

Absorption Process for Mitigating Green Oil Formation in Petrochemical Plants



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The reaction of hydrochloric acid with hydrocarbons in petrochemical plants produces a viscous hydrocarbon compound called green oil. This oil can cause corrosion problems in the internal parts of equipment. As an alternative to the adsorption process used to remove hydrochloric acid, a simulation model is presented to efficiently absorb hydrochloric acid from an off-gas stream from an industrial process. Five suggested organic solvents were used in addition to water. Operating conditions that could affect HCl removal were investigated and optimized for all proposed solvents. Furthermore, an economic study was performed for all proposed solvents based on required utility and capital cost estimates. The results showed that glycolic acid followed by ethylene glycol ranked second and third after water among the proposed solvents in terms of highest solubility, lowest solvent flowrate, and lowest capital and utility costs. Design Expert software was used to statistically analyze the simulation results.

Keywords

absorption process, green oil, water solvent, organic solvents, process simulation

Introduction

In petrochemical plants and refineries, the presence of halides and especially hydrogen chloride in the naphtha catalytic reforming unit can cause serious operational problems in compressors and subsequent hydroprocessing units.^{1,2} If hydrogen chloride is not removed from the hydrocarbon stream, it may cause corrosion of all equipment and catalysts, and affect the process products.^{3,4} It is therefore important to remove hydrogen chloride from hydrocarbon streams.

There are several techniques used to remove hydrogen chloride from hydrogen gas streams. These techniques are catalytic hydrochlorination, electrochemical dechlorination, pyrolysis, and adsorption. In the catalytic hydrochlorination process, the catalyst always converts organic chloride into hydrochloric acid, and caustic treatment is always the method of removing hydrochloric acid.^{5–11}

The adsorption process is the common method for removing hydrochloric acid from different streams.¹¹ The adsorbent used can be activated alumina, enhanced alumina, alumina, metal oxides, mixed metal oxide, or zeolite.^{12–15} Reinforced and activated alumina was the first type of adsorbent used to capture hydrogen chloride.¹¹

Lee *et al.*¹⁶ used NaOH-supported activated carbon (NaOH/C) in a fixed bed reactor to treat gas containing hydrochloric acid. They found that NaOH/C is a good adsorbent for removing hydrochloric acid, and its treatment capacity increases with increasing water content by up to 27 %. They also found that the hydrochloric acid processing capacity of NaOH/C is about 6 times that of commercial alumina.

Zeolite has been widely used by many researchers because of its advantages. It is suitable for all phases (liquid and gases), green oil will not form on its surface like alumina, and it has a high adsorption capacity for chloride.^{11,17–20}

The work on absorption of hydrochloric acid from refineries and chemical gas streams using solvents has attracted researchers.^{21–23} Some researchers have studied the solubility of hydrochloric acid in some organic solvents, such as acids, esters, alcohols, and ethers. Liu *et al.*²¹ studied the separation of hydrochloric acid from a mixture of trifluoromethane gas and hydrochloric acid using different organic solvents, such as alkane, alcohols, chlorinated solvents, ketones, ethers, and esters. They found that alcoholic solvents such as methanol, glycerol, and butanol have high solubility in hydrochloric acid. Among these alcohols high solubility was achieved by glycerol. Jin *et al.*²³ introduced a

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rotating stator reactor as an absorber to remove hydrochloric acid from flue gas using glycerol as a solvent. They studied the effects of glycerol flow rate and temperature, rotation speed, and gas flow rate on hydrochloric acid recovery. Some other researchers have studied ionic liquids (IL) as absorbents in capturing hydrochloric acid. These liquids are molten salts that have a melting point close to room temperature. These absorbents are non-volatile, possess high thermal stability, and offer tunable solubility for both polar and non-polar substances.²⁴ However, their practical application is limited due to high viscosity, high cost, and questionable environmental friendliness.²⁵ He *et al.*²⁴ studied the solubility of HCl in three ILs at various temperatures and pressures: 1-butyl-3-methylimidazolium chloride, 1-hexyl-3-methylimidazolium chloride, and 1-octyl-3-methylimidazolium chloride. The results showed that these ILs achieved high HCl solubility, which decreased with increasing length of the alkyl substituents.

As an alternative to ionic liquids, deep eutectic solvents (DESs) have attracted considerable attention due to their gas absorption capabilities and favorable properties.^{25–27} DESs are non-volatile, non-toxic, non-flammable, and can be regenerated. Choline chloride (Ch-Cl)-based DESs, combined with various hydrogen bond donors such as carbohydrates, polyols, carboxylic acids, and amides, are particularly attractive due to their low cost, biodegradability, and non-toxicity.^{25,26} Zhu *et al.*²⁶ studied the solubility of hydrochloric acid gas in Ch-Cl-urea, Ch-Cl-glycolic acid, and Ch-Cl-glycerol. They found that Ch-Cl-urea exhibited the highest solubility in hydrochloric acid, followed by Ch-Cl-glycerol and Ch-Cl-glycolic acid. Feng *et al.*²⁷ studied the solubility of HCl in six Ch-Cl-DESs using ethylene glycol, glycerol, glycolic acid, lactic acid, oxalic acid, and malonic acid. They found that the highest HCl solubility was achieved with Ch-Cl-ethylene glycol and Ch-Cl-glycerol, followed by Ch-Cl-glycolic acid and Ch-Cl-lactic acid, and finally by Ch-Cl-oxalic acid and Ch-Cl-malonic acid.

Sequential absorption using caustic soda followed by water has also been reported as an effective method for absorbing hydrochloric acid from tail gases. Liu and Yang²⁸ proposed a two-step absorption process for HCl removal from synthesized tail gas. In the first step, hydrochloric acid is absorbed using an aqueous alkali solution; in the second step, water is used to absorb the remaining HCl. This technology has been applied in a refinery in Upper Egypt. A single absorption tower is used, divided into two sections. The lower section is a countercurrent between the caustic soda and the tail gas exiting the catalytic reformer, while the upper

section is a countercurrent between the tail gas exiting the lower section of the absorption tower and water. Additional studies have also explored alkali-based absorption methods.^{29–32}

The development of a new, energy-efficient, and cost-effective absorption process is essential for the industrial recovery of hydrochloric acid gas. Therefore, it is necessary to develop a method for treating tail gases containing hydrochloric acid, especially to efficiently produce pure hydrogen chloride for sale or reuse as a raw material for certain chemicals in the chemical industry.²⁵

Most prior studies on the absorption of hydrochloric acid from the gas stream in the petrochemical industry have been based on small-scale laboratory experiments, and lack integration of the absorption and solvent regeneration processes.^{21–27} Typically, the regeneration of the HCl-saturated solvent is carried out without recycling the regenerated solvent in a closed-loop system. In addition, critical design aspects such as heating duty in the regenerator, and the design parameters of the absorber and regenerator (packing type, diameter, packing number, etc.) are often omitted.

The purpose of this work was to investigate various solvents for HCl removal from a hydrogen gas stream using predictive simulation models developed in Aspen HYSYS. Notably, current literature lacks any comprehensive evaluation of water as a solvent for HCl absorption. This study presents the first simulation models of HCl absorption using different solvents. It also introduces a novel capital expenditure (CAPEX) optimization approach for the absorption and stripping process using Aspen Economics. This work may be considered the first to propose a low-cost solvent coupled with full economic evaluation.

Water and five organic solvents—ethylene glycol, glycolic acid, glycerol, lactic acid, and malonic acid—were proposed and compared. These solvents were used in a closed absorption cycle with recirculation of the regenerated solvent. For each solvent, optimal design conditions were determined to maximize HCl recovery in the absorption and regeneration process, including solvent flow rate and temperature, absorption pressure, stripper reflux ratio, and stripper reboiler duty. The proposed absorption process simulates a real industrial scenario for HCl removal from gas streams. The regenerated solvent is circulated from the stripping tower to the absorption tower to reabsorb HCl from the continuous feed gas stream in a closed loop. All design parameters for the absorption and stripping towers, including tower diameter, packing material, packing number, packing type, height, and dimensions, were fully specified.

Methodology

The aim of this work was to design and simulate a proposed absorption process to remove HCl from a hydrogen gas stream originating from an existing continuous catalyst regeneration process. To achieve this, various organic solvents were proposed and used in addition to water. Firstly, the proposed absorption process was simulated using Aspen HYSYS version 11, with water used as the base-case solvent.

Secondly, the optimal number of stages for the absorption and stripping towers was determined based on an estimate of the capital and utility costs of the proposed absorption process. The optimum number of stages was defined as the one that minimizes overall operating and capital costs. The number of theoretical stages in both absorber and stripper towers was assumed, while the solvent flow rate was adjusted to ensure 100 % HCl removal in the absorber—necessary to prevent green oil formation in the downstream process. Other parameters, such as reflux ratio, were fixed, taking into account the required utilities such as cooling water for the condenser (top of the stripper) and low-pressure steam in the bottom of the stripper. To reduce the heating energy required for stripping the HCl during regeneration, the pressure of the HCl-rich water stream exiting the bottom of the absorber was lowered, consequently decreasing the number of the stages in the stripper tower, and subsequently reducing capital and utility costs. Additionally, tuning the pressure of the stripper inlet stream helped minimize water entrainment with HCl in the overhead vapor, thus reducing solvent makeup requirements. For each assumed number of stages, capital and utility costs were evaluated. The effect of the various operational design conditions—including absorber pressure, solvent circulation rate, inlet solvent temperature, feed gas flow rate, hydrochloric acid loading in the feed gas, and hydrochloric acid loading in the recycling solvent—on HCl absorption and recovery for all proposed solvents was studied and optimized. An economic analysis was conducted for all proposed solvents, based on the calculation of utility and capital costs using Aspen Economics. This tool proved valuable in optimizing both capital expenditure (CAPEX) and operational expenditure (OPEX) and provided a foundation for future industrial-scale cost estimation.

Finally, Design Expert version 13 was used to statistically analyze the simulated data of the absorption process.

Simulation assumptions

Based on literature data, simulations were performed using Aspen HYSYS version 11 to determine suitable operating conditions for an industrial

hydrochloric acid absorption process. Absorption temperature in the absorber tower was assumed to range from 20–50 °C, as suggested by Jin *et al.*²³ The absorption pressure was assumed to range from 50–450 kPa.^{23–26} The Wilson liquid activity model was used as a thermodynamic properties package, since Wilson mostly deals with non-ideal systems suitable for chemical streams and equilibrium models.³³

Binary interaction parameters for hydrogen chloride and the studied organic solvents besides water were available in the Aspen HYSYS properties database. The absorber tower was simulated at 450 kPa. The temperature and pressure of the make-up solvent were 25 °C and 100 kPa, respectively. The effect of operating parameters (solvent flow rate, solvent inlet temperature, absorber pressure, feed gas flow rate, HCl loading in the circulating solvent, and HCl concentration in the feed gas) on the HCl recovery efficiency was studied and evaluated using Aspen HYSYS software. The HCl recovery efficiency was calculated according to Eq. (1).³⁴

$$\text{HCl recovery} = \frac{\text{HCl}_{\text{feed gas}} - \text{HCl}_{\text{outlet gas}}}{\text{HCl}_{\text{feed gas}}} \quad (1)$$

Statistical analysis

Design Expert version 13 software was used to determine the significant effects of the factors and their interactions on the response. The statistical analysis of the simulation data obtained from Aspen HYSYS simulation software for the hydrochloric acid recovery efficiency and the studied operational variables (solvent flow rate, solvent inlet temperature, absorber pressure, and feed gas flow rate) were statistically analyzed, evaluated, and examined using the Response Surface Methodology (RSM) design type (quadratic polynomial model) in Design Expert software. An analysis of variance (ANOVA) in Design Expert was conducted to evaluate the significance of each parameter. Two tests were used in the ANOVA analysis: the P-value (probability value) test, and the R-squared (R^2) test. The P-value test indicates the significant parameters in the model. A P-value less than 0.05 indicates that the model parameters are significant, whereas a P-value greater than 0.1 indicates that the model parameters are not significant and are excluded from the model. R-squared is a statistical measure that indicates how much of the variation of a dependent variable is explained by an independent variable in a regression model. The R^2 test is used to examine the predictive ability of the model. It includes R^2 , adjusted R^2 , and a predicted R^2 . An R^2 close to one means that the model fits the data, an adjusted R^2 close to one means that the parameters and their interactions are

significant, and a predicted R^2 close to one means that the model predicts the response to new observations well.^{34,35}

Catalytic reforming unit process description

An existing catalytic reforming unit was selected as a case study (Fig. 1). In this unit, straight-run naphtha is first processed in a naphtha hydrotreater (NHT), where light and heavy naphtha are separated. The heavy naphtha then passes through the reaction section of the catalytic reforming unit.

The primary objectives of the catalytic reforming unit (also known as the octane unit) are:

- To produce gasoline with a high octane number and rich aromatic content.
- To generate hydrogen gas as a valuable by-product for use in other units (diesel hydrotreater, naphtha hydrotreater, isomerization unit, etc.).

Due to coke deposition on the surface of the catalyst in the catalytic reactor (spent catalyst), the catalyst must be continuously regenerated. This process, referred to as continuous catalyst regeneration (CCR), involves the injection of chloride and pure hydrogen gas, as shown in Fig. 1.²¹

The CCR section ensures the catalyst is continuously regenerated during normal operation, maintaining a constant coke level in the reactors to sustain optimal operating conditions for the reformer unit. Once the coke level in the catalyst reaches be-

tween 3–7 wt.%, catalyst regeneration will begin according to the following steps:

- Combustion (coke burning)
- Oxychlorination
- Calcination
- Reduction.

In the combustion section, the coke deposited on the spent catalyst is burned off using hot nitrogen containing a low concentration of oxygen. This combustion step generates high temperatures, which lead to the sintering of platinum particles of the catalyst and a decrease in the weight percentage of chlorine on the catalyst surface. The subsequent oxychlorination step aims to restore the ideal metallic phase dispersion of the platinum-based catalyst and replenish the chlorine content on the catalyst using a chlorinating agent.²⁸ In the calcination step, hot air is used to dry the catalyst and remove moisture. The final regeneration stage involves the reduction of platinum oxide to the active metal form using >99 % pure H_2 gas, typically sourced from a pressure swing adsorption (PSA) purification unit or membrane unit.²¹

To enhance platinum dispersion and restore catalyst acidity, CCR units inject a chlorinating agent during the oxychlorination step. Chlorination of the catalyst can be achieved using chlorine gas (Cl_2), as reported by Marczewski *et al.*³⁶ and Ayame *et al.*³⁷ or gaseous HCl .^{38–41} However, the use of chlorinating agents results in hydrogen chloride formation in the hydrogen stream exiting the CCR unit. This hydrogen stream and the hydrogen pro-

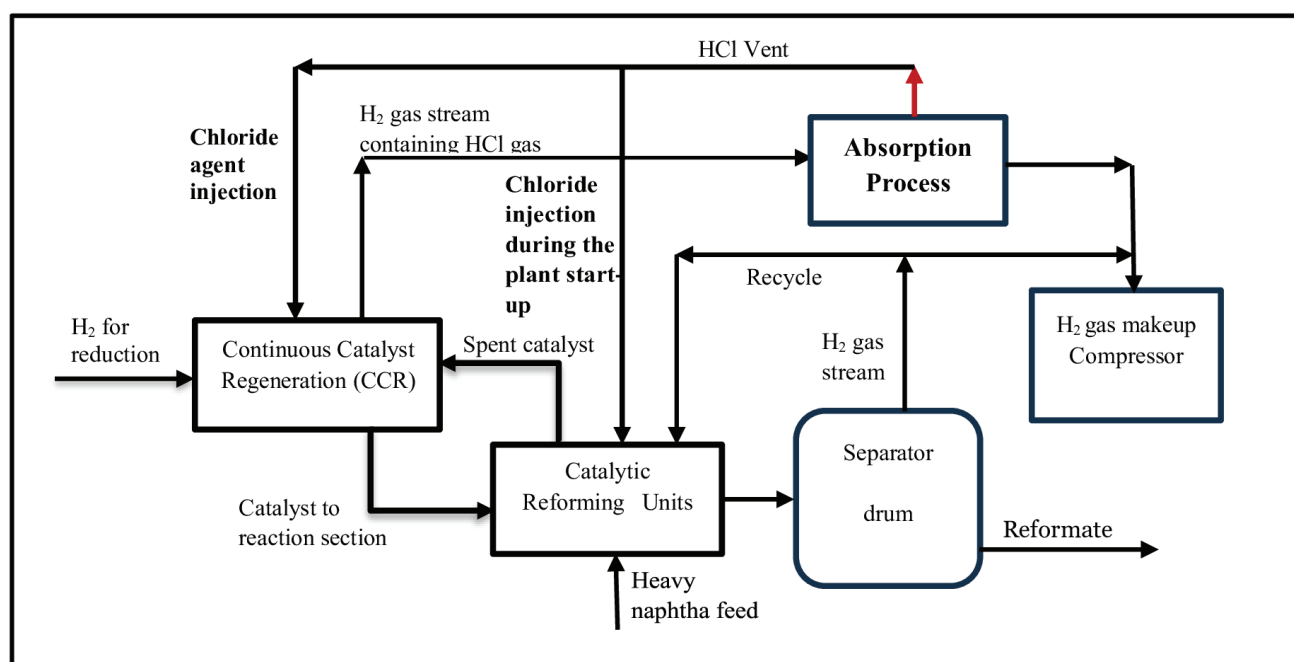


Fig. 1 – Proposed catalytic reforming unit with absorption process installed at the outlet of the continuous catalyst regeneration unit

duced in the catalytic reforming reaction, is routed to the downstream processes. Hydrogen consumed in downstream processes can be adversely affected by even trace amounts of hydrochloric acid present in the hydrogen gas stream. In addition, this may cause corrosion problems in compressors, valves, and other equipment. Furthermore, a common problem with CCR units is the formation of long-chain polymerized hydrocarbons, also known as “green oils”. The H_2 gas stream from the catalyst reduction section is always saturated with chloride due to the injection of chloride into the oxychlorination step of the continuous catalyst regeneration. This stream is considered the main reason for the formation of green oil because it is in direct contact with heavy hydrocarbons from the reaction section at the top of hydrogen make-up compressor.

Green oils are the byproducts of unwanted polymerization reactions occurring across the surface area of the catalyst, where hydrocarbons react with hydrochloric acid to form chlorinated hydrocarbons. The olefin polymerization reaction will be promoted by the presence of HCl downstream of the reaction section. Chemical combinations of relatively small molecules with enormous chain-like or network-structured molecules are the main components of these reactions. This type of polymerization produces complex multi-chain chemistries with high boiling points and generally waxy molecules. These molecules were thought to be oligomers of light olefinic hydrocarbons. They are green or red, mostly composed of C_6 – C_{18} hydrocarbons, and may have a tail above C_{40} with a few aromatic nuclei present in the configurations. It is necessary to eliminate HCl from gas or liquid hydrocarbon streams because it can lead to unfavorable catalytic reactions and contaminate the downstream units’ catalyst systems. Furthermore, since HCl is regarded as a hazardous material, it is imperative to prevent its release into the environment.²²

Reciprocating compressors are the most commonly used type of compressor in industrial applications. Because of their high-pressure ratio, reciprocating compressors are essential components in the process, but their maintenance costs are approximately 3.5 times higher than those of centrifugal compressors.⁹

Due to the formation of hydrochloric acid in the hydrogen gas stream exiting the catalytic reforming unit and to mitigate green oil formation in the hydrogen gas stream compressor, an adsorption unit was implemented in this studied catalytic reforming unit. The catalyst used in this catalytic reforming unit consisted of alumina (Al_2O_3) as well as a promoter (aluminum, sodium, or calcium) to enhance the adsorption of HCl from gas streams.

However, this process has several limitations: The catalyst in the adsorption process is not regenerated and is typically discarded at end-of-life. Chloride salts may be formed when aluminum, sodium, or calcium (catalyst activators) react with hydrochloric acid on alumina-based adsorbents. Adsorption beds can also produce green oil when the green oils are produced in fixed bed adsorption, this leads to fouling and premature failure of the adsorbent, which is explained by an increase in delta P across the bed. The life and efficiency of the adsorbent depend on the chloride content in the hydrogen gas stream.^{12–15}

This work presents a detailed design of the HCl absorption process as an alternative technology for the adsorption process, with the choice of solvent type. In the existing catalytic reforming unit, an adsorption process is used to adsorb all the hydrogen chloride in the hydrogen gas stream into the adsorbent layer and is not recovered. In the absorption process proposed in this study, the recovered hydrogen chloride from the stripping tower can be redirected for use as a chloride agent in the oxychlorination zone of the regenerator tower in the CCR process, and for catalyst activation during plant start-up, as presented in Fig. 1. The presented absorption process effectively removed all HCl with high efficiency. The H_2 gas stream exiting the CCR process goes directly to the absorption tower to remove all the HCl gas, and then to the H_2 make-up compressor without chloride contamination.

Modeling the hydrogen chloride absorption process using water solvent as the base case

Fig. 2 illustrates the proposed absorption process. The H_2 gas stream from the CCR reduction chamber section with a mass flow of about 160 kg h^{-1} (Table 1) enters the absorption tower, where it contacts a water solvent stream. The absorption of HCl into the solvent depends on the equilibrium solubility of HCl in the solvent used. The hydrogen gas stream of the upper product of the absorption tower is free of any HCl gas. The bottom product of the absorption tower is water saturated with hydrochloric acid (L1 stream) and is sent directly to the stripper section to recover water from hydrochloric acid. The recovered water (L4 stream) is then cooled, mixed with makeup water, and pumped to the absorption tower as a closed loop to maintain the solvent flow rate. The HCl gas product from the top of the stripper (HCl vent stream) can combine with heavy naphtha feed to be used for chloride injections during plant start-up to protect the catalyst. In addition, it can be used as a chloride agent in the oxychlorination step of the CCR process. Absorption and stripping towers are simulated as packing towers.

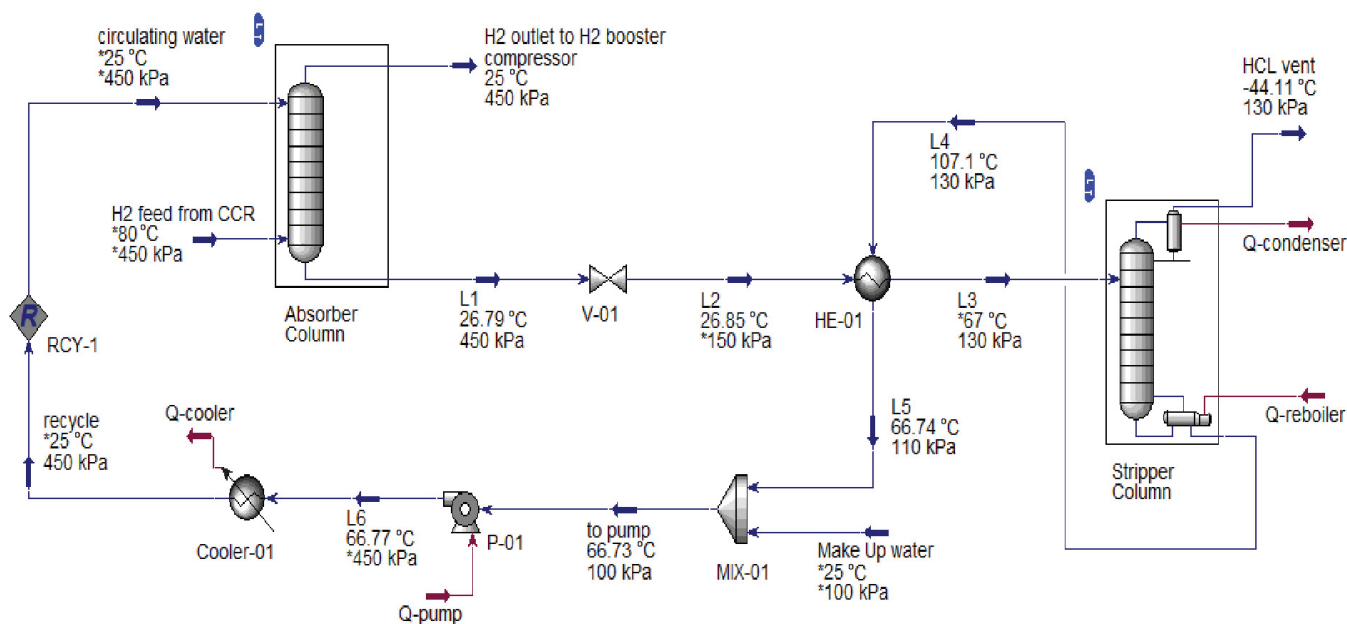


Fig. 2 – Proposed absorption process model for removing hydrochloric acid from the hydrogen gas stream leaving the CCR process

Table 1 – Hydrogen feed gas conditions and composition entering the absorber

Hydrogen gas specifications exiting the CCR unit	
Temperature, °C	80
Pressure, kPa	450
Mass flow rate, kg h ⁻¹	160
Molar flow, kg mol h ⁻¹	71.22
Composition (mol, %)	
Hydrogen	99.04
HCl	0.05
H ₂ O	0.2
Methane	0.08
Ethane	0.05
Propane	0.02
i-Butane	0.01
n-Butane	0.0
Nitrogen	0.55

Results and discussion

Simulation of the hydrogen chloride absorption process

Aspen HYSYS simulation software (version 11) was used to simulate the proposed absorption process presented in Fig. 2.

Determining the optimum number of absorber and stripping tower stages

To determine the optimal number of stages for the absorber and stripper towers, simulations were conducted with absorber pressure set at 450 kPa, feed gas temperature at 80 °C, and solvent (water) temperature at 25 °C, 7 stages at stripper tower, and stripper reflux rate at 3 kg mol h⁻¹. The number of absorber stages were varied from 15 to 30. For each suggested stage number, the solvent flow rate was adjusted to ensure complete absorption of HCl from the feed gas stream. Once the solvent flow rate was determined, the cooling water requirement for the condenser and steam demand for the reboiler were calculated. Capital and operating costs for each case were then estimated using Aspen HYSYS, with the results presented in Table 2. It was observed that the minimum total cost for the absorption and stripping towers was achieved with 26 absorption stages. At this configuration, the solvent flow rate was 12,575 kg h⁻¹, the cooling water flow rate in the stripper condenser was 6,341 kg h⁻¹, and the low-pressure steam flow rate in the reboiler was 1,024 kg h⁻¹.

In this study, the stripper tower was configured with 7 stages, which was found to be the minimum number of stages required to effectively strip all HCl from the stripper feed. If 5 stages or any number less than 7 were to be used, the HCl would appear at the stripper bottom (Fig. 3), necessitating a higher steam flow rate in the reboiler to achieve full stripping. This would increase both the size and the cost of the reboiler and reduce overall process efficiency.

Table 2 – Effect of the number of stages on the absorber/stripper costs

Absorber column		Stripper column			Capital cost, (USD)	Utility cost, (USD yr ⁻¹)
Number of stages	Solvent flow rate, kg h ⁻¹	R*	Cooling water flow rate in stripper condenser, kg h ⁻¹	Low-pressure steam flow rate in stripper reboiler, kg h ⁻¹		
15	19850	3	6360	1352	4,047,350	124,849
16	16120	3	6353	1296	4,008,710	122,240
17	15490	3	6351	1248	4,007,000	119,272
18	14980	3	6361	1209	4,006,090	117,806
19	14510	3	6352	1173	4,005,790	116,181
20	14270	3	6372	1154	3,948,080	115,692
21	13780	3	6360	1117	3,932,600	113,719
22	13470	3	6360	1093	3,932,600	113,711
23	13290	3	6335	1079	3,912,190	111,748
24	13090	3	6335	1064	3,907,920	111,094
25	12890	3	6330	1048	3,906,880	110,441
26	12575	3	6341	1024	3,903,140	109,412
27	12675	3	6333	1032	3,905,630	109,752
28	12610	3	6341	1027	3,905,210	109,543
29	12690	3	6344	1033	3,905,630	109,806
30	12640	3	6336	1029	3,905,630	109,785

* Solvent circulation reflux ratio of the stripper

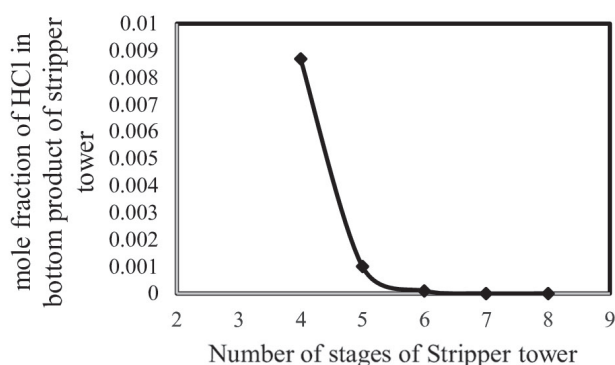


Fig. 3 – Effect of the number of stages of stripper tower on HCl mole fraction in the bottom product of stripper tower

Influence of operating conditions of the proposed absorption process on HCl recovery

The absorption process shown in Fig. 2 was simulated using other solvents: ethylene glycol, glycolic acid, glycerol, malonic acid, and lactic acid.

The same absorber and stripper configurations were used (26 stages for absorber, and 7 stages for stripper) as determined for the base case using water. The effect of the following operating conditions on the proposed absorption process was evaluated

and optimized for each solvent: solvent flow rate and temperature, absorber pressure, feed gas flow rate, and HCl loading in both the feed gas and the circulating solvent.

Effect of solvent flow rate on HCl recovery

To study the effect of solvent flow rate on HCl recovery, the proposed absorption process was simulated for all cases at $T = 25\text{ }^{\circ}\text{C}$ for inlet circulating solvent and inlet makeup solvent, $P = 450\text{ kPa}$ for absorption pressure, $P = 130\text{ kPa}$ for stripping pressure, and hydrogen gas feed stream from Table 1. Results are shown in Fig. 4. In all cases, HCl recovery increased with increasing solvent flow rate until it reached a maximum at a certain value of the solvent. Beyond this value, no change in HCl recovery was observed. Fig. 4a shows that with the water solvent, maximum HCl recovery occurred at a standard volume flow rate of $13\text{ m}^3\text{ h}^{-1}$, while in the case of ethylene glycol, glycolic acid, lactic acid, glycerol, and malonic acid, the required flow rates increased to 60, 70, 70, 70, and $80\text{ m}^3\text{ h}^{-1}$, respectively. Note that the flow rate of water solvent is the lowest among the solvents studied, followed by ethylene glycol, glycolic acid, glycerol, and lactic acid. The high solubility of HCl in water resulted in a

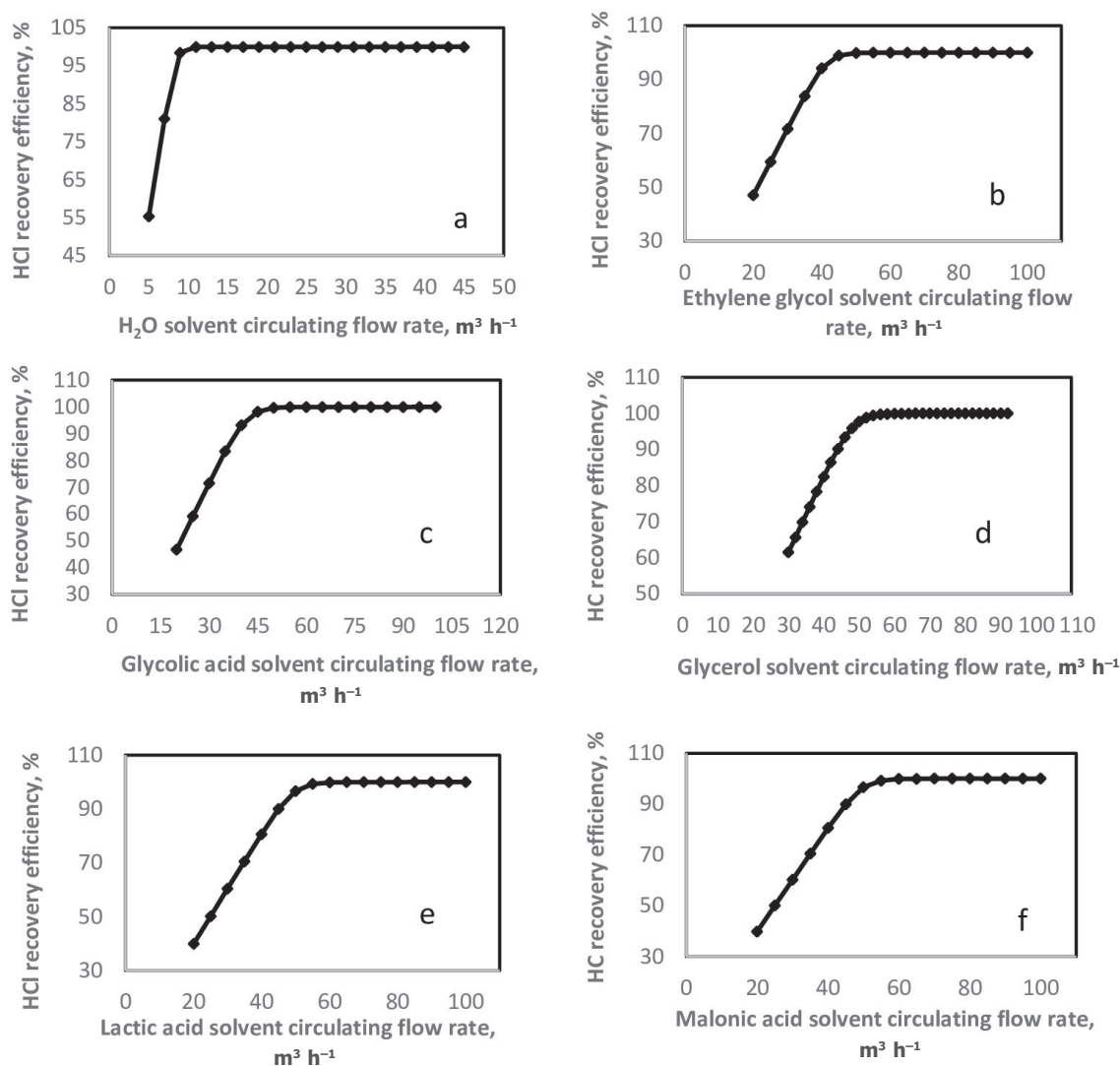


Fig. 4 – Effect of solvent circulation rate on HCl recovery efficiency % in case of using different solvents; (a) water; (b) Ethylene glycol; (c) Glycolic acid; (d) Glycerol; (e) Lactic acid; (f) Malonic acid

lower flow rate of water solvent required to fully remove the HCl (1.3093 kg h^{-1}) in the hydrogen gas stream compared to other proposed solvents. It is also noted that the flow rate of malonic acid solvent was the highest among all solvents used ($80 \text{ m}^3 \text{ h}^{-1}$). This suggested that the solubility of HCl in malonic acid was the lowest compared to other solvents used.

Similar results were obtained by Jin *et al.*²³ They found that by increasing the solvent flow rate from 2 L h^{-1} to 6 L h^{-1} when using glycerol as solvent, the HCl recovery increased from 93.5 % to 96.1 %. They explained that an increase in the glycerol flow rate led to an increase in the speed of the glycerol in the reactor, thus increasing the turbulence of the liquid and reducing the resistance to mass transfer between the gas and the liquid, which led to an increase in the recovery of hydrochloric acid. Other results were reported by Feng *et al.*²⁷

They used six organic solvents (ethylene glycol, glycerol, glycolic acid, lactic acid, oxalic acid, and malonic acid) mixed with choline chloride. They found that when the mixture ratio between choline chloride and different organic solvents was 1:1, the highest solubility of HCl was achieved in the choline chloride-ethylene glycol mixture and the lowest in choline chloride– malonic acid mixture.

Effect of inlet solvent temperature on HCl recovery

To evaluate the effect of inlet solvent temperature on HCl recovery, the proposed absorption process was simulated at $P = 450 \text{ kPa}$ (absorber pressure), $P = 130 \text{ kPa}$ (stripping pressure), make-up solvent temperature at 25°C , and pressure at 100 kPa , and the inlet solvent temperature was set at $T = 25\text{--}80^\circ \text{C}$ for all proposed solvents used. Fig. 5 shows the results obtained for all solvents. For water, ethylene glycol, and glycerol, the HCl recovery

decreased when the temperature of the circulating solvent to the absorber increased above 35 °C. On the other hand, for glycolic acid, lactic acid, and malonic acid, the HCl recovery decreased when the temperature of the solvent entering the absorber increased above 40 °C. As presented by Feng *et al.*²⁷ the solubility of HCl increases as the pressure increases and temperature decreases. This study proposes that the absorber pressure be the same as the outlet pressure of the hydrogen gas stream from the catalytic reforming process (450 kPa) to avoid using the compressor before the absorber, and thus avoiding the formation of green oil in any new compressor added. The lowest suggested solvent temperature at the absorption pressure used was 25–35 °C for water, ethylene glycol, and glycerin, and 25–40 °C for lactic acid, glycolic acid, and ma-

lonic acid. Jin *et al.*²³ found that by increasing the temperature of the glycerol solvent from 20 to 50 °C, the HCl recovery decreased. They explained that an increase in temperature can reduce the density and viscosity of the solvent, which improves the diffusion of hydrochloric acid in the solvent. However, the mass transfer resistance to absorption of HCl into the solvent lies mainly on the gas side, so the effect of the increase in the diffusion coefficient of HCl in the solvent is insignificant to the effect of HCl removal. What happens is the opposite, increasing the temperature will reduce the solubility of hydrochloric acid in the solvent, which is not suitable for the absorption of hydrochloric acid and has a greater effect on the removal of hydrochloric acid.

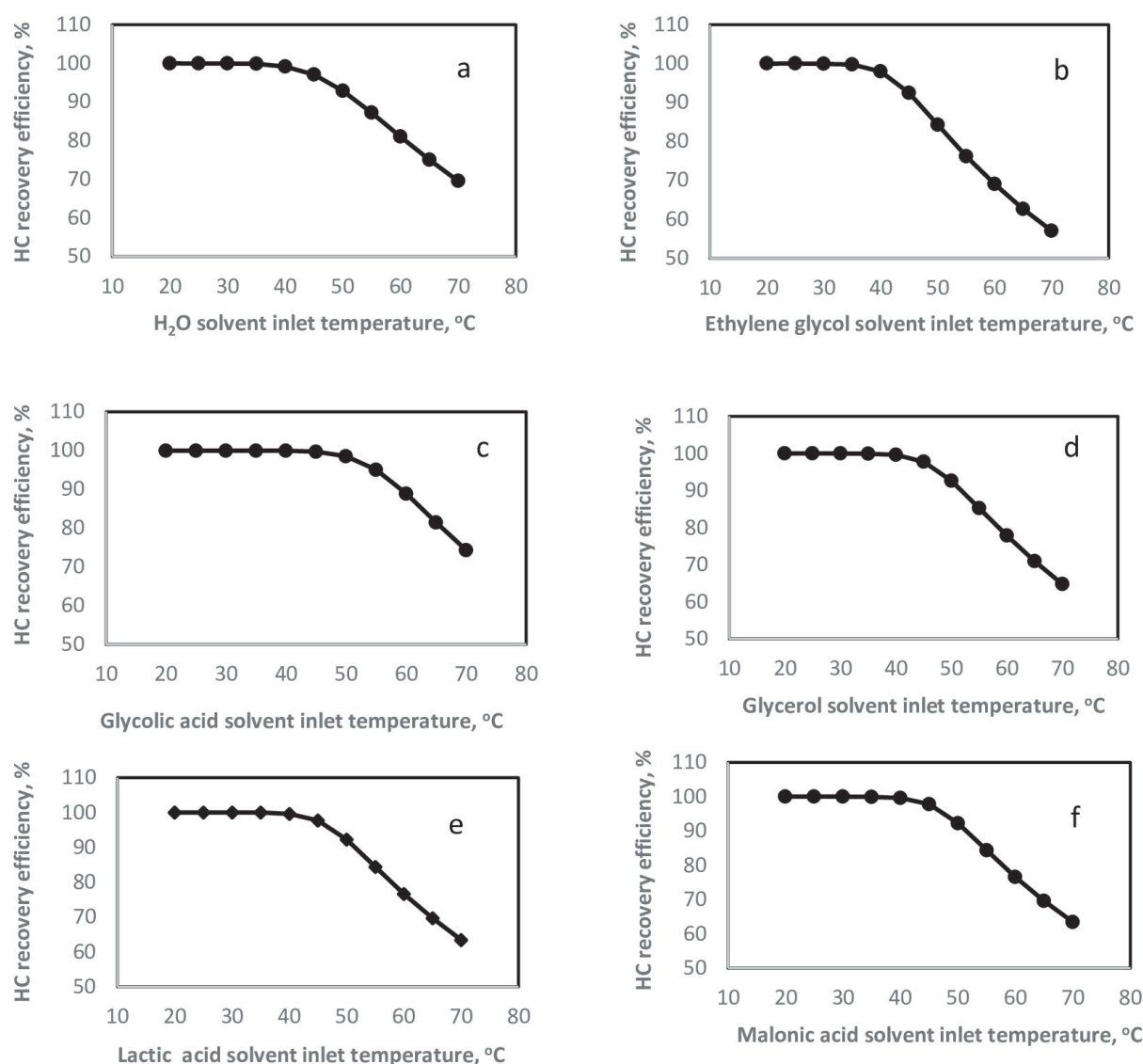


Fig. 5 – Effect of solvent temperature on HCl recovery efficiency % in case of using different solvents; (a) water; (b) Ethylene glycol; (c) Glycolic acid; (d) Glycerol; (e) Lactic acid; (f) Malonic acid

Effect of absorber pressure on HCl recovery

To study the effect of absorption pressure on HCl recovery, the proposed absorption process was simulated at $T = 25\text{ }^{\circ}\text{C}$ for the circulating solvent, $P = 130\text{ kPa}$ for stripper pressure, $T = 25\text{ }^{\circ}\text{C}$ and $P = 100\text{ kPa}$ for inlet make-up solvent, and the absorber pressure at $P = 100\text{--}450\text{ kPa}$. Fig. 6 shows the relationship between the flow of HCl in the hydrogen gas stream exiting the absorber for all proposed solvents and the absorption pressure. The results show that, for all proposed solvents, increasing the absorption pressure led to a decrease in mass flow of HCl in the gas stream exiting the absorption reaching 0 kg h^{-1} (maximum recovery). The pressure at which maximum removal of hydrochloric acid was achieved varied from one solvent to another. For water, the pressure that yielded zero HCl mass flow in the gas leaving the absorber was 250 kPa , beyond which the HCl recovery remained at maximum.

For the other solvents, the required absorber pressures were $400, 360, 440, 440,$ and 390 kPa for ethylene glycol, glycolic acid, glycerol, lactic acid, and malonic acid, respectively. Increasing the absorber pressure beyond these values had no effect on the HCl recovery, and maintained it at maximum.

Effect of the feed gas flow rate on HCl recovery

The effect of changing the feed gas flow rate on HCl recovery was evaluated by simulating the absorption process at a feed gas flow rate ranging from 40 to 400 kg h^{-1} . Fig. 7 shows the results for all proposed solvents. Fig. 8 shows that the HCl recovery remained at its maximum value until it reached a certain point, beyond which the HCl recovery began to decline. This point varied from one solvent to another. For water, ethylene glycol, and glycerol, the HCl recovery started decreasing once

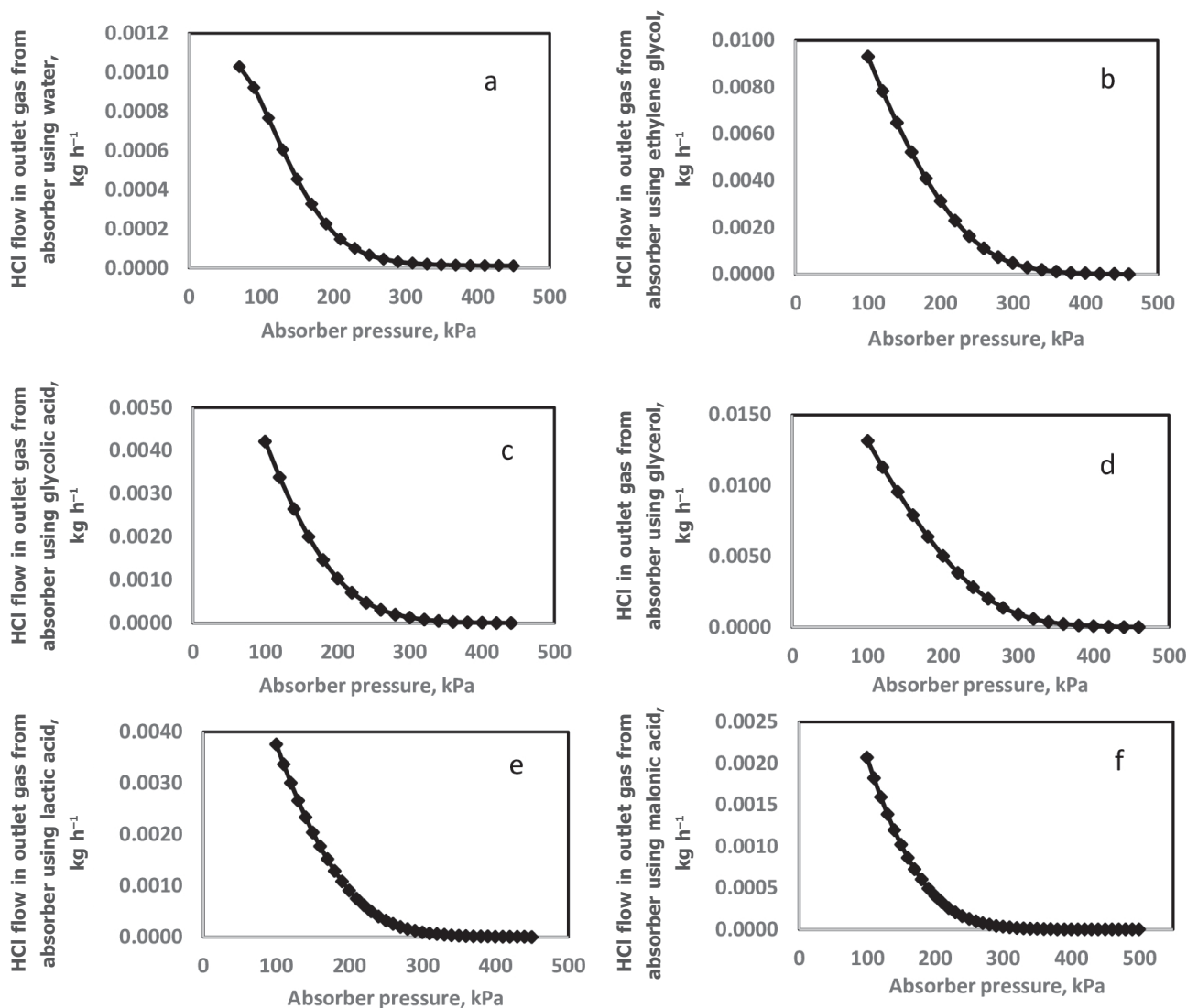


Fig. 6 – Effect of absorber top pressure on HCl flow in outlet gas from absorber using different solvents; (a) water; (b) Ethylene glycol; (c) Glycolic acid; (d) Glycerol; (e) Lactic acid; (f) Malonic acid

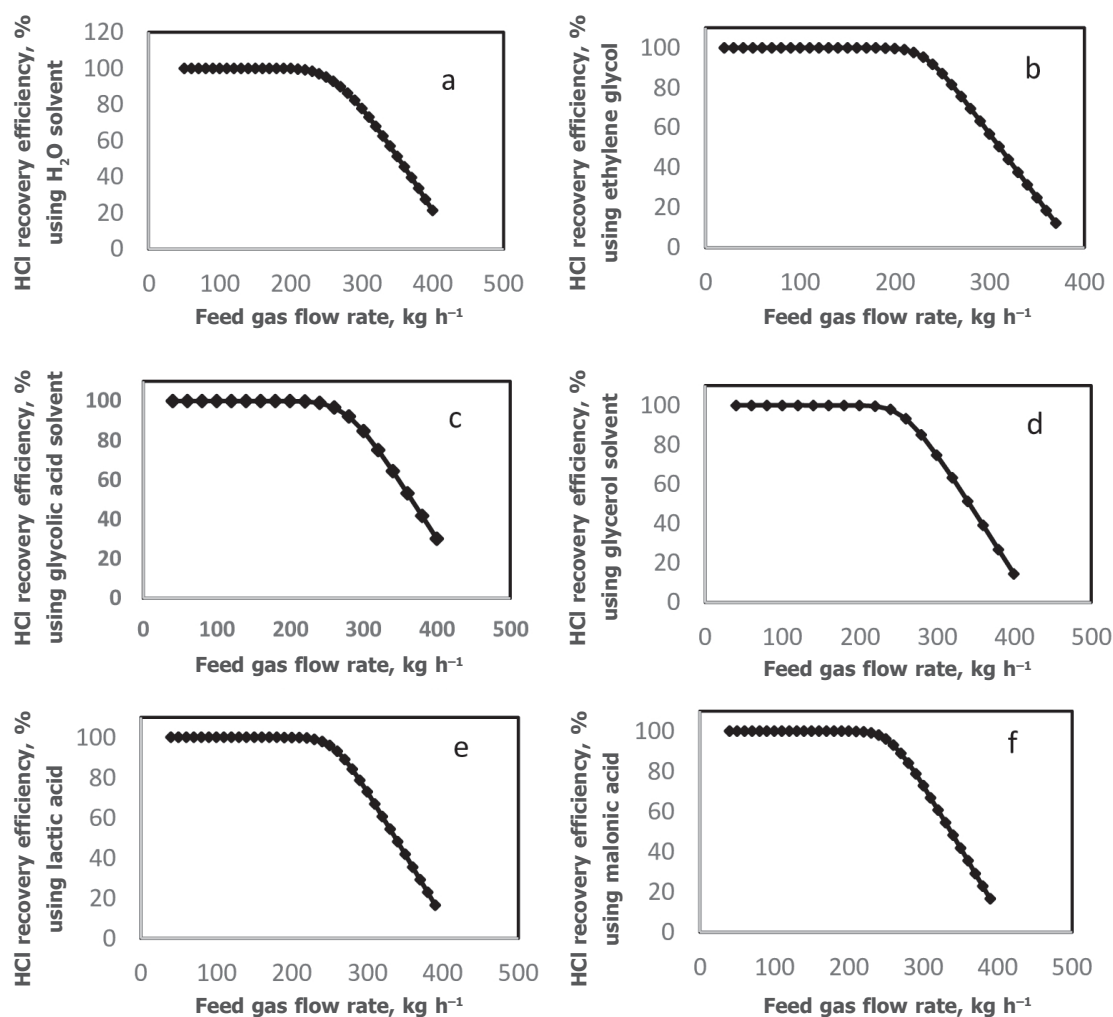


Fig. 7 – Effect of feed gas flow rate on HCl recovery efficiency % in case of using different solvents; (a) water; (b) Ethylene glycol; (c) Glycolic acid; (d) Glycerol; (e) Lactic acid; (f) Malonic acid

the gas flow rate exceeded 200 kg h⁻¹. Between 200 to 240 kg h⁻¹, the HCl recovery decreased gradually; above 240 kg h⁻¹, the HCl recovery dropped sharply. The current flow rates for water, ethylene glycol, and glycerol solvents were 13, 60, and 70 m³ h⁻¹, respectively. The flow of these quantities was sufficient to fully absorb the hydrochloric acid present in the feed gas stream (160 kg h⁻¹) and any increase in gas flow up to 200 kg h⁻¹. Above 200 kg h⁻¹ feed gas flow, the solvent flow in this case becomes insufficient to absorb all the HCl in the feed gas flow, and a mass flow of HCl would appear in the gas leaving the absorber. On the other hand, for glycolic acid, lactic acid, and malonic acid, the HCl recovery remained at its maximum when the gas flow rate increased from 40 to 220 kg h⁻¹. By increasing the gas flow from 220 to 260 kg h⁻¹, the HCl recovery decreased slowly, and above 260 kg h⁻¹, the HCl recovery decreased sharply. The results of this work are consistent with the results obtained by Jin *et al.*²³ They showed that the HCl recovery first decreases slowly and then decreases rapidly with

increasing feed gas flow rate if glycerol is used as a solvent. They justified this by saying that increasing the gas flow beyond a certain value led to a decrease in the residence time of the gas in the absorber. Therefore, the contact time between gas and liquid was insufficient, resulting in low HCl recovery.

Effect of HCl concentration in feed gas flow rate on HCl recovery

To assess the effect of changing HCl concentration in the inlet feed gas on HCl recovery, simulations were conducted with HCl mole fractions ranging from 0.0 to 0.08. Fig. 8 shows that HCl recovery remained at its maximum across this concentration range for all solvents. This indicated that the high current solvent flow rates of the five solvents (column 1 in Table 4) were sufficient to absorb any increases in the HCl concentration in the feed gas. These results agree with those of Jin *et al.*,²³ who found that with increasing HCl concentration in the feed gas stream from 700 to 2400 mg m⁻³, the HCl recovery remained around 94.5 %.

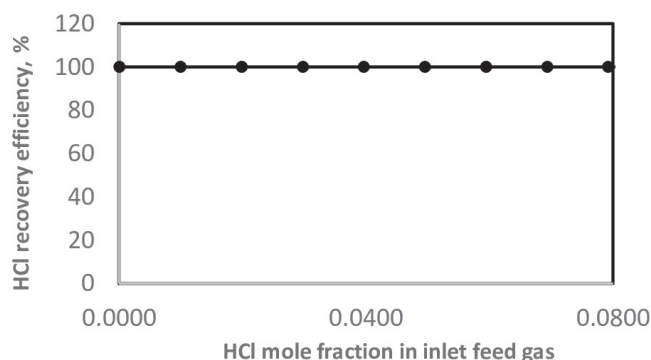


Fig. 8 – Effect of changing HCl mole fraction in feed gas stream on HCl recovery efficiency % in case of using different solvents

Effect of changing HCl concentration in the circulating solvent on HCl recovery

To study the effect of changing the concentration of HCl in the circulating solvent, the proposed absorption process was simulated at HCl molar

fractions ranging from 0.0 to 0.0002 mol. The results are shown in Fig. 9. For water, ethylene glycol, glycolic acid, and malonic acid, HCl recovery remained at maximum from 0.0 to 0.0001 mol, and no mass flow of HCl in the gas leaving the absorber (0.0 kg h^{-1}) was detected. As the molar fraction of HCl increased above 0.0001 mol, the HCl recovery decreased, and a mass flow of HCl appeared in the gas exiting the absorber. However, glycerol (Fig. 9d) and lactic acid (Fig. 9e), were found to be the most sensitive solvents to any presence of hydrochloric acid in their flow. It was found that by increasing the HCl mole fraction from 0.0 to 0.000001 mol, no HCl mass flow was detected in the gas exiting the absorber, but by increasing the HCl mole fraction above 0.000001, the HCl mass flow would be detected in the exit gas. These results are consistent with Jin *et al.*,²⁵ who reported that by increasing the mass fraction of HCl in the circulating glycerol solvent from 0.0 to 0.03 g g^{-1} , the HCl recovery

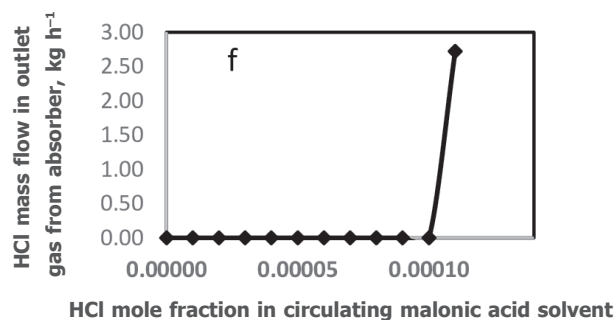
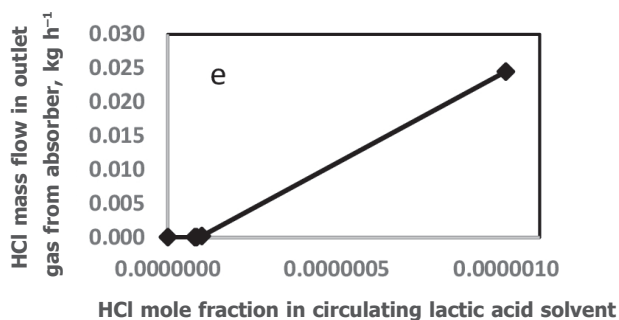
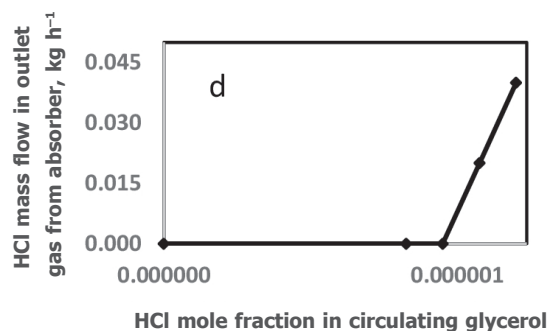
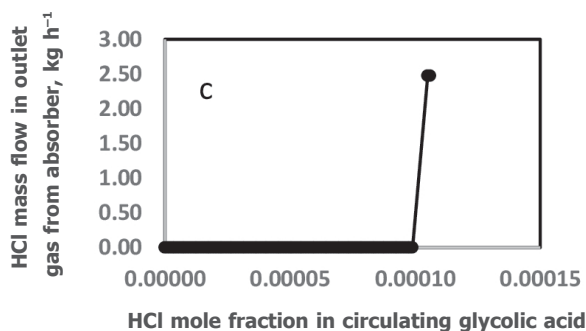
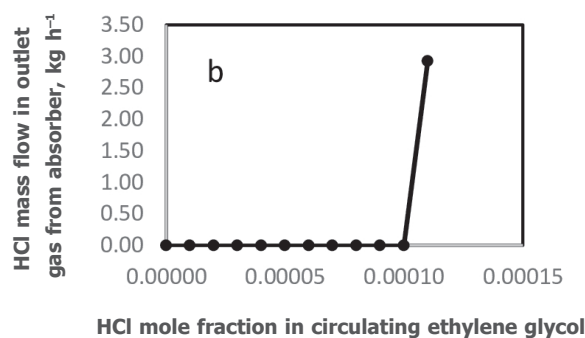
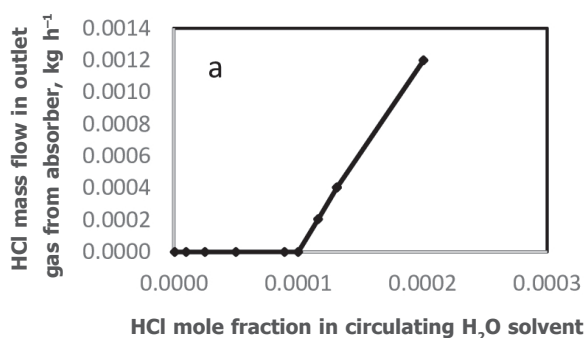


Fig. 9 – Effect of HCl mole fraction in circulating solvent on HCl mass flow in outlet gas from absorber in case of using different solvents; (a) water; (b) Ethylene glycol; (c) Glycolic acid; (d) Glycerol; (e) Lactic acid; (f) Malonic acid

slowly decreased, and with a further increase in the HCl molar fraction to 0.04 g g⁻¹, the HCl recovery decreased sharply. They concluded that an increase in the HCl concentration in the circulating solvent means a decrease in the HCl concentration difference between the solvent and the feed gas, which leads to a decrease in the mass transfer driving force for HCl absorption.

Solvent regeneration and economic analysis

Density and viscosity play an important role in the thermal stability of a solvent during the regeneration process. The high thermal stability is conducive to regeneration and can effectively avoid volatilization.^{23,25,27} The physical properties (boiling point, density, and viscosity) of the proposed sol-

vents were determined from Aspen HYSYS, and are shown in Table 3. All solvents were used at a temperature of 25 °C, which is well below their boiling points. Thus, they exhibited high thermal stability and negligible volatility. Table 3 also shows that the thermal stability of glycerol and malonic acid are the highest among other proposed solvents, since malonic acid has the highest density (1.496 g cm⁻³) and glycerol has the highest viscosity (76.27 mPa s). The second-highest solvent in viscosity is lactic acid (7.162 mPa s) followed by glycolic acid. Therefore, more energy is required for the regeneration of these solvents with higher viscosity and density.

Table 4 shows that malonic acid, followed by glycerol and lactic acid require the most energy in the regeneration process—18,900, 16,690, and 10,580 kW are required to desorb HCl from malonic acid, glycerol, and lactic acid, respectively. The high energy required in the regeneration process means higher utility and capital costs, as shown in Table 4 (columns 7 and 8). Water is the best solvent that can be used to mitigate hydrochloric acid from industrial gas streams followed by glycolic acid and ethylene glycol—639, 7653, and 8271 kW—are the energies required to extract hydrochloric acid from water, glycolic acid, and ethylene glycol, respectively.

Table 5 summarizes the energy consumption of the absorption process for all the solvents studied. The energy consumption in the cooler-01 (Q-cooler) and the stripping tower reboiler (Q-reboiler), presented in Fig. 2, had the highest energy consump-

Table 3 – Physical properties of proposed solvents

Item	Boiling point (°C) at $P = 100$ kPa	Density (g cm ⁻³) at $P = 130$ kPa (solvent to stripper)	Viscosity (mPa s) at $P = 130$ kPa (solvent to stripper)
Water	147.9	0.9662	0.8589
Ethylene glycol	251.5	1.076	4.052
Glycolic acid	216	1.313	6.506
Lactic acid	269.73	1.248	7.162
Glycerol	347.3	1.204	76.27
Malonic acid	371.1	1.496	0.5035

Table 4 – Optimum operating conditions, utility and capital costs for the proposed studied solvents in mitigating HCl

Solvent type	Solvent circulation flow rate, m ³ h ⁻¹	Absorber pressure, kPa	Solvent temp., °C	Stripper tower reflux ratio	Heat required in reboiler of Stripper*, kW	Utilities cost, USD yr ⁻¹	Capital cost, USD
Water (base case)	13	250–450	25	3	639	110,692	3,932,19
Glycolic acid	70	360–450	25	3	7,653	1,855,43	4,408,15
Ethylene glycol	60	400–450	25	0.5	8,271	3,840,62	4,570,64
Lactic acid	70	440–450	25	1	10,580	4,896,340	6,036,940
Glycerol	70	440–450	25	3	16,690	6,288,245	6,466,210
Malonic acid	80	390–450	25	3	18,900	7,120,394	6,562,77

*Stripper pressure = 130 kPa

Table 5 – Energy streams of absorption process for all solvents studied

Absorption process	Water solvent	Glycolic acid	Ethylene glycol	Lactic acid	Glycerol	Malonic acid
Q-cooler, kW	635	7692	8306	10,610	16,720	18,930
Q-pump, kW	1.724	9.74	8.72	10.7	13.19	12.11
Q-condenser, kW	39.81	3.27	6.26	12.44	14.38	15.29
Q-reboiler, kW	639	7653	8271	10,580	16,690	18,900

Table 6 – Design parameters of absorber and stripper towers using water and ethylene glycol solvents

Parameter	Water solvent		Ethylene glycol solvent	
	Absorber design	Stripper design	Absorber design	Stripper design
Tower diameter, m	0.7	1.3	1.5	4
Internal type	Packed	Packed	Packed	Packed
Section packed height, m	0.5	0.5	0.5	0.5
Packing dimension	0.5 IN OR 13 MM	15 MM	0.5 IN OR 13 MM	0.5 IN OR 13 MM
Packing material	CERAMIC	CERAMIC	CERAMIC	CERAMIC
Packing vendor	GLITSCH	RASCHIG	GLITSCH	GLITSCH
Packing type	RASCHIG	RASCHIG	RASCHIG	RASCHIG
Maximum Stage Liquid Holdup [m ³]	0.00122	0.00442	0.00563	0.006
Void fraction	0.64	0.7	0.64	0.64
Maximum % Capacity (Constant L V ⁻¹) [%] = Approach to flood, %	74.89	41.38	54.88	66.73
Section pressure drop, mbar	1.63	0.36	0.2562	0.956
Average pressure drop/height [mbar m ⁻¹]	3.27	0.719	0.5123	1.913

Table 7 – Design parameters of absorber and stripper towers using glycolic acid and lactic acid solvents

Parameter	Glycolic acid solvent		Lactic acid solvent	
	Absorber design	Stripper design	Absorber design	Stripper design
Tower diameter, m	1.5	3	1.5	5
Internal type	Packed	Packed	Packed	Packed
Section packed height, m	0.5	0.5	0.5	0.5
Packing dimension	0.5-IN OR 13-MM	0.5-IN OR 13-MM	0.5-IN OR 13-MM	0.5-IN OR 13-MM
Packing material	CERAMIC	CERAMIC	CERAMIC	CERAMIC
Packing vendor	GLITSCH	GLITSCH	GLITSCH	GLITSCH
Packing type	RASCHIG	RASCHIG	RASCHIG	RASCHIG
Maximum stage liquid holdup [m ³]	0.006	0.047	0.00593	0.0889
Void fraction	0.64	0.64	0.64	0.64
Maximum % capacity (Constant L V ⁻¹) [%] = Approach to flood, %	58.75	73.92	59.09	55.99
Section pressure drop, mbar	0.263	2.10	0.273	1.052
Average pressure drop/height [mbar m ⁻¹]	0.525	4.21	0.547	2.104

Table 8 – Design parameters of absorber and stripper towers using glycerol and malonic acid solvents

Parameter	Glycerol solvent		Malonic solvent	
	Absorber design	Stripper design	Absorber design	Stripper design
Tower diameter, m	1.5	6	1.5	5
Internal type	Packed	Packed	Packed	Packed
Section packed height, m	0.5	0.5	0.5	0.5
Packing dimension	0.5-IN OR 13-MM	0.5-IN OR 13-MM	0.5-IN OR 13-MM	0.5-IN OR 13-MM
Packing material	CERAMIC	CERAMIC	CERAMIC	CERAMIC
Packing vendor	GLITSCH	GLITSCH	GLITSCH	GLITSCH
Packing type	RASCHIG	RASCHIG	RASCHIG	RASCHIG
Maximum stage liquid holdup [m ³]	0.006	0.130	0.00599	0.0976
Void fraction	0.64	0.64	0.64	0.64
Maximum % capacity (Constant L V ⁻¹) [%] = Approach to flood, %	83.38	84.29	44.27	64.26
Section pressure drop, mbar	2.05	6.68	0.152	2.44
Average pressure drop/height [mbar m ⁻¹]	4.11	13.37	0.304	4.87

tion in the absorption process for all the solvents studied. This is due to the high energy required to strip the absorbed HCl from the solvent in the stripping tower, and the energy required to cool the recycled solvent before entering the absorption tower.

Tables 6, 7, and 8 show the detailed design parameters of the absorption and stripping towers in the proposed absorption and desorption process with the studied solvents as calculated using Aspen HYSYS. The design of these towers differs in the case of using water as a solvent from other solvents because the sensitivity to flooding is very high in the case of organic solvents due to the high flow rate of the solvent used. To avoid flooding phenomena, the diameters of the absorber and stripper were increased. The maximum allowable capacity (flood percentage, %) in Aspen HYSYS software is 88 % (safety factor). The diameter of the absorption tower was found to be 0.7 m when using water as the solvent, and 1.5 m with other organic solvents. Regarding the stripper tower, the diameter of the stripper was 1.3 m for the water solvent, but 3, 4, 5, and 6 m for glycolic acid, ethylene glycol, lactic acid, malonic acid, and glycerol, respectively.

A mixture of any of the studied organic solvents with water at a ratio of 1:1²⁷ is expected to be an effective alternative to pure organic solvents in practical hydrochloric acid separation applications, due to lower costs compared to pure organic solvents without mixing with water, and its high regenerability. According to the economic analysis presented in this paper, the hydrochloric acid absorption process using water as a solvent was the least expensive, followed by absorption using glycolic acid and ethylene glycol, while absorption us-

ing malonic acid was the most expensive. Using water, glycolic acid, or ethylene glycol as a solvent is the optimal choice for recovering hydrochloric acid from the hydrogen gas stream exiting a catalytic reformer.

Evaluation of data extracted from Aspen HYSYS program

The simulation data obtained from Aspen HYSYS for the effect of operating parameters (factors) of the proposed hydrochloric acid absorption process on the hydrochloric acid recovery efficiency (response) were transferred to Design Expert version 13 for statistical analysis. As shown in the above analysis by Aspen HYSYS, each studied parameter had a significant effect on the HCl recovery efficiency when the other parameters were held constant. Design Expert is used to model the relationship between the hydrochloric acid recovery efficiency resulting from the proposed simulated absorption process and all operating parameters at the same time. RSM is used to predict the correlation equation between the studied operating parameters (absorber pressure (P), solvent inlet temperature (T_s), solvent flow rate (F_s), and feed gas flow rate (F_f)) and the hydrochloric acid recovery efficiency. Design Expert checks whether the studied operating parameters by Aspen HYSYS had a significant effect on the hydrochloric acid recovery efficiency as determined by Aspen HYSYS. The predicted correlation equations relating the studied operating parameters and the HCl recovery efficiency for all proposed solvents are described in Eqs. (2) – (7), as analyzed by Design Expert.

$$\begin{aligned} \% \text{HCl Recovery}_{\text{water}} = & -107.51519 + 0.006899 P + 0.940426 T_s + 21.37634 F_s + \\ & + 0.750454 F_f - 0.017728 T_s^2 - 0.873547 F_s^2 - 0.002203 F_f^2 \end{aligned} \quad (2)$$

$$\begin{aligned} \% \text{HCl Recovery}_{\text{Glycolic acid}} = & -56.79218 + 1.54387 T_s + 2.20171 F_s + 0.674252 F_f - \\ & 0.024435 T_s^2 - 0.017101 F_s^2 - 0.001734 F_f^2 \end{aligned} \quad (3)$$

$$\begin{aligned} \% \text{HCl Recovery}_{\text{Ethylene glycol}} = & -107.5614 + 1.06244 T_s + 5.28755 F_s + 0.700681 F_f - \\ & 0.022073 T_s^2 - 0.049840 F_s^2 - 0.002141 F_f^2 \end{aligned} \quad (4)$$

$$\begin{aligned} \% \text{HCl Recovery}_{\text{Lactic acid}} = & -116.7588 + 0.007333 P + 1.28673 T_s + 3.86192 F_s + \\ & + 0.759073 F_f - 0.022935 T_s^2 - 0.028760 F_s^2 - 0.002086 F_f^2 \end{aligned} \quad (5)$$

$$\begin{aligned} \% \text{HCl Recovery}_{\text{Glycerol}} = & -136.49956 + 1.06643 T_s + 4.72249 F_s + 0.896828 F_f - \\ & 0.022119 T_s^2 - 0.037595 F_s^2 - 0.002581 F_f^2 \end{aligned} \quad (6)$$

$$\begin{aligned} \% \text{HCl Recovery}_{\text{Malonic acid}} = & -121.51854 + 1.49223 T_s + 3.72271 F_s + 0.783778 F_f - \\ & 0.023947 T_s^2 - 0.026790 F_s^2 - 0.002057 F_f^2 \end{aligned} \quad (7)$$

where P is the absorber pressure, kPa; T_s is the solvent inlet temperature, °C; F_s is the solvent flow rate, m³ h⁻¹; F_f is the feed gas flow rate, kg h⁻¹. Eqs. (2)–(7) were applied at absorber pressure range of 100–450 kPa, solvent temperature range of 20–80 °C, solvent flow rate range of 5–80 m³ h⁻¹, and feed gas flow rate range of 50–400 kg h⁻¹. These ranges were determined by the simulation of the proposed HCl absorption process. The ANOVA statistical analysis in Design Expert shows that, the individual effect of the operating parameters studied were statistically significant, as illustrated in Table 9, column 2. The P-value of all parameters were less than 0.05. All the individual parameters (P , T_s , F_s , F_f) were significant terms in the models presented for water and lactic acid solvents in Equations (2) and (5). In addition, the quadratic terms of T_s^2 , F_s^2 , and F_f^2 were significant terms in all the models presented for all solvents. Note that the interaction between the studied parameters, the quadratic term P^2 , and the P term (Equations (3), (4), (6), and (7)) were insignificant terms, whose P-value were greater than 0.1 and were therefore excluded from the models. The R^2 , adjusted R^2 , and predicted R^2 were close to one for all the predictive models (Table 9, column 3). This suggested that these models fitted the data, were important, and well predicted the response to new observations.^{34,35} Fig. 10 shows the relationship between the data collected from Aspen HYSYS for the HCl recovery efficiency from the

suggested absorption process and the predicted HCl recovery efficiency by the Design Expert. The predicted results are in good agreement with the simulation data with a standard deviation less than 5 % for all suggested solvents. These models are effective in predicting new HCl recovery efficiency for the presented HCl absorption process for all suggested solvents under the same range of studied operating parameters.

Conclusion

This research presents a new simulation model using Aspen HYSYS for the hydrochloric acid absorption process to remove hydrogen chloride from the hydrogen stream exiting the catalyst regeneration section from the catalytic reforming unit. Water and other five organic solvents were proposed for absorption of HCl from the feed gas stream. These solvents were ethylene glycol, glycolic acid, glycerol, lactic acid, and malonic acid. The optimum solvent flow rate was 13, 70, 60, 70, 70, and 80 m³ h⁻¹, for water, glycolic acid, ethylene glycol, lactic acid, glycerol, and malonic acid, respectively. Water provided the best absorption capacity compared to the other solvents. Moreover, glycerol and malonic acid required the most energy for the regeneration process, while water required the least amount of energy for regeneration (639 kW).

Table 9 – Statistical analysis

Solvent	ANOVA analysis	
	P-value	R^2
Water	P-value for P was <0.0494 and for T_s , F_s , F_f , T_s^2 , F_s^2 , and F_f^2 were < 0.0001	$R^2 = 0.9930$ Adjusted $R^2 = 0.9914$ Predicted $R^2 = 0.9761$
Glycolic acid	P-values for T_s , F_s , F_f , T_s^2 , F_s^2 , and F_f^2 were < 0.0001	$R^2 = 0.9914$ Adjusted $R^2 = 0.9903$ Predicted $R^2 = 0.9800$
Ethylene glycol	P-values for T_s , F_s , F_f , T_s^2 , F_s^2 , and F_f^2 were < 0.0001	$R^2 = 0.9929$ Adjusted $R^2 = 0.9921$ Predicted $R^2 = 0.9889$
Lactic acid	P-values for P was < 0.0076 and T_s , F_s , F_f , F_f^2 , F_s^2 , and F_f^2 were < 0.0001	$R^2 = 0.9952$ Adjusted $R^2 = 0.9945$ Predicted $R^2 = 0.9923$
Glycerol	P-values for T_s , F_s , F_f , T_s^2 , F_s^2 , and F_f^2 were 0.0001	$R^2 = 0.9937$ Adjusted $R^2 = 0.9933$ Predicted $R^2 = 0.9909$
Malonic acid	P-values for T_s , F_s , F_f , T_s^2 , F_s^2 , and F_f^2 were < 0.0001	$R^2 = 0.9958$ Adjusted $R^2 = 0.9955$ Predicted $R^2 = 0.9941$

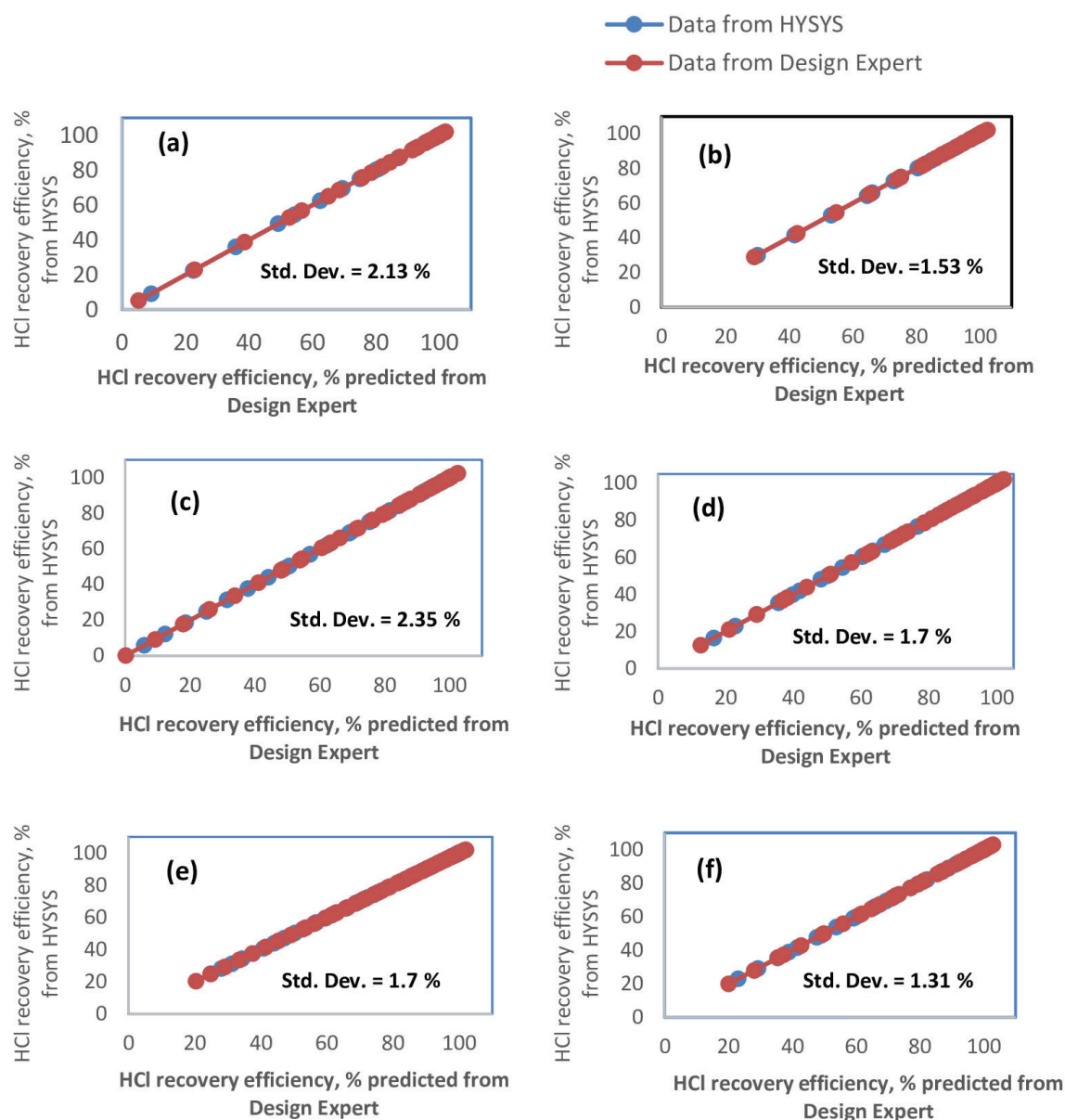


Fig. 10 – HCl recovery efficiency % as estimated by HYSYS and predicted by Design Expert programs for all studied solvents; (a) water; (b) Glycolic acid; (c) Ethylene glycol; (d) Lactic acid; (e) Glycerol; (f) Malonic acid

Based on these findings, water was selected as the base case to optimize the design of both absorber and stripper. The optimum number of stages in absorber and stripper towers were found to be 26, and 7 packing stages, respectively. In addition, optimal operating conditions (solvent flow rate, absorber pressure, inlet circulating solvent temperature) that provide maximum HCl recovery or zero mass flow of HCl in the outlet gas from the absorber were studied and determined.

Water exhibited several advantages over the other solvents, including low required flow rate, low cost, and high HCl solubility. The response surface methodology in Design Expert 13 was used to statistically analyze the simulation data extracted

from Aspen HYSYS and to model the hydrochloric acid recovery efficiency and the operating parameters studied. The recovery efficiency results from Aspen HYSYS showed good agreement with the predictive model results.

Abbreviations

ANOVA	– Analysis of variance
CAPEX	– Capital expenditure
Ch-Cl	– Choline-chloride
CCR	– Continuous catalyst regeneration
F_f	– Feed gas flow, kg h^{-1}
F_s	– Solvent flow, $\text{m}^3 \text{h}^{-1}$

NHT	– Naphtha hydrotreater
OPEX	– Operating expenditures
<i>P</i>	– Absorber pressure, kPa
PSA	– Pressure swing adsorption
RSM	– Response surface methodology
<i>T</i>	– Solvent inlet temperature, °C

AVAILABILITY OF DATA AND MATERIAL

The data that support the findings of this study are available on request.

COMPETING INTERESTS

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

AUTHORS' CONTRIBUTIONS

Walaa Mahmoud Shehata participated in the supervision, conceptualization, methodology, software, data curation and analysis, and editing of the current research paper. Ahmed Hassan Abdel Hady participated in conceptualization, methodology, software, validation, and writing-original draft. Professor Fatma K. Gad participated in supervision, conceptualization, data curation, and analysis.

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References

1. Sergio, K., The impact of oil field chemicals on refinery corrosion problems; NACE: Houston, TX, (2003), Paper No. 03649
2. Fan, X. J., Zhu, J. H., Song, H. F., Wu, B. C. H., The identification and quantitation of organochlorine in naphtha by gas chromatography with ECD, *Pet. Sci. Technol.* **29** (2011) 867.
doi: <https://doi.org/10.1080/10916460903436788>
3. Mittal, D., Chloride management in the reformer product stream, *Pet. Technol. Q.* **1** (2020) 95.
4. Erfan, M., Chloride removal in refineries, *Pet. Technol. Q.* **16** (2011) 1.
5. Lu, Y., He, M. Y., Shu, X. T., Zong, B. N., Interactions of n alkanes within a restrictive pore system under fluid catalytic cracking (FCC) conditions, *Energy Fuels* **17** (2003) 1040.
doi: <https://doi.org/10.1021/ef030021p>
6. Grause, G., Matsumoto, S., Kameda, T., Yoshioka, T., Pyrolysis of mixed plastics in a fluidized bed of hard burnt lime, *Ind. Eng. Chem. Res.* **50** (2011) 5459.
doi: <https://doi.org/10.1021/ie102412h>
7. Śrębowata, A., Juszczak, W., Kaszukur, Z., Karpinski, Z., Hydrodechlorination of 1,2-dichloroethane on active carbon supported palladium-nickel catalysts, *Catal. Today* **124** (2007) 28.
doi: <https://doi.org/10.1016/j.cattod.2007.02.010>
8. Śrębowata, A., Juszczak, W., Kaszukur, Z., Sobczak, J. W., Karpinski, Z., Hydrodechlorination of 1,2 dichloroethane and dichlorodifluoromethane over Ni/C catalysts: The effect of catalyst carbiding, *Appl. Catal. A: General* **319** (2007) 181.
doi: <https://doi.org/10.1016/j.apcata.2006.12.004>
9. Jalil, A. A., Triwahyono, S., Razali, N. A. M., Hairom, N. H. H., Idris, A., Muhid, M. N. M., Ismail, A., Yahaya, N. A. M., Ahmad, N. A. L., Dzinun, H., Complete electrochemical dechlorination of chlorobenzenes in the presence of various arene mediators, *J. Hazard. Mater.* **174** (2010) 581.
doi: <https://doi.org/10.1016/j.jhazmat.2009.09.091>
10. Richard, M. A., Gurevich, V., Faz, C. E., Removal of halogenated organic compounds from hydrocarbon streams. U.S. Patent US59285001999, 1997.
11. Kumar, S., Kumar, P., Jasra, R. V., Sorption of HCl from an aromatic hydrocarbon mixture using modified molecular sieve zeolite 13X, *ACS Omega* **6** (2021) 28742.
doi: <https://doi.org/10.1021/acsomega.1c03450>
12. Paereli, S., Sorption of hydrogen chloride on solid sorbents. NTNU, Nor. Univ. Sci. Technol. **6** (2015) 1.
<http://hdl.handle.net/11250/2351696>
13. Sun, Z., Yu, F. C., Li, F., Li, S., Fan, L. S., Experimental study of HCl capture using CaO sorbents: Activation, deactivation, reactivation, and ionic transfer mechanism, *Ind. Eng. Chem. Res.* **50** (2011) 6034.
doi: <https://doi.org/10.1021/ie102587s>
14. Li, M., Shaw, H., Yang, L. C., Reaction kinetics of hydrogen chloride with calcium oxide by Fourier transform infrared spectroscopy, *Ind. Eng. Chem. Res.* **39** (2000) 1898.
doi: <https://doi.org/10.1021/ie990628m>
15. Kameda, T., Uchiyama, N., Park, K. S., Grause, G., Yoshioka, T., Removal of hydrogen chloride from gaseous streams using magnesium-aluminum oxide, *Chemosphere* **73** (2008) 844.
doi: <https://doi.org/10.1016/j.chemosphere.2008.06.022>
16. Lee, M. T., Wang, Z. Q., Cang, J. R., Activated-carbon-supported NaOH for removal of HCl from reformer process streams, *Ind. Eng. Chem. Res.* **42** (2003) 6166.
doi: <https://doi.org/10.1021/ie0207055>
17. Micoli, L., Bagnasco, G., Turco, M., HCl removal from biogas for feeding MCFCs: Adsorption on microporous materials, *Int. J. Hydrogen Energy* **38** (2013) 447.
doi: <https://doi.org/10.1016/j.ijhydene.2012.09.102>
18. Dou, B., Pan, W., Ren, J., Chen, B., Hwang, J., Yu, T. U., Single and combined removal of HCl and alkali metal vapor from high-temperature gas by solid sorbents, *Energy Fuels* **21** (2) (2007) 1019.
doi: <https://doi.org/10.1021/ef060266c>
19. Kim, J. Y., Kyung, D. H., Park, Y. C., Jo, S. H., Ryu, H. J., Park, Y. S., Moon, J. H., The adsorption and desorption breakthrough behavior of hydrogen chloride gas mixture on zeolite 13X Pellet in a fixed bed reactor, *J. Chem. Eng. Jpn.* **48** (3) (2015) 202.
doi: <https://doi.org/10.1252/jcej.14we183>

20. Sharma, R., Segato, T., Delplancke, M. P., Terryn, H., Baron, G. V., Denayer, J. F. M., Cousin-Saint-J. Remi, Hydrogen chloride removal from hydrogen gas by adsorption on hydrated in-exchanged zeolites, *Chem. Eng. J.* **381** (2020) 122512.
doi: <https://doi.org/10.1016/j.cej.2019.122512>
21. Liu, C., Li, C. X., Meng, H., Wang, Z. H., Solubility of trifluoromethane and hydrochloride gas in different solvents, *J. Chem. Eng. Chin. Univ.* **22** (2008) 1.
22. Kim, J. Y., Park, Y. C., Jo, S. H., Ryu, H. J., Baek, J. I., Moon, J. H., The absorption breakthrough characteristics of hydrogen chloride gas mixture on potassium-based solid sorbent at high temperature and high pressure, *Energy Fuels* **30** (2016) 2268.
doi: <https://doi.org/10.1021/acs.energyfuels.5b02473>
23. Jin, H., Xiao, H., Zhang, Y. L., Wu, T. Y., Song, Y. H., Yun, L., Shao, L., Study on HCl removal by glycerol in a rotor-stator reactor and desorption of HCl, *Chem. Eng. Process.: Process Intensif.* **190** (2023) 109410.
doi: <https://doi.org/10.1016/j.ccep.2023.109410>
24. He, R. H., Long, B. W., Lu, Y. Z., Meng, H., Li, C. X., Solubility of hydrogen chloride in three 1-alkyl-3-methylimidazolium chloride ionic liquids in the pressure range (0 to 100) kPa and temperature range (298.15 to 363.15) K, *J. Chem. Eng. Data* **57** (11) (2012) 2936.
doi: <https://doi.org/10.1021/jc3003783>
25. Pan, Y., Liu, Y., Zhang, X. M., Shi, M. Z., Tu, Z. H., Hu, X. B., Wu, Y. T., Design of deep eutectic solvents with multiple-active-sites for HCl separation and storage, *Sep. Purif. Technol.* **300** (2022) 121799.
doi: <https://doi.org/10.1016/j.seppur.2022.121799>
26. Zhu, J., Shao, H., Feng, L., Lu, Y. Z., Meng, H., Li, C. X., Absorptive separation of HCl GAS BY choline chloride-based deep eutectic solvents, *J. Mol. Liq.* **341** (2021) 116928.
doi: <https://doi.org/10.1016/j.molliq.2021.116928>
27. Feng, L., Meng, H., Lu, Y. Z., Li, C. X., Efficient and reversible absorption of HCl gas by ChCl-based deep eutectic solvents-Insights into the absorption behavior and mechanism, *Sep. Purif. Technol.* **281** (2022) 119994.
doi: <https://doi.org/10.1016/j.seppur.2021.119994>
28. Liu, D., Yang, G., Method for removing hydrogen chloride in chemically synthesized tail gas, CN101658758A, (2010).
29. Bal, M., Reddy, Th. T., Meikap, B. C., Removal of HCl gas from off gases using self-priming venturi scrubber, *J. Hazard. Mater.* **364** (2019) 406.
doi: <https://doi.org/10.1016/j.jhazmat.2018.10.028>
30. Kurella, S., Balla, M., Bhukya, P. K., Scrubbing of HCl gas from synthesis gas in a multistage dual flow sieve plate wet scrubber by alkaline solution, *Chem. Eng. & Proc. Tech.* **6** (2015) 2.
doi: <https://doi.org/10.4172/2157-7048.1000250>
31. Bandyopadhyay, A., Biswas, M. N., SO₂ scrubbing in a tapered bubble column scrubber, *Chem. Eng. Commun.* **193** (2006) 1562.
doi: <https://doi.org/10.1080/00986440600584466>
32. Han, B., Kim, H., Kim, Y.-J., Han, K.-S., Removal characteristics of gaseous contaminants by a wet scrubber with different packing materials, *KSAE* **23** (2007) 744.
doi: <https://doi.org/10.5572/KOSAE.2007.23.6.744>
33. Aspen HYSYS, Customization Guide, Aspen Technology, Inc., 2011.
34. Shehata, W. M., Abd-elhamid, E. I., Gad, F. K., Monitoring, modeling, and optimization of parameters affecting the recovery efficiency of acid gases from a sweetening unit, *Egypt. J. Pet.* **32** (4) (2023) 21.
doi: <https://doi.org/10.1016/j.ejpe.2023.11.001>
35. Shehata, W. M., Mohamed, M. F., Gad, F. K., Monitoring and modelling of variables affecting isomerate octane number produced from an industrial isomerization process, *Egypt. J. Pet.* **27** (4) (2018) 945.
doi: <https://doi.org/10.1016/j.ejpe.2018.02.006>
36. Marczewski, M., Derewinski, M., Malinowski, S., The influence of gaseous chlorine on the chemical and catalytic properties of alumina, *Can. J. Chem. Eng.* **61** (1983) 93.
doi: <https://doi.org/10.1002/cjce.5450610116>
37. Ayame, A., Sawada, G., Sato, H., Zhang, G., Ohta, T., Izumizawa, T., Characterization of chlorine-treated alumina surfaces, *Appl. Catal.* **48** (1989) 25.
doi: [https://doi.org/10.1016/S0166-9834\(00\)80263-8](https://doi.org/10.1016/S0166-9834(00)80263-8)
38. Koerin, R., Influence du mode de synthèse de la boehmite sur l'état de surface de l'alumine-gamma mise en forme: application au reformage catalytique: Doctoral dissertation, IFPEN, Université de Caen Basse-Normandie 2015.
39. Bailey, R. R., Wightman, J. P., Interaction of gaseous hydrogen chloride and water with oxide surfaces: I. Alumina, *J. Colloid Interface Sci.* **70** (1979) 112.
doi: [https://doi.org/10.1016/0021-9797\(79\)90014-6](https://doi.org/10.1016/0021-9797(79)90014-6)
40. Tanaka, M., Ogasawara, S., Infrared studies of the adsorption and the catalysis of hydrogen chloride on alumina and on silica, *J. Catal.* **16** (1970) 157.
doi: [https://doi.org/10.1016/0021-9517\(70\)90209-5](https://doi.org/10.1016/0021-9517(70)90209-5)
41. Kytokivi, A., Lindblad, M., Root, A., IR and 1H NMR studies on the adsorption of gaseous hydrogen chloride on γ -alumina, *J. Chem. Soc. Faraday Trans.* **91** (1995) 941.
doi: <https://doi.org/10.1039/FT9959100941>