FULL PAPER

UPSCALING THE PRODUCTION OF POTASSIUM SULPHATE (K_2SO_4) FROM STILLAGE

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Abstract

Stillage contains considerable amounts of potassium, which has attracted its use for fertigation. The infrastructure that is needed for fertigation requires huge capital investment, so that only fields close to the ethanol plant benefit, albeit salinising the soil, and acidifying and destroying the conveyance infrastructure. Therefore, making baggable potassium sulphate is a way of mitigating the challenges of stillage fertigation. This idea has been validated at a laboratory scale, by following the wet digestion method. In this scaled-up model, stillage from the Triangle Ethanol Plant (TEP) was analysed for its elemental constituents, and it contained 2.20% (± 0.18%) of potassium. The extracted potassium was recovered as potassium sulphate through the processes of digestion, clarification, evaporation, crystallisation and decolourisation. The optimised process produced 1.13 kg of potassium sulphate with a purity of 95.79% from a 60 L batch of stillage. The process had a cost-benefit of 26.96%, compared to purchasing a 50-kg bag of the same product on the market.

Keywords: Stillage, fertigation, potassium, optimisation, cost-benefit, validated

Introduction

Stillage, also known as vinasse, is the dark-brown, viscous waste that comes from distilleries. Its distinguishing features include the high concentration of organic matter, nitrogen compounds, Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), potassium and sulphates, as well as its acidic and caustic properties (Fuess and Garcia, 2014). At the Triangle Ethanol Plant in Zimbabwe, a substantial volume of stillage is primarily acquired as a secondary by-product of cane sugar production, whereby the primary by-product, molasses, undergoes fermentation and distillation to produce ethanol. Sugarcane-based stillage contains considerable amounts of potassium and this has attracted its use in fertigation (Mikucka and Zielińska, 2020). The potassium concentration in stillage is a result of its luxurious consumption by sugarcane during its lifecycle. Potassium is not a constituent of any part of the structural components of sugarcane, and neither is it retained in any of the main products, namely sugar and molasses, hence its fate lies in the stillage.

Ethanol plants normally produce 10 to 15 litres of stillage for every litre of ethanol that is produced (Pant and Adholeya, 2007; Satyawali *et al*., 2008; Mohana *et al*., 2009; Giacobbo *et al*., 2013). With an estimated yearly production capacity of 40 million litres of ethanol (Mutete and Mutatu, 2021), the Triangle Ethanol Plant would produce about 520 million litres of stillage if the average rate of stillage production was 13 litres per litre of ethanol.

The stillage from the Triangle Ethanol Plant is mixed with irrigation water and fertigated to the sugarcane-producing fields around the plant. Only the fields that are closer to the distillery benefit, because there is not enough infrastructure to carry it to all the fields in the industry. The distribution of stillage to other places further from the plant would require a huge capital investment in infrastructure development. According to Fuess and Garcia (2014), prolonged fertigation with stillage is associated with adverse environmental impacts, such as the risk of soil salinisation, the clogging of soil pores, a reduction in microbial activity, a significant

depletion of the dissolved oxygen concentration in water bodies, contamination by means of nitrates and eutrophication, the destabilisation of the soil structure and the possible acidification of soil and water resources.

Most distillery plants struggle with containing and managing the disposal of stillage (Montiel-Rosales *et al*., 2022). The desire is to have zero liquid discharge from the distilleries; however, this is unfortunately not feasible in many nations, due to the infrastructure and energy requirements associated with incineration (Balasubramanian and Kannan, 2016). Various techniques have been investigated for the management and disposal of stillage, including biological (aerobic and anaerobic), physicochemical (coagulation/flocculation, electrocoagulation, adsorption, ozonation and membrane processes) and thermal techniques (Getachew *et al.*, 2019). The main drawback of these processes is their high cost. In this study, a novel way of utilising distillery stillage was conducted, in which potassium was extracted as potassium sulphate crystals, by following the wet digestion method. The utilisation of stillage as a raw material for potassium sulphate production presents a remarkable reduction in the problems that are posed by its disposal. The production of potassium sulphate from stillage has several advantages, including a decrease in land and water pollution, as well as a reduction in the fertiliser input costs that are incurred by the sugar industry. The recycling of the potassium in stillage will make it more like a renewable resource, thereby reducing the reliance on mineral-based fertilisers. The transportation and storage of solid K_2SO_4 is easier, compared to that of liquid stillage.

The concept of producing baggable potassium sulphate can be a breakthrough with regard to cutting down on the cost of fertilisers in sugarcane production. Besides reducing the input costs, the process also reduces the negative environmental impacts associated with stillage disposal and prolonged fertigation. This idea has been validated at a laboratory scale by following the wet digestion method (Chauke *et al*., 2022). The process was optimised and had a projected cost-benefit of 22.27%, compared to the purchase of the same product on the market. By following product development protocols, this paper demonstrates the technical and commercial feasibility of producing potassium sulphate from the same stillage, and it also presents a cost-benefit analysis for the possible commercialisation of the process.

Materials and Methods

Materials

Analytical grade reagents were used to characterise raw stillage and the produced K_2SO_4. In the wet digestion process, 98% industrial-grade sulphuric acid was used. A 60 L stainless steel vessel was used as a dual reactor and evaporator, and a 20 L High-Density Polyethylene (HDPE) vessel was used as a crystallisation dish.

Stillage sampling and analysis

Stillage samples were collected in 25-litre plastic containers from a stillage storage dam at the Triangle Ethanol Plant and taken to the laboratory for analysis. The dry ashing method was employed for the elemental analysis of the stillage composition. A 1 g portion of thoroughly-mixed stillage was weighed into a porcelain crucible and then ashed at 500^{O}C in a Gallenkamp QPR/M 066 BH muffle furnace for an hour. The sample was allowed to cool in a fume hood at room temperature before the consecutive addition of 2 ml of deionised water and 3 ml of aqua regia. The sample was filtered into a 100 ml volumetric flask by using Whatman No 91 filter paper and the vessel was filled to the mark with deionised water. The filtrate was analysed for cations (K, Ca, Mg, Zn, Cu, Fe and Mn) against the calibration standards on a Varian SpectrAAS50 Atomic Absorption Spectrometer. The sample phosphate content was also analysed from the same filtrate by pipetting 10 ml into a 50-volumetric flask and adding 4 ml

of molybdovanadate reagent for colour development (Rambwawasvika *et al.*, 2022). The phosphate content was determined by using a Spectroquant Ultra Violet-Visible Spectrometer at 420 nm. The stillage pH and Electrical Conductivity (EC) were determined by dipping the respective electrodes in the fresh samples of stillage, using a Mettler-Tolledo Seven Excellency Multi-parameter. The Total Dissolved Solids (TDS) were determined by putting 100 ml of stillage in a pre-weighed porcelain crucible and heating it in a water-bath at 100ºC until all the water had evaporated, which was evidenced by a constant mass on further heating. The TDS was calculated by subtracting the mass of the empty crucible from the mass of the crucible containing the dried stillage sample, and it was expressed as a percentage of the wet stillage. The sulphur content was determined by using a Leco TruSpec CN and S analyser, whereby 0.35 g of fresh stillage sample was weighed into a combustion boat and placed in the sulphur module furnace which was regulated at 950ºC in a pure oxygen environment. The combustion of the sample freed the sulphur from the stillage and converted it to SO_2 gas, which was then detected by the infra-red detectors of the instrument and reported as a percentage of the total mass.

Production of K_2SO_4 from stillage

The process started with the acid digestion of 60 L of stillage by using 3 L of 98% industrial-grade sulphuric acid. The stillage and acid contents were heated to 100ºC in a 70 L capacity stainless steel pot, using a gas stove at a very low heat, with occasional stirring for six hours. The digested mixture was left to cool and clarify at room temperature. The sediment organic cake was removed by filtration with a 50-micron filter fabric to remain with the supernatant. The filtrate was evaporated to remove the excess solvent and to increase the potassium concentration. The overall evaporation step took three hours to complete until a 10 L solution was left. This volume was then allowed to cold crystallise in a High-Density Polyethylene (HDPE) vessel at room temperature. The formed crystals were separated from the mother liquor by decanting and washing them with ice-cold water. Recrystallisation and decolourisation were employed by using activated carbon to improve the purity and quality of the produced crystals. A schematic flow chart of the process is shown in Figure 1.

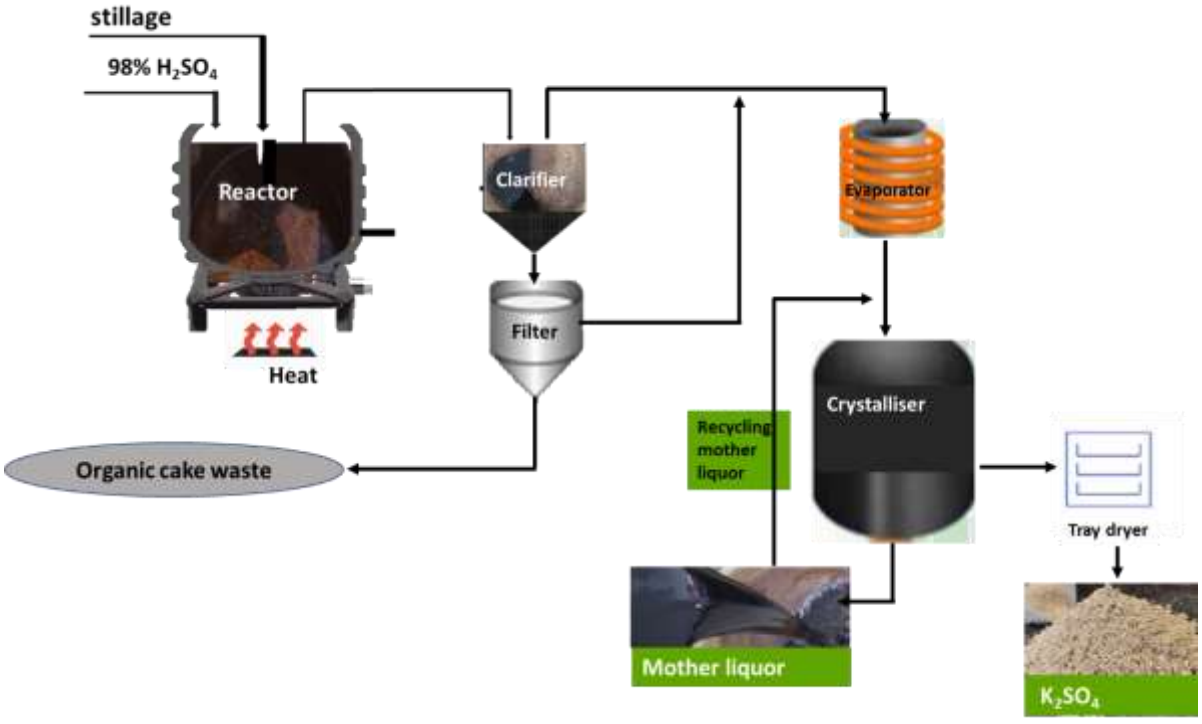

Figure 1. Flow process for the production of K_2SO_4 from stillage waste

Purification by recrystallisation and decolourisation with activated carbon

Re-crystallisation was carried out by dissolving the crystals in deionised water, followed by filtration. The filtrate was then re-subjected to the processes of evaporation and crystallisation, in order to allow the crystals to be formed again. Recrystallisation resulted in crystals of better purity, compared to those of the first crystallisation. The crystal purity was determined by using the AAS instrument to determine the potassium content. The decolourisation process involved dissolving the crystals in deionised water and mixing them with activated carbon, targeting the removal of melanoidins, which contributed to the dark colour. In the decolourisation step, gold-grade coconut-shell-activated carbon was used as a decolouriser. A 30 g portion of the AC was used for every litre of the dissolved crystal solution. The spent activated carbon was filtered out and the crystals were recovered by using the usual evaporation and crystallisation techniques.

Characterisation of the produced K_2SO_4 and the filter cake waste

The K_2SO_4 product was analysed for its K content, solubility and pH. The K content was analysed by using the same procedure for analysing stillage with AAS. The filter cake carbon content was estimated by using the Total Ignition method (Bojko and Kabała 2014). The solubility of the product was tested by putting a known mass of the product in a known volume of water, until no more could dissolve. The mixture was filtered and dried. The mass of the dried sample was subtracted from the initial mass of the product. The produced K_2SO_4 was analysed for its pH and EC by dissolving 10% (w/v) in deionised water and dipping the respective electrodes, which was followed by taking readings on the seven excellence multi-parameter instrument.

Cost-benefit analysis

To assess the commercial viability of the process, the estimated cost of manufacturing a 50-kg bag of K_2SO_4 from stillage was compared against the cost of purchasing a commercial product. The direct costs involved in all three classes of the produced crystals (the first crystallisation, re-crystallisation and decolourisation) were used to formulate the cost of production. The energy consumption was based on the amount of gas used to complete the batch process. The Cost Benefit (CB) was calculated by using Equation 1:

$$CB\ (\%) = \frac{Cost\ of\ purchasing\ a\ 50\ kg\ commercially\ -\ Estimate\ cost\ of\ producing\ a\ 50\ kg}{cost\ of\ 50\ kg\ commercial\ product} x100 \qquad (1)$$

Results and Discussion

Stillage from the Triangle Ethanol Plant was characterised and found to contain an average of 2.20% potassium. This percentage was used to calculate the expected yield from a 60 L batch. Processing 60 L of stillage produced 1.13 kg of potassium sulphate. The table below shows the constituents and characteristics found in the stillage that was used in this study.

Table 1. Chemical properties of TEP stillage. All values are expressed as means of the triplicates ± standard deviation

Parameter	Quantity	Analytical precision (SD)
K (%)	2.20	± 0.38
Ca (%)	0.51	± 0.07
Mg (%)	0.38	± 0.11
P (%)	0.186	± 0.103
Cu (%)	0.0046	± 0.0001
Fe (%)	0.0321	± 0.0001
Mn (%)	0.028	±0.005
S (%)	0.309	± 0.21
TDS(g/L)	1 040	± 25
EC (dS/m)	3.860	± 0.103
pH	4.35	± 0.24

Optimisation of process parameters and unit operations

Some of the process parameters and unit operations conformed to the optimised gram scale that was produced by Chauke *et al.* (2022). However, due to the increase in the scale of production, other process unit operations, like digestion and evaporation, needed to be optimised at a kilogram scale.

Digestion time

Using optimised H_2SO_4 to stillage of 1:20 (Chauke *et al.*, 2022), the digestion time was optimised by collecting samples at hourly intervals. The samples were dry-ashed and analysed for their K concentration. The absence of any significant further increase in potassium concentration over time indicated the completion of digestion. It was noted that the digestion time was directly proportional to the increase in the K content in the solution. The digestion of a 60 L volume of stillage with 3 L H_2SO_4 took an optimum of six hours, which resulted in 10.59% K in solution. Figure 2 below shows the optimised digestion time against the K concentration in solution. It can be seen from the graph that there was no drastic increase in the K concentration with a digestion time of six hours and beyond; this was therefore concluded to be the optimum digestion time.

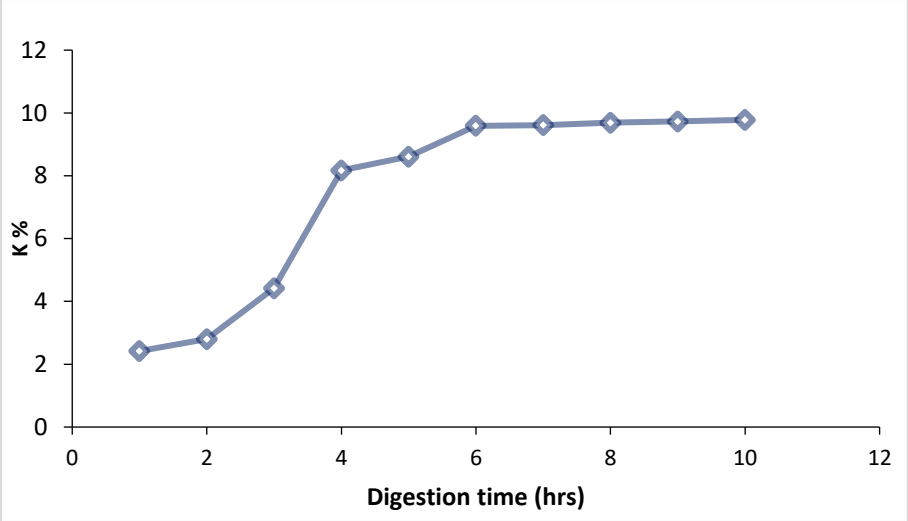

Figure 2. The plot of the recovered K% against the digestion time during the optimisation process

Evaporation and crystallisation

The evaporation time had a great impact on crystallisation and close monitoring was required. The concentration of the K in the solution kept on increasing with an increase in the evaporation time. The loss of water from the solution after evaporation concentrated the K (Figure 3).

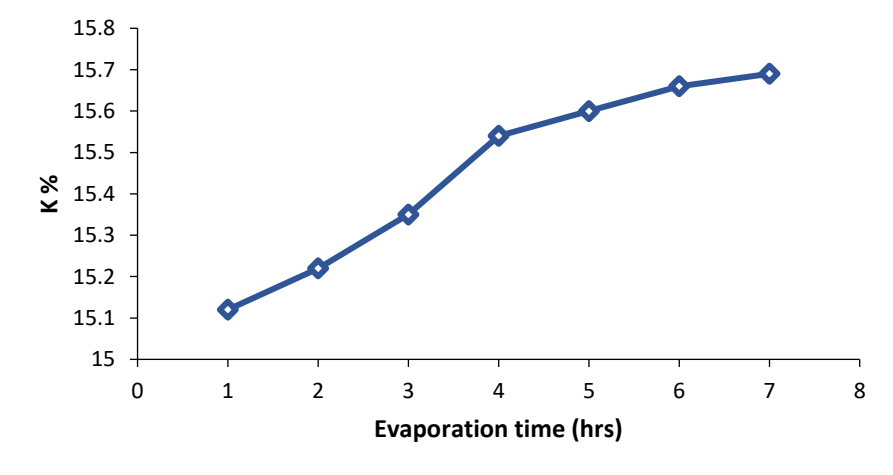

Figure 3. The plot of K% against the evaporation time for the optimisation of evaporation

Evaporation greatly affected crystallisation, with the volume of the solution that was left for crystallisation affecting the quality of the crystals. Evaporating for a shorter time and leaving more water resulted in purer crystals; however, they took too long to form. Leaving too little water in the solution by evaporating for too long resulted in impure crystals. Evaporating for an hour resulted in a 20 L solution being left for crystallisation. However, this did not result in crystal formation in 24 hours. Evaporating to remain with 15 L of saturated solution gave crystals albeit lower yields due to dissolution losses. Leaving them for a longer time, however,

produced good-quality crystals. The best crystals were obtained after evaporating the solution for 3 hours to remain with 10L. A 10L supersaturated solution started crystalising within 24 hours. Leaving a saturated solution of 10 L was achieved after three hours of evaporation. Evaporating beyond the 10 L saturation resulted in over-saturation and the formation of dirty crystals and caking. Therefore, an evaporation time of three hours, which resulted in a 10 L supersaturated solution, was taken as the optimum. These differences in the crystal nature were attributed to the degree of supersaturation of the solution, which is the driving force for both crystal nucleation and growth (Pritula and Sangwal, 2015). High supersaturation resulted in bogus nucleation, which was accompanied by mass crystallisation in the solution, and hence, the caking of the crystals (Pritula and Sangwal, 2015). At a low supersaturation, crystals grow faster than they nucleate, which results in a larger crystal size, whilst at a higher supersaturation, crystal nucleation dominates the crystal growth, ultimately leading to smaller crystals. Therefore, to get a better crystal size distribution, the evaporation stage needs to be monitored for optimum crystal formation. If the solution becomes over-saturated, rapid and uncontrolled crystal growth occurs, which leads to caking. Therefore, the evaporation rate was controlled to maintain a suitable level of supersaturation for controlled growth (Figure 4).

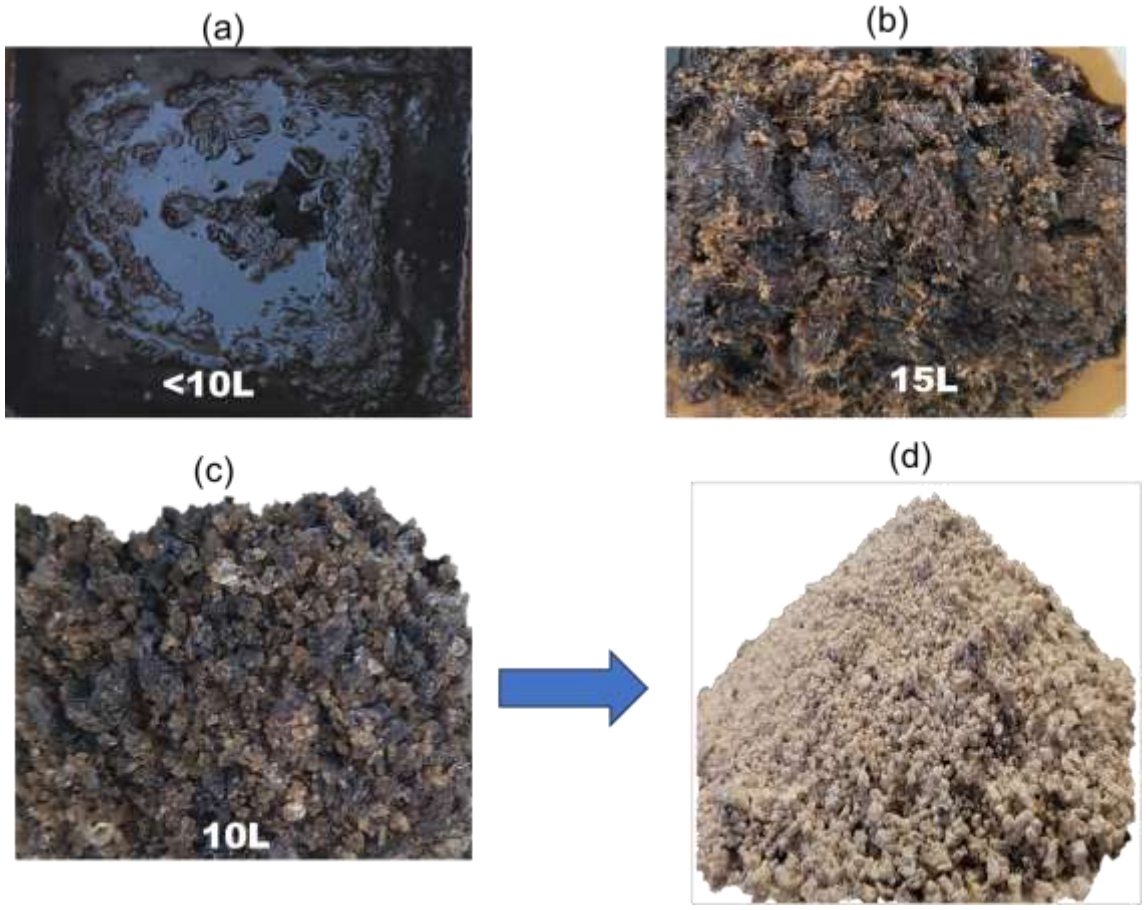

Figure 4. Crystals formed from different saturation levels: (a) formed when evaporation volume was left at less than 10 L, causing caking; (b) dendritic crystals from a 15 L saturation; (c) formed from a volume of 10 L; and (d) washed crystals from a 10 L saturation

Crystal purification techniques

Re-crystallisation (2nd crystallisation) and decolourisation were employed to improve the purity of the produced crystals. The crystals from the first crystallisation, the second crystallisation

and decolourisation stages were compared, in terms of the product quality, process time, recovery rate and cost-effectiveness of the process. Crystals obtained from the first crystallisation process had a lower purity, compared to the subsequent purification methods (Table 2). This could have been because of residual impurities that co-precipitated within the crystals. However, the differences in the purities were too small to warrant a reduction in the cost-benefit that comes with further purification, considering that the product is targeted for application as a fertiliser. The purification data are important as a basis for diversification in the use of the product. However, further purification resulted in an increased overall time consumption (Table 2).

Table 2. Comparison of the different purification processes (first crystallisation, second crystallisation and decolourisation) on the quality of the crystals (purity, processing time and cost of production)

Parameter	1st Crystallisation	2nd Crystallisation	Decolourisation
K%	42.41	42.88	43.01
K_2SO_4%	94.74	95.79	96.80
Overall time consumption of the process (hrs)	27.00	46.00	46.00
Estimated cost of producing 50-kg bag (US$)	31.10	31.77	42.57
*CB (KCl)%	28.51	26.96	2.14
*CB (K_2SO_4)%	40.19	38.90	18.13

*CB is cost-benefit

The crystals that went through the first crystallisation and decolourisation appeared to be purer, clearer and whitish, compared to those that were subjected to the first crystallisation only, or to the first and second crystallisation only. The visual appearance of the crystals is shown in Figure 5.

Figure 5. The visual appearance of K_2SO_4 crystals after different purification processes (a) crystals from first crystallisation, (b) second crystallised crystals, and (c) decolourised crystals

Characteristics of the produced K_2SO_4 and the filter cake waste

The different stillages produced by K_2SO_4 had different solubilities, ranging from 11.58 to 118.32 g/L against 120g/L of commercial product. The purest product (subjected to first crystallisation and then decolourisation) had the highest purity of 118.32. Solubility is important in fertilisers, as it determines the phyto-availability of the fertiliser's nutritional elements in the soil. The stillage that produced K_2SO_4 had a low pH of 5.41, 5.74 and 6.80 for the first crystallised, second crystallised and decolourised products, respectively. All the products had a lower pH, compared to the commercial product, which had an almost neutral pH of 7.10. The low pH of the products suggests a good fit in alkaline soils. The purer product (decolourised) had a high pH, which implies that they could be best-suited for soils with a low pH. Thus, purification serves to raise the product pH and it can be used to produce diverse products, depending on the pH of the soil. The reason for the low pH in less pure products could be the residual sulphuric acid on the crystals. There were no special trends in the electrical conductivities of the products, as shown in Table 3.

Table 3. Solubility, pH and EC characteristics of the K_2SO_4 products, in comparison to commercial products

K_2SO_4 Class	**Solubility(g/L)**	**pH**	**EC (µS/cm)**
Commercial grade	120.00	7.10	130
First crystallisation	111.58	5.41	143
Second crystallised	116.04	5.74	122
Decolourised	118.32	6.80	120

Processing 60 L of the stillage yielded an average of 1.073 kg (± 0.5 kg) of a highly-organic filter cake. The filter cake was analysed for its constituents and was found to contain an estimated 87.25% organic material, Ca of 2.29%, K of 0.376% and sulphur of 0.309, among other nutritional elements (Table 4). The low pH and appreciable amounts of Ca might result in the use of the filter cake as an ameliorant for sodic soils. Sodic soils are characterised by a high pH and sodium content. The high pH of sodic soils can be lowered by the acidity of the filter cake, while the high sodium can be replaced by Ca in the waste filter cake. Future research may be needed to assess the possibility of this endeavour.

Table 4. The chemical composition of the waste filter cake and its pH

Parameter	**Quantity**	**Analytical precision (SD)**
Estimate organic material (%)	87.25	± 2.450
K (%)	0.376	± 0.020
Ca (%)	2.29	± 0.070
Mg (%)	0.40	±0.113
P (%)	0.076	± 0.100
Cu (%)	0.043	± 0.001
Fe (%)	1.356	± 0.001
Mn (%)	0.092	± 0.005
S (%)	0.309	± 0.210
pH	2.31	± 0.24

Conclusion

Scaling up potassium sulphate production from stillage holds up a green light for its commercialisation. The scale-up model proved its feasibility and yielded an average of 1.13 kg K_2SO_4, with a purity and recovery rate of 95.79% and 89.23%, respectively, from a 60 L batch. Controlling the evaporation stage was the key factor in determining the formation of crystals. Evaporating 83% of the water during evaporation was optimum for the production of

a reasonably high yield of quality crystal. Purification processes, such as recrystallisation and decolourisation, enhanced the product quality, but resulted in an increased processing time and lower yields. The processes of purification by the second crystallisation and decolourisation are only necessary when the product is to be used for purposes other than soil fertility, besides which, the processes can be omitted.

Recommendations

Proper unit operations should be used to optimise the process further, by conducting in-depth research on reaction kinetics, heat transfer, as well as agitation parameters, for maximum potassium extraction and process efficiency. A lot of water is evaporated in the process; therefore, ways of recycling the steam should be explored. The scaled-up model used a gas stove for heating, but safer and sustainable energy sources should be used for large-scale production. The process produced 1.073 kg of acidic and highly carbonaceous filter cake, which can be used in the manufacture of activated carbon, or as a soil amendment for highly-alkaline soils.

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