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A SUSTAINABLE AND EFFICIENT APPROACH TO BROMOETHAN SYNTHESIS

Keywords: ethyl bromide, residual aqueous acid solution, thiols, regenerated sodium bromide.

An optimized and sustainable method for the synthesis of ethyl bromide (C_2H_5Br) via the reaction of ethanol with a halide salt (KBr/NaBr) in the presence of concentrated sulfuric acid (H_2SO_4) has been presented. The molar ratios of 1:1.2:2:5, 1:1.2:4.5:11.2, and 1:2:3.5:13.2 (KBr/NaBr: C_2H_5OH:H_2SO_4: H_2O) depending on the order of reagent mixing were found to favor higher yields. In addition, other factors like synthesis duration, temperature and catalyst were also studied. The overall maximum achieved yield was 93-95%. To address the large excess of acid when a molar ratio 1:1.2:4.5:11.2 and 1:2:3.5:13.2 is used, a closed-loop recycling approach was introduced: the residual aqueous acid solution from the first synthesis was reused in subsequent batches by adjusting the H_2SO_4, stoichiometry to 1.1-2.1 equivalents, minimizing waste without compromising efficiency. In order to save the cost of the reagents, especially the halide salts for the synthesis process and address environmental risks associated with the discharge of sodium bromide as a byproduct, regenerated sodium bromide from a classical method of thiol synthesis process was utilized in the preparation of ethyl bromide under same conditions which also resulted in obtaining high yields. The effectiveness of the synthesis process using sodium bromide solution has also been presented. The obtained product from sodium bromide solution also exhibited high purity profile same as the product obtained from commercial halide salts. The product was isolated by simple distillation and characterized by gas chromatography and boiling point confirming high purity. The presented results has also shown the potential application of the synthesis process at a larger scale.

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УСТОЙЧИВЫЙ И ЭФФЕКТИВНЫЙ ПОДХОД К СИНТЕЗУ БРОМОЭТАН

Ключевые слова: бромоэтан, остаточный водный раствор кислоты, тиолы, регенерированный бромид натрия.

Представлен оптимизированный и надежный метод синтеза бромистого этила (C_2H_5Br) путем взаимодействия этанола с галогенидной солью (KBr/NaBr) в присутствии концентрированной серной кислоты (H_2SO_4). Было обнаружено, что молярные соотношения 1:1.2:2:5, 1:1.2:4.5:11.2, и 1:2:3,5:13,2 (KBr/NaBr: C_2H_5OH:H_2SO_4:H_2O) в зависимости от порядка смешивания реагентов способствуют повышению выхода. Кроме того, были изучены и другие факторы, такие как продолжительность синтеза, температура и катализатор. Общий максимальный достигнутый выход составил 93-95%. Для устранения большого избытка кислоты при использовании молярных соотношений 1:1,2:4,5:11,2 и 1:2:3,5:13,2 был применен метод рециркуляции по замкнутому циклу: остаточный водный раствор кислоты из первого синтеза повторно использовали в последующих партиях, доводя стехиометрию H_2SO_4 до 1,1-2,1 эквивалента, что сводит к минимуму количество отходов без ущерба для эффективности. Для снижения затрат на процесс синтеза и устранения экологических рисков, связанных с выделением бромида натрия в качестве побочного продукта, для получения бромистого этила в тех же условиях был использован регенерированный бромид натрия, полученный в процессе синтеза тиола, что также привело к получению высоких выходов. Полученный продукт из раствора бромида натрия также продемонстрировал высокую степень чистоты, аналогичную продукту, полученному из коммерческих галогенидных солей. Продукт был выделен путем перегонки и охарактеризован с помощью газовой хроматографии и температуры кипения, подтверждающих его высокую чистоту. Представленные результаты также продемонстрировали потенциальную возможность применения процесса синтеза в более крупных масштабах.

Introduction

Ethyl bromide (bromoethane, C_2H_5Br) is a colorless, versatile, flammable alkyl halide liquid with an ether-like odor and has significant applications in organic synthesis like in Grignard reactions [1,2] and as an ethylating agent in various chemical reactions [3-8]. C_2H_5Br is also used as a raw material for the synthesis of pesticides, pharmaceuticals, as a refrigerant, and a fumigant [9-12].

The growth of industrial sectors has led to an increased demand for ethyl bromide, thereby necessitating the development of safe and efficient synthesis processes to meet this demand.

Many traditional chemical methods have been studied and applied to synthesize ethyl bromide, through different reaction mechanisms. One of the earlier methods of synthesis presented is the free radical halogenation substitution reactions of alkanes in which a halogen atom replaces a hydrogen atom from an alkane [13]. In the case of ethyl bromide synthesis, a mixture of ethane and Br_2 either as gases or in a solvent are irradiated with ultraviolet (UV) or visible light. The bromination process can be grouped into two categories called initiation and propagation [14]. This method is advantageous as it involves the direct use of ethane, a cheap hydrocarbon and it does not require strong acids or phosphorus reagents. However, low selectivity of the product comes as a result of the formation of multiple brominated products like di-and tri- brominated ethane.

Ethyl bromide can be obtained from the reaction of Phosphorus tribromide (PBr_3) with ethanol. The reaction is a substitution reaction where the hydroxyl group (-OH) of ethanol is replaced by a bromine atom [15,16]. Like other alkyl bromides, ethyl bromide can be prepared by reacting the alcohol with an adduct formed by the reaction of triphenylphosphine and bromine. In the synthesis, the alcohol displaces bromide ion from the pentavalent adduct giving an alkoxy phosphonium intermediate. The intermediate phosphonium ion then undergoes nucleophilic attack by bromide ion, displacing triphenylphosphine oxide [17]. One of the methods that is widely interested and applied due to its high efficiency is the synthesis of Ethyl bromide through the reaction of ethanol with hydrobromic acid directly or through the reaction of ethanol with halide salt (KBr/NaBr) in the presence of sulfuric acid [18,19]. Earlier literature data on this method has shown that the excess use of alcohol leads to the formation of ether which reduces the yield of the desired product when treating the crude ethyl bromide for the removal of ether [20]. Another disadvantage of the method is the harmful and corrosive nature of HBr when directly used [21,22]. Ethyl bromide is also synthesized by the reaction of ethylene with HBr [23,24] or via nucleophilic substitution methods like the Appel reaction using carbon tetrabromide as a halide source [25,26]. However, the cost and availability of the reagent make its use avoided on an industrial scale.

Despite the widespread application of ethyl bromide, its synthesis faces several challenges like low yields due to the formation of byproduct and costly reagents in most of the methods. Other challenges include the use of reagents with a corrosive nature like liquid or gas hydrogen bromide and phosphorus tribromide.

One of the solutions to reduce the cost of the synthesis process is to save the maximum amount of reagents. In our experience with the process of thiol synthesis from alkyl bromides and sodium hydrosulphide (NaHS), a large amount of NaBr (40-50wt.%) is produced and not recycled for use in chemical processes, its discharge poses significant environmental risks due to the high mobility and persistence of the bromide anion (Br□). Once in the aquatic environment, Br□ facilitates the formation of genotoxic brominated disinfection byproducts (DBPs) in public water supplies, raising serious ecological and health concerns [27-30]. To mitigate this issue and adhere to green chemistry principles and at the same time reducing the cost of the synthesis, a sustainable approach to C_2H_5Br synthesis in this work was taken and it involved the utilization of NaBr solution, a byproduct generated from a conventional process of preparing alkyl thiols from alkyl bromides and sodium hydrosulphide (NaHS) [31].

In this study, the synthesis of ethyl bromide from ethanol and halide salts in acidic medium was systematically and thoroughly carried out to optimize the reaction conditions thereby improving the yield and quality of the product. Specifically, factors such as molar ratio of reactants and mixing order of reagents were carefully adjusted and studied to determine the optimal conditions for the synthesis of ethyl bromide. Commercial KBr/NaBr was used as halogen source to evaluate the conversion of ethanol to ethyl bromide under different conditions, thereby determining the most suitable reaction parameters.

In addition, a sustainable process was proposed based on the recycling principle, in which NaBr recovered from thiol synthesis was reused in the synthesis of ethyl bromide. This method not only helps to reduce the consumption of input materials but also contributes to improving the sustainability of the production process without reducing the reaction efficiency or the quality of the final product. The results show that the optimization of reaction conditions and the application of the circular process have contributed to improving the economic and environmental efficiency of ethyl bromide synthesis process in the research scope.

Experimental

Reagents

Reagents employed in this study possess high purity levels and do not require further purification, including: NaBr (98.94%, Russia), KBr (98.94%, Russia), Na_2CO_3 (99.8%, Russia), $ZnSO_4{*}7H_2O$ (98%, China), K_2CrO_4 (99.5%, China), $AgNO_3$ (99.9%, China), ethanol (99.7%, Russia), concentrated H_2SO_4(98.0%, Russia).

The salt solution containing 40-50wt. % NaBr was obtained as a by-product from the synthesis of thiols from sodium hydrosulfide and alkyl halides at the Center "AhmadullinS" LLC, Kazan, Russia.

Analytical methods

Mohr method was used to determine the content of NaBr in the solution obtained from the synthesis of thiols. The method involves the direct titration of bromides with a solution of silver nitrate in the presence of potassium chromate indicator, with the formation of an insoluble precipitate. In this research work, the first stage of the analysis involved the precipitation of sulfides and hydrosulfides followed by titration. Titration is carried out in neutral or slightly alkaline solutions at pH from 6.5 to 10 [32].

The percentage weight of sodium bromide *(X_{NaBr})* was determined by the formula:

$$X_{NaBr} = \frac{V_1 \cdot 0.01029 \cdot V_2 \cdot 100}{m \cdot V_3}$$

where V_1 is the volume of 0.1 M silver nitrate solution consumed for titration, mL;

V_2 – total filtrate solution, mL;

V_3 – is the volume of filtrate taken for analysis, mL;

0.01029– is the mass of sodium bromide in grams, corresponding to 1mL of 0.1M silver nitrate solution;

m – is the mass of the byproduct solution,

In the case of an incomplete thiol reaction process, the presence of residual sulfide ions (S^2□) in the sodium bromide byproduct solution was quantitatively monitored using potentiometric titration method UOP-209-00. The analysis is based on the precipitation titration of sulfide ions with silver nitrate. The endpoint of the titration is determined potentiometrically by monitoring the change in potential of a silver/sulfide ion-selective electrode relative to a reference electrode. A sharp change in the millivolt (mV) reading indicates the point at which all sulfide ions have been precipitated as silver sulfide (Ag□S) [33].

The purity of the synthesized ethyl bromide and the identification of potential organic impurities were determined using Gas Chromatography with a flame ionization detector (GC-FID Khromatek-Kristall 5000, № 254183). Chromatographic separation was performed on a Khromatek-Kristall 5000 gas chromatograph (serial number: 254183) equipped with a split/splitless injector and a flame ionization detector (FID). Separation was achieved using an HP-FFAP capillary column (50 m length × 0.32 mm internal diameter × 0.5 µm film thickness), which is a polar stationary phase suitable for the separation of volatile organic compounds and acids.

The analysis was carried out under the following optimized conditions: Injector; temperature was set at 150 °C, operating in split mode with a split ratio of 30:1; carrier gas: Helium was used at a constant flow rate of 2.3 mL/min; oven temperature program: The initial oven temperature was held at 35 °C for 10 minutes, followed by a ramp of 6 °C/min to a final temperature of 150 °C, which was then held for 20 minutes. The total runtime was 49.17 minutes: Detector; the FID temperature was maintained at 250 °C. The detector gases were set at flows of 250 mL/min for air and 25 mL/min for hydrogen~~.~~

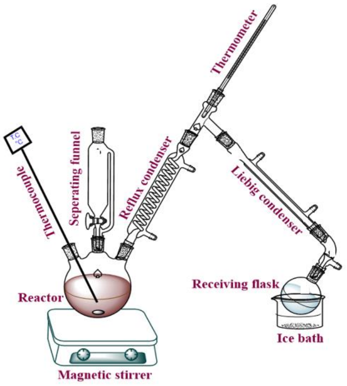
Experimental procedure

The synthesis of ethyl bromide was carried out using the halide salts, potassium bromide (KBr, 36.19% solution) and sodium bromide (NaBr, 53.59% solution), in a 2-liter three-neck round-bottom flask (RBF) placed on a magnetic stirrer IKA, C-MAG HS 7 as shown in **Scheme 1**. The three-neck round-bottom flask was equipped with a thermocouple, a cooling system, and a 250 ml product collection flask.

The synthesis of ethyl bromide was carried out as follows: the potassium bromide/sodium bromide solution was added to the three-neck round-bottom flask and stirred at a stirring speed of 1000 rpm. For the synthesis using potassium bromide, 236 mL of ethanol was added to the flask, followed by 813 mL of concentrated sulfuric acid being added dropwise to the mixture to ensure that the reaction temperature did not exceed 40°C. The resulting mixture was then heated to 120 for 5 hours. After the reaction was completed, the reaction mixture was cooled, and the aqueous acid solution was separated from the salt. The resulting ethyl bromide was washed with water and dried with CaCl□.

For the synthesis of ethyl bromide from sodium bromide, a mixture of 450 mL of ethanol and 603 mL sulfuric acid was added dropwise to the reaction flask containing the sodium bromide solution while stirring. After the reaction was completed, the resulting mixture was distilled to separate the ethyl bromide. The mixture was slowly heated for about 6 hours, after which the product was washed with water and dried with CaCl□.

In another synthesis, after determining the content of NaBr in the byproduct solution, 1500g of the solution was mixed with ethanol 242 mL in a 5-liter three-necked RBF. While mixing, H_2SO_4 1055mL was added dropwise. After all the acid was added, the mixture was slowly heated up to 120°C for 6h after which the product was washed with water and dried with $CaCl_2$.



Scheme 1 - Experimental scheme for the synthesis of ethyl bromide from NaBr/KBr and ethanol in the presence of sulfuric acid

Results and discussion

Optimization of ethyl bromide synthesis from pure KBr/NaBr

To obtain higher yields in the synthesis of ethyl bromide, different molar ratios of KBr/NaBr: C_2H_5OH:H_2SO_4: H_2O were used. It was noticed that the reagent mixing order during the synthesis slightly affected the yield of the product.

When the order of reagent mixing used was adding ethanol to a salt solution of KBr/NaBr followed by the dropwise addition of H_2SO_4, the highest yields of up to 91% based on the salt were obtained at a C_2H_5OH:H_2SO_4: H_2O ratio of 1:1.2:3.5:13.2 **(Fig. 1a)**. Since the reaction is an equilibrium process, moderate excess ethanol in this case improves the conversion of KBr/NaBr to C_2H_5Br by shifting the equilibrium toward the product. However, there should be a limit to the excess ethanol used as the molar ratio 1:>2 of KBr/NaBr: C_2H_5OH led to low yields as treating the obtained C_2H_5Br having large amounts of ether led to the reduction in the quantity of the main product.

An increase in the yield of C_2H_5Br was observed when excess acid was added to the reaction. Depending on the order of reagent mixing, and or the ratio of the halide salt to other reagents, a ratio KBr:H_2SO_4: H_2O of 1:2:5 and a ratio KBr:H_2SO_4: H_2O of 1:4-6:13.2 produced higher yields compared with earlier literature [20]. A moderate excess acid ratio1:4-6 of KBr:H_2SO_4 led to yields of up to 93% of C_2H_5Br **(Fig. 1b)**. This can be explained by the complete conversion of KBr/NaBr to HBr which maximizes the amount available for ethyl bromide formation. H_2SO_4 also drives the reaction forward as it absorbs water, shifting the equilibrium towards ethyl bromide production (Le Chatelier's principle). Exceeding the acid ratio i.e. 1:7 of KBr:H_2SO_4 led to a reduction of C_2H_5Br yield possibly due to the oxidation of HBr to Br_2. Excess H_2SO_4 also slightly promoted diethyl ether ($C_2H_5OC_2H_5$) formation.

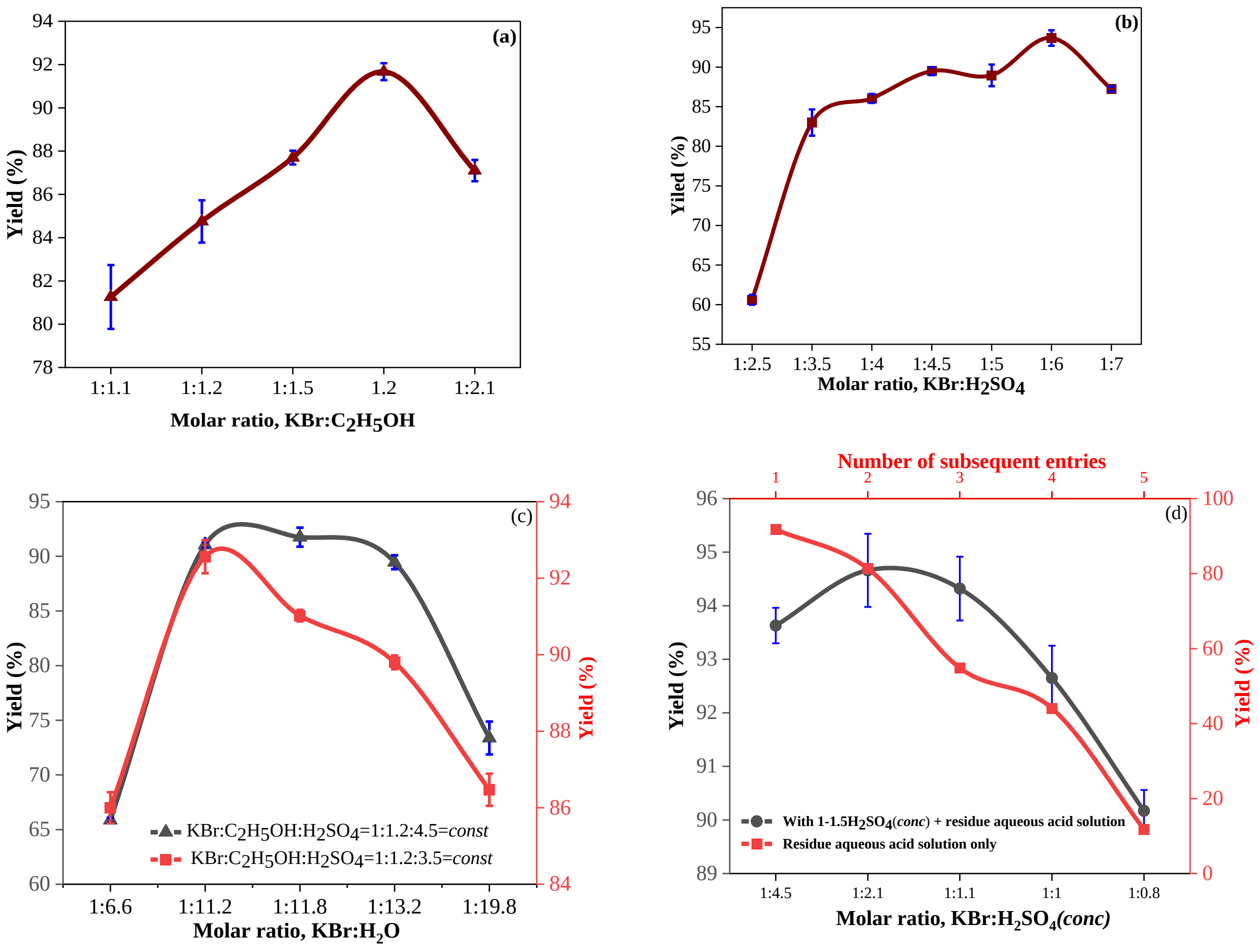


Fig. 1 - C_2H_5Br yield dependence on the molar ratios of KBr: C_2H_5OH:H_2SO_4: H_2O when heated to 120°C for 4-6h (a-c), d – reuse of residue aqueous acid solution with and without the addition of concentrated sulfuric acid

In the literature [20], C_2H_5Br was synthesised with and without H_2O by mixing the acid and ethanol followed by the addition of the salt. The maximum yield obtained was 85% after preparing with and without using H_2O. When we tried to synthesis ethyl bromide without water with the mixing order ethanol, salt then acid, yields of less than 50% were obtained due to the loss of *in situ* formed HBr that escaped from the reaction mass. Adding water to the reaction reduced the amount of the HBr lost which led to an increase in the yield. Adding just enough water to dissolve the salt followed by the addition of ethanol then acid led to yields ≥ 90 % of C_2H_5Br **(Fig. 1c)**. However, there is a limit to the quantity of water that should be added. Adding excess H_2O led to the reduction in the yield of the product probably due to the shifting of the equilibrium to the left, promoting the reverse reaction i.e. the hydrolysis of ethyl bromide back into C_2H_5OH and HBr. Low yields might also be due to the dilution of HBr and ethanol which may lead to the reduction of effective collision rate resulting in incomplete conversions. Since the acid in the reaction acts as a proton source to generate HBr from KBr/NaBr and as a dehydrating agent to drive the reaction forward by removing water, excess water might dilute the acid reducing its effectiveness in both roles. It was noticed that the yields of C_2H_5Br with a constant ratio KBr: C_2H_5OH of 1:1.2 slightly differed depending on the ratio of KBr: H_2SO_4. Higher yields were obtained when 1:4.5 ratio of KBr: H_2SO_4 was used compared to a 1:3.5 ratio with 1:11-20 ratios of KBr: H_2O in both cases **(Fig. 1c)**.

To address the excess sulfuric acid used in the synthesis, the residual aqueous acid solution from the one synthesis was reused in subsequent batches by adjusting the H_2SO_4, stoichiometry to 1.1-2.1 equivalents and without adding H_2O to the reaction as the quantity of water from the residual aqueous acid solution is enough for the synthesis **(Fig. 1d)**. High yields were obtained when the residual aqueous acid solution was utilized together with small quantity of concentrated H_2SO_4 whereas, when the residual aqueous acid solution was utilized in a synthesis without additional concentrated sulfuric acid (i.e., only KBr, C_2H_5OH, and residual aqueous acid solution in the synthesis), a drop in the product yield was observed **(Fig. 1d)**.

Since the reaction proceeds via protonation of ethanol by H_2SO_4 to form a better leaving group (H_2O), followed by nucleophilic attack by bromide (Br-), diluted acid provides fewer H^+ ions, slowing the protonation step and reducing the concentration of the reactive intermediate ($C_2H_5OH_2^+$) **(Scheme. 2)**. This is accompanied by lower reaction rate and yield respectively. Reusing the residual aqueous acid solution minimizes waste without compromising the efficiency of the synthesis.

$$C_2H_5OH + H^+ \rightleftharpoons C_2H_5OH_2^+ \quad \textbf{(Protonation of ethanol)}$$

$$C_2H_5OH_2^+ + Br^- \longrightarrow C_2H_5Br + H_2O \quad \textbf{(S}_\textbf{N}\textbf{2 Substitution)}$$

Scheme 2 - Reaction mechanism of C_2H_5Br synthesis

To reduce the volume of the reaction mass especially when preparing C_2H_5Br in large amounts, a 1:1.2:2:5 ratio of KBr/NaBr: C_2H_5OH:H_2SO_4: H_2O was employed. When the order of reagent mixing was salt solution followed by C_2H_5OH and then dropwise additional of H_2SO_4, the maximum yield obtained was 88±0.8963%. At the ratio 1:5 of KBr/NaBr: H_2O, reducing the amount of ethanol or sulfuric acid i.e. 1:<1.2 ratio of KBr/NaBr: C_2H_5OH and 1:<2 ratio of KBr/NaBr: H_2SO_4 respectively, led to the drop in the percentage yield of the product. Adding a salt solution to a mixture of C_2H_5OH and H_2SO_4 also gave yields of up to 88%. One disadvantage of this order of reagent mixing was the crystallization of the salt in the separating funnel during the dropwise addition of the solution to the ethanol-acid mixture. The solution was saturated as the water was not enough to dissolve all the salt. When the reagent mixing order was changed to the dropwise addition of ethanol-acid mixture to the salt solution using 1:1.2:2:5 ratio of KBr/NaBr: C_2H_5OH:H_2SO_4: H_2O, yields of up to 91% were obtained.

Optimization of of ethyl bromide synthesis from sodium bromide solution (a by-product of thiol synthesis reaction)

The conventional synthesis of alkyl bromides, including ethyl bromide, typically relies on the use of commercially sourced, reagent-grade sodium or potassium bromide. While effective, this approach overlooks significant opportunities for waste minimization and resource efficiency within the chemical industry. Hitherto, this work addressed this limitation by implementing a circular economy model for the bromide ion source. Sodium bromide, a byproduct generated from a conventional process of preparing alkyl thiols from alkyl bromides and sodium hydrosulphide (NaHS) **(Scheme 3)** was utilized. After thiol production, the aqueous solution containing dissolved NaBr was filtered and prepared for actual concentration determination. Depending on the thiol reaction process the byproduct solution obtained may also contain small amounts of sulfide from unreacted NaHS (**Table 1**). Potentiometric titration method was used to determine the residual sulfide ions. This method was critical for ensuring the effective purification of NaBr and for verifying the success of the sulfide removal protocol prior to its use in ethyl bromide synthesis. The sulfide was removed by adding sulfuric acid to the solution. The produced hydrogen sulfide was trapped in an alkaline solution.

$$R\text{-}Br + NaHS \longrightarrow R\text{-}SH + NaBr$$

Scheme 3 - Synthesis of thiols from alkyl halides and sodium hydrosulphide

Table 1 - Thiol byproduct solution content

№ of entries	Byproduct solution yield, g	NaBr, wt. %	S^{2-}, wt. %
1	250	46	0.34
2	500	44	1.12
3	1000	43	1.23
4	1500	42	2.44
5	2000	42	2.40

Before experiments were conducted to optimize the synthesis of C_2H_5Br from sodium bromide solution obtained from a thiol synthesis process, a sample of NaBr solution was titrated with silver nitrate ($AgNO_3$) using potassium chromate (K_2CrO_4) as an indicator (Mohr's method). The endpoint is marked by the formation of a reddish-brown silver chromate (Ag_2CrO_4) precipitate, indicating complete precipitation of AgBr. The NaBr concentration is calculated based on $AgNO_3$ consumption. The quantity of NaBr obtained depends on the degree of completion of the thiol synthesis process. To prepare C_2H_5Br calculated amount of ethanol was added to the salt solution followed by dropwise addition of sulfuric acid while stirring. Yields of up to 95% were obtained after a duration of 4-6h and reaction mass temperature of up to 120°C. Using a moderate excess of acid and ethanol (0.2 ratio of salt to acid and 0.8 ratio of salt to ethanol) like in other reactions with pure halide salts showed an increase in the yield of the product (**Fig. 2**). The optimized parameters of ethyl bromide synthesis from sodium bromide byproduct solution showed high effectiveness (**Fig. 3).**

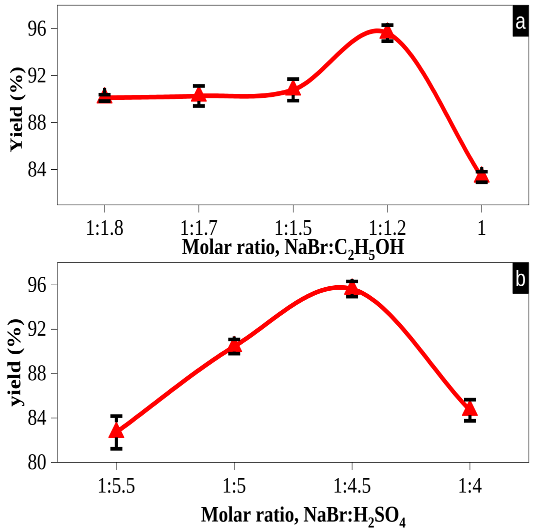


Fig 2 - (a) C_2H_5Br yield dependence on the molar ratio of an aqueous salt solution (from the synthesis of thiols) to ethanol when heated to 120°C for 4-6h. NaBr: H_2SO_4=1: 4.5= const, (b) C_2H_5Br yield dependence on the molar ratio of an aqueous salt solution (from the synthesis of thiols) to H_2SO_4 when heated to 120°C for 4-6h. NaBr: C_2H_5OH=1: 1.2 = const

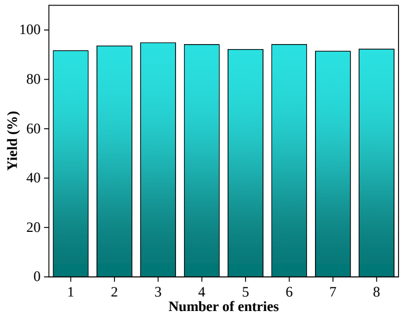


Fig. 3 - Effectiveness of ethyl bromide synthesis from NaBr byproduct solution (mole ratio, NaBr:C_2H_5OH:H_2SO_4=1:1.2:4.5)

To further evaluate the efficiency of the synthesis procedure, using both commercial and regenerated sodium bromide (NaBr), the purity of the ethyl bromide obtained was determined by gas chromatography (GC) and distillation. The product when distilled was obtained at 38°C.

Chromatographic analysis of the ethyl bromide sample synthesized from commercial NaBr revealed a high degree of purity. The primary peak in the chromatogram, corresponding to ethyl bromide, was dominant, accounting for 99% of the total integrated area with minor impurities, constituting 1% of the total composition **(Fig. 4a)**. A consistent and identifiable peak was attributed to diethyl ether, a common by-product known to form under the reaction conditions from the acid-catalysed dehydration of ethanol [19]. Additional, very minor peaks were observed and classified as unknown impurities

Remarkably, the ethyl bromide produced from the regenerated NaBr—obtained as a byproduct from thiol synthesis exhibited a virtually identical purity profile **(Fig. 4b)**. The GC chromatogram was largely superimposable with that of the product from commercial sources. The target ethyl bromide peak again constituted 99% of the ethyl bromide. Diethyl ether and other impurities constituted 1% of the total composition.

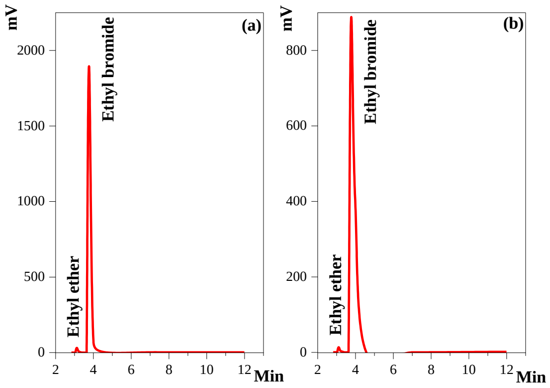


Fig. 4 - Overlaid gas chromatograms of ethyl bromide synthesized from commercial NaBr (a) and regenerated NaBr (b). The major peaks at 3.763 and 3.772 min corresponds to ethyl bromide. Analytical conditions: HP-FFAP column (50 m × 0.32 mm × 0.5 µm), split injection (30:1), temperature program: 35°C (hold 10 min) to 150 °C at 6 °C/min (hold 20 min)

This parity in purity between the two products is a significant and strongly indicates that the regeneration and purification process applied to the waste NaBr solution was highly effective in removing organic contaminants and inorganic salts that could have otherwise acted as catalysts for side reactions or introduced new impurities. The fact that the impurity profile is unchanged suggests that the side-reaction are inherent to the reaction chemistry between ethanol and hydrobromic acid in situ, and are not influenced by the origin of the bromide ion, provided it is of sufficient purity.

Factors affecting the synthesis of ethyl bromide

Effect of Temperature and duration of the synthesis

With regards to the temperature and duration of ethyl bromide synthesis, high yields are obtained by slowly heating the reaction mass so as to maintain lower boiling temperature for the product distillation and to also allow the complete reaction of C_2H_5OH. Abruptly heating the reaction mass leads to a rapid increase of the boiling temperature enabling most of the ethanol to be distilled off before it completely reacts with the HBr. Heating of the reaction mass was stopped when the distillation of the product stopped and in other cases when the boiling temperature was close or equal to 80-100°C as only water was distilled off.

The duration of the reaction therefore varies according to the heating of the reaction mass and in our case, it usually takes 4-6 hours with reaction mass temperature of up to 117-120°C from the temperatures of the first drop of product during distillation (**Table. 2**).

Effect of $ZnCl_2$ Catalyst on the synthesis

In an effort to enhance the synthesis of C_2H_5Br from C_2H_5OH and KBr/NaBr in the presence of an acid, zinc chloride ($ZnCl_2$) was tested as a potential catalyst. However, the addition of $ZnCl_2$ did not improve the yield of ethyl bromide compared to the uncatalyzed reaction. It was observed that increasing the quantity of $ZnCl_2$ led to a progressive decrease in yield contrary to expectations **(Fig. 5).**

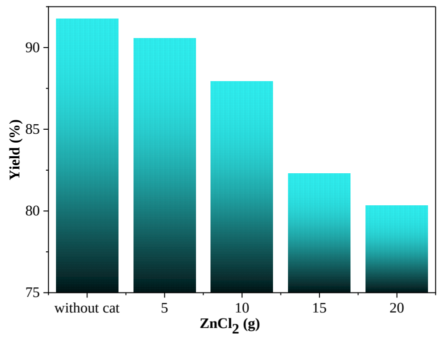


Fig. 5 - C_2H_5Br yield dependence on the quantity of $ZnCl_2$ added to the reaction in an attempt to enhance the synthesis process

$ZnCl_2$ is well documented as a catalyst for alkyl halide (especially chlorides) formation where it acts as a Lewis

Acid to stabilize carbocation intermediates particularly effective for secondary and tertiary alcohols [34]. However, in this work, the inverse relationship between $ZnCl_2$ concentration and yield suggests possible complications one of which could be that $ZnCl_2$ could have bound Br^- from the salt reducing their ability for substitution.

Table 2 - Reaction mass temperature range and synthesis duration of C_2H_5Br

№ of entries	Molar ratio of components				Reaction temperature range, ºC	Reaction time, h	Yield, %
	KBr/NaBr	C_2H_5OH	H_2SO_4	H_2O			
1	1	1.2	6	13.2	77-119	5	93.69
2	1	1.2	7	13.2	67-120	4.30	87.23
3	1	1.2	7	13.2	34-120	4.30	91.04
4	1	1.2	4.5	11.2	34-118	4.30	91.04
5	1	1.2	4.5	11.9	85-120	4.30	91.75
6	1	2	3.5	13.2	90-119	5.30	87.44
7	1	2	3.5	13.2	90-120	5.30	86.49
8	1	2	3.5	13.2	90-120	5.30	88.49
9	1	1.2	1.87	5	62-117	6	89.18
10	1	1.2	1.87	5	50-120	6	91.08

Conclusion

This study has successfully demonstrated a sustainable and efficient strategy for the synthesis of ethyl bromide, pivoting on the principles of process optimization and waste valorization. Molar ratios of 1:1.2:2:5, 1:1.2:4.5:11.2, and 1:2:3.5:13.2 gave higher yields >90% with the suitable reagent mixing order of (NaBr/KBr solution, C_2H_5OH, H_2SO_4). A closed-loop recycling approach of excess acid used in the synthesis was effective for the high-yielding (>90%) synthesis of high-purity ethyl bromide. Furthermore, this study effectively utilized regenerated NaBr, a byproduct obtained from a separate thiol synthesis reaction and obtained high yields of ethyl bromide (>90%) with high purity comparable to the product obtained from commercial, reagent-grade NaBr.

The successful integration of waste valorization with process optimization in this work, underscores the potential for implementing greener and cheaper methodologies in routine organic synthesis without compromising on the quality of the final product. This approach not only offers an economical route for producing ethyl bromide but also serves as a model for the sustainable management of byproducts in chemical manufacturing.

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