Simulation and design of tar recovery and gas decarbonization process

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Abstract. A multi-production system including pulverized coal molding, pyrolysis and activation is designed to solve the key problems of powder coal pyrolysis in Northern Shanxi. As the pulverized coal molding is just a physical procedure, so more attention is arranged on the preliminary design of Shenfu coal pyrolysis process. As coal tar can be converted to gasoline by hydrocracking technology, the pyrolyzation gas is cooled and coal tar is reclaimed by a spray tower, then a decarbonization unit is introduce to separate CO_2 by MEA absorption. In the design process, process simulation and performance parameters optimization were carried out by Aspen Plus. At the same time, corresponding safety measures and relevant wastes treatment suggestions for the whole process were put forward.

1. Introduction

At present, China faces a very seriously challenge of energy saving and emission reduction. The responsibility of the coal industry is particularly arduous. The environmental problems caused by direct combustion of coal have not been effectively cured. Therefore, how to greatly develop the clean utilization of coal is an important issue that needs to be faced. Coal, as one of the main by-products of low temperature coal carbonization, is a dark brown viscous liquid with a density usually between 0.95g/cm^3 and 1.10g/cm^3. Although the tar content in the crude gas is mainly related to the nature of the raw coal and the low-temperature dry distillation method, suitable tar recovery process and gas purification process also have a significant impact on tar recovery rate, which can provide a guarantee for improving tar quality index. This paper analyzes and compares various technologies of tar recovery and gas carbonization. the sections of tar recovery and gas decarbonization are simulated and optimized.

2. Analysis and improvement of tar recovery technology

The tar recovery process is widely used in system of gas production and using, including purification of coke oven gas and pyrolysis gas, and collection and utilization of tar[1]. Generally, the gas temperature of the gas purification and tar recovery system is 300-500℃, and the tar content is 50-200 g/Nm^3[2] . Therefore, the general purification process includes main processes such as cooling, washing, and post-treatment. The conventional process of tar recovery is to directly spray 70-75℃ cycling ammonia into the high-temperature crude gas to lower it to 80-82℃, then let the gas enter the primary cooler and cool it to 25-35℃with cooling water, then output to the subsequent section. The sprayed cycling ammonia water, the condensed tar and condensed ammonia and tar from the primary cooler are sent to the mechanized ammonia liquor decanter, and are divided into three parts: ammonia

water, tar and tar slag. The tar is sent to the tar workshop through the tar intermediate tank, and the remaining ammonia water is phenol wastewater with high concentration which goes to the wastewater treatment process after oil removal and solvent dephenolics[3]. This traditional process has the following problems:

(1) Directly sprayed circulating ammonia water to the high temperature gas to 25 to 35℃, the residual heat in the gas cannot be used.

(2) A large amount of cooling water is still required to cool after spraying the cycling ammonia water.

(3) In order to make the heavy tar flow with the ammonia water, the sprayed ammonia water is greatly excessive, so a large amount of phenol wastewater is produced, and the treatment cost is high.

In order to avoid the shortcomings in the above technology, and considering the small scale of the design, the design intends to use the high-temperature gas from the outlet of the carbonization furnace to pass the high-efficiency cyclone for dry dedusting, and the collection efficiency reaches 80%~95%, then the tar is recovered by indirect cooling of the gas, low-temperature light tar spray cooling gas, and oil-water separation[4][5]. Compared to traditional processes, this process has the following advantages:

(1)The steam recovered from indirect cooling of gas can be used in the section of char activation to maximize the utilization of raw materials.

(2)Using low-temperature light tar circulating spray to achieve the effect of cooling the gas, without the need for ammonia spray, greatly reducing wastewater discharge;

(3)After the tar spray tower, a high-efficiency electro tar precipitator is set up, the recovery rate of tar is up to 99.99%, and the tar content of the outlet gas is less than 20mg/Nm^3.

3. Comparison and selection of gas decarbonization technology

According to the reaction of the CO_2 separation process, the method for separating CO_2 can be divided into chemical-solvent method, physical separation method, Physicochemical separation method.Among them, methods of organic amines, hot carbonate process are commonly used in the chemical solvent method, and the physical solvent method, the molecular sieve method, and the membrane separation method are commonly used in the physical separation method.Due to the large amount and complex components of coal-fired flue gas,and pressure and content of CO_2 are relatively low , the physical solvent method and membrane separation method are not economical[6].The oxyamine process is currently the most commonly used technique for CO_2 capture in coal-fired flue gas.In the process of removing CO_2 by oxyamine process, common solvents are MEA, DEA, MDEA, and the characteristics of these three solvents are compared as follows[7][8]:

(1)Characteristics of MEA (monoethanolamine)

a.Strong solvent reaction, good chemical stability, easy to regenerate;

b.Mature process and high purification;

c.Compared with other alcohol amine solvents, it has low molecular weight, low viscosity and high solubility in water;

d.The highest relative rate of CO_2 absorption and low selectivity to H_2S and CO_2;

e.It is highly corrosive, so the solvent concentration used is generally not more than 20%.

(2)Characteristics of DEA(diethanolamine)

a.Less solvent loss than MEA;

b.Purification is not as good as MEA;

c.Suitable for processing raw materials containing organic sulfur.

(3)Characteristics of MDEA(methyldiethanolamine)

a.With good selectivity, it can make acid gas thicker;

b.Since there is no active hydrogen atom on the nitrogen atom in the MDEA molecule, it cannot directly react with CO_2, COS, and CS_2, so no degradation products are produced;

c.The weakest alkaline and the least corrosive;

d.Generally suitable for large-scale devices.

Through the comprehensive consideration of design background and process characteristics, combined with process investment and operating cost comparison, it is more advantageous to use MEA for the removal of CO_2 in the 100 thousand t/a briquette pyrolysis and activation multi-production process.

4. Process design

The process flow after the improvement of the traditional tar recovery and gas decarburization process is shown in the figure1.

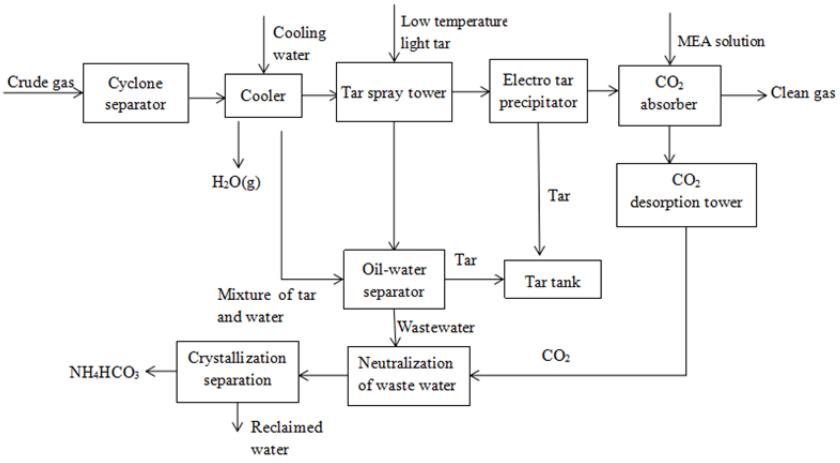

Figure 1. Process flow diagram.

The process flow is described as follows:

(1)The pyrolysis gas and activated gas are discharged at a temperature of about 550℃. The high temperature cyclone removes the dust from the gas by 90% and then enters the tar recovery section.

(2)In the tar recovery section, the gas first enters the coil cooler to cool to about 250℃, at which point some of the tar condenses and enters the oil-water separator.

(3)The gas continues to pass through the light tar spray tower, and the gas is sprayed with a large amount of low temperature and light tar to reduce the gas temperature to 25-30℃. The tar after spraying and the tar condensed during the cooling process are separated by the oil water separator，then get tar into the tar tank.

(4)Gas from the tar spray tower enters the electro tar precipitator to remove the tar fog, and then enters the gas decarbonization section.

(5)In the gas decarbonization section, the MEA absorption method is used to remove CO_2, and about 80% of the CO_2 in the gas is removed, then the clean gas enters the gas container.

(6)The rich liquid after absorbing CO_2 enters the desorption tower, and the desorbed CO_2 enters the wastewater neutralizing tank together with the weak alkaline wastewater in the tar recovery section , and after precipitation and separation, ammonium bicarbonate and reclaimed water are obtained, and the desorption solution(MEA) is recycled.

5. Process simulation

5.1. Establishment of tar model

The composition of tar: The composition of tar is complex, and can be roughly classified into the volatile component and asphalt depending on the boiling point. In order to simplify the calculation, for the former, 25 real components with mass composition greater than 0.02% are selected (see Table 1),

and the content of the volatile components in the actual tar is more than 90%;For asphalt, the virtual component AB-1 is used to represent it, and the real boiling point data is used for regression prediction. At 101.33 KPa, the distillation real boiling point data are shown in Table 2.

Thermodynamic model：For the Aspen Plus simulation process, the accurate selection of physical methods is critical to the accuracy and reliability of the process simulation. Based on the simplified the model of car, this paper selects the UNIQ-RK physical method to calculate the thermodynamic properties[10].

Table 1. A table with headings spanning two columns and containing notes[9].

Number	Component	Boiling point/℃	Mass fraction/w%	Number	Component	Boiling point/℃	Mass fraction/w%
1	Water	100.00	2.00	14	Fluoranthene	382.00	3.50
2	Benzene	80.10	0.21	15	Pyrene	393.00	2.80
3	Toluene	110.80	0.35	16	Pyridine	115.30	0.04
4	M-xylene	139.30	0.17	17	2-Methylpyridine	129.00	0.03
5	Indene	181.00	0.42	18	Quinoline	237.30	0.42
6	Tetralin	207.20	0.42	19	Isoquinoline	243.00	0.14
7	Naphthalene	217.90	16.80	20	Indole	253.00	0.28
8	1-Methylnaphthalene	244.40	1.68	21	Phenol	181.80	0.70
9	2-Methylnaphthalene	241.10	2.52	22	o-Cresol	190.95	0.28
10	Dimethyl naphthalene	220.00	1.68	23	m-Cresol	202.80	0.56
11	Fluorene	297.90	2.80	24	p-Cresol	202.00	0.28
12	Anthracene	340.00	2.52	25	Xylenol	217.10	0.70
13	Phenanthrene	340.00	8.40	26	Asphalt	>360	50.30

Table 2.True boiling point data of asphalt[11].

Number	Flow Fraction/%	T/℃
1	0.00	360.00
2	5.00	480.97
3	30.00	568.49
4	50.00	608.99
5	70.00	631.08
6	90.00	705.69
7	98.00	736.75

5.2. Process simulation

The composition of crude gas entering the tar recovery section is shown in Table 3.

Table 3. Composition of raw gas[12].

Component	H_2	CH_4	CO	CO_2	H_2O	Tar
Mass fraction/%	9.5	3.9	15.3	42.3	11.5	17.5

The material balance and heat balance of this design are based on the Aspen Plus simulation and optimization results of the tar recovery and gas decarbonization process.The Aspen model diagram of tar recovery and gas decarbonization process is shown in Figure 2.

From the Aspen Plus simulation results, this design achieved the expected results and can be applied to industrial production.

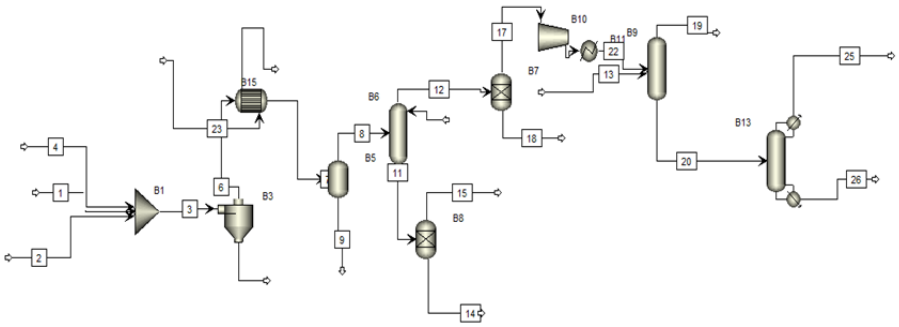

Figure 2. Aspen model diagram of process.

6. Simulation results and analysis

6.1. Effect of MEA temperature on CO_2 absorption

The relationship between the CO_2 absorption rate and the temperature of the MEA solution is shown in Figure 3. The temperature range of the selected MEA solution is 25-50℃[13]. It can be seen from Figure 3 that the temperature of the MEA solution is not sensitive to the CO_2 absorption.When the solution temperature is lower than 40℃, the temperature increases and the CO_2 absorption rate increases slowly.

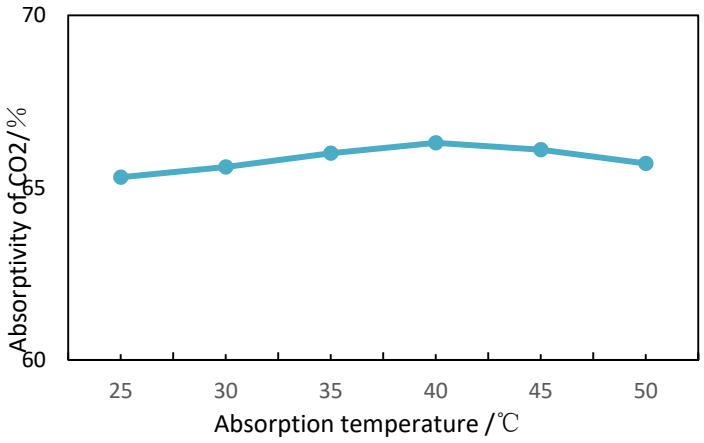

Figure 3. Effect of MEA temperature on CO_2 absorption.

6.2. Effect of concentration of MEA solution on CO_2 absorption

The relationship between the CO_2 absorption rate and the mass concentration of the MEA solution is shown in Figure 4. The concentration of the MEA solution selected for the simulation calculation ranges from 22.3% to 42.5%[14]. As shown in Figure 4, the CO_2 absorption rate increases with the increase of the mass concentration of MEA solution. Due to the influence of gas-liquid mass transfer and reversible reaction equilibrium conditions, the concentration of MEA solution increases, the CO_2 absorption rate increases correspondingly, and finally reaches a stable value. Under this simulated condition, the optimum concentration of MEA solution for CO_2 capture is 35%-40%.

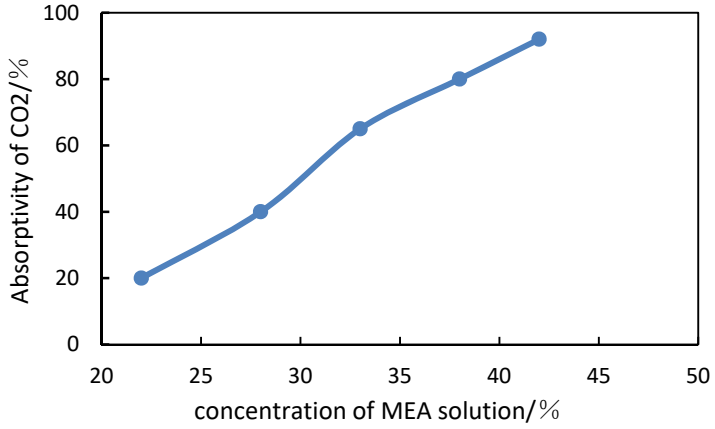

Figure 4. The relationship between the CO2 absorption rate and the mass concentration of the MEA solution.

6.3. The composition of the outlet gas

Table 4 shows the composition of the outlet gas after tar recovery and decarburization. It can be seen that the design process can effectively remove the tar and CO_2 in the coke oven gas, and the outlet gas reaches the standard of the coke oven net gas[15].

Table 4. The composition of the outlet gas.

Temperature ℃	38.06
Pressure psia	145.23
Vapor Frac	1.00
Mole Flow lbmol/hr	1298.93
Mass Flow lb/hr	8480.88
Volume Flow cuft/hr	54014.88
Enthalpy MMBtu/hr	-16.01
Mass Frac	
H_2	0.574
CH_4	0.258
CO	0.061
CO_2	0.029
H_2O	0.014
Tar	0.064

7. Conclusions

In summary, the improved tar recovery process improves tar yield, shortens processing cycles, and reduces processing costs. The MEA gas decarbonization process has good purification effect and the process flow is mature. In the treatment of waste gas and wastewater, the wastewater source of the project mainly includes weakly alkaline waste water condensed from the crude gas in the tar recovery section. It is introduced into the wastewater neutralizing tank together with the waste gas(CO_2) absorbed from the gas decarburization section, and then, byproduct ammonium bicarbonate was obtained by crystallization separation.

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