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Research paper

Integrated process for potassium sulfate and a mixture Of ammonium chloride/potassium sulfate salts production

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Abstract

Relatively pure and coarse crystalline potassium sulfate of about 52 wt % K_2O content and almost chlorine free has been obtained by reacting commercial potassium chloride and commercial ammonium sulfate in a stirred tank reactor at moderately low temperature. To increase the yield of potassium sulfate to a reasonable value, an evaporation stage located between the reactor and the crystallizer is used. The main steps of the production process include dissolution, reaction, evaporation, crystallization, centrifuging, drying, and then cooling. It is found that the best operating parameters to produce potassium sulfate of good quality, quantity, and crystal size are 1:1 as $KCl/(NH_4)_2SO_4$ mole ratio, 60 ºC reaction temperature, 1 hour reaction time, about one third of the total water used in the dissolution step is to be evaporated, 10 ºC crystallization temperature, 1 hour crystallization time, and 160 and 60 rpm agitation speeds in the reactor and the crystallizer respectively. Applying these operating conditions, a potassium sulfate yield of about 78 % can be achieved. Also, a fully soluble complex salt as a mixture of ammonium chloride and potassium sulfate is obtained by further treatment of the mother liquor. Further concentration of the mother liquor by further water evaporation of about 40 wt % and then crystallization of the slurry at 25 ºC can recover up to about 60 wt % of the remaining solid in the mother liquor as a complex salt. The total yield of potassium sulfate is found to be about 95 wt % and the whole value of the solid product obtained is about 79 wt %.

Keywords: *Ammonium Chloride; Ammonium Sulfate; Crystallization; Potassium Sulfate; Potassium Chloride.*

1. Introduction

Potassium as a source of K exists as a single fertilizer like potassium chloride (KCl), potassium sulfate K_2SO_4, and potassium hydroxide (KOH) or as NPK fertilizers like mono potassium phosphate (MKP), and potassium nitrate (KNO_3). Potassium (K) fertilizer is commonly added to improve the yield and quality of plants growing in soils that are lacking an adequate supply of this essential nutrient. Most potassium fertilizer comes from ancient salt deposits located throughout the world. The word “potash” is a general term that most frequently refers to potassium chloride (KCl), but it also applies to all other K-containing fertilizers, such as potassium sulfate (K_2SO_4) [1], [2].

Potassium sulfate is an organic crystalline salt with a chemical formula K_2SO_4, produced in a crystalline or a powder form. It is white, odorless, bitter tastes, nontoxic, nonflammable, and soluble in water. It contains 48 to 54 % potassium (as K_2O) and supplies 18.4 % of sulfate, and it is considered as the second largest tonnage of potassium compound and is primarily used as a fertilizer [3]. Potassium sulfate is a valuable chemical commodity and it is typically employed as a fertilizer especially for certain crops that do not tolerate the chloride ions well, also most crops need more sulfate than chloride. This fertilizer is a rich source of potassium and sulfur which offers a high concentration of nutrients readily available to plants. Potassium sulfate is also used in the manufacture of glass and production of potassium alums [4].

1.1. Potassium sulfate production processes

Historically potassium sulfate has been made primarily from potassium chloride and sulfuric acid when the byproduct HCl was the dominant product. However, over the year the HCl market has had more competition and “natural” K_2SO_4 with lower capital and operating coasts has begun to dominate its production in some countries with natural complex salts. Nowadays, potassium sulfate can be manufactured by several processes such as: Mannheim process, yield from natural complex salts, naturally occurring brines, the Ochoa process, production of potassium sulfate from potash and sodium sulfate, production of potassium sulfate by reacting ammonium sulfate with potassium chloride. A brief description of these processes in addition to disadvantages will be given below.

1.1.1. Mannheim process

The Mannheim process was originally developed for sodium sulfate production. For the production of potassium sulfate, sodium chloride is replaced with potassium chloride. The required raw materials (potassium chloride (KCl) and sulfuric acid (H_2SO_4)) are poured into the center of a muffle furnace heated to above 600 ºC [5]. Potassium chloride reacts with sulfuric acid during the slow mixing of the ingredients in the gas heated Mannheim furnace consisting of cast iron muffle with rotating plough which helps to agitate the mixture. The hydrochloric acid produces during the reaction is cooled and absorbed into water to produce 33 % hydrochloric acid as a byproduct. The precipitated potassium sulfate is cooled, filtered and the lumps are crushed and granulated [6], [7]. The following reactions take place during the production process:

$KCl + H_2SO_4 \rightarrow KHSO_4 + HCl$

$KHSO_4 + KCl \rightarrow K_2SO_4 + HCl$

Although the Mannheim process is the most widely process for K_2SO_4 production but it has many disadvantages

1) Mannheim process needs high production cost.
2) It needs a high temperature (> 550 °C) which means high energy consumption.
3) Mechanical problems and some difficulties encountered due to corrosion.
4) The Mannheim kiln is of necessity constructed from special bricks which have high resistance to direct flame, intense heat and acid, while the stirrer must be heat- and acid-proof.

1.1.2. Recovery from natural complex salts

Complex salts containing magnesium sulfate and potassium sulfate occur naturally in many potash ores, such as the potash ores that are found in the European deposits and in the Permian Basin. The chief natural complex salts that are the source of the potassium sulfate are; Kainite ($KCl.MgSO_4.3H_2O$), Langbeinite ($K_2SO_4.3MgSO_4$), and Carpathian polmineral ores. The natural process involves the initial conversion with recycled K_2SO_4 end liquor “mined” kainite or langbeinite to form an intermediate product schoenite. All processes are based on intercrystalline reactions of ion exchange.

The process comprises four basic units: preparation of the ore and flotation, production of schoenite and its recovery, leaching of the schoenite to potassium sulfate, and liquor treatment. The kainite is repulped with recycled brine, screened, and directed to ball mills and hydro-classifiers. Overflows go to a thicker and main filter and underflows to flotation and filtration. Float material, after filtration, is combined with the solid fraction from the main filter and directed to the schoenite reactors and separating cyclones. After a two-step hydro-separation, centrifugation, and filtration, schoenite is directed to the leaching reactors. After decomposition of the schoenite, product is directed to final centrifuges and a dryer; the overflows are cooled and crystallized. After additional thickening, the product is centrifuged and dried. The product specification ensures that the K_2O content is not lower than 50% and the chlorine content is less than 1% [8].

1.1.3. Production of potassium sulfate from potash and sodium sulfate

Potassium chloride can be reacted with various sulfate salts to form a double salt that can be decomposed to recover potassium sulfate. The most common raw material employed for this purpose is sodium sulfate. A saturated solution of sodium sulfate is added to a saturated solution of potassium chloride to produce glaserite, which is the double sulfate of sodium and potassium. The solution obtained can be filtered to remove insoluble matter, and is then subjected to crystallization, such as evaporative crystallization or cooling crystallization in which glaserite crystallizes out of solution. The obtained solution is filtered to separate the produced potassium sulfate from the mother liquor. The resulting mother liquor undergoes evaporative crystallization in which sodium chloride is produced, and then it is separated by filtration from the mother liquor and recovered as a co product [9-11]. The main disadvantages of this method are summarized as follows:

- This process takes a very long time and this is the most serious disadvantage.
- There are numerous problems associated with the solid/liquid separation of glaserite. Since known processes produce a fine glaserite. Somewhat larger glaserite crystals can be obtained by out-salting, but this requires a longer residence time and more sophisticated crystallization equipment.
- Dilution of the solution being cooled with water permits obtaining quality glaserite, but its yield is only 5 to 10 wt % of the theoretical. In addition, the refrigeration is so expensive.
- In addition, as a result of evaporation of the glaserite solutions, a thick crust of glaserite, difficult to remove, is formed on the apparatus surface, which reduces the heat transfer coefficient.

1.1.4. Recovery of potassium sulfate from polyhalite

The process utilizes polyhalite, water and energy to produce three main products soluble potassium sulfate, standard potassium sulfate, and granular potassium sulfate. Processing polyhalite to produce potassium sulfate by this technique involves crushing, washing, calcinations, leaching, crystallization, and granulation. This method can be effective in areas, which have high evaporation rate and low rainfall and only with brines that contain very high sulfate levels, while in reality lakes with sufficient brine mineral levels are rare. Potassium sulfate production from such sources is usually complex because of the presence of many other salts in significant proportions, which leads to the use of a combination of a mechanical type of separation step with a solubility process step in order to make the latter more efficient. The recoveries of potassium sulfate are less than the optimum due to the greatest difficulty encountered in effecting a clean separation of these several salts because of the presence of the sodium chloride. In most cases, potassium sulfate is not recovered directly from natural brine sources; however, potassium chloride is commonly recovered and then used as a raw material for the production processes of potassium sulfate [12], [13].

1.1.5. Naturally occurring brines

In this process evaporate minerals comprising mixtures of relatively coarse salts are treated in a manner such that certain salts are converted by recrystallization to very finely divided form and then separated from the coarse salts by size classification. The ore should be calcined at 450 °C to remove the water of crystallization and render the material soluble in a hot water leach. Polyhalite which is a row material in this process crystallizes in the triclinic system. There are various operations in this process and the process can only be effective in areas which have plenty of water resources. The treatment being especially useful in a process for the recovery of potassium sulfate from marine evaporates mixtures [14]. The main disadvantage of this technique is its high energy and cost are needed in addition to that it requires high rate of equipment maintenance.

1.1.6. Production of potassium sulfate by reacting ammonium sulfate and potassium chloride

In this production process, potassium sulfate is produced by reacting ammonium sulfate and potassium chloride at a temperature of about 30 to 40 °C to produce a slurry containing $K_2SO_4 \cdot (NH_4)_2SO_4$ double salt, and reacting this double salt with an aqueous solution containing potassium chloride at a temperature of about 30 °C to produce a slurry containing potassium sulfate. The slurry containing potassium sulfate is subjected to a solids/liquid separation step to obtain potassium sulfate crystals having a size in the range of about 20 to about 150 meshes. The filtrate from solids/liquid separator flows to a settler, where this filtrate is separated into fines, which are recycled back, and an overflow liquor; reacting the overflow liquor with sodium sulfate and either calcium chloride or calcium sulfate dihydrate at a temperature of 30° C to produce a slurry containing syngenite, $CaSO_4 \cdot K_2SO_4 \cdot xH_2O$, and passing the slurry containing syngenite into a solids/liquid separator to produce a filtrate and solid syngenite [15], [16].

After reviewing most of the available commercial potassium sulfate production processes and based on the availability of the raw materials, the advantages, and disadvantages of the mentioned processes especially the huge quantity of energy required by most of the available production processes and their environmental effect, it is necessary to seek a more feasible and more environmentally friendly production process with less energy consumption.

1.1.7. Description of the present production method

Production of potassium sulfate by the present process starts by charging both commercial potassium chloride (KCl) and ammonium sulfate ($(NH_4)_2SO_4$) to two separate jacketed dissolution tanks to prepare potassium chloride and ammonium sulfate saturated solutions. In order to obtain the saturated solutions of both of these materials, it is necessary to raise the temperature of the solution up to 60 ^{o}C under an agitation. The two saturated solution (streams 1 and 2) are transferred to a jacketed continuous stirred reactor where the reaction temperature is kept constant for the whole period of reaction time. The stoichiometric reaction between potassium chloride and ammonium sulfate obeys the following reaction equation:

$$2KCl_{aq} + (NH_4)_2SO_{4\ aq} \rightarrow K_2SO_{4\ s} + 2NH_4Cl_{\ aq} \qquad (1)$$

Fig. 1 shows the process flow sheet for the production of potassium sulfate according to the laboratory experimental work carried out. On completion of the reaction, the resulted solution (stream 3) that consists of dissolved potassium sulfate and ammonium chloride is transferred from the reactor to the kettle evaporator as shown in the process flow sheet. Steam will be used in the kettle evaporator to rise up the solution temperature from 60 ^{o}C up to 100 ^{o}C to allow water to be evaporated and hence increase the concentration of the potassium sulfate in the solution.

Reducing the temperature of the solution after the required amount of water has been evaporated will bring the solution far away below the crystallization temperature of potassium sulfate. The output solution from the kettle evaporator (stream 5) will be fed to the batch crystallizer where the hot solution is cooled down from about 100 ^{o}C to the crystallization temperature (varies between 5 to 28 ^{o}C). Chilled water will be circulated in the jacket of the crystallizer to cool the solution down to the set crystallization temperature; the crystallization temperature must be kept constant for the whole period of the crystallization step.

On completion of the crystallization step, solid potassium sulfate crystals will be formed leaving the more soluble compound (ammonium chloride) dissolved in the solution. During the crystallization step, the mixture should be agitated with a stirring speed that is enough to keep the potassium sulfate crystals suspended in the solution, this will allow for larger potassium sulfate crystals to grow up. If the agitation speed is not high enough to suspend the formed crystals, then a fine product will be obtained because the formed crystals will settle down and accumulate over each other hence preventing crystals growth step to take place.

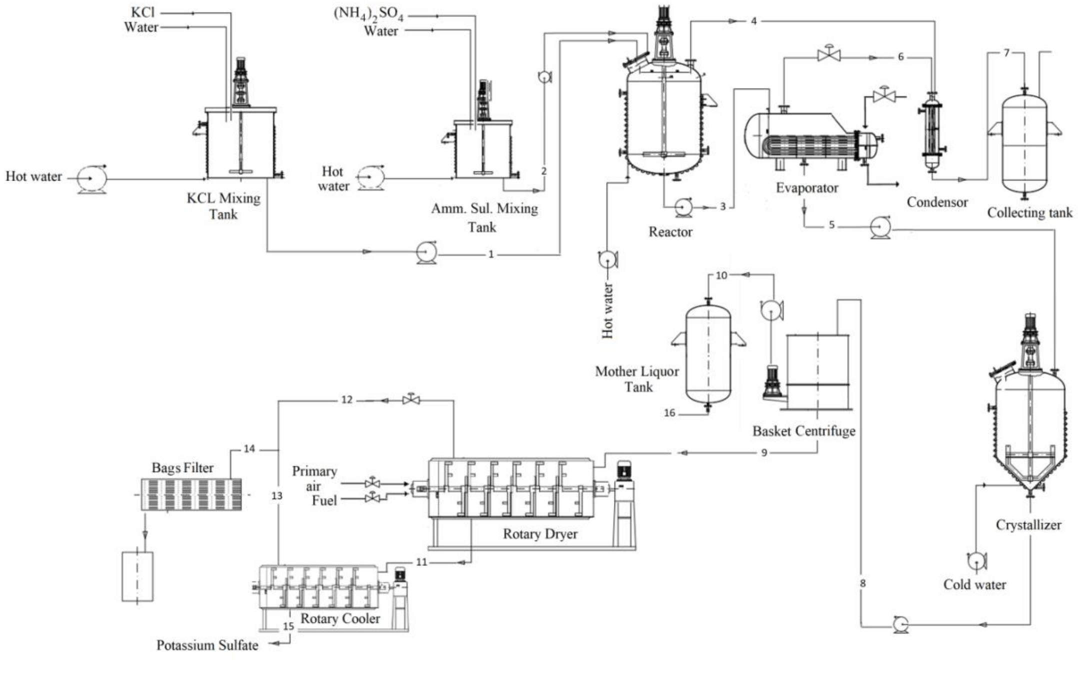

Fig. 1: Process Flow Sheet of Potassium Sulfate Production.

The resulting slurry of potassium sulfate crystals and the mother liquor flows via stream 8 to the centrifuge where the separation of potassium sulfate crystals from the mother liquor takes place under the very high speed of rotation of the internal basket of the centrifuge. The moist potassium sulfate crystals (stream 9) need further drying while the mother liquor (stream 10) is pumped to a storage tank for further processing and recovery. The mother liquor contains valuable compounds such as dissolved ammonium chloride and soluble potassium sulfate that must be recovered.

To get rid of the excess moisture content within the obtained potassium sulfate crystals and obtain crystals with the standard specifications, a rotary dryer is used where the wet crystals flow via stream 9 from the centrifuge to the rotary dryer. The wet crystals flow counter-currently into the rotary dryer where they will be in contact with hot air blown into the dryer with a temperature of 122 ^{o}C. Potassium sulfate crystals (stream 11) leave the rotary dryer at a moisture content of about 0.05 % and at a temperature of 60 ^{o}C. To prevent the dried potassium sulfate crystals from gaining some moisture from the air and then agglomerate while they are in storage, a cooling step is required to cool down the end product from about 55 ^{o}C down to room temperature. Dust from both, the rotary dryer (stream 12) and the cooler (stream 13) are sent to a bag filter to recover any potassium sulfate fine crystals and to clean the exit air from solid pollutants. Also, water vapor from the reactor and the evaporator is collected and condensed to reduce the amount of water consumed.

The mother liquor (stream 16) that contains mainly the dissolved ammonium chloride and the unrecovered potassium sulfate is treated as shown in Fig. 2 to obtain a complex salt of both of these compounds. The treatment process starts with the further evaporation of water to increase the concentration of the salts in the liquor. The saturated solution (stream 18) is then transferred to crystallizer 2 that operates at a temperature of 25 ^oC to allow the salts crystal to nucleate and grow up. By the end of the crystallization process, the suspension (stream 19) is centrifuged to separate the solid salt formed from the second mother liquor. The obtained sold salt (stream 20) is dried using a rotary dryer to remove the excess moisture.

Many experimental runs were done to determine the best operating parameters for producing potassium sulfate by reacting ammonium sulfate and potassium chloride. There are many operating parameters need to be optimized such as mole ratio of KCl to $(NH_4)_2SO_4$, reaction temperature, reaction time, crystallization temperature and crystallization time. In the present work, five variables were investigated to achieve the best-operating conditions that lead to a maximum yield of K_2SO_4 with better crystals quality. These variables are: the reaction temperature (40, 60, 80 and 100 ^{0}C), the reaction time (0.5, 1, 2 and 4 hour), the crystallization temperature (5, 10, 15 and 28 ^{0}C), the crystallization time (0.25, 0.5, 1 and 2 hour), and the percentage of water evaporated (15, 24 and 32 %). Also, to recover potassium sulfate/ammonium chloride complex salt from the main mother liquor, the percentage of water evaporated and the crystallization temperature were studied. The percentage of water evaporated varied as 0, 15, 30, 40, and 50 wt % while the crystallization temperature varied as 5, 10, 15, 25, and 30 ^{0}C.

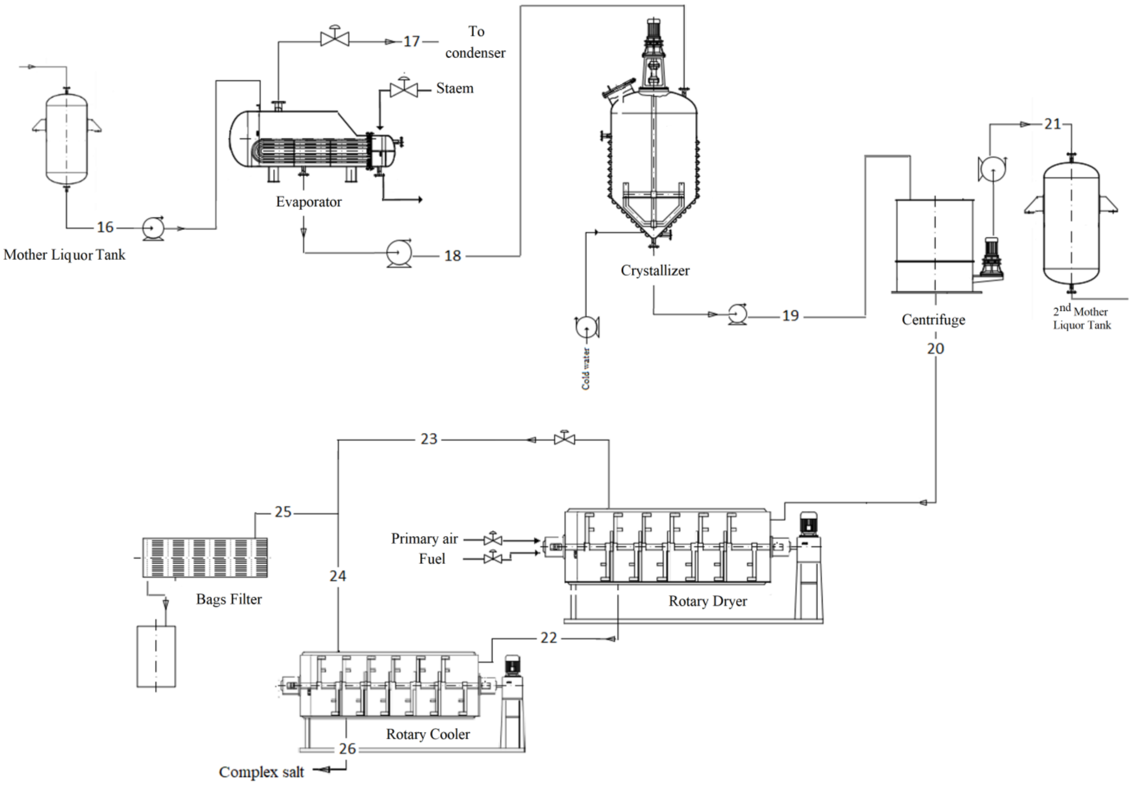

Fig. 2: Process Flow Sheet of Mother Liquor Treatment.

2. Materials and methods

2.1. Materials used

A standard potassium chloride (KCl) supplied by the Arab Potash Company and has the following specifications: purity = 96.6 %, potassium oxide (K_2O) = 61 wt %, moisture content = 0.35 wt %, particle size (90 % minimum) between 0.212-1.7 mm, bulk density = 1300-1358 kg/m^3 [17]. Commercial ammonium sulfate ($(NH_4)_2SO_4$) with the following specifications: ammoniacal nitrogen = 21 wt %, water soluble sulphur = 24 wt %, moisture content = 0.2 wt %, mean particle size = 1.1 mm, loose bulk density = 1040 kg/m^3, and color = whitish.

2.2. Experimental procedure followed

The following block flow diagram (Figure 3) summarizes the procedure adopted in the experimental work to produce both potassium sulfate and the complex salt. Both raw materials were used as received to prepare the saturated solutions from which the two products were obtained.

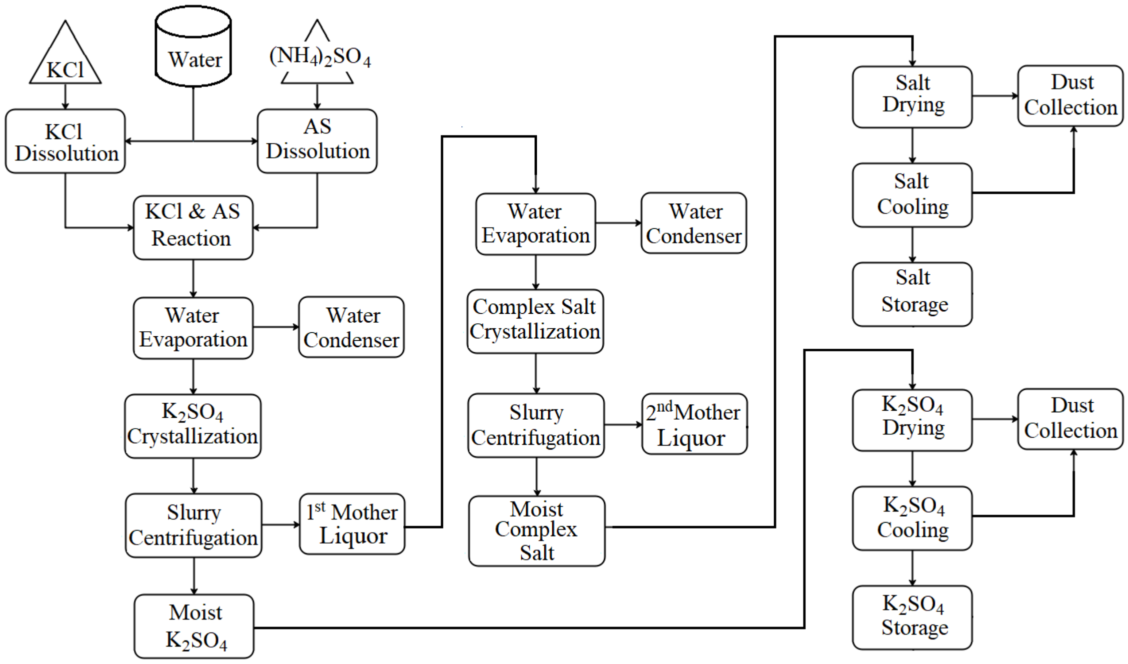

Fig. 3: Block Flow Diagram for Potassium Sulfate and Potassium Sulfate/Ammonium Chloride Complex Salt Production.

3. Results and discussion

In this proposed method two products can be produced; the main is the crystalline potassium sulfate while the other byproduct is a mixture of ammonium chloride and potassium sulfate salts. Below the effect of the operating parameters on the yield, chemical analysis, and physical appearance of the products will be presented.

3.1. Effect of operating parameters on the potassium sulfate production

3.1.1. Reaction temperature effect

To investigate the effect of the reaction temperature on the yield of potassium sulfate, four experiments were carried out at different reaction temperatures (40, 60, 80 and 100 °C) while all other parameters were kept fixed at: molar ratio of KCl/$(NH_4)_2SO_4$ = 1/1, reaction time = 60 min, crystallization temperature = 10 °C, crystallization time = 60 min, and evaporated water ratio = 15 %. The effects of the reaction temperature on the potassium sulfate yield and crystals size are presented in Fig. 3. It is obvious that in general, increasing the reaction temperature increases the K_2SO_4 yield. Increasing the temperature from 40 to 60 °C, increases the yield by about 5 wt %, while increasing the reaction temperature from 40 to 100 °C, increases K_2SO_4 yield by about 15 wt %. On the other hand, increasing the reaction temperature from 60 to 100 °C, increase the yield by about 6 wt % only.

The obtained potassium sulfate crystals were all white and shiny except the crystals obtained at a reaction temperature of 40 °C; the K_2SO_4 crystals were very fine in size and less shiny. Since the obtained K_2SO_4 crystals at a reaction temperature of 40 °C are not acceptable in terms of crystal size and physical appearance, and since increasing the reaction temperature above 60 °C does not increase the yield significantly, it is concluded that the best reaction temperature to adopt is 60 °C. Figure 4 shows microscopic graphs of the obtained potassium sulfate crystals obtained by crystallization saturated solutions reacted at different temperatures. All samples were crystallized at a crystallization temperature of 10 °C.

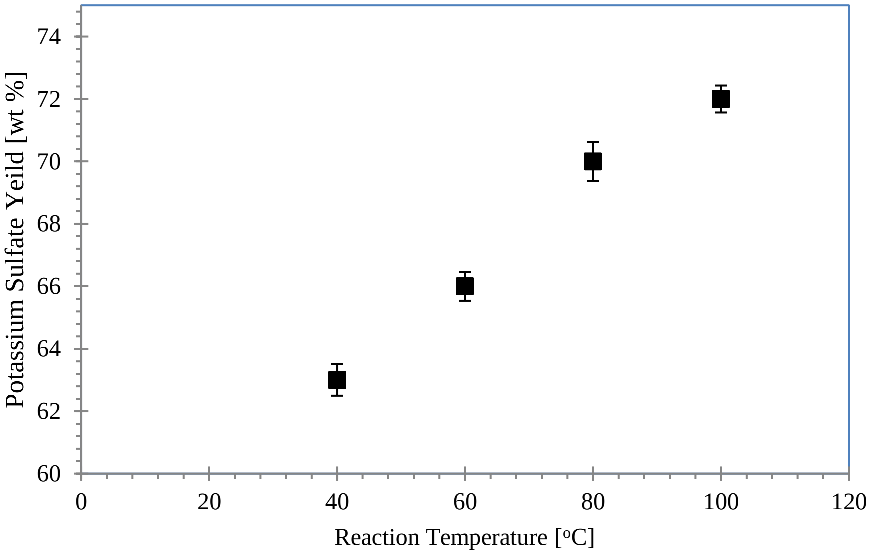

Fig. 3: Percentage of Potassium Sulfate Yield as a Function of Reaction Temperature while the other Parameters were Kept Fixed at 60 Min Reaction Time, 10 ^{O}C Crystallization Temperature, 60 Min Crystallization Time and 15 wt % Evaporated Water Ratio.

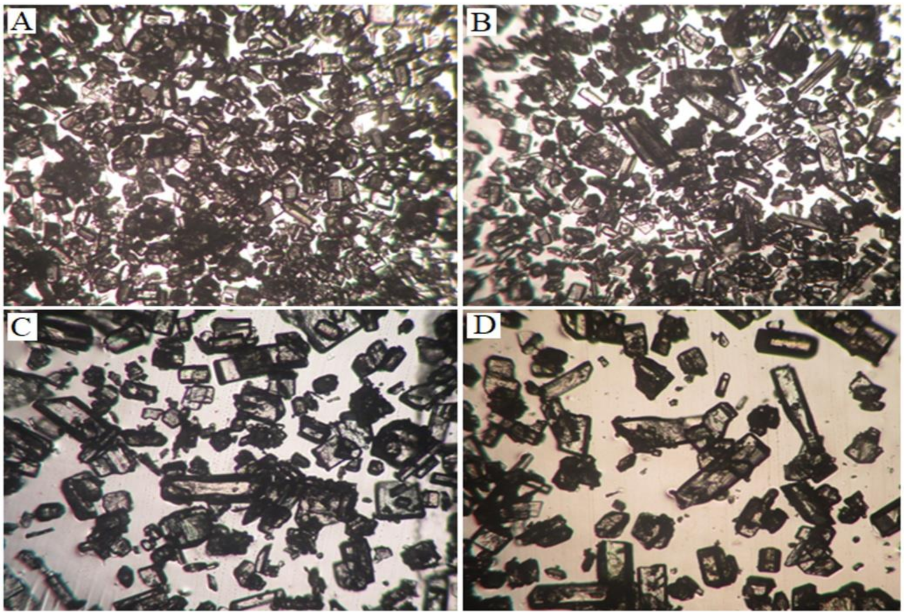

Fig. 4: Microscopic Images of Potassium Sulfate Crystals Crystallized at 10 ^{o}C From Solutions Reacted at A) 40 B) 60 C) 80 D) 100 Oc.

3.1.2. Reaction time effect

To reveal the reaction time effect on the K_2SO_4 yield, four trials were conducted at 0.5, 1, 2 and 4 hours reaction time while the other operating parameters were kept constant at: molar ratio of $KCl/(NH_4)_2SO_4$ = 1/1, reaction temperature = 60°C, crystallization temperature = 10°C, crystallization time = 60 minutes, and evaporated water ratio = 15 %. Fig. 5 presents the effect of the reaction time on the yield of the potassium sulfate crystals. The results show that increasing the reaction time form 30 min to 60 min increases the potassium sulfate yield by about 10 wt % and increasing the reaction time to 120 minutes increases the yield by about 13 wt % only. Further increment in the reaction time does not increase the yield significantly and nearly similar yield values were obtained for reaction times of 1, 2 and 4 hours. Also, it is noticed that the amount of K_2SO_4 nuclei and fine crystals formed during the reaction step after 30 minutes was very little compared with the amount formed after 60 minutes. As a result of this, a reaction time of 60 minutes can be considered as the best reaction time. Fig. 6 shows microscopic graphs of the obtained potassium sulfate crystals by crystallization saturated solutions reacted at 60 ^{o}C for different times. All samples were crystallized at a crystallization temperature of 10 ^{o}C.

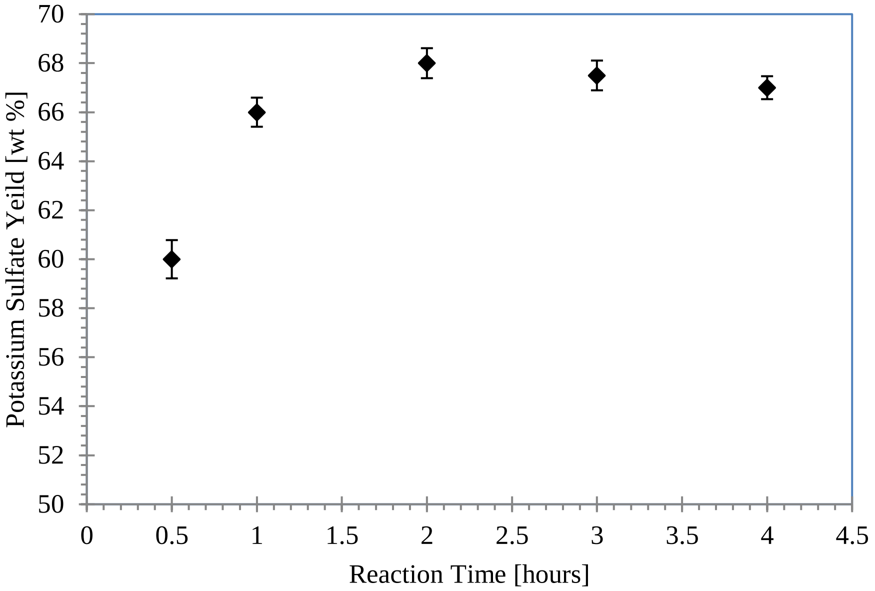

Fig. 5: Percentage of K_2SO_4 Yield as a Function of Reaction Time while the other Parameters were Kept Fixed at 60 ^{O}C Reaction Temperature, 10 ^{O}C Crystallization Temperature, 60 Min Crystallization Time and 15wt % Evaporated Water Ratio.

3.2.3. Crystallization temperature effect

One of the most widely used methods for achieving the supersaturation essential for crystallization is cooling of a solution. On completion of the reaction between the potassium chloride and ammonium sulfate, the slurry is transferred to the crystallizer to allow further nucleation and growth of K_2SO_4 crystals and hence increase the yield of potassium sulfate. Knowing that the solubility of ammonium chloride [18] (39.5 g/100 g water at 25 ^{o}C) is over three times the solubility of potassium sulfate [19] (12 g/100 g water at 25 ^{o}C), and then cooling a saturated solution containing both of these salts will allow potassium sulfate to crystallize initially. In the present study, slurries from the reactor were cooled at different crystallization temperatures to investigate the effect of the crystallization temperature on K_2SO_4 yield; the crystallization temperatures covered were 5, 10, 15 and 28°C. The other parameters were kept constant at: molar ratio of $KCl/(NH_4)_2SO_4$ = 1/1, reaction temperature = 60°C, reaction time = 60 minutes, crystallization time = 60 minutes, and evaporated water ratio = 15 %. The cooling temperature is known to influence the rate of growth and size of crystals through its effect on supercooling [20-22].

It is clearly seen in Fig. 7 that decreasing the crystallizer's temperature will increase the yield of K_2SO_4 crystals as a result of the supercooling which leads to excessive nucleation. Decreasing the crystallization temperature from 28 ^{o}C to 10 ^{o}C increases the K_2SO_4 yield by 20 wt %. Since the difference in the yield values is almost negligible (less than 2 wt %) if the crystallization temperature reduces from 10 to 5 ^{o}C, then there is no need to reduce the crystallization temperature further. Hence, it is believed that 10 ^{o}C might be a suitable crystallizer temperature at which a reasonable amount of K_2SO_4 can be recovered. The microscopic images of Fig. 8 show that increasing the crystallization temperature increases the size of the obtained crystals, at lower crystallization temperature the nucleation rate is high and hence smaller size of crystals will be obtained [23], [24].

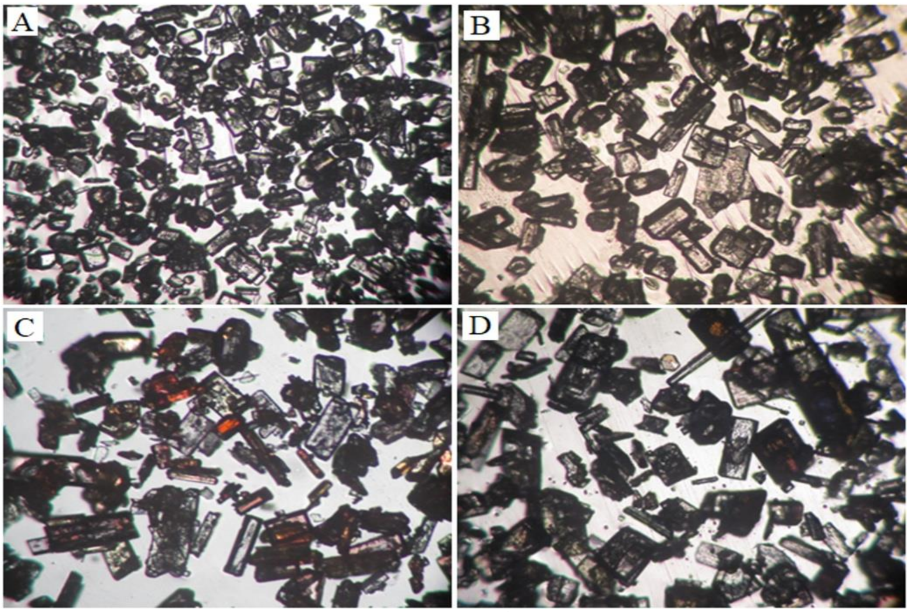

Fig. 6: Microscopic Images of Potassium Sulfate Crystals Crystallized at 10 ^{O}C from Solutions Reacted at 60 ^{o}C for A) 0.5 B) 1 C) 2 D) 4 Hr.

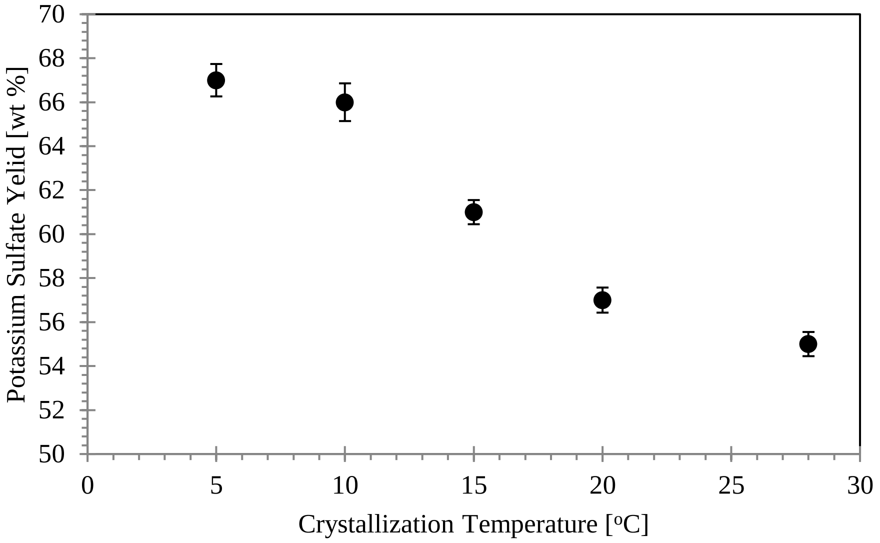

Fig. 7: Percentage of K_2SO_4 Yield as a Function of Crystallization Temperature; the other Parameters were Kept Fixed at 60 ^{O}C Reaction Temperature, 60 Min Reaction Time, 60 Min Crystallization Time and 15 wt % Evaporated Water Ratio.

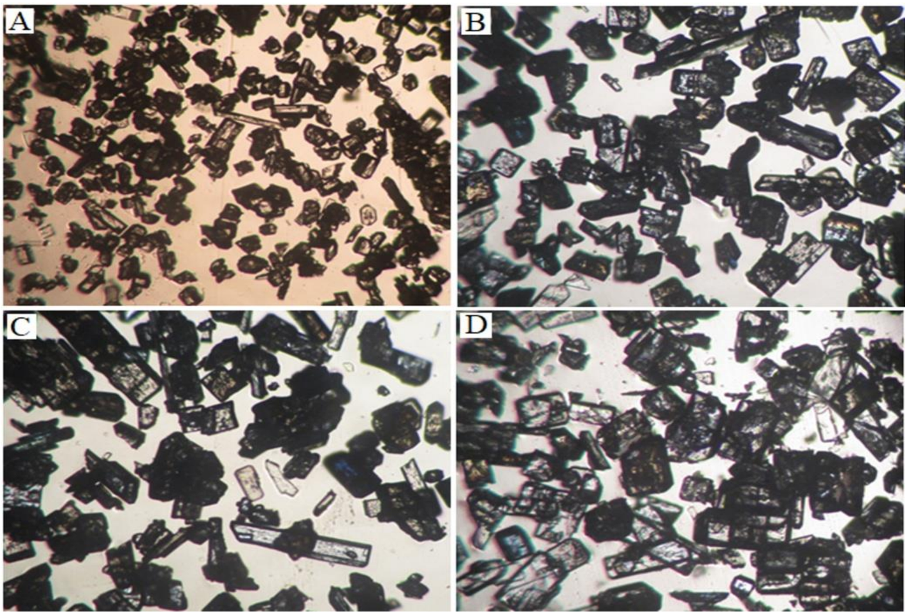

Fig. 8: Microscopic Images of Potassium Sulfate Crystals Crystallized for One Hour at Different Temperatures A) 5 B) 10 C) 15 D) 28 ^{O}C.

3.2.4. Crystallization time effect

As expected, the crystal yield increases with time [25], the effect of crystallization time was studied by setting the crystallization time to 0.25, 0.5, 1, and 2 hours, while the other variables were set at: molar ratio of $KCl/(NH_4)_2SO_4$ = 1/1, reaction temperature = 60°C, reaction time = 60 minutes, crystallization temperature = 10°C, and evaporated water ratio = 15 %. As expected, increasing the crystallization time will increase the K_2SO_4 yield as presented in Fig. 9. The figure reveals that the yield increases by about 14 wt % when the crystallization time increases from 30 to 60 minutes, while the yield increases by about 16 wt % when the crystallization time increases from 30 to 120 minutes. Since the increment in the K_2SO_4 yield is very small as the crystallization time increases from 60 to 120 minutes and in order to save more energy and to reduce the process time, it is suggested to stop the crystallization stage after 60 minutes. The microscopic graphs obtained (Fig. 10) reveals that reducing the crystallization time will decrease the final size of the crystals as a result of the insufficient time for crystals to grow up.

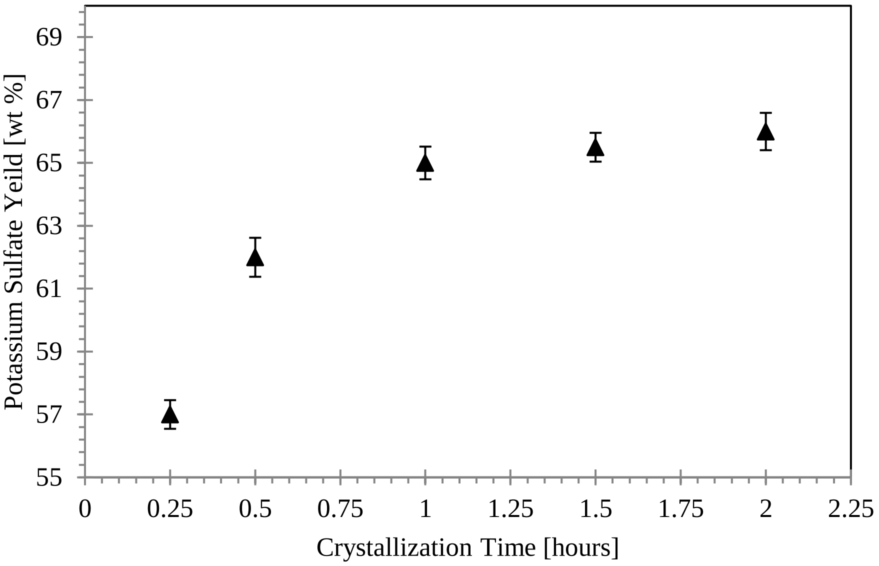

Fig. 9: Percentage of Potassium Sulfate Yield as a Function of Crystallization Time while the other Parameters were Kept Fixed at 60 ^{O}C Reaction Temperature, 60 Min Reaction Time, 10 ^{O}C Crystallization Temperature and 15 wt % Evaporated Water Ratio.

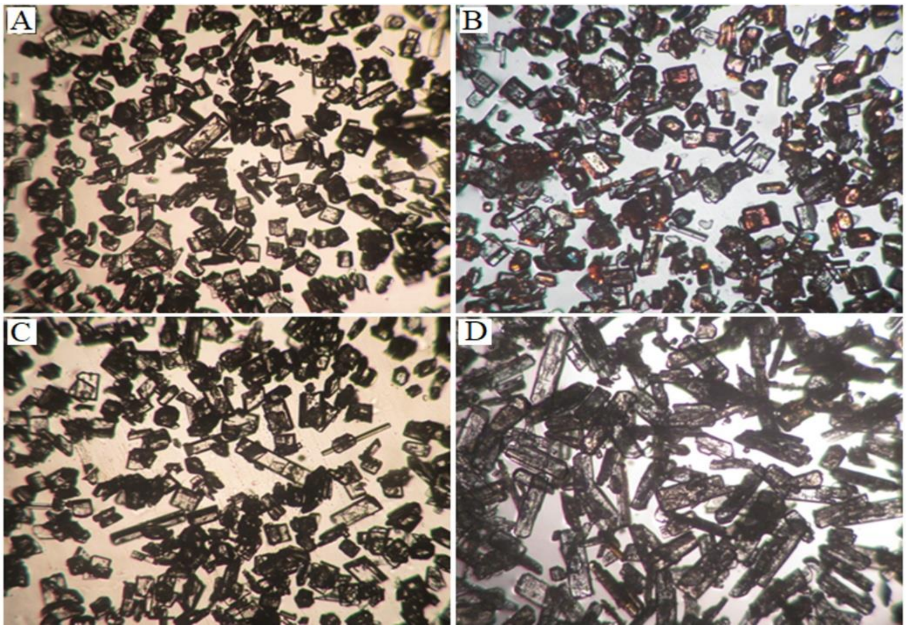

Fig. 10: Microscopic Images of Potassium Sulfate Crystals Crystallized at 10 ^{O}C for Different Periods of Time A) 0.25 B) 0.5 C) 1 D) 2 Hr.

3.2.5. Water evaporation ratio effect

In order to prepare the two saturated solutions of potassium chloride and ammonium sulfate, it is necessary to use a large quantity of water to dissolve the solid raw materials at the required temperature (60 ^{o}C). The total percentage of water at the beginning of the reaction stage is about 65 wt % of the total feed. The presence of this high quantity of water limits and reduces the K_2SO_4 yield; hence a very low yield was obtained when this large quantity of water remains in the solution during the crystallization stage. It is necessary to evaporate part of this water to increase the concentration of the salts in the solution and allow the less soluble salt (K_2SO_4) to crystallize at a reasonable crystallization temperature. The effect of the percentage of water evaporation prior to crystallization was studied by setting the ratio of the water evaporation at 0, 15, 24 and 32%, while all other parameters were set at: molar ratio of $KCl/(NH_4)_2SO_4$ = 1/1, reaction temperature = 60 °C, crystallization temperature = 10°C, reaction time = 60 minutes, and crystallization = 60 minutes. Fig. 11 presents the effect of the percentage of water evaporation on the K_2SO_4 yield. It can be clearly seen that increasing water evaporation leads to higher yield; the yield increases from 42 to 65 wt % by water evaporation of about 15 wt % of the total water exist in the solution. By increasing the percentage of water evaporation to 32%, about 100% increment in the K_2SO_4 yield can be achieved (about 85 wt % of K_2SO_4 is recovered); further increase in water evaporation does not increase the yield much. As a result of this conclusion, a 32 percentage of water evaporation will be considered as the best. This percentage of water evaporation means that around 1.5 tons of water must be evaporated for each ton of potassium sulfate production. This amount of water is considered reasonable if we compare it with the 10 tons of water that must be evaporated per ton of potassium sulfate as mentioned by Sardisco in his patent [26].

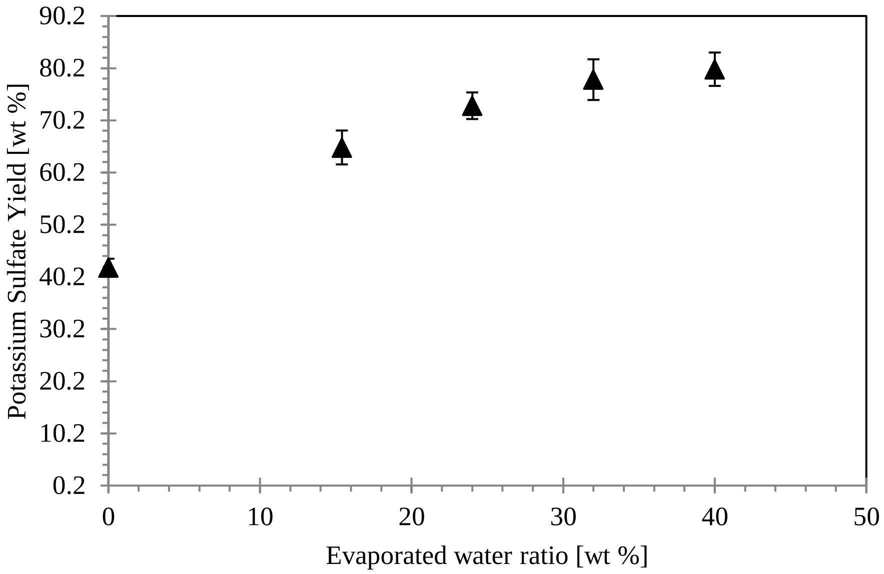

Fig. 11: Percentage of K_2SO_4 Yield as a Function of Evaporated Water Ratio; the other Parameters were Kept Fixed At 60 ^{O}C Reaction Temperature, 60 Min Reaction Time, 10 ^{O}C Crystallization Temperature and 60 Min Crystallization Time.

3.2.6. Best operating parameters for K_2SO_4 production

To verify the obtained results in this study, a triplicate identical experiments were conducted at the obtained best-operating conditions: molar ratio of $KCl/(NH_4)_2SO_4$ = 1/1, 60 °C reaction temperature, 60 minutes reaction time, 10 °C crystallization temperature, 60 minutes crystallization time, and 32 wt % water evaporation. About 78 wt % of the K_2SO_4 was recovered as a white and shiny solid crystals as shown in Fig. 11. The chemical analysis of the obtained K_2SO_4 crystals is presented in Table 1. In addition to the chemical analysis, the microscopic graphs shown in Fig. 12 is another evidence that the obtained crystals are potassium sulfate crystals which is in agreement with what is reported in the literature [27], [28].

Table 1: Specifications of the Obtained Potassium Sulfate Crystals Produced at the Best Operating Parameters

Element	Description
Color	White
State	Free flowing
Appearance	Shiny crystals
Solubility	Fully soluble
K^+	43.2 wt %
K_2O	52.2 wt %
Cl^-	0.5 wt %
N^-	0.2 wt %
SO_4^{-2}	55.2 wt %
moisture	0.8 wt %

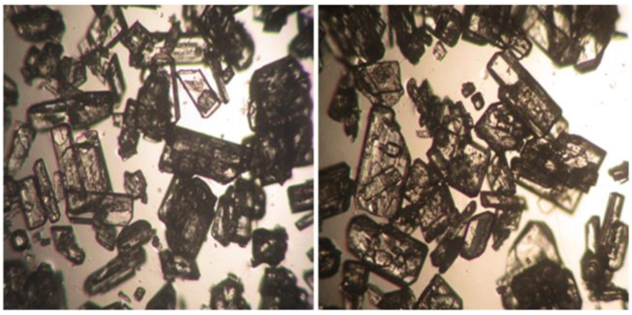

Fig. 12: Microscopic Graphs of Potassium Sulfate Crystals Obtained by Applying the Recommended Operating Parameters.

3.3. Effect of operating parameters on the complex salt production

3.3.1. Mother liquor treatment

The mother liquor that contains a considerable amount of dissolved K_2SO_4 in addition to a large quantity of ammonium chloride can be treated further to produce ammonium chloride/potssium sulfate slat. In the present study, two main factors affetcting the yield of the salt were studied; these are the water evaporation ratio and the crystallization temperature.

3.3.2. Effect of water percentage evaporation on the yield of the complex salt

The mother liquor leaves the K_2SO_4 centrifuge still has a reasonable fraction of unrecovered potassium sulfate in addition to the whole ammonium chloride. It is crucial to recover these valuable materials from the solution, different trials were conducted to recover as much as possible out of these materials. The recovered salt is a mixture of ammonium chloride and potassium sulfate. It has been found that the percentage of recovered salt is very low if crystallization is applied on the mother liquor without any water evaporation, the very high solubility of ammonium chloride prevents the crystallization step to take place with the existence of the huge quantity of water in the solution. Hence it was necessary to get rid of part of the water exist in the solution prior to the crystallization step. Keeping the crystallization temperature fixed at 25 °C, Fig. 13 shows the effect of water evaporation % on the yield of the salt, as shown in the figure, the recovered quantity of the salt is very little (< 10 wt %) if no water evaporation takes place. Up to 59 wt % of the dissolved salts in the mother liquor can be recovered if 40 wt % of the water is evaporated. The percentage of yield may reach 67 wt % by further evaporation (50 wt % of the water is evaporated) but the viscosity of the slurry inside the evaporator will be high and this may cause handling and transferring problems.

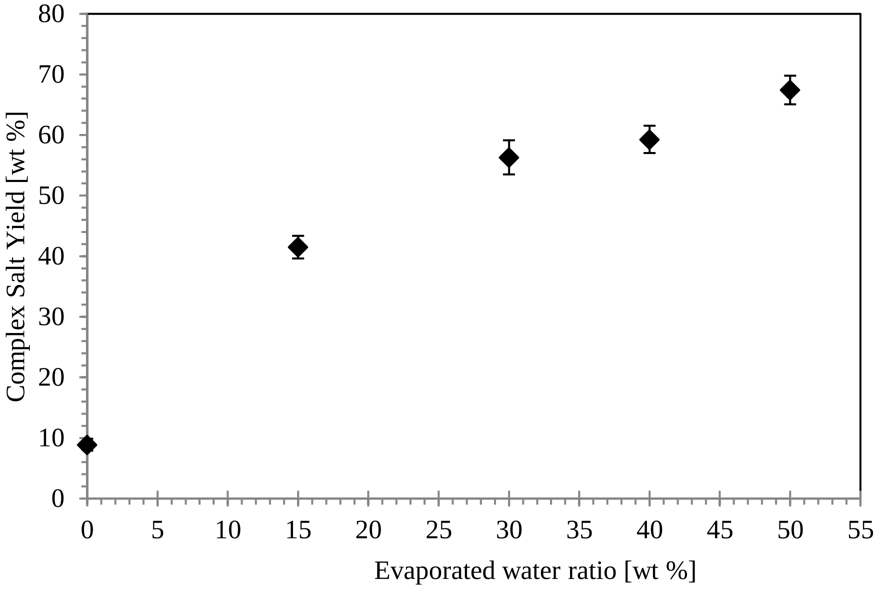

Fig. 13: Percentage of the Complex Salt Yield as a Function of Evaporated Water Ratio. Samples were Crystallized at 25 ^{O}C for 60 Min.

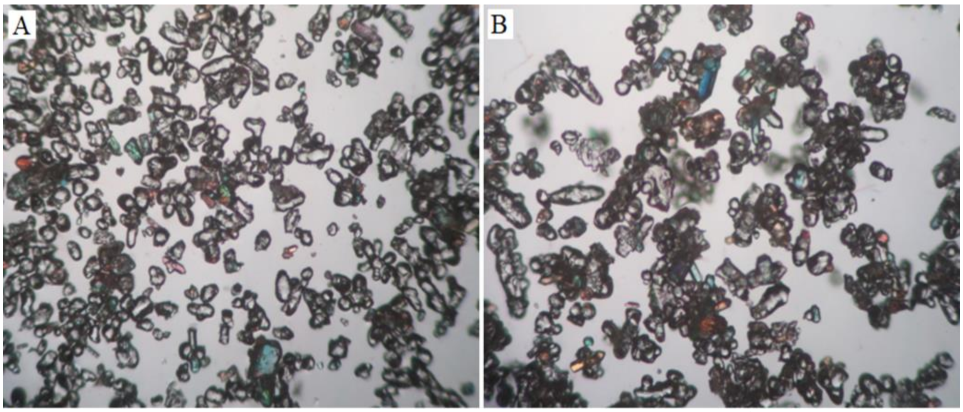

Fig. 14: Microscopic Graphs of Complex Salt Crystals Obtained by Crystallizing the Mother Liquor at 25 ^{O}C after Water Evaporation of A) 40 wt % B) 50 wt %.

Also, it has been found that the crystals obtained from solutions with high viscosity are hard to be dried and the flowability of the particles are less compared to crystals obtained from solution with less viscosity as shown in Fig. 14. As a result of this, it is decided to keep the percentage of evaporation around 40 wt %.

3.3.3. Effect of crystallization temperature

It has been found that once the solution is concentrated, the complex salt will start to precipitate even at high temperature. The effect of the crystallization temperature on the percentage of salt yield is presented in Fig. 15. Each point on the curve represents an individual experiment, all experiments were conducted by keeping the percentage of evaporation around 40 wt % while keeping the crystallization time fixed at 60 minutes and varying the crystallization temperature. Four crystallization temperatures were tested; 5, 10, 25 and 30 ^{o}C. The results show that if the crystallization temperature reduces from 30 to 5 ^{o}C, then an additional amount of 6 wt % of the complex salt can be obtained. This additional amount reduces to 3 wt % if the crystallization temperature decreased from 25 to 5 ^{o}C. Since cooling the crystallizer to 5 ^{o}C will cost more and needs a longer period of time, it is recommended to use a crystallizer temperature of 25 ^{o}C at which about 59 wt % of the complex salt can be recovered.

Table 2 shows the chemical analysis of the complex salt obtained. Detailed experimental values for the feed, main product (K_2SO_4) and the complex salt in addition to the chemical analysis of each item and the percentage of yield are tabulated in Table 3. These values were obtained by conducting a complete experimental run using the suggested operating parameters to produce potassium sulfate as well the complex salt.

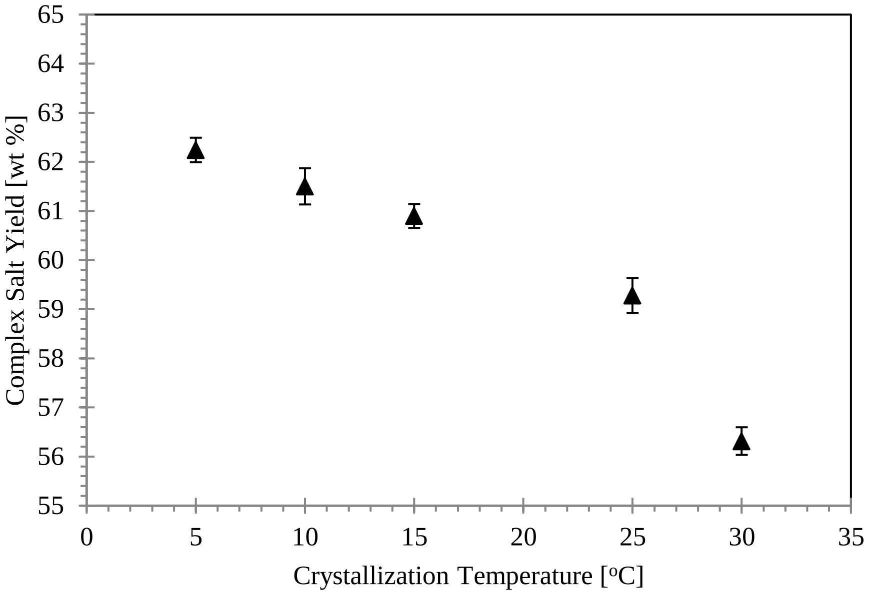

Fig. 15: Percentage of the Complex Salt Yield as a Function of Crystallization Temperature; the Crystallization Time was Kept at 60 Min and the Percentage of Water Evaporation was 40 %.

Table 2: Chemical Analysis of the Obtained Complex Salt Produced From the Main Mother Liquor after 40 wt % Water Evaporation and Then Crystallization at 25 °C

Element	Description
Color	white
State	Free flowing
Appearance	Crystals
Solubility	Fully soluble
NH_4Cl (63.8 %)	NH_4^+: 21.5 % Cl^-: 42.3 %
K_2SO_4 (35.3%)	K^+: 15.9 % SO_4^{-2}: 19.5 %
Moisture	0.8 %

Table 3: Chemical Analysis of the Feed and the Obtained Products as Well as the % Yield. the Operating Parameters were: 60 °C Reaction Temperature, 60 Minutes Reaction Time, 10 °C (K_2SO_4), and 25 °C (Complex Salt) Crystallization Temperature, 60 Minutes Crystallization Time, and 32% (Main Solution) and 40% (Mother Liquor) Water Evaporation

	Mass (g)	Composition	(g)	Theoretical	Mass (g)	Yield	%
Feed	291						
KCl (96% purity)	156	52.4% K^+	78.7	K_2SO_4	174.25	K_2SO_4	95.4
		47.6% Cl^-	71.3	NH_4Cl	107	NH_4Cl	52.5
		Other	6			K^+	93.2
$(NH_4)_2SO_4$ (98% purity)	135	72.8% SO_4^{-2}	96			Cl^-	52.1
		21.2% N^-	28			N^-	52.4
		6.05% H^+	8			SO_4^{-2}	96.8
		Other	3		Total solid yield		79.1
Main Product	138						
K_2SO_4	135.8						78
		43.2% K^+	59.62				
		55.2% SO_4^{-2}	76.18				
NH_4Cl	1.05						1.0
		0.5% Cl^-	0.69				
		0.2% N^-	0.28				
		0.06% H^+	0.08				
Moisture	1.1	0.8% H_2O	1.1				
Complex Salt	86.3						
K_2SO_4	30.5						17.5
		15.9 % K^+	13.7				
		19.5 % SO_4^{-2}	16.8				
NH_4Cl	55.1						51.5
		42.3% Cl^-	36.5				
		16.7% N^-	14.4				
		4.8% H^+	4.2				
Moisture	0.7	0.8% H_2O	0.7				

4. Conclusions

Potassium sulfate with high purity and clarity is produced by reacting commercial potassium chloride with commercial ammonium sulfate at moderately medium reaction temperature. The chemical analysis of the obtained K_2SO_4 crystals shows that the product has about 52 wt % K_2O and less than 0.5 wt % chlorine content. The addition of an evaporation step before the crystallization step will increase the K_2SO_4 yield from about 64 wt % up to 78 wt %. Large crystals of potassium sulfate have better features and have more satisfying aesthetics for the customers; also the separation of these crystals from the mother liquor and drying will be easier.

A potassium sulfate yield of about 78 wt % and a reasonable crystal size can be obtained if the production process is carried out at the recommended operating conditions obtained from the experimental study. A reaction temperature of 60 °C, a reaction time of 1 hour, a crystallization temperature of 10 °C, a crystallization time of 1 hour, and a water evaporation ratio of 32 wt % were found to be the best-operating conditions.

Further treatment of the mother liquor leads to production of a complex salt containing about 15 wt % N, 22 wt % K_2O, and 38 wt % Cl which can be used as NPK fertilizer if a source of phosphorous is added. It has been found that a water evaporation ratio of 40 wt % and a crystallization temperature of 25 °C will yield about 17.5% of the remaining K_2SO_4 in addition to about 51.5 wt % of the ammonium chloride.

About 93 wt % of the total input K can be recovered as 75.8 wt % in the K_2SO_4 and 17.5 wt % in the complex salt. On the other hand, about 40 wt % of the total input nitrogen can be recovered in the complex salt as ammonium chloride. Both of the obtained products are free-flowing with a moisture content of less than 0.8 wt %, both salts are fully soluble in water and leave no turbidity.

Compared with the Mannheim process for K_2SO_4 production, the present method requires much lower energy and it is free of chlorine gas emission, hence environmentally friendly process. While the Mannheim process requires a reaction temperature of at least 600 °C, the present process requires a reaction temperature of 60 °C only. Potassium sulfate produced by the present method have a shiny, clear, and larger crystals size compared to the powder form obtained by the Mannheim technique. In terms of equipment’s materials of construction; the present process does not require expensive alloys to fabricate the equipment from. Instead of stainless steel or special alloys, carbon steel or mild steel can be used since there is no corrosive acids exist.

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