CHEMICAL ENGINEERING TRANSACTIONS

VOL. 88, 2021

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Petar S. Varbanov, Yee Van Fan, Jiří J. Klemeš

ISBN 978-88-95608-86-0; **ISSN** 2283-9216

DOI: 10.3303/CET2188036

Comparison of Equilibrium-Stage and Rate-Based Models of a H_2S Scrubber for Purification of Coke Oven Gas

Nikolett Rado-Foty[a], Attila Egedy[a,*], Lajos Nagy[a], Ivan Hegedus[b]

[a] Univ. of Pannonia, Dep. Process Engineering, Egyetem St. 10., 8200 Veszprém, Hungary
[b] ISD Kokszoló Kft., Vasmu Sq. 1-3., 2400 Dunaújváros, Hungary
egedya@fmt.uni-pannon.hu

In recent years, one of the most important challenges worldwide is to meet increasingly stricter environmental regulations while maintaining the profitability of plants. Modelling particular parts of existing technologies can help efficient operation, reduce energy consumption, minimize emissions, and keep operating costs low. Furthermore, adequately validated models provide the opportunity to examine different equipment designs, operating parameters side by side without hindering the technological process. The coke oven gas purification technology of a Hungarian coke oven plant was studied in this research work. As a by-product of coke production, approximately 40,000 - 60,000 m^3 crude coke oven gas is generated every hour, which has to be cleaned before being used for energy purposes. First, the cooled crude coke oven gas is fed into the hydrogen sulfide scrubber in a counter-current flow. Then, the hydrogen sulfide is absorbed in an ammonia-rich washing liquid coming from the following two ammonia scrubbers. In this study, two mathematical models, equilibrium-stage and rate-based models, were used to simulate the removal of H_2S from coke oven gas in the Aspen Plus process simulator program. The validation of the models was performed by using the operating measurements of the outlet streams. The results closely approximate the measured composition of the outflows. However, the simulation results predicted by the rate-based model show better agreement than the equilibrium model compared with the experimental data. With the use of the rate-based model, a sensitivity analysis was made, taking into account the parameters that have a tremendous impact on the cleaning process and can also be controlled by appropriate intervention. The creation of this model was the first step in building the simulation of the entire gas purification process, which will be used to optimize the operation and create an operator training system.

1. Introduction

In the past, coke oven plants have frequently caused severe pollution problems. Although the emission of coking plants is still unavoidable, national and international agreements were concluded to prevent and control pollution arising from industrial activities. European Directive lays down rules to prevent, or, where that is not practicable, to reduce emissions to achieve a high level of environmental protection (Directive 2010/75/EU, 2010). The Commission Implementing Decision establishing the Best Available Techniques (BAT) conclusions on industrial emissions for iron and steel production, including coke oven plants. It specifies the standards for the coke oven gas (COG) as well. The residual H_2S concentration in cleaned coke oven gas must be < 300 – 1,000 mg/Nm^3 using an absorption system and < 10 mg/Nm^3 using wet oxidative desulphurization. Moreover, it fixes that using cleaned coke oven gas, the emission level is < 200 -500 mg/Nm^3 for SO_x and < 350 – 650 mg/Nm^3 for NO_x (Commission Implementing Decision 2012/135/EU, 2012).
Coke is a primary raw material of the iron and steel industry and is produced by high-temperature pyrolysis of coal blends. A significant amount of raw coke oven gas is generated during the coking process, which can be considered a by-product or a waste gas used as an energy substitute for natural gas. The quality of the coal blend determines the composition of both the coke and the gas, so moisture, ash, volatile, sulphur and special coal quality parameters (e.g. dilatation, swelling index) must meet the prescribed criteria (Babich and Senk, 2019). The raw coke oven gas, collected from coke oven chambers, mainly contains coal tar, water, light oil (benzene, toluene, xylene and other aromatic hydrocarbons) and impurities like NH_3 H_2S or HCN, which have

Paper Received: 4 June 2021; Revised: 20 August 2021; Accepted: 3 October 2021
Please cite this article as: Rado-Foty N., Egedy A., Nagy L., Hegedus I., 2021, Comparison of Equilibrium-Stage and Rate-Based Models of a H_2S Scrubber for Purification of Coke Oven Gas, Chemical Engineering Transactions, 88, 217-222 DOI:10.3303/CET2188036

to be removed. Firstly, the gas is precooled, so coal tar and water are separated from the gas. Next, the gas is passed through electric precipitators to remove fine drops of tar and coolers. Then the impurities are removed in an absorption section. Finally, the light oil is recovered in washing towers, and the cleaned gas can be used partly to heat the coke oven chambers, and the rest is burned in gas engines. The cleaned coke oven gas consists of mainly hydrogen and methane, which has a high net calorific value. Therefore, it can be used as a fuel in boilers and oven firing systems in different parts of integrated steel plants. Thus natural gas consumption can be reduced, making the whole steel production more economically and environmentally sustainable (Porzio et al., 2014).

Aqueous ammonia absorption is the most widely used technology in plants operating in America and Europe for removing the impurities from coke oven gas. However, it appears that the trend for new operations is toward the use of other, more efficient absorbents (e.g. Takahax, Stretford, Sulfiban process etc.). The developed, new processes can be designed to avoid adverse effects of trace impurities in the gas and provide higher removal efficiency (Kohl and Nielsen, 1997). Though in the case of existing plants, the changeover and installation of these new processes is relatively costly and often unfeasible because of the continuous operation and the lack of free area in the plant. One hour of malfunction in the gas purification technology can cause approximately 15% extra cost, not to mention the environmental impact. Improving the existing coke oven gas purification unit is frequently required, which is often not to upgrade the process and equipment of the technology but to optimize and adequately manage the process. Implementing these possible solutions can be significantly assisted by flowsheet simulators, which can be valuable for existing installations. They can find the optimal mode of operation of technology and train the operational staff (Komulainen et al., 2012). Furthermore, a detailed and validated process simulator helps understanding general and specific features of technology behaviour. As a result, the number of experiments could be reduced, and process operation could be supported effectively (Chaves et al., 2016). However, creating the simulation of this system is complicated since the purification of this gas represents a complex multi-component separation process combined with countless parallel chemical reactions.

Several studies focus on the development of coke oven gas purification technology, but only a few concerning modelling, simulation or optimization. A German research group developed a rigorous dynamic two-phase model based on two-film theory and carried out steady-state and dynamic experiments in a pilot-scale gas scrubber, which were in good agreement with experimental data (Mayer et al., 1999). Another German research team investigated and simulated the chemical absorption for the system NH_3-CO_2-H_2S-NaOH-H_2O. The system was described with a non-equilibrium heat and mass transfer model, validated by experimental studies. The developed model can be extended easily to include other reactive components like monoethanolamine (MEA) or methyl diethanolamine (MDEA). In terms of selective removal of H_2S, an optimal pH range was derived (Thiele et al., 2004). A few years later, this research group developed a rate-based model for a coke oven gas purification process and investigated the multi-component mass transfer of the impurities in aqueous potassium hydroxide (KOH) or potash (K_2CO_3) solutions. Their model was validated using data obtained from a pilot plant and from industrial measurements. Moreover, the industrial process was systematically optimized using evolutionary algorithms, which resulted in a decrease of 30% in operating costs while still complying with the restrictions for the gas outlet concentration (Thiele et al., 2007).

A Brazilian research team developed a model to evaluate solutions that allow greater removal of H_2S from coke oven gas. For model validation, data from an industrial plant was used. Three different process configurations were tested, and the best one represented a 5% increase in removal efficiency. That improvement can allow for the use of coal with a higher sulphur content (Carneiro et al., 2020).

In this study, an industrial plant's purification technology is studied to understand better this complex separation process, which is a necessary step for creating the process simulator of the technology. Creating the process simulator is challenging due to the lack of technical information and the limited measured data. Furthermore, the design of the scrubber and the packing are unique, so the parameters from the databank of the commercial software are not suitable for this technology. Nevertheless, creating a good process simulator can help optimize the operation (e.g. optimized amount of deacidified water can decrease the energy demand of the pumps) and provide constant gas composition even under changing conditions. Thus coke oven gas can be used in the other parts of the integrated steel plant, and the use of natural gas can be decreased.

1.1 Chemical reactions

The following parallel reversible liquid-phase reactions were taken into account:

$$2\,H_2O \leftrightarrow \mathrm{H_3O^+} + OH^- \tag{1}$$

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \tag{2}$$

$$H_2S + H_2O \leftrightarrow HS^- + H_3O^+ \quad (3)$$

$$HS^- + H_2O \leftrightarrow S^{2-} + H_3O^+ \quad (4)$$

$$HCN + H_2O \leftrightarrow CN^- + H_3O^+ \quad (5)$$

$$CO_2 + 2\,H_2O \leftrightarrow HCO_3^- + H_3O^+ \quad (6)$$

$$HCO_3^- + H_2O \leftrightarrow CO_3^{2-} + H_3O^+ \quad (7)$$

$$NH_3 + HCO_3^- \leftrightarrow NH_2COO^- + H_2O \quad (8)$$

Eqs(6-7) obey first and second-order kinetics, while the other reactions are based on simple proton transfers. Thus they can be regarded as instantaneous by the corresponding mass action law equations. The selectivity of the purification process significantly depends on choosing and providing the right conditions for the required reactions (Kohl and Nielsen, 1997). CO_2 is also a major impurity in the coke oven gas, but it is unnecessary to remove gases used as fuel. The partial removal of CO_2 is beneficial to improve the heating value of the gas, while complete CO_2 elimination is desirable for gases undergoing processes at very low temperatures (e.g. gas purification to provide clean hydrogen for ammonia synthesis). However, removing the other impurities is necessary when the concentration is high enough to cause pollution, not to mention operating problems such as corrosion, deposition or plugging (Kohl and Nielsen, 1997).

1.2 Gas purification technology

In this study, the H_2S scrubber of a Hungarian coke oven plant was investigated. This scrubber is the first unit of the coke oven gas purification process. Therefore, for understanding the input streams, the whole purification technology has to be described.

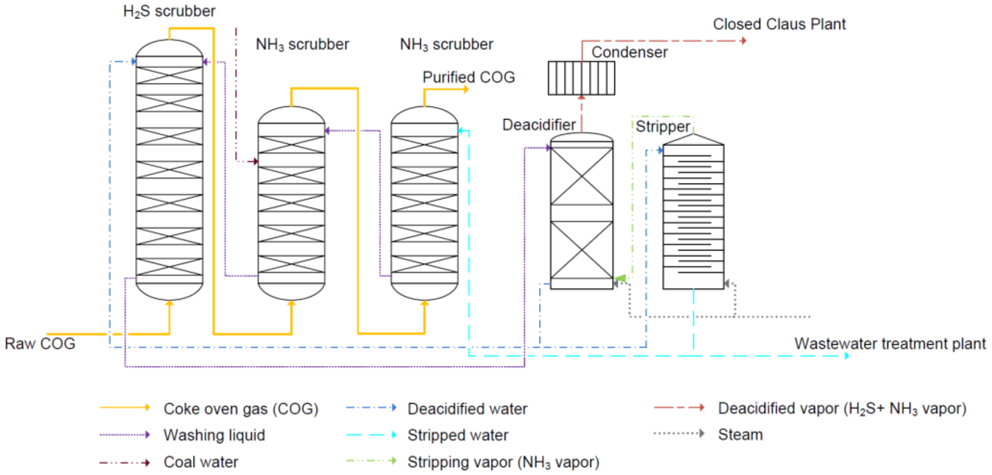


Figure 1: The coke oven gas purification technology

As Figure 1 shows, the cooled raw coke oven gas is passed through three scrubbers (a H_2S scrubber and two NH_3 scrubbers) in a series arrangement, in which the gas and the washing liquids are in counter-current flow. The washing liquid, leaving the towers, is regenerated firstly in a deacidification column and secondly in a stripping column. The bottom product of the deacidification column is called deacidified water, and a certain amount of it is fed to the H_2S scrubber. The head product of the deacidification column is fed to the stripping column. The stripped water leaves the column at the bottom and is partly fed to the second NH_3 scrubber, and the surplus is transferred to the waste treatment plant. The vapour fraction of the stripping column is fed to the closed Claus technology, where it is passed through a crack reactor, two catalytic reactors, and sulphur separators. Water from the moisture content of the coal blend (coal water) is also added to the first NH_3 scrubber.

2. Process modelling

During this research work, the aim was to create the stationary model of the H_2S scrubber. The model was built using the Aspen Plus process simulator program, which is widely used in the commerce and scientific fields. It was validated with industrial data from a Hungarian coking plant. In the introduced purification process, there is a large amount of electrolytes in the liquid phase. Due to the strong intermolecular interaction between these electrolytes, the liquid phase is strongly non-ideal. The Electrolytic Non-Random Two-Liquid (ENRTL) model was used for evaluating the behaviour of the liquid phase. This excess Gibbs energy model implements a rigorous thermodynamic framework for calculating various electrolyte thermodynamic properties, such as osmotic coefficients, average ionic activity coefficients and fugacities (Chen and Song, 2004). The Henry constants for every component were taken from the databank of Aspen Plus. In the model, Eqs(1-8) reactions were considered. Only a few research works concern coke oven gas purification modelling, but two approaches are available for modelling absorption, equilibrium-stage model and rate-based model. The equilibrium-stage model is based on the assumption that the gas and liquid streams leaving any particular stage are in equilibrium with each other. However, equilibrium can be rarely reached, so the usual way to deal with departure from equilibrium is to incorporate stage efficiency (Ramesh et al., 2007). On the other hand, gas and liquid phases are balanced separately by considering mass and heat fluxes across the interface in the rate-based approach. It requires physical properties, reaction rate parameters and column specific data and avoids the approximation of efficiency entirely. Furthermore, it takes into account reaction kinetics, thus mainly depends on residence time. (Afkhamipour and Mofarahi, 2013). In this study, these approaches were examined to determine which model is the most adequate for this complex technology.
The H_2S scrubber was built according to the information collected in Table 1 and Table 2.

Table 1: Specification of the scrubber

	H_2S scrubber
Number of stages	16
Diameter (m)	3.56
Packing type	SHEET-PACK
Packing material	Metal
Packing dimension	350Y
Total height (m)	32
Total pressure drop (mbar)	1.35

Table 2: Input parameters

	COG	Washing liquid	Deacidified water
Temperature (°C)	24	21	24
Pressure (bar)	1.168	1.138	1.140
Flow rate (m^3/h)	46,190	44	60
Composition (kg/h)			
H_2O	-	43,055.76	58,113.05
H_2	2,700.84	-	-
NH_3	73.47	516.12	1,422.29
H_2S	341.20	33.00	81.27
CO_2	1,920.63	395.12	379.81
HCN	12.21	-	3.59
CO	2,567.05	-	-
CH_4	8,366.47	-	-
C_2H_6	2,034.02	-	-
N_2	2,886.90	-	-

3. Results

Both the equilibrium-stage model and the rate-based model were created with input streams data from Table 2. The concentration profiles of the three main impurities in the gas phase, along with the scrubber, are shown in Figure 2. A break-point can be observed at stage 6, caused by the introduction of deacidified water at that point. As the charts show, there is a significant difference between the two concentration profiles.

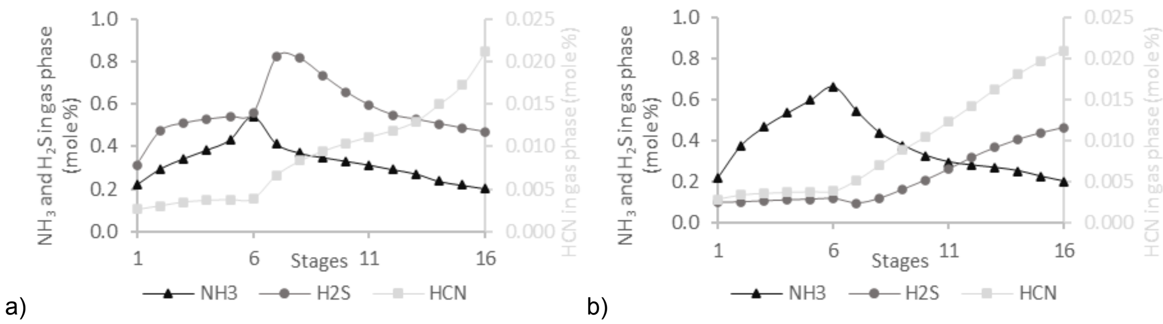


Figure 2: Concentration profile by the equilibrium-stage model (a) and rate-based model (b)

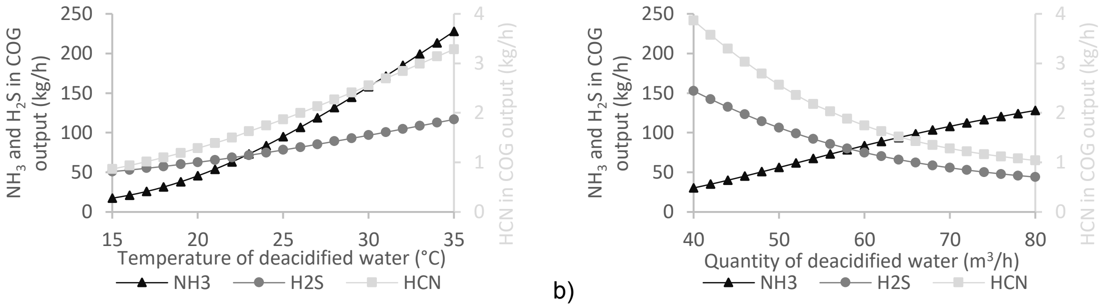
However, in the H_2S profile, there is a difference between the trends and quantities. Using the equilibrium-stage model, the amount of H_2S is increasing along the column instead of decreasing. Unfortunately, the gas flow was sampled only at 3 points along with the scrubber; adding more measurements points will increase the reliability of the data. Therefore, the technical implementation is in progress to sample the gas at more points along the column simultaneously, which would give a more reliable representation of the concentration profiles. Table 3 shows the impurities in the output coke oven gas stream, measured and calculated with two mathematical models. The measured values are averages for the impurities. The results of the equilibrium-stage model were just slightly different from the measured concentrations, except for the amount of H_2S, which was significantly higher than the measured value. Due to the equilibrium circumstance, CO_2 could absorb in the washing liquid better than H_2S. We also show the results without CO_2, and it shows that without CO_2, the amount of H2S is significantly decreased in the output gas stream. However, the other two component flows are larger than the measured. Using a rate-based model, the problems were eliminated, and the concentration results of the components closely approximate the measured values.

Table 3: Measured and calculated results of the impurities in the output coke oven gas

Mass flow (kg/h)	Measured results	Equilibrium-stage model results	Equilibrium-stage model results without CO_2	Rate-based model results
NH_3	85.91	84.27	162.04	83.67
H_2S	75.74	238.92	62.20	74.81
HCN	1.75	1.59	2.69	1.74

3.1 Sensitivity analysis

To perform detailed studies on the system, the Aspen simulator and MATLAB were connected. This step is beneficial since it makes it easier to examine different parameters over a wide range of intervals. Furthermore, the simulator results can be saved and evaluated through MATLAB than with the Aspen Plus sensitivity analysis tool. To better understand the purification process, sensitivity analyses were made. For the sensitivity analysis, the most influential parameters were implemented. These were the quantity and the temperature of the input flows because these parameters can be modified easily, except the quantity of coke oven gas. It depends on the coal blend and cannot be controlled. Additionally, the composition of input streams was examined since they may change due to the different operation conditions.
Among the parameters studied, only the temperature and quantity of deacidified water on impurities in COG output flow are introduced in this article as examples. Figure 3 shows the achieved results.



a) b)

Figure 3: The effect of the temperature (a) and the quantity (b) of deacidified water on impurities in COG output flow

As Figure 3a shows, the higher the temperature of the deacidified water, the higher the amount of impurities in the output flow of coke oven gas. That means the rising temperature of the deacidified water is not beneficial for the purification process. Therefore, especially in summer, special attention must be paid to the temperature of the input deacidified water. There is a non-linear relationship between concentration and temperature, so it is necessary to find the optimum temperature that is economically and technologically feasible while keeping the harmful components low. As Figure 3b shows, increasing the quantity of the deacidified water causes the decrease of H2S and HCN in output coke oven flow but increases NH_3. It is caused since deacidified water contains relatively large quantities of NH_3, which desorbs to the gas. The amount of ammonia is reduced in the following two absorbers, as shown in Figure 1. Thus this growth might not cause emission problems. However, choosing a lower volume of deacidified water is recommended, as a higher pump delivery capacity is required, increasing operating costs.

4. Conclusions

This study used the equilibrium-stage model and rate-based model to simulate the H_2S scrubber used for the coke oven gas purification process in a Hungarian coke oven plant. It was created with the help of the Aspen Plus process simulator program, and it was validated by using the operating measurements of the output streams. The simulation results predicted by the rate-based model show a higher level of agreement than the equilibrium-stage model compared with the experimental data. Compared to the results calculated with the rate-based model and the measured values, the difference was 2.6 % for NH_3, 1.2 % for H_2S and 0.6% for HCN. Then a sensitivity analysis was made, taking into account the parameters that have a particularly large impact on the process and can also be controlled by appropriate intervention. That is why the effect of the temperature and quality of deacidified water were presented as examples. Based on these results, the rate-based model will be used for creating the other two scrubbers of the technology. The sensitivity analysis can be extended for the whole process, which will be beneficial for the optimization task. As the steady-state model of the technology is working properly, the dynamic model can be built. With the help of this tool, the technology can be operated more consciously, and the occurrence of breakdowns and malfunctions can be significantly reduced.

Acknowledgements

Prepared with the professional support of the Doctoral Student Scholarship Program of the Co-operative Doctoral Program of the Ministry of Innovation and Technology financed from the National Research, Development and Innovation Fund.

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