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A Modified Four-Coefficient Model for Plus Fraction Characterization of a Supergiant Gas Condensate Reservoir

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Abstract

Properties and chemical composition of plus fraction in a petroleum fluid have a considerable impact on the fluid phase behavior. Understanding the trend of changes in molecular weight of successive single carbon number (SCN) groups in a plus fraction requires an accurate and reliable distribution function. Different distribution function models proposed so far may be applicable for certain types of reservoir fluids. In this work, analysis of 30 representative fluid samples in a supergiant gas condensate reservoir indicated a discontinuity in molecular weights of SCN groups at SCN=8, and SCN=13. The exponential, gamma, four-coefficient, and modified four-coefficient distribution functions were applied to these samples to predict the composition of SCN components. Results showed that the exponential distribution function does not predict the distribution of SCN composition accurately, especially in the aforementioned compositional discontinuities. Furthermore, the gamma distribution function was successful in predicting the jump in SCN=8 but failed at SCN=13. On the other hand, the modified four-coefficient model did predict the jumps in both SCN=8 and SCN=13. The overall error of calculations was 37.19%, 12.04% and 10.71% for exponential, gamma and modified four-coefficient models. Comparing four-coefficient and modified four-coefficient prediction results showed that the model parameters are strongly dependent on the fluid nature and need to be optimized based on available field data.

Keywords: Gas Condensate, plus fraction, distribution function, four-coefficient model

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Introduction

Phase behavior and thermodynamic properties of petroleum fluids are normally determined using equations of states (EOS). Proper application of EOS requires information such as physical and critical properties, acentric factor, binary interaction parameters and molecular weight of all components that exist in the petroleum fluid.

Routine separation techniques can identify some components, leaving most of them impossible to separate and characterize (Whitson and Brule, 2000). The light components, including hydrocarbon compounds up to C₆ and non-hydrocarbon components, i.e. N₂, CO₂, and H₂S are almost clearly identifiable through experimental measurements.

Other hydrocarbon compounds are usually lumped as a plus fraction (C_{7+}) to avoid further analysis of hydrocarbon components, which is limited by separation techniques, preventing extra time for reservoir production and process simulations (Danesh, 1998). Characterization of plus fraction is one of the key steps in reservoir fluid phase behavior studies. In the absence of extended compositional measurements, lumping all components into a single pseudo heavy component can cause large errors in predicting phase behavior of reservoir fluids (Ahmed, 1989). In order to characterize the plus fraction, it is first split into a number of SCN groups and then lumped into pseudo components (Pedersen and Christensen, 2007). Several techniques have been proposed for splitting heavy ends; these techniques are based on the nature of hydrocarbons that exist in the plus fraction. Pedersen et al. (1983, 1984) studied a large number of fluid samples and proposed a semilog relationship between molecular weight and composition of SCN groups for SCN>6. This relationship, also known as exponential distribution function, has been extensively implemented to characterize plus fraction of gas condensate samples (Du and Mansoori, 1987; Mansoori et al., 1989). However, Whitson (1983) observed that the mole fraction of SCN groups versus corresponding molecular

weight in the plus fraction does not always follow the exponential distribution function trend, as the experimental trend shows a discontinuity at SCN=8. He proposed the threeparameter, gamma probability distribution function to predict distribution of hydrocarbons in the plus fraction. The use of variance as an adjustable parameter in this approach makes it more flexible in a wider range of components (Ahmed, 1989).

Ahmed et al. (1985) integrated the exponential and gamma distribution functions to introduce a new, linear distribution function to account for the discontinuity in SCN=8. Similar to exponential distribution function, they introduced the semilog function for composition and molecular weight of SCN groups, except for the SCN=8, which was modeled by two linear functions. Hosein et al. (2012) studied 20 petroleum and gas condensate samples and observed the discontinuity at SCN=8, 13. They extended the Ahmed et al. (1985) two coefficient model to a four-coefficient distribution function, called four-coefficient model. They reported the accuracy of predictions by four-coefficient model as AAD=7.0% for selected samples, compared to AAD% of 10.8% by Ahmed et al. (1985) model.

As stated before, all available models have adjustable parameters that can be calculated through an optimization algorithm using experimental data. It is expected that these parameters are subject to change as a function of fluid nature, composition and phase behavior. The objective of this study is to modify the parameters of the four-coefficient model and customize them using PVT data of a supergiant gas condensate field. A global optimization algorithm procedure will be introduced to include all PVT data simultaneously, rather than individual optimization followed by averaging the optimized parameters. In the next sections, field data are introduced first. Then, modeling and optimization approach is presented. Next, results of optimization approach are presented and discussed. Concluding remarks appear in the end.

Field PVT data and modeling

PVT data were collected from a supergiant gas condensate field located in the Middle East. These data were selected from among a comprehensive data set after a careful screening and quality control of sampling conditions using standard protocols. Several guality control procedures have been proposed in the literature (Drohm et al., 1988; Trengove et al., 1991; Kikani and Ratulowski, 1996; Moffatt and Williams, 1998; Cobenas and Crotti, 1999). The integrated quality control of PVT and DST data (Osfouri et al., in press) was used to select 30 valid data sets out of more than 70 available samples. The sampling depth and temperature were 8900-11300 ft and 188-220 F. Table 1 gives the average composition and range of variations for successive SCN groups. Figure 1 shows compositional analysis versus SCN for one of the samples. The decreasing trend of composition is interrupted at SCN=8, 13, same as those reported by Hosein et al. (2012).

The four-coefficient model proposed by Hosein et al. (2012) will be modified and applied to selected gas-condensate data. To test the ability of this model, results of model predictions are compared with exponential and gamma distribution functions, defined as equations (1) and (2):

(1) $\ln z_i = A + BM_i$

(2)
$$F(M) = \frac{(M-\tau)^{(\alpha-1)} e^{\left(\frac{(M-\tau)}{\beta}\right)}}{\beta^{\alpha} \Gamma(\alpha)}$$

Table 1: Average and variance of composition of SCN groups and molecular weight of plus fraction in the data set (Osfouri et al., in press).

SCN	(%) Composition
7	0.076 ± 0.507
8	0.064 ± 0.412
9	0.056 ± 0.246
10	0.042 ± 0.241

11	0.029 ± 0.168
12	0.022 ± 0.130
13	0.023 ± 0.115
14	0.018 ± 0.086
15	0.016 ± 0.071
16	±0.012 0.050
17	0.011 ± 0.041
18	0.010 ± 0.034
19	0.008 ± 0.027
20+	0.036 ± 0.079
M ₇₊	3.213 ± 137.679

 α , M and τ are model parameters that describe the distribution form, molecular weight and minimum molecular weight in the plus fraction. β is calculated by equation (3):

$$(3) \beta = \frac{M_{C7+} - \tau}{\alpha}$$

 M_{C7+} is the molecular weight of C_{7+} fraction, defined by equation (4):

(4)
$$F_i = -\exp\left(\frac{\tau}{\beta}\right) \cdot \left[\exp\left(-\frac{M_i}{\beta}\right) - \exp\left(-\frac{M_{i-1}}{\beta}\right)\right]$$



Figure 1: Mole percent distribution of pseudocomponent SCN in a gas condensate sample (Osfouri et al., in press).

The mole fraction of each pseudo SCN, z_{i} , is calculated by equation (5) using composition of plus fraction, z_{1} :

(5)
$$z_i = z_+ \cdot F_i$$

The four-coefficient model divides the composition distribution of plus fraction into four distinct zones, as shown by equations (6) and (7):

(6)
$$M_{n+} = M_{7+} + S(n-7)$$
 for $7 \le SCN \le 12$

(7) $M_{n+} = M_{12+} + S(n-12)$ for $12 \le SCN \le 19$

Hosein et al. (2012) suggested that values of adjustable parameter S are selected from table 2 for each SCN and used equations (6) and (7) to calculate molecular weight of plus fraction, M_{n+} . Composition of each SCN pseudocomponent is calculated by equation (8), as suggested by Ahmed et al. (1985):

(8)
$$z_n = z_{n+} \left[\frac{M_{(n+1)+} - M_{n+}}{M_{(n+1)+} - M_n} \right]$$

If the plus fraction is to be split up to SCN=20, equation (8) will be used to calculate composition of SCN=7-19, and composition of C_{20+} is calculated by mass balance, equation (9):

(9)
$$\sum_{n=7}^{20} z_n = z_{C_{7+}}$$

Table 2: Constant for equations (6) and (7) (Hosein et al., 2012).

SCN	n=8	n<13>8	n=13	n>13
S	12.5	16	13	14.5

RESULTS AND DISCUSSION

As stated before, Hosein et al. (2012) calculated adjustable model parameters for every single sample by applying the optimization algorithm on that sample. They reported the mean or average values of adjustable parameters as the optimum model parameters for the data set. We have implemented a global optimization procedure to calculate the four model coefficients by using

all PVT data simultaneously. The total average absolute deviation (TAAD), defined by equation (10), is used as an objective function:

(10) TAAD =
$$\frac{1}{K} \sum_{j=1}^{K} \left(\frac{1}{L} \sum_{n=7}^{20} \left| \frac{Z_n^{Cal} - Z_n^{Exp}}{Z_n^{Exp}} \right|_j \times 100 \right)$$

The optimum parameters are calculated by minimizing equation (10).

K and L are the total number of experimental data sets and number of SCN groups in the plus fraction splitting. The minimization was performed using the Marquardt optimization program for minimizing TAAD (Chandler, 1985). Table (3) summarizes the S-values of the four coefficient model for 30 gas condensate data sets used in this study.

For the same data set, the exponential distribution parameters A and B were calculated as 0.981 and -0.018, and the gamma distribution parameters, α and τ , were calculated as 0.97 and 86. The molecular weight of C₇₊ for each sample is used to calculate model parameters in gamma distribution function.

Trend of plus fraction molecular weight (M_{n+}) versus SCN group can be calculated using optimized models. Figures 2 and 3 show the M_{n+} versus SCN calculated by a modified four-coefficient model for a gas condensate sample of this reservoir.

The optimized models can be used to calculate the composition of SCN groups for each sample.

For example, figure 4 compares model predictions with experimental data of SCN compositions for a gas condensate sample of this reservoir. It is clear from this figure that the modified four-coefficient model can predict experimental data very well.

Table 3: New adjusted constants of the 4 coefficient model.

SCN	n=8	n<13>8	n=13	n>13
S	13.14	14.07	12.41	13.21



Figure 2: Changes in molecular weight of SCN=8 for one of the gas-condensate samples (a) Molecular weight between SCN=7-8 (b) Molecular weight between SCN=8-12.



Figure 3: Changes in molecular weight of SCN=13 for one of the gas-condensate samples (a) Molecular weight between SCN=12-13 (b) Molecular weight between SCN=13-19.

Table 3 summarizes average absolute deviation (AAD%) of model predictions for all samples. According to this table, the optimized four-coefficient model (this work) has AAD% equal to 10.71, while the exponential, gamma, and original four-coefficient models give AAD% equal to 37.19, 12.04 and 16.04, respectively. According to this table, the modified four-coefficient model shows the best match with experimental data.

On the other hand, the exponential model shows large error in predicting the composition of SCN groups for all samples used in this study, although it was suggested by Mansoori et al. (1989) for gas-condensate systems.

Figure 5 compares prediction results of modified four-coefficient and optimized gamma distribution function. Both models can predict the compositional discontinuities at SCN=8; however, the gamma distribution function cannot predict second discontinuity at SCN=13, although it gives better predictions for some SCN groups.

Overall, better results are obtained by the simpler four-coefficient model modified for selected data set. This model is easier to use with less calculation complexity and requires less calculation steps.



Figure 4: Comparison of modified four-coefficient model (solid line) with experimental data (black circles) for gas condensate sample.



Figure 5: Average absolute deviation for composition of SCN groups in all samples. Black columns: modified fourcoefficient model (this work); Grey columns: gamma distribution function

Sample name	Exponential	Gamma	CM 4	This work
S1	40.75	8.35	10.06	8.38
S2	34.62	6.54	10.99	5.24
S3	12.89	8.58	8.07	6.71
S4	11.55	9.68	12.30	5.87
S5	12.25	13.64	11.09	7.37
S6	16.90	10.04	14.64	9.59
S7	13.90	11.41	18.31	8.46
S8	23.29	7.04	10.79	5.94
S9	63.69	14.18	20.97	15.50
S10	15.43	10.28	15.76	11.69
S11	23.91	10.97	15.38	9.99
S12	84.82	10.12	13.03	8.97
S13	75.89	9.92	12.09	8.90
S14	34.55	17.42	25.56	14.84
S15	13.73	13.69	16.73	11.50
S16	32.86	13.63	19.98	12.71
S17	29.16	14.05	14.94	13.14
S18	22.00	13.61	15.74	12.91
S19	22.65	12.73	16.79	11.67
S20	22.65	12.47	14.46	12.66
S21	40.90	11.84	17.05	10.31
S22	30.22	11.87	14.67	10.96
S23	124.04	13.63	19.75	12.60
S24	100.58	14.08	20.10	12.94
S25	96.94	12.93	19.15	12.28
S26	22.42	12.31	16.79	11.34
S27	20.06	16.60	25.90	14.75
S28	20.63	13.72	16.19	11.70
S29	21.00	12.63	16.89	11.10
S30	31.55	13.35	16.98	11.28
TAAD	37.19	12.04	16.04	10.71

Table 4: Average absolute deviation of samples and total average deviation of different distribution functions

Conclusions

Gas condensate samples taken from the supergiant reservoir under study showed discontinuities or jumps in molecular weight at SCN=8, 13. Results showed that ignoring discontinuities can result in large errors when applying exponential distribution function. The gamma distribution function can predict compositional discontinuities at SCN=8 but failed at SCN=13. On the other hand, the

modified four-coefficient model was shown to successfully predict both discontinuities with the best accuracy compared to exponential, gamma, and original four-coefficient models. Results also showed that the parameters of distribution function are strongly dependent on fluid nature and better results are obtained upon optimizing the selected model using experimental field data.

NOMENCLATURE

AAD	Average Absolute Deviation	
F	Distribution function	
М	Molecular weight	
c	Adjustable parameters of	
3	equations 6 & 7	
Sn	Sample name, in table 3	
SCN	Single Carbon Number	
TAAD	Total Average Absolute Deviation	
Z	Molar composition of SCN group	
GREEK LETTER		
А	Distribution form	
	Minimum molecular weight in the	
I	plus fraction	
	SUPERSCRIPTS	
Cal	Calculation	
Ехр	Experimental	
	SUBSCRIPTS	
+	Plus fraction	
N	Number of SCN group	

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Fabrication and Characterization of Polymer Blend Membranes for CO2/CH4 Separation

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Abstract

In the last two decades, various modifying techniques have been employed to improve membranes performance including mixed matrix, cross linking, grafting, polymer blending, making composite or hybrid membrane. Blending of polymeric membrane is a cost and time effective approach and an advanced technique for gas separation, where two or more polymers are mixed to produce a new material with different and desired physical, chemical and mechanical properties. This work reports on the separation performance of a novel polymeric blend membrane based on poly(amide-bethylene oxide) and polyethersulfone blends. These flat sheet membranes were synthesized using solution-casting in different ratios (10-40%) in order to improve membrane separation performance of CO_2/CH_4 gas mixtures. Prepared membranes were then characterized by Fourier Transformed Infra-Red Spectroscopy (FTIR) where spectral changes indicated existence of molecular interaction among the polymeric blends, highlighting their compatible nature. Permeabilities of pure gases (CO_2 and CH_4) were also examined at room temperature. Results indicated that increasing wt.% PES in the Pebax[®]/PES blend membranes increased selectivity of CO_2/CH_4 and decreased pure gas permeabilities.

Keywords: Blending, gas separation, poly(amide-b-ethylene oxide), polyethersulfone

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Introduction

Gas separation membrane is a semipermeable barrier, separating one or more gases from a multicomponent gas mixture by permitting the transport of certain molecules under the influence of some forms of chemical potentials such as pressure or concentration gradient (Mulder, 1997; Baker, 2000).

There are many known industrial processes involving separation of carbon dioxide from other gases including purification of synthesis gas to obtain high purity hydrogen for fuel cells, removal of carbon dioxide in natural gas sweetening, separation of carbon dioxide from industrial flue gases for greenhouse gas sequestration and removal of carbon dioxide from breathing air in space crafts or spacesuits (Dortmundt and Doshi,1999; Chung et al., 2007). Table 1 summarizes several sweetening technologies commercialized to date for such purposes (Maddox and Morgan, 1998).

Among these techniques, membrane separation has attracted much attention due to its compact and modular devices, mild operating

conditions, simple equipment without moving parts (Ismail and Kusworo, 2007; Shekhawat et al., 2003), while it could be scaled up easily for design purposes (Shekhawat et al., 2003) and does not require sorbent regeneration or desorption (An et al., 2011).

A desirable membrane should satisfy several structural and functional properties including a combination of high permeation rate, high species selectivity, low fouling rate, long and reliable service life, and adequate mechanical, thermal and chemical stabilities under certain operating conditions (Meinema et al., 2005). However, a single membrane cannot surpass all above requirements and hence, attempts are continually being made to compensate for these using polymeric blend membranes which offer extensive processability.

As far as the ratio of glass transition and application temperatures are concerned, there are two types of polymeric membranes: glassy and rubbery. The former have a glass transition temperature higher than application temperature, while the latter refers to those polymeric membranes having glass transition temperatures well below their application

CO ₂ Removal Mechanism	Process Type	Technology	Commercial Name
Chemical	Regenerative, continuous	Potassium carbonate	MEA, DEA, MDEA, DIPA, DGA, formulated solvents
absorption	Non regenerative, continuous (usual arrangement : lead/lag)	Sodium hydroxide	Benifielf, Catacarb, Giam macro-Vetrocoke,etc.
Physical absorption	Regenerative, continuous	Physical solvents	-
Physical-chemical absorption	Regenerative, continuous	Physical-chemical solvents	Selexol,Rectisol, Purisol, Fluor Solvent, IFPexol, etc.
Physical adsorption	Regenerative, continuous(adsorption/ desorption sequence)	Molecular sieves	Z5A (Zeochem), LNG-3 (UOP), etc.
Permeation	Continuous	Membranes	Separex, Cynara, Z-top, Medal, etc.

Table 1- Classification of sweetening Technology

temperatures (Mulder, 1997). A limiting challenge in the industrial application of polymeric membrane is their low permeability and selectivity, for which blending with other polymers are thought to be the right approach in meeting this challenge.

poly(amide-b-ethylene oxide) (Pebax®1657) seems to be a suitable choice for this as it is a rubbery copolymer containing PEO segments as the permeable phase, with the polyamide crystalline phase giving the required mechanical strength to the membrane. It also has a high CO₂ permeability due to the high affinity of its PEO segment with respect to the polar CO₂ molecule, making it a promising material for CO₂ capturing of flue gas and in natural gas sweetening processes (Car et al., 2008; Okamoto et al., 1995; Bondar et al., 2000). Polyethersulfone (PES) on the other hand, offers high chemical resistance, and is stable against oxygen and thermal degradation with high CO₂/CH₄ selectivity while being commercially attractive (Cakal, 2009). Therefore, adding PES to Pebax® may improve the CO₂/CH₄ selectivity of this rubbery polymer, and hence in this study, we first prepared the Pebax®/PES blend membranes with different ratios and characterized them before gas transport properties of the blend membranes were investigated and compared with those of the neat Pebax[®]. To the best of our knowledge. apart from our own research papers currently under review, blending of these rubbery/glassy polymers has not been reported elsewhere in the literature.

Experimental

Material

Pebax® 1657 was purchased from Arkema and PES was supplied from BASF, with their chemical structure being presented in Fig. 1. Dimethylacetamide (DMAc) was purchased from Merck and used as solvent in its received form.

Preparation of films

Polymeric blend membranes with various

compositions (10/90, 20/80, 30/70, 40/60 wt.%) were prepared by solution-casting and evaporation method. First, PES in stipulated quantity was dissolved in DMAc using a magnetic stirrer for 12 h. Subsequently, Pebax® was added while stirring was continued at 90 °C to allow complete mixing of the polymers. The solution was cast into a 10 cm diameter Petri-dish, and kept in an oven at 60 °C for 16 h. All membranes were kept under vacuum at room temperature overnight before testing was conducted on them.



Fig. 1- Chemical structures of (a) Pebax[®] and (b) PES

Characterization

Fourier transform infrared (FTIR) spectra were recorded using a Bruker Alpha FTIR to examine the chemical interaction between the polymers. Measurements were carried out using the attenuated total reflectance (ATR) technique.

Gas permeability

Pure gas permeation properties were determined using constant pressure/variable volume method for both CO₂ and CH₄. All measurements were performed at room temperature and volume change under constant feed pressure was measured by means of a capillary tube.

Permeability, an intrinsic property of the membrane material, is defined according to the following equation:

(1)
$$P_i = \frac{LN_i}{\Delta P_i}$$

where Pi represents the permeability for penetrant component i, L is the membrane thickness (cm) and N_i refers to the flux passing through the film (cm³/sec). Its unit is commonly expressed in Barrer (1 Barrer = $1 \times 10-10$ cm³ (STP) cm/(cm² sec cmHg)). The ability of a membrane in separating two molecules, for example, i and j, is referred to as the ratio of their permeabilities, or better known as the membrane selectivity. In this study, ideal gas selectivity was calculated from the ratio of pure gas permeability according to equation (2) below (Mulder, 1997):

(2)
$$\alpha_{i,j} = \frac{P_i}{P_j}$$

Results and discussion

FTIR Analysis

Fig. 2 demonstrates FTIR-ATR spectra of Pebax®, PES and Pebax®/PES (20 wt.%) blend membranes. As can be seen, -C=O and -C-Ostretching vibrations in Pebax® were located at 1731 and 1090 cm-1, respectively. Moreover, bands at 1635 and 3296 cm⁻¹ could be attributed to presence of both C=O and N-H of the amide functional group, respectively (Kim and Lee, 2001), while the band at 1540 may be related to N-H bending. In the PES spectrum, the S=O stretching peaks were situated at 1143 cm⁻¹and 1007 cm⁻¹, while the C-H stretching peak of benzene ring was located at 3096 cm⁻¹. Other bands at 1574, 1482 and 1402 cm-1 might be assigned to aromatic skeletal vibrations. The characteristic peaks at 1320 cm⁻¹ and 1230 cm⁻¹ may also be attributed to C-O-C stretching (Qu et al., 2010).

As for the Pebax®/PES (20 wt.%) blend membrane, apart from Pebax® characteristic peaks which were clearly evident, the N-H peak was found to be gradually split into two peaks; the free N-H in the Pebax® structure as well as a hydrogen bonded one with S=O group appeared at 1542 cm⁻¹. In other words, an intermolecular hydrogen bond may have been formed between the amidic hydrogen and the sulfone group. This weak intermolecular interaction, has

led to longer N-H bond and hence wavelength vibration of the bonded N-H has become higher than the free one. This could be treated as evidence for PES being kept in the Pebax® matrix.



Fig. 2- FTIR-ATR of (a) pure Pebax[®] (b) pure PES (c) Pebax[®]/PES (20 wt.%)

Permeability results

Figs. 3 and 4 illustrate pure gas permeabilities and ideal selectivities of both neat and blend membranes using CO₂ and CH₄, respectively. In general, CO₂ permeability is higher than CH₄, and CO₂ has greater solubility in Pebax® polymer. The kinetic diameter of CO₂ (3.3 Å) (Bakhtiari et al., 2011; Li et al., 2013) is also smaller than that of CH₄ (3.8 Å) (Li et al., 2013; Karkhanechi et al., 2012), which leads to its greater diffusivity.

Compared to pure Pebax® membrane, blend

membranes exhibit improved CO₂ selectivity perhaps due to the presence of PES in the blend, while compared to pure PES membrane, these membranes exhibit improvement in the permeability due to the presence of Pebax® in the blend. Adding PES as glassy polymer to Pebax® matrix has led to a decrease in the chain mobility of the Pebax®, and hence reduced permeability. Because of size sieving properties of the glassy polymers, PES presence in Pebax® has apparently increased selectivity here.



Fig. 3 – Pure gas permeabilities for Pebax®/PES blend membranes



Fig. 4 – Ideal selectivities for Pebax®/PES blend membranes

Conclusion

In fabricating a novel polymeric blend membrane to separate CO₂/CH₄ gas mixtures, based on poly(amide-b-ethylene oxide) and polyethersulfone blends, flat sheet membranes were synthesized using solution-casting in different ratios (10-40%), where all prepared membranes were of clear and homogeneous films. FTIR analysis confirmed presence of PES in Pebax® matrix. Spectral changes indicated existence of molecular interaction among the polymeric blends, highlighting their compatible nature. Increasing wt.% PES in the Pebax®/PES blend membranes, increased selectivity of CO₂/ CH, while decreasing pure gas permeabilities. Gas permeabilities of flat sheet blend membranes varied monotonically between those of the two pure polymers. For further work we intend to add fillers in the blend, in order to enhance even further the polymeric blend membrane performance.

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Performance Comparison and Analysis of the Genetic Algorithms and Particle Swarm Optimization Methods to Optimize the Pressure-Flow Equations in Gas Transmission and Distribution Networks

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Abstract

One of the most important goals of gas engineering is to optimally distribute gas in gas transmission and distribution networks; however, this process often suffers from some inevitable distribution network problems such as errors caused by inaccurate estimates of pressure at various points in the network. Recently, statistical optimization methods have been proposed to solve this problem. Particle Swarm Optimization (PSO) and Genetic Algorithm (GA) are common methods for this purpose. The purpose of this study is to compare the performances of these two procedures. If similar constraints and computational loads are applied to both methods, PSO can provide more accuracy and speed compared to GA, although repeatability of GA was found to be better.

Keywords: Gas network, optimization, particle swarm optimization, genetic algorithm

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Introduction

After producing natural gas from the underground reservoir, the first process is to transport the natural gas to operation and filtration units. There are a number of options for transporting natural gas from oil and gas fields to market. These include pipelines, liquefied natural gas (LNG), compressed natural gas (CNG), and gas to solids (GTS), i.e., hydrates, gas to power (GTP) and any possible method. If technical and economic hurdles can be overcome, these pipelines can become effective. Pipelining is the method that is preferred. In the last decade, on average, over 12,000 miles per year of new gas pipelines have been completed, most of which are transnational (Mokhatab, S. et al., 2014).

To keep gas flowing in these networks, pressure-boosting stations are installed along the delivery system. The stations use fossil energy or electricity to operate flowing of gas depending on gas volume. The performance of these compressors depends on many factors, the most important of which is gas pressure in the delivery system. In addition, the most important sites along the system are gas delivery points. To estimate pressure, pressureflow equations are used, and Bernoulli's Equation is one of the most widely used ones for estimating gas pressure in a gas delivery system (Schroeder, 2001). Such equations always show an inevitable degree of error. To tackle this problem a few number of methods have been proposed (Mokhatab, S. et al., 2012; Golshan et al., 2000; Haji Ali Akbari and Reza Mosaiebi Behbahani, 2014).

Recently, researchers have studied the optimization algorithms in a wide variety of fields (Edgar et al., 2001; Rao, 2009). Genetic algorithm (GA) and particle swarm optimization (PSO) are the most popular optimization algorithms, which are called population-based algorithms (Goldberg et al., 1988; Gen et al., 2008; Kennedy and James, 2010; Poli et al., 2007; Haupt, R. L. and Haupt, S. E, 2004). GA was proposed by John Holland in the 1970s based on Darwin's theory of evolution (Holland, J.H,

1975). In GA, the solutions (chromosomes) are evaluated based on fitness values (or objective function values) for a randomly generated initial population. The fitness or objective function values of all solutions are evaluated for reproduction. Thereafter, the population of the new generation is formed based on the selected individual crossover and mutation operations in an iterative manner until maximum number of generations or convergence is reached. Inspired by the social behavior of bird flocking, Kennedy and Eberhart introduced PSO in the 1990s (Eberhard and Kennedy, 1995). The general procedure of PSO is to propagate in the design space the optimal solution over a number of iterations (moves) for an initial population which is randomly generated. In this algorithm, every solution is known as a particle which contains three parameters: position, velocity, and the population of solutions (swarm of particles). Thereafter, selection is made for reproduction to update velocity, and the position is determined for each individual particle based on fitness values. This process is repeated until the stopping criterion is reached. In this paper, the performances of GA and PSO for pressure equation tuning in natural gas transmission and distribution networks are compared. To the best of our knowledge, this is the first time that a performance comparison is made between GA and PSO in tuning gas networks. In this study, performance evaluation of the optimization algorithms is practically demonstrated through examining the performance of a natural gas network in Western Azerbaijan Province (as a national site of the Iranian Transmission and Distribution Gas Network).

In recent decades, the optimization algorithms have been studied by the researcher in a wide variety of fields (Rao, 2009; Edgar et al., 1988). Genetic algorithm and particle swarm optimization are the most popular optimization algorithms which are called population based algorithms (Goldberg et al., 1988; Kennedy, 1993; Kennedy and Eberhart, 1995). Genetic algorithm (GA) was defined by John Holland in the 1970s based on the Darwinian theory of evolution applied to biology (Holland, 1992). In GA the solutions (chromosomes) are evaluated based on fitness value (or objective function value) for a randomly generated initial population. For all solutions, fitness or objective function values are evaluated for reproduction. The population of new generation is formed based on the selected individuals crossover and mutation in an iterative manner until maximum number of generations or convergence is reached. Kennedy and Eberhart Particle introduced the swarm optimization (PSO) in the 1990s inspired by the social behavior of birds flocking (Kennedy and Eberhart, 1995; Eberhart and Kennedy, 1995). The general procedure of PSO is to propagate in the design space towards the optimal solution over a number of iterations (moves) for a randomly created initial population. In this algorithm, every solution known as particle contains parameters of position and velocity, and the population of solutions is called a swarm of particles. Thereafter, based on fitness, selection is done on the particles for reproduction to update velocity and position for each individual. This process is repeated until stopping criterion is reached.

In this paper, the performances of GA and PSO for tuning of pressure equation in natural gas transmission and distribution networks are compared. To the best of our knowledge, this is the first time that a performance comparison between GA and PSO for tuning the gas networks is presented. Performance evaluation of the optimization algorithms is practically demonstrated through Western Azerbaijan Province (a part of the Iranian transmission and distribution gas network).

Problem Description

Gas transmission and distribution networks

Gas Network Management

Gas network management means setting the pressure and input equipment's power so that

there is no pressure drop or abnormal pressure in the network. The manager tool for this purpose is dispatching, which is a set of tools and software connecting the equipment and engineers. The equipment generally has little specified error value that will be negligible by calibration. But the software is more challenging. This will be discussed below.

General Flow Equation

Based on the assumptions that there is no elevation change in the pipeline and that the condition of flow is isothermal, the integrated Bernoulli's equation is expressed by the following Equation (Schroeder, 2001):

$$Q_{sc} = C\left(\frac{T_b}{P_b}\right) D^{2.5} \left(\frac{P_1^2 - P_2^2}{f \chi G T_a Z_a L}\right)^{0.5} E \quad (1)$$

Qsc: standard gas flow rate (measured at base temperature and pressure, ft3/day) Tb: gas temperature, base conditions, 519.6°R Pb: gas pressure, base conditions, 14.7 psia P1: inlet gas pressure, psia P2: outlet gas pressure, psia D: inside diameter of pipe, inches f: Moody friction factor E: flow efficiency factor γ_{G} : gas specific gravity Ta: average absolute temperature of pipeline Za: average compressibility factor L: pipe length, miles C: 77.54 (a constant for the specific units used).

Pipelines are usually not horizontal; however, as long as the slope is not too great, a correction for the static head of fluid (Hc) may be incorporated into the following equation (Schroeder, 2001).

$$Q_{sc} = C\left(\frac{T_b}{P_b}\right) D^{2.5} \left(\frac{P_1^2 - P_2^2 - H_c}{f \Im G T_a Z_a L}\right)^{0.5} E \quad (2)$$

Where

$$H_{\rm c} = \frac{0.0375 \, g(H_2 - H_1) P_{\rm a}^2}{Z_{\rm a} T_{\rm a}}$$

H1: inlet elevation, ft H2: outlet elevation, ft g: gravitational constant, ft/sec2

Error definition

Based on the review of data taken from network measurement system a significant amount of error has been observed.

Error in performed analysis means the difference between the pressure data that has been read from the pressure control station (And outbound of the network) and the predicted quantities from the equations used in the software.

$$E = P_{out}$$
 (measurement) $- P_{out}(P,D,z,L,T,\mu,...)$

This value has been reduced with passage of time by providing newer equations.

Sources of Error

Perhaps the first question that comes to mind is: "Why is it that no equation which provides an accurate answer is available?"

The answer is the condition of pipelines and their performance in the future is ambiguous. For example:

- Aging of the pipes: This factor is influenced by many parameters (such as temperature tubes per minute, precise amounts of alloy composition, metallurgy metal tube materials, gas ...).
- Environment: Temperature and weather forecast for the next few days is an approximation so exact temperature and weather forecasting for over than 30 years is impossible.

The only way in this issue is using statistical optimization for fixing the equations which are

used in the software.

Such corrections are common in developed countries, for example (in 2012), ATMOS international limited has carried out extensive research on the Subsea Pipeline Models (Hanmer et al., 2012) which leads to better estimates of the hydraulic capacity and the Estimated Time of Arrival will be achieved by tuning the effective roughness and the heat transfer of the pipeline models.

Evolutionary algorithms

All evolutionary algorithms consist of three main components. In the first part, the population is randomly initialized. Possible solutions based on the cost function are evaluated and ranked in the second step. Thereafter, in the last step some of the solutions are selected and new population is generated. As mentioned previously, the purpose of this paper is to compare the PSO and GA in natural gas transmission and distribution networks for tuning of pressure equation. Therefore, the main characteristics and general process of each of these algorithms are described in the following sections.

Genetic Algorithms

There are many ways to implement a genetic algorithm, but the overall process of this algorithm is shown in Fig. 1. The algorithm can be summarized as follows:

- An initial population is randomly generated.
- Objective function values for each solution are calculated (chromosome).
- Better chromosomes are selected (chromosomes with higher objective function values have a higher probability to be chosen).
- A pair of offspring chromosomes are produced by GA parameters such as crossover and mutation.
- New population is created and the process is repeated until stop criterion is satisfied.



Particle Swarm Optimization

One of the drawbacks of previous methods is the lack of data, which limits the search and may even become divergent. In addition, calculation of this method is less. The overall process of the method is shown in Fig. 2. The searching procedure of PSO can be summarized as follows:

- The velocity and position of all particles are randomly initialized.
- Objective function of each particle is evaluated.
- Position and velocity of particles in iteration are updated according to:

$$v_{i}^{k} = \omega v_{i}^{k-1} + c_{1} r_{i1}^{k-1} (x_{B} - x_{i}^{k-1}) + c_{2} r_{i2}^{k} (x_{G} - x_{i}^{k-1})$$
(3)

(4)
$$x_i^k = x_i^{k-1} + v_i^k$$

- When the size of population, inertia weight, and two positive constants called cognitive and social parameters, and random numbers uniformly distributed within the range.
- Personal best and global best are updated by the following:
- The algorithm is repeated until a certain number of iterations is met.

Result and discussion

As mentioned earlier, the results of the gas engineering software (the gas transmission networks) always show an error in predicting pressure in different parts of the network (these default error values are shown in Table 1). To construct a pipeline, from the conventional equation of gas transmission network, AGA is one of the common equations in National Iranian Gas Company's software. The fully turbulent AGA equation has the following formula in Imperial Units (Haji Ali Akbari and Mosaiebi, 2014).

$$Q_b$$
(5) = 38.774 $\left(\frac{T_b}{P_b}\right) D^{2.5} \left(\frac{P_1^2 - P_2^2 - E}{GT_{ave}Z_{ave}L}\right)^{0.5} \left(4\log \right)$

where

Qb: gas flow rate at base conditions, SCF/D Tb: gas temperature, base conditions, 519.6°R Pb: gas pressure, base conditions, 14.7 psia P1: inlet gas pressure, psia P2: outlet gas pressure, psia D: inside diameter of pipe, inches E: flow efficiency factor Ta: average absolute temperature of pipeline Za: average compressibility factor L: pipe length, miles Ke: roughness

The equation can be rewritten as below (Haji Ali Akbari, 2014; Ahmed, 1989):

(6)
$$= \sqrt[2]{P_{in}^2 - [(gasdensity * L * T * Z_{ave} * A^2) - E]}$$

After one year, the data are gathered from this gas network, and accordingly two sets of data can be obtained. As mentioned earlier, the data were gathered from the Iranian Transmission and Distribution Gas Network, Western Azerbaijan Province.

- Series pressures calculated in the software: This series is calculated by physical specifications of the gas network, its volume, properties of the gas, and specifications of the equipment used.
- Series of reports from pressure measurement systems: This series of data is obtained from the real system and is normally used for system performance analysis. In the next section, some criteria for data analysis are introduced.

Objective function for default value
=
$$\sum |P_m^2 - P_{calc}^2|_i = 1547273$$

Therefore, statistical optimization methods are the only way to eliminate the errors in the gas transmission network. In this paper two approaches of genetic algorithm (GA) and Particle Swarm Optimization algorithm (PSO) were applied and evaluated on a small portion of the gas transmission network.

Exact Value	Default Value	Error	$ P_{M}^{2} - P_{CLC}^{2} $
1070	1069.127	-0.873	1867.458
1069.65	1030.482	-39.168	82257.97
1069.73	990.6736	-79.0564	162888.1
1069.81	949.197	-120.613	243518.5
1061.82	1059.937	-1.883	3995.268
1061.78	1051.636	-10.144	21438.49
1061.63	1051.33	-10.3	21763.49
1057.62	887.1947	-170.425	331445.6
1045.41	1046.629	1.219	2550.196
1026.49	1031.204	4.714	9699.97
1007.02	1015.033	8.013	16202.71
994.085	1003.845	9.76	19499.8
990.617	893.691	-96.926	182638.4
983.183	763.3859	-219.797	383890.8
986.481	997.5334	11.0524	21928.12
986.948	997.2169	10.2689	20375.19
985.903	996.6532	10.7502	21312.88

Table 1: The default error values

PSO

Evaluated network (part of the Iranian transmission and distribution gas network– Western Azerbaijan Province) based on equations AGA and Colebrook-White is modeled and the values of roughness by PSO have been modified so that the error (the difference between the measured pressure and calculated pressure) approaches zero (Figure 3).

As is clear from Figure 3, the objective function value is reduced to about 2,300.



Figure 3. The objective function value per iteration





GA

The variation of the objective function according to generations is shown in Figure 4. As shown in Figure 4 an objective function value is reduced to about 2500.

PSO & GA speed and accuracy analysis

In the previous sections, the error rates of the two methods were analyzed. In this section, the speed and accuracy of the methods are analyzed under equal conditions (Table 2).

GA	PSO
lower bound=400	lower bound=400
upper bound=500	upper bound=500
population	swarm size=3500
size=3500	
generation=200	maximum number of
	iteration=200

Table 2: Conditions and constraints of the optimizer

Under equal conditions, according to Table 2, both of the methods were tested: the run time needed for GA and PSO were found to be 392 and 223 sec. respectively. As a result, PSO was 76% faster.

In Figs 5-6, roughness values are shown for both GA and PSO methods for the 17 points of the network system. As the values indicate, both of the methods show reasonable degrees, but according to gas engineering analysis, the answers observed in PSO results seem to be more reliable.

Furthermore, the changes in roughness from one point to another were found to be relatively greater in PSO. Yet, in most of the points, the roughness in GA was observed to be less than that of PSO. According to Figs. 5-6, the maximum and minimum roughness rates were obtained in the PSO method. This finding showed that the rate of roughness changes in this method was greater and that in practice the method can problematize roughness changes.

It should be also noted that after about 500 tests on both methods, repeatability of GA was found to be much better than that of PSO. More specifically, the 500 tests on the two methods involved 500 optimization processes conducted on the sample under equal conditions to evaluate repeatability and to verify the performance of the methods. Figs. 6-7 show the variance of the answers based on the results.

As Table 3 shows, variance was used to compare roughness in the two methods. As a result, the degree of changes in PSO was found to be considerably higher (approximately two times greater), which would complicate its implementation. Figs. 6-7 illustrate the pattern of values and their variance for roughness of the two methods. As can be seen, the variance of values for GA is more limited; so one can arrive at the conclusion that the repeatability of roughness values was better in GA than in PSO (Table 3, Figures 5, 6). As mentioned above, the two methods GA and PSO were used to optimize roughness rates in the gas network under study.

Both methods did actually decrease network errors, but to compare them objectively, three criteria were taken into account: error rate, speed, and accuracy. As a result, PSO showed fewer errors and increased the speed and accuracy of the answers.

Yet, at the same time, the degree of pointto-point changes of PSO was found to be high. As a result, users are recommended to first calculate rate of roughness through PSO, and then rely on GA. Through this hybrid process, the results observed will have more speed and accuracy, while they will show fewer changes

in answers.

Title	PSO	GA
Pipe 1	9637.214	95649.17
Pipe 2	7323317	1822185
Pipe 3	2550420	2546315
Pipe 4	7041421	2469718
Pipe 5	27928.93	57971.79
Pipe 6	1933637	3131380
Pipe 7	7225785	2062032
Pipe 8	342.2096	2175652
Pipe 9	4291376	1086471
Pipe 10	2972490	2106808
Pipe 11	2455181	2058235
Pipe 12	4520820	643426.8
Pipe 13	6774454	1001154
Pipe 14	8326615	1230682
Pipe 15	1619731	1153129
Pipe 16	7659232	4622807
Pipe 17	2588888	2756354
Total	67321276	31019970

Table 3: Result Variance

Conclusion

Clearly, it is essential to eliminate the errors in gas engineering software in the process of estimating pressure in different parts of gas distribution networks. In line with this, in the present study, PSO and GA algorithms were used to discover degrees of pipe roughness of each point. The results of this study indicated that the PSO method was faster than GA (the process time for GA was 76% more than that of PSO). Moreover, the objective function graphs showed that through reducing the number of generations, PSO could be much more accurate than GA. In other words, in this study, PSO was found to be more accurate than GA in providing answers. Moreover, PSO was found to be slightly faster.

Yet, GA, compared to PSO, showed more reliable answers. In other words, the distribution of PSO answers was found to be relatively higher than that of GA. Given the relative advantage of PSO in terms of speed and accuracy, and the



Figure 5: PSO's answers distribution





slight advantage of GA in the third parameter, one can obtain optimized values by combining the two methods.

The general conclusion of the tuning process is that fuel costs can be cut in the pressure compressor stations, less time is wasted, and it is an exemplar of engineering. In other words, the process involves the design, development, and forecast of the structure, while machines function according to economical and safe goals. Thus, in future studies, an integrated model of GA and PSO can be investigated to provide better roughness values and answers with more accuracy, speed, and distribution.

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Preliminary Hydrocarbon Potential Evaluation of Hojedk Formation in Kerman Coaly Syncline (KCS), Iran: Geochemical Approach

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Abstract

To evaluate the hydrocarbon potential of coal seams (D and E horizons) and their country rocks of Hojedk Formation (Middle to Upper Jurassic) at Kerman Coaly Syncline (KCS), 32 coal and 46 shale samples were collected. These samples were studied geochemically, and their quantity, quality and thermal maturity of organic matter were studied as well. According to Rock-Eval pyrolysis data, it was found that the total organic carbon (TOC) content of coal samples is in excellent condition. Such a situation is, more or less, the same for the shales. Genetic potential (GP) also indicated that the majority of the samples have acceptable potential for gas and oil generation. Therefore, the organic matter quality of Hojedk Formation was evaluated as good to excellent generally. The use of hydrogen Index (HI) as one of the most important factors determining the quality of source rocks showed that the coal and shale samples of Hojedk formation have fewer than 50 to over 600 mgHC/g rock, and majority of the samples fall in 50-200 and 200-300 mgHC/g rock category and therefore, it can be stated that the quality of organic matter varies from without potential to gas and oil potential. The existing kerogen types in these samples are mainly of the III and II-III and consequently, gas and oil generation in the region is likely. Relative high values of S2/S3 (3.70 to 402.36) confirmed the above-mentioned products. In order to evaluate the thermal maturity of organic matter, two different methods (Tmax and vitrinite reflectance) were used. Tmax values revealed that most samples of KCS are in the early to late oil generation window conditions. The highest Tmax (overmature condition) is related to the Tikdar stratigraphic section and this is probably due to its proximity to the Kuhbanan fault. Measurements of vitrinite reflectance also showed that Ro% ranges from 0.5 to 2% and the mean value of this factor is 1.18% and therefore, corresponds to the condition of oil generation window. Finally, based on the quantity, quality and thermal maturity of organic matter at KCS, it can be said that the region has adequate potential for gas and to a minor extent oil generation. Moreover, coal seams, because of enough liptinite contents (up to 22%), are in a better condition in general.

Keywords: Kerman Coaly Syncline (KCS), Hojedk, Hydrocarbon potential, Pyrolysis, Kerogen.

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Introduction

For many years, it has been well recognized that the source rocks of terrestrial origin have favorable potential for oil and gas generation worldwide (Hunt, 1996). For example, in the Gippsland Basin of southeastern Australia, such cases have been reported (Shanmugam, 1985; Burns et al., 1987; Bishop, 2000). Mahakam Delta of Indonesia (Huc et al., 1986; Peters et al., 2000) and Nigerian Delta (Tuttle et al., 1999) have a similar situation. Although such circumstances have been reported in many regions of the world and in spite of the wide spread of continental suitable sediments, this issue has still not been addressed in Iran seriously.

Between 4000 to 7000 meters of late Triassic to late Jurassic non-marine and marine deposits consisting of shale, coaly shale, siltstone, argillite, sandstone and limestone interlayer were exposed over 2200 square kilometers in the northern parts of Kerman Province. Outside the scope of this study, in Central Iran, especially in Yazd Province, outcrop of these strata covers several thousand square kilometers.



Fig. 1. Geographic and location map of north Kerman area. Main coal mines represented by numbers 1-9.

Additionally, extensive outcrops of Paleozoic deposits with suitable lithology as potential for hydrocarbon source rocks are reported in the central parts of Iran, such as Kerman Province (Abbasloo et al., 2013). Considering the fact that fourteen petroleum systems with Upper Jurassic source rocks contain one-fourth of the world's discovered petroleum (Klemme, 1994), study of Jurassic source rocks is important in Iran.

In the Kerman area, several coal mines (various types) are in operation (Fig. 1). Existence of gas $(CH_4, H_2, CO_2, N_2...)$ in these coal mines is one of the undesirable factors for exploitation and unfortunately sometimes gas explosion occurs. Moreover, gas seepage and rarely oil seeps have been observed in the area. For example, it has been observed that after several years of Babnizu coal mine closure, gas outflow from mine wells continues.

Organic geochemical assessment for hydrocarbon potential of the Jurassic strata, as economic resources, is the main purpose of this research. These deposits have been subdivided into four stratigraphic formations (Nayband, Shemshak, Badamu and Hojedk), and we focus on the Hojedk formation (Bajocian-Bathonian) only. Therefore, defining the situation of stratigraphy, organic geochemistry and hydrocarbon potential of the succession was considered. Determination of TOC value, kerogen types and thermal maturity of organic matter in these deposits are the most important evaluations in this area.

Geological setting

According to Zarand 1:100,000 geological map (Vahdati Daneshmand, 1995) and 1:50,000 geological map of the Kerman coal deposits (Technoexport, 1969), in the northern Kerman area, a very thick sequence of different formations from Upper Proterozoic to Quaternary has been exposed. Due to the importance of Mesozoic deposits in the generation of hydrocarbon resources, these formations are studied in more detail.

General structure of the area is a large

syncline with the northwest - southeast direction axis direction (Fig. 2) which is called Kerman coaly syncline (KCS). Geological studies of Triassic-Jurassic deposits in northern Kerman province were carried out for the first time by Huckriede et al (1962) and Poliansky and Safronov (1974). According to Poliansky and Safronov (1974), these formations are subdivided into 8 stratigraphic suites. These suites have been named as Dahrud, Darbidkhun and Toghrajeh of Triassic, and Neizar, Babnizu, Gumrud, Dashtkhak and Asadababd of Jurassic age. Based on nomenclature of the Mesozoic strata in Zarand area (Vahdati Daneshmand, 1995), the equivalent of these stratigraphic suites are Naiband, Shemshak, Badamu and Hojedk formations (Fig. 3).

A total of 6 coal horizons in the Mesozoic sequence in the KCS is known and named as A, B, C, D, E and F (Fig. 3). Each of these horizons consists of many coal seams; for example, the D horizon contains over 20 thin to thick coal layers. Relatively, the D horizon is more important than others and lies in the Hojedk Formation. This formation consists of shale, sandstone, argillite and carbonate interlayers. Carbonate interlayers of Hojedk Formation and ammonite (belemnite) bearing limestone of Babnizu suite (Badamu Formation) under the Hojedk Formation indicate the presence of marine environment.

Presence of gas bearing coal seams in the Hojedk Formation (D and E Horizon) and gas seeps accompanied with coal mines has led us to the hypothesis that the gas (and probably oil) reservoirs may be formed in this area. In order to investigate this hypothesis, a total of 13 sections of Hojedk Formation were evaluated geochemically. These sections are shown in Fig. 2 and consist of Eshkeli, Hojedk, Tikdar, Babnizu, Darbidkhun, north Darbidkhun, Sarapardeh, Khomrud, south and main Pabdana, Komsar, Hashuni and Hamkar.

Materials and Methods

For the purpose of organic geochemical evaluation of Hojedk Formation and

considering principles of sampling (Hunt, 1996), 46 samples were collected from exposed black (and gray) shale in 6 sections. Furthermore, 30 samples were collected from D horizon coal seam. Moreover, 2 samples were collected from E horizon at Hamkar mine (Fig. 2). These samples (coal and carbonaceous shale), in the first step, were crushed, ground and dried at 105 °C oven. All samples were then analyzed by Rock-Eval II pyrolysis in the Research Institute of Petroleum Industry (RIPI) in Tehran. Geochemical parameters S1, S2, S3 and Tmax were obtained from pyrolysis and based on these parameters, the values of total organic carbon (TOC), hydrogen index (HI), oxygen index (OI), total production index (TPI), pyrolysed carbon

(PC) and remnant (residual) carbon (RC) were calculated. The method of calculation of these parameters is presented in Table 1 briefly.

In the next step, 37 samples of coal and shale (with the best TOC contents) were analyzed for study of organic material. Petrography of organic matter and measurement of vitrinite reflectance were conducted by a Leitz-MPV-SP polarizing microscope equipped with photomultiplier in the same laboratory as pyrolysis (RIPI). A sapphire glass standard with 0.584% reflectance value was used for calibration. A combination of these two methods (pyrolysis and petrography) was used for achieving the aims of the research.



Fig. 2. A. General geological map (modified after Technoexport, 1969) and B. satellite image (after GoogleEarth) of Kerman coaly syncline (KCS). Location of sampling: 1. Eshkeli, 2. Hojedk, 3. Tikdar, 4. Babnizu, 5. S-Darbidkhun, 6. N-Darbidkhun, 7. Sarapardeh, 8. Khomrud, 9. S-Pabdana, 10. Main Pabdana, 11. Komsar, 12. Hashuni and 13. Hamkar.

Parameter	Formula	Description
S ₁ (mgHC/g Rock)		Free hydrocarbon (HC)
S ₂ (mgHC/g Rock)		Hydrocarbon generated through thermal cracking
S ₃ (mgCO ₂ /g Rock)		Amount of CO ₂ produced during
S ₄ (mgCO ₂ /g Rock)		Amount of CO ₂ produced during combustion
Tmax (°C)		The temperature of S ₂ peak
PI	S ₁ /(S ₁ +S ₂)	Production Index
PC (%)	0.1[.83(S ₁ +S ₂)+0.273S ₃ + 0.429(S ₂ CO+0.53S ₂ ′CO)]	Pyrolysable organic carbon
RC (%)	RC CO+ RC CO ₂	Residual organic carbon
TOC (%)	PC+RC	Total organic carbon
BI (mgHC/g TOC)	100S ₁ /TOC	Bitumen Index
HI (mgHC/g TOC)	100S ₂ /TOC	Hydrogen Index
OI (mgCO ₂ /g TOC)	100S ₃ /TOC	Oxygen Index

Table 1. Rock-Eval parameters and calculations (Johannes et al., 2007).

Results and discussion

Theory

A petroleum source rock may be defined as fine-grained sediments that has generated and released enough hydrocarbons to form an accumulation of oil and gas while potential source rock is one that is not mature to generate petroleum in its natural setting but will form significant quantities of petroleum when required thermal maturity is attained (Hunt, 1996; Hunt et al., 2002).

Accurate characterization of the oil generation potential of source rocks is essential

for hydrocarbon accumulation assessment in a petroleum system (Kwan-Hwa Su et al., 2006). The petroleum potential of any source rock is evaluated by determining the quantity, type and thermal maturity of organic matter contained in such rock. These parameters are discussed briefly in Table 2.

As presented in Table 2, the quantity of organic matter in source rocks is usually expressed as the total organic carbon (TOC). The minimum acceptable TOC values for various types of source rocks are 0.5% for shales, 0.3% for carbonates and 1.0% for clastic type rocks (Killops and Killops, 1993). A minimum of 1.5-2% TOC has generally been accepted for defining



Fig. 3. Correlation of Mesozoic formations (not to scale), coal seams and situation of Hojedk Formation as subject of this study.

good source rocks (Hunt, 1996).

The amount of hydrocarbon isolated from the bitumen extracted from finely ground rock samples can also provide a useful indication of whether any oil potential exists. Oil source rocks are generally considered to require a minimum hydrocarbon content of 200-300 ppm (Killops and Killops, 1993). The genetic potential (GP) expressed in milligram hydrocarbon per gram of rock (mgHC/g rock) can also be used to evaluate the maximum quantity of hydrocarbon that a particular rock had already generated (S1) and would be generated (S2) if exposed to a sufficient prolonged thermal stress i.e. (S1+S2). Both the S1 and S2 values can be obtained from the Rock-Eval pyrolysis of rocks.

The quality of organic matter contained in rocks can be determined by optical and physiochemical methods. Maceral examination can be carried out using reflected light microscopy of thin sections of the whole rock or of isolated organic particles. Transmitted light microscopy can also be used for isolated maceral concentrates. Shape and degree of transmittance or reflectance and also fluorescence under UV-illumination can be used to identify broad maceral groups (liptinite, exinite, vitrinite and inertinite).

Elemental analysis of kerogen concentrate from rock is the most reliable method of

characterizing the types or quality of organic matter. It is based on the major constituents (C, H, O), which have been used to define main types of kerogen based on the plot of H/C versus O/C in Van Krevelen diagram. The plot of hydrogen index (HI) vs. oxygen index (OI) provides an analogue to the van Krevelen diagram. Both the HI and OI can be obtained from Rock-Eval pyrolysis. Based on the plot of H/C vs. O/C and HI vs. OI, kerogen can be classified into types I to IV which are broadly equivalent to the maceral groups, liptinite, exinite, vitrinite and inertinite respectively for coals (Killops and Killops, 1993).

Information on the level of maturity of organic matter in the source rock is needed to determine if the source rock has reached the stage of hydrocarbon generation or not. The

maturity status of source rock can be determined from Rock-Eval pyrolysis, petrographic and biomarker analyses. The major maturity parameters from the Rock-Eval pyrolysis are production index (PI) or transformation ratio (TR) and Tmax. These parameters increase with increasing maturation. The PI or TR expressed as the ratio of S1/S1+S2 measures the extent to which the genetic potential of the rock has been effectively utilized. It is expressed as the ratio of the hydrocarbon already generated to the total genetic potential. Generally, the threshold of the oil zone is fixed at about 0.1. The ratio reaches about 0.4 at the bottom of the oil window and increases to 1.0 when the hydrocarbon generative capacity of the kerogen has been exhausted. The Tmax

Quantity	TOC(wt%)	S1(mgHC/gRock)	S2(mgHC/gRock)	S1+S2
Poor	0.5	0.5	0-2.5	0-3
Fair	0.5-1	0.5-1	2.5-5	3-6
Good	1-2	1-2	5-10	6-12
Very good	2+	2+	10+	12+
Quality	H/C	S2/S3	HI(mgHC/gTOC)	Kerogen type
Oil	>1.5	>15	>600	
Oil	1.2-1.5	10-15	300-600	II
Gas and oil	1.0-1.2	5-10	200-300	11/111
Gas	0.7-1.0	1-5	50-200	111
None	< 0.7	< 1	< 50	IV
Maturation		Tmax (°C)	Ro%	TAI
Immature		< 435	0.2 - 0.6	1.5-2.6
Early		435-445	0.6 - 0.65	2.6-2.7
Peak		445-450	0.65 - 0.9	2.7-2.9
Late		450-470	0.9 -1.35	2.9-3.3
Postmature		> 470	> 1.35	> 3.3

Table 2.	Guide	elines for	[,] pyrolysi	s pa	rameters	(and	petrogra	phic d	ata) of qu	uality,
quantit	y and	thermal	maturity	of	organic m	atter	(from Pe	ters ar	nd Cassa,	1994).

Sam.	S1	S2	S3	OI	ні	Tmax	PI	RC	тос	S1+S2	S2/S3	Coal Laver	Ref.**
Ham 1	5.17	98.55	1.58	2	154	449	0.05	55.34	63.95	87.17	62.37	D2	1
Ham2	1.29	20.15	24.58	37	30	454	0.06	64.77	66.55	83.29	0.82	D4	
Ham3	0.44	3.91	40.22	73	7	436	0.1	54.46	54.82	82.44	0.1	E2	
Ham4	0.59	6.57	35	73	14	439	0.08	47.66	48.25	82.59	0.19	E3	
Has1	2.05	174.95	0	0	218	454	0.01	65.53	80.22	84.05		D2	2
Has2	2.78	158.11	0	0	240	449	0.02	52.65	66	84.78		D4	
Has3	1.97	147.76	0	0	209	443	0.01	58.28	70.71	83.97		D2	3
Has4	1.58	93.33	0	0	210	451	0.02	36.53	44.41	83.58		D6	
Pab1	2.67	74.21	1.35	2	100	463	0.03	66.25	73.52	84.67	54.97	D3	4
Pab2	4.98	141.02	2.5	3	179	457	0.03	70.22	78.7	86.98	56.41	D2	
Pab3	3.56	83.1	1.02	1	103	468	0.04	67.71	80.26	85.56	81.47	D6	
Pab4	4.33	152.33	2.07	3	193	458	0.02	71.02	78.8	86.33	73.59	D2	
Pab5	3.88	73.7	0.27	0	104	472	0.05	61.02	70.32	85.88	272.96	D1	
Pab6	5.03	177.01	1.9	3	238	469	0.02	67.23	74.42	87.03	93.16	D4	
Pab7	4.57	167.18	2.4	3	210	457	0.02	71.28	79.6	86.57	69.66	D2	
Pab8	2.16	107.27	1.07	1	143	473	0.02	62.02	75.15	84.16	100.25	D5	
Pab9	2.05	13.66	26.66	40	20	461	0.13	65.53	66.83	84.05	0.51	D2	5
Pab10	2.44	86.29	1.92	3	140	443	0.03	54.24	61.6	84.44	44.94	D3	
Pab11	3.76	145.65	0.47	1	229	445	0.03	51.22	63.62	85.76	309.89	D2	3
S-Pab	4.08	129.85	0.49	1	179	475	0.03	61.5	72.62	86.08	265	D2	
Kho	1.4	59.25	0	0	124	448	0.02	42.81	47.84	83.4		D2	
Sar1	8.54	151.25	2.45	3	202	443	0.05	61.7	74.96	90.54	61.73	D2	
Sar2	6.97	148.34	0	0	211	445	0.04	57.32	70.21	88.97		D3	
Sar3	6.5	171	0	0	217	442	0.04	64.23	78.96	88.5		D3	
Sar4	9.87	175.73	2.43	3	252	440	0.05	54.21	69.61	91.87	72.32	D3	
Sar5	10.73	154.38	2.47	4	229	444	0.06	53.83	67.53	92.73	62.5	D4	
Sar6	5.31	175.87	2.14	3	218	446	0.03	65.53	80.57	87.31	82.18	D5	
Sar7	4.41	174.1	2.4	3	217	445	0.02	65.53	80.35	86.41	72.54	D6	
Sar8	3.35	94.6	2.1	4	158	456	0.03	51.85	59.98	85.35	45.05	D8	
Bab	1.16	18.11	1.67	4	39	445	0.06	45.24	46.82	83.16	10.84	D2	6
Ној	3.89	146.61	0.95	1	188	462	0.03	65.53	78.02	85.89	154.33	D2	
Esh	7.91	112.66	0.28	0	155	466	0.07	62.62	72.63	89.91	402.36	D2	

Table 3. Rock-Eval pyrolysis data of coal samples at KCS (raw data of this study).

*- Sample location: Ham (Hamkar), Has (Hashuni), Pub (Pabdana), S-Pub (South Pabdana), Kho (Khomrud), Sar (Sarapardeh), Bab (Babnizu), Hoj (Hojedk) and Esh (Eshkeli).

**- Reference: 1. Ziaaldini (2012), 2. Safinejad (2013), 3. Dashtbozorgi et al. (2012), 4. Sohrabi (2013), 5. Mollaei (2013) and 6. Shakibi et al. (2013).
indicates the temperature of the maximum generation of S2 peak. Generally, the threshold of the oil zone is fixed at Tmax of 430-435 °C for type II and III kerogen while gas zone ranges from 450-455 °C and 465-470 °C for type II and type III respectively (Killops and Killops, 2005).

Organic petrography researchers also developed series of maturation indicators, the most reliable of which is vitrinite reflectance (Hunt et al., 2002). The use of vitrinite reflectance as a technique for determining the maturity of oil in sedimentary rocks was first described by Teichmuller (1958). Today, vitrinite reflectance is a widely used indicator of thermal stress because it extends over a longer maturity range than any other indicator (Hunt et al., 2002). Vitrinite reflectance can be used to assess thermal maturity in types II and III but cannot be used for type I kerogen due to absence of vitrinite. Vitrinite reflectance values for main phase of oil generation ranges from 0.65-1.3%Ro and values greater than 2.0%Ro indicate dry gas generation (Tissot and Welte, 1984).

Quantity of organic carbon

The first parameter in the process of evaluating a source rock is defining the quantity of organic carbon value. Values of TOC, S1 and S2 can provide good estimates of the quantity of organic carbon in a source rock (Peters and Cassa, 1994). In the studied samples, the amounts of total organic carbon from the

Sam. No.*	S1	S2	S3	Tmax	OI	ні	PI	PC	RC	тос	S1+S2	S2/S3	Ref.**
Ham1	0.07	0.2	0.2	478	20	20	0.28	0.02	0.97	0.99	0.27	1.00	1
Ham2	0.06	0.23	1.6	483	68	10	0.21	0.04	2.34	2.38	0.29	0.14	
Ham3	0.64	13.7	1.25	444	12	127	0.04	1.19	9.57	10.76	14.34	10.96	
Ham4	0.07	0.58	0.58	463	42	42	0.11	0.05	1.32	1.37	0.65	1.00	
Ham5	0.2	6.34	0.35	451	5	99	0.03	0.54	5.85	6.39	6.54	18.11	
Ham6	1.66	43.7	0.22	451	1	256	0.04	3.76	13.28	17.04	45.36	198.64	
Has 1	0.09	0.23	1.36	443	425	73	0.28	0.03	0.29	0.32	0.32	0.17	2
Has2	0.6	23.52	0	456	0	133	0.02	2	15.69	17.69	24.12		
Has3	0.14	2.35	0	456	0	226	0.06	0.21	0.83	1.04	2.49		
Has4	0.19	2.42	0	470	0	109	0.07	0.22	2.01	2.23	2.61		
Has5	1.11	50.08	0	449	0	204	0.02	4.25	20.35	24.6	51.19		
Has6	0.27	5.75	0	455	0	179	0.04	0.5	2.71	3.21	6.02		
Pab1	0.21	5.22	0	447	0	74	0.03	1.74	5.28	7.02	5.43		
Pab2	0.06	0.59	0.31	580	129	246	0.09	0.05	0.19	0.24	0.65	1.90	
Pab3	0.16	1.8	0.18	450	9	93	0.08	0.16	1.78	1.94	1.96	10.00	
Pab4	0.12	1.33	0.13	448	11	113	0.08	0.12	1.06	1.18	1.45	10.23	

Table 4. Rock-Eval pyrolysis data of shale samples at KCS (raw data of this study).

Pab5	0.09	0.61	0.69	490	66	59	0.13	0.06	0.98	1.04	0.7	0.88	
Pab6	0.06	0.39	0.17	529	212	488	0.13	0.04	0.04	0.08	0.45	2.29	
Pab7	0.06	0.46	0.78	472	67	40	0.12	0.04	1.12	1.16	0.52	0.59	
Pab8	0.07	0.5	1.44	505	78	27	0.12	0.05	1.8	1.85	0.57	0.35	
Sar	1.43	23.83	0	444	0	247	0.06	2.1	7.55	9.65	25.26		
Bab1	0.64	13.7	1.25	444	12	127	0.04	1.19	9.57	10.76	14.34	10.96	
Bab2	0.07	0.58	0.58	463	42	42	0.11	0.05	1.32	1.37	0.65	1.00	
Bab3	0.2	6.34	0.35	451	5	99	0.03	0.54	5.85	6.39	6.54	18.11	
Bab4	1.66	43.7	0.22	451	1	256	0.04	3.76	13.28	17.04	45.36	198.64	
Bab5	0.2	0.19	0.1	467	31	53	0.51	0.03	0.33	0.36	0.39	1.90	
Bab6	0.34	0.35	0.2	465	27	43	0.49	0.06	0.75	0.81	0.69	1.75	
Bab7	0.06	0.19	0.16	441	36	43	0.24	0.02	0.42	0.44	0.25	1.19	
Bab8	0.13	1.67	0.35	442	19	91	0.07	0.15	1.68	1.83	1.8	4.77	
Bab9	0.06	0.13	0.03	539	6	27	0.31	0.02	0.47	0.49	0.19	4.33	
Bab10	0.05	0.13	0.02	559	20	130	0.28	0.01	0.09	0.1	0.18	6.50	
Bab11	0.1	0.69	0.31	448	28	62	0.13	0.07	1.04	1.11	0.79	2.23	
Bab12	0.04	0.15	0.06		8	20	0.21	0.02	0.74	0.76	0.19	2.50	
Bab13	0.06	0.02	0.01		25	50	0.75	0.01	0.03	0.04	0.08	2.00	
Tik1	1.47	7.25	2.17	490	27	91	0.17	0.72	7.27	7.99	8.72	3.34	3
Tik2	0.11	0.44	0.26	466	36	61	0.2	0.05	0.67	0.72	0.55	1.69	
Tik3	0.53	3.35	7.31	476	54	25	0.14	0.16	13.46	13.62	3.88	0.46	
Tik4	0.27	2.35	6.17	501	49	19	0.1	0.22	12.41	12.63	2.62	0.38	
Tik5	0.12	0.77	0.12	490	38	241	0.13	0.08	0.24	0.32	0.89	6.42	
Tik6	0.16	1.26	0.18	540	33	233	0.11	0.12	0.42	0.54	1.42	7.00	
Tik7	0.15	1.01	0.05	525	21	421	0.13	0.1	0.14	0.24	1.16	20.20	
Tik8	0.14	1.06	0.14	460	70	530	0.12	0.1	0.1	0.2	1.2	7.57	
Tik9	0.6	4.54	0.21	430	29	631	0.12	0.43	0.29	0.72	5.14	21.62	
Tik10	0.18	0.66	0.09	541	53	388	0.21	0.07	0.1	0.17	0.84	7.33	
Tik11	0.15	0.88	0.31	496	56	160	0.15	0.09	0.46	0.55	1.03	2.84	
Tik 12	0.11	1.17	0.07	588	25	418	0.09	0.11	0.17	0.28	1.28	16.71	

*- Sample location as same as Table 3. **- References: 1. Ziaaldini (2012), 2. Safinejad (2013), 3. Hemmatafza (2014).

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Fig. 4. Comparison of TOC, S1 and S2 of coal (A, C and E) and shale samples (B, D and F) from various parts of KCS.

pyrolysis were investigated. It is clear that the organic carbon content of coal samples should be high. In these samples, TOC content varies from 44.41 wt% to 80.57 wt% with a mean value of 68.68 wt% (Table 3). Obviously, the amount of TOC alone may not reflect the high quality of the rock and other quantitative parameters should be considered (Fig. 4A).

Total organic carbon content of the shale samples varies from 0.04 wt% to 24.6 wt% with a mean value of 4.16 wt% (Table 4). Comparison of TOC content in different samples indicates that all coal samples and most of the shale samples have sufficient organic carbon content as a source rock. However, TOC content of shale samples ranges from poor to excellent (Fig. 4B).

In addition to the TOC, the S1 parameter is used to evaluate the quantity of hydrocarbon source rocks (Peters and Cassa, 1994). In the present research, S1 contents of coal samples varies from 0.44 to 10.73 mgHC/g rock with a mean value of 4.04 mgHC/g rock. Accordingly, based on Peters and Cassa (1994), S1 content of the coal samples ranges from very good to excellent (Fig. 4C). Moreover, shale samples have S1 values from 0.04 to 1.66 (mean 0.32) mgHC/g rock and range from poor to good, but most of the samples are located at poor situation. In coal samples, the maximum value of S1 is related to Sarapardeh mine and in shale samples, Hashuni, Babnizu and Hamkar have higher values (Fig. 4D).

S2 is the other evaluating factor in determining quantity of hydrocarbon source rocks. Indeed, this parameter is the present potential of source rocks and consists of kerogen, bitumen and heavy hydrocarbons. Data obtained from pyrolysis of coal samples show that the S2 in these samples varies from 3.91 to 177.01 mgHC/g rock, and therefore the content of S2 represents very good to excellent condition (Fig. 4E). S2 values of shale samples of KCS range from 0.02 to 50.08 with a mean value of 6.00 mgHC/g rock and therefore, the values show poor to good conditions (Fig. 4F). The majority of these samples are plotted at poor to fair condition. One of the criteria for determining



Fig. 5. Log-plot of S1 vs. S2 for determining the genetic potential (GP) of KCS, A. non-coal and B. coal samples.

the quantity of source rocks is genetic potential (GP). As presented in Table 1, this parameter is the sum of S1 and S2 values. Based on Peters and Cassa (1994), the high values of GP can indicate the high quantity of source rocks. The mean value of GP for shale and coal samples of KCS is 6.33 and 86.04 mgHC/g rock respectively (Tables 3 and 4). These values also indicate that both shale and coals have sufficient potential for hydrocarbon generation, but the coal samples are in much better condition. Plotting S1 against S2 (log-plot) also shows that the coal samples, compared to the shale samples, have higher potential and fall in the very good to excellent field (Fig. 5).

Briefly, quality of organic material in the coal samples is obviously better than the shale samples, but, the shale samples are not so undesirable. In other words, shale strata at KCS can also be considered acceptable as a source rock.

Quality of organic material

Often when talking about the quality of source rocks, the amount of hydrogen and kerogen type is considered. The quality of the organic matter contained in the coal and shale samples was evaluated from pyrolysis data. Using HI vs. OI plot and HI vs. Tmax plot, the kerogen type and source of organic carbon in the source rocks can be determined.

In coal samples of KCS, the hydrogen index ranges from 7 to 252 with a mean value of 160 mgHC/g rock and indicates ability of gas generating as well (Table 3). The hydrogen index of shale samples has a greater extent and variability. In these samples, HI values range from 10 to 631 with a mean value of 154 mgHC/g rock. Based on this parameter and considering the guidelines provided by Peters and Cassa (1994), the shale samples represent potential for oil and gas. Plots of HI against OI, for the samples are shown in Figs. 6 and 7. As shown in Fig. 6A, most of the coal samples have a moderate hydrogen index and low oxygen index. In contrast, variation of these two parameters is much more for shale samples (Fig. 6B).

For a more general estimate of the position



Fig. 6. Hydrogen index vs. oxygen index (Hunt, 1996) and position of A. coal samples and B. shale samples from KCS.

of kerogen types, all 78 samples of coal and shale are plotted in a single diagram (Fig. 7). As shown in Fig. 7, most of the samples fall in the III and II/III kerogen types (55 samples, 70.5% of the total samples). In a lesser amount, a few samples (18 samples, 23% of the total samples) were plotted in IV type. Finally, 4 samples (5% of the total samples) and only one sample fall in the field of II and I kerogen type respectively. Also, it can be seen that the majority of coal



Fig. 7. Definition of kerogen types and hydrocarbon generating potential of KCS coal and non-coal samples in HI vs. OI cross plot.

samples are plotted near the axis of hydrogen index and this indicates that the samples are poor oxygenated compounds. Moreover, it is clear that most of these samples can produce gas and a lesser amount of oil.

In addition to the previous plots, for determining the kerogen types and generating hydrocarbon potential, we have used S2 vs. TOC diagram (Langford and Blanc-Valleron, 1990) (Fig. 8). In this diagram, two different clusters of samples can be seen. One of these clusters (arrow1) covers the non-coal samples and is plotted near the lower left corner of the diagram. In contrast, coal samples cluster with a more extensive area (arrow2) covers important parts of III and mixed II-III kerogen types fields. Based on this diagram, it is clear that most coal samples are located in the area of gas (and gas and oil) production. It should be noted that the results of this diagram are confirmed by the results of HI-OI plots (Figs. 6 and 7).

Thermal maturity of organic material

Pyrolysis data

The quantity and quality of organic matter alone is not sufficient to produce adequate hydrocarbon. In addition to these two factors, maturity of organic matter should be adequate enough to generate oil and gas. As mentioned above, thermal maturity can be reflected by pyrolysis data. Tmax alongside the production index (PI) are the two determining parameters. Moreover, using HI vs. Tmax plot is one of the multipurpose diagrams in organic geochemistry. This diagram can be used to determine the thermal maturity and kerogen types.

According to available pyrolysis data, the HI vs. Tmax plot (Hunt, 1996) was drawn for KCS samples (Fig. 9). As shown in Fig. 9A, all of the coal samples fall within the range of 430 to 470 °C tmax, and therefore thermal maturity of



Fig. 8. S2-TOC cross-plot (Langford and Blanc-Valleron, 1990) and location of coal and non-coal samples.



Fig. 9. Hl vs. Tmax cross plot (Hunt, 1996) for determining thermal maturity and kerogen types of KCS. A. Coal samples and B. Non-coal samples.

the samples is presently within the oil window. Locating all data between lines of 0.5% and 1.35% vitrinite reflectance has confirmed the result too.

Despite the limited extension of coal samples in HI vs. Tmax, shale samples cover a wide range in this plot (Fig. 9B); therefore, maturity of these samples ranges from mature to overmature condition. Considering this plot and maturity conditions, coal samples are in the stage of oil and wet gas production and shale samples are in the stage of wet gas, condensate and dry gas. Also, the values of hydrogen index represent potential of gas and oil for majority of samples.

Petrography and vitrinite reflectance

In order to define thermal maturity and organic petrography, microscopic studies in reflected light were used. On this basis, the organic composition of 36 coal and shale samples was investigated. Although maceral identification in all samples was done, only 8 cases were examined to determine the percentage of macerals.

These investigations were carried out according to the definition and description of macerals given by Taylor et al. (1998).

In a general overview, all samples of KCS are vitrinite rich (Table 5). The percentage of vitrinite ranges from 49.3% to 75% with a mean value of 60.80%. In terms of frequency, total fusinite plus semifusinite macerals with an average of 23.8% are in the second rank (Fig. 10).

The liptinite group contains cutinite, sporinite, exsudatinite, fluorinite, resinite, bituminite, suberinite and liptodetrinite. Liptinite, as a hydrogen rich maceral, can be found in all samples of KCS considerably (Table 5, Fig. 10).

This maceral as an accessory maceral ranges from 5% to 22.2% with an average of 15.46%. The highest value of liptinite (22.2%) is related

Sample No.	Vitrinite %	Fusinite %	Semifusinite %	Liptinite %
Ham1	75	5	15	5
Ham2	63.5	9.78	10	17.6
Ham3	65	10	12	11
Has	54	18	12	16.8
Kom	53.3	18.6	13	16.7
M-Pab	49.3	19.7	9	22.2
Dar	66.81	9.1	8	16.38
Tik	60	14	8	18
Avg.	60.86	13	10.8	15.46

Table 5. Percentage of maceral groups in coal samples of KCS (data arter Shayestehfar et al. 2007).

to Main Pabdana mine. Relative high amount of liptinite in Pabdana coal mine has been reported previously by Shayestehfar et al. (2007). However, this amount of liptinite in KCS coal samples indicates oil production capability by the rock. Moreover, Jones (1987) suggested that if the liptinite contents (exinite plus resinite) reach over 10-15% in coal, in addition to increasing the hydrogen index, it is possible to generate liquid hydrocarbon by such coal.



Fig. 10. Comparative frequency of maceral groups from KCS coals, (data after Shayestehfar et al. 2007).

Table 6. Petrography and vitrinite reflectance in emersion oil of coal and	i shale	samples.
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Location	Sample type	Maceral type(s)	Ro%	Variation	Tmax
	Coal-D2	F	1.3		
	Shale	V+L	2		
	Shale	F+V	0.6		
	Coal-D3	F+L	0.85	Min: 0.5	
Sarapardeh	Shale	F	F 0.5		
	Coal-D4	V+F	1.7	Mean: 125	
	Coal-D5	V+F	2	Mean. 1.25	
	Coal-D6	F+V	0.5		
	Coal-D8	F+V	1.8		

	shale	V+F+L	1.9		
	Coal-D6	F+V	1.5		
	shale	V+L	2		
	shale	F	1	Min: 0.73	
Hashuni	Coal-D4	V+F	1.8	May 2	
	shale	F	1	Mdx. Z	
	shale	F	1.5	Mean: 1.48	
	Coal-D2	V+L+F	2		
	shale	F	1.4		
	Coal-D2		0.73		
Hamkar	Coal-D2	V+S+F	0.8	Min: 0.8	
Панткат	Coal-D4	V+S+F	0.89	Max: 0.89	
	Shale	F	0.9		469
	Coal-D3	L	1.9		463
	shale	F	1.1		473
Pabdana	shale	F	1.1		472
	Coal-D2	F+V+L	1.2		457
	shale	F+L	1.1	Min: 0.59	457
	shale	V	1.2	Max: 1.9	458
	Coal-D4	V+F	1	Mean: 1.02	469
	shale	V+F+L	0.9		447
	Coal-D2	V+L	0.59		461
S-Pabbana	Coal-D2	V+L	0.69		443
	Coal-D2		0.71		
	Coal-D2		0.96		
	shale	V+F+L	0.77	Min: 0.77	
Tikdar	shale	V+F+L	0.92	Max: 0.92 Mean: 0.84	



Fig. 11. Comparative assessment of vitrinite reflectance variations in different location of KCS.

In addition to petrography and definition of macerals, in 36 samples of coal and shale, measurement of vitrinite reflectance was done by polarizing microscope and photomultiplier. These measurements were carried out using a Leitz-MPV-SP microscope in organic petrography laboratory of Research Institute of Petroleum Industry. A sapphire glass standard with 0.584% reflectance value was used for calibration. The reflectance of vitrinite remains the most definitive measure of coal rank and maturity of source rocks, because, it is unaffected by oxidation, by changes of sample

		Q	Quantity			Quality			Therma naturit	l y	Hydrocarbon potential			
Locality	Sample Type	TOC %	S1 Ave	S2	HI Avg.	Krogen Type	S2/S3	Tmax °C	PI	Ro%	None	Gas	Gas and Oil	Oil or Gas Seepage
Hamkar	Coal (D, E)	E	G	E	50- 200	Ш	15.8	EM	0.07	0.84				
Hamkar	Shale	E	Р	E	50- 200	Ш	38.3	EM	0.07					
Usebuni	Coal	E	VG	E	200- 300	, -	243	PM	0.01	1.56				
Hashuni	Shale	E	Р	E	50- 200	III	14.05	LM	0.08					-
Dahdana	Coal	E	VG	E	50- 200	Ш	118.57	LM	0.03	1.03				
Pabdana	Shale	G	Р	Р	50- 200	III	3.7	ОМ	0.09					-

Table 7. Summarized geochemical characteristics of KCS coal and shale samples.

Khomrud	Coal	E	G	E	50- 200	III	-	PM	0.02			
Commendation	Coal	E	E	E	200- 300	, -	66.05	PM	0.04	1.25		
Saraparden	Shale	E	G	E	200- 300	, -	-	EM	0.06			
Dahaiau	Coal	E	VG	E	0-50	IV	10.84	PM	0.06			
Babnizu	Shale	VG	Р	VG	50- 200	III, IV	19.68	PM	0.24			
Tikdar	Shale	Р	Р	Р	200- 300	, -	7.96	ОМ	0.18	0.84		
Hojedk	Coal	E	E	E	50- 200		154.33	LM	0.03	1.05		
Eshkeli	Coal	E	E	E	50- 200		402.36	LM	0.07	0.73		

type, or by carbonate mineral matrix.

As can be seen in Table 6, in the majority of the samples, vitrinite was found as main maceral. Also, the mean value of this maceral in 6 semiquantitative measurements (Table 5) reaches 60.86%. Measurements of vitrinite reflectance in various location and sample types revealed that this parameter ranges from 0.5% to 2% with an average of 1.18%. These values clearly show that the majority of samples lie within the oil window.

A comparative estimate (Fig. 11) indicates that across regions, Hashuni, Sarapardeh and Pabdana have the highest Ro% and maturity (with average values of 1.48%, 1.25% and 1.02% respectively). However, because of scarcity of samples, this result should not be considered definitive. This estimate also shows that the average maturity of the samples correspond to the early to late oil window.

Conclusion

In the present research, the quantity, quality, thermal maturity and hydrocarbon potential of D (and E) coal horizon and its carbonaceous country rocks (Hojedk Formation), as a potential

source rock were studied in KCS. To achieve these goals, the pyrolysis and petrographic techniques were used. Raw data were evaluated by standard procedures and hydrocarbon potential of the area studied. Based on this analysis, the following results were obtained (Table 7).

The quantity of carbonaceous rocks and coal seams in KCS using TOC content, S1 and S2 parameters were evaluated and it was found that in most cases, the amount of organic carbon is excellent. Due to the nature of the coal samples, the high organic carbon content is obvious (Fig. 4A). However, the shale samples (Fig. 4B) also have an acceptable condition. The value of S1 ranges from poor to excellent and coal samples have a better condition compared to shale samples (Figs. 4C and D). Finally, according to the S2 parameter as a quantity indicator, it was found that majority of samples fall in the excellent condition (Figs. 4E and F).

In order to evaluate the quality of shale and coal samples, hydrogen index (HI) was used. For the purpose of simplification, average of HI from each location was classified (Table 7) and compared to Peters and Cassa (1994) guidelines. Although the range of hydrogen index values of various samples of KCS is relatively high, the data can be categorized and placed in one of the five definitive classes (0-50, 50-200, 200-300, 300-600 and >600). Based on this classification, the average values of HI of 9 locations (from 14 locations), fall in the 50-200 class, four cases lie in the 200-300 class and only one case is classified in 0-50 class

Thus, it is clear that the majority of the samples are capable of generating gas and some are capable of generating oil and gas.

As can be inferred from Figs. 6, 7, 8 and 9 (and Table 7), type III kerogen is dominant in most cases, but in some cases (especially in coal samples), mixed II/III kerogen type also has been detected (Fig. 8). Considerable amounts of liptinite in some coal samples (up to 22% at Pabdana) support this finding. Therefore, kerogen types in Hojedk formation are suitable for gas and oil generation. Moreover, high S2/S3 ratio in most cases (Table 7) support oil generation hypothesis in the KCS.

After determining the amount and quality of organic matter, thermal maturity evaluation of the KCS was conducted.

According to Tmax values, it can be stated that the majority of the samples have passed adequate maturation to generate oil and gas. Table 7 also shows that in most cases, Tmax reflects early to late maturation corresponding to oil window and only in a few cases, overmaturation occurred. Vitrinite reflectance (Ro%) studies also confirmed that in most cases (Fig. 11), the maturity of the samples are in accordance to the oil generation window (top to bottom).

Finally, it can be stated that the quantity, quality (kerogen types) and thermal maturity of coal seams and its country rocks of Hojedk formation in KCS have sufficient potential for gas and to a lesser amount oil generation. Existence of gas and rarely oil seepage in the area confirm this claim.

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Prediction of Optimal Sulfinol Concentration in Khangiran Gas Treating Unit via Adaptive Neuro-Fuzzy Inference System and Regularization Network

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Abstract

The concentration of H₂S in the inlet acid gas is an important factor that sulfur plant designers must consider when deciding on the right technology or configuration to obtain high sulfur recovery efficiency. Using sterically-hindered solvents such as promoted tertiary amines and various configuration for gas treating unit are several alternatives for acid gas enrichment (AGE) to reduce the concentration of carbon dioxide and heavy aromatic hydrocarbons while enriching the H₃S content of SRU feed stream. The present article uses combinations of Aspen-HYSYS software and two distinct networks (namely, Regularization network and adaptive neuro-fuzzy inference system) to compare the AGE capability of sulfinol-M (sulfolane + MDEA) solvent at optimal concentration to traditional MDEA solution when both of them are used in a conventional gas treating unit (GTU). The simulation outcomes demonstrate 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 H₂S in the SRU feed stream increases the conventional 33.48 mole% to over 57mole%. Increased H₂S selectivity of optimal Sulfinol-M aqueous solution will elevate the CO, slippage through sweet gas stream at around 4.5mole% which is still below the permissible threshold.

Keywords: AGE, BTEX, Regularization network, MLP, ANFIS

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Introduction

Sour unconventional natural gas often has a higher CO,:H,S ratio than conventional gas sources, which results in leaner acid gas feed streams (lower H₂S concentration). Moreover, acid gases from both of these sources frequently contain contaminants such as heavy hydrocarbons (e.g. Benzene, Toluene, Ethylbenzene and xylene (BTEX)), ammonia and methanol which all can cause operating problems in sulfur recovery units (SRUs). Excessive amount of such impurities in acid gas stream entering SRU Claus process drastically decreases the combustion chamber temperature and reduces the overall elemental sulfur recovery efficiency (Chludzinski et al., 1993). A preferential method for reducing the concentration of these contaminants in the acid gas of SRU feed stream is to utilize proper acid gas enrichment (AGE) process at upstream of the sulfur recovery unit.

The recent development and success of applying various kinds of machine learning modeling approaches to tackle various complex engineering problems has attracted much attention to their potential applications in the natural gas industry (Zhou et al., 2013). These powerful tools are traditionally used for their capability of nonlinear mapping and lack of necessity for detailed mechanistic knowledge (Anifowose et al., 2011). The capability of artificial neural networks (ANNs) and adaptive neuro-fuzzy inference system (ANFIS) to model nonlinear and highly complex systems in order to extract underlying truth from noisy data are memorable.

Acid gas enrichment process depends on multiple input variables which possess strong coupling between them with severe uncertainty. 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 along with ANFIS particularly attractive.

The principle of acid gas enrichment process originates from proper selective removal of H₂S at the presence of other impurities (specially CO₂) which can be accomplished in three distinct routes (Seagraves et al., 2011; Palmer et al., 2006):

A)Sterically-hindered amines, controlling the selectivity primarily in the absorber.

B) Various design (configuration) options of gas treating unit (GTU) and absorber internals, affecting the difference in CO₂ and H₂S mass transfer kinetics.

C)Promoted tertiary amines, focusing more on enhanced regeneration and thus leading to lower H₂S loadings.

For selective H₃S absorption in the first route, a molecular structure would be selected which suppresses carbamate formation and, consequently, the rate of CO₂ absorption, without affecting the rate of H₂S absorption. Sterically hindered amines, either primary or secondary amines with large bulky alkyl or alkanol groups attached to the nitrogen (Seagraves et al., 2011), show suitable result for selectively absorbing H,S in the presence of CO₂. Appropriate molecular configuration leads to an unstable carbamate formed with CO, which is readily hydrolyzable, resulting in the formation of bicarbonate as the end product. This phenomenon results in a theoretical ratio of one mole of CO, per mole of amine.

The chemistry of acid gas reactions with sterically hindered amines is discussed in some detail by Sartori and Savage (1983) and by Weinberg et al. (1983). Furthermore, Chludzinski and lyengar (1993) describe the application of sterically hindered amines to AGE units as well as outline the operating conditions and some of the possible unit configurations. FLEXSORB-SE amine, which was recognized by Exxon-Mobil scientists in 1981, is a kind of sterically hindered solvent that was successfully used for selective H₂S absorption purposes (Parks et al., 2010). Different kinds of sterically hindered amines such as amino-2-methyl-1-propanol (AMP), tertiary butyl amino ethanol (TBE), tertiary butyl amino ethoxyethanol (TBEE), MAMP (2-N-methylamino-2-methyl-propan-1-ol), EETB (Ethoxyethanol-t-butylamine), MEEETB (Methoxyethoxyethoxyethanol-tertbutylamine) were tested for their selectivity toward H₂S (Mandal et al., 2004; Lu et al., 2006; Siskin et al., 2013).

In the second route, necessary modifications can be applied to an existing gas treatment unit (GTU) configuration while using the conventional solvent. Various schemes are used to enhance the selectivity of H_2 S over CO₂ (Mak et al., 2015; Al Utaibi et al., 2010; Way et al., 2013).

Finally in the third route, the advanced promoter (e.g. sulfolane) would be added to conventional solvent in order to enhance the selectivity of tertiary amines and also make the release of H₂S from rich amine in the regenerator column easier. Tetra methylene sulfone (TMS) or sulfolane is an excellent industrial solvent with capability of removing H₂S, COS, and CS₂ from various sour gas streams. Aromatic and heavy hydrocarbons such as BTEX and CO, are soluble in sulfolane to a lesser degree (Vahidi et al., 2013). Sulfolane is usually blended with alkanol amines (specially methyl diethanol amine (MDEA)) to form adequate mixed solvent (known as sulfinol-M) to capture various impurities, simultaneously (Vahidi et al., 2013; Mokhatab et al., 2012).

Different powerful software along with various mathematical techniques have been used for simulation and modeling of gas treating unit respectively. The results of some recent works will be reviewed in the following section.

Darwish and Hilal (2008) used ANN to detect and diagnose process faults in the dehydration plant. They have concluded that ANN successfully detects the disturbance severity levels in the input variables considered for the contactor. Faults in the stripper–regenerator unit have been perfectly predicted by the ANN for two symptoms (TEG emissions and BTEX emissions in vents).

Fu et al. (2013) developed a neural network to predict overall mass transfer coefficient for carbon dioxide absorption into aqueous diethylenetriamine (DETA). The inlet CO_2 loading, solvent concentration, liquid flow rate, CO_2 partial pressure, and liquid feed temperature were selected as input parameters. They have reported that ANN is a suitable tool for predicting the absorption performance of packed columns. Angaji et al. (2013) examined the performance of various concentrations of sulfolane in the Sulfinol solvent for GTUs of Khangiran natural gas refinery. They concluded that providing 40.2%wt sulfolane, 21.2% wt H₂O and 37.7%wt MDEA in liquid mixture of Sulfinol-M could increase 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 MDEAsulfolane solutions. Limited parameters such as condenser and reboiler duties were investigated in order to optimize sulfolane concentration.

Abdulrahman and Sebastine (2013) used Aspen HYSYS V.7.3 to simulate the Khurmala (Iraqi-Kurdistan region) gas sweetening process. They have tested several amine blends (MEA and MDEA), circulation rate and concentration instead of DEA with flow rate of 400 m³/hr. Their optimization showed that using DEA 35% is the best recommended process.

Abdulrahman and Sebastine (2013) analyzed the effect of the lean amine temperature on the acid gas content in the sweetened gas and saturated the amine solution by using Aspen HYSYS software. They reported that the optimal temperature for the regenerated amine solution, at which the maximum sweetening of the gas is achieved with minimum amine circulation rate, is within the range 38°C-45°C.

Ghanbarabadi and Karimi (2014) simulated Khangiran gas refinery in order to optimize the concentration and flow rate of MDEA, thermal load of restoration and other operating parameters by using Aspen HYSYS software. They reported that optimum performance of MDEA solvent is 45-50% wt concentration at 55-63°C.

The superior performances of ANN and ANFIS have been proved in a wide variety of applications (Zhou et al., 2013; Rahmanian et al., 2012).

In the present article, a conventional GTU is simulated by resorting to the powerful Aspen-HYSYS software V.8.3. Instead of using the traditional MDEA solution as solvent, various concentrations of MDEA and sulfolane (known as sulfinol solution) will be used to predict the concentration of H,S 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 MDEAsulfolane solutions. The limited data collected from Aspen-HYSYS simulations using various sulfinol concentrations will be employed as the training data to optimize an adaptive neurofuzzy inference system and regularization network. The trained network performances will be initially compared with the performance of conventionally used neural network toolbox of MATLAB software and finally they will be recruited to provide reliable interpolation hyper-surfaces for practical uses.

Importance of AGE and BTEX elimination in a conventional GTU

One of the keys to achieving good Claus plant performance is to maintain a stable flame and high temperatures in the main reaction furnace (>926°C, 1700°F). Higher temperatures increase the conversion of H₂S to elemental sulfur. Contaminants in the acid gas stream can seriously impact the operability and reliability of a sulfur plant. Carbon dioxide and other impurities in the acid gas feed stream to SRU unit acts diluents, reducing reaction furnace temperatures and hence, drastically limit the elemental sulfur capacity. In the worst scenario, excessive amounts of such inert constituents can completely quench the combustion chamber flame.

To achieve high temperatures in the Claus furnace an acid gas feed stream typically requires at least 50 mole percent H₂S. If the H₂S concentration in the acid gas from the acid gas removal unit is lower than 50%, several Claus plant design options are available out of which the most common is the split flow design (Mokhatab et al., 2012; Kidnay et al., 2006). Although other options such as split flow design, acid gas or air preheat plus oxygen enrichment are available to increase the overall sulfur recovery efficiency none of them is as preferable as the acid gas enrichment process.

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.

Two significant problems occur when high concentrations of BTEX are passed through SRU. The first is general deactivation of the catalyst in the catalytic chamber due to accumulation of carbon and/or carsul (a variety of heavy carbonsulfur compounds) in the pores of the catalyst due to coking of the hydrocarbons (Kidnay et al., 2006; Zarenezhad et al., 2008). This problem affects all Claus catalysts, both alumina and titania. The second problem with BTEX is rapid deterioration of hydrolysis catalysis in titania catalysts. Nowadays, titania catalysts are used in many plants that require high sulfur recovery efficiency, because it is proved that this catalyst significantly improves the degree of COS and CS, hydrolysis over that of alumina catalysts, especially at lower temperatures.

Unfortunately, field experience and recent laboratory testing have shown that titania catalysts are especially prone to rapid decline in the amount of hydrolysis they catalyze when exposed to BTEX. It is therefore crucial to oxidize and recover energy from BTEX completely in the combustion chamber. 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 (Crevier et al., 2001; Zarenezhad, 2011).

Installing proper acid gas enrichment process or using suitable adsorption system such as carbon active is an available alternative to mitigate BTEX content of SRU feed stream at upstream section.

Various mixtures of sulfolane and MDEA solutions (sulfinol solvent) will be considered for their performances of the enrichment efficiency in the Khangiran refinery GTU. Effective AGE increases the H₂S content of SRU feed stream and alleviates SRU existing complications such

as flame temperature and BTEX issues.

Characteristics of Sulfinol solvent

Mixed or hybrid (or composite) solvents composed of a non-aqueous physical solvent and an aqueous amine take advantage of both physical and chemical absorptions. The best known example of such mixed solvents is the Sulfinol solvent which was 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.

The sulfinol-M solution is mainly used for the selective absorption of H_2S from natural gas in the presence of CO_2 . As it was mentioned before, solubility of aromatic hydrocarbon and carbon dioxide are in a lesser degree compared to the sulfur compounds (Mokhatab et al., 2012).

The advantages of sulfinol-M are higher acid gas loading, lower energy requirements for regeneration, lower corrosion rates, relatively poor hydrocarbon selectivity and lower foaming tendency. Thermodynamic modeling of aqueous sulfolane solutions (in the absence of alkanolamines) for prediction of their thermal and physical properties have well received remarkable attention in numerous studies (Zong et al., 2011; Shokouhi et al., 2013).

Optimization of sulfolane concentration in the proposed sulfinol-M solvent instead of MDEA solvent in the Khangiran natural gas refinery treating unit via Regularization network and ANFIS is the essence of this work. In the following section, brief review of RN and ANFIS will be presented.

Intelligent Systems

Modern computer hardware technology together with intelligent software solutions makes it possible to process the large amount of data at low cost. Some well-known analysis methods and tools that are used for data mining are statistics (regression analysis, discriminant analysis, and principal component analysis), time series analysis, decision trees, cluster analysis, neural networks, fuzzy models and neuro-fuzzy models. These approaches are particularly useful when data are abundant and modeling knowledge is missing (Zhou et al., 2013).

Adaptive neuro-fuzzy inference system (ANFIS)

The learning ability of neural networks combined with fuzzy modeling has created the adaptive network based fuzzy inference system (FIS). ANFIS is a rule-based fuzzy logic model whose rules are developed during the model training. In general, rule based models can be classified into four categories: fuzzy relational, linguistic, neural network based, and Takagi-Sugeno-Kang (TSK) fuzzy models. ANFIS is the combination of low level calculation of ANN along with the high reasoning ability of a fuzzy logic system (Rahmanian et al., 2012). At the computational level, ANFIS can be regarded as a flexible mathematical structure that can approximate a large class of complex nonlinear systems to a desired degree of accuracy. Appendix A contains a detailed review of ANFIS rules and related structure. Figure 1 shows block diagram representation of training algorithm for optimized ANFIS used in the present article.

The ANN method, either alone or in combination with the least squares method, is employed for tuning of the adjustable parameters for obtaining an optimized ANFIS structure during the training phase. For a fixed value of consequent parameters, backpropagation (BP) ANN based on gradient descent method finds the optimal value of premise parameters. The output of the ANFIS is calculated first by employing the consequent parameters. Next, the output error is used to adjust the premise parameters by means of a standard BP algorithm. When both the premise and consequent parameters need tuning, the combination of least squares and gradient descent method based BP-ANN is adopted for parameter optimization. The least squares method is used to optimize the consequent parameters by forward pass keeping the value of premise parameters fixed. Once the optimal consequent parameters are found, the backward pass starts immediately to optimize the premise parameters using the

gradient decent BP-ANN. In the present article, a Sugeno-type FIS using subtractive clustering is generated using *genfis2* function to provide an initial set of membership functions for the training of ANFIS. Figure 2 shows our training algorithm for optimizing ANFIS (Rahmanian et al., 2012).

Artificial neural networks

Artificial Neural Networks (ANNs) are aptly suited for investigating of ill-understood problems with imprecise data which can successfully 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). Many neural networks have been constructed to perform approximation of multi-dimensional function by solving the hyper-surface reconstruction problem. This form of learning is closely related to classical approximation techniques such as regularization theory. The solution of multivariate regularization theory leads to a class of three-layer networks called Regularization networks which is reviewed in the following section (Haykin, 1999).

A brief review of Regularization networks

Poggio and Girosi proved that the ultimate solution of the ill-posed problem of multivariate regularization theory could be represented in the concise form of (Poggio et al., 1990; Shahsavand, 2000):

$$(G + \lambda I_N) \underline{w}_{\lambda} = y \tag{1}$$

where G is the N×N symmetric Green's matrix which usually is factorizable isotropic Gaussian basis function with certain spread , λ the regularization parameter, I_N is the N×N identity matrix, \underline{w}_{λ} is the N×1 linear synaptic weight vector and \underline{y} is the real response values corresponding to input vector $\underline{x}_i = 1, 2, ..., N$. The structure of RN and Gaussian basis function parameters are elaborated in Appendix B. Figure 2 depicts the Flow diagram representation of our in-house optimal training algorithm for a Regularization network. The performance of



Figure 1. Block diagram representation of training algorithm for optimized ANFIS.

Regularization network strongly depends on the appropriate choice of the isotropic spread and the proper level of regularization which is described in Appendix B. In the following figure, e_k is the N×1 unit vector in which all elements (except the kth one) are zero.

Simulation case study: GTU of Khangiran (Or Hasheminejad) natural gas refinery

Khangiran is the major gas field in North East of Iran, near the Turkmenistan border, and it supplies gas to six north eastern provinces through Khangiran (Hasheminejad) refinery which has been operational since late 1970s

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with around 50 sour gas wells. According to recent reports, total gas intake of the refinery, whether sour or sweet, amounts to 57 MMSCMD and by completion of underway development projects, the gas sweetening capacity of the refinery will increase by 10 MMSCMD to reach 67 MMSCMD. Sulfur production capacity of Khangiran gas refinery stands at 2,600 tons a day while the actual production is 2,000 tons. At present, it consists of five sour gas treating units (GTUs) along with four sulfur recovery units with maximum total sulfur production capacity. All sweetening units were designed using 34wt% DEA in water as the solvent (Shahsavand et al. 2010; Moaseri et al., 2013; Shahsavand et al., 2011). Since 2006, 47 wt% 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. The wet sour gas analysis for the contactor feed of the Khangiran GTUs has been presented in our previous article (Shahsavand et al. 2010).

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 0C), 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 simulator (Aspen HYSYS V.8.3 contains a special acid gas property package which supports various Sulfolane-M solutions.) using the actual operating conditions which has been described in full detail in our previous article (Shahsavand et al. 2010). The simulation was



Figure 2. Flow diagram representation of our inhouse optimal training algorithm for a Regularization network

initially calibrated by validation with real plant data. The most important operating conditions are summarized in Table 1. Figure 3 shows the simplified schematic diagram of Khangiran gas refinery showing all output parameters of artificial neural network (*in italic fonts*). Both ANFIS and in-house RN are used to investigate the effects of inputs (sulfolane and MDEA weight percent in the lean amine solution) on actual operational variables such as benzene, toluene and ethylbenzene (BTE) escape factors (Defined as: (moles of BTE escaping from regenerator to SRU / total BTE moles entering GTU)×100), H₂S mole fraction and total moles of SRU feed, reboiler temperature and mole fraction of CO, in sweet gas.

Networks predictions

Figure 4 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 training data of appendix C is used to train networks including conventional MATLAB ANFIS Editor Toolbox and exact fit networks (which is equal to RN, but λ =0) along with Regularization network and optimized ANFIS.

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).

Figure 5 presents typical recall performances of all above four networks for benzene escape factor (%) (out of six other recall performances) which is significantly appropriate. A person unfamiliar with the over-fitting concept may take proper recall performance as a reliable basis to accept all predictions of such network. Figure 6, which shows the corresponding generalization performances over 100×100 mesh, clearly

Р	Temp.(°C)	Pres. (psia)	Flow (Kgmole/hr)	H ₂ S(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	18650	0.03	0.01
Rich Amine (From Contactor)	72	1050	19380	1.35	2.21
Lean Amine (To Flash Drum)	57	90	70	0.03	0.01
Rich Amine (To Regenerator)	99	90	19445	1.35	2.19
Lean Amine (From Regenerator)	121	27	18670	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

Table 1: Some operational conditions of Khangiran GTUs.



Figure 3. Simplified schematic diagram of Khangiran gas refinery unit.



Figure 4. Sulfolane and MDEA input data for training our in-house optimal RN and optimized ANFIS.



Figure 5. Typical recall performances of various ANN and ANFIS for Benzene escape factor.



Figure 6. Typical generalization performances of Benzene escape factor (%) in SRU feed stream versus MDEA and sulfolane (wt%) variation in lean amine for various networks.

illustrates that such a naive presumption can lead to catastrophic results when the trained network is used for generalization purposes.

It should be emphasized that un-regularized networks (Exact fit network) tend to follow (fit) the noise (or measurement errors associated with real data) and lead to severely oscillatory generalization performances as shown in Figure 6. A similar oscillatory trend can be observed at MATLAB ANFIS toolbox generalization performance.

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 performance. generalization the Both Regularization network and optimized ANFIS provide almost similar generalization performance over the entire domain. From now on, only the generalization performances of these two networks will be presented.

According to both fully optimized RN and optimized ANFIS networks of Figure 6, 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.

Figure 7 depicts the generalization performances of toluene escape factor versus MDEA and sulfolane (wt%) variation in lean amine via Regularization and optimized ANFIS 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.

Similarly, Figure 8 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% H₂O provides minimum escape factors for all BTE components. Small fluctuations observed in predictions of optimally tuned RN for Ethylbenzene escape factor indicate 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 hypersurfaces.

Figure 9 depicts two similar generalization



Figure 7.Generalization performances of Toluene escape factor (%) in SRU feed stream versus MDEA and sulfolane (wt%) variation in lean amine (Left: RN, Right: ANFIS)



Figure 8.Generalization performances of Ethylbenzene escape factor (%) in SRU feed stream versus MDEA and sulfolane (wt%) variation in lean amine (Left: RN, Right: ANFIS)

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 CO₂ 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.

Figure 10 illustrates two similar generalization



Figure 9. Generalization performances of SRU feed stream molar flow (kgmole/hr) versus MDEA and sulfolane (wt%) variation in lean amine (Left: RN, Right: ANFIS)

performances for hydrogen sulfide mole fractions of SRU feed streams versus MDEA and sulfolane concentrations in lean amine solutions. Figure 10 clearly shows that the H₂S 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% H₂O), the SRU feed stream contains around 34 mole% H₂S while, by using a solvent containing 37 wt% sulfolane, 47 wt% MDEA and 16% H₂O, the H_2S content of acid gas stream entering SRU will raise to more than 57mole% which indicates around 62% H_2S enrichment. It is anticipated that such a 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 Figure 11



Figure 10.Generalization performances of hydrogen sulfide mole fraction in SRU inlet feed stream versus MDEA and sulfolane (wt%) variation in lean amine (Left: RN, Right: ANFIS)

depict the generalization performances of the optimally regularized and optimized ANFIS networks for reboiler temperature of GTU regenerator column versus MDEA and sulfolane concentrations. Severe oscillations are still revealed 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 cannot 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 of the above techniques. The bottom-left 3D plot of Figure 11 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 Figure 13 illustrates that visual optimization of regularization level successfully captures the true underlying trend embedded in the training data when proper value of (σ =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) (Reza et al., 2006; Chakma et al., 1997). However, lots of parameters can affect the degradation process and must be taken into account. Amine solutions are prematurely degraded by reaction with CO₂, oxygen, organic sulfur compounds, and other gas impurities to form heat-stable salts and amine degradation products. Most scientific literature agree that MDEA thermal degradation temperature starts at 127°C (260 °F) in the presence of H₂S and CO₂. In other words, to achieve a 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 Figures 11 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 rebolier 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.



Figure 11.Generalization performances of reboiler temperature (0C) of regenerator column versus MDEA and sulfolane (wt%) variation in lean amine.

Figure 12 shows two nearly equal generalization performances of both networks for carbon dioxide mole 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 mole percent (Mokhatab et al., 2012; Kidnay et al., 2006). As it is anticipated, high concentrations of sulfolane will reject the carbon dioxide from acid gas stream and increase the mole fraction of CO₂ inside the sweetened gas stream. Therefore, the

previously determined optimal concentrations of 37 wt% sulfolane and 45 wt% MDEA can lead to excessive CO₂ rejection rate. Fortunately, Figure 12 shows that the CO₂ mole fraction of the contactor overhead is around 4.5 mole% which is still well within the permissible range. Table 2 summarizes all simulation results including various escape factors and different constituents molar flow and compositions for several locations of the GTU process operating with optimal concentration of Sulfinol-M solution (37 wt% Sulfolane, 45 wt% MDEA).



Figure 12 .Generalization performances of carbon dioxide mole fraction in sweet gas stream (mole%) versus MDEA and sulfolane (wt%)variation in lean amine (Left: RN, Right: ANFIS)

Benzene Escape Factor	Toluene Escape Factor	Ethylbenzene Escape Factor	SRU Molar Flow	H ₂ S mole% in SRU feed	Reboiler Temp.	CO ₂ mole% in sweet gas
%	%	%	kgmole/hr	%	٥C	mol%
20	0	0	415	57	129	4.5

Table 2: Summery of simulation results at optimal concentration of Sulfinol-M solution. (37 wt% Sulfolane, 45 wt% MDEA)

Conclusion

Contaminants in the acid gas stream can seriously impact the operability and reliability of a sulfur plant. Therefore, designers must determine the most economical means of removing or destroying these contaminants so that they do not negatively affect the performance of the facility. Selective removal of H_2S in the presence of CO_2 and other impurities 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 their performances for the H,S enrichment efficiency were evaluated. Optimized ANFIS network 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 (ANFIS Editor and exact fit networks). It was clearly shown that two fully optimized ANFIS 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 ANFIS network via minimization of error provide a distinguished performance. The optimal concentrations of 37 wt% sulfolane and 45 wt% MDEA were 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 H₂S in the SRU feed stream also increased from 33.48 mole% to over 57mole% when using the optimal Sulfinol-M aqueous solution.

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Appendix A

A schematic structure of an ANFIS network which has five distinct layers is shown in Fig. 1.A. For simplicity, it is presumed that the fuzzy inference system has two inputs (x, y) and just one output (f). The following rules can be written for a first order Sugeno fuzzy model:

Rule 1: If x is A₁ and y is B₁, then $f_1 = p_1 x + q_1 y + r_1$

Rule 2: If x is A₂ and y is B₂, then $f_2 = p_2 x + q_2 y + r_2$

In the above rules: p_1 , q_1 , r_1 and p_2 , q_2 , r_2 are the consequent parameters. Also A_1 , B_1 , A_2 , and B_2 are the linguistic labels. As shown in figure 1, fuzzy inference system consists of five distinct layers which are described below:

Layer 1 (or Fuzzification layer):

The fuzzy part of ANFIS is mathematically incorporated in the form of membership functions (MFs) to divide dimensions of each input. In most practical applications, Gaussian function presented in equation 1, because of minimum training and testing errors compared to the other shapes, was chosen as the best membership function ($\mu_{Ai}(x)$):

$$\mu_{\mathrm{A}i}(x) = \exp\left[-\left(\left(\frac{x-c_i}{a_i}\right)^2\right)^{b_i}\right]$$
(1.A)

Where a_i, b_i and c_i are a constant (referred to premise parameters) that define the bellshaped of membership function. Every node i in this layer is an adaptive node with a node function:

$$O_{1,i} = \mu_{Ai}(x)$$
 for $i = 1, 2$ or

$$O_{1,i} = \mu_{Bi-2}(x) \text{ for } i = 3, 4$$
 (2.A)

Generally, X (or y) is the input variable of node i and A_i (or B_{i-2}) is a linguistic label associated with this node. Therefore, $O_{1,i}$ is the membership grade of a fuzzy set (A_1, A_2, B_1, B_2) .

Layer 2 (Rule layer):

Every node in this layer is a fixed node labeled as π and the output of nodes in this layer is the product of all the incoming signals:

$$O_{2i} = W_i = \mu_{Ai}(x) \cdot \mu_{Bi}(y)$$
 $i = 1, 2$ (3.A)

Every node in this layer computes the multiplication of the input values and gives the product as the output. The membership values represented by $\mu_{Ai}(x)$ and $\mu_{Bi}(y)$ are multiplied in order to find the firing strength of a rule where the variables x and y have the linguistic values A_i and B_i , respectively.

Layer 3 (Normalization Layer):

Each node in this layer normalized the related firing strengths (w_i). The ratio of firing strength of each rule to the sum of all rules firing strength is calculated according to the following equation:

$$O_{3,i} = \overline{w}_i = \frac{w_i}{w_1 + w_2}$$
 i=1,2 (4.A)

where O_{3i} is the output of layer 3 and \overline{w}_i is the normalized firing strength.

Layer 4 (Defuzzification Layer):

Every node in this layer is an adaptive node with a node function, indicating the contribution of each rule towards the overall output.

$$O_{4,i} = \overline{w}_i f_i = \overline{w}_i (p_i x + q_i y + r_i) \quad i=1, 2$$
(5.A)

Layer 5 (Output Layer):

The single node in this layer is a fixed node labeled sum, which computes the overall output as the summation of all incoming signals:

Overall output =
$$O_{5,i} = \sum_{i} \overline{w}_{i} f_{i} = \frac{\sum_{i} w_{i} f_{i}}{\sum_{i} w_{i}}$$
 i=1,2 (6.A)



Figure 1.A ANFIS structure for a two-input Takagi-Sugeno model

Appendix B

Generally, Regularization refers to a process of introducing additional information in order to solve an ill-posed problem or to prevent over-fitting phenomena. This information is usually of the form of a penalty for complexity, such as restrictions for smoothness or bounds on the vector space norm. Many regularization techniques correspond to imposing certain prior distributions on model parameters.

Poggio and Girosi showed that regularization principles lead to approximation schemes which are equivalent to networks with one hidden layer which are called Regularization Networks (RN). In particular, they have described that a certain class of radial stabilizer (associated priors in the equivalent Bayesian formulation) lead to subclass of Regularization Network which is already known as a Radial Basis Function (Shahsavand et al., 2007).

Figure 1.B 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.

For a special choice of stabilizing operator, the Green's function reduces to the following multidimensional factorizable isotropic Gaussian basis function with infinite number of continuous derivatives (Shahsavand et al., 2005).

$$G(\underline{x}, \underline{x}_j) = \exp\left[-\frac{\left\|\underline{x} - \underline{x}_j\right\|^2}{2\sigma_j^2}\right] = \prod_{k=1}^p \exp\left[-\frac{(x_k - x_{j,k})^2}{2\sigma_j^2}\right]$$
(1.B)

In the above equation, σ_i denotes the isotropic spread of the jth Green's function and is assumed to be identical for all input dimensions. 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 $G(\underline{x}, \underline{x}_i)$ centered at a particular data point \underline{x}_i . The influence of the regularization parameter λ is embedded in the unknown synaptic weights w.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 (Shahsavand et al., 2007). 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

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in our recent article (Niknam Shahrak et al., 2013). The optimal value of ridge regression parameter is case dependent and as before, the LOOCV criterion (among many others) can be used to provide the best value of I for

the problem at hand. Our fully optimized inhouse training algorithm for the isotropic Regularization network has been discussed in sufficient detail elsewhere (Shahsavand et al., 2009).



Figure 1.B. Schematic representation of Regularization network with single hidden layer

Appendix C

MDEA Conc.	Sulfolane Conc.	Benzene Escape Factor	Toluene Escape Factor	Ethylbenzene Escape Factor	SRU Molar Flow	H ₂ S mole% in SRU feed	Reboiler Temp.	CO ₂ mole% in sweet gas
wt%	wt%	%	%	%	kgmole/ hr	mol%	°C	mol%
0.47	0	59.5	98.8	100	729	0.35	120.9	0.009
0.47	0.1	89.5	99.9	100	687.5	0.36	121.9	0.0157
0.47	0.2	99.9	50.9	29.2	591.1	0.42	123.6	0.0292
0.47	0.3	54.1	26.8	13.4	481.8	0.52	126.7	0.0437
0.47	0.32	48.0	23.3	11.3	464.9	0.54	127.7	0.044
0.47	0.37	39.3	3.3	6.7	413.2	0.57	128.3	0.045
0.44	0	52.3	93.8	98.9	730.7	0.35	120.7	0.0093
0.44	0.1	77.7	99.9	100	697	0.36	121.6	0.0142
0.44	0.2	99.8	94.0	38.7	616.5	0.41	122.9	0.0257
0.44	0.3	64.6	32.8	17.2	507.1	0.50	125.4	0.0405
0.44	0.32	57.4	28.9	14.7	489.2	0.51	126.2	0.0429
0.4	0	44.1	82.5	88.6	730.7	0.35	120.3	0.0091
0.4	0.1	64.7	99.7	100	704.6	0.36	121.1	0.0129
0.4	0.2	96.0	99.5	81.1	640.1	0.39	122.2	0.0223
0.4	0.3	99.9	41.9	23.7	541.9	0.46	124.1	0.036
0.4	0.35	60.5	31.1	16.1	493.6	0.51	125.7	0.0424
0.35	0	35.8	68.4	70.7	728.2	0.35	120	0.0092
0.35	0.1	51.9	94.2	99.1	704.8	0.36	120.7	0.0124
0.35	0.2	77.7	99.8	98.9	654.2	0.38	121.6	0.0199
0.35	0.25	94.6	97.4	51.3	617.4	0.41	122.2	0.0253
0.35	0.3	99.8	60.5	33.8	574.8	0.44	123	0.0314
0.35	0.35	99.9	42.1	23.8	529	0.48	124	0.0377
0.35	0.38	88.7	35.5	19.0	503.5	0.50	124.9	0.0412
0.3	0	29.1	56.1	55.1	716.6	0.35	119.8	0.0101
0.3	0.1	41.7	80.0	86.4	693.1	0.36	120.3	0.0133
0.3	0.2	61.8	99.4	99.9	651.8	0.39	121.1	0.0196
0.3	0.3	93.6	83.8	46.0	589.3	0.43	122.1	0.0289
0.3	0.35	99.7	55.1	33.6	549.8	0.46	122.9	0.0345
0.3	0.38	99.9	46.7	27.5	528.2	0.48	123.5	0.0376
0.25	0	23.5	45.0	41.9	678.8	0.37	119.5	0.014
0.25	0.1	33.5	65.1	68.0	657.6	0.38	119.9	0.0174
0.25	0.2	49.4	91.9	98.4	626.2	0.40	120.6	0.0223
0.25	0.25	60.5	99.1	99.7	603	0.42	121.1	0.0259
0.25	0.3	75.1	95.5	60.5	579.7	0.43	121.5	0.0294
0.25	0.35	92.7	68.6	45.0	551.8	0.46	122.1	0.0336
0.25	0.38	98.7	58.7	37.6	533.2	0.47	122.5	0.0363

Investigating the Effect of Replacing Modern High Effective Random Packings on Natural Gas Purification

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Abstract

This investigation attempts to evaluate and compare the effect of packing type on the mass transfer and pressure drop along the gas sweetening absorption column. To this aim, modern packings such as Super Ring, Ralu Ring, Ralu Flow and the second-generation packing (Pall Ring), have been used in simulated columns by using of Aspen HYSYS modeling software. Flooding calculation is made possible by linking Aspen HYSYS with MATLAB programing. The selected models validity is checked by comparison to empirical data from a real gas plant. It should be noted that empirical data is available just for second-generation packing. Comparison of these packings performance shows that Super Rings provide low pressure drop, Ralu Rings lead to high mass transfer and Ralu Flow packings can provide high mass transfer and low pressure drop in absorption columns. According to results, the capacity of gas treatment units can be significantly increased by replacing Pall Ring with Ralu Flow.

Keywords: Natural gas sweetening, absorption column, packing, mass transfer, pressure drop

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Introduction

Nowadays, one of the most common methods to increase the capacity of a plant for gas purification is absorption column internal modification which is usually realized through replacement of packed beds. Development of packings initiated in 1950 when the secondgeneration Pall Ring and Intalox packings were designed and later continued by creating the third-generation International Metal Tower Packing (IMTP) and Cascade Mini-Ring (CMR). Due to packing key role in absorption and desorption processes, packings developed in recent years have been widely employed. Super Rings, Ralu Rings and Ralu Flows are the fourth-generation packings which have prominent characteristics compared to the other types. Billet and Schultes (1999) made an effort to predict the mass transfer in columns with dumped and arranged packings. Schultes (2003) investigated the characteristics of some third-generation packings including Nutter Ring, CMR, IMTP and also Super Ring as a fourth-generation packing. Darakchiev et al. (2005) compared the gas distribution in packed columns with IMTP and Ralu Flow packings. Nako et al. (2007) compared the effective areas of some highly effective packing. Darakchiev and Semko (2008) investigated the effect of modern high effective packings on waterethanol rectification. Mackowiak (2009)predicted the pressure drop of some packings by extended channel model.

Arachchige et al. (2012) compared the effect of second-generation packings on energy consumption of CO₂ capture processes by using of Aspen Plus. As previous studies have been based on predicting the characteristics of packings and assessing the performance of second and third generation packings, this paper investigates the effect of replacing fourth generation random packings on energy consumption and capacity of gas purification plants (MDEA-based). To this aim, Aspen HYSYS simulation software (V8.3) is used for modeling of packed column.

Rate-based modeling and validation

In this paper, a real life case study data (BIDBOLAND gas refinery, Iran) has been used for validation of simulation results. The entire refinery has four parallel gas treatment units (GTU) with 4 absorbers and 4 regenerators. The absorbers have an internal diameter of 2.9 meters and two sections. Each section is 6.54 meters in height and filled with plastic random packing (2-inch Pall rings). The regenerator column has 17 sieve trays and internal diameter of 3.96 meters. Based on tray spacing of 27 inch, the height of the column is 11.66 m. Table 1 shows the current operation conditions of the mentioned units.

The traditional approach of modeling absorption and Regenerator columns is using the equilibrium stages. In this model the column is divided into a number of stages and it assumes that the vapor and liquid phase leaving a stage are at equilibrium. This assumption is used to simplify the modeling and rarely happens in reality.

The departure from equilibrium is corrected by applying tray efficiency like the Murphree efficiency for tray columns or the height equivalent to a theoretical plate (HETP) for packed columns. For reactive separation processes, the deviations from the equilibrium model are very large and the use of efficiencies does not work well. Hence, rate-based models are suggested for modeling these systems. This model assumes that the vapour-liquid equilibrium occurs only at interface. In this work, the RadFrac distillation model was used to model the absorber and stripper columns. It is a rigorous model for simulating absorption and stripping where chemical reactions are occurring. The rate-based mode of RadFrac, called ASPEN RateSep, allows for the rate-based modeling of absorption and desorption columns and uses the two-film theory in mass and heat transfer models. According to the above-mentioned, the validity of the simulation results depends heavily on selection of equilibrium and mass transfer models used in simulation. In this study, the ACID GAS thermodynamic package and

Absorption Column					
Type of packing	2-inch, Pall ring				
Number of section	2				
Column Pressure, bar	54				
H ₂ S in Gas Feed, ppm	1950				
%CO ₂ in Gas Feed, mole	1.74				
Gas Feed Temperature, °C	30.0				
%Amine Conc. in Solvent, wt	40				
Inlet lean Amine Temperature, °C	34				
Amine Flow Rate, kmol.h ⁻¹	4615				
Feed Gas Flow Rate, kmol.h ⁻¹	15860				

Table 1. Current operation conditions of BIDBOLAND gas refinery units

Table 1. Current operation conditions of BIDBOLAND gas refinery units (cont'd)

Regenerator Column				
Column Pressure, bar	1.4			
Condenser Temperature, °C	33.0			
Feed Temperature, °C	93.60			
Bottom Temperature, °C	116.70			

ELECNRTL package (PMDEA Data package) are selected for process simulation in Aspen HYSYS (V 8.3) and Aspen Plus (V 8.2), respectively. It should be noted that both of these packages use electrolyte NRTL models in the property package for the thermodynamics, and also use a mass-and-heat transfer rate-based calculation method. Aspen Rate-Based distilation uses well known and accepted correlations to calculate binary mass transfer coefficients for the vapour and liquid phases, interfacial areas, heat transfer coefficients and liquid holdup. The simulation results and operating data of the BIDBOLAND treatment unit are provided in Table 2. As seen in Table 2, ACID GAS Package which has been inserted in Aspen HYSYS (V 8.3) software simulated the treatment unit with an acceptable accuracy and this simulator is used for the following investigation steps. It should be mentioned that selected mass transfer and interfacial models that provide best results are shown in Table 3.

Table 2. Simulation results of BIDBOLAND GTU using ELECNRTL and ACID GAS packages

Parameters	Plant Data	ACID GAS	ELECNRTL
H ₂ S in Sweet Gas, ppm	4.00	4.02	3.12
% CO ₂ in Sweet Gas, mole	1.1065	0.9834	1.4893
Rich Amine Temperature, °C	21.20	20.81	20.67
(Acid Gas Loading*(Rich amine	0.328	0.327	0.294
Reboiler Duty, kJ.hr ⁻¹	10 ^{8×} 1.19	10 ^{8×} 1.08	10 ^{8×} 1.05

*moles of acid gases per mole of amine

Table 3. Mass transfer and interfacial models (ACID GAS and ELECNRTL)

Models	Absorbtion column		Regenerator column		
	Section 1	Section 2	Bubble cap	Sieve tray	
Mass transfer	onda	Hanley	Gerster	Chen & Chuang	
Interfacial	onda	Hanley	Scheffe	Zuiderweg	

Results and discussion

Replacing the Fourth-Generation Packings

In this study, the method of Billet and Schultes (1999) has been used for calculating flooding percentage. This calculation has been done by written MATLAB Code that linked to Aspen HYSYS. Table 4 shows the characteristics of used packings as well as required constants for calculation of flooding percentage. It should be noted that attempts have been made to avoid using metal packings due to occurrence of corrosion in amine sweetening units. The simulation results are shown in Figs.1, 2, 3 and 4 in order to study the effect of used packings on sweetening and energy consumption of gas treatment units of BIDBOLAND refinery.

Amine circulation rate

Figure 1 shows the required amine circulation rate in presence of various packings for achieving 4ppm H₂S in sweet gas stream. As it is observed, the required amine circulation rate in presence of Pall Ring (4615 kmol.h⁻¹) is not much different from that in presence of Super Ring (4810 kmol.h⁻¹), while amine consumption rate significantly decreases in presence of Ralu Ring (25mm) and Ralu Flow (NO-1).
to reduce

Packing Type(size)	Specific Area(m ² /m ³)	Void Fraction	C _h	C _{fi}
Pall Ring(50mm)	110	0.920	0.593	1.757
Super-Ring(NO-2)	100	0.960	0.720	2.096
Ralu Ring(25mm)	190	0.940	0.719	1.989
Ralu Ring(38mm)	150	0.930	0.640	1.812
Ralu Flow(NO-1)	165	0.940	0.640	2.401
Ralu Flow(NO-2)	100	0.945	0.640	2.174

is using

Table 4. Constants and characteristics of used packings (Billet and Schultes, 1999)



Figure 1. Required amine circulation rate in presence of various packings (4 ppm H2S in sweet gas stream)

Energy consumption

Energy consumption of the unit in presence of various packings is presented in Figure 2. According to Figure 1, as in presence of Ralu Ring (25mm) and Ralu Flow (NO-1), the amine circulation rate is at lowest level; using these two packing types leads to maximum reduction in energy consumption of unit. sweetening unit energy consumption, investigating operating considerations and avoiding flooding phenomenon are among the most important aspects of this research. Figure 3 shows the calculated flooding percentage in absorption column of gas sweetening unit in presence of different packings. As seen in this diagram, using Ralu Ring packing (25mm) increases the risk of flooding in the column whereas there is no such drawback by selecting Ralu Flow (NO-1).

appropriate packing



Figure 2. Unit energy consumption in presence of various packings (4 ppm H2S in sweet gas stream)

Another important factor in selecting the type of packing is acid gas loading in rich

Operational constrains

Although the main purpose of this paper



Figure 3. Predicted flooding percentage in presence of various packings (4 ppm H2S in sweet gas stream)



Figure 4. Acid gas loading in rich amine in presence of various packings (4 ppm H2S in sweet gas stream)

amine solution. According to Figure 4, if Ralu Flow packing is used to achieve 4ppm hydrogen sulfide in sweet gas stream, acid gas loading in rich amine will increase more than critical limit (0.5 mole/mole for MDEA) (Kohl and Nielsen, 1997). At the same time, as shown in Table 5, when concentration of 2 ppm is achieved for hydrogen sulfide, acid gas loading in rich amine will reach the allowed limit while the unit energy consumption will be lower than that using other types of packings in similar conditions.

Increasing capacity

In this study, according to the performance of sweetening unit of BIDBOLAND refinery, flooding critical limit in absorption column is considered to be 65%.

According to this parameter and the results presented in Table 6, the refinery capacity can be increased up to 18% by replacing Pall Ring with Ralu Flow.

Packing Type	Amine Flow (kmol.h ⁻¹)	CO ₂ in sweet gas (mole %)	Rich Loading	Flooding (%)	Total Energy (kj/hr)
Ralu Flow (4 ppm)	2894	1.0892	0.530	51.15	100836732
Ralu Flow (2 ppm)	3413	1.0397	0.479	53.08	123807485

Table 5. Comparison of unit performance in presence of Ralu flow packing to achieve 2 and 4 ppm H2S in sweet gas stream (Sour gas flow: 9 MMSCMD)

Table 6. Comparison of unit performance in presence of Ralu flow packing to achieve 9 and 11 MMSCMD capacity (H2S concentration in sweet gas: 2 ppm)

Sour Gas Flow (MMSCMD)	Amine Flow (kmol.h ⁻¹)	CO ₂ in sweet gas (mole %)	Rich Loading	Flooding (%)	Total Energy (kj/hr)
9.00	3413	1.0397	0.479	53.08	123807485
11.00	3940	1.11735	0.467	62.41	142188391

Conclusion

Analysis of simulation results of gas treatment unit of BIDBOLAND refinery shows that changing the type of packing in the absorption column can decrease not only flooding risk, but also energy consumption.

Comparing the performance of modern random packings of Super Ring, Ralu Ring, and Ralu Flow indicates the reduction of flooding risk in the absorption column in the presence of Super Ring packing.

The results reveal that using Super Ring packing will not make any change to the level of absorption of acid gases, energy consumption and the unit capacity compared to Pall ring packing.

At the same time, using Ralu Flow packings (NO-1) largely increases hydrogen sulfide absorption. Although this issue reduces the amine circulation rate, it raises the level of acid gases loading in rich amine solution over the allowed limit.

To solve this problem, amine circulation rate is increased which in turn reduces acid gases loading and increases sweet gas purity.

As seen in the results, using Ralu Flow packing (NO-1) in the absorption column decreases flooding and allows for increasing the unit capacity up to 1.18 times of the current capacity.

It should be noted that like Ralu Flow packing, using Ralu Ring packing (25mm) will decrease the unit energy consumption. However, due to its failure in decreasing flooding, it cannot increase the unit capacity.

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ارائه مدل تصحیح شده چهار ضریبی برای مشخصه سازی جزء سنگین در یک مخزن فوق عظیم گاز میعانی

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چکیـــده

خواص و ترکیب برش جمعی یک سیال نفتی تأثیر قابل توجهی بر رفتار فازی سیال دارد. شناخت روند تغییرات جرم مولکولی گروه های متوالی تک کربن برش جمعی مستلزم داشتن یک تابع توزیع دقیق و قابل اعتماد است. مدل های مختلف تابع توزیع موجود برای انواع خاص سیال قابل استفاده است. در این مقاله، تحلیل ۳۰ سیال معرف یک مخزن گاز میعانی فوق عظیم نشان داد که ناپیوستگی در جرم مولکولی های گروه های تک کربن ۸ و ۱۳ است. توابع توزیع نمایی، گاما، چهارضریبی و چهارضریبی تصحیح شده بر این داده ها اعمال شد تا ترکیب گروه های تک کربن پیش بینی شود. نتایج نشان داد که تابع توزیع نمایی دقت لازم برای پیش بینی توزیع ترکیبات تک کربن به ویژه در نقاط ناپیوستگی ترکیب را ندارد. به علاوه، تابع توزیع گاما ناپیوستگی ترکیب در عدد کربنی ۸ را به خوبی پیش بینی کرد ولی دقت لازم در عدد کربنی ۱۳ را ندارد. به علاوه، تابع توزیع گاما ناپیوستگی ترکیب در عدد کربنی ۸ را به خوبی پیش بینی کرد ولی دقت ازم در عدد کربنی ۱۳ را ندارد. به علاوه، تابع توزیع گاما ناپیوستگی ترکیب در عدد کربنی ۸ را به خوبی پیش بینی کرد ولی دقت ازم در عدد کربنی ۱۳ را ندارد. خطای کلی محاسبات برای روش های نمایی، گاما و چهارضریبی تصحیح شده به تر تیب برابر با ۳۷٫۹

به شدت وابسته به ماهیت سیال است و بر اساس داده های میدانی موجود نیازمند بهینه سازی میباشد.

واژگان كليدى: گاز ميعانى، برش جمعى، تابع توزيع، مدل چهارضريبى

ساخت و ارزیابی غشاهای آمیزه پلیمری برای جداسازی CO2/CH4

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چکیـــده

واژگان کلیدی: آمیزهسازی، جداسازی گازی، پلی(آمید-b-تیلن اکساید)، پلیاترسولفون

مقایسه و آنالیز عملکرد بهینه سازی معادلات Pressure-Flow در شبکه خطوط انتقال و توزیع گاز به دو روش الگوریتم ژنتیک و الگوریتم اردحام

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چکیـــده

یکی از مهمترین اهداف مهندسی گاز، توزیع بهینه گاز در شبکه های انتقال و توزیع گاز است. هرچند که اغلب این فرایند از مسائل غیر قابل اجتنابی مانند وجود خطا در تخمین نادقیق فشار در نقاط مختلف شبکه رنج می برد. اخیرا روشهای بهینه سازی آماری برای حل این مشکل پیشنهاد شده است. روش های ازدحام ذرات و الگوریتم ژنتیک روشهای مرسوم بهینه سازی برای این هدف هستند. هدف از این مطالعه مقایسه عملکرد این دو روش در یک مثال واقعی از شبکه ایران است و با انجام آزمایش ۹۹٬۹۹ درصد دقت بدست آمد. در شرایط اعمال محدودیت و بار محاسبات یکسان بر دو روش، عملکرد روش ازدحام ذرات سریعتر و دقیقتر از الگوریتم ژنتیک مشاهده گردید. هر چند که تکرار پذیری روش الگوریتم ژنتیک بهتر از روش ازدحام ذرات بود.

واژگان كليدى: شبكه انتقال گاز، بهينه سازى، الگوريتم ژنتيك

ارزیابی مقدماتی توان هیدروکربن زایی سازند هجدک در ناودیس زغالی کرمان، ایران: رویکرد ژئوشیمیایی

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چکیـــدہ

به منظور براورد توان هیدروکربن زایی لایه های زغالسنگ (افق های D و E) و سنگ دربردارنده آن ها در سازند هجدک (ژوراسیک میانی– پایانی) در ناودیس زغالی کرمان، ۳۲ نمونه زغالسنگ و ۴۶ نمونه شیل برداشت شد. این نمونه ها به طریقه ژئوشیمیایی مورد مطالعه قرار گرفت و کمیت، کیفیت و بلوغ حرارتی مواد آلی آنها تعیین شد. براساس داده های حاصل از پیرولیز راک- اول مشخص شد که محتوای کل کربن آلی (TOC) در نمونه های زغالسنگ در وضعیت عالی قرار دارد. این شرایط برای نمونه های شیل نیز کم و بیش مشابه است. همچنین بررسی پتانسیل زایشی (GP) نیز نشان داد که اغلب نمونه ها پتانسیل قابل قبولی برای تولید گاز و نفت دارند. بنابراین، کمیت مواد آلی سازند هجدک در مجموع در شرایط خوب تا عالی ارزیابی شد. با بهره گیری از اندیس هیدروژن (HI) به عنوان یکی از مهمترین شاخص های تعیین کننده کیفیت سنگ های منشاء مشخص شد که نمونه های زغالسنگ و شیل سازند هجدک دارای اندیس هیدروژن از کمتر از ۵۰ تا بیش از ۶۰۰ میلی گرم هیدروکربن بر گرم سنگ بوده و عمده نمونه ها در بازه های ۵۰ تا ۲۰۰ و ۲۰۰ تا ۳۰۰ قرار می گیرند و بنابراین می توان کیفیت این مواد را از فاقد توان تولید هیدروکربن تا دارای توان تولید گاز و نفت در نظر گرفت. نوع کروژن موجود در این نمونه ها نیز در گروه های III و III–II قرار می گیرد و در نتیجه تولید گاز و نفت برای این ناحیه محتمل است. بالا بودن نسبت ST/S۲ (۳.۷۰ تا ۴۰۲.۳۶) نمونه ها نیز تولید محصولات یادشده را تأیید می کند. به منظور براورد بلوغ حرارتی مواد آلی از دو روش Tmax و انعکاس ویترینایت استفاده شد. مقادیر Tmax اغلب نمونه های مورد بررسی نشانگر قرارگیری آن ها در ابتدا تا انتهاى ينجره نفتى است. بالاترين مقدار Tmax مربوط به منطقه تيكدر است كه اين بلوغ بالا (شرايط فوق بالغ) احتمالا به خاطر مجاورت با گسل کوهبنان است. اندازه گیری های قدرت انعکاس ویترینایت نیز از نشان داد که مقدار انعکاس از ۰.۵ تا ۲ درصد در تغییر بوده و میانگین آن ۱.۱۸ است و این مقدار با پنجره نفتی مطابقت دارد. در نهایت، براساس کمیت، کیفیت و بلوغ حرارتی مواد آلی در ناودیس زغالی کرمان می توان اظهار داشت که این ناحیه پتانسیل کافی برای تولید گاز و به مقدار کمتر نفت را دارد. بعلاوه، لایه های زغالي در مجموع به خاطر داشتن مقادير بالاتر محتواي ليپتينايت (تا ۲۲ درصد) از شرايط بهتري برخوردارند.

واژگان کلیدی: ناودیس زغالی کرمان، هجدک، پتانسیل هیدروکربن زایی، پیرولیز، کروژن

پیش بینی غلظت بهینه سولفینول در واحد تصفیه گاز پالایشگاه خانگیران از طریق سیستم استنتاج تطبیقی عصبی- فازی و شبکه ر گولاریزاسیون

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چکیـــدہ

غلظت سولفید هیدروژن در گاز اسیدی ورودی به واحد بازیافت گوگرد از جمله پارامترهای مهم و تاثیر گذار می باشد که باید طراحان آن واحدها در هنگام تصمیم گیری برای انتخاب فرآیند یا ساختار درست جهت بدست آوردن بیشترین بازده بازیافت گوگرد در نظر داشته باشند. استفاده از حلال های ممانعت فضایی شده مانند آمین های نوع سوم ارتقاء یافته و همچنین ساختارهای متفاوت برای واحد تصفیه گاز، از جمله گزینه های مختلف برای غنی سازی گاز اسیدی (AGE) که به منظور کاهش غلظت دی اکسید کربن و هیدروکربن های آروماتیکی سنگین و افزایش غلظت سولفید هیدروژن در جریان خوراک ورودی به واحد بازیافت گوگرد انجام می گیرد، خواهد بود. در مقاله حاضر با استفاده از تلفیق نرم افزار اسپن-هایسیس و دو شبکه مجزا (به نام های شبکه رگولاریزاسیون و سیستم استنباط فازی- عصبی تطبیقی) نسبت به مقایسه توانایی غنی سازی گاز اسیدی حلال سولفینول-M (سولفولان+ADAR) در غلظت بهینه و فازی- عصبی تطبیقی) نسبت به مقایسه توانایی غنی سازی گاز اسیدی حلال سولفینول–M (سولفولان+ADAR) در غلظت بهینه و حلال رایچ ADDA، هنگامی که هر دوی آن ها به عنوان حلال واحد تصفیه گاز مورد استفاده قرار می گیرد، اقدام شده است. نتایج تاصل از شبیه سازی حاکی از آن بود که در غلظت بهینه حلال سولفینول–M (شامل ۷۳% وزنی سولفولان و ۵۴% وزنی MDEA) شمای تولوئن و اتیل بنزن و همچنین ۸۰% از بنزن ورودی به واحد تصفیه گاز ، از خوراک ورودی به واحد بازیافت گوگرد حذف خواهند شد. علاوه بر این، کسر مولی سولفید هیدروژن در خوراک ورودی به واحد تصفیه گاز، از خوراک ورودی به واحد بازیافت گوگرد خذف خواهند شد. علاوه بر این، کسر مولی سولفید هیدروژن در خوراک ورودی به واحد تصفیه گاز، از خوراک ورودی به واحد بازیافت گوگرد مذف خواهند

واژگان كليدي: غنى سازى گاز اسيدى، بنزن- تولوئن-اتيل بنزن، شبكه رگولاريزاسيون، سيستم استنباط فازى- عصبى تطبيقى

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بررسی اثر جایگزینی آکنه های مدرن با کارآئی بالا در فرآیند تصفیه گاز طبیعی

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چکیـــده

در این تحقیق، اثر نوع آکنه بر نرخ انتقال جرم و میزان افت فشار در برجهای شیرین سازی گاز طبیعی مورد ارزیابی قرار گرفته است. بدین منظور از میان آکنه های مدرن، انواع Super Ring، Ralu Ring، Ralu Flow و همچنین از میان نسل دوم آکنههای موجود، نوع Pall Ring انتخاب شده و اثر جایگزینی هریک از آنها درون برجهای تماس، توسط نرم افزار مذکور، امکان پیشبینی پدیده است. لازم بذکر است که با توسعه یک برنامه محاسباتی در MATLAB و فراخوانی آن توسط نرم افزار مذکور، امکان پیشبینی پدیده طغیان فراهم شده است. به منظور اعتبار سنجی مدل های انتخابی نیز، نتایج شبیه سازی با اطلاعات استخراج شده از یک واحد واقعی مانیان فراهم شده است. به منظور اعتبار سنجی مدل های انتخابی نیز، نتایج شبیه سازی با اطلاعات استخراج شده از یک واحد واقعی مانیان فراهم شده است. به منظور اعتبار سنجی مدل های انتخابی نیز، نتایج شبیه سازی با اطلاعات استخراج شده از یک واحد واقعی مانیان فراهم شده است. به منظور اعتبار سنجی مدل های انتخابی نیز، نتایج شبیه سازی با اطلاعات استخراج شده از یک واحد واقعی مانیان فراهم شده است. به منظور اعتبار سنجی مدل های انتخابی نیز، نتایج شبیه سازی با اطلاعات استخراج شده از یک واحد واقعی مانیان فراهم شده است. به منظور اعتبار سنجی مدل های انتخابی نیز، میام مازی با اطلاعات استخراج شده از یک واحد واقعی مانیاده نموده است. نتایج نشان می دهد که استفاده از آکنه Super Ring منجر به کاهش افت فشار و همچنین استفاده از نوع Ralu استفاده نموده است. نتایج نشان می دهد که استفاده از آکنه Super Ring منجر به کاهش افت فشار و همچنین استفاده از نوع Ring باعث افزایش نرخ انتقال جرم خواهد شد. این در حالی است که استفاده آکنه Ralu Flow ، به تنهایی می تواند هر دو هدف را

واژگان کلیدی: شیرین سازی گاز طبیعی، ستون جذب، پر کن، انتقال جرم، افت فشار



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