

## STUDY OF THE EFFECT OF THE RATIO OF SULFURIC ACID TO NITRIC ACID IN THE SYNTHESIS OF NITROCELLULOSE FROM BIOMATERIALS AS AN ALTERNATIVE RAW MATERIAL

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### ABSTRAK

Dinamika lingkungan strategis global mendorong penguatan kemandirian industri pertahanan melalui pengembangan propelan berbasis nitroselulosa. Penelitian ini bertujuan untuk mengkaji pengaruh rasio campuran asam penitrasi terhadap kadar nitrogen dan karakteristik nitroselulosa berbasis selulosa biomaterial sebagai alternatif bahan baku propelan. Metode penelitian dilakukan melalui studi literatur sistematis terhadap publikasi ilmiah sepuluh tahun terakhir yang relevan dengan sintesis nitroselulosa, variasi rasio asam, serta kondisi reaksi. Hasil kajian menunjukkan bahwa kadar nitrogen nitroselulosa dipengaruhi secara signifikan oleh rasio  $H_2SO_4 : HNO_3$ , konsentrasi asam, suhu, dan waktu reaksi. Rasio asam dengan fraksi  $H_2SO_4$  rendah menghasilkan rendemen tinggi namun kadar nitrogen rendah, sedangkan peningkatan fraksi  $H_2SO_4$  hingga kondisi optimum meningkatkan derajat nitrasi dengan kadar nitrogen mencapai 13,39%, mendekati nilai teoritis 14,14%, bahkan pada kondisi tertentu mencapai 16,76%. Namun, rasio  $H_2SO_4$  yang berlebihan berpotensi menyebabkan degradasi selulosa sehingga menurunkan efektivitas reaksi.

Kata Kunci: Nitroselulosa, Biomaterial, Propelan.

### ABSTRACT

*The dynamics of the global strategic environment drive the strengthening of defense industrial self-reliance through the development of nitrocellulose-based propellants. This study aims to examine the effect of nitrating acid ratio on nitrogen content and the characteristics of nitrocellulose derived from bio-based cellulose as an alternative propellant raw material. A systematic literature review was conducted on relevant scientific publications from the past ten years, focusing on nitrocellulose synthesis, acid ratio variation, and reaction conditions. The results indicate that nitrocellulose nitrogen content is strongly influenced by the  $H_2SO_4:HNO_3$  ratio, acid concentration, reaction temperature, and reaction time. Lower  $H_2SO_4$  fractions produce higher yields but lower nitrogen content, whereas increasing the  $H_2SO_4$  ratio to an optimum level enhances the degree of nitration, yielding nitrogen contents up to 13.39%, approaching the theoretical maximum of 14.14%, and in certain conditions reaching 16.76%. However, excessive  $H_2SO_4$  leads to cellulose degradation, thereby reducing reaction efficiency.*

**Keywords:** Nitrocellulose, Biomaterials, Propellant.

### INTRODUCTION

The dynamics of the current global strategic environment are increasingly unpredictable, necessitating the optimization of supporting elements for national defense preparedness. National defense encompasses the maintenance of territorial integrity and regional stability, both of which face growing and complex challenges (Dwi Amanda et al., 2023). Consequently, defense industrial self-reliance is essential, defined as a country's capacity to independently produce major defense equipment to safeguard national sovereignty and security. In Indonesia, strengthening defense industrial self-reliance has become a strategic component of national development aimed at enhancing defense capabilities while reducing dependence on imported defense systems. This effort

is realized through the development of seven priority programs in the national defense industry, namely fighter aircraft, submarines, tanks, rockets, missiles, radar systems, and propellants. Within this framework, the development of the propellant industry represents a key strategy for supporting national defense autonomy (Efendie et al., 2022).

The propellant industry plays a critical role in meeting domestic ammunition requirements, as propellants function as fuels that generate thrust energy through controlled combustion and the release of high-temperature gases ((Restasari et al., 2019). However, the development of the propellant industry in Indonesia remains constrained by limited availability of raw materials, resulting in a high dependence on imports from countries such as Korea, Taiwan, Belgium, and Yugoslavia. Therefore, mastery of nitrocellulose-based propellant production technology is a crucial factor in achieving national self-sufficiency in propellant supply (Saragih et al., 2015).

Nitrocellulose is synthesized through the nitration of cellulose using a mixed acid system of nitric acid and sulfuric acid, in which nitro groups substitute hydrogen atoms in the hydroxyl groups of cellulose. This compound is widely utilized in defense applications as a propellant and energetic material for ammunition (Cahyono et al., 2023). Indonesia possesses abundant renewable cellulose resources, one of which is derived from biomaterials such as water hyacinth (*Eichhornia crassipes*), a fast-growing invasive aquatic plant that frequently disrupts aquatic ecosystems. Despite its negative environmental impact, water hyacinth exhibits significant potential as an environmentally friendly raw material due to its biodegradability and high cellulose content. The synthesis of nitrocellulose involves delignification, bleaching, and nitration stages, with hydrogen peroxide employed as a relatively safe bleaching agent that preserves cellulose integrity (Pramujo, 2020). The nitration process utilizes a mixture of nitric and sulfuric acids, where the nitrating acid ratio plays a decisive role in determining the nitrogen content and physicochemical characteristics of the resulting nitrocellulose. Nevertheless, studies addressing variations in nitrating acid ratios for the synthesis of nitrocellulose derived from water hyacinth cellulose remain limited. Therefore, this study aims to determine the optimum synthesis conditions for producing nitrocellulose suitable as a propellant raw material.

## **METHODOLOGY**

This study employed a literature review approach aimed at systematically collecting, examining, and evaluating scientific publications related to the effect of sulfuric acid-to-nitric acid ratios in the synthesis of nitrocellulose derived from biomaterials as alternative propellant raw materials. This approach was selected to provide a comprehensive understanding of previous research outcomes, while also identifying existing challenges and potential development opportunities in the utilization of biomaterial-based cellulose for propellant applications. Data were collected through a systematic search of academic databases, including Google Scholar, PubMed, and ScienceDirect. The literature search was conducted using relevant keywords associated with the influence of sulfuric acid to nitric acid ratios in nitrocellulose synthesis from water hyacinth (*Eichhornia crassipes*) cellulose, alternative propellant raw materials, and the development of Indonesia's propellant industry. The reviewed literature was limited to publications from the past ten years to ensure the relevance and currency of the analyzed data.

Literature selection was carried out using clearly defined inclusion and exclusion criteria. Included studies comprised articles employing valid research methodologies,

reporting scientifically significant findings, and addressing cellulose extraction processes, nitration stages in nitrocellulose production, and the application of biomaterials in ammunition or propellant industries. The selected literature was subsequently subjected to critical analysis and data synthesis to identify key methodological approaches and principal findings. The compiled data were compared and interpreted in relation to propellant performance requirements, with consideration given to economic and environmental aspects. Through this approach, the literature review is expected to provide a comprehensive assessment of the influence of sulfuric acid-to-nitric acid ratios on the synthesis of biomaterial-based nitrocellulose as an alternative propellant feedstock.

## RESULT AND DISCUSSION

Nitrocellulose is a highly flammable material with explosive potential. Its initiation can be triggered by open flames, mechanical impact, or sufficiently strong friction. Under normal storage and usage conditions, nitrocellulose is relatively stable; however, it must be protected from exposure to high temperatures, moisture, and other conditions that may induce degradation. During combustion, nitrocellulose generates a large volume of hot gases, including nitrogen, carbon dioxide, and water vapor. These gases contribute to the generation of thrust in propulsion systems that utilize nitrocellulose as a propellant material (Waruwu et al., 2013).

Indonesia possesses abundant cellulose resources, one of which is derived from biological sources, commonly referred to as biomaterials.

### Result

Table 1: Comparison of Nitrocellulose

Materials	Composition			Characteristics	
	Purity $\alpha$ -celullose (%)	Lignin Content (%)	Yield Nitrocelullose (%)	Nitrocelullose color	Nitrogen Content (%)
Straw	25-45	10-15	86	Yellowish	
Cotton	86-98	<5	68	White	
Water hyacinth	24,5	8,6	16,76		16,76
Pineapple leaf	69,5-71,5	12	86,2		11,56

Based on Table 1, nitrocellulose exhibits color variations ranging from white to yellow, which are influenced by the lignin content of the raw materials used. Lignin is one of the major structural components of cellulose and plays a significant role in imparting color to lignocellulosic fibers. The use of raw materials with relatively high lignin content in nitrocellulose production tends to result in products with a more yellowish appearance. In contrast, raw materials with lower lignin content generally yield nitrocellulose with a whiter coloration (P et al., 2012).

Halim et al., (2021) reported the use of a nitrating reagent consisting of 65% nitric acid (HNO<sub>3</sub>) combined with 98% sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) as a catalyst at a ratio of 1:2, with temperature variations applied during the nitration process. According to Saragih *et al.* (2009), the highest nitrogen functional group content was obtained at temperatures between 10°C and 20°C, as indicated by lower transmittance values compared to the ranges of 5°C–10°C and 15°C–20°C. In the present study, temperature variables of 10°C, 15°C, and 30°C were employed. The resulting outcomes are presented as follows:

Table 2: Correlation of time and temperature with nitrogen content

Temperature (°C)	15	30	45
	minutes	minutes	minutes
(%N)			
10	8,74	8,94	11,18
20	4,79	16,24	5,58
30	6,34	16,76	8,94

The data presented in the table indicate that increasing nitration temperature and prolonging reaction time generally lead to higher nitrogen content in fiber-derived nitrocellulose; however, reaction time exhibits an optimum point. This optimum condition was subsequently fixed as a constant parameter in the nitration process while varying the mixed acid ratio. This behavior can be attributed to the occurrence of reversible reactions, in which a portion of the product reverts to the reactants or the reaction rate shifts toward the reactant side, resulting in a decrease in the overall product yield beyond the optimum condition.

According to Setiadi et al., (2017), nitration was carried out using various nitrating acid ratios (1:2, 1:3, 1:4, 2:1, 7:3, 3:1, and 4:1), while other reaction parameters were maintained constant. The nitration process employed 95% sulfuric acid ( $H_2SO_4$ ) and 65% nitric acid ( $HNO_3$ ).

Table 3: Correlation of ratio with nitrogen content

No	$H_2SO_4 : HNO_3$	% Yield	% N
1	1 : 4	98,6 %	5,25 %
2	1 : 3	97,8 %	5,6 %
3	1 : 2	97,0 %	5,95 %
4	2 : 1	92,4 %	7,7 %
5	7 : 3	88,8 %	8,75 %
6	3 : 1	86,2 %	11,56 %
7	4 : 1	83,4 %	6,3 %

According to (Purnawan, 2010) Table 4 the nitration process was carried out using 65% nitric acid ( $HNO_3$ ) and 97% sulfuric acid ( $H_2SO_4$ ) and Table 5 4 the nitration process was carried out using 100% nitric acid ( $HNO_3$ ) and 97% sulfuric acid ( $H_2SO_4$ )

Table 4: Correlation of ratio with nitrogen content

No.	$H_2SO_4 : HNO_3$	Yield (%)	Content N (%)
1	1 : 8	54,42	1,48
2	1 : 6	36,40	3,17
3	1 : 4	33,29	5,53
4	1 : 2	32,76	2,19
5	2 : 1	31,73	1,87
6	3 : 1	34,62	1,29

At ratios above 4, nitrogen content decreased. This indicates that an excess of  $H_2SO_4$  leads to partial degradation of cellulose, reducing the amount of cellulose available for reaction. Similarly, increasing the  $HNO_3$  concentration shifts the reaction equilibrium toward greater product formation.

Table 5: Correlation of ratio with nitrogen content

No.	$H_2SO_4 : HNO_3$	Yield (%)	Content N (%)
1	1 : 8	155,33	13,25
2	1 : 6	153,57	13,31
3	1 : 5	152,34	13,39
4	1 : 4	151,22	13,27

5	1 : 3	150,36	12,87
6	1 : 2	149,28	12,29
7	2 : 1	133,05	11,97

According to Handono & Kusmartono, (2017), nitric acid (HNO<sub>3</sub>) at a concentration of 65% and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) at 95% were used as reagents in the nitration reaction of cellulose to produce nitrocellulose.

Table 6: Correlation of ratio concentration with nitrogen content

No.	H <sub>2</sub> SO <sub>4</sub> : HNO <sub>3</sub>	Produk (%)	N (%)
1	1 : 4	93,6	7,00
2	1 : 3	93,2	7,23
3	1 : 2	92,6	8,31
4	2 : 1	92,0	10,07
5	7 : 3	91,0	11,47
6	3 : 1	73,0	8,36
7	4 : 1	50,0	6,20

An increase in the H<sub>2</sub>SO<sub>4</sub> to HNO<sub>3</sub> ratio resulted in a decrease in product yield due to partial cellulose degradation and dissolution in sulfuric acid, leading to material loss during the filtration process. However, the mixed-acid ratio strongly influenced the nitrogen content, as H<sub>2</sub>SO<sub>4</sub> acts both as a catalyst and a dehydrating agent that binds water generated during the nitration reaction. At low H<sub>2</sub>SO<sub>4</sub> ratios, unbound water inhibits the substitution of hydroxyl (–OH) groups by nitro (–NO<sub>2</sub>) groups. Conversely, increasing the H<sub>2</sub>SO<sub>4</sub> fraction reduces the activation energy and enhances the reaction rate up to an optimal condition. The maximum nitrogen content was achieved at an H<sub>2</sub>SO<sub>4</sub>:HNO<sub>3</sub> ratio of 7:3, reaching 11.47%, whereas higher ratios led to a decline in nitrogen content due to cellulose degradation. This value is considered favorable when compared with the theoretical maximum nitrogen content of nitrocellulose (14.14%).

According to Rizkiah et al., (2021), a 65% nitric acid (HNO<sub>3</sub>) solution and a 95% sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) solution were employed as nitrating agents in the conversion of cellulose into nitrocellulose.

Table 7: Correlation of ratio concentration with nitrogen content

No.	H <sub>2</sub> SO <sub>4</sub> : HNO <sub>3</sub>	N (%)
1	1 : 1	12,26
2	2 : 1	13,23
3	3 : 1	12,97

As shown in the table, all experimental variations meet the nitrogen content requirement for propellant applications, exceeding the minimum standard of 11%. The highest nitrogen content was obtained in sample B at an H<sub>2</sub>SO<sub>4</sub>:HNO<sub>3</sub> ratio of 2:1, achieving a nitrogen content of 13.23%.

## Discussion

The nitration of cellulose to nitrocellulose is strongly affected by the nitrating acid ratio, acid concentration, reaction temperature, and reaction time, which collectively govern nitrogen content and product yield. The use of 65% HNO<sub>3</sub> and 98% H<sub>2</sub>SO<sub>4</sub> at a 1:2 ratio demonstrates that increasing temperature and reaction time up to an optimum enhances the degree of nitration, yielding a maximum nitrogen content of 16.76% at 30 °C for 30 min (Halim *et al.*, 2021). However, excessive reaction time leads to a decrease in nitrogen content due to cellulose degradation, consistent with the reversible nature of the nitration process (Saragih *et al.*, 2009). Previous studies reported that higher HNO<sub>3</sub> fractions result in high yields but relatively low nitrogen contents (5.25–5.95%), whereas increasing the H<sub>2</sub>SO<sub>4</sub> fraction improves nitrogen incorporation up to 11.56% at a 3:1 ratio,

albeit with reduced yield, confirming the critical role of H<sub>2</sub>SO<sub>4</sub> as both a catalyst and an effective dehydrating agent (Setiadi *et al.*, 2017).

Studies employing highly concentrated acids, such as 100% HNO<sub>3</sub> and 97% H<sub>2</sub>SO<sub>4</sub>, achieved higher nitrogen contents ranging from 11.97% to 13.39%, approaching the theoretical maximum of 14.14%, although excessive acidity increases the risk of cellulose degradation and reduced product stability (Purnawan, 2010). At moderate acid concentrations, optimum nitrogen contents of 11.47–13.23% were obtained at H<sub>2</sub>SO<sub>4</sub>:HNO<sub>3</sub> ratios between 7:3 and 2:1, fulfilling the minimum nitrogen requirement for propellant-grade nitrocellulose (>11%) (Handono & Kusmartono, 2017; Rizkiah *et al.*, 2021). In contrast, low H<sub>2</sub>SO<sub>4</sub> ratios provide insufficient dehydration, limiting –OH to –NO<sub>2</sub> substitution, while excessive H<sub>2</sub>SO<sub>4</sub> promotes cellulose destruction and reduces nitration efficiency. Overall, these findings indicate that achieving high-quality nitrocellulose requires balanced optimization of acid ratio, concentration, temperature, and reaction time to ensure effective nitration without compromising cellulose integrity.

## CONCLUSION

The nitrogen content of nitrocellulose is influenced by the nitrating acid ratio, concentration, and reaction conditions. The optimum H<sub>2</sub>SO<sub>4</sub>:HNO<sub>3</sub> ratio increases the degree of nitration and produces a nitrogen content of up to 13.39%, approaching the theoretical value of 14.14%, and even reaching 16.76% under certain conditions. However, excess H<sub>2</sub>SO<sub>4</sub> can cause cellulose destruction, thus reducing the effectiveness of the reaction.

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