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Strategies for Clean Production in Methyl Isocyanate Synthesis for Pesticide Raw Materials

Deni Faisal[1,2], Fatah Sulaiman[1,2], Marta Pramudita [1,2,3*]

[1]Master's Program in Chemical Engineering, Universitas Sultan Ageng Tirtayasa, Cilegon, Indonesia

[2]Department of Chemical Engineering, , Universitas Sultan Ageng Tirtayasa, Cilegon, Indonesia

[3]Biomass Valorization Laboratory, Universitas Sultan Ageng Tirtayasa, Cilegon, Indonesia

*Email: marta_pramudita@untirta.ac.id

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Abstract

The increasing demand for pesticides in agriculture has led to a rise in the production of methyl isocyanate, a key intermediate in carbamate pesticide manufacturing. However, this process generates sodium sulfate as a by-product, dissolved in an aromatic solvent, which, if not adequately managed, contributes to environmental pollution and resource inefficiency. Chemical and environmental engineering are crucial in addressing this issue by developing effective separation and recovery methods. One potential solution is the distillation process, which separates sodium sulfate based on boiling point differences with water. However, the effectiveness of this method depends on operational conditions, particularly pressure and sulfuric acid concentration. This research focuses on optimising the recovery of sodium sulfate from methyl isocyanate production waste by investigating different operating pressures (atmospheric, vacuum, and combined) and sulfuric acid concentrations (0 M, 0.07 M, 0.15 M, 0.22 M, and 0.30 M). A recovery efficiency of sodium sulfate as high as 92.5% using vacuum distillation at a 0.22 M sulfuric acid concentration. Additionally, the condensate water contained 98.7% purity, making it suitable as a precursor for struvite fertiliser. Sodium sulfate is used as a raw material in producing insecticidal pesticides, with a purity level of 97.3%. This study demonstrates that an optimised distillation process can enhance the efficiency of pesticide production by minimising waste and maximising resource utilisation, contributing to cost efficiency and environmental in industrial pesticides.

Keywords: distillation, methyl Isocyanate, pesticide, sodium sulfate recovery

INTRODUCTION

Pesticides enhance agricultural productivity by controlling pests, weeds, and plant diseases that can significantly reduce crop yields. Without pesticides, food production could decline drastically, threatening food security and increasing the risk of crop failure (Sharma et al., 2019). Moreover, the demand for pesticides continues to rise in response to population growth and higher food requirements. The increasing demand for pesticides in the agricultural sector has led to a surge in pesticide production, particularly in the carbamate group, which relies on methyl isocyanate (MIC) as an intermediate compound. MIC is a key precursor in carbamate pesticide production, widely used to protect crops from pests, ensuring food security and agricultural productivity (Carvalho, 2017).

As a fundamental component in pesticide synthesis, its availability and production efficiency directly impact the pesticide industry and agricultural supply chains. MIC is specifically chosen due to its unique reactivity in forming carbamate pesticides such as aldicarb, carbofuran, and methomyl. Unlike alternative intermediates, MIC enables an efficient synthesis route with high yields and controlled product quality (Rivas & Cintas, 2022). While other compounds, such as organophosphates and pyrethroids, serve as pesticide precursors, MIC-based carbamates are preferred due to their biodegradability, broad-spectrum efficacy, and lower environmental persistence compared to organochlorine pesticides (Paidi et al., 2021).

It is important to note that conventional MIC production generates hazardous waste, particularly sodium sulfate, ammonia emissions, and residual organic solvents (Spooren et al., 2020). If not properly managed, the amount of sodium sulfate by-product poses significant environmental risks, including water pollution and toxic gas emissions (Kavitha et al., 2022). On the other hand, a resource-efficient MIC production process is essential to maintaining a stable pesticide supply while minimising environmental and economic costs.

Clean production offers a proactive approach by minimising waste generation at the source, improving resource efficiency, and reducing operational costs (Zhang et al., 2021). Improper waste disposal leads to environmental contamination and imposes additional disposal costs on the industry (Ferronato et al., 2019). The pesticide industry, which manufactures carbamate pesticides using MIC synthesised through the cyanate process, generates sodium sulfate waste that holds economic potential if properly recycled (Kumari et al., 2023). However, current waste management practices involve third-party disposal, which is costly and inefficient. Addressing this issue requires chemical and environmental engineering approaches to enhance resource efficiency and reduce environmental impact (Fenibo et al., 2021).

This study uses a distillation-based separation method to introduce an optimised approach for sodium sulfate recovery from MIC process waste. Unlike conventional disposal methods, which primarily rely on third-party waste management or neutralisation processes that add environmental burdens, this research explores a more sustainable and resource-efficient alternative. Previous studies on sodium sulfate recovery have focused on conventional crystallisation and precipitation techniques, with limited emphasis on integration into a cleaner production framework (Sahu et al., 2021).

This research focuses on applying

process intensification strategies, particularly vacuum distillation, to reduce energy consumption and control acidification to enhance recovery efficiency (Guzman & Lucia, 2021). This study aims to determine the optimal concentration for sodium sulfate recovery from MIC process waste using a distillation method, enabling its reuse as a raw material in pesticide production. This aligns with clean production principles in MIC synthesis by minimising waste and repurposing by-products, such as utilising condensate water for struvite fertiliser production, to enhance resource efficiency and reduce environmental impact (Tian et al., 202). This research aligns with circular economy principles, ensuring minimal waste generation and maximum resource recovery. Through this approach, the study reduces disposal costs and contributes to pesticide production by promoting cleaner manufacturing and improving overall process efficiency.

METHOD

The method used to separate dissolved sodium sulfate from MIC waste is distillation, conducted with variations in process pressure and sulfuric acid concentration. The initial stage of this research involves preparing methyl isocyanate waste for the separation process of sodium sulfate from water, aiming to achieve optimal conditions for sodium sulfate recovery through variations in separation processes using atmospheric pressure, vacuum pressure, and a combination of operating pressures, followed by determining the optimal concentration for sulfuric acid addition; after establishing the optimal conditions from the variations in operating pressure and sulfuric acid concentration during sodium sulfate recovery, tests on the obtained sodium sulfate and water will be conducted. Subsequently, the data gathered from all research phases will undergo data processing and analysis. The stages of the process in this research are illustrated in Figure 1.

Materials used in this research are MIC waste and sulfuric acid. MIC waste was obtained from a pesticide chemical industry in the industrial area of Serang Regency. The distillation apparatus used to separate sodium sulfate from MIC waste is shown in Figure 2.

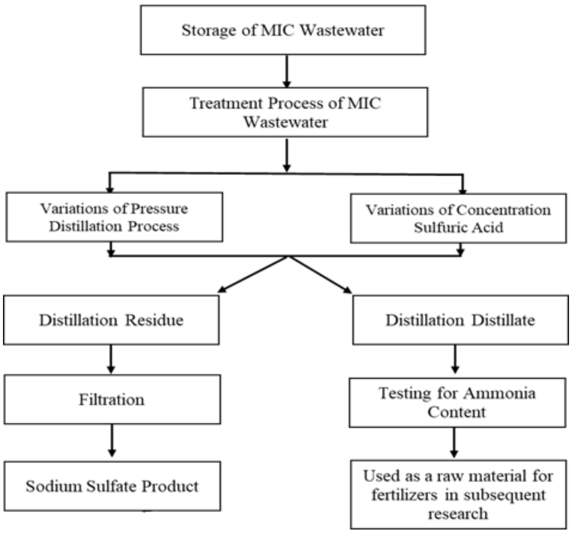

Figure 1. Stages of Research on Sodium Sulfate Recovery from MIC Waste

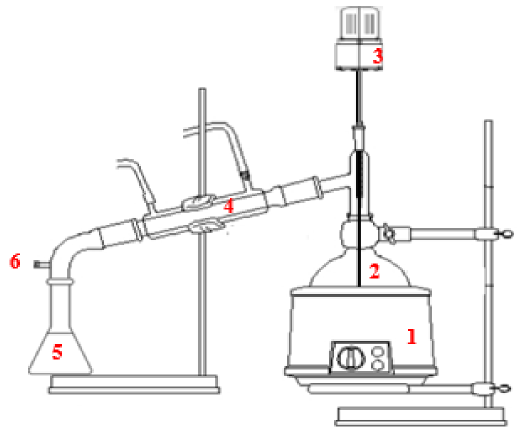

Figure 2. Distillation equipment:
1. Oil bath, 2. Distillation flask, 3. Stirrer, 4. Condenser, 5. Erlenmeyer flask, 6. Vent/Vacuum inlet.

Separation of sodium sulfate from MIC waste

The research commenced with preparing equipment and materials to distil 1000 mL of MIC waste, which was placed in a distillation flask. During the distillation process, sulfuric acid was added at the beginning of the stages. The distillation was conducted for 8 hours under varying atmospheric and vacuum pressures. For combined pressure variations, the distillation was performed for 4 hours at atmospheric pressure followed by 4 hours at vacuum pressure. The distilled water was analysed to determine the ammonia content, while the distillation residue, consisting of sodium sulfate, was filtered, weighed, and analysed for sodium sulfate concentration.

Qualitative analysis of sodium sulfate was carried out using acid-base titration with sodium carbonate 0.1 N as the secondary solution. The concentration of sodium sulfate was calculated using the formula presented in Equation 1. Description: W is sample weight (g), N is the Normality of Na_2CO_3 (N), % w/w is weight percentage, EW Na_2SO_4 is 71.02 g/ek, Va is the volume of 0.1 N Na_2CO_3 for Sample Titration (mL), and Vb is the volume of 0.1 N Na_2CO_3 for Blank Titration (mL).

$$Na_2SO_4\,(\%b/b) = \frac{(Vb-Va)\ x\ N\ x\ 71.02}{W} \quad (1).$$

Analysis of ammonia was conducted using a UV-Vis spectrophotometer. Ammonia concentration can be calculated using the formula in equation 2, which is C = concentration in ppm and fp = Dilution Factor. The concentration value is the result of reading the test sample concentration from the calibration curve.

$$\text{Ammonia Concentration (mg N/L)} = C \times fp \quad (2).$$

This research will employ a factorial design with two factors: distillation process pressure (3 levels) and sulfuric acid concentration (5 levels).

RESULTS AND DISCUSSION

Effect of Pressure and Sulfuric Acid Concentration on the Sodium Sulfate Recovery Process

The effect of pressure and sulfuric acid concentration on the distillation of MIC waste is illustrated in Figure 3. Under atmospheric operating pressure conditions, the yield of sodium sulfate is directly proportional to the concentration of sulfuric acid in the waste, with an optimum sodium sulfate weight of 190.483 grams at a concentration of 0.30 M. The exact yield pattern is observed under vacuum pressure conditions, where the amount of sodium sulfate obtained at each sulfuric acid concentration is more significant than that at atmospheric pressure, with an optimum sodium sulfate weight of 214.916 g at a concentration of 0.30 M. In combined pressure conditions, the yield of sodium sulfate tends to increase with an increase in sulfuric acid concentration in the waste. However, a decrease in sodium sulfate yield occurs at a sulfuric acid concentration of 0.22 M, which may be due to the sulfuric acid having already reacted completely with sodium bicarbonate. In combined pressure variations, the optimum sodium sulfate weight obtained at a concentration of 0.30 M is 215.166 grams. Based on research conducted by the Research and Development Division, MIC waste contains sodium bicarbonate, a by-product of the reaction between NaOCN and water. The sodium bicarbonate in the MIC waste can react with sulfuric acid to produce sodium sulfate, water, and carbon dioxide.

An optimisation approach was applied by adjusting pressure and sulfuric acid concentration to determine the best conditions for sodium sulfate recovery. The goal was to ensure that the process was efficient and cost-effective and that no liquid waste was generated (in line with the zero liquid discharge principle). The right combination of pressure and H_2SO_4 concentration is crucial to maximising separation without producing brine (Bruinsma et al., 2021). The pressure and chemical conditions influence sodium sulfate deposition in supercritical water gasification, which aligns with Bruinsma et al. (2021), who found that optimising pressure and sulfuric acid concentration is crucial for efficient sodium sulfate recovery without producing brine (Zhang et al., 2019).

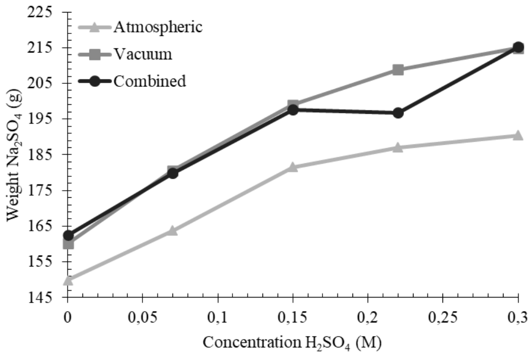

Figure 3. Effect of pressure conditions and sulfuric acid concentration on the quantity of sodium sulfate

Determination of the Optimal Pressure Conditions for the Sodium Sulfate Recovery Process

In this research, a series of experiments was conducted with variations in atmospheric, vacuum, and combined pressure to evaluate the effect of distillation pressure on the recovery rate of sodium sulfate and the purity of the final product.

Based on the experimental results, it was found that pressure significantly affects the quantity of sodium sulfate recovered. Among the tested conditions, vacuum pressure was the most optimal for sodium sulfate recovery. Under vacuum, solvent evaporation becomes more efficient, leading to a higher concentration of sodium sulfate in the solution and promoting maximum crystallisation. It is attributed to the reduction in vapour pressure, which accelerates the precipitation of sodium sulfate from the solution.

The data show that at a vacuum pressure of 60 mmHg, the weight of sodium sulfate obtained reached 192.73 g—the highest yield compared to 174.56 grams under atmospheric pressure and 190.35 grams under combined pressure. Vacuum distillation is widely recognised as one of the key methods used in various industries to efficiently separate components with high boiling points. Currently, many researchers are focusing on improving the efficiency of this process to support more environmentally sustainable production. Optimising Distillation temperatures adjusting holding times, and applying repeated partial condensation have significantly enhanced product purity (Xu et al., 2023).

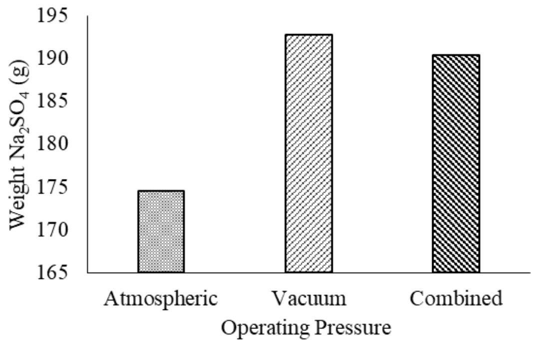

Figure 4. Effect of pressure conditions on the quantity of sodium sulfate

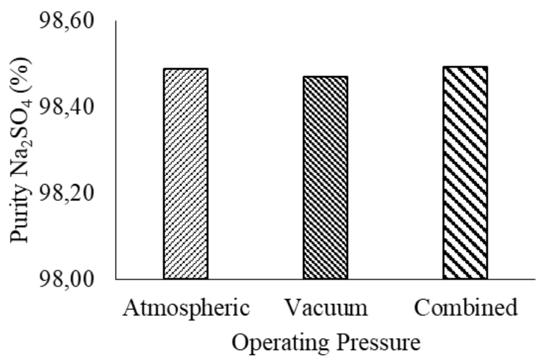

Figure 5. Effect of pressure conditions on the quality of sodium sulfate

The quality of sodium sulfate across

various pressure conditions is relatively consistent, with purity levels exceeding 98.450%, as shown in Figure 4. Under the combined pressure condition, the sodium sulfate product exhibits slightly higher purity, reaching 98.492%. The consistently high purity across all pressure variations suggests that MIC waste contains sodium sulfate that can be effectively recovered. The state that the reaction produces approximately 1.5 kg of solid waste (Na_2SO_4) for every 1 kg of MIC generated. Developing isocyanate protection strategies using castor oil modifications to enhance storage stability and performance as waterborne adhesive additives (Choi et al., 2020).

Effect of Sulfuric Acid Addition on the Sodium Sulfate Recovery

An experiment on the effect of sulfuric acid in the distillation of MIC waste was conducted by varying the sulfuric acid concentration in the total waste solution. Theoretically, adding sulfuric acid converts the sodium bicarbonate present in the MIC waste into sodium sulfate.

The experiment results demonstrate the effect of sulfuric acid addition on the quantity of sodium sulfate produced. As the concentration of sulfuric acid added to the MIC waste increases, more sodium sulfate can be recovered. Based on the research conducted by the Research and Development Division, sulfuric acid reacts with sodium bicarbonate to form sodium sulfate, thereby maximising the amount of sodium sulfate that can be effectively recovered.

Figure 6 shows that the quality of the produced sodium sulfate is in line with its quantity, where an increase in sulfuric acid concentration correlates with an increase in the purity of the sodium sulfate obtained. This research demonstrates that the addition of sulfuric acid significantly impacts the sodium sulfate recovery process from MIC waste, both in terms of quantity and quality. Adding sulfate compounds—either sodium sulfate or sulfuric acid—increases the efficiency and selectivity of the recovery process for specific metals or inorganic compounds (Mustafa, 2019). The addition of concentrated sulfuric acid to the solution can help adjust the acid content in the evaporation process, which can potentially affect the recovery of anhydrous sodium sulfate (Porvali et al., 2019)

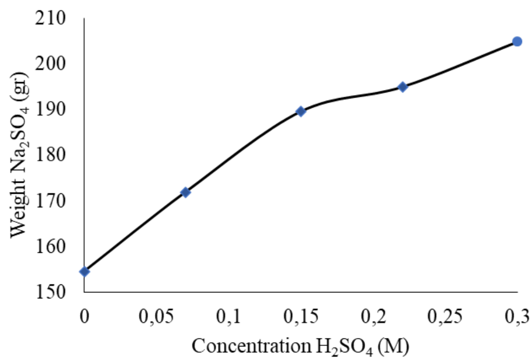

Figure 6. Effect of sulfuric acid addition on the quantity of sodium sulfate

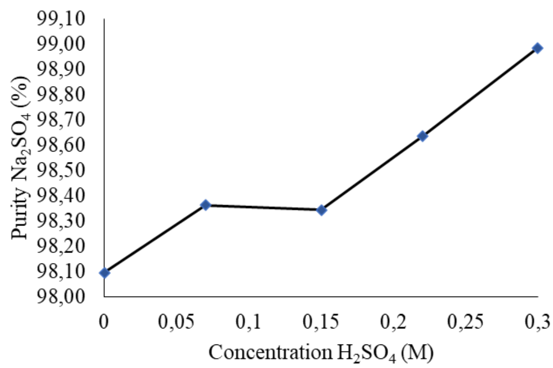

Figure 7. Effect of sulfuric acid addition on the quality of sodium sulfate

Analysis of Ammonia Content in Distillate.

Ammonia in MIC waste originates from the reaction between sodium cyanate and water. The analysis of ammonia content in the distillate is crucial as a reference for treating distillate

Table 1. Factorial ANOVA a x b

Source of Variation	dk	JK	KT	F_{Count}	F table	
					α = 0,05	α = 0,01
Average	1	1,508,791.30	1,508,791.30			
Treatment						
Pressure (A)	2	14,325.41	7,162.70	2,392.04	3.32	5.39
Cencentration (B)	4	2,838.47	709.62	236.98	2.69	4.02
A x B	8	407.16	50.89	17.00	2.27	3.17
Mistake	30	89.83	2.99			
Amount	45	1,526,452.16	-	-		

7 shows that under each operating condition, the ammonia concentration tends to decrease with an increase in sulfuric acid concentration. It is consistent, where NH_3 reacts reversibly with water to form NH_4OH. Temperature and pH significantly influence the equilibrium between NH_3 (unionised ammonia) and NH_4^+ (ionised ammonia). By lowering the pH, the solubility of ammonia in water increases. Adding sulfuric acid reduces the pH, producing less ammonia evaporation at higher sulfuric acid concentrations. Atmospheric pressure conditions yield higher ammonia levels than vacuum or combined pressure conditions, indicating the influence of temperature on the ammonia evaporation process.

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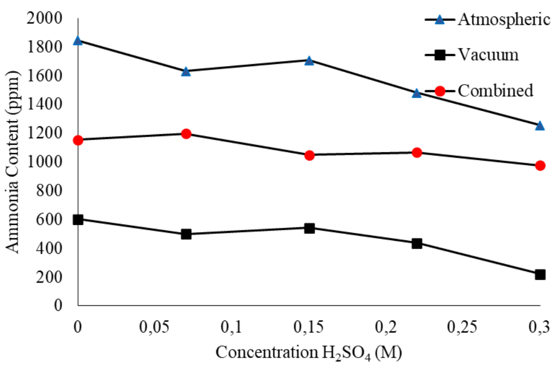

Figure 8. Ammonia content in distillate

The distillate obtained from the distillation process contains ammonia, which will form NH_4OH and can be used as a raw material for Struvite. Struvite ($NH_4MgPO_4 \cdot 6H_2O$) is a white crystal formed from the reaction between Mg^{2+}, NH_4^+, and PO_4^{3-} ions in a molar ratio 1:1:1 (Ariyanto et al., 2020).

Statistics

The method used in this research employs a factorial design with two factors: distillation pressure conditions with three levels and sulfuric acid concentration with five levels, each replicated three times.

Based on the calculations in the ANOVA table, the calculated F value for the factor of distillation pressure conditions is 2,392.04, which is greater than the F table value at a 95% confidence level of 3.32 and a 99% confidence level of 5.39. This indicates that the variable of distillation pressure conditions significantly affects the weight of the sodium sulfate obtained. For the variation in sulfuric acid concentration, the calculated F value is 236.98, more significant than the F table value at a 95% confidence level of 2.69 and a 99% confidence level of 4.02. This indicates that the sulfuric acid concentration variable also significantly affects the weight of sodium sulfate obtained. Strategies for clean production in the synthesis of methyl isocyanate (MIC)—a key intermediate in pesticide manufacturing, must focus on minimising emissions, improving reaction efficiency and ensuring the safety of workers and the surrounding environment.

One crucial aspect of this is the ability to detect exposure to MIC, a highly toxic compound, accurately. Liquid chromatography techniques have demonstrated high sensitivity in detecting exposure biomarkers. For example, Donkor et al. (2022) used this method to identify phenylmethyl carbamate released from haemoglobin following a reaction with MIC, offering a highly selective exposure verification approach. Incorporating such advanced analytical methods into clean production strategies strengthens occupational health monitoring and aligns with sustainable chemical manufacturing practices. Implementing clean production strategies in synthesising MIC for pesticide raw materials strongly supports several Sustainable Development Goals, particularly Good Health and Well-being, Clean Water and Sanitation, Industry, Innovation, and Infrastructure), and Responsible Consumption and Production. This research is highly beneficial, as it contributes to safer chemical manufacturing processes, reduces environmental pollution, and enhances occupational health monitoring.

CONCLUSION

In this research, the optimal condition for distilling MIC waste is under vacuum pressure. The vacuum pressure condition is more energy-efficient, requiring lower heat than other conditions. It results in the highest quantity of sodium sulfate, with an average weight of 192.76 grams. Adding sulfuric acid to MIC waste significantly increases the quantity of sodium sulfate produced. At a sulfuric acid concentration of 0.30 M, the highest quantity of sodium sulfate obtained was 214.916 grams. The addition of sulfuric acid reacts with the sodium bicarbonate contained in the MIC waste, thereby increasing the amount of sodium sulfate that can be recovered. The purity of the sodium sulfate produced in this study is relatively high, with an average purity above 98.45% under all pressure conditions. The highest purity was achieved under atmospheric pressure with a sulfuric acid concentration of 0.30 M, reaching 98.985%. Based on ANOVA analysis, both distillation pressure and sulfuric acid concentration have a highly significant effect on the quantity of sodium sulfate obtained, with the calculated F value being more significant than the F table value at the 95% and 99% confidence levels. This indicates that both of these variables play a crucial role in the recovery process of sodium sulfate from MIC waste.

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