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Numerical Simulation and Process Package Optimization of a New Type of Citrate Desulfurization System

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Abstract. In order to further study the process of flue gas desulfurization by citrate process, A numerical model for the removal of SO_2 from packed absorption tower is established by using chemical process simulation software Aspen Plus, The influence of operation parameters on desulfurization efficiency was analyzed and optimized. The simulation results are in good agreement with the literature. The model calculation results show that: The desulfurization rate increases with the increase of pH value and liquid gas ratio of the absorption liquid;With the increase of inlet mass concentration of SO_2 and the increase of inlet flue gas flow rate, The results show that the pH value and the liquid gas ratio are the main factors affecting the flue gas desulfurization efficiency of citrate process. The established model of citrate flue gas desulfurization process is accurate and reasonable, The simulation results can provide reference and reference for the actual operation of desulfurization system and the influence of various operation parameters on desulfurization efficiency.

Modeling and Module Selection

Such as the establishment process of Aspen model is shown in Figure 1, the desulfurization process is decomposed into three parts: 1) the use of packing section of the absorption tower to strengthen the gas-liquid mass transfer process, sulfur-containing flue gas since the packing tower is entered, the citrate absorption liquid enters from the upper end of the packing tower, gas-liquid reverse contact in the tower, the enhancement of mass transfer process that makes the sulfur dioxide in the flue gas is absorbed by the absorption to meet the national standards, the flue gas is absorbed from the upper end of the packing tower after discharge, the absorption liquor from the bottom and then discharged into the desorption tower to continue treatment, the process selects the RadFrac model simulation; 2) -- from the absorption desorption output by the absorption liquor after entering the heat exchanger absorption desorption tower, rich liquid into self desorption tower top, and high temperature steam in the tower of reverse contact, the sulfur dioxide absorption desorption liquid rich in to In the water vapor, the sulfur containing water flows out from the upper end of the desorption tower, and the product stream is obtained after subsequent treatment. After desorption desorption tower section from lean liquid outflow, the heat exchanger is returned to the absorption section for recycling, the process of selecting RadFrac model simulation; 3) mixer output - desorption tower desorption solution is returned to the poor absorption tower for recycling, but in the whole process of absorption liquid will therefore need to loss. Adding citric acid salt fresh absorption liquid, so use the mixer to mix fresh absorption liquid and absorption liquid circulation, the highest degree of economic, so the selection of Mixer module. The corresponding relationships between these modules and the process equipment referred to in this process are shown in table 1.

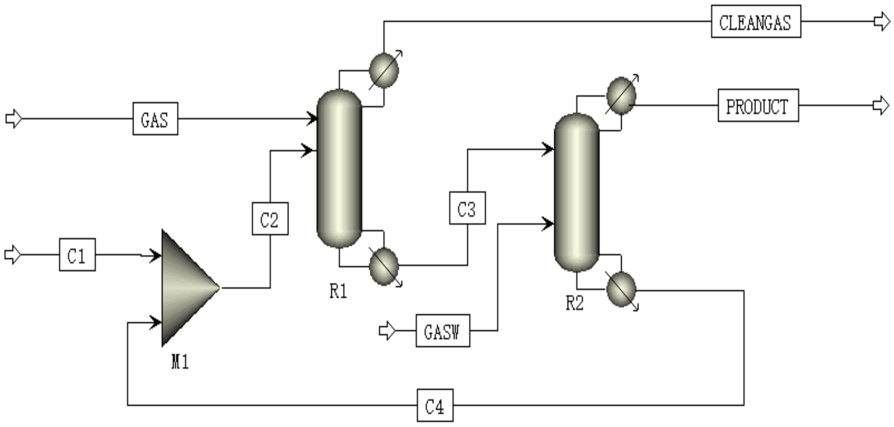
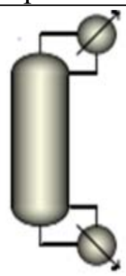
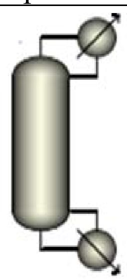
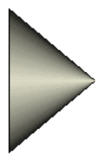


Fig.1. Aspen model flow

Table 1 Relationship between citrate process equipment and Aspen Plus module

Citrate process equipment	Absorption section	Desorption section	mixer
Aspen Module legend			
Aspen	RadFrac	RadFrac	Mixer

Regression thermodynamic equilibrium model

Processing of phase equilibrium experimental data

According to the experimental data of [1] using regression software to carry on the regression function of thermodynamic equilibrium operation, the new Properties-Data in the three data sets, which were named as VLE1, VLE2, VLE3, Setup in Category Phase equilibrium Data type option is selected; choose "TPXY" data type. Fill in the following table, as:

Table 2 Data-VLE1

Usage	TEMPERATURE	PRESSURE	X	X	Y	Y
	C	mmHg	SO2	C6H8O7	SO2	C6H8O7
STD-DEV	0.1	0.10%	0.10%	0	0%	0
DATA	40	136.6	0.006	0.994	0.022	0.978
DATA	40	150.9	0.044	0.956	0.144	0.856
DATA	40	163.1	0.084	0.916	0.227	0.773
DATA	40	183	0.187	0.813	0.37	0.63
DATA	40	191.9	0.242	0.758	0.428	0.572
DATA	40	199.7	0.32	0.68	0.484	0.516
DATA	40	208.3	0.454	0.546	0.56	0.44
DATA	40	210.2	0.495	0.505	0.574	0.426
DATA	40	211.8	0.552	0.448	0.607	0.393
DATA	40	213.2	0.663	0.337	0.664	0.336
DATA	40	212.1	0.749	0.251	0.716	0.284
DATA	40	204.6	0.885	0.115	0.829	0.171
DATA	40	200.6	0.92	0.08	0.871	0.129
DATA	40	195.3	0.96	0.04	0.928	0.072

Table 3 Data-VLE2

Usage	TEMPERATURE	PRESSURE	X	X	Y	Y
	C	mmHg	SO2	C6H8O7	SO2	C6H8O7
STD-DEV	0.1	0.10%	0.10%	0	0%	0
DATA	70	548.6	0.0065	0.9935	0.0175	0.9825
DATA	70	559.4	0.018	0.982	0.046	0.954
DATA	70	633.6	0.131	0.869	0.237	0.763
DATA	70	664.6	0.21	0.79	0.321	0.679
DATA	70	680.4	0.263	0.737	0.367	0.633
DATA	70	703.8	0.387	0.613	0.454	0.546
DATA	70	710	0.452	0.548	0.493	0.507
DATA	70	712.2	0.488	0.512	0.517	0.483
DATA	70	711.2	0.625	0.375	0.597	0.403
DATA	70	706.4	0.691	0.309	0.641	0.359
DATA	70	697.8	0.755	0.245	0.681	0.319
DATA	70	679.2	0.822	0.178	0.747	0.253
DATA	70	651.6	0.903	0.097	0.839	0.161
DATA	70	635.4	0.932	0.068	0.888	0.112
DATA	70	615.6	0.975	0.025	0.948	0.052

Table 4 Data-VLE3

Usage	TEMPERATURE	PRESSURE	X	X	Y	Y
	C	mmHg	SO2	C6H8O7	SO2	C6H8O7
STD-DEV	0.1	0	0	0	1%	0
DATA	78.45	760	0	1	0	1
DATA	77.4	760	0.0248	0.9752	0.0577	0.9423
DATA	77.2	760	0.0308	0.9692	0.0706	0.9294
DATA	76.8	760	0.0468	0.9532	0.1007	0.8993
DATA	76.6	760	0.0535	0.9465	0.1114	0.8886
DATA	76.4	760	0.0615	0.9385	0.1245	0.8755
DATA	76.2	760	0.0691	0.9309	0.1391	0.8609
DATA	76.1	760	0.0734	0.9266	0.1447	0.8553
DATA	75.9	760	0.0848	0.9152	0.1633	0.8367
DATA	75.6	760	0.1005	0.8995	0.1868	0.8132
DATA	75.4	760	0.1093	0.8907	0.1971	0.8029
DATA	75.1	760	0.1216	0.8784	0.2138	0.7862
DATA	75	760	0.1291	0.8709	0.2234	0.7766
DATA	74.8	760	0.1437	0.8563	0.2402	0.7598
DATA	74.7	760	0.1468	0.8532	0.2447	0.7553
DATA	74.5	760	0.1606	0.8394	0.262	0.738
DATA	74.3	760	0.1688	0.8312	0.2712	0.7288
DATA	74.2	760	0.1741	0.8259	0.278	0.722
DATA	74.1	760	0.1796	0.8204	0.2836	0.7164
DATA	74	760	0.1992	0.8008	0.3036	0.6964
DATA	73.8	760	0.2098	0.7902	0.3143	0.6857
DATA	73.7	760	0.2188	0.7812	0.3234	0.6766
DATA	73.3	760	0.2497	0.7503	0.3517	0.6483
DATA	73	760	0.2786	0.7214	0.3781	0.6219
DATA	72.7	760	0.3086	0.6914	0.4002	0.5998
DATA	72.4	760	0.3377	0.6623	0.4221	0.5779
DATA	72.3	760	0.3554	0.6446	0.4331	0.5669
DATA	72	760	0.4019	0.5981	0.4611	0.5389
DATA	71.95	760	0.4184	0.5816	0.4691	0.5309
DATA	71.9	760	0.4244	0.5756	0.473	0.527
DATA	71.85	760	0.447	0.553	0.487	0.513
DATA	71.8	760	0.4651	0.5349	0.4934	0.5066
DATA	71.75	760	0.4755	0.5245	0.4995	0.5005
DATA	71.7	760	0.51	0.49	0.5109	0.4891
DATA	71.7	760	0.5669	0.4331	0.5312	0.4688
DATA	71.75	760	0.5965	0.4035	0.5452	0.4548
DATA	71.8	760	0.6211	0.3789	0.5652	0.4348
DATA	71.9	760	0.6425	0.3575	0.5831	0.4169
DATA	72	760	0.6695	0.3305	0.604	0.396
DATA	72.1	760	0.6854	0.3146	0.6169	0.3831

Usage	TEMPERATURE	PRESSURE	X	X	Y	Y
DATA	72.3	760	0.7192	0.2808	0.6475	0.3525
DATA	72.5	760	0.7451	0.2549	0.6725	0.3275
DATA	72.8	760	0.7767	0.2233	0.702	0.298
DATA	73	760	0.7973	0.2027	0.7227	0.2773
DATA	73.2	760	0.8194	0.1806	0.7449	0.2551
DATA	73.5	760	0.8398	0.1602	0.7661	0.2339
DATA	73.7	760	0.8503	0.1497	0.7773	0.2227
DATA	73.9	760	0.8634	0.1366	0.7914	0.2086
DATA	74.1	760	0.879	0.121	0.8074	0.1926
DATA	74.3	760	0.8916	0.1084	0.8216	0.1784
DATA	74.7	760	0.9154	0.0846	0.8504	0.1496
DATA	75.1	760	0.9367	0.0633	0.8798	0.1202
DATA	75.3	760	0.9445	0.0555	0.8919	0.1081
DATA	75.5	760	0.9526	0.0474	0.9038	0.0962
DATA	75.7	760	0.9634	0.0366	0.9208	0.0792
DATA	76	760	0.9748	0.0252	0.9348	0.0652
DATA	76.2	760	0.9843	0.0157	0.9526	0.0474
DATA	76.4	760	0.9903	0.0097	0.9686	0.0314
DATA	77.15	760	1	0	1	0

Regression and selection of thermodynamic phase equilibrium model

In Regression, the new regression models are Wilson, NRTL, and UNIQUAC (because the three models can describe the system better by choosing the experience of the thermodynamic model). The phase equilibrium model obtained by the regression of three thermodynamic models and the two element interaction parameters of sulfur dioxide and citric acid described by different thermodynamic models are obtained。

Different thermodynamic models describing the sulfur dioxide citric acid two element interaction parameter are presented below:

Table 5 Fitting two element interaction parameter

	NRTL	UNIQUAC	WILSON
Component i	C6H8O7	C6H8O7	C6H8O7
Component j	SO2	SO2	SO2
Temperature units	C	C	C
Source	R-R-1	R-R-2	R-R-3
Property units			
AIJ	0.061653	-0.716431	2.69032
AJI	-2.37216	1.30625	0.298825
BIJ	689.318	-384.608	-222.81
BJI	-446.39	309.229	-13.7663
CIJ	0.3	0	0
DIJ	0	0	0
EIJ	0	0	0
EJI	0	0	0
FIJ	0	0	0
FJI	0	0	0
TLOWER	40	40	-273.15
TUPPER	78.45	78.45	726.85

By comprehensively comparing the two element interaction parameters described by the three thermodynamic models, it is found that the NRTL thermodynamic model is the most appropriate to describe the process. Therefore, the NRTL thermodynamic model is selected to do the calculation after the simulation, and the SO2 / citric acid two element interaction parameter is taken as the calculation model.

Simulation Results

Detailed information about the logistics components and status parameters of each node of the system is listed in table 6-7。

Table 6 Status and components of logistics(1)

project	C1	C2	C3	C4
molar flow rate kmol/hr				
water	2.92E+05	1.79E+07	1.71E+07	1.80E+07
atmosphere	0	5.48E-86	28132.48	5.63E-86
citric acid	7875	4.98E+05	4.98E+05	4.98E+05
sulfur dioxide	0	5.56E-58	26.96592	5.62E-58
continued 4-10				
project	C1	C2	C3	C4
Mol percentage				
water	0.9737098	0.9729554	0.9701911	0.973041
atmosphere	0	2.98E-93	1.59E-03	3.05E-93
citric acid	0.0262902	0.0270446	0.0282129	0.0269589
sulfur dioxide	0	3.02E-65	1.53E-06	3.05E-65
Total flow kmol/hr	3.00E+05	1.84E+07	1.76E+07	1.85E+07
Total flow kg/hr	6.77E+06	4.18E+08	4.05E+08	4.19E+08
Total flow l/min	1.01E+05	6.73E+06	6.34E+06	6.75E+06
temperature C	20	93.48749	72.41015	94.61731
pressure bar	1.01325	1.01325	1.01325	0.8106

Table 7 Status and components of each logistics (2)

	CLEANGAS	GAS	GASW	PRODUCT
molar flow rate kmol/hr				
water	7.90E+05	0	2.10E+06	1.25E+06
atmosphere	3090.025	31222.5	0	28132.48
citric acid	2.26E-04	0	0	2.12E-04
sulfur dioxide	0.5340799	27.5	0	26.96592
Mol percentage				
water	0.9961051	0	1	0.9779331
atmosphere	3.89E-03	0.99912	0	0.0220457
citric acid	2.85E-10	0	0	1.66E-10
sulfur dioxide	6.73E-07	8.80E-04	0	2.11E-05
Total flow kmol/hr	7.93E+05	31250	2.10E+06	1.28E+06
Total flow kg/hr	1.43E+07	9.06E+05	3.78E+07	2.33E+07
Total flow l/min	4.06E+08	1.42E+07	1.08E+09	8.01E+08
temperature C	100.6276	60	105	94.01374
pressure bar	1.01325	1.01325	1.01325	0.8106

Enter the necessary given conditions and restrictions, as aforesaid under the assumption that by running the above model, the amount of flue gas: 700000Nm3/h per hour processing as shown in the table of the flue gas composition, the system consumes citrate 41kg/h, water 16.2t/h, liquid gas 7.5L/Nm3, desulfurization efficiency of the system can reach 95%.

5 simulation results analysis3.1 Influence of inlet flue gas SO2 concentration on desulfurization efficiency

Sensitivity analysis of the model is carried out, and other process conditions are kept constant. The inlet flue gas SO2 concentration is adjusted, and the relationship between the flue gas SO2 concentration and the desulfurization efficiency is obtained, as shown in figure 1. Calculation conditions: the amount of flue gas is 700000 Nm3/h, the absorption liquid circulation is 5250m3/h, the liquid gas ratio is 7.5L/m3, and the citrate absorption liquid flow rate is 1008 kg/h.

Can be seen from Figure 2, in the same condition, the desulfurization efficiency of the system decreased with the increase of entrance flue gas SO2 concentration, flue gas SO2 concentration increased from 1000mg/Nm3 to 5500mg/Nm3, the desulfurization efficiency is reduced from 98% to 88.5%. This is mainly due to the influence of the increase of SO2 concentration in the gas phase on the interphase mass transfer effect。

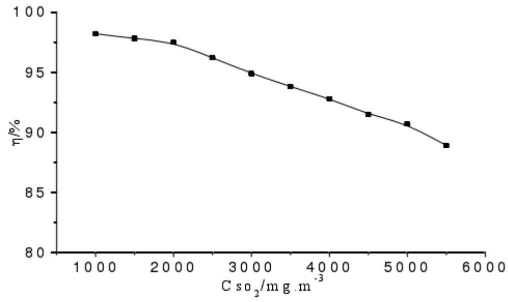


Fig.2. Effect of inlet flue gas SO2 concentration on desulfurization efficiency3.2liquidEffect of gas ratio on desulfurization efficiency

Sensitivity analysis of the model is carried out, and other process conditions are kept constant, and the ratio of liquid to gas is adjusted. The influence diagram of liquid gas ratio on desulfurization efficiency is shown as shown in figure 3. Calculation conditions: the amount of flue gas is 700000 Nm3/h, the inlet flue gas SO2 concentration is 2.73g/Nm3, and the citrate flow is 1008 kg/h. As can be seen from Figure 3, under the same conditions, the desulfurization efficiency increases with the increase of liquid gas ratio. The ratio of liquid to gas increases by about 11.5L/m3 from 2.5L/m3, and the desulfurization efficiency increases from 63% to 97%. Under actual operation conditionConsidering the desulfurization efficiency and operation cost, the ratio of liquid to gas in the flue gas desulfurization system of citrate method is chosen 7.5L/m3-10L/m3, which can meet the requirements of desulfurization efficiency greater than 95%.

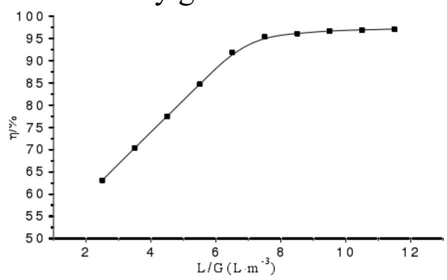


Fig.3. Effect of liquid gas ratio on desulfurization efficiency

Influence of flue gas volume on desulfurization efficiency

The sensitivity analysis of the model, the constant of other process conditions, the adjustment of the inlet flue gas amount, and the influence of the amount of flue gas on the desulfurization efficiency are shown as shown in figure 4. Calculation conditions: the absorption liquid circulation is 5250m3/h, the inlet flue gas SO2 concentration is 2.73g/Nm3, the citric acid salt flow rate is 1008kg/h. As can be seen from Figure 4, under the same conditions, the desulfurization efficiency of the system decreases with the increase of the amount of flue gas, the amount of flue gas increases from 250000Nm3/h to 700000Nm3/h, and the desulfurization efficiency is reduced from 99% to 95%. For a specific absorption tower, under the condition of other conditions unchanged, increasing the amount of flue gas, desulfurization efficiency will decline, on the contrary, efficiency will rise.

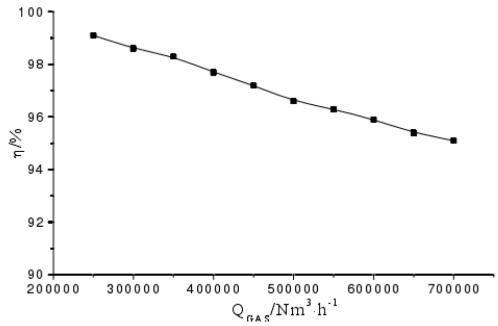


Fig.4 .Effect of flue gas volume on desulfurization efficiency

Conclusion

In this paper, the theoretical analysis of the absorption of sulfur dioxide by citrate method and the numerical simulation of absorption tower and desorption tower in the main part of the desulfurization system are carried out, and the following conclusions are obtained:

(1) draw the process flow chart and equipment connection diagram, and understand the citrate method more directly.

(2) the phase equilibrium experimental data regression to two yuan of sulfur dioxide and citric acid parameters, of which two yuan NRTL thermodynamic model of interaction parameters under AIJ=0.061653 description, can well describe the actual situation. The citrate method desulfurization process of materialbalance, the results are as follows: the amount of flue gas per hour when dealing with 700000Nm3/h system consumes citrate 41kg/h, water 16.2t/h, oxidation air requirement for 2000kg/h, liquid gas ratio 7.5L/Nm3, desulfurization efficiency of the system can reach 95%.

Through the simulation analysis, it is concluded that the desulfurization efficiency of the system decreases with the increase of inlet flue gas SO2 concentration. When the concentration of SO2 in the flue gas is below 3000mg/m3, the desulfurization efficiency can be guaranteed to be above 95%. Increased with the increase of the ratio of liquid to gas, liquid gas ratio of 7.5 and above, can achieve a good desulphurization effect, and after the liquid gas ratio increases, desulfurization efficiency changed little; reduce with increase of amount of flue gas and flue gas in the amount can be within 700000m3/h to get better effect of desulfurization; absorption amount increased with the increase of citric acid absorption liquid, but increased to a certain extent after the change are not obvious.

The optimum conditions are as follows: the inlet gas concentration is 3000mg/m3, the flue gas volume is 700000m3/h; the absorption liquid gas ratio is 7.5; the citrate consumption is 41kg/h. In actual production, the actual situation needs to be considered.

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