of the coal and lower its calorific value [12].

ILs are not utilized as often in the industry because they are more expensive to produce than conventional solvents. A green alternative to traditional ILs would be biodegradable and have high thermal and chemical stabilities. Deep eutectic solvents (DESs) are one of these options. Since they are made at room temperature, they are relatively cheap and can be used on a large scale in the industry [13]. DESs are similar to conventional ILs in their physical and chemical properties, including melting points close to room temperature, undetectable vapor pressure, non-volatility, non-flammability, and exceptional solubility for a variety of substances. Although they are comparable, DESs and ILs offer superior characteristics. The components in DESs are less expensive and more biodegradable than those in ILs. In other words, DESs outperform ILs in terms of cost and toxicity. Additionally, the synthesis of DESs is entirely atom-economic, simple to handle, and does not require purification, making their application on a large scale possible. DESs have been used in various processes, including material preparation, substance dissolving, separation procedures, electrochemistry, catalysis, and extraction. Several DESs have effectively removed sulfur from oil more than traditional and functionalized ILs. DES is an excellent extractant (EODS) for systems involving extractive and oxidative desulfurization [14]. Up to this point, a

few investigations into extraction, desulfurization, and oxidation utilizing DESs have been published [10]. DESs were a novel material for absorbing gases, including CO₂, SO₂, and NO_x [15]. Since CO₂ and SO₂ adsorption and sequestration are now critical topics aimed at minimizing global warming, researchers are interested in CO₂ and SO₂ capture [2,16,17]. Yang et al. [16], claimed that several DESs, including choline chloride (ChCl)-glycerol, imidazole-glycerol, and ChCl-ethylene glycol (EG), are potential absorbents for SO₂ absorption. Using different DESs will affect extraction efficiency. Therefore, choosing appropriate DESs is essential [2].

The white salt potassium carbonate (K₂CO₃) dissolves in water to form a highly alkaline solution with a melting point of 891 °C [13]. Ethylene glycol (EG) is a non-volatile organic solvent with a low viscosity that is odorless and colorless. It is the most basic diol and has various distinct properties due to its unique structure of two hydroxyl (OH) groups at adjacent locations along a hydrocarbon chain. It is completely miscible in water and does not crystallise quickly. It finally solidifies to form a substance that resembles glass after cooling to a highly viscous, super-cooled mass [18].

This study aims to determine the efficiency of the mixture of potassium carbonate and ethylene glycol in removing organic sulfur in coal. As potassium-based salts are not previously used in DES manufacturing, they can be considered a new form of DES for coal desulfurization. A one-cycle coal desulfurization experiment was conducted using an ultrasonic-assisted extraction technique at various K₂CO₃:EG molar ratios, temperatures, and times. A previous study [19] found that a two-step extraction process using a magnetic stirrer took two to three hours to achieve the same result; thus, the sonication technique was used to reduce the processing time in this work. The ultrasonic leaching shockwaves create microscopic cracks on the surface of the coal, bringing the reagent closer to the coal particles. Sulfur and carbon in the coal matrix separate when the chemical bonds that bind them together are broken [19]. The optimum molar ratio, temperature, and processing time for the coal desulfurization process were determined using the Central Composite Design-Response Surface Methodology (CCD-RSM) to minimize the number of experimental runs.

EXPERIMENTAL

Preparation of Coal Sample

The sample of high sulfur coal from Jambi Province, Indonesia, was supplied by SGS (Malaysia) Sdn. Bhd. The coal was pulverized and sieved through successively smaller screens to reach particle sizes of 212 μm. The pulverized coal was sieved for 30 minutes in an Endecott Shaker Model EFL2 MK3 before being dried in an oven at 60 °C for 24 hours and kept in a securely

screw-capped bottle to remove moisture [20]. The proximate and ultimate analyses and forms of sulfur of the raw coal are displayed in Table 1.

Preparation of the Mixture of Potassium Carbonate (K₂CO₃) and Ethylene Glycol (EG)

The potassium carbonate was obtained from R&M Chemicals, while the ethylene glycol 98% was obtained from Merck. The solution was prepared by mixing the potassium carbonate and ethylene glycol in a molar ratio (mol/mol) of 1:8, 1:12, 1:16, and 1:19, respectively, as shown in Table 2. The liquid was stirred at 25 °C for 1-2 hours with a hot plate stirrer until a clear solution was obtained. The pH of each DES was measured using the Metrohm 827 pH Lab, and the results indicated that all solutions had a pH of 13, indicating that they were extremely basic. The viscosity of DES was determined with a Brookfield viscometer. All the solutions were prepared and stored in sealed Schott bottles to avoid contamination and moisture.

Extraction Process

The K₂CO₃:EG mixture was mixed with 3 g of coal in a 1:20 coal-to-solution ratio (g:mL) [20]. The mixture was then subjected to ultrasonic extraction at 40 kHz according to the temperatures and times listed in Table 3. After filtering, the mixture was thoroughly washed with hot distilled water until the litmus test remained neutral. The residue was dried in an oven at 60 °C for 24 hours. A list of the optimization parameters, including temperature, processing time, and the K₂CO₃: EG mixing ratio, is presented in Table 2. The experiment was repeated twice to get an accurate result. Under optimum circumstances, the blank samples were created by pre-treating coal with a combination of K₂CO₃:H₂O and EG.

Sulfur Assay Studies

Total sulfur (T_s) in coal was tested using ASTM D3177-02 (2012) [21], while ASTM D2492-02 (2012) [22] was used to quantify sulfate sulfur (S_s) and pyrite sulfur (P_s). The organic sulfur (O_s) was calculated by subtracting the sum of sulfate and pyritic sulfur from

the total sulfur using Equation 1, while the organic sulfur removal percentage was calculated using Equation 2.

$$O_s = T_s - (P_s + S_s) \quad \text{Equation 1}$$

$$\text{Percent } O_s \text{ removal (\%)} = (T_s - O_s) / T_s \times 100 \quad \text{Equation 2}$$

Fourier Transform Infrared Spectroscopy (FTIR) Study

FTIR analysis was performed on raw and treated coal to determine and compare the changes in functional group absorption peaks in both samples. The sample was dried overnight at 80°C before the FTIR analysis to reduce the impact of moisture. The coal samples were ground with KBr at a 1:50 coal-to-KBr mass ratio and compressed into tiny pellets. A Perkin Elmer FTIR Spectrometer with a scan range of 400–4000 cm⁻¹ was employed, and it was then scanned 64 times with a resolution of 4 cm⁻¹ [23].

Experimental Design

Three variables were selected to study their effects on the percent of organic sulfur removal from coal, including the molar ratio of K₂CO₃:EG (mol/mol), temperature (°C), and time (min). The variables are denoted by the letters (A), (B), and (C), respectively, and the percent of organic sulfur removal in coal was the study's output. These parameters were optimized using Central Composite Design (CCD) under RSM in Design Expert V13, where 18 experimental runs were proposed. The studies were conducted at random to reduce response error. The parameters A, B, and C are quantitative factors that change according to the ranges listed in Table 2. The effect of the extraction parameters A, B, and C was computed using Design Expert V13. An Analysis of Variance (ANOVA) is used to fit the parameters A, B, and C and the response output into a quadratic polynomial model to investigate the significance of each experimental parameter and their interactions during the desulfurization process. The optimal conditions were derived from the generated response surface models.

Table 1. Characterization of raw coal.

Proximate analysis (wt% db)		Ultimate analysis (wt% daf)		Forms of sulfur (wt% db)		Calorific Value (MJ/kg)
Ash	14.83	Carbon	61.26	Total sulfur (T _s)	3.94	25.49
Volatile matter	44.40	Hydrogen	5.03	Sulfate sulfur (S _s)	0.89	
Fixed carbon	40.77	Nitrogen	1.38	Pyrite sulfur (P _s)	1.36	
		Sulfur	3.94	Organic sulfur* (O _s)	1.69	
		Oxygen*	28.39			

db = dry basis weight unit
daf = dry-ash-free basis weight unit
* = calculated by difference

Table 2. List of variables, codes, and design coordinates.

Coded	Parameter	Units	Minimum	Maximum	-1 Actual	+1 Actual
A	Molar ratio	mol	8	16	8	19
B	Temperature	°C	30	70	30	84
C	Time	min	40	60	33	67

RESULTS AND DISCUSSION

Model Fitting and Analysis of Variance (ANOVA)

Table 3 displays the experimental and predicted percentages of organic sulfur removal for every 18 experimental runs conducted by CCD with various extraction parameters. The appropriate quadratic model is determined by adjusting the values from the two repetition samples with a range difference of 0.2 to 0.6. Equation 3 illustrates the effect of each experimental parameter and its correlation with other parameters.

$$\text{Percent of organic sulfur removal (\%)} = + 53.82 + 6.60*A - 2.53*B + 5.24*C - 3.76*AB - 0.48*AC - 3.69*BC - 3.07*A^2 - 4.89*B^2 - 1.22*C^2 \quad \text{Equation 3}$$

In Table 4, the statistical significance of the model is determined using the F-statistic test in ANOVA. The validity of model terms may be described by Probability (P) > F values. The model term is significant if (P > F) values less than 0.05. Significant model terms are likely to influence the response. In contrast, the model term is insignificant if (P) values are higher than 0.10. Table 4 shows that the chosen quadratic model is significant as it has a (P > F) value of < 0.0001. The model's F-value of 537.17 suggests

that it is significant. There is just a 0.01% possibility that this F-value is the product of noise. The significant extraction parameters are A, B, C, AB, AC, BC, A², B² and C² as they have (P > F) values less than 0.05. A significant Lack of Fit means that the model does not match the data within the range of variation seen in replicates. The Lack of Fit for F-value in this study is 0.34, indicating that it is insignificant compared to the pure error. The Lack of Fit for F-value has an 80.09% probability of being caused by noise. This value of non-significant for Lack of Fit is good. The Predicted and Adjusted R-squared (R²) should be within 0.20 to avoid a problem with the data or the model. In this case, the Predicted R² (0.9983) and Adjusted R² (0.9965) show that the model correctly predicts the results because the difference between the two is less than 0.2. The signal-to-noise ratio is measured using Adequate Precision. It compares the predicted value range at the design points with the average prediction error. The ratio of 97.28 shown by this study suggests an adequate signal. A ratio larger than 4 is preferable. This model may be used to explore the design space. Figure 1(a) displays the normal distribution of the Normal Plot of Residuals, while Figure 1(b) displays the Predicted vs Actual percent of organic sulfur removal, demonstrating that the values are still within acceptable limits.

Table 3. CCD Experimental Design with Experimental and Predicted Percentages of Organic Sulfur Removal.

Run	Molar ratio (A)	Temperature (B)	Time (C)	Organic sulfur removal (%)	
				Actual value	Predicted value
1	1:8	70	60	45.29	45.41
2	1:19	50	50	56.11	56.24
3	1:12	84	50	44.11	44.24
4	1:16	70	40	48.17	47.98
5	1:16	30	60	61.76	61.88
6	1:8	70	40	43.46	43.25
7	1:8	30	60	40.11	40.21
8	1:8	30	40	23.37	23.29
9	1:16	70	60	52.05	52.04
10	1:12	50	33	41.19	41.55
11	1:12	50	67	59.41	59.18
12	1:12	50	50	53.53	53.82
13	1:12	50	50	54.70	53.82
14	1:12	50	50	54.11	53.82
15	1:12	50	50	54.11	53.82
16	1:12	50	50	52.94	53.82
17	1:16	30	40	43.27	43.06
18	1:12	50	50	53.53	53.82

Table 4. ANOVA analysis for percentage removal of organic sulfur in coal.

Source	Sum of squares	Degree of freedom (df)	Mean square	F-value	P-value
Model	1368.84	9	152.09	537.17	< 0.0001 ^a
A-Molar ratio	380.42	1	380.42	1343.60	< 0.0001 ^a
B-Temperature	55.90	1	55.90	197.44	< 0.0001 ^a
C-Time	375.20	1	375.20	1325.15	< 0.0001 ^a
AB	113.10	1	113.10	399.46	< 0.0001 ^a
AC	1.81	1	1.81	6.38	0.0355 ^a
BC	108.93	1	108.93	384.72	< 0.0001 ^a
A ²	70.56	1	70.56	249.22	< 0.0001 ^a
B ²	179.33	1	179.33	633.39	< 0.0001 ^a
C ²	19.84	1	19.84	70.07	< 0.0001 ^a
Residual	2.27	8	0.28		
Lack of Fit	0.38	3	0.13	0.34	0.8009 ^b
Pure Error	1.89	5	0.38		
Cor Total	1371.10	17			R ² = 0.9983
Std. Deviation	0.53				Adjusted R ² = 0.9965
Mean	48.96				Predicted R ² = 0.9940
Coefficient variation (C.V. %)	1.09				Adequate Precision = 97.28

^aSignificant value: P value less than 0.0500.

^bInsignificant value: P value greater than 0.1000.

Analysis of the Ethylene Glycol and DES Viscosities

Viscosity is useful in coal desulfurization because it can measure the solvent's fluidity and flow resistance. Temperature also affects DES viscosity, which assesses its applicability and predicts the energy required for

processing [24]. Figure 2 illustrates the trendline for EG and DES viscosities as a function of temperature. The graph demonstrates that the viscosities of the K₂CO₃: EG mixtures are greater than the EG alone, and as the temperature increased, the viscosities decreased. The following sequence shows the decrease in the viscosity of DES and EG.

1:8 > 1:12 > 1:16 > 1:19 > EG.
 \rightarrow
decreasing viscosity

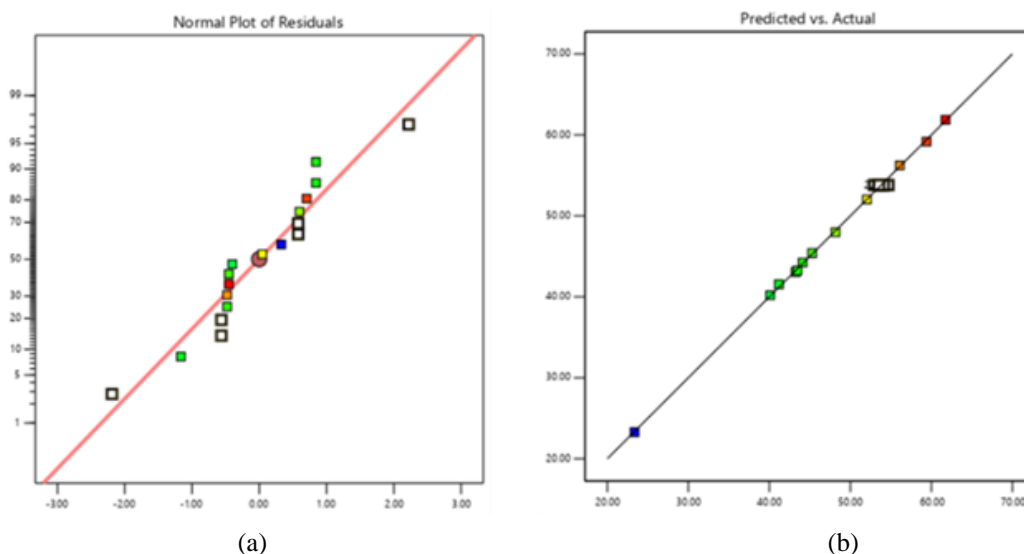


Figure 1. (a) Normal probability plot of Residuals and (b) Plot of Predicted Vs Actual

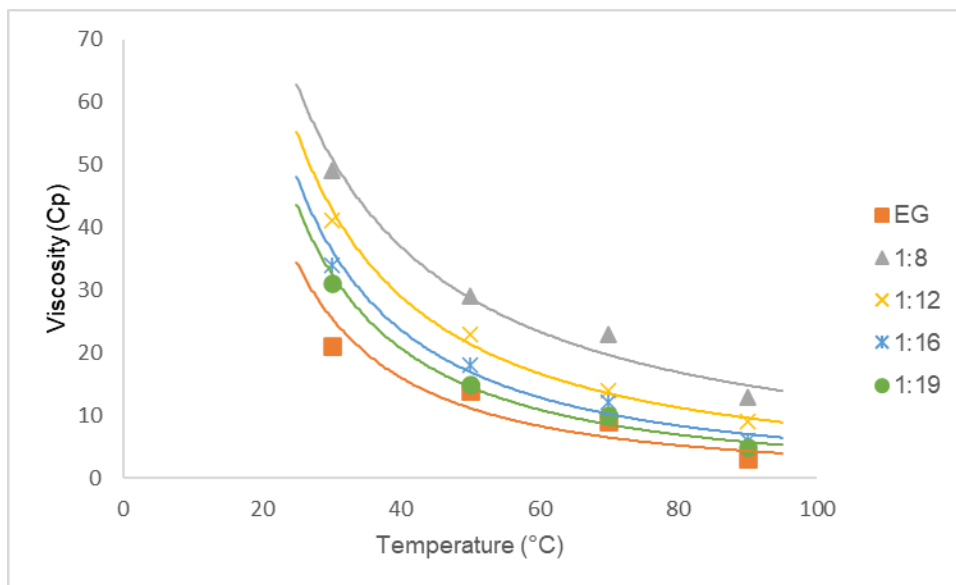


Figure 2. The trendline of DESs viscosities as a function of temperature.

The Effect of DES Solvents and Extraction Parameters on Coal Desulfurization

Figures 3(a), 3(b), and 3(c) display the patterns of the response surface as a result of changing the extraction parameters. According to the ANOVA analysis in Table 4, the molar ratio (A) and time (C) significantly impacted the amount of organic sulfur extracted from coal due to their high F-values.

The Effect of Molar Ratio on Coal Desulfurization

As shown in Figure 3(a), the highest removal of organic sulfur occurs at a molar ratio of 1:6 at 30 °C. As the molar ratio of EG increases from 8 to 16 mol, organic sulfur removal also increases to 61.76%. Lee et al. [10] stated that sulfur removal efficiency is highly dependent on the molar ratio of hydrogen bond acceptor (HBA) to hydrogen bond donor (HBD), as well as the types of HBA and HBD used in DES. However, increasing the amount of EG (HBD) up to a molar ratio of 1:19 did not improve the extraction efficiency compared to the molar ratio of 1:16. As the molar ratio of EG as HBD increased, the extraction efficiency increased due to the number of carbon atom chains and a decrease in hydrogen bond interactions because of steric hindrance. HBD surrounds the anion, stabilising the group and supplying more active hydrogen. More sulfur can therefore be eliminated [2,25]. However, further increases in HBD content did not improve the extraction efficiency [26]. The study by Rogosic and Kucan [27] discovered that increasing or reducing the EG content of DES is not always suitable for organic sulfur extraction. It was sometimes the ideal medium for other aromatic structures like toluene or pyridine. The effectiveness of organic sulfur extraction from coal is also affected by other variables, including temperature.

The Effect of Temperature on Coal Desulfurization

According to Figure 3(b), as the time passed from 40 to 60 minutes, the percentage of organic sulfur elimination at 30 °C increased. Similar trends were seen at 50 °C, where 30 to 70 minutes reaction times resulted in more organic sulfur elimination. However, other samples indicated that the amount of organic sulfur removed was unaffected by the higher temperature. The percent elimination of organic sulfur was observed to decrease between 70 and 84 °C. These findings revealed that high temperatures inhibited the K_2CO_3 :EG extraction-desulfurization process, but low temperatures for a more extended reaction period made the desulfurization process work better. The pattern is consistent with Makos and Boczkaj [26] finding that raising the temperature from 20 to 40 °C enhanced extraction efficiencies while increasing the temperature from 40 to 70 °C decreased extraction efficiencies. The results of Yang et al. [16] were consistent with the temperature effect on SO_2 absorption capacities, which showed a reduction from 20 to 60 °C. Acid-base complexation, an exothermic reaction, may have slowed the reaction process. Additionally, electrophilic substitution occurs more rapidly at higher temperatures. Therefore, the treatment may be done at any ambient temperature [25].

The Effect of Time on Coal Desulfurization

Figures 3(b) and 3(c) show the interaction of processing temperature and DES molar ratio with time on the percentage of organic sulfur removal. According to the data, extending the time from 33 to 67 minutes had no consistent effect on the percentage of organic sulfur removal. The ANOVA analysis in Table 4 revealed that the DES molar ratio affects coal organic sulfur extraction since the molar ratio had the highest F-

value for the significant factor, followed by processing time. The molar ratio and reaction time appeared proportional to the percentage of organic sulfur removed as shown in Figure 3(c). A molar ratio of 1:16 resulted in the highest removal of organic sulfur after 60 minutes of reaction time. Similar trends were seen for molar ratios of 1:8 and 1:12, in which the percentage of organic sulfur removed increased as the processing period was prolonged. It is believed that the low viscosity of the molar ratio of 1:16 and the 60 min of processing time has contributed to the highest removal of organic sulfur. As shown in Figure 2, a molar ratio of 1:16 DES has a lower viscosity than 1:8 and 1:12. The low solvent viscosity promotes free volume and high energy that allows solvent molecules or ions to flow around the sample [24]. The molar ratio of 1:16

has spread out the coal and revealed suitable-sized holes, while the extended processing time assists in sulfur extraction [24]. In conclusion, the organic sulfur removal percentage increased as the molar ratio and extraction time increased.

Optimization Study

The molar ratio, temperature, and reaction time were all set within the study range, while the percent of organic sulfur removal was set to its maximum value to determine the experiment's optimal condition. The optimized reaction parameters given by RSM-CCD were found to be at a molar ratio of 1:16, a temperature of 40°C, and a time of 60 minutes that yielded the maximum percent of organic sulfur removal of around 62.27%.

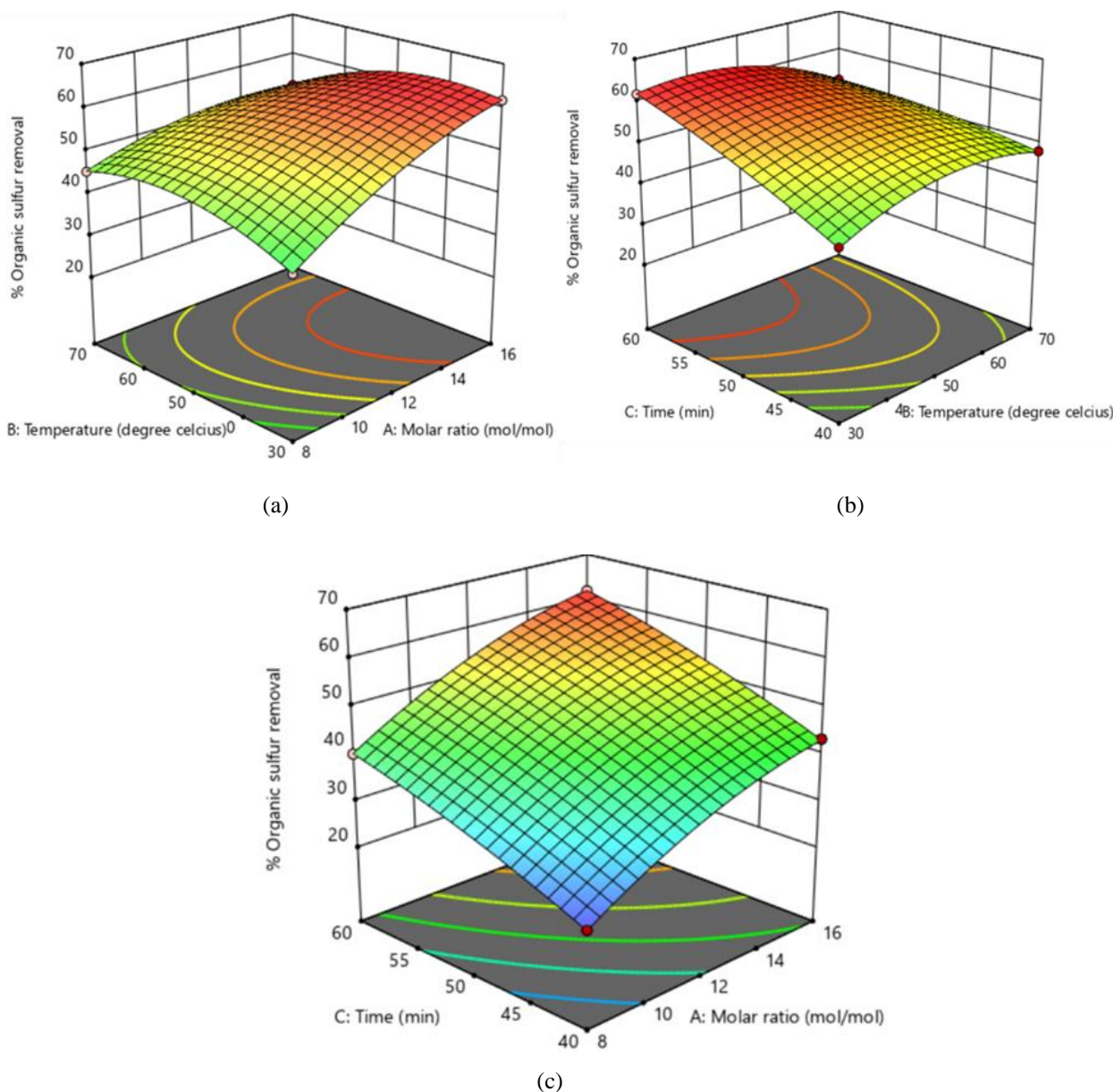


Figure 3. Response surface to show the effect of (a) the molar ratio and temperature, (b) the temperature and time, and (c) the molar ratio and time on the percent of organic sulfur removal.

Validation

A verified run for the optimized parameter was performed thrice to validate the percent organic sulfur removal. The percent elimination rates achieved were 64.02, 65.68, and 66.45%, with an average value of 65.38%, which is greater than the value predicted by CCD-RSM at 62.27%. However, the findings are supported by Makos and Boczkaj [26], who studied the effect of extraction temperature on extraction efficiency. The extraction efficiencies were found to increase with an increase in temperature from 20 °C to 40 °C. But, a further increase in temperature, from 40 °C to 70 °C, reduced extraction efficiency. Lee et al. [10], also discovered that desulfurization effectiveness was temperature insensitive. The value can increase with rising temperatures or decrease as temperatures increase.

Fourier Transform Infrared Spectroscopy (FTIR) of the Optimized Sample

The FTIR analysis describes the desulfurization outcomes in the coal microstructure before and after the pre-treatments. Figure 4 shows the FTIR analysis of raw and treated coal under optimal conditions and

coal treated with $K_2CO_3:H_2O$ and coal-EG alone. The peaks at 1420 cm^{-1} and $2525\text{-}2600\text{ cm}^{-1}$ are related to thiophene rings and thiol (S-H stretch) in raw coal, respectively [28]. The absorption peaks at $1330\text{-}1125\text{ cm}^{-1}$ and $1060\text{-}1030\text{ cm}^{-1}$ show the existence of sulfoxide (S=O) and sulfone (O=S=O), respectively [29]. The absorption peaks at $705\text{-}570\text{ cm}^{-1}$ and $620\text{-}600\text{ cm}^{-1}$ indicate the stretching vibration of the C-S and S-S of disulfide bonds, respectively [30]. The peak at $1450\text{-}1615\text{ cm}^{-1}$ corresponds to the aromatic ring reduction (C=C-C) [23]. The peaks from $843\text{-}600\text{ cm}^{-1}$ are linked to coal's inorganic and organic mineral materials [31] indicating that the three pre-treatments quickly removed these compounds. The peaks for thiophene, aromatic ring (C=C-C), disulfide (C-S and S-S bonds), and sulfoxide for treated coal seemed to have changed and shifted towards the higher wavenumber side, indicating that the mass of the molecules was reduced in comparison to the peak of raw coal. Coal-treated $K_2CO_3:H_2O$ significantly affects the thiophene, sulfoxide, and disulfide bonds, while coal-treated EG affects the sulfone and disulfide bonds. In conclusion, the mixture of $K_2CO_3:EG$ as a coal pre-treatment may enhance the extraction of organic sulfur from coal more than when coal- $K_2CO_3:H_2O$ and coal-EG were used alone.

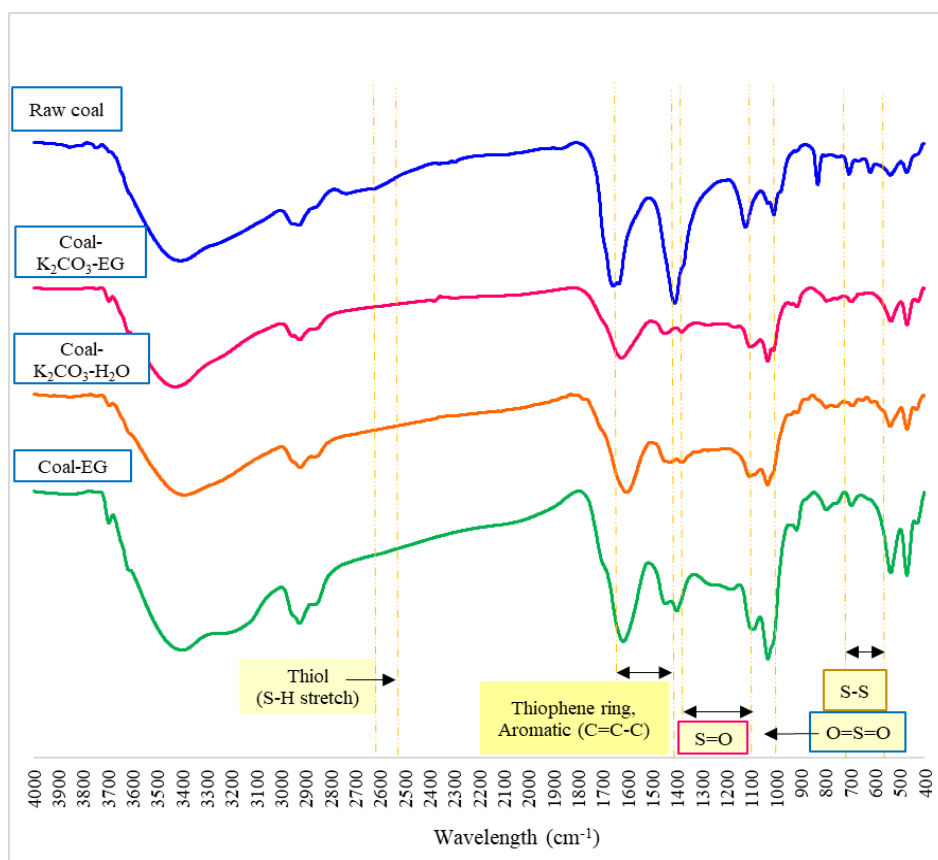


Figure 4: FTIR results of (a) raw and treated coal using (b) coal- $K_2CO_3:EG$ under optimal condition, (c) coal- $K_2CO_3:H_2O$ and (d) coal-EG.

CONCLUSION AND RECOMMENDATION

From the sulfur assay study, it was found that the mixture of K_2CO_3 :EG was efficient for removing organic sulfur in coal. The experimental results showed that all the specified molar ratios, temperatures, and times in Table 3 could eliminate organic sulfur in coal by at least 20 to 62%. The optimum parameters suggested by CCD-RSM were found at a molar ratio of 1:6 at 40°C for 60 minutes of processing time. The results were also supported by FTIR data, which showed that the efficiency of K_2CO_3 :EG for coal desulfurization caused the peaks of thiophene and organic sulfates to change practically. However, further tests using Gas Chromatography-Mass Spectroscopy (GC-MS) and Nuclear Magnetic Resonance spectroscopy (NMR) are required to establish the type of organic sulfur eliminated in this research since specific organic sulfur that has a heterocyclic structure is challenging to extract from coal.

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