

# Discussion on Wastewater Treatment Process of Coal Chemical Industry

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**Abstract:** Coal chemical wastewater has such characteristics as high concentration of oil, ammonia nitrogen and COD. In this paper, treatment process of coal chemical industry is described mainly, such as pretreatment process, biochemical treatment process and polishing process. Through the recovery of phenol and ammonia and the treatment of wastewater from abroad, the new technology of wastewater treatment in coal chemical industry was expounded. Finally, The development of coal chemical wastewater treatment technology is prospected, and the pretreatment technology is emphasized. According to the diversification and utilization of water, zero discharge of coal chemical wastewater will be fulfilled.

## 1. Introduction

In order to make up for the shortage of energy structure in our country, the project of using coal to make oil and natural gas and other chemical materials has been rising all over the country. During the process of combustion, gasification, cooling and washing, a large amount of wastewater is produced. The composition of the wastewater is very complicated. Coal chemical wastewater is not only related to coal quality, but also closely related to the process of gasification. According to the gasification temperature, the gasifier can be divided into high temperature gasifier and low temperature gasifier. High gasification temperature is about 1350~1750 degrees, such as GSP, SHELL, multicomponent slurry etc.. Low gasification temperature is about 950 ~ 1300 degrees, such as pulverized coal gasifier, Lurgi etc.. Pulverized coal gasifier is the most difficult to deal with.

## 2. Basic characteristics of coal chemical wastewater

The coal chemical wastewater are mainly composed by gas washing wastewater with high concentration, which contains a large number of toxic and harmful substances, such as phenol, cyanogens, oil and ammonia nitrogen. COD is generally in 300 ~ 5000mg/L, Ammonia nitrogen is in 150 ~ 400mg/L. The coal chemical wastewater is typical industrial wastewater, which is difficult to degrade, because of containing organic pollutants, including phenols, polycyclic aromatic hydrocarbons and heterocyclic compounds containing nitrogen and sulfur. The degradable organics are mainly phenolic compounds and benzene compounds; pyrrolidone, naphthalene, furan, Dialkylimidazolium. Refractory organics include pyridine, carbazole, biphenyl, terphenyl etc..

The basic difference of comprehensive wastewater with different gasification processes is shown in table 1:



**Table 1.** Comprehensive wastewater with different gasification processes

project	High temperature gasification process (mg/L)	Low temperature gasification process (mg/L)
Total ammonia (NH <sub>3</sub> )	150~220	200~400
COD	300~350	3500~5000
BOD <sub>5</sub>	100~150	1170~2000
Phenols	-	200~300
polyhydric phenols	-	420~500
oil	10~20	100~200
cyanide	5	5~10
Salinity	2800	3600
The quality of water	①Low organic concentration. ②Benzene and heterocyclic substances are not included. ③ Higher concentration of ammonia nitrogen. ④Low oil and grease. ⑤Less toxic inhibitory substances. ⑥Low chroma. ⑦Low TDS. ⑧ Relatively small amount of wastewater.	①High organic concentration. ② Refractory organics are included, such as phenols, polyphenols and other units containing phenyl and heterocyclic compounds, which have certain biological toxicity. The decomposition of these substances in aerobic environment is difficult, which can open loop and degrade in anaerobic/anoxic environment. ③The high concentration of ammonia nitrogen is difficult to dispose. ④ It contains floating oil, dispersed oil, emulsified oil and dissolved oil. The main components of dissolved oil are aromatic hydrocarbons. Emulsified oil needs to be removed by air flotation. Dissolved phenols need to be removed by biochemical and adsorption methods. ⑤Toxic inhibitory substances deal with phenols, polyphenols, ammonia and other toxic substances in wastewater. Through inhibition, enhance the microbial acclimation antitoxic ability, which need to select the appropriate process to improve the resistance capacity of the system. ⑥Higher chromaticity, The substances which having a part of chromogenic groups contain in wastewater. ⑦High TDS. All the salt needs to be removed. ⑧The amount of wastewater is relatively large.

From table 1, there is a great difference in the water quality of the gasifier at different temperatures. Low temperature gasification wastewater contains polycyclic aromatic compounds (such as benzene, phenol and polyhydric phenol) and heterocyclic compounds. There are many refractory organics. Some of them have biological toxicity. The concentration of ammonia nitrogen is high, and organic nitrogen contains in the wastewater. The substances which having a part of chromogenic groups contain in wastewater, make the water has deep colour. High alkalinity and salinity make equipments and pipes are easy to scale and clog in actual operation. The process of phenol ammonia recovery, the selection of extractant and the pretreatment effect of phenols have a great influence on the subsequent wastewater treatment in a low temperature gasifier. In addition, the same process with different coal also produces different wastewater. The composition of phenols in wastewater is complicated during gasification by low quality coal, such as long flame coal and

lignituous coal, and the treatment of wastewater is difficult.

### **3. Basic process of wastewater treatment in coal chemical industry**

Biochemical method is major technique of treating coal chemical wastewater. It has good effects on the removal of phenol and benzene compounds, but the quinoline, indole, pyridine, carbazole and some refractory organic matter treatment effect is poor. The COD of wastewater is difficult to achieve emission standards. Phenol ammonia recovery and wastewater treatment technology are used to treat gas water which is produced by Pulverized coal gasification in our country. Because of low gasification operation temperature, the decomposition of organic matter in coal is not complete, and the problem is that the gas water is large and the composition is complex. Although treatments are used, the wastewater reach the discharge standard is still very difficult. Volatile phenols and other issues still exist in the treatment process. The process of wastewater treatment is long and fluctuates greatly about projects in the construction. The stability of treatment effect needs to be validated. For the current domestic wastewater, the pretreatment process mainly includes adjustment, deoiling, sedimentation and flotation. The main goal of biological treatment is to remove COD, improve biodegradability, and remove nitrogen, such as acidification, hydrolysis, A/O process, SBR process, etc.. The three stage treatment process of coagulation, filtration, ozone, biological aerated filter (BAF) and activated carbon (coke) adsorption and its combination are adopted. And membrane separation technology, such as UF, RO and so on, is used in the desalting treatment process. Each process is described below.

#### *3.1 Pretreatment process*

The purpose of pretreatment is to remove substances that cannot be removed by biochemistry, but can affect biochemical treatment. Oil is the focus of pretreatment. The oily wastewater adopts the combined process of horizontal flow separation, inclined plate oil separation and air flotation. Recently, there are many sophisticated equipments to treat oily wastewater, such as regulating tank, oil-water separator, air flotation device and so on. Main pretreatment process has been formed by sophisticated equipments. The removal of emulsified oil, dissolved oil and subdivision oil requires addition of drugs and even multi-stage flotation.

#### *3.2 Biochemical treatment process*

There are many biochemical treatment processes. Conventional activated sludge treatment processes include oxidation ditch, SBR, A/O, common activated sludge process and MBR process. The biological membrane process mainly includes contact oxidation process and BAF process. Each treatment process has its own characteristics and is suitable for different water quality. Coal chemical wastewater which contains high COD belongs to high concentration sewage. The biochemical process selected to treat Coal chemical wastewater should improve the biochemical performance and high efficiency of nitrogen removal, and it is beneficial to long-term stable operation and convenient operation. Because anaerobic treatment has low energy consumption and high running load, it may be considered to choose hydrolysis or anaerobic treatment as the preceding stage of biochemical treatment. However, the gasification wastewater of the low temperature gasifier is very toxic, and the operation condition of the anaerobic treatment process is harsh, the commissioning cycle needs to be more than half a year. A large quantity of substandard water should be stored during commissioning. After hydrolysis or anaerobic process, A/O process with nitrogen removal function, oxidation ditch process and SBR process can be adopted. Mixing biological treatment with shock resistance is the key to achieve biological stability and achieve treatment effect in the first stage of biochemical treatment. Secondary biological treatment can adopt the plug flow operation mode.

#### *3.3 The third wastewater treatment processes*

There are a small amount of ammonia nitrogen and organic substances in secondary biochemical

effluent, which can not meet the discharge standards and water requirements. After treatment, it can be used as circulating cooling supplementary water, production and living miscellaneous water, and green water. To meet the local discharge standards and total pollutant control requirements, sewage can be discharged. Tertiary treatment process include biological aerated filter (BAF), contact oxidation, filtration, ozonation, biological carbon / activated carbon, disinfection, membrane treatment, biological oxidation pond and other combined processes. Because of the low B/C value and poor biodegradability of the second biochemical treatment, ozone and hydrogen peroxide are needed to improve the biodegradability, and then to remove the low concentration organic compounds by biological methods. Or adopt the DHA process, a new technique to improve the B/C ratio, to improve the biodegradability of sewage. Ozone oxidation, only participates in the reaction of  $O_3$ , without any reagent in the reaction process, does not lead to salinity in sewage, and the process is simple. Flocculation, air flotation, ozone oxidation, biological aerated filter (BAF) and filtration adsorption process can be adopted in the third treatment process. The biochemical performance of sewage was improved by ozone modification.  $NH_3-N$  and COD in sewage were further removed by BAF, and COD and SS in water were removed by adsorption and filtration.

### *3.4 Sludge treatment process*

The technology of mechanical dehydration is quite mature at present. The main applications in the project are belt pressure filter, centrifugal dehydrator and plate and frame filter, etc.. The sludge produced by the sewage treatment biochemical system is mainly flocculation sludge and biological excess sludge, which is dehydrated by belt type pressure filter. The equipment is running well. The power consumption is low, and the equipments can be made in China. The sludge produced by lime softening is inorganic sludge, containing inorganic particles, which is more abrasion to the equipment. It is suitable to choose a box, plate and frame filter press to improve the solid content of mud cake. At present, the screw type dehydrator and centrifugal dehydrator are widely used. Due to the high precision of centrifuge manufacturing, most of the imported products are used.

### *3.5 Waste gas treatment process*

Harmful waste gas is produced by the pretreatment unit and the sludge treatment unit of sewage biochemical treatment, which mainly occurs in the treatment unit, such as the regulating pond, the sewage regulating tank, the acidification hydrolysis tank and the biological sludge dewatering room. The main components of odor are  $H_2S$ ,  $NH_3$  and so on. The main treatment methods are activated carbon adsorption, liquid absorption, absorption oxidation, biological deodorization and so on. Activated carbon adsorption: Put the gas into the adsorber with activated carbon.  $H_2S$  is adsorbed by activated carbon. Then  $H_2S$  is oxidized to elemental sulfur and water. 5% aqueous ammonium is used to wash sulfur, activated carbon can continue to use. The advantages of activated carbon adsorption are quick reaction, short contact time and high treatment capacity. Biological deodorization is a method of deodorizing artificially by natural microorganisms, which control the biota within a particular facility. The essence of the process is to convert the harmful substances of gas stream into simple organics by the decomposition of microorganisms. Microbial deodorization usually takes place under normal temperature and pressure. There is no pollution during biological treatment, which is environmental friendly technology.

### *3.6 Wastewater reuse treatment process*

After pretreatment + the second biochemical treatment + the third treatment, the salt has not been removed. Desalination is required to meet the needs of industrial reuse of the recirculating water system. At present, the desalting process has been used in our country, such as chemical desalting and membrane separation technology. Ion exchange water treatment technology is quite mature and suitable for the wastewater with low salt content. But in the technology, a large amount of acid and alkali wastewater is produced during the regeneration of resin. Membrane separation technology has

the advantages of easy operation, compact equipment, safe working environment, saving energy and medicament, therefore reverse osmosis membrane method is widely used in wastewater reuse system. With the gradual maturity of anti fouling membrane products, RO membrane desalination is the most widely used treatment process in the field of water reuse. The effect of pretreatment facilities is the key factor affecting the effect of membrane treatment. Air flotation can be used to remove oil and small suspended matter that may be contained in water. Filters were used to further reduce suspended solids. Ultrafiltration is used to further remove residual contaminants in water. The purpose of these processes is to minimize the pollution load of RO membrane and improve the high efficiency cycle of equipment. When the wastewater has a certain degree of hardness, lime softening method is adopted to reduce the hardness of water inflow, to reduce subsequent treatment facilities and to protect reverse osmosis membrane. Ultrafiltration and reverse osmosis membranes require low oil content. When oil content is high of the inlet water, the walnut shell filter can be arranged before the ultrafiltration, to protect the safety of the further treatment facilities. To sum up, biochemical wastewater reclamation and desalting process can be softened by petrochemical softening + walnut shell filter + gas water backwash filter + ultrafiltration + primary reverse osmosis treatment process. In order to reduce evaporation unit size, salt content can be checked. When the salt content is allowed, the concentrated brine at the first grade RO can be re pressurized, desalted and concentrated so as to increase the recovery rate.

### *3.7 Standard treatment or concentration treatment of concentrated brine*

After enrichment by membrane method, the amount of concentrated brine is still large. and concentrated brine contains a certain amount of organic pollutants. Without treatment, direct emissions can cause heavy pollution to the local environment. In areas where emissions are allowed, NH<sub>3</sub>-N and COD emission standards cannot be met. Concentrated brine can be treated by catalytic oxidation of nitrogen adding process.

When there is a zero emission requirement, it is very uneconomical to evaporate the concentrated brine directly from the double membrane process, because of its large size, high equipment investment and a large amount of energy. There are many companies at home and abroad of brine study the reconcentration by double membrane method, in order to make the salt content reach 6% ~ 8%, who increase salinity, reduce subsequent evaporator size and reduce the investment and saving energy as far as possible. The concentrated brine process in foreign countries mainly includes HERO highly effective reverse osmosis process, nanofiltration membrane concentration process and shock film enrichment process, but its equipment investment is high, domestic application is few. There are some domestic companies in the study of brine concentration process. Nanofiltration + reverse osmosis membrane process has been applied to undertake the project by DongHua Science and Technology. The process has the characteristics of high water recovery rate, low equipment investment and good water quality. And the quality of the concentrated brine is stable, which is beneficial to the safe and long-term operation of the follow-up evaporator.

### *3.8 Evaporation crystallization process*

The concentration of concentrated brine is high by biochemical treatment processes, about 6%~8%, which is difficult to be recycled. In order to realize the "zero discharge" of wastewater, further evaporation and crystallization treatment is needed. The mechanical steam compression circulation evaporator further concentrates the concentrated brine to about 20%. The purpose of evaporator is to reduce the volume of waste water, produce high quality distilled recycled water, and maximize the concentration of sewage. Forced circulation technology is used in crystallizer. And the concentrated waste brine passes through a crystallizer or a dryer to crystallize various salts dissolved in the sewage and become solid. The concentrated brine passes through a crystallizer or dryer to crystallize various salts dissolved in sewage and become solid disposal. Falling film evaporators are formed by the action of gravity, which can evaporate high viscosity, cut heating time, suit for heat sensitive materials, not

easy to crystallization and scaling materials. According to the current domestic coal chemical wastewater zero discharge of practical engineering experience, no matter whether the crystallization device is set up or not, the evaporation pond must be set up in the boundary area to cope with the storage of open parking sewage and accidental sewage.

#### 4. Recovery of phenol ammonia from Lurgi and wastewater treatment

Lurgi Phenosolvan phenol recovery process adopts continuous countercurrent extraction process which has five stage mixing and clarification tanks. After treatment with phenol recovery unit, the content of light oil and particles in gas water is less than 50 $\mu$ g/g, the content of phenol is less than 20 $\mu$ g/g, the extraction rate of polyphenol was 85%, the extraction rate of total phenol was more than 99%, and COD content in the stripping gas water of the waste water treatment unit can be remarkably reduced. The separation of solvent and crude phenol is achieved in a distillation column, which using waste heat from ammonia recovery unit. The solvent loss is small and the energy consumption is low. Efficient deasphalting tower, which have patented design, can produce phenol. But Lurgi's phenol recovery process has never been implemented in China. After CLL ammonia recovery treatment of Lurgi, the content of free ammonia in gas water is less than 50 $\mu$ g/g, and the content of COD is less than 3000mg/L, which is suitable for further biochemical treatment. Ammonia and sulfuric acid gas are recovered by stripping and washing process without additional chemicals and solvents. The anhydrous ammonia liquid is pressurized or frozen to be used as an agricultural or chemical grade product. With certain pressure, acid gas without ammonia will send to sulfur recovery unit.

Lurgi said, according to the above gas water treatment process, coupled with the subsequent sewage biological treatment, the wastewater discharge can meet the most stringent environmental standards. Gas water treatments which design by Lurgi and cooperative foreign company, can meet the strict emission standards for local, such as Sasol gas water in South African (1600t/h) and North Dakota plains coal gas plant in U.S.A (640t/h). After treatment by other methods, water reuse can be used as process cooling water or boiler feed water. Zero discharge of wastewater can be realized.

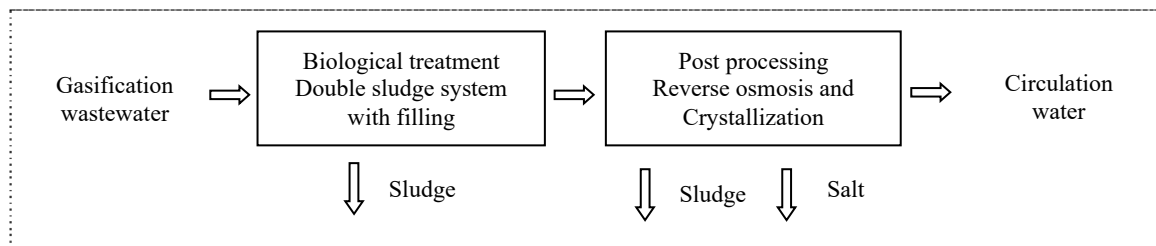
Table 2 shows the application of phenol ammonia treatment in foreign project by Lurgi Technology.

**Table 2.** Application of phenol ammonia treatment in foreign project by Lurgi Technology

project	unit	Influent of recovery of phenol and ammonia	Influent of sewage treatment plant
flow	m <sup>3</sup> /h	800	800
PH		8.5	9
NH <sub>3</sub>	mg/L	1.2 $\times$ 10 <sup>4</sup>	250
Total phenol	mg/L	4400	125
BOD	mg/l		600
COD	mg/L		1700-3000
oil	mg/L		<5
cyanide	mg/L		5
sulfide	mg/L		10

According to the data in the table 2, the removal rate of NH<sub>3</sub> is about 97.9%, and the total phenol removal rate is about 97.2%. A phenol ammonia recovery plant in South African has sewage tanks for 3 days storage, in order to store wastewater under shutdown and accident conditions.

German company and USA Company, who work with Lurgi, have sewage treatment experiences. The process of sewage treatment is shown in figure 1.



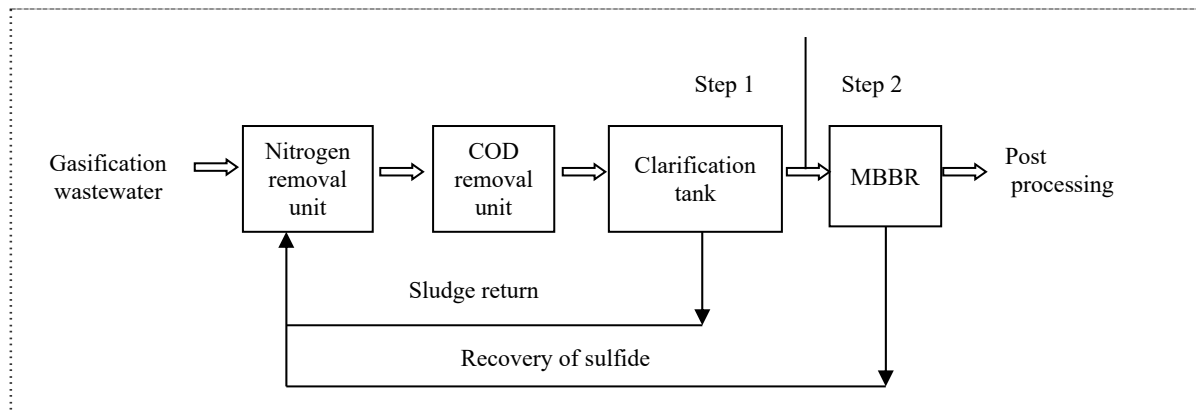
**Figure 1.** The process of sewage treatment

Biological treatment technology comes from a company in Germany. It is divided into 2 steps.

Step 1: High load activated sludge method is used for nitrogen removal, removal of COD and hydrolysis of toxic substances.

Step 2: Low load nitrification process. MBBR using biological carrier filler provides recirculation of nitrating liquid and dilution of water quality.

The flow chart is shown in figure 2.



**Figure 2.** Biological treatment technology from a German company

If the coal gasification wastewater of the low temperature gasifier is separated by Lurgi gas water separation and phenol ammonia recovery, the effluent quality can be stably achieved. It will play a crucial role in the subsequent sewage treatment.

The fixed bed low temperature gasifier wastewater is difficult to treat in the existing gasification unit in our country. The water quality fluctuates greatly and the processing flow is long. In the non environmental capacity area, investment, operation and management of sewage treatment are complex. And environmental risks are relatively large. After analyzing the water quality of the phenol ammonia recovery unit supplied by Lurgi Company, it is found that there is little difference between the domestic sewage treatment process and the domestic wastewater treatment process. In accordance with the current domestic sewage treatment level of similar projects, after the recovery of phenol and ammonia, there should be no problem to treat the coal chemical wastewater to meet the standard and reuse by domestic technology.

## 5. Conclusion

Coal chemical wastewater has the characteristics of complex water quality, large amount of water and difficult to deal with. The existing technology cannot meet the requirements of national environmental protection, so it is very necessary to develop Integrated and complete process with stable system, shock resistance, low treatment cost and good effluent effect, to achieve near zero emissions coal

chemical wastewater.

### *5.1 Strengthening sewage pretreatment technology*

Because of toxic and harmful substances which will affect the subsequent biochemical treatment, the biodegradability of coal chemical wastewater is poor. So it is necessary to strengthen the pretreatment technology to improve the biodegradability of the sewage and reduce biological toxicity. Optimize the existing process, such as ammonia distillation and removal of phenol, to improve the treatment effect.

### *5.2 Bioaugmentation*

Biological nitrogen removal is one of the key and difficult parts of coal chemical wastewater. It is the key technology to select the biological treatment process with strong toxicity resistance and to cultivate and adapt activated sludge for treating coal chemical wastewater.

### *5.3 Intensified post-treatment*

Postprocessing technique is the key of meeting the requirements for water reuse by treating coal chemical wastewater. Also it is the key technology to realize the zero discharge of the real coal chemical wastewater. Advanced oxidation and membrane assembly process are the main processes for advanced treatment. But the cost is still high. Still there are a series of problems, such as membrane fouling. Therefore, how to reduce the treatment cost and control membrane fouling, including the final concentrated water treatment, will be further studied.

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