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Preliminary studies on conversion of potassium chloride into potassium sulfate using membrane reactor

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Abstract

The trials of KCl conversion with sulfuric acid into sulfate salt were performed in a membrane reactor. The conversion process proceeded on the feed side of the membrane distillation system. HCl—the gaseous product of the conversion was continuously separated by means of the membrane, whereas non-volatile $KHSO_4$ and H_2SO_4 were completely retained in the feed solution. The model solutions containing HCl and H_2SO_4 or KCl and H_2SO_4 were applied as the feed. The influence of the feed composition on the HCl molar flux and volumetric flux through the membrane was studied. Potassium bisulfate was precipitated from the reaction liquor after cooling of the reaction mixture. Potassium sulfate was obtained as a result of desalting from $KHSO_4$ solution using methanol.

The results of the current studies were promising and showed a potential of applying a combination of reactor with membrane distillation in production of potassium sulfate.

Keywords: Membrane reactor; Direct contact membrane distillation; HCl separation; KCl conversion into potassium bisulfate

1. Introduction

Potassium is one of the three essential elements (NPK) in the life cycle of all plants. In agriculture, complex fertilizers almost always contain potassium chloride as a potash constituent, readily recoverable from naturally occurring potash raw materials. There are a number of reasons why other potassium salts are in fact more desirable as fertilizer materials than the chloride, but they are considerably more expensive [1]. Many crops (e.g. citruses, tobacco, potatoes, tomatoes) are chloride-sensitive, therefore, a fertilizer containing chlorides could be harmful or even toxic. Moreover, the application of the potassium chloride causes higher salinity and acidulation of the soil. Potassium sulfate is recommended to be used as a fertilizer due to its excellent physical properties and a low salt index [1].

Potassium sulfate can be obtained by acidulation of potassium chloride [1]. In this process, potassium chloride reacts with sulfuric acid forming potassium bisulfate and hydrogen chloride in the first step, according to the following reaction:

$$2KCl + H_2SO_4 \rightleftarrows KHSO_4 + 2HCl \tag{1}$$

The final product, potassium sulfate can be formed at high temperature, about 600–700 °C (the classical Mannheim process) [1] or at ambient temperature by desalting the salt using a 40% methanol solution [2]:

$$2KHSO_4 \xrightarrow{CH_3OH_{aq}, 298\,K} K_2SO_4 + H_2SO_4 \tag{2}$$

During the conversion of KCl with H_2SO_4, HCl could be separated from the liquor to shift the reaction. The results of our previous work [3–6] have demonstrated, that the hydrochloric acid is effectively separated from solutions by membrane distillation (MD). The MD process is a promising method for HCl recovery from spent metal pickling solutions [5,6]. The separation mechanism of MD is based on the vapour/liquid equilibrium of a liquid mixture. The driving force of the process is established by a vapour pressure difference across a hydrophobic membrane resulting from the temperature and compositions of solutions in the layers adjacent to the membrane [3]. Therefore, under MD conditions non-volatile species should be completely retained in the feeding solution, whereas the volatile species will be transferred across a hydrophobic, microporous membrane

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[3]. The MD membranes are made from such polymers as polytetrafluoroethylene (PTFE), poly(fluorovinylidene) (PVDF) or polypropylene (PP) which are thermally and chemically resistant [3–6]. Their hydrophobic properties do not permit for the flow of aqueous solutions through the membrane. Hydrogen chloride is a volatile product of the KCl and H_2SO_4 conversion; therefore, it can be transferred across a membrane during the membrane distillation process [7].

The aim of the work was to investigate the possibility of the direct contact membrane distillation (DCMD) application for HCl separation from reaction mixture during the conversion KCl with H_2SO_4 in the membrane reactor as well as the possibility of obtaining potassium bisulfate free of chlorides using the reactor.

2. Materials and methods

The DCMD process was carried out in a laboratory-scale installation. The experimental set-up for the direct contact membrane distillation studies with a capillary membrane module is presented in Fig. 1. The MD module was equipped with polypropylene capillaries, $d_{in}/d_{out} = 1.8/2.6$ mm, produced by Membrana GmbH, Germany. The effective area of the capillary membranes was 226 cm^2. The membrane module was set in the MD installation in a vertical position. In all the experiments, the warm feed and cold distillate streams flowed in the module in a co-current mode, from the bottom to the upper part of the module. Such an arrangement ensures the venting of the module and easy transfer of the HCl through the membrane. Moreover, it protects the module against collecting of gas in its upper part. The feed flowed inside the capillaries, whereas the distillate flowed through the intercapillary space. The process solutions were circulated in the thermostated systems. The inlet feed temperature amounted to 343 K. Due to the evaporation of water at the interface of feed solution and the membrane pores interface, and heat transfer through the membrane, the temperature of the reaction mixture in the feed tank was lower, and amounted to 333 K. The liquor was then heated to 343 K in a heat exchanger. The inlet temperature of distillate was equal to 293 K for all the experiments.

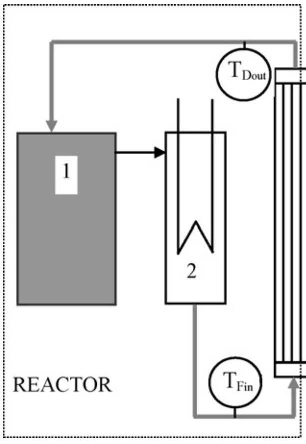

Fig. 1. Scheme of the MD experimental set-up: (1) feed tank; (2) heating system; (3) capillary module; (4) distillate tank; (5) cooling system.

In the first step, the studies were performed using as a feed the model solutions containing 50 g of hydrochloric acid and various amounts of sulfuric acid equal to 50, 107 or 250 g/dm^3. For the conversion process solutions containing KCl and H_2SO_4 were applied. The molar ratio of the substrates was as 1:1. The cold system was initially supplied by distilled water. During the experiments associated with the conversion process, the solution was concentrated close to the saturated state, when crystals were precipitated from the reaction mixture after cooling. The changes of volume of the cold distillate were measured every hour. The HCl flux across the membrane was calculated from the material balance of HCl performed every hour taking into account the changes of volume and the acid concentration in the distillate. The calculation was previously described in detail in references [3–5]. Simultaneously, the composition of the feed was analysed. The composition of the precipitate separated from the reaction mixture was analysed chemically (after dissolution) and/or using X-ray diffraction method.

3. Results and discussion

The potassium bisulfate was produced in the membrane reactor by the conversion of potassium chloride with sulfuric acid using the membrane distillation. The products of the conversion constitute potassium bisulfate and HCl. Therefore, the reaction mixture contains the following ions: K^+, H^+, Cl^- and SO_4^{2-}. The removal of volatile HCl moves the reaction in the desired direction to form $KHSO_4$. At the beginning of the studies, experiments were performed to evaluate the efficiency of HCl separation from model solutions containing a mixture of hydrochloric and sulfuric acids. During MD of the solution nonvolatile sulfuric acid was concentrated in the feed, whereas both gaseous HCl and the water vapour were transferred through the pores of the PP membrane. The vapour was condensed directly in the solution in the cold compartment (intercapillary space) in which HCl was dissolved. In accordance with the liquid/vapour equilibrium, the permeate composition is affected by the concentration of both hydrochloric and sulfuric acid in the feed. Therefore, the studies concerning the influence of sulfuric acid concentration in the feed on the transport of hydrogen chloride were performed.

Fig. 2 presents the changes of HCl concentration in the feed in the MD process as a function of time, at various initial concentration of sulfuric acid in the feed. According to water vapour and HCl partial pressure equilibrium with hydrochloric acid solutions, the partial pressure of gaseous HCl rises sharply when the HCl concentration in the solution increases above 300 g/dm^3, at ambient temperature. For higher temperatures of the liquid phase, the solubility of gaseous HCl decreases and the HCl partial pressure rises at lower content of the compound in the solution [8]. The results of the experiments showed that the presence of sulfuric acid in the feed containing HCl decreased the solubility of the volatile HCl, causing enrichment of vapour. Since H_2SO_4 is non-volatile compound, therefore it was concen-