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Conceptual design of a modified phenol and ammonia recovery process for the treatment of coal gasification wastewater

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HIGHLIGHTS

- The new process utilizes low-pressure steam instead of medium-pressure steam.
- The conceptual design of the new process is suggested based on simulation results.
- The binary interaction parameters between ammonia and phenol are regressed.

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ABSTRACT

This paper proposes an improved process for phenol and ammonia recovery, which mainly utilizes low-pressure steam (LPS) for treating industrial coal-gasification wastewater. A conceptual design of the proposed process is suggested based on simulation results. To improve the accuracy of the simulation, binary interaction parameters between ammonia and phenol are regressed. It is expected that the performance of the new process is better, where the concentrations of phenol, total phenols and COD can be reduced to approximately 15 mg/L, 240 mg/L and 240 mg/L, respectively. Upon implementation of the new process, the total consumption of steam is lower, and most of the medium-pressure steam (MPS) can be replaced by LPS. Therefore, the financial investments by the factory will be greatly reduced, causing a significant increase in profits.

1. Introduction

At present, approximately 30 large-scale coal chemical factories are expected to convert the use of more than 300 million tons of low-rank coal per year into alternate fuel sources. In the process of coal conversation, Lurgi fixed bed gasifiers, such as the Mark IV, have been demonstrated to be reliable and beneficial for low-rank coal conversion. These gasifiers are widely used in the chemical industry, and play an important role in the energy supply in China. However, using Lurgi gasifiers for low-rank coal gasification produces a considerable amount of organic wastewater, which is not easily biodegradable. According to industrial data, the conversion of 1 ton of coal produces approximately 0.8–1.1 tons of wastewater. Coal gasification wastewater generally contains various pollutants, such as phenols, ammonia, hydrogen sulfide, carbon dioxide, oil, and fatty acids. The total concentrations for phenol, ammonia and chemical oxygen demand (COD) of the wastewater are typically above 5000, 6000 and 20,000 mg/L, respectively. Hence, the phenol and ammonia recovery (P&AR) process is adopted to improve the biodegradability of the wastewater and recover valuable by-products, such as raw phenol and ammonia. The P&AR process consists of stripping and extraction units and is specifically used to remove most ammonia, phenols, carbon dioxide, and hydrogen sulfide from the wastewater. Several types of P&AR processes are currently being used. For example, the Phenosolvan™ phenol recovery process [1] and the CLL™ ammonia recovery process have been effectively implemented for more than 30 years in Sasol at Secunda, South Africa. According to experimental results [2,3], the removal performance of phenol is strongly affected by the pH value of wastewater. However, because phenol extraction is performed before ammonia stripping, and the pH value of the wastewater is more than 8.5 resulting in the decrease of phenol removal. Therefore, there is additional room for improving the removal performance of phenol.

In some factories, the phenolic contaminants in the wastewater are very difficult to remove. The total phenol content and the COD are too high, even after treatment through processes similar to the

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Phenosolvan™ process. Treating wastewater and meeting the discharge standards by biological treatment methods remain difficult. To improve the removal performance of phenols and COD, several types of improved P&AR processes have been proposed in previous works [4–6], where ammonia stripping is performed before phenol extraction. After ammonia stripping, industrial process data has shown that the pH of the wastewater can be reduced from ⩾8.5 to ⩽6.5. This is because of high concentrations of fatty acids, such as acetic acid and propionic acid. When the pH value is less than 8, the dissociation of the phenols in the wastewater sharply declines. Compared with the performance by the Phenosolvan™ or other similar P&AR processes, the phenol removal performance in the wastewater can be significantly improved.

The P&AR process techniques, as proposed in our previous works [4–6], are currently applied in approximately 30 sets of industrial units. The total annual treatment capacity for the coal gasification wastewater is over 60 million tons. Although the process techniques work effectively in recovering phenols and ammonia, the energy consumption is still high. The steam consumption for 1 ton of wastewater is 280–350 kg, of which steam with a pressure of ⩾1.0 MPag (hereinafter referred to as the medium-pressure steam, MPS) is over 180 kg.

In the coal gasification plants that use the Lurgi gasifiers, low-pressure steam with a pressure of ⩽0.5 MPag (hereinafter referred to as low-pressure steam, LPS) is produced from the waste heat boilers. This steam is combined with the coal gasifiers and is a surplus. Because it cannot be efficiently or fully utilized, a power plant equipped with LPS electricity generators must be constructed. Such construction efforts are bound to cause a large increase in investment, with low proceeds. In addition, MPS must be drawn directly from steam boilers. The demand and supply of LPS and MPS is not reasonable. Therefore, the development of a new P&AR process, which mainly uses LPS, can greatly increase the economic efficiency of these plants. The growth of the low-rank coal conversion industry (since 2005) in various countries, such as China, Indonesia, and Vietnam, will provide significant economic benefits with the application of the new process technique.

In the past 40 years, the technology of chemical thermodynamics for process simulations has developed significantly. And several electrolyte activity coefficient models have been proposed for aqueous solutions with volatile weak electrolytes. Many of them have been shown to be effective and accurate [7–11]. In particular, the electrolyte non-random two liquid (ELECNRTL) model is universally recognized. When the ELECNRTL model is used to describe a non-ideal system, the binary interaction parameters are regressed from actual or experimental phase equilibrium data. However, there were few studies between 1980 and 2005 on coal gasification wastewater. This was because there were only a few coal chemical factories that used low-rank coal as raw material. In addition, the development of this technology was slow. Many important parameters, such as the binary interaction parameters for the wastewater system, have not been determined or regressed. It causes that the simulations probably deviate seriously from actual data. Therefore, the accuracy of the simulations for industrial coal gasification wastewater treatment units needs to be improved further. These tasks should promote the simulation, design, and optimization of the treatment process of coal gasification wastewater.

2. Steam production and demand in the Lurgi gasifier modules and the P&AR units

A typical Lurgi gasifier (Mark IV) module is shown in Fig. 1. The raw gas produced in the gasifier flows into the quench cooler where it is washed and cooled down to 190–210 °C. A part of the quench water changes into steam. Next, the mixture of raw gas and steam flows into the waste heat boiler. In the boiler, heat is exchanged between the mixture and boiler feed water. As a result, part of the boiler feed water evaporates and flows into the LPS pipe network. A part of the gas liquor from the bottom of the waste heat boiler is initially pumped into the following gas liquor separation unit. In the separation unit, the fuel gas and most of the oil in the wastewater are removed. This gas liquor is then pumped into the P&AR unit.

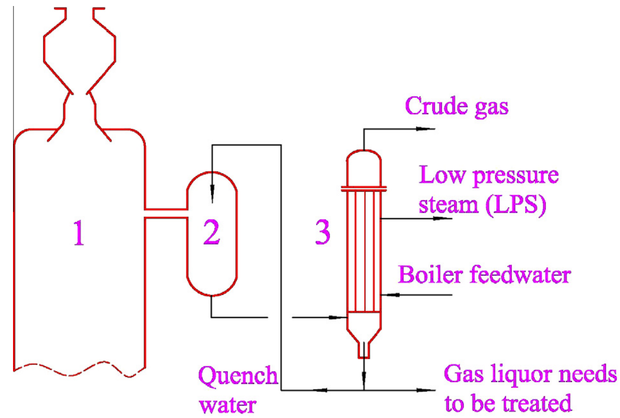

Fig. 1. Lurgi gasifier and waste heat recovery system schematic flow sheet: 1: Lurgi gasifier; 2: quench cooler; 3: waste heat boiler.

A typical synthetic natural gas (SNG) factory has an annual production capacity of 4 billion normal cubic meters. Using lignite as raw materials, approximately 1900 tons of wastewater is produced and needs to be treated by the P&AR unit on site. The actual supply and demand data for LPS and MPS are collected and shown in Fig. 2. Approximately 390 ton/h MPS is needed by the phenol and ammonia units. MPS is usually drawn from the steam boilers, which are located far from the gasifier module. A large amount of LPS, nearly 668 ton/h, is produced as surplus.

3. Analysis of the current P&AR processes

The quality data of wastewater to be treated by the P&AR unit are shown in Table 1. Before the wastewater is treated by the biochemical treatment process, the concentrations of total phenol, ammonia, and hydrogen sulfide should be reduced to less than 500, 150, and 50 mg/L, respectively.

In our previous work, several types of improved P&AR processes were proposed. One of the most widely used processes is shown in Fig. 3. In this process, which includes the sour water stripper T1′, the sour gas and ammonia are simultaneously stripped out from the wastewater. The side draw of T1′, which mainly contains raw ammonia gas and steam, is partially condensed three times to

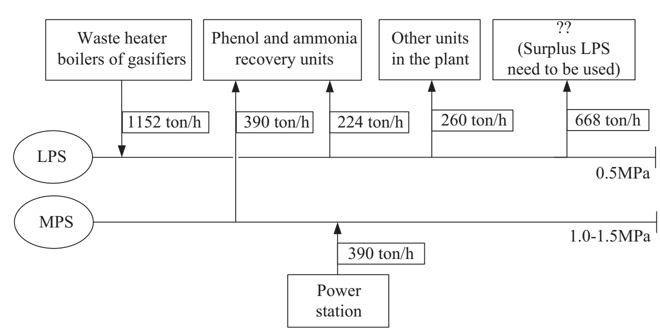

Fig. 2. Steam supply and demand in the Lurgi gasifier modules and the P&AR units.