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Reliable estimation of optimal sulfinol concentration in gas treatment unit via novel stabilized MLP and regularization network

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ABSTRACT

Proper technology or configuration for sulfur recovery units (SRUs) strongly depends on H_2S concentration of inlet acid gas stream. Various acid gas enrichment (AGE) schemes with different solvents can be used to reduce the concentration of carbon dioxide and heavy aromatic hydrocarbons while enriching the H_2S content of SRU feed stream. The present article uses combinations of Aspen-HYSYS software and two in-house artificial neural networks (namely, Regularization and stabilized multilayer perceptron networks) to compare the AGE capability of sulfinol-M (sulfolane + MDEA) solvent at optimal concentration with traditional MDEA solution when both of them are used in a conventional gas treating unit (GTU). The simulation results indicate that the optimal concentration of Sulfinol-M aqueous solution (containing 37 wt% Sulfolane and 45 wt% MDEA) will completely eliminate toluene and ethylbenzene from the SRU feed stream while removing 80% of benzene entering the GTU process. Furthermore, mole fraction of H_2S in the SRU feed stream increases from the conventional 33.48 mol % to over 57 mol %. Increased H_2S selectivity of optimal sulfinol-M aqueous solution will elevate the CO_2 slippage through sweet gas stream at around 4.5 mol % which is still below the permissible threshold. To the best of our knowledge, the stabilized MLP network has not been addressed previously.

1. Introduction

Acid gas enrichment (AGE) is crucial when treating exceedingly high CO_2 (or other inert impurities) content sour gases, in which the resulting acid gas stream is likely to contain relatively low H_2S concentrations making it unsuitable feed for Sulfur Recovery Units (SRU). Excessive amount of inert impurities in acid gas stream entering SRU Claus process will drastically decreases the combustion chamber temperature and reduces the overall elemental sulfur recovery efficiency. AGE has become an increasingly economic option in the last two decades (Chludzinski and Iyengar, 1993).

Artificial neural networks (ANNs) are widely accepted as a technology offering an alternative way to tackle complex and ill-defined problems. Properly trained neural networks can derive meaning from complicated or imprecise data (e.g. can extract the underlying truth from noisy data). These powerful tools are traditionally used for their capability of nonlinear mapping and lack of necessity for detailed mechanistic knowledge (Mahmoodzadeh Vaziri and Shahsavand, 2013).

Acid gas enrichment process depends on multiple input variables which posse's strong coupling between them with severe uncertainty. The difficulties presented in using conventional modeling techniques to model such nonlinear and highly complex systems with large numbers of input and output variables, make the application of ANNs particularly attractive.

Two main approaches are usually recruited for acid gas enrichment. In the first scheme, suitable solvent is chosen in conventional gas treating unit (GTU) to absorb more selectively H_2S while inhibiting CO_2 absorption. Sterically hindered amines, either primary or secondary amines with large bulky alkyl or alkanol groups attached to the nitrogen (Seagraves and Weiland, 2011), show suitable result for selective absorption of H_2S in the presence of CO_2 (by reducing carbamate stability).

Secondly, necessary modifications can be applied to an existing GTU configuration while using the conventional solvent. Various schemes are used to enhance the selectivity of H_2S over CO_2 (Palmer, 2006; Mak et al., 2009; Al Utaibi and Al Khateeb, 2010; Way and Viejo, 2013).

Tetra methylene sulfone (TMS) or sulfolane is an important industrial solvent with capability of removing acid gases such as CO_2 and H_2S from various sour gas streams. Furthermore, sulfolane is able to extract monocyclic aromatic hydrocarbons (such as

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Benzene-Toluene-Ethylbenzene-Xylene (BTEX)) from different petroleum products. Sulfolane is usually blended with alkanol amines (specially methyl diethanol amine (MDEA)) to form adequate mixed solvent (known as sulfinol) to capture various impurities, simultaneously (Vahidi and Moshtari, 2013).

In 1981, Exxon-Mobil scientists recognized the effect of molecular structure of the GTU solvent on the performance of natural gas sweetening process and synthesized the so called "FLEXSORB-SE" amine for high H_2S selective absorption (Royan et al., 1992; Parks et al., 2010).

In a similar research, in 1983, Satori et al. had compared H_2S selectivity and moles of H_2S and CO_2 loadings per moles of amine for various solvents (tertiary butyl amino ethoxyethanol (TBEE), tertiary butyl amino ethanol (TBE) and MDEA). The results indicated that TBEE has a significant higher selectivity than other two solvents for the above purposes (Sartori et al., 1983).

In 2004, Mandal et al. had investigated selective absorption of H_2S from different sour gas streams containing various H_2S and CO_2 concentrations via aqueous solutions of MDEA and 2-amino-2-methyl-1-propanol (AMP). The acid gas mass transfer has been modeled using two different approaches. The equilibrium-mass-transfer-kinetics-based-combined model is used for CO_2 absorption and gas-phase-transport-equation-based approximation is recruited for modeling of H_2S absorption. Negligible interactions between CO_2 and H_2S in both gas and liquid phases were assumed. They reported that proper agreement existed between experimental measurements and simulation results (Mandal et al., 2004).

Lu et al. (2006) used a unique mixture of TBEE and MDEA (1 kmol/m^3 TBEE +1.5 kmol/m^3 MDEA) in a packed column at atmospheric pressure and constant liquid flow rate to absorb H_2S and CO_2 from different acid gases. The aqueous blend of MDEA and TBEE has been found to be an exceedingly efficient mixed solvent for selective H_2S removal over traditional amines (Lu et al., 2006).

In 2011, Koolivand Salooki et al. designed a neural network to predict the output parameters of gas sweetening regeneration column of Khangiran refinery. The simulation results had close agreement with plant data (Koolivand Salooki et al., 2011).

In 2011, Saghatoleslami et al. developed a neural network based genetic algorithm (GA) to optimize the absorption column of Khangiran refinery. They have used GA to determine the number of neurons in the hidden layers, the momentum and learning rates parameter. Operating variables such as inlet gas flow rate and corresponding gas pressure and temperature, lean amine temperature and its flow rate were selected as the input parameters while acid gas and rich amine flow rates considered as the outputs of ANN. They have reported that the model was in good agreement with experimental data (Saghatoleslami et al., 2011).

In 2013, Angaji et al. examined the performance of various concentrations of sulfolane in the Sulfinol solvent for GTUs of Khangiran natural gas refinery. They have concluded that providing 40.2%wt sulfolane, 21.2% wt H_2O and 37.7%wt MDEA in liquid mixture of Sulfinol-M could increases the capacity of sour gas treatment from 173 to 220 MSCMH. The version of Aspen Plus software which has been used for the entire simulation is unable to provide proper property package for mixtures of MDEA-sulfolane solutions. Limited parameters such as condenser and reboiler duties were investigated in order to optimize sulfolane concentration (Torabi Angaji et al., 2013).

In 2013, Adib et al. developed a support vector machine (SVM) to estimate process output variables of contactor and regenerator of Khangiran gas treatment unit over 13 series of input–output plant data each consisting of 145 exemplars. They have claimed that SVM based model showed to be in better agreement with operating plant data compared to artificial neural networks based models (Adib et al., 2013).

In 2014, Kazemi et al. simulated Sulfinol-M, LO-CAT and mixed amine process via Aspen plus software v.8.1 for natural gas sweetening. Feed contained 5 mol% H_2S, 1.33 mol% CO_2 and the remaining (93.67 mol %) was methane. Aspen process economic analyzer was used to economically evaluate the entire processes in order to meet the pipeline specifications. They have claimed that LO-CAT process is the more appropriate choice when capital and operating costs along with acid gas loading are taken into account (Kazemi et al., 2014).

In the present article, a conventional GTU is simulated by resorting to power full Aspen-HYSYS software V.8.3. Instead of using traditional MDEA solution as solvent, various concentrations of MDEA and sulfolane (known as sulfinol solution) will be used to predict the concentration of H_2S and BTEX components in the acid gas stream leaving GTU. The above version of Aspen-HYSYS software is capable of providing adequate property package for all mixtures of MDEA-sulfolane solutions. The limited data collected from Aspen-HYSYS simulations using various sulfinol concentrations will be employed as the training data to optimize two stabilized artificial neural networks. The trained networks performances will be initially compared with the performance of conventionally used neural network toolbox of MATLAB software and then finally they will be recruited to provide reliable interpolation hypersurfaces for practical uses.

2. Why AGE and BTEX elimination in a conventional GTU?

As it was mentioned previously, treating of sour gases with high amounts of impurities (e.g. CO_2) can lead to lean acid gas streams which contain significant amounts of inert constituents such as CO_2. Excessive amounts of carbon dioxide available in the acid gas stream entering SRU can dramatically reduce the combustion chamber temperature and hence drastically limit the elemental sulfur capacity. In other words, extreme dilution of SRU feed stream by very high amounts of CO_2 may cause severe flame instability in combustion chamber and in the worst scenario, it can completely quench the combustion chamber flame (Palmer, 2006). Moreover, effective elimination of carbon dioxide from acid gas streams via a successful acid gas enrichment scenario can dramatically decrease the size of a conventional Claus unit in the design stage or significantly increase the plant throughput for an existing SRU facility. Selim et al. experimentally studied the effect of CO_2 and N_2 content of SRU feed on sulfur recovery and overall conversion efficiency. They reported that increasing the concentration of carbon dioxide in acid gas stream drastically deteriorates the performance of the Claus process. Carbon dioxide reduced the probability of sulfur recovery where most of H_2S is converted to SO_2. Conversely, nitrogen tends to act as an inert medium, and was found to have less severe effect as compared to carbon dioxide (Selim et al., 2012).

The majority of existing acid gas streams contains significant quantities of other contaminants (such as BTEX) that should be destroyed in the Claus furnace (providing high enough combustion chamber temperatures) to protect the downstream Claus reactors catalysts. However, relatively high carbon dioxide concentrations tend to lower the furnace flame temperature, thereby often making thermal destruction of these contaminants difficult (or even impossible).

Deleterious effects of heavy hydrocarbons and particularly aromatics in an SRU plant feed stream are essentially known and well documented (Crevier et al., 2001). Fig. 1 shows the variations of combustion chamber adiabatic flame temperature versus H_2S content of acid gas stream entering the SRU process. As it can be seen, destruction of aromatics (BTEX) can't be commenced when acid gas contains less than 35 mol % H_2S (Zarenezhad, 2011). In many practical situations, the destruction of Benzene starts at

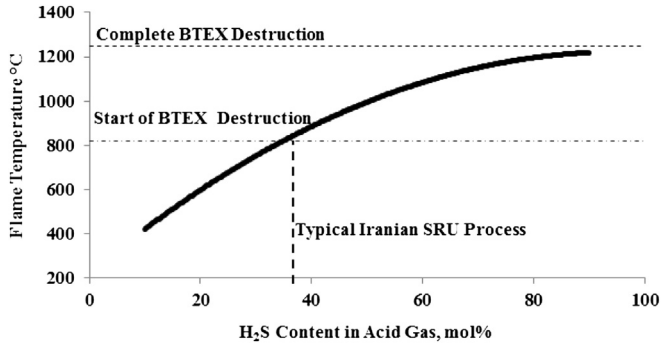

Fig. 1. Adiabatic flame temperature of combustion chamber versus H_2S concentration (Zarenezhad, 2011).

around 820 °C while other heavy aromatic hydrocarbons begin to dissociate and burn at around 940 °C (Schöbel et al., 2001).

When BTEX is not sufficiently destructed in the reaction furnace, it deposits on various Claus catalyst beds (especially the first bed) resulting rapid fouling of all catalysts which will lead to short lifespan of catalyst and more frequent turnarounds. Incomplete destruction of such aromatic compounds can result in contamination of the final elemental sulfur product (production of dark yellowish sulfur) and deactivation of the catalysts. Several studies have shown that catalyst coking has been tied directly to aromatic content of acid gas stream with toluene being the primary contributor (Zarenezhad and Hosseinpour, 2008).

As it was emphasized before, a minimum reaction furnace temperature of 1050 °C (1920 °F) is recommended for adequate destruction of BTEX. The split design scheme (where part of the acid gas is bypassed around the reaction furnace) may not be also effective due to excessive fouling of the first convertor catalyst by the slipped BTEX in the bypassed stream.

Evidently, increasing the H_2S concentration of SRU feed stream via AGE can effectively increase reaction furnace temperature and will lead to proper destruction of BTEX components. Various mixtures of sulfolane and MDEA solutions (sulfinol solvent) will be considered in this research and their performances of the enrichment efficiency of the Khangiran refinery GTU will be investigated. Effective AGE increases the H_2S content of SRU feed stream and alleviates SRU existing complications such as flame temperature and BTEX issues.

2.1. Characteristics of sulfinol solvent

Sulfinol is a composite solvent which is initially introduced by Shell company in 1963. It is a mixture of Sulfolane ($C_4H_8O_2S$), water and diisopropanolamine (DIPA, $C_6H_{15}NO_2$) or MDEA known as Sulfinol-D or Sulfinol-M, respectively. Unlike alkanolamines, sulfinol physically bonds with the above species and enhances the removal of hydrogen sulfide, carbon dioxide, carbonyl sulfide, mercaptans and organic sulfur components from natural gas.

Proper heat economy, small solvent losses because of the low vapor pressure of the sulfolane, relatively poor hydrocarbon selectivity and reduction of corrosion rate are other advantages of these hybrid solvents (Mokhatab and Poe, 2012). Thermodynamic modeling of aqueous sulfolane solutions (in the absence of alkanolamines) for prediction of their thermal and physical properties are well received remarkable attention in numerous studies (Zong and Chen, 2011; Vahidi and Moshtari, 2013; Shokouhi et al., 2013).

Optimizations of sulfolane concentration in the proposed sulfinol-M solvent instead of MDEA solvent in the Khangiran natural gas refinery treating unit via artificial neural network is the essence of this work.

3. A brief review of artificial neural networks

Artificial Neural Networks (ANNs) are multifaceted tools that can be successfully used to model and predict various complex and highly non-linear processes. ANNs have been widely applied in many fields such as process modeling, control, optimization, estimation and forecasting (Haykin, 1999). Single Perceptron concept is initially presented by Rosenblatt in 1958 and widely used in last 55 years in multilayer Perceptron (MLP) networks to successfully model highly non-linear systems. Lipmann presented the perceptron convergence algorithm in 1987 (Haykin, 1999). In the following sections, a brief description of the un-stabilized ANNs and two in-house stabilized MLP and Regularization networks have been presented. To the best of our knowledge, the stabilized MLP network has not been addressed previously.

3.1. Our modified un-stabilized MLP network

Feed-forward multilayer Perceptrons (MLP) networks were able to successfully map a set of multidimensional input data $(\underline{x}_i;\ i=1,\cdots,N)$ onto a set of appropriate multidimensional outputs$(\underline{y}_i;\ i=1,\cdots,N)$. The MLP configuration has been extensively used for static regression applications and it consists of one input layer, one or more hidden layer(s) and one output layer. MLP network utilizes a supervised learning technique called back propagation for training the network (Haykin, 1999). All input variables $(x_1,\cdots,x_p)$ are initially projected into a scalar for the jth neuron $(j=1,\cdots,M)$ neuron by using a set of linear weights $(w_i,\ i=1,\cdots,p)$. Ultimately, a proper nonlinear activation function (φ), such as such as threshold, piecewise-linear, sigmoid and hyperbolic tangent, performs a pre-defined mathematical operation over its argument and provides the model predictions $(\widehat{y})$.

The MLP network is often trained by adapting the synaptic weights using a back-propagation technique or any other optimization procedure. During the training phase, network output(s) is (are) compared with the desired target value(s). The obtained sum of squared error(s) between these two values is used to adapt the weights. This rate of adaptation may be controlled by a learning rate parameter. A high learning rate will make the network adapt its weights quickly, but will make it potentially unstable (Shahsavand, 2000). Setting the learning rate to zero, will make the network keep its weights constant. The steepest descent optimization technique with variable learning rate (step length) parameters is used in this work. As shown in Fig. 2, additional linear weights $(\alpha_1,\ldots,\alpha_M)$ are used in our modified MLP network for two reason: 1) to accelerate the network convergence for a single hidden layer MLP network, 2) to provide a vehicle for mimicking large values outputs with limited number of hidden layer neurons.

Fig. 2 also depicts that the optimal values of linear parameters $(\underline{\alpha})$ for conventional MLP network should be updated after each iteration of back-propagation method using the following update rule:

$$\left(\Phi^T\Phi\right)\underline{\alpha}=\Phi^T\underline{y} \tag{1}$$

Where $\Phi_{i,j}=\phi\cdot(z_{i,j}),\ i=1,\cdots,N$ and $j=1,\cdots,M$ and y is the $N\times 1$ vector of measured values. The parameters N and M represent the number of training exemplars and the number of hidden layer neurons, respectively. All inputs of training data should be scaled between −1 and 1 to assure that the original S shape of sigmoid function is preserved for all cases.

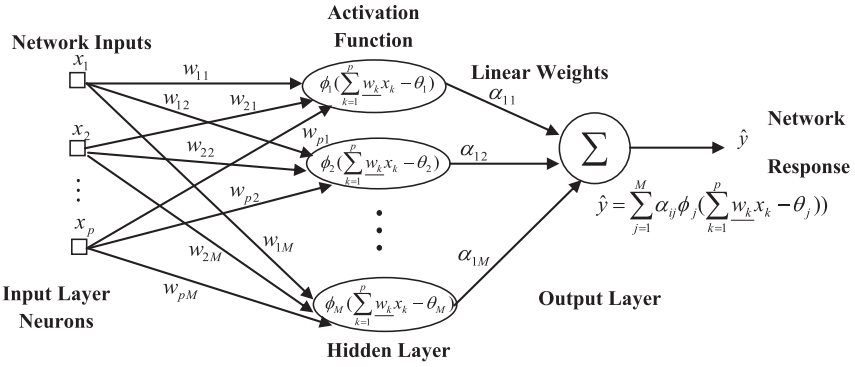

Fig. 2. Schematic representation of a single hidden layer MLP network for MIMO problem.

3.2. Novel stabilized MLP network

In most practical engineering applications, the number of available measurements (N) is limited and all measurements are inevitably contaminated with measurement error (noise). On the other hand, the neural network model should have large number of neurons (M) to obtain sufficient degrees of freedom and have high flexibility to reconstruct the data points. Consequently, the response of such networks will eventually lead to oscillatory and highly degenerate solution which is due to ill conditioning or singularity of the related matrices. In order to eliminate or alleviate such oscillatory phenomena, a stabilization technique is required to filter out the noise and capture the true underlying trend embedded in the noisy data.

As mentioned above, the $M \times M$ matrix $\Phi^T\Phi$ will be severely ill condition or even singular when $M >> N$ and equation (1) will have large number of highly degenerate and oscillatory solutions. By resorting to singular value decomposition (SVD) technique will help to select a relatively optimum solution, but SVD may lead to a large number of zero singular values which results in losing most of the information content of matrix Φ (Shahsavand, 2000).

In order to dispel large oscillations in the elements of the solution vector ($\underline{\alpha}$), the so called ridge regression can be used. To minimize the oscillations, the following constrained optimization should be introduced (Shahsavand and Pourafshari Chenar, 2007).

$$\text{Minimize} \quad \Im(\underline{\alpha}) = \frac{1}{2}\sum_{i=1}^{N}\left(\widehat{y}\left(x_i\right) - y_i\right)^2 = \frac{1}{2}\left(\Phi\underline{\alpha} - \underline{y}\right)^T\left(\Phi\underline{\alpha} - \underline{y}\right)$$
$$\text{Subject to} \quad : \quad \underline{\alpha}^T\underline{\alpha} \le \gamma \tag{2}$$

When γ is any arbitrary constant. By resorting to Lagrangian multiplier concept, the constraint can be combined into original merit function as the following penalized sum of square error (PSSE) or penalized least square (PLS) objective function:

$$\text{Minimize} \quad \Im\ (\underline{\alpha}) = \frac{1}{2}\left(\Phi\underline{\alpha} - \underline{y}\right)^T\left(\Phi\underline{\alpha} - \underline{y}\right) + \frac{1}{2}\lambda(\underline{\alpha}^T\underline{\alpha} - \gamma) \tag{3}$$

Evidently extremely large values of the so called Lagrangian multiplier (λ) or ridge regression parameter pulls away the *over-smoothen* final solution from the original data and reinforces the *a priori* information, while very tiny λ's ignore the *a priori* assumption and provide the final (oscillatory) solution such that it is totally compatible with original (noisy) data. Differentiating equation (3) with respect to model parameter ($\underline{\alpha}$) and simplifying the corresponding equations leads to:

$$\left(\Phi^T\Phi + \lambda I\right)\underline{\alpha} = \Phi^T\underline{y} \tag{4}$$

Where I is an $M \times M$ identity matrix. Evidently, the optimal value of ridge regression parameter is case dependent and a reliable automatic method should be devised to provide the optimal value of λ^* for the problem at hand. The leave one out cross validation technique (LOOCV) is frequently used for automatic selection of optimal ridge regression level. A detailed comparison of LOOCV with other techniques such as Generalized cross validation (GCV), L-curve, modified L-curve, U curve and modified U-curve method have been presented in our recent article (Niknam Shahrak et al., 2013).

The above so-called "Stabilized MLP network" leads to equation (4) which seems very similar to the ultimate result of zero order (Thikonov) regularization theory. We should emphasize here that these two concepts are entirely different and should not be mixed with each other. In stabilization, a penalty function is added to the original least square merit function to reduce the oscillations in linear weights, while in (Thikonov) regularization theory one will add a penalty term based on its *a priori* information about the shape (or distribution) of the actual solution.

3.2.1. Automatic selection of ridge regression parameter

Golub and Van-loan derived the following equation for computation of leave one out cross validation criteria (Golub and Van Loan, 1996):

$$\text{LOOCV}(\lambda) = \frac{1}{N}\sum_{k=1}^{N}\left[\frac{\underline{e}_k^T[I - H(\lambda)]\underline{y}}{\underline{e}_k^T[I - H(\lambda)]\underline{e}_k}\right]^2 \tag{5}$$

Where $H(\lambda) = \Phi(\Phi^T\Phi + \lambda I)^{-1}\Phi^T$ is the $N \times N$ smoother matrix and e_k is a column vector which all of its elements are zero except the kth element which is unity.

The inversion of $M \times M$ matrix$(\Phi^T\Phi + \lambda I)^{-1}$ at each value of λ requires an order of M^3 mathematical operations which can be extremely time demanding, especially for large data networks. This gigantic amount of computation can be avoided by resorting to the SVD technique as summarized below:

$\Phi = USV^T;\ \Phi \in \Re^{N\times M},\ U \in \Re^{N\times N},\ S \in \Re^{N\times M}\left(\text{diagonal}\right),\ V \in \Re^{M\times M}$

U and V are orthonormal $U^TU = UU^T = I_N\ \&\ V^TV = VV^T = I_M$

$$H(\lambda) = U\begin{bmatrix} \sigma_1^2/\left(\sigma_1^2+\lambda\right) & 0 & \cdots & 0 \\ 0 & \sigma_2^2/\left(\sigma_2^2+\lambda\right) & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & \sigma_N^2/\left(\sigma_N^2+\lambda\right) \end{bmatrix} U^T \tag{6}$$

Where $\sigma_i;\ i = 1,\cdots,N$ are the singular values of matrix Φ(or square roots of eigenvalues of matrix$(\Phi^T\Phi)$. Using the above approach, the number of mathematical operations required for the entire LOOCV criteria calculations reduces from $n\times M^3$ order of magnitude to $n\times M$ order of magnitude, where n is the number of trial values for ridge regression parameter (λ). Fig. 3 illustrates the entire training algorithm for novel stabilized MLP network when LOOCV is used for automatic selection of optimal ridge regression parameter and SVD technique is employed to promote the speed of computations (Shahsavand, 2000).

3.3. A brief review of regularization networks

Learning an input–output mapping from a set of data in can be considered as a multi-dimensional function approximation tool. Many neural networks have been constructed to perform this issue by solving hyper-surface reconstruction problem. This form of learning is closely related to classical approximation techniques such as regularization theory (Poggio and Girosi, 1990a).

The solution of multivariate regularization theory leads to a three layer networks called Regularization networks (Poggio and Girosi, 1990a). Regularization Networks is proved to be a strong technique for solving certain problems of learning, in particular the regression problem of approximating a multivariate function from sparse data. In other words, Regularization network is a method for solving ill-posed function interpolation problems. Radial Basis Function (RBF) is a special case of such network (Girosi et al., 1995). An obvious property of this technique is that it can be implemented by a simple network with just one layer of hidden neuron. Learning algorithm, which implements a set of approximating functions $f(x,\omega)$, where ω is a set of parameters of an arbitrary nature. Given a noisy function $y(x)$, the goal is to find function $f(x,\omega_0)$ that minimizes (overall possible parametersω) the functional:

$$R\left(\omega,\lambda\right) = \|y(x) - f(x,\omega)\|^2 + \lambda\,\Omega[f(x,\omega)] \tag{7}$$

Here $\Omega[f(x,\omega)]$ is a non-negative penalty term which penalizes non-smooth function $f(x,\omega)$, and λ is the regularization parameter (Cherkassky and Ma, 2009). Poggio and Girosi (1990b) showed that the following equation minimizes the merit function of. $R(\omega,\lambda)$

$$(G + \lambda I_N)\,\underline{w}_\lambda = \underline{y} \tag{8}$$

where G is the $N\times N$ symmetric Green's matrix, λ the regularization parameter, I_N is the $N\times N$ identity matrix,$\underline{w}_\lambda$ is the $N\times 1$ linear synaptic weight vector and $\underline{y}$ is the real response values corresponding to input vector $\underline{x}_i = 1,2,\cdots,N$. Fig. 4 illustrates the equivalent network (known as the Regularization network (RN)) for the above equation with N being the number of both training exemplars and neurons of RN. These neurons (or centers) should be positioned exactly at the locations of training exemplars.

The network consists of a single hidden layer with N neurons and the activation function of the jth hidden neuron is a Green's function $G(\underline{x},\underline{x}_j)$ centered at a particular data point $\underline{x}_j$. The influence of the regularization parameter λ is embedded in the unknown synaptic weights $w_j s$.

The performance of Regularization network strongly depends on the appropriate choice of the isotropic spread and the proper level of regularization. Small values of λ lead to oscillatory solutions due to fitting of the noise, while excessively large levels of regularization parameter will over-smooth the Regularization network predictions. Same as our novel stabilized MLP, the optimal value of ridge regression parameter is case dependent and as before, the

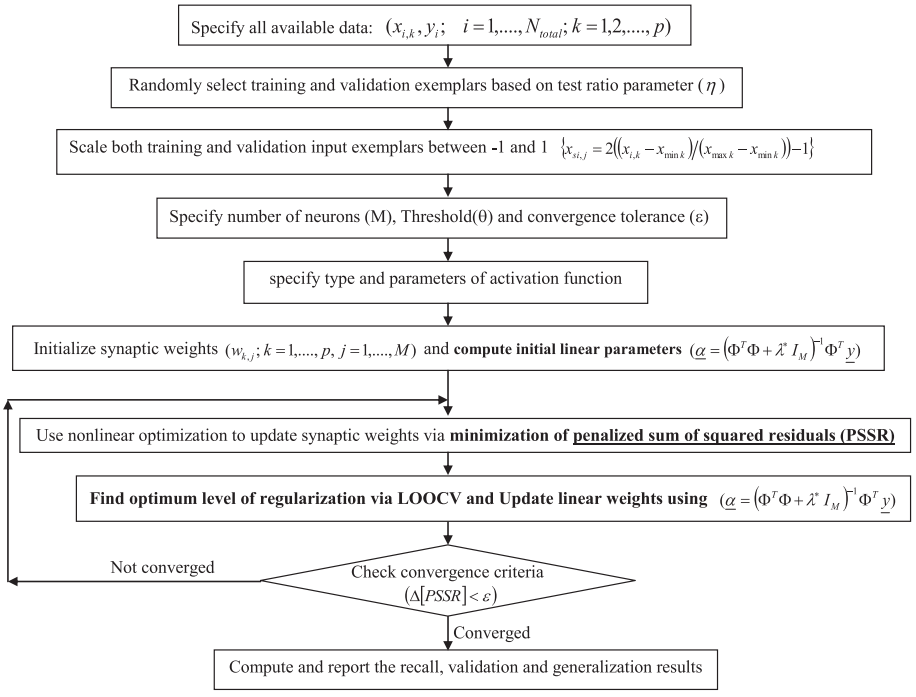

Fig. 3. Block diagram representation of training algorithm for a stabilized MLP network.

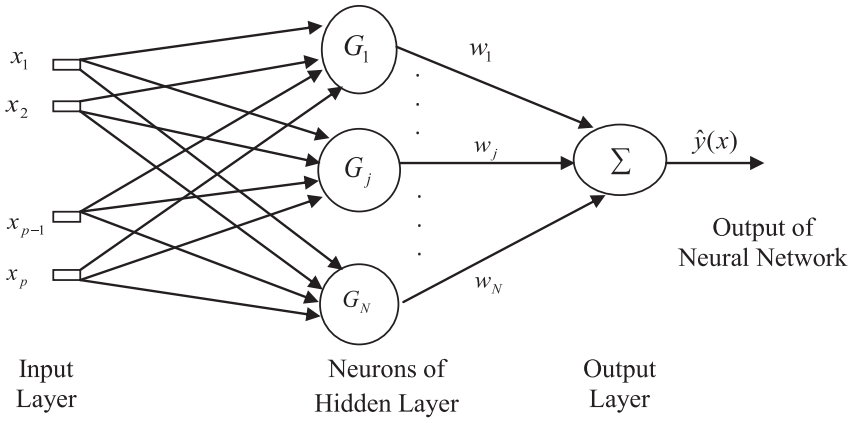

Fig. 4. Schematic representation of Regularization network with single hidden layer.

LOOCV criterion (among many others) can be used to provide the optimal value of λ^* for the problem at hand. Our fully optimized in-house training algorithm for the isotropic Regularization network has been discussed in sufficient detail elsewhere (Shahsavand and Ahmadpour, 2005; Shahsavand and Pourafshari Chenar, 2007; Shahsavand, 2009). To avoid excessive degrees of freedom (flexibility) of The RN, all isotropic spreads of N neurons are assumed to be the same in our proposed algorithm.

4. Simulation case study: GTU of Khangiran natural gas refinery

Khangiran natural gas refinery which is located in the north eastern of Iran was founded in late 1970s and commissioned in early 80s. It was expanded in several steps in 2000 and 2004 (Shahsavand and Garmroodi Asil, 2010; Moaseri et al., 2013). At the present, it consists of five sour gas treating units (GTUs) with maximum total capacity of around 50MMSCMD, four sulfur recovery units with maximum total sulfur production capacity of 2600 tons per day and two topping plants with each receiving 183.6 CMD (1155 bbl/day) sweet condensate (Moaseri et al., 2013).

All sweetening units were designed using 34wt% DEA in water as the solvent. Since 2006, 47wt% MDEA solution in water was replaced for DEA solution, to decrease amine circulation rate and hence save energy in regenerator reboilers and provide extra sweetening capacity for sour gas treatment. Table 1 presents the wet sour gas analysis for the contactor feed of the Khangiran GTUs (Shahsavand and Garmroodi Asil, 2010).

Each GTU consists of two parallel trains with two distinct absorbers and two strippers. Therefore, the entire refinery has 10 contactors (with 2.895 m inside diameter (ID), 21 m height (H) and 20 valve trays (T)) and 10 regenerators (with ID = 3.8 m, $H = 24$ m, $T = 24$). Although, both trains of each GTU share the same amine and gas flash drums, however, it is always assumed that each train performs independently and there is no interaction between two adjacent parallel contactors or strippers. The rich amine stream enters regenerator over the fourth tray at around 99 °C (Shahsavand and Garmroodi Asil, 2010; Shahsavand et al., 2011).

Table 1
Wet sour gas analysis (mole%) of Khangiran refinery GTUs feed.

Components	**C_1**	**C_2**	**C_3**	**iC_4**	**nC_4**	**iC_5**	**nC_5**	**H_2O (Vap.)**
mole%	88.57	0.53	0.06	0.01	0.03	0.01	0.014	0.38
Component	**C_6^+(MW = 156)**	**H_2S**	**N_2**	**CO_2**	**C_6H_6**	**C_7H_8**	**C_8H_{10}**	
mole%	0.03	3.57	0.37	6.43	0.015	0.005	0.002	

The acid gas leaving Khangiran refinery's GTU contains about 35% hydrogen sulfide. Such low quality SRU feed stream requires split flow with pre-heat scheme for 500 tons per day production of elemental sulfur by each sulfur recovery unit. In the absence of sufficient pre-heat, serious operational problems will be encountered, such as combustion chamber low flame temperature (around 860 °C), unburned BTEX components, low quality and impure produced elemental sulfur with dark yellowish color. Low acid gas quality combined with the premature catalyst deactivation rapidly decreases the overall efficiency of the entire Claus process from the standard value of 97% to less than 90%.

The entire Khangiran GTU process was initially simulated using Aspen HYSYS (version 8.3[1]) simulator using the actual operating conditions which has been described in full detail in our previous article (Shahsavand and Garmroodi Asil, 2010). The simulation is initially calibrated by validation with real plant data. The most important operating conditions are summarized in Table 2. To ensure the reliability of the recruited software, prior to simulation of Khangiran GTU using sulfionl solvent to, the accuracy of acid gas property package for prediction of equilibrium data of Sulfolane plus MDEA mixture were compared with available experimental data borrowed from literature (Macgregor and Mather, 1991; Murrieta-Guevara et al., 1994; Zong and Chen, 2011). The predicted values for equilibrium constants via Aspen-HYSYS software had close agreement with the experimental data at corresponding operating conditions.

Fig. 5 shows the simplified schematic diagram of Khangiran gas refinery showing all output parameters of artificial neural network (*in italic fonts*). Both our novel stabilized MLP (SMLP) and in-house RN are used to investigate the effects of ANN inputs (sulfolane and MDEA weight percent in the lean amine solution) on actual operational variables such as benzene, toluene and ethylbenzene (BTE) escape factors[2], H_2S mole fraction and total moles of SRU feed, reboiler temperature, condenser and reboiler duties, molar flow of H_2S to flare and mole fraction of CO_2 in sweet gas.

Fig. 6 maps the entire input domain of the ANN and illustrates 37 concentration pairs used as training exemplars for MDEA and sulfolane in the range of (25–47 wt%) and (0–37 wt%), respectively. The Aspen HYSYS V.8.3 software was used to compute the values of previously mentioned 10 output variables for training exemplar (run). All training data set are presented in Appendix 1.

[1] Aspen HYSYS V.8.3 contains a special acid gas property package which supports various Sulfolane-M solutions.

[2] Defined as: (moles of BTE escaping from regenerator to SRU/total BTE moles entering GTU) × 100.

Table 2
Some operational conditions of Khangiran GTUs.

Stream	Parameter				
	Temperature (°C)	Pressure (psia)	Flow (kmole/h)	H_2S (mol%)	CO_2 (mol%)
Sour gas (To contactor)	52	1050	7319	3.57	6.43
Treated Gas	36	1050	6574	0	0.66
Lean Amine (To Contactor)	57	1050	18,650	0.03	0.01
Rich Amine (From Contactor)	72	1050	19,380	1.35	2.21
Lean Amine (To Flash Drum)	57	90	70	0.03	0.01
Rich Amine (To Regenerator)	99	90	19,445	1.35	2.19
Lean Amine (From Regenerator)	121	27	18,670	0.03	0.01
Acid Gas (From Flash Drum)	69	90	28.5	0.04	6.81
Acid Gas (From Regenerator)	55	27	755	33.48	56.05

5. ANNs predictions

The training data of appendix 1 is used to train several artificial neural networks (ANNs) including conventional MATLAB neural network toolbox back-propagation and exact fit networks along with two un-stabilized and two fully optimized (stabilized) MLP and RN networks. After training, the trained network can be used for predicting outputs for one or some of the training data (recall) or computing outputs for some exemplars outside the training set but inside the training domain (generalization).

For all cases, the numbers of hidden layer neurons were selected to be equal to the number of training exemplars to ensure sufficient degrees of freedom for all scenarios. Both stabilization and regularization techniques will kick-in (if necessary) and will prevent the over-fitting phenomena.

Fig. 7 presents typical recall performances of all above six networks for benzene escape factor (%) (out of nine other recall performances). As can be seen, the un-stabilized networks with $\lambda = 0$ (especially our two un-stabilized MLP and RN networks) performs much better than the stabilized networks. Somebody unfamiliar with the over-fitting concept may take proper recall performance as a reliable basis to accept all predictions of such network. Fig. 8 which shows the corresponding generalization performances over 100×100 mesh, clearly illustrate that such naive presumption can lead to catastrophic results when the trained network is used for generalization purposes.

It should be emphasized that un-regularized (or un-stabilized) networks tend to follow (fit) the noise (or measurement errors

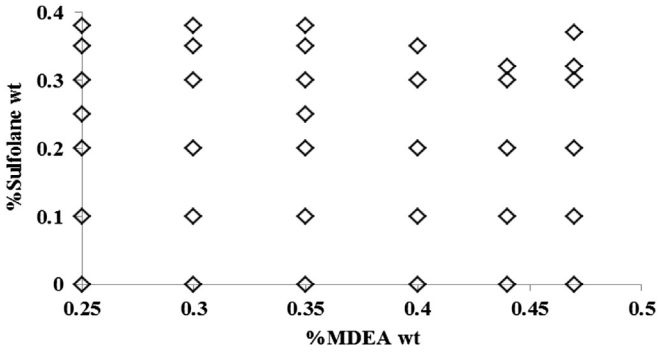

Fig. 6. Sulfolane and MDEA input data for training our in−house optimal RN and SMLP.

associated with real data) and hence provide better recall performance but lead to severely oscillatory generalization performances as shown in Fig. 8 (note the vertical axis values).

The optimum level of regularization eliminates the ill-conditioning problem and leads to a more reasonable generalization performance. It is quite clear that LOOCV criterion is relatively successful to stabilize the generalization performance. Both Regularization network and stabilized MLP provide almost similar generalization performance over the entire domain. From now on, only the generalization performances of these two networks will be presented.

It should be emphasized that the standard neural network toolbox of MATLAB software has not equipped with any stabilization or noise filtering facility. To make sure that comparison is fair and nothing is missed, the same optimal parameters which have been computed in our in-house optimized networks are exactly substituted in the MATLAB toolbox networks and the most optimal learning procedures available in MATLAB were used. As mentioned earlier, the so called “exact fit' network refers to a network which has same number of neurons as the training data, which is compatible with Regularization network. Otherwise, the so called 'fewer neuron' network should be used. No early-stopping training was used in the case of “back-propagation trained” networks.

According to both fully optimized RN and stabilized MLP network of Fig. 8, sulfolane and MDEA concentrations of (0,0.25) and (0.37, 0.47) can be considered as the optimal choices based on minimization of benzene escape factor entering SRU, which only permits 20% of the total inlet benzene entering GTU passing to the SRU feed stream. Evidently, the first point (i.e. 0 & 0.25) seems much more attractive from both economical and operational view points. However, other considerations (as will be discussed in the following sections) will indicate that the other optimal point will be more appropriate for sustainable production.

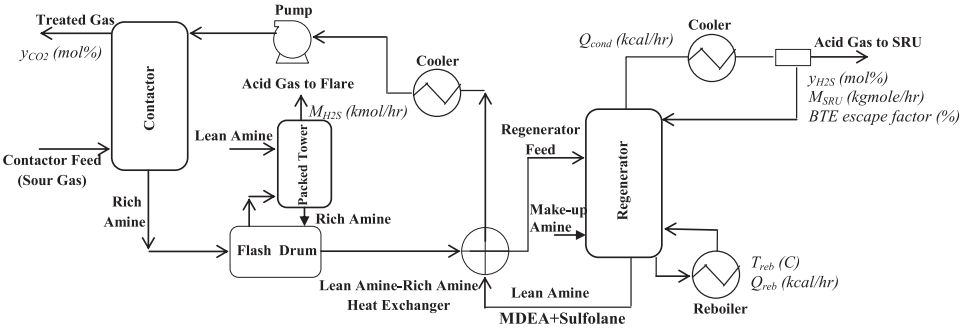

Fig. 5. Simplified schematic diagram of Khangiran gas refinery unit.

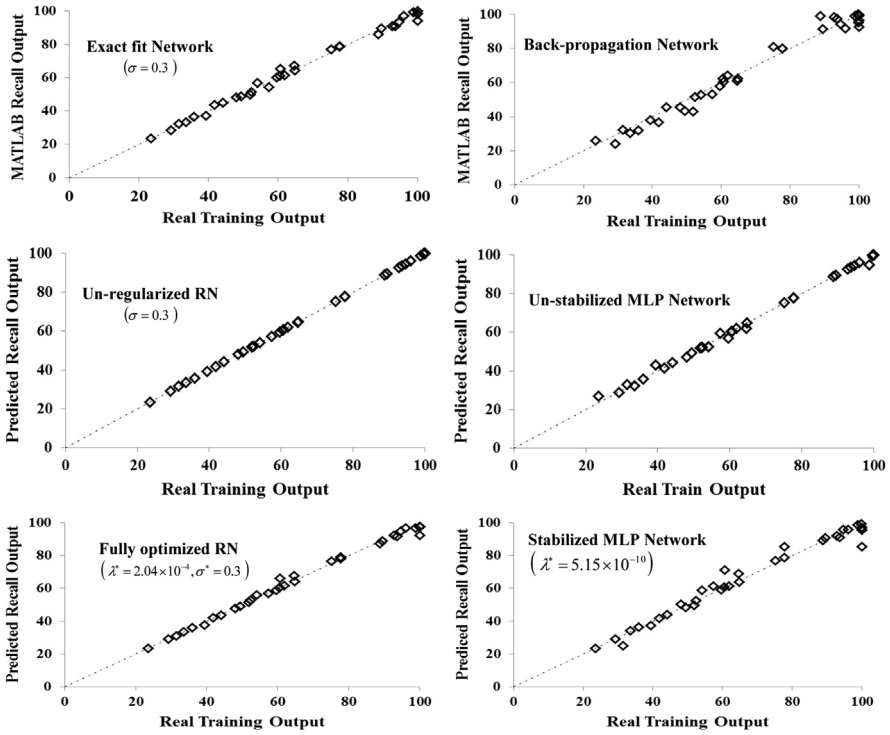

Fig. 7. Typical recall performances of various ANN for Benzene escape factor.

Fig. 9 depicts the generalization performances of toluene escape factor versus MDEA and sulfolane (wt%) variation in lean amine via Regularization and stabilized MLP networks. As before, the generalization performances of both networks are practically the same and no distinct difference can be distinguished.

Both generalization performances indicate that at the global optimum point of (0.37, 0.47), almost the entire toluene content of SRU feed stream has been eliminated. Evidently, the other suboptimal point of (0, 0.25) will lead to the relatively high concentrations of toluene.

In the same manner, Fig. 10 shows that the optimal point of (0.37, 0.47) provides minimum Ethylbenzene escape factor and practically removes all Ethylbenzene from GTU feed stream. In light of the above results, a mixture of 37 wt% sulfolane, 47 wt% MDEA and 16 wt% H_2O provides minimum escape factors for all BTE components. Small fluctuations observed in predictions of optimally tuned RN for Ethylbenzene escape factor indicates that LOOCV criterion relatively fails to totally filter the noise embedded in the training exemplars. Other techniques such as modified U curve method can lead to more stable hyper-surfaces.

Fig. 11 depicts two similar generalization performances for the total molar flow rates (kgmole/hr) entering SRU versus MDEA and sulfolane (wt%) variation in lean amine solution. Evidently, lower molar flow rates are more desirable since they indicate higher levels of acid gas enrichments due to efficient CO_2 rejection. Both Figures indicate that as before, the optimal point of (0.37, 0.47) provides minimum molar flow rate of 415 kgmole/hr for the SRU feed stream. About 43% drop in the total molar flow rate of SRU inlet stream (compared to 725 kgmole/hr at (0 & 0.47)) will dramatically reduce the size of a conventional Claus unit in the design stage or significantly increase the plant throughput at an existing SRU facility.

Fig. 12 illustrates two similar generalization performances for hydrogen sulfide mole fractions of SRU feed streams versus MDEA and sulfolane concentrations in lean amine solutions. Fig. 12 clearly shows that the H_2S mole percent in SRU feed stream increases more rapidly when sulfolane wt% increases. In an original GTU with no AGE (which uses a solvent containing 47 wt% MDEA and 52 wt% H_2O), the SRU feed stream contains around 34 mol % H_2S while, by using a solvent containing 37 wt% sulfolane, 47 wt% MDEA and 16% H_2O, the H_2S content of acid gas stream entering SRU will raise to more than 57 mol % which indicates around 62% H_2S enrichment. It is anticipated that such high amount of H_2S mole fraction in SRU inlet stream, which is due to large slippage (rejection) of CO_2 and other impurities such as BTE, can severely increase the furnace temperature of Claus unit and alleviate the catalytic deactivation while increasing the sulfur recovery efficiency.

Two 3D plots shown in top of Fig. 13 depict the generalization performances of the optimally regularized and stabilized networks for reboiler temperature of GTU regenerator column versus MDEA and sulfolane concentrations. It is quite clear that LOOCV criterion is relatively successful to stabilize the generalization performance of the stabilized MLP network, however, severe oscillations still remains in the generalization performance of the regularization network. Evidently, LOOCV criterion fails to provide the optimal level of regularization parameter for the regularization network. Hence, it can't successfully filter out the noise and extract the true underlying trend embedded in the noisy data set. Our previous work (Niknam Shahrak et al., 2013) summarized various techniques (such as visual, L-curve, modified L-curve, U-curve and modified U-curve methods) for automatic selection of the optimum ridge regression or regularization parameter.

In the absence of a reliable method for successful estimation of the optimal regularization level, the computed values for the optimal spreads has no practical meaning and both the optimal values of the isotropic spread and the regularization level should be recomputed using one the above techniques. The bottom-left 3D plot of Fig. 13 clearly shows that visual optimization of regularization level dramatically fails when improper value is selected for the Gaussian isotropic spread (note the value of vertical axis). On the other hand, The bottom-right 3D plot of Fig. 13 illustrates that visual

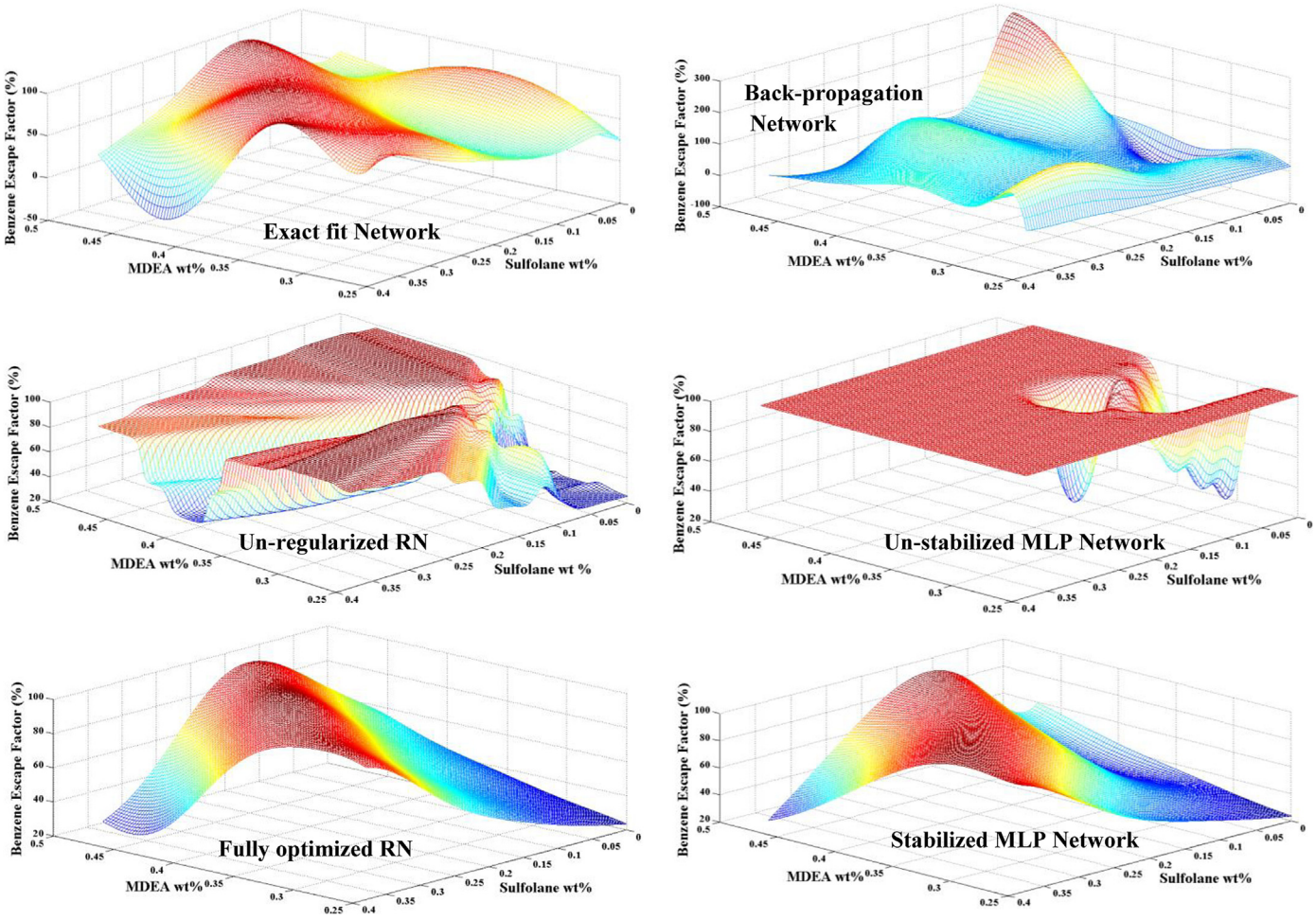

Fig. 8. Typical generalization performances of Benzene escape factor (%) in SRU feed stream versus MDEA and sulfolane(wt%) variation in lean amine for various networks.

optimization of regularization level successfully captures the true underlying trend embedded in the training data when proper value of ($\sigma = 1.0$) is selected for the Gaussian isotropic spread.

It is proved that maximum recommended skin temperature (tube wall temperature) for MDEA is 178 °C (350 F) and the temperature when MDEA degradation starts is advised as 182 °C (360 F) (Chakma and Meisen, 1997; Reza and Trejo, 2006). But lots of parameter can affect the degradation process and must be taken to account. Amine solutions are prematurely degraded by reaction with CO_2, oxygen, organic sulfur compounds, and other gas impurities to form heat-stable salts and amine degradation products. Most of scientific literature agree that MDEA thermal degradation temperature start at 127 °C (260 °F) in presence of H_2S and CO_2. In other words, to achieve reliable and steady operating system, it is recommended that the maximum amine temperature should be kept below 127 °C (260 °F).

Both right 3D plots of Fig. 13 indicate that the reboiler temperature essentially remains independent of MDEA concentration, especially for extremely low sulfolane concentrations. The previously found optimal solution containing 37 wt% sulfolane and 47 wt % MDEA still leads to reboiler temperature of around 129 °C which can cause excessive degradation of MDEA. To ensure more sustainable operation, the sulfinol solution of 37 wt% sulfolane and 45 wt% MDEA may be recommended.

Figs. 14 and 15 shows the similar generalization performances of fully optimized RN and SMLP networks for both condenser and reboiler duties (kcal/hr) of the regenerator column versus MDEA and sulfolane (wt%) concentrations, respectively. As before, although both ANNs predictions predict similar trends, the generalization performances of the Regularization network for the reboiler duty shows slight oscillations. Increasing the sulfolane and MDEA concentrations in the lean amine solution decrease both condenser and reboiler duties. Figs. 14 and 15 clearly demonstrate that using sulfinol solvent with optimum concentration of 37 wt% sulfolane and 47 wt% MDEA (the remaining 16 wt% is water) can easily lead to 70% and 35% energy savings in the condenser and reboiler duties, respectively compared to original GTU solvent (47% MDEA, 53% water). A more close examination of the above figures shows that approximately the same amount of energy savings can be accomplished by using the sulfinol solution containing 37 wt% sulfolane and 45 wt% MDEA (the remaining 18 wt% is water).

Fig. 16 shows the completely similar generalization performances of RN and SMLP for prediction of hydrogen sulfide molar flow (kgmole/hr) slipped to the atmosphere from the overhead of packed bed column. Due to strict environmental legislations, H_2S emission should not be exceeded the threshold limit of 3 mol % of hydrogen sulfide entering GTU process. Once again, the previously determined optimal concentrations of 37 wt% sulfolane and 45 wt% MDEA will practically lead to insignificant values of H_2S slippage and almost just pure CO_2 will be slipped from the overhead of packed bed column to atmosphere.

Fig. 17 which shows two nearly equal generalization performances of both fully optimized ANNs for carbon dioxide mole

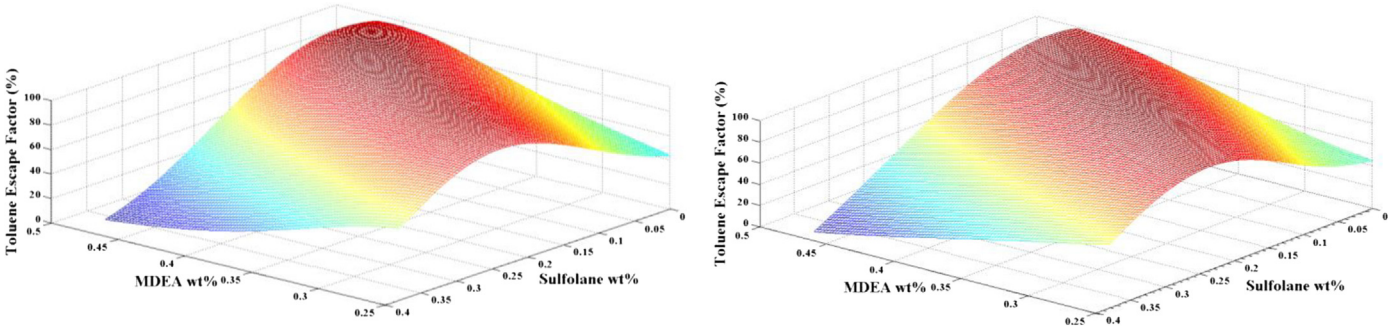

Fig. 9. Generalization performances of Toluene escape factor (%) in SRU feed stream versus MDEA and sulfolane(wt%) variation in lean amine (Left:RN, Right: SMLP).

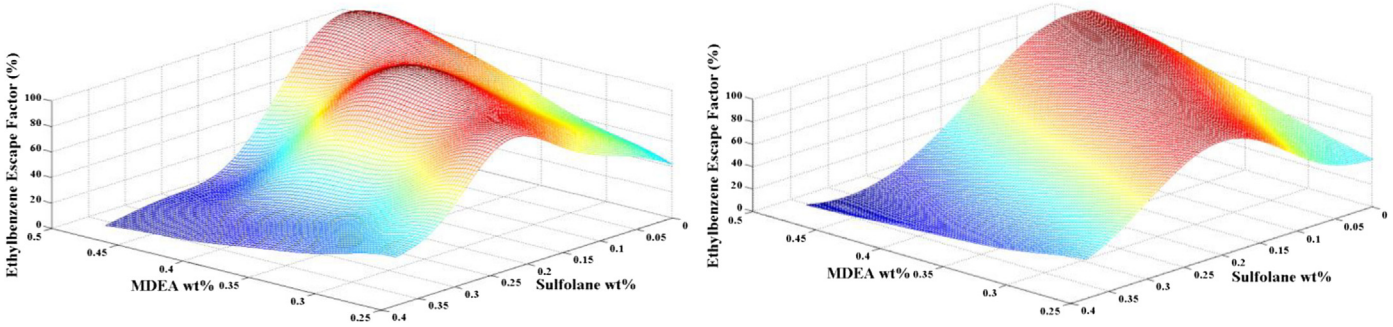

Fig. 10. Generalization performances of Ethylbenzene escape factor (%) in SRU feed stream versus MDEA and sulfolane(wt%) variation in lean amine (Left:RN, Right: SMLP).

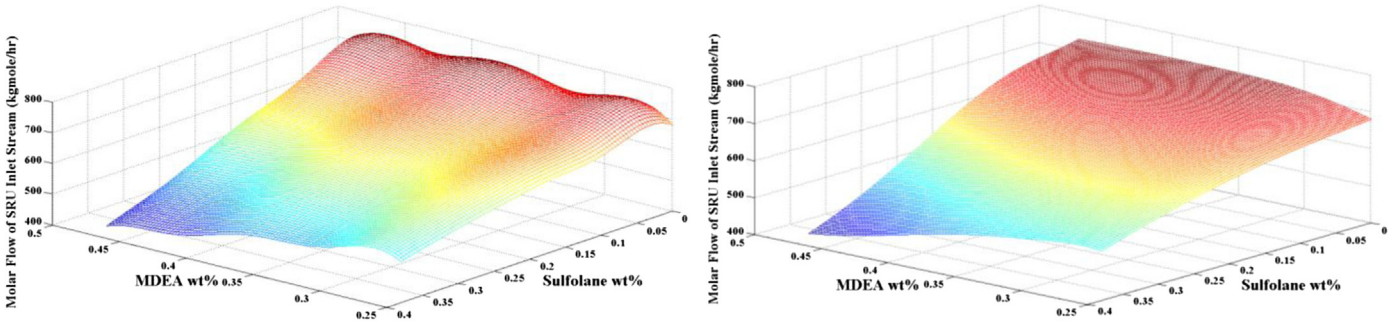

Fig. 11. Generalization performances of SRU feed stream molar flow (kgmole/hr) versus MDEA and sulfolane(wt%) variation in lean amine (Left:RN, Right: SMLP).

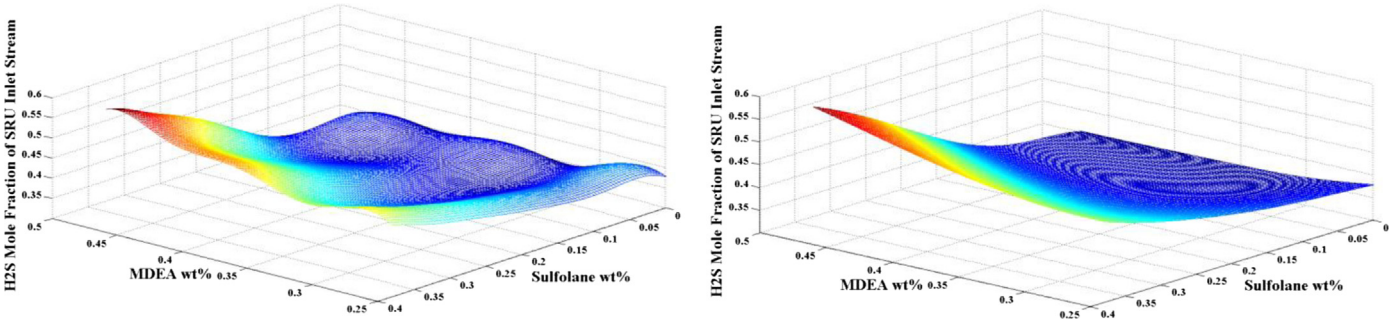

Fig. 12. Generalization performances of hydrogen sulfide mole fraction in SRU inlet feed stream versus MDEA and sulfolane(wt%) variation in lean amine (Left:RN, Right: SMLP).

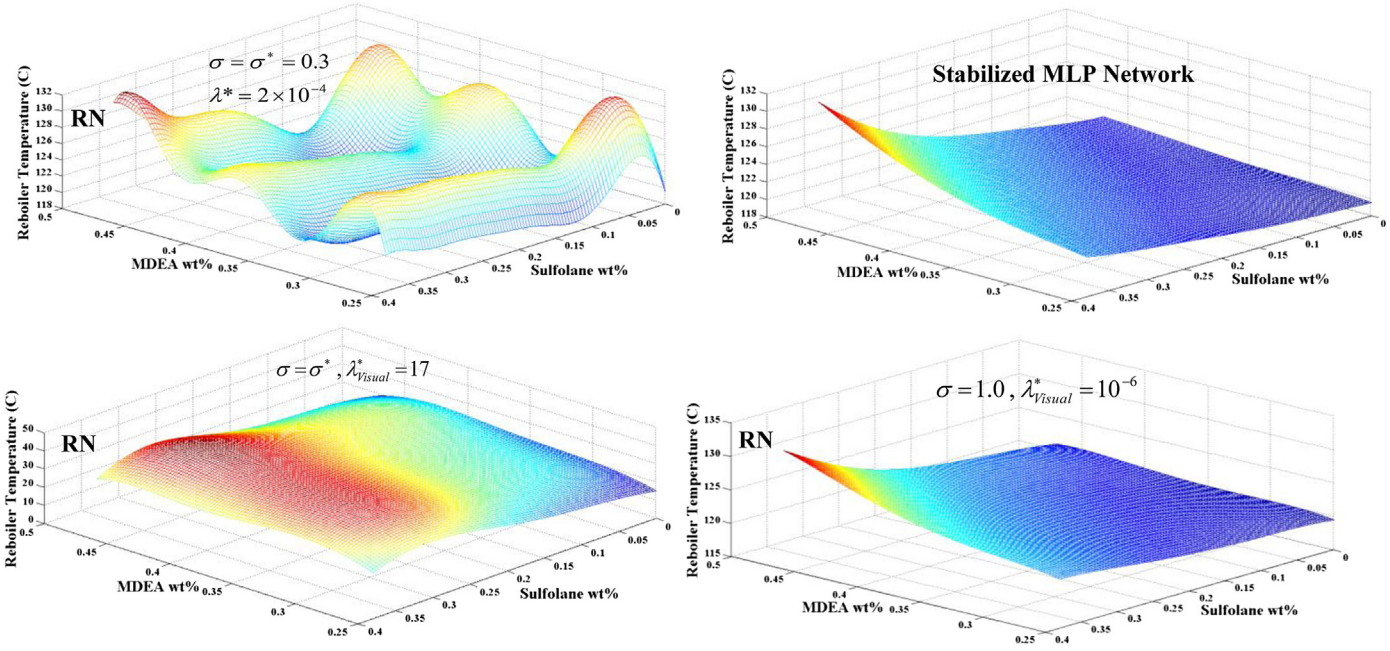

Fig. 13. Generalization performances of reboiler temperature (°C) of regenerator column versus MDEA and sulfolane(wt%) variation in lean amine.

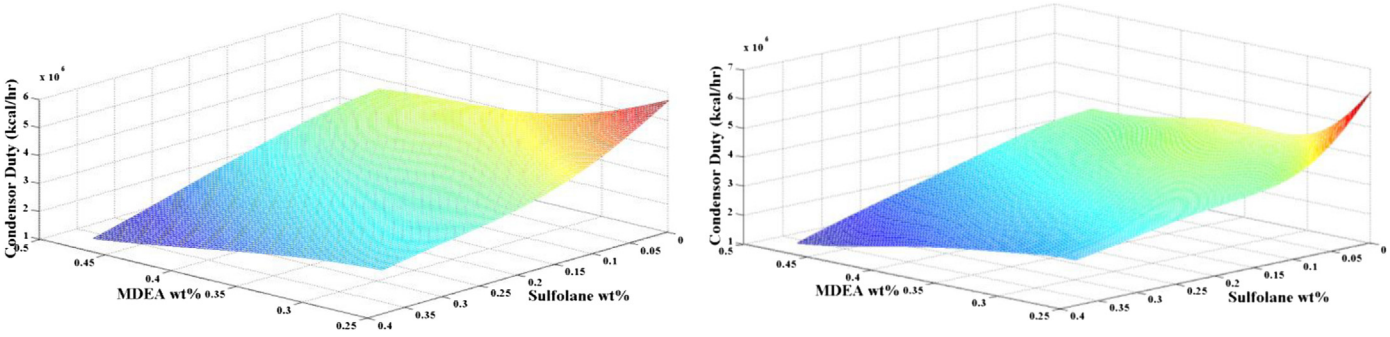

Fig. 14. Generalization performances of condenser duty (kcal/hr) of regenerator column versus MDEA and sulfolane(wt%) variation in lean amine (Left:RN, Right: SMLP).

fraction in sweet gas stream (mole %) leaving the contactor. Conventionally, the carbon dioxide content of the sweet gas entering the trunk line should be around 2–5 mol percent (Kidnay and Parrish, 2006; Mokhatab and Poe, 2012). As it is anticipated, high concentrations of sulfolane will reject the carbon dioxide from acid gas stream and increases the mole fraction of CO_2 inside sweetened gas stream. Therefore, the previously determined optimal concentrations of 37 wt% sulfolane and 45 wt% MDEA can lead to excessive CO_2 rejection rate. Fortunately, Fig. 17 shows that the CO_2 mole fraction of the contactor overhead is around 4.5 mol % which is still well inside the permissible range. Table 3 compares several obtained results via stabilized MLP network and fully optimized RN for different target values (including BTE escape factors and various constituents' molar flows and compositions for

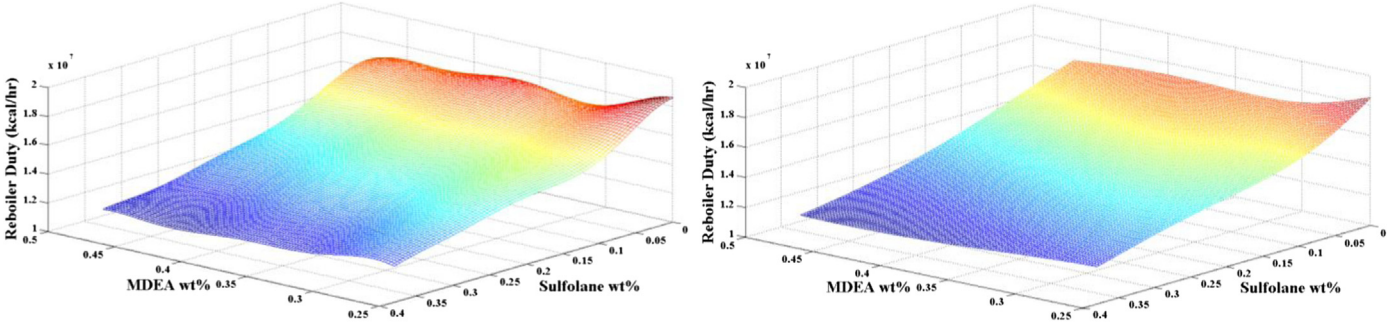

Fig. 15. Generalization performances of reboiler duty (kcal/hr) of regenerator column versus MDEA and sulfolane(wt%) variation in lean amine (Left:RN, Right: SMLP).

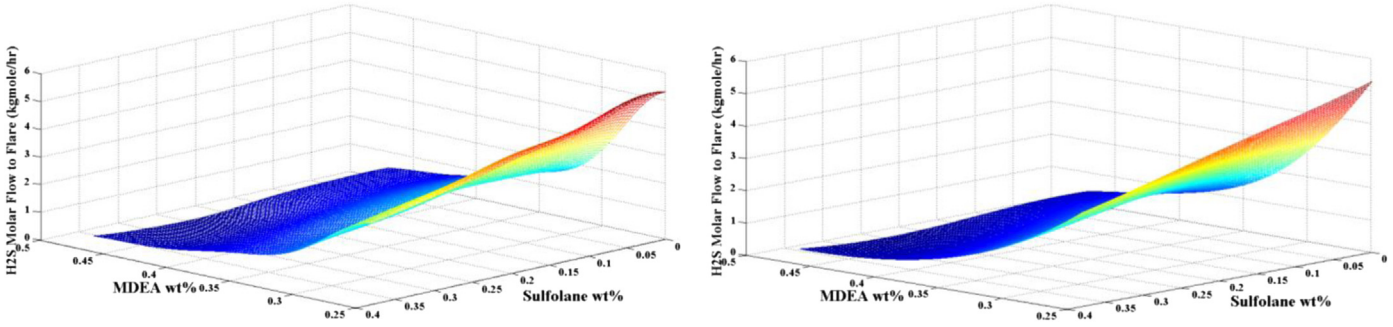

Fig. 16. Generalization performances of hydrogen sulfide molar flow (kgmole/hr) slipped to atmosphere from acid gas to flare stream versus MDEA and sulfolane (wt%) variation in lean amine (Left:RN, Right: SMLP).

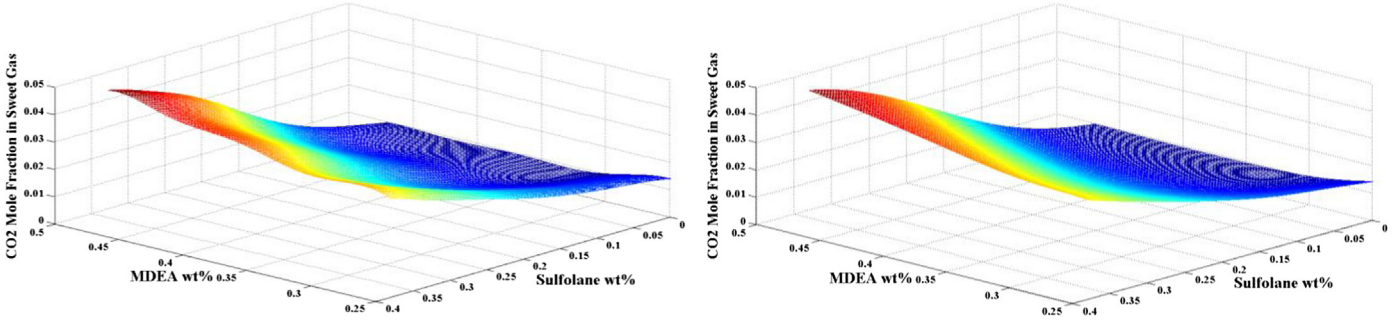

Fig. 17. Generalization performances of carbon dioxide mole fraction in sweet gas stream (mole %) versus MDEA and sulfolane(wt%)variation in lean amine (Left:RN, Right: SMLP).

Table 3
Comparison of neural networks predictions and Aspen-HYSYS simulations at optimal concentration of Sulfinol-M solution. (37 wt% Sulfolane, 45 wt% MDEA).

	Benzene escape factor%	Toluene escape factor %	Ethylbenzene escape factor %	SRU molar flow kgmole/hr	H_2S mole % in SRU feed %	Reboiler temp. °C	Condenser duty ($*10^6$) kcal/hr	Reboiler duty ($*10^7$) kcal/hr	H_2S molar flow to flare kgmole/hr	CO_2 Mole % in sweet gas mol%
NN	22	3	4	415	57	129	1.3×10^6	1.18×10^7	0.3	4.5
A/H	21.3	2.3	5.0	421.3	56.4	128.6	1.27×10^6	1.23×10^7	0.26	4.4
%Er	3.3	30	25	1.5	1	0.3	2.4	4	15	2

several locations of the GTU process) at optimal concentration of Sulfinol-M solution (37 wt% Sulfolane, 45 wt% MDEA). The comparison shows that both neural networks (stabilized MLP and fully optimized RN) can successfully predict the output parameters especially for sufficiently large parameters (outputs).

6. Conclusion

Selective removal of H_2S is essential for production of H_2S enriched acid gas streams which provides better-quality Claus process feed stream for attaining proper sulfur recovery efficiency. Various mixtures of sulfolane and MDEA solutions (Sulfinol solvent) were used to simulate the conventional GTU process of Khangiran natural gas refinery via Aspen-HYSYS V.8.3 and investigated their performances for the H_2S enrichment efficiency. A novel stabilized MLP artificial neural network is introduced for the first time and its recall and generalization performances were compared with our previously developed in-house Regularization network and two other networks borrowed from conventional MATLAB neural network toolbox (back-propagation and exact fit networks). It was clearly shown that two fully optimized (stabilized) MLP and RN networks provided more reliable interpolation hyper-surfaces for ten outputs in order to find optimal sulfolane concentration in the sulfinol-M solvent.

The outstanding generalization performance of the RN network is the result of its strong theoretical backbone due to the powerful multivariate regularization theory coupled with the efficient technique of leave one out cross validation (CV) criterion. Also, strong noise filtering capabilities of stabilization techniques made our novel stabilized MLP network to provide a distinguished performance. The optimal concentrations of 37 wt% sulfolane and 45 wt% MDEA was selected for the GTU process of Khangiran refinery which can successfully eliminate the entire toluene and ethylbenzene from the SRU feed stream while removing 80% of benzene entering the GTU process. The mole fraction of H_2S in the SRU feed stream was also increased from 33.48 mol % to over 57 mol % when using the optimal sulfinol-M aqueous solution.

Acknowledgment

The authors wish to acknowledge the valuable contribution of Khangiran gas refinery officials for their financial support and providing us with up to date SRU and GTU plants data.

Nomenclature:

Symbols

$\underline{x}$	input data vector
$\underline{y}$	output data vector
N	number of input data
w	synaptic weights
p	dimensions of input data
M	number of neurons
z	projected input variable
I	identity matrix
H	smoother matrix
e	zero column vector
U	orthonormal matrix
V	orthonormal matrix
S	diagonal matrix
G	green matrix

Greeks

θ	threshold
φ	activation function
α	linear weights
Φ	input matrix
$\Im$	merit function
$\underline{\alpha}$	linear weights
γ	constant
λ	Lagrangian multiplier ridge regression parameter
λ	regularization parameter
λ^*	optimum ridge regression or optimal regularization parameter
σ	singular values
σ	isotropic spread
σ^*	optimum value of σ

Abbreviations

AGE	acid gas enrichment
ANNs	artificial neural networks
BTE	benzene − toluene − ethyl benzene
BTEX	benzene − toluene − ethyl benzene − xylene
CMD	cubic meter per day
DIPA	diisopropanol amine
GA	genetic algorithm
GCV	generalized cross validation
GTU	gas treatment unit
LOOCV	leave one out cross validation
MDEA	methyl diethanol amine
MLP	multilayer perceptrons
MMSCMD	million standard cubic meter per day
MW	molecular weight
RN	regularization Network
SMLP	stabilized multilayer perceptrons
SRU	sulfur recovery unit
SVD	singular value decomposition
SVM	support vector machine

Appendix

MDEA conc. wt%	Sulfolane conc. wt%	Benzene escape factor%	Toluene escape factor%	Ethylbenzene escape factor%	SRU molar flow kgmole/hr	H_2S mole % in SRU feed mol%	Reboiler temp. °C	Condensor duty (*10^6) kcal/hr	Reboiler duty (*10^7) kcal/hr	H_2S molar flow to flare kgmole/hr	CO_2 mole % in sweet gas mol%
0.47	0	59.5	98.8	100	729	0.35	120.9	3.62	1.68	0.43	0.009
0.47	0.1	89.5	99.9	100	687.5	0.36	121.9	3.19	1.52	0.4	0.0157
0.47	0.2	99.9	50.9	29.2	591.1	0.42	123.6	2.50	1.35	0.2	0.0292
0.47	0.3	54.1	26.8	13.4	481.8	0.52	126.7	1.78	1.23	0.15	0.0437
0.47	0.32	48.0	23.3	11.3	464.9	0.54	127.7	1.64	1.22	0.19	0.044
0.47	0.37	39.3	3.3	6.7	413.2	0.57	128.3	1.21	1.19	0.32	0.045
0.44	0	52.3	93.8	98.9	730.7	0.35	120.7	3.73	1.70	0.56	0.0093
0.44	0.1	77.7	99.9	100	697	0.36	121.6	3.34	1.55	0.6	0.0142
0.44	0.2	99.8	94.0	38.7	616.5	0.41	122.9	2.72	1.38	0.4	0.0257
0.44	0.3	64.6	32.8	17.2	507.1	0.50	125.4	2.00	1.24	0.24	0.0405
0.44	0.32	57.4	28.9	14.7	489.2	0.51	126.2	1.87	1.22	0.25	0.0429
0.4	0	44.1	82.5	88.6	730.7	0.35	120.3	3.86	1.71	0.84	0.0091
0.4	0.1	64.7	99.7	100	704.6	0.36	121.1	3.52	1.58	0.94	0.0129
0.4	0.2	96.0	99.5	81.1	640.1	0.39	122.2	2.96	1.42	0.76	0.0223
0.4	0.3	99.9	41.9	23.7	541.9	0.46	124.1	2.28	1.27	0.49	0.036
0.4	0.35	60.5	31.1	16.1	493.6	0.51	125.7	1.95	1.21	0.46	0.0424
0.35	0	35.8	68.4	70.7	728.2	0.35	120	4.24	1.73	1.45	0.0092
0.35	0.1	51.9	94.2	99.1	704.8	0.36	120.7	3.69	1.60	1.6	0.0124
0.35	0.2	77.7	99.8	98.9	654.2	0.38	121.6	3.21	1.46	1.43	0.0199
0.35	0.25	94.6	97.4	51.3	617.4	0.41	122.2	2.91	1.38	1.23	0.0253
0.35	0.3	99.8	60.5	33.8	574.8	0.44	123	2.60	1.30	1.04	0.0314
0.35	0.35	99.9	42.1	23.8	529	0.48	124	2.28	1.24	0.9	0.0377
0.35	0.38	88.7	35.5	19.0	503.5	0.50	124.9	2.10	1.20	0.87	0.0412
0.3	0	29.1	56.1	55.1	716.6	0.35	119.8	4.21	1.70	2.75	0.0101
0.3	0.1	41.7	80.0	86.4	693.1	0.36	120.3	3.80	1.60	2.77	0.0133
0.3	0.2	61.8	99.4	99.9	651.8	0.39	121.1	3.37	1.48	2.46	0.0196
0.3	0.3	93.6	83.8	46.0	589.3	0.43	122.1	2.83	1.34	1.96	0.0289
0.3	0.35	99.7	55.1	33.6	549.8	0.46	122.9	2.54	1.27	1.76	0.0345
0.3	0.38	99.9	46.7	27.5	528.2	0.48	123.5	2.37	1.23	1.61	0.0376
0.25	0	23.5	45.0	41.9	678.8	0.37	119.5	6.22	1.86	5.29	0.014
0.25	0.1	33.5	65.1	68.0	657.6	0.38	119.9	3.83	1.57	4.6	0.0174
0.25	0.2	49.4	91.9	98.4	626.2	0.40	120.6	3.40	1.47	4.05	0.0223
0.25	0.25	60.5	99.1	99.7	603	0.42	121.1	3.17	1.41	3.68	0.0259
0.25	0.3	75.1	95.5	60.5	579.7	0.43	121.5	2.95	1.35	3.37	0.0294
0.25	0.35	92.7	68.6	45.0	551.8	0.46	122.1	2.71	1.29	3.07	0.0336
0.25	0.38	98.7	58.7	37.6	533.2	0.47	122.5	2.56	1.25	2.92	0.0363

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