Desalination and Water Treatment
www.deswater.com
doi: 10.5004/dwt.2018.22289

113 (2018) 326–334
May

Simulation of a pilot plant for water deoxygenation using circulating stripping gas

Xinghua Han[a,b,*], Hao Bai[c], Ting Dong[a], Yanhong Wang[a], Weizhou Jiao[b]

[a]*School of Chemical and Environmental Engineering, North University of China, Taiyuan 030051, China*
[b]*Shanxi Province Key Laboratory of Higee-Oriented Chemical Engineering, North University of China, Taiyuan 030051, China, Tel. +86-351-3922116, Fax +86-351-3922118, email: hxh@nuc.edu.cn (X. Han)*
[c]*CFHI Dalian Design and Research Institute, Dalian 116000, China*

Received 25 May 2017; Accepted 2 April 2018

ABSTRACT

A compact pilot plant was designed to remove dissolved oxygen from water for water injection in an oilfield. Two stage static mixers were selected to explore a more efficient scheme and flexible layout. In addition, a compact plate heat exchanger and air booster were chosen. Key process features of the proposed module are the air booster, and the static mixer and plate heat exchanger selected to design a compact pilot plant. The pilot plant process was simulated by Aspen Hysys software. The air booster was modeled separately in Matlab Simulink. The stripping process was simulated to optimize theoretical stage numbers, oxygen concentration, and molar flow rate of the stripping gas. A sensitivity analysis of flow rate and temperature was performed to investigate their influence. The simulations showed that the proportion of oxygen in 10 m^3/h water after treatment was less than 20 ppbw, which meets the strict requirements for two stage static mixers at 250 kPa and 40 kg/h stripping gas flow rates.

Keywords: Deoxygenation; Water injection; Stripping; Water treatment

1. Introduction

Deoxygenation of water is one of the most important topics in ocean engineering for water injection and ballast water treatment [1]. In the context of oil and/or gas extraction, hydrocarbon reservoir strata typically consist of a gas layer, an oil layer, and a water layer in sequence downwards from cap rock to source rock. Oil particles are not found in the water layer, but in porous layers of rock [2]. During the oil/gas the oil and gas from the porous strata. Surface water contains substantial levels of dissolved oxygen, which has an adverse effect on sustaining injection water pressure and the quality of the produced oil. Another consideration is that high pressure injection water pipe lines are usually made of carbon steel, which is prone to corrosion by the dissolved oxygen in the water because the dissolved oxygen helps to create differential aeration cells beneath scale deposits on metal surfaces [2]. Dissolved oxygen also promotes the growth of aerobic bacteria and enhances the synergistic effect between different species of bacteria. Aerobic acid-producing bacteria deplete the oxygen and produce acids that act as nutrients for sulfate-reducing bacteria [3].

Corrosion rates are determined by the oxygen concentration, the diffusion of the dissolved oxygen, flow velocity, etc. [4,5]. In general, the dissolved oxygen level is 20–50 ppbw [3,6–8] in different situations (the exact value may be obtained from reports or from laboratory studies). Several deoxygenation technologies have also been developed (thermal processes, vacuum processes, and stripping processes [9,10]).

In the stripping process, the inert stripping gas is usually nitrogen or natural gas [10]. Nitrogen has the advantage that it can be catalytically purified and recycled [11], if natural gas is used instead of nitrogen, the process is simpler, but a heater may be required in some cases [12]. Thermomechanical processes using steam are preferably adopted when steam is already available from other operations. Compared with the conventional vacuum process and natural gas stripping process, nitrogen stripping has many advantages: it has a smaller footprint, a shorter overall

*Corresponding author.

system height, lower operating weight, and produces lower concentrations of dissolved oxygen [6].

The pilot plant in this paper is based on the Minox Technology system, which is a gas stripping process where ultra pure nitrogen gas is used to remove dissolved oxygen from water without the use of oxygen-scavenging chemicals [13,14]. Nitrogen gas is continuously circulated and regenerated in a closed loop. Oxygen reacts with methanol and releases heat in a fixed-bed catalytic reactor, so that hot effluent steam transfers heat to the cold reactor inlet stream [6,15].

Key processes in the proposed module are the air booster, static mixer, and plate heat exchanger, selected to develop a compact pilot plant. Each unit can be tailor-made to fit into a given space. This makes it suitable for installation on existing platforms, or when conventional deaeration systems are being upgraded. The module is flexible in design and capacity. The following describes the simulation of a steady state pilot plant process to determine the optimal design parameters, using the commercial software Aspen Hysys. The air booster operations were simulated using Matlab Simulink.

2. Materials and methods

2.1. The principle of the deoxygenation process

The principle of the stripping process is that the gas-liquid equilibrium between the dissolved components in the water and the "on-compressible" components obeys Henry's Law.

2.2. Stripping unit model

On the assumption that the presence of nitrogen and carbon dioxide each has a negligible effect on the equilibrium of oxygen, a simplified counter-current stripping column model was developed to determine the relationship between the gas: water ratio, the oxygen content in the purified cycling gas, and the number of stripping stages.

In a differential-contact plant such as the stripping operation in the counter-current column is illustrated in Fig. 1, variations in composition are continuous from one end of the plant to the other. The material balances for the stripping section of the column in Fig. 1 are given by:

$$G(y_2 - y_1) = L(x_2 - x_1) \tag{1}$$

$$\left(\frac{G}{L}\right)_{min} = \frac{x_2 - x_1}{y_2^* - y_1} = \frac{x_2 - x_1}{mx_2 - y_1} \tag{2}$$

$$\left(\frac{G}{L}\right) = f * \left(\frac{G}{L}\right)_{min} \tag{3}$$

where G is the molar flow rate of the stripping gas (kmol/s) and L is the molar flow rate of the liquid phase (kmol/s). In Eq. (1), y_1 and y_2 represent the entry and exit mole fraction of oxygen component in stripping gas, and x_1 and x_2 are the exit and entry mole fraction of the oxygen component in water. All concentrations are in molar. In Eq. (2), y_2^* is the equilibrium point of x_2 and m is the Henry's constant, equal to 1.4576×10^4 at conditions of 15°C and 250 kPa [15]. In Eq. (3), f is the ratio of G/L to $(G/L)_{min}$. The value of G/L is important in the economics of absorption in a counter-current column. The oxygen-water system is a dilute solution, and is constant. The system is isothermal, so the Kremser equation is applicable. Thus, we obtain the following equation when A is not equal to 1:

$$N = \frac{1}{lnS} ln\left[(1-A)\left(\frac{x_2 - y_1/m}{x_1 - y_1/m}\right) + A\right] \tag{4}$$

where $A = \frac{L}{mG}$ and $S = \frac{1}{A}$.

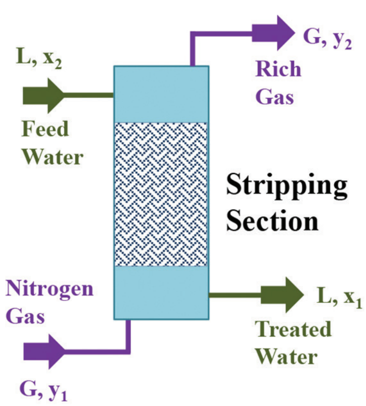

Fig. 1. Material balance diagram for a packed column.

2.3. Process description

The deoxygenation process may be either a linear or recyclic process, depending on the flow model of the stripping gas. Only the recyclic process is discussed in this report. The overall process comprises a nitrogen stripping section and a regeneration section. A typical deoxygenation process is shown in Fig. 2a in a commercial-scale plant. It consists mainly of a stripper, a heat exchanger, a reactor, and a reciprocating blower. Feed water flows into the mixing zone and merges with the stripping nitrogen gas. The oxygen is moved from the water to enrich the nitrogen. The nitrogen is then sent from the first stage tower to the regeneration system for purification using a catalytic combustion process, in which the oxygen is removed by preheating the nitrogen using either a heater or a gas-gas exchanger. Methanol is added to fuel the reaction, and the nitrogen-methanol stream is passed over the reactor. Oxygen is combusted producing water and CO_2,which eventually dissolves in the water [6]. The ultra-low oxygen nitrogen gas then passes through a blower to be pressurized, and finally flows back into the mixing zone for reuse.

Static mixers are efficient devices for physical or chemical transformations when accompanied by heat transfer, having high productivity and comparatively low energy costs [16]. The main features that have promoted the use of these devices in chemical, pharmaceutical, food processing, polymer synthesis, pulp and paper, paint, resin and water treatment are that they occupy only a small space, and have low equipment operation and maintenance costs, sharp residence time distribution, improved selectivity through intensified mixing and isothermal operation, by-product reduction and greater safety [17,18]. The driving force for the flow is provided by a compressor and air-driven booster [19]. The latter is a cost effective way of compressing ambient air or bottled gas to meet the range of requirements for higher pressure and lower volumes of air or gas [20,21]. Compared to multistage high pressure compressors, static mixers have the advantages of compact size, light weight, fewer moving parts and seals, less maintenance, and low noise. In addition, the heat exchanger maybe a shell-and-tube type or a plate-evaporator type. Performance results indicate that the overall footprint area is significantly reduced if a plate evaporator heat exchanger is adopted [22]. On that basis, an air booster static mixer and plate heat exchanger were selected for the design of a compact pilot plant. The pilot plant comprised the same subsections as a commercial scale plant, except that the second static mixer is located before the air booster to operate at lower pressures (Fig. 2b), which is beneficial for the stripping process.

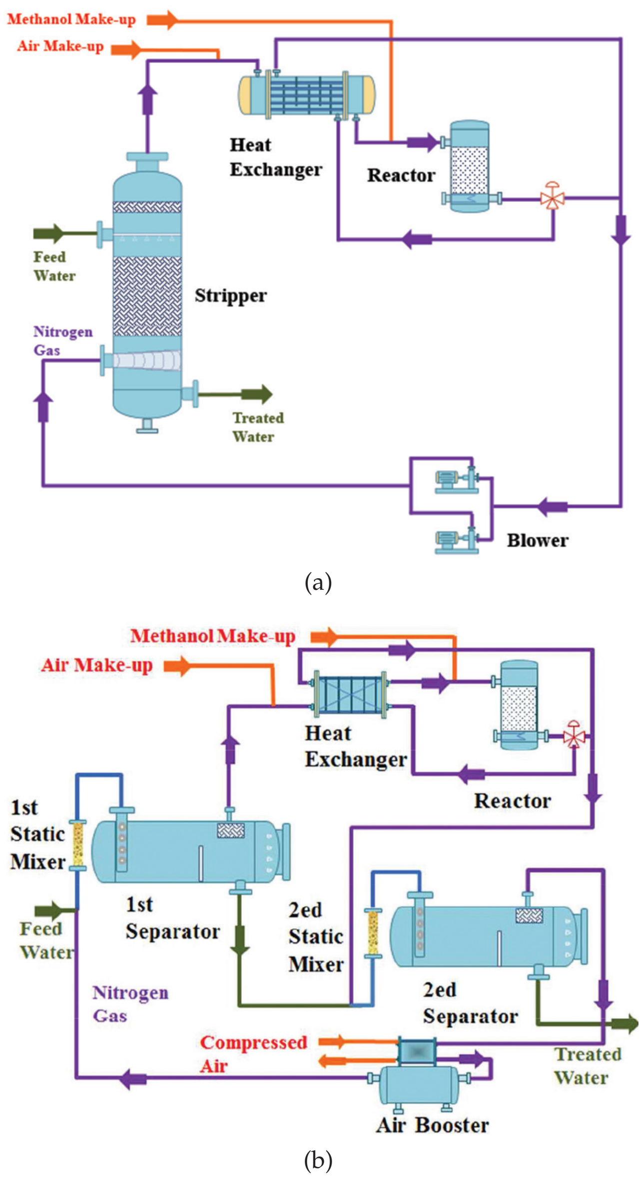

Fig. 2. Schematic flow diagram of deoxygenation: (a) commercial scale, and (b) pilot plant.

2.4. Process simulation

2.4.1. Selection of the thermodynamics method

An appropriate thermodynamics method must be chosen, because it directly influences the simulation results. As mentioned above, Henry's Law is applicable to the system, so an on random two liquid (NRTL) model was selected, being suitable for dilute systems and producing the required accuracy for a vapor-liquid equilibrium (VLE) system. Hysys incorporates Henry's Law automatically. The Peng-Robinson (PR) property model within Hysys applies a functionality to specific component–component interaction parameters. Key components receiving special treatment include N_2, CO_2, H_2O, and CH_3OH, etc, which were also present in the system. The process was modeled using the dual thermodynamic package NRTL-PR, with vapor phase non-ideality taken into account.

2.4.2. Establishment of unit models

The static mixer, plate heat exchanger, and separator were selected to be simulated using a build-in valve, separator and heat exchanger library models in Aspen Hysys v8.6. The process flow diagram of the deoxygenation process model is shown in Fig. S1. The fixed-bed catalytic reactor model was simplified by using a conversion reactor for which the conversion percentage is calculated by an adjusting unit.

Because an air booster replaced the compressor in the pilot plant, an air booster was modeled separately in Matlab Simulink. The feasibility analysis was considered by simulation. Matlab software provided a pneumatic actuation circuit demonstration model, which included a directional five-way valve, pipe, orifice, and double action pneumatic actuator unit. This model was modified for use in the present simulation, as described in Section 2.5.

2.5. Air booster model

The air booster was driven by compressed air supplied either by an available shop air or by an air compressor, rather than by an electrically driven compressor and blower. It mainly included pilot valves, check valves, air chambers, gas-air chambers, a piston and muffler, as shown in Fig. 3. When in operation, compressed air alternately flowed into the left- and right-hand air chambers with the flow direction controlled by pilot valves, simultaneously driving the reciprocal motion of the compressed air drive head and piston. The reciprocating motion of the piston caused the gas to flow from the low-pressure inlet to the high pressure node (outlet).

A stable and continuous flow rate is necessary for the stripping process, so a model of the gas booster system

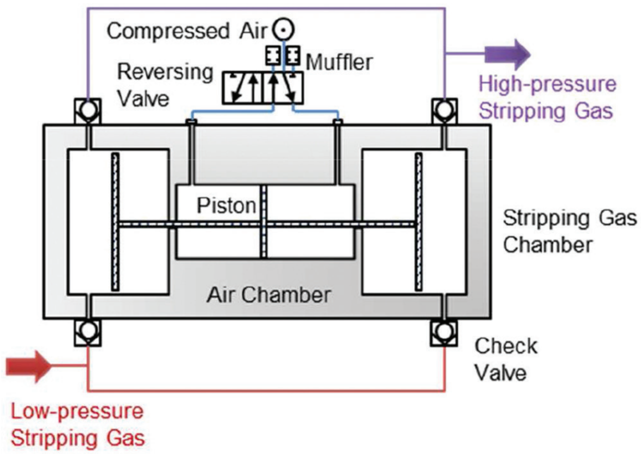

Fig. 3. Schematic of double-acting, single stage air booster.

was developed in Matlab Simulink was used to investigate the operation and check its applicability (Fig. S2). The air booster model network included mechanical units, thermal elements, logic operations, and signal blocks in the Matlab library. The model was functionally divided into two translational pneumatic piston chambers for air and process gas, respectively. The pneumatic piston chamber unit was based on the ideal gas law, comprising a continuity equation, an energy equation, and a force equation.

To simulate convectional heat transfer, a convective heat transfer element was used. Air flow reversal modeling incorporated a five-way directional valve system consisting of variable are a pneumatic orifices and logic operations, the control strategy being that the flow direction was reversed when the piston reached the ends of each chamber. The detailed description of the equations are available in Matlab Help and on the Math Works website https://www.mathworks.com.

3. Calculation results

3.1. Stripping unit

Before proceeding with the simulation, the primary boundary conditions were specified to ensure reasonable parameters and to assist in model convergence. The two boundary conditions to be confirmed were the oxygen content in the feed water (x_2) and the desired oxygen content in the treated water (x_1). Natural saturated oxygen concentration is approximately 10 ppmw at atmospheric pressure. As discussed above, the target for oxygen content was 20 ppbw in the treated water, which is sufficient to avoid corrosion and bacteria-plugging problems for water injection in oilfield use. The details of the feed water are listed in Table 1.

When the O_2 concentration (y_1) increased from 1 ppbw to 100 ppmw and f increased from 10 to 10000, the relationships between stage number (N), O_2 concentration (y_1) and ln(f) were as shown in Fig. 4. For stage number = 1, large stripping gas flow was needed, especially for high oxygen concentration. Therefore, log normal coordinates were used in Fig. 4 to conveniently plot the large f values.

Table 1
Design basis of feed water

Feed water parameters	Values
Flow rate (L), m^3/h	10
Temperature, °C	15
Pressure, kPa	250
Oxygen content (x_1), ppbw	20
Oxygen content (x_2), ppm	5.63

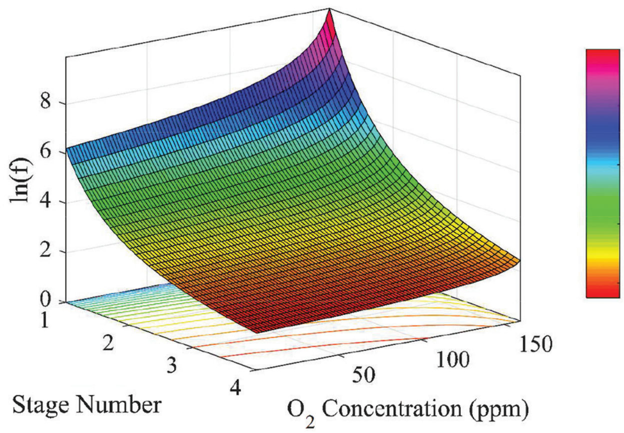

Fig. 4. Relationships between stage number, O_2 concentration, and ln(f).

For stage numbers ≥ 2, the required amounts of stripping gas were reduced drastically, hence linear coordinates was used in Fig. S3. Regardless of stage number, increasing the oxygen concentration led to a sharp increase in stripping gas as equilibrium was approached. Increasing the stage number decreased the stripping requirements, which implied high initial investment and a large space requirement; thus the design was a compromise between investment and operating costs. It is recommended that the number of stripping stages should be two, at which the oxygen content in the purified cycling gas is 100 ppm in molar fractions.

3.2. The influence of stripping gas mass flow

The effects of stripping gas mass flow on the O_2 concentration (x_1), make-up air, reactor temperature, and the conversion of methanol are shown in Fig. 5. Increasing G increases the G/L ratio while L remains constant, which reduced x_1 in the treated water and in the conversion of methanol and reactor temperature, however, the mass flow rate of the make-up air was almost constant. The stripping gas mass flow was higher than 40 kg/h, which had a limited impact on$x_1$inthe range of 10.1–8.3 ppbw, corresponding to methanol conversion in the range of 80.7–79.5% and reactor temperature in the range of 206–192°C.

The G/L ratio is important in the economics of stripping in a counter-current column. Increasing G/L increases the driving force in the column. However, using a larger amount of gas increases power consumption in the air booster

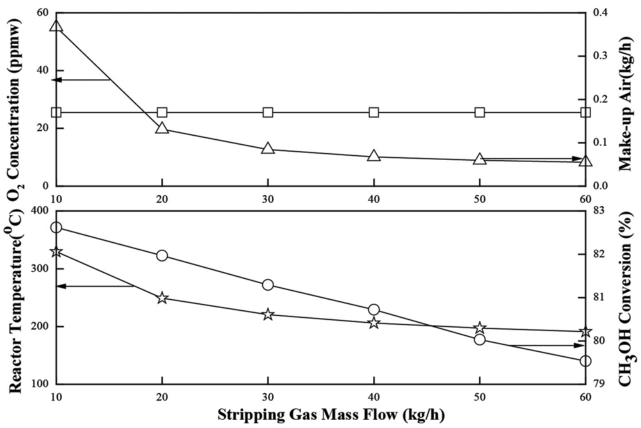

Fig. 5. Effects of stripping gas mass flow on the deoxygenation process.

and increases gas resistance, thus requiring a greater pipe diameter. The optimum stripping gas mass flow was 40 kg/h, obtained by balancing the operational costs for both units against the fixed costs of the equipment.

3.3. Influence of feed water temperature

In this case, the flow rates of the feed water and stripping gas, the pressure distribution of system, and the oxygen content of the purified stripping gas from the reactor remained constant at 10 m^3/h, 40 kg/h, and 250 kPa at the second separator for a pressure drop of 120 kPa and 100 ppmw.

The effect of the effluent temperature on the conversion of methanol, the flow rate of the make-up air, and the concentration of oxygen in the product water were studied. The results are presented in Fig. 6. When feed water temperature was increased, the effluent temperature and conversion of reactor decreased approximately linearly, as did the flow rate of the make-up air and the concentration of oxygen in the treated water. This indicated that a high temperature benefited the stripping process, and if lower oxygen concentration was desired, it was recommended that the feed water temperature be increased. In winter, despite seawater temperatures as low as 3°C, the oxygen concentration in the treated water still remained at less than 20 ppbw, as required.

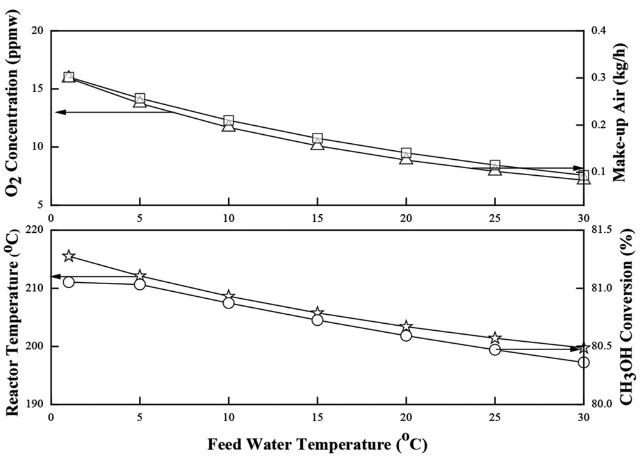

Fig. 6. Effects of feed water temperature.

3.4. Air booster

In Fig. 7, the plot of the reciprocating motion of the piston is approximately triangular and the flow curve is approximately columnar. The frequency is approximately 42/min. The position of the piston is located within the stroke distance. The stripping gas flow rate and the air consumption can be checked by frequency and chamber volume, which are available in the operation process. Because, as expected, the flow was not stable, a buffer tank was needed during the stripping process. The statistical flow rate of 11.26 kg/s was the numerical average of instantaneous flows.

Fig. 8 indicates that the flow rate of the air booster is mainly determined by the pressures of the compressed air, and by the pressures at the low pressure inlet and the

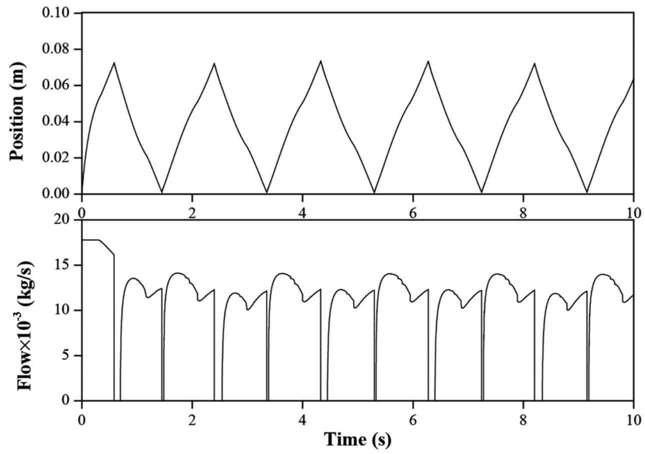

Fig. 7. Piston position (upper graph) and flow curve.

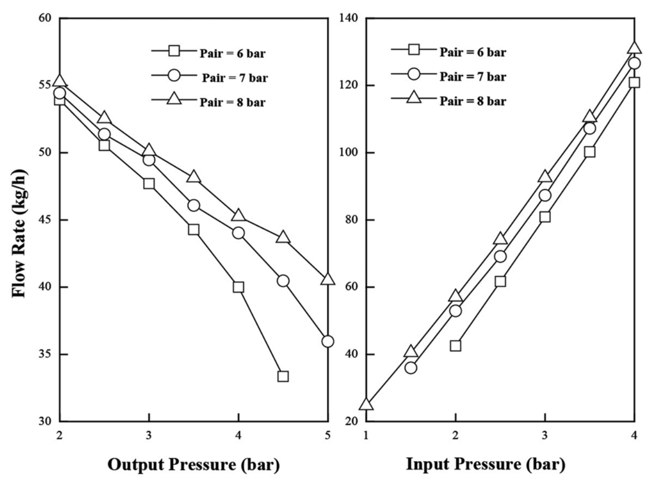

Fig. 8. The flow characteristic curve.

high pressure outlet. The flow rate increased linearly with increasing input pressure at the inlet. Conversely, increasing outlet pressure produced an almost linear reduction in flow rate. From this information, the desired operating pressures and flows may be obtained by the use of regulating valves.

4. Conclusions

A compact water deoxygenating pilot plant is proposed, utilizing a gas stripping process in which ultrapure nitrogen gas was used to remove dissolved oxygen from water. The air booster, static mixer, and plate heat exchanger were selected to design an innovative, compact, and lightweight system for deoxygenating water. The optimal parameters obtained from process simulation in Aspen Hysys were: capacity 10 m^3/h; concentration, 100 ppmw; and stripping gas mass flow, 40 kg/h. The treated water contained< 20 ppbw oxygen. Depending on the operating curve of the air booster, a buffer tank should be installed to produce stable flow rates. It should be noted that if the water quality varies, the dissolved oxygen level may also vary. The design should then be modified to meet special requirements, such as combining a stripping sub-process and a chemical reaction sub-process to take account of equipment investment and operating costs. The proposed design is capable of modification to meet practical pilot plant demands for reduction of the oxygen content in water.

Acknowledgements

The project was supported by Shanxi Province Key Laboratory of Higee-Oriented Chemical Engineering (No. CZL201508), Shanxi Province Foundation for Youths (No. 2015021056) and Science Foundation of North University of China (No. 110246, 110121).

References

[1] M.N. Tamburri, K. Wasson, M. Matsuda, Ballast water deoxygenation can prevent aquatic introductions while reducing ship corrosion, Biol. Conserv., 103 (2002) 331–341.
[2] D. Robinson, Oil and gas: Water treatment in oil and gas production-does it matter? Filtr. Sep., 47 (2010) 14–18.
[3] C.F. Tsang, J.A. Apps, Underground Injection Science and Technology, 5th edn., Elsevier, Amsterdam, (2005), pp. 204–214.
[4] R.W. Revie, H.H. Uhlig, Corrosion and Corrosion Control: An Introduction to Corrosion Science and Engineering, 4th edn., John Wiley, Hoboken, New Jersey, (2008), pp. 116–117.
[5] R. Heidersbach, Metallurgy and Corrosion Control in Oil and Gas Production, John Wiley, Hoboken, New Jersey, (2011), pp. 150–163.
[6] C.L. Deuel, Compact seawater deoxygenation system improvements for floating production facilities, SPE International Petroleum Conference and Exhibition, Mexico, (2002).
[7] I. Comanescu, R.E. Melchers, C. Taxen, Life time assessment of offshore water injection pipelines as a function of microbiologically influenced corrosion, Proc. 22nd International Offshore and Polar Engineering Conference, Rhodes, Greece, (2012).
[8] National Energy Administration, Water quality standard and practice for analysis of oil field injecting waters in clastic reservoirs, Petroleum Industry Press, Beijing, (2012).
[9] J.R.A. Peel, The mass transfer and hydrodynamics of a gas liquid centrifugal deoxygenator (PhD thesis), University of Newcastle-upon-Tyne, Newcastle, (1995).
[10] A. Lydersen, Method for the removal of oxygen from water, US Patent 4565634, (1986).
[11] I.M. Daniels, Developments in compact deoxygenation: The Minox 'compact tower' process. The 4th International Water Management Offshore Conference, Aberdeen, (1995).
[12] K.Y. Wu, A.T. Lee, L. Vuong, E.K. Liu, K.T. Chuang, Process and apparatus for removal of oxygen from seawater, US Patent 8449656, (2012).
[13] S.S. Jogwar, M. Baldea, P. Daoutidis, Dynamics and control of reactor-feed effluent heat exchanger networks, American Control Conference, Washington, (2008).
[14] http://www.minox.no/products-references/deoxygenation-process/.
[15] R. Battino, T.R. Rettich, T. Tominaga, The solubility of oxygen and ozone in liquids, J. Phys. Chem. Ref. Data, 12 (1983) 331–341.
[16] A. Ghanem, T. Lemenand, D.D. Valle, H. Peerhossaini, Static mixers: Mechanisms, applications, and characterization methods-A review, Chem. Eng. Res. Des., 92 (2014) 205–228.
[17] R.K. Thakur, C. Vial, K.D.P. Nigam, E.B. Nauman, G. Djelveh, Static mixers in the process industries-A review, Chem. Eng. Res. Des., 81 (2003) 787–826.
[18] S. Ferrouillat, P. Tochon, C. Garnier, H. Peerhossaini, Intensification of heat transfer and mixing in multifunctional heat exchangers by artificially generated streamwise vorticity, Appl. Therm. Eng., 26 (2006) 1820–1829.
[19] Y. Shi, Y. Wang, H. Liang, M. Cai, Power characteristics of a new kind of air-powered vehicle, Int. J. Energy Res., 40 (2016) 1112–1121.
[20] Z. Li, Y. Zhao, L. Li, P. Shu, Mathematical modeling of compression processes in air-driven boosters, Appl. Therm. Eng., 27 (2007) 1516–1521.
[21] Y. Shi, M. Cai, Working characteristics of two kinds of air-driven boosters, Energy Convers. Manage., 52 (2011) 3399–3407.
[22] Z. Ge, C. Yang, Y. Liu, X. Du, L. Yang, Y. Yang, Analysis of plate multi-effect distillation system coupled with thermal power generating unit, Appl. Therm. Eng., 67 (2014) 35–42.

Supplementary data

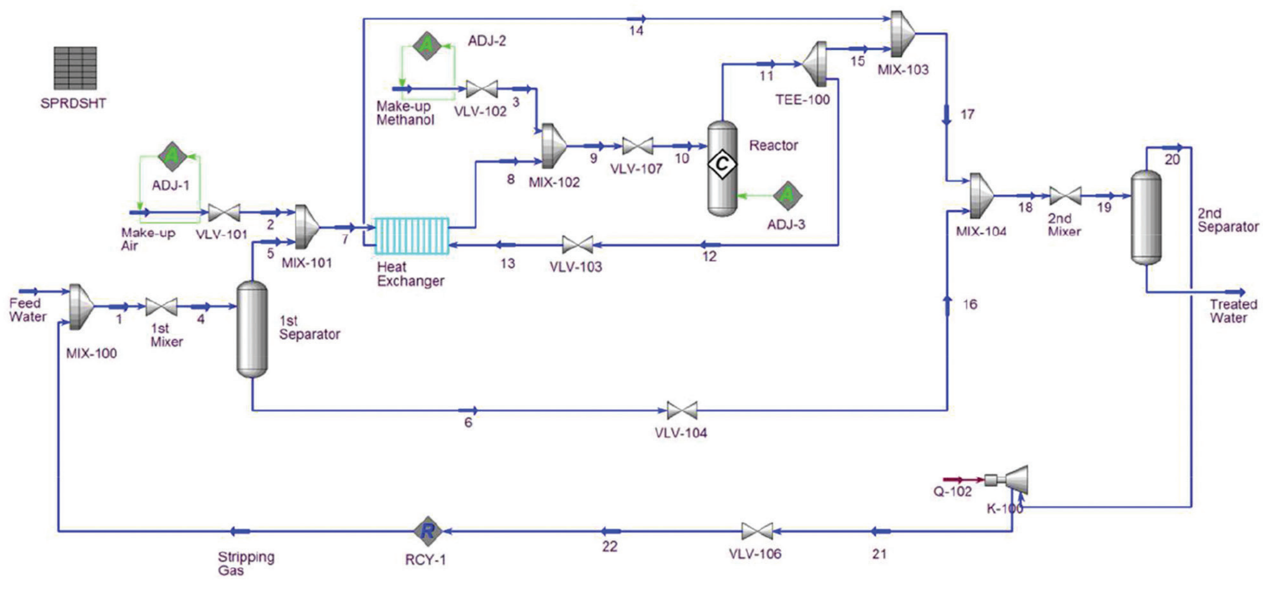

Fig. S1. The process flow diagram of deoxygenation process in HYSYS.

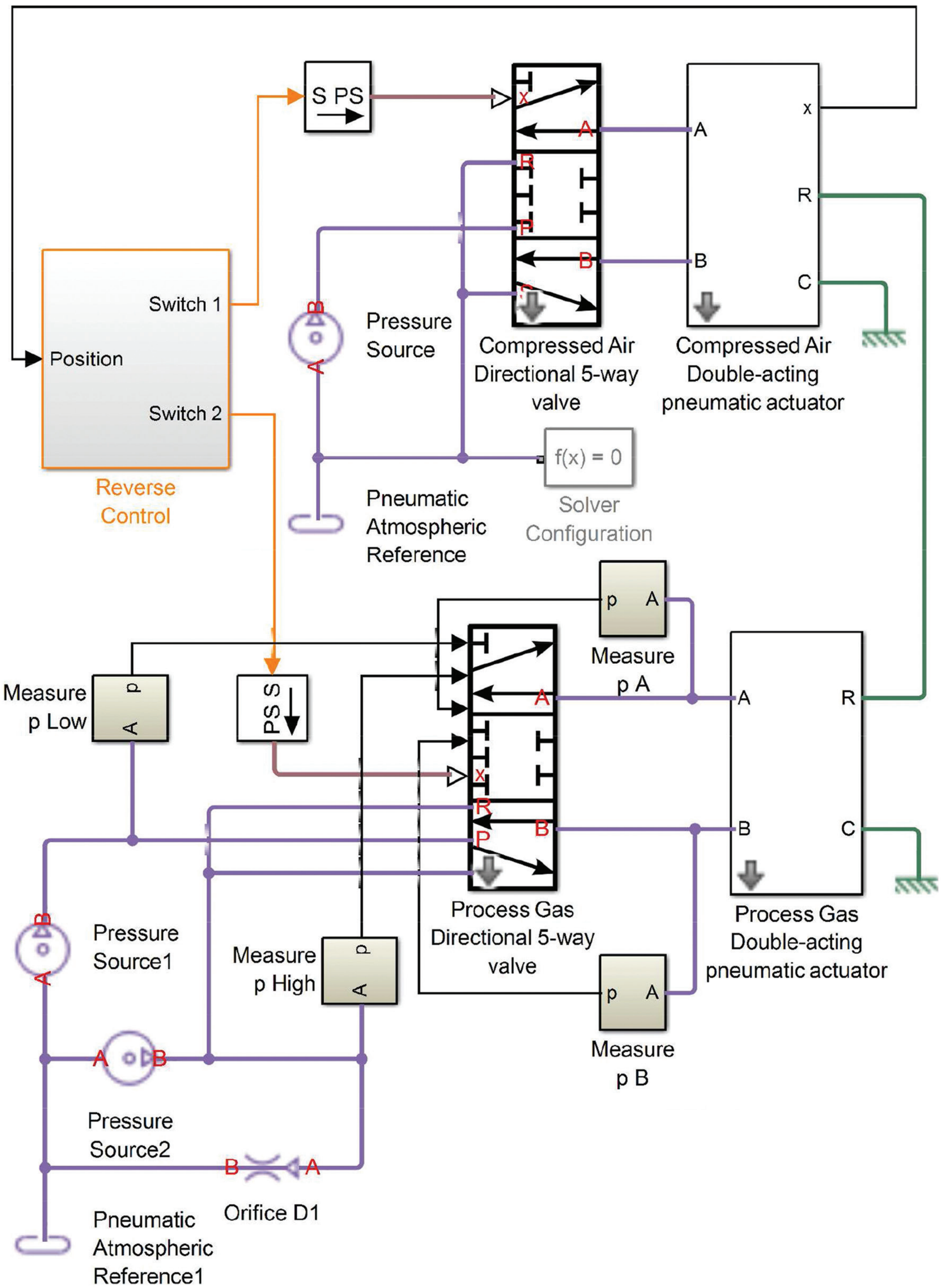

Fig. S2. The process flow diagram flowsheet of air booster in Simulink.

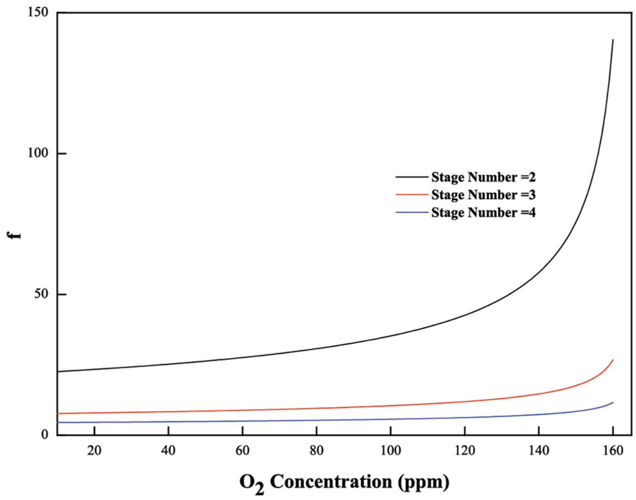

Fig. S3. The relations among stage number, O_2 concentration and ln(f).