Experimental Analysis of Reaction Heat of CO₂ Absorption of Phase Change Absorber AEP-DPA at Low Partial Pressure

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Abstract: The reaction heat of CO_2 absorption by organic amines is directly related to the regenerative heat consumption of absorbers. Therefore, it is necessary to study and determine the heat of absorption reaction and heat of regeneration reaction of CO_2 capture solvent before its industrial validation and application. According to the law of thermodynamics, a computer model of the heat of absorption reaction and desorption reaction is established and verified. The heat of reaction of the AEP-DPA phase transition absorption system was studied under different ratios, absorption temperatures, reaction concentrations and reaction pressures. The heat of reaction increases with concentration and decreases with pressure. The reaction heat of the AEP-DPA phase transition absorption system and MEA were compared. The optimum reaction conditions were as follows: AEP-DPA ratio 6:4, absorption temperature 40 °C. The reduction rate of absorption heat and regenerative heat of the AEP-DPA phase change absorption system is more than 35% and 31%, respectively.

Keywords: CO_2; phase change absorbent; reaction heat; absorption; regeneration

1. Introduction

The use of fossil fuels has greatly promoted the development of contemporary industries. The average share of fossil fuels in today's world energy structure is as high as 65.59% [1]. However, the massive use of fossil fuels has also caused a series of environmental problems, among which the greenhouse effect is most significant. At present, the environmental problems caused by carbon dioxide are still very serious. Reducing the emission of carbon dioxide and absorbing carbon dioxide are difficult problems we face. Through unremitting efforts and continuous research, methods to absorb carbon dioxide have been developed, and organic amine chemical absorption method is one of them.

The organic amine chemical absorption method is the most mature method of flue gas CO₂ capture at present and has achieved large-scale engineering demonstration application [2]. However, there are problems such as the current absorption process, high energy consumption and high cost. Therefore, to develop a low cost absorption system and evaluate the state of current research, renewable energy is the key to the absorption system evaluation index, the reaction of the economy and the advancement of the absorbent. In organic amine chemistry, reaction heat is an important part of energy consumption in the CO₂ absorption process for organic amine. Reaction heat is closely related to the amount of CO₂ absorbed and energy consumed. The higher the unit reaction heat, the higher the regenerative energy consumption; the lower the unit heat of reaction, the lower the energy

consumption of regeneration. The higher the total reaction heat, the higher the absorption load; the smaller the total reaction heat, the smaller the absorption load.

The heat of the absorption reaction [3] is the heat released by the gas-liquid in the process, and the heat of the regeneration reaction is the heat consumed in the process of the heating and decomposition of reaction products. The total heat consumed by the regeneration process includes the heat consumed by the gas heating in the reactor (called the reactor heat capacity), the heat consumed by the solution heating, the heat consumed by the regeneration reaction (theoretically the same as the heat value of the absorption reaction) and the latent heat of vaporization of the water during the heating process. The reaction heat data is crucial for the design of a CO_2 capture device, as it reflects the steam consumption (regenerative energy consumption) required in the process of absorbent heating regeneration, which is directly related to the reaction balance [4].

Therefore, before the industrial verification and application of CO_2 capture solvent, it is necessary to study and measure the heat of the absorption reaction and regeneration reaction of the solvent. The calculation or measurement of the heat of absorption reaction is a necessary step in studying the energy consumption of chemical absorption regeneration. In this paper, a mechanism model is introduced to verify that the CO_2 reaction heat of the AEP-DPA phase transition absorption system is studied under different conditions to find the best reaction conditions for large-scale production. Based on this, it is of great significance to accurately measure the heat of CO_2 reaction in the AEP-DPA phase transformation absorption system [5].

2. Experimental Materials and Methods

2.1. Experimental Materials

The items used in this experiment are CO_2 gas, N_2 gas, PH meter, MEA, DPA, reaction heat tester, AEEA, DIPA, DEEA, AEP, AMP, DSBA, BDA, DAP, MACA, D_2EHA, DMBA, DPEA, DMCA, PNA and MOR absorbent.

A reaction heat tester was developed for CO_2 chemical absorption, which can measure the reaction heat under adiabatic conditions with high accuracy. The reaction heat test system consists of an adiabatic reactor part, an inlet preheating pressure regulation and metering part, a stirring and mixing part, a tail gas cooling regulation and metering part, ga heating power regulation part and a real-time control and data collection part, as shown in Figure 1.
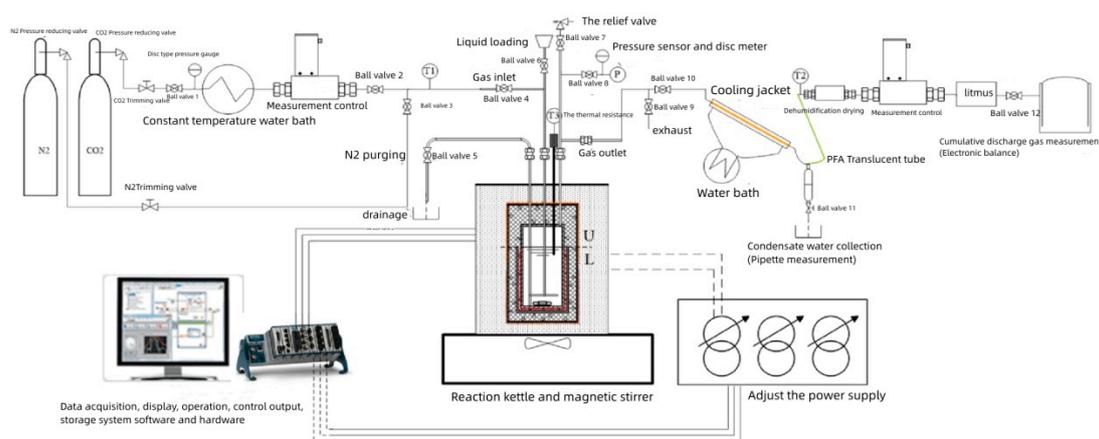
Figure 1. Composition of reaction heat test device.

The main part is the reactor and the design concept of "synchronous temperature control + aerogel insulation" is used to ensure its thermal insulation environment. The design model is shown in Figure 2.
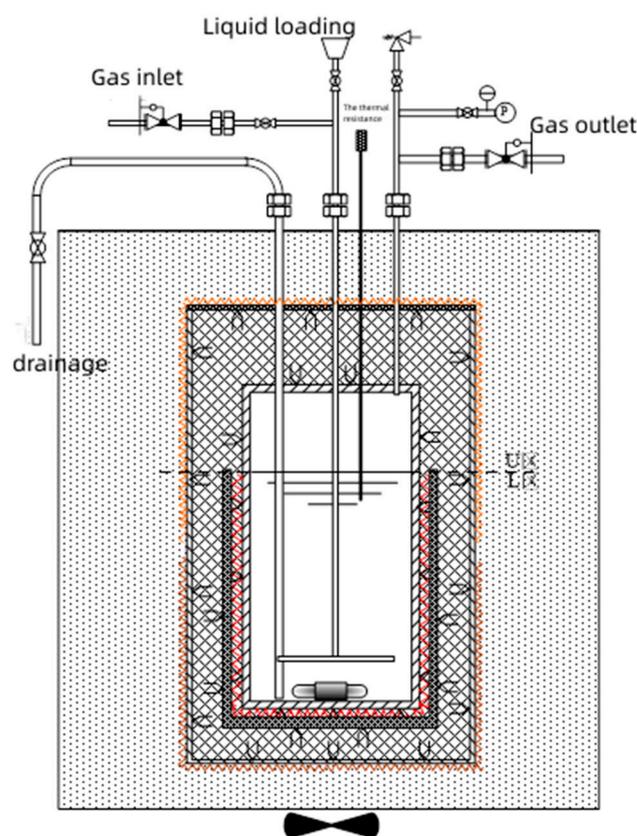
Figure 2. Reactor design model of reaction heat tester.

2.2. Experimental Method

2.2.1. Experimental Process of Absorption Reaction Heat Test

① Before the test, preheat the power supply for 45 min and set the constant temperature sink to 40 °C; turn on the dc regulated power supply and adjust to preset mode. Establish a communication connection between the NI acquisition board and Lab VIEW software (2014 version, National Instruments (NI), Austin, TX, USA).

② Before the test, N_2 was used to purge the air and other impurities in the system. The inlet flow rate was set at 600 mL/min in the LabVIEW control system and the purge time was set at 5 min.

③ Add 500 mL absorption liquid from the nozzle, turn on the stirrer and stir evenly. Heat the reactor to 40 °C (absorption reaction temperature) and start synchronous temperature control.

④ CO_2 was injected, the internal pressure of the reactor was set to 50 kPa and the absorption reaction began. The reaction temperature, reaction pressure and reaction heat value of the process were recorded.

⑤ When the CO_2 intake volume is less than 20 mL/min and the absorption temperature remains unchanged for 2 min, the absorption reaction test is considered to be over and the intake valve and control system are closed.

2.2.2. Regeneration Reaction Heat Test Process

① Start regeneration test. Open the reactor water bath heating and the re-gas exhaust valve.

② Adjust the heating temperature to the regeneration temperature required by the absorption liquid, set the reactor pressure to 20 kPa, set the initial heating temperature to the absorption reaction stable value and start the regeneration reaction thermal test.

③ When the re-gas outlet flow rate is less than 20 mL/min and the re-gas condensate is a plunger, turn off the heating power, record the heat of regeneration reaction and the regeneration test is over.

④ After the reaction heat temperature drops to room temperature, the solution is discharged with N_2 and the valves of the system are closed.

2.3. Mechanism Model of Reaction Heat Calculation

In the absorption process of the device, CO_2 gas enters by the inlet valve and the outlet is closed. At this time, the reaction is carried out in the opening system. Assuming that the total energy value of the system at time t is $E_t + e_1 dm_1$, then the total energy at $t + dt$ is $E_{t+dt} + e_2 dm_2$ and the total energy change of the open system in dt time can be calculated by the following test [6]:

$$dE = (E_{t+dt} + e_2 dm_2) - (E_t + e_1 dm_1) \tag{1}$$

$$dE = dE_{CV} + (e_2 dm_2 - e_1 dm_1) \tag{2}$$

With E_f representing the total energy of the flowing medium, the calculation formula is:

$$E_f = U + \frac{V^2}{2} + gh \tag{3}$$

In the above formula, U is the internal energy J, V is the flow medium rate m/s and h is the height m of the inlet interface relative to the datum level.

In the process of reaction absorption heat research, CO_2 enters the reactor as the flow medium and CO_2 and water vapor flow out of the reactor in the process of reaction desorption heat research, which can be called a semi-open system. The key difference between a semi-open system and a closed system is that there is a working medium inside and outside the boundary of the system, which is accompanied by the flow work of the medium, representing the energy carried by the flow medium, expressed by pv.

For the reaction heat test, the work value of the semi-open system should include the flow work difference value $p_2 v_2 - p_1 v_1$ at the inlet and outlet boundary and the net work done externally dW_{net}, so the expression of the total external work is:

$$dW = (p_2 v_2 - p_1 v_1) + dW_{net} \tag{4}$$

According to the first law of thermodynamics:

$$dQ = dE + dW \tag{5}$$

If the above two equations are substituted, then:

$$dQ = dE_{CV} + (E_{f2} + p_2 v_2)dm_2 - (E_{f1} + p_1 v_1)dm_1 + dW_{net} \tag{6}$$

Since the internal energy U is the state function and pv is the work of the flowing medium, it can be obtained as follows:

$$H = U + pv \tag{7}$$

H is the specific enthalpy value of the flowing medium, then the energy balance equation can be changed into:

$$dQ = dE_{CV} + (H_2 + \frac{v_2^2}{2} + gz)dm_2 - (H_1 + \frac{v_1^2}{2} + gz)dm_1 + dW_{net} \tag{8}$$

Since the reaction heat test system only has the inflow of CO_2, no outflow of any other flowing media and no external work is done, it can be shown that:

$$m_2 = 0; \quad dW_{net} = 0 \tag{9}$$

Then Equation (5) is:

$$dQ = dE_{CV} - (H_1 + \frac{v_1^2}{2} + gz)dm_1 \tag{10}$$

According to the measured parameter temperature rise value, the specific heat capacity of the absorption liquid, the inlet temperature and flow rate and the thermal equivalent of the system, the heat of CO_2 absorption reaction was calculated. Suppose that the real-time inlet air volume in the reaction process is L_{CO_2} mL/min, the inlet air temperature is T_{CO_2} °C, the inlet air flow rate is v_{CO_2} m/s, the inlet air temperature is T_0 °C, the initial absorption temperature of the absorption liquid in the reactor is T_I °C, the temperature at absorption equilibrium is T_E °C and the enthalpy value of the inlet CO_2 is H_{T_0}. At the beginning of the reaction, the enthalpy of CO_2 was H_{T_I}, the mass of absorption liquid was M_{ABS} kg, the average specific heat was C_{PABS}, the absorption load of CO_2 was α mol, the molar molecular weight was M_{CO_2} and the volume of absorbed CO_2 was V_{CO_2} L. The heat of reaction for CO_2 absorption is Q_{ABS} kJ/mol CO_2 and the molar volume of CO_2 is V_M.

The height difference between the inlet pipeline and the reactor is basically negligible, so $z \approx 0$. In the process of the absorption reaction heat test, since there is no heat exchange between CO_2 and the boundary (adiabatic state) and no work is performed to the outside, its enthalpy value can be considered equal to the ideal state. The enthalpy value of CO_2 in the ideal state is:

$$H_{CO_2} = A + BT' + CT'^2 + DT'^3 + ET'^4 + FT'^5 \tag{11}$$

A = 4.77805, B = 0.114433, $C \times 10^3$ = 0.101132, $D \times 10^6$ = −0.02649, $E \times 10^{10}$ = −0.034706, $F \times 10^{14}$ = −0.01314.

T' value is Fahrenheit temperature plus 460, so:

$$T' = 1.8T + 492 \tag{12}$$

There are:

$$T'_0 = 1.8T_0 + 492 \tag{13}$$

$$T'_I = 1.8T_I + 492 \tag{14}$$

Suppose the mass at t moment is M_t, then the mass at $t + dt$ moment is M_{t+dt}, then:

$$M_{t+dt} - M_t = \frac{L_{CO_2}}{V_M} M_{CO_2} dt \tag{15}$$

E_{CV} is the calorific value change of the system in dt time, including the calorific value change of the absorption liquid and the reactor shell, as shown below:

$$dE_{CV} = C_{PABS} M_{t+dt} dT + H_E dT \tag{16}$$

Then the heat release of absorption reaction within the dt micro period is as follows:

$$dQ_{ABS} = C_{PABS}(M_{ABS} + \frac{L_{CO_2}}{V_M} M_{CO_2} dt)(T_{t+dt} - T_t) + H_E(T_{t+dt} - T_t) - (H_{T'_I} - H_{T'_0} + \frac{v^2_{CO_2}}{2})\frac{L_{CO_2}}{V_M} M_{CO_2} dt \tag{17}$$

Let the moment of absorption equilibrium be t_E, then the heat value of absorption reaction is:

$$Q_{ABS} = C_{PABS}(M_{ABS} + \int_0^{t_E} \frac{L_{CO_2}}{V_M} M_{CO_2} dt)(T_E - T_I) + H_E(T_E - T_I) - (H_{T'_I} - H_{T'_0} + \frac{v^2_{CO_2}}{2})\int_0^{t_E} \frac{L_{CO_2}}{V_M} M_{CO_2} dt \tag{18}$$

For the regeneration reaction, the CO_2 inlet valve is closed and the exhaust valve is opened, so the regenerated CO_2 and water vapor flows out. Similar to the absorption process, the system is also semi-open system. Equation (15) is also suitable for a regeneration reaction.

In the regeneration process, m_1 is 0 and dW_{net} represents the heating value of the power supply to the system input, which is simplified as follows:

$$dQ = dE_{CV} + (H_2 + \frac{V_2^2}{2} + gz)dm_2 + dW_{net} \tag{19}$$

The exploratory experimental study found that $(h_2 + \frac{v_2^2}{2} + gz)m_2$ is less than 1 kJ.

$$(h_2 + \frac{v_2^2}{2} + gz)m_2 \ll dE_{CV} \tag{20}$$

Then Equation (17) can be simplified as:

$$dQ = dE_{CV} + dW_{net} \tag{21}$$

According to the measured parameter temperature rise value, absorption liquid specific heat capacity, inlet temperature and flow rate and system thermal equivalent, CO_2 regeneration reaction heat is calculated. The initial regeneration temperature of the absorption liquid in the reactor is T_E °C and the temperature at the end of regeneration is T_F °C. The mass of the absorption liquid is M_{DES} kg, the average specific heat is C_{PDES}, the CO_2 absorption load is α mol, the molar molecular weight is M_{CO_2} and the exhaust volume is V_{GAS} L. The heat of CO_2 regeneration reaction is Q_{DES} kJ/molCO$_2$ and the molar volume of CO_2 is V_M.

Because the regenerative heating process is accompanied by water vaporization and evaporation, the liquid water produced during condensation is discharged together with the regenerated CO_2. Since the change of condensate quality is a continuous process, the condensate volume can be averaged into the regenerated CO_2 volume to make the calculation model conform to the actual process as far as possible. Then, in dt time, the amount of re-gas and condensate discharged is:

Total outflow of gas and liquid = outflow of CO_2 × (1+ total condensate mass/total CO_2 regeneration mass)

Suppose that the mass at t time is M_t, then the mass at $t + dt$ time is M_{t+dt} and the system quality changes as follows:

$$M_{t+dt} - M_t = -\frac{M_{CO_2}L_{GAS}}{V_M}dt(1 + \frac{M_{H_2O}V_M}{M_{CO_2}L_{GAS}}) \tag{22}$$

Assume that the latent heat value of steam vaporization in the regeneration process is h_{H_2O} and the calorific value change of the system in dt time includes the calorific value change of absorption liquid heating, the calorific value change of the system and the latent heat of water vaporization, and the relation equation is:

$$dQ_{DES} = dQ_{HEAT} - C_{PDES}(M_{DES} - \frac{M_{CO_2}L_{GAS}}{V_M}(1 + \frac{M_{H_2O}V_M}{M_{CO_2}L_{GAS}})dt) - H_E(T_{t+dt} - T_t) - h_{H_2O}dM_{H_2O} \tag{23}$$

Assume that the end time of regeneration is t_F, then the heat value of regeneration reaction is:

$$Q_{DES} = Q_{HEAT} - C_{PDES}(M_{DES} - \int_0^{t_F} \frac{M_{CO_2}L_{GAS}}{V_M}(1 + \frac{M_{H_2O}V_M}{M_{CO_2}L_{GAS}})dt)(T_F - T_E) - H_E(T_F - T_E) - h_{H_2O}M_{H_2O} \tag{24}$$

2.3.1. Validation of Mechanism Model

In order to verify the accuracy of the reaction heat mechanism calculation, MEA, the most widely used organic amine absorber, was selected as a reference. The following table lists the data of foreign well-known scholars [2,7,8] using C80, CPA122 and other self-designed calorimeters to measure MEA absorption heat. Here, although Mathonat and Hugues and other scholars used C80, they designed their own flow units and established their own mechanism calculation models. The experimental data and maximum error are shown. It can be seen from Table 1 that the variance of reaction heat obtained by testing and calculating the mechanism model of this subject is the smallest and is consistent with the results calculated or tested by foreign scholars.

Table 1. Statistical data for absorption heat [2,7,8].

Category	Instrument/Mechanism	MEA Concentration/ (mol/L)	Temperature/K	Pressure/kPa	Heat of Absorption Reaction/(kJ/mol)	Variance/%
Mathonat 1998	C80	5	313~393	20~100	81~102	7
Carson 2000	Independent development	2~5	298	2. 65	81~83	4
Kim 2007	CPA122	5	313~393	1~3	84~110	3
Hugues 2011	C80	5	322~373	5~30	83~96	5
This topic	Independent development	5	313~351	10	83~93	3

2.3.2. System Heat Capacity Measurement

The heat capacity of the empty reactor system without absorption solution should be checked prior to the experimental measurement of reaction heat. Under the same test conditions, the heat capacity H_E of the air system at different temperatures was measured by the heating method.

The initial equilibrium temperature measured in the empty reactor was 25 °C and the heating temperature difference was 5 °C. By measuring the heating power of the reactor system, H_E can be obtained as follows:

$$H_E = \frac{\int_0^{t_E} UI dt}{T_E - T_I} \tag{25}$$

In the above two equations, U is the voltage value, I is the current value, t_E is the time when equilibrium is reached, T_E is the system temperature when equilibrium is reached and T_I is the initial temperature. Test data of heat capacity at different temperatures are shown in Table 2 below.

Table 2. Thermal equivalent measurement data of air system.

Temperature/°C	Heat Capacity/kJ/K	Fitting Error	Temperature/°C	Heat Capacity/kJ/K	Fitting Error
20	1.051	0.43%	85	1.038	0.24%
25	1.029	0.26%	90	1.049	−0.23%
30	1.016	0.67%	95	1.054	−0.45%
35	1.003	−1.12%	100	1.059	−0.14%
40	0.983	0.37%	105	1.062	0.28%
45	0.959	1.06%	110	1.072	0.63%
50	0.971	0.23%	115	1.093	−0.41%
55	0.982	−0.29%	120	1.104	−0.21%
60	0.997	−0.92%	125	1.112	0.57%
65	1.005	−0.13%	130	1.134	−0.47%
70	1.008	0.22%	135	1.138	−0.22%
75	1.012	0.77%	140	1.141	0.16%
80	1.028	−0.02%	/	/	/

The least square method is used to fit the measured data with the change of temperature and the fitting formula is $H_E = \sum_{i=1}^{n} Y_i x^i$. The fifth-order equation is used for fitting, set T_I as the initial temperature, T_E as the equilibrium temperature and taking $x = \frac{(x_i - \frac{T_I + T_E}{2})}{\frac{T_E - T_I}{2}}$, the numbers of each system can be obtained as follows: $Y_1 = 1019.36$, $Y_2 = 77.23$, $Y_3 = -46.39$, $Y_4 = 31.46$, $Y_5 = 98.25$, $Y_6 = -47.75$, can solve $x = \frac{T - 314}{60}$, curve fitting diagram is shown in Figure 3. As can be seen from the figure, for the heat capacity of empty containers, the fitting difference of most temperature points is less than 1%, indicating good fitting compliance.

Proposed and interval.
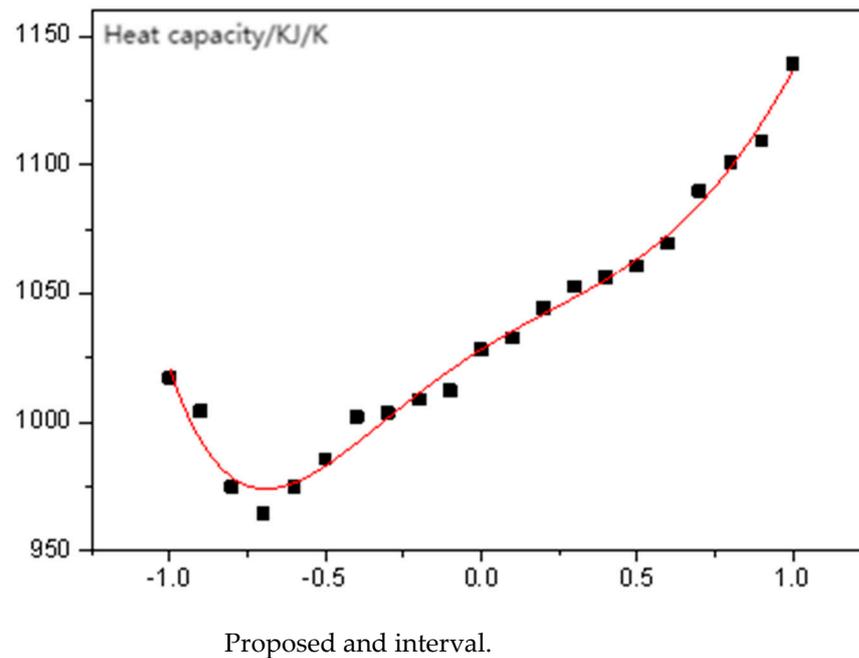
Figure 3. System thermal equivalent H_E fitting curve.

3. Uncertainty Analysis for Phase Transition Nanofluids

The uncertainty of the reaction heat test value of phase transition nanofluid was analyzed. The absorption reaction heat is an indirect measurement value. Equation (18) shows that the absorption reaction heat is a function of time, temperature and inlet flow rate, and can be obtained as follows:

$$\frac{\partial Q_{ABS}}{\partial t_E} = C_{PABS}\frac{L_{CO_2}}{V_M}M_{CO_2}(T_E - T_I) - (H_{T_I'} - H_{T_0'} + \frac{v^2_{CO_2}}{2})\frac{L_{CO_2}}{V_M}M_{CO_2} \tag{26}$$

$$\frac{\partial Q_{ABS}}{\partial T_E} = C_{PABS}(M_{ABS} + \int_0^{t_E}\frac{L_{CO_2}}{V_M}M_{CO_2}dt) + H_E \tag{27}$$

$$\frac{\partial Q_{ABS}}{\partial v_{CO_2}} = -v_{CO_2}\int_0^{t_E}\frac{L_{CO_2}}{V_M}M_{CO_2}dt \tag{28}$$

The standard uncertainty of the heat of absorption reaction is then:

$$u_{Q_{ABS}} = \sqrt{(\frac{\partial Q_{ABS}}{\partial t_E})^2 u_{t_E}^2 + (\frac{\partial Q_{ABS}}{\partial T_E})^2 u_{T_E}^2 + (\frac{\partial Q_{ABS}}{\partial v_{CO_2}})^2 u_{v_{CO2}}^2} \tag{29}$$

The heat of the desorption reaction is also measured indirectly and from Equation (24) it can be shown that the heat of desorption reaction is a function of time and temperature, giving:

$$\frac{\partial Q_{DES}}{\partial t_F} = C_{PDES}\frac{M_{CO_2}L_{GAS}}{V_M}(1 + \frac{M_{H_2O}V_M}{M_{CO_2}L_{GAS}})(T_F - T_E) \tag{30}$$

$$\frac{\partial Q_{DES}}{\partial T_F} = -C_{PDES}(M_{DES} - \int_0^{t_F}\frac{M_{CO_2}L_{GAS}}{V_M}(1 + \frac{M_{H_2O}V_M}{M_{CO_2}L_{GAS}})dt) - H_E \tag{31}$$

The standard uncertainty of the heat of desorption reaction is then

$$u_{Q_{DES}} = \sqrt{(\frac{\partial Q_{DES}}{\partial t_F})^2 u_{t_F}^2 + (\frac{\partial Q_{DES}}{\partial T_F})^2 u_{T_F}^2} \tag{32}$$

3.1. Reaction Heat Studies of Base Liquids

The absorption reaction temperature was set at 40 °C, the absorption pressure was 10 kPa and the regeneration temperature was carried out according to the values measured in Chapter 2. The absorption reaction heat and regeneration reaction heat of 1 mol/L base solution under saturated absorption conditions were compared, as shown in Tables 3–6, with AEP < AMP < DEEA

< AEEA < DIPA, and AEP had the minimum value of the base solution reaction heat, where the absorption reaction heat was 59.91 kJ/mol CO_2 and the regeneration reaction heat is 72.63 kJ/mol CO_2; this conclusion is consistent with the conclusions for base liquid comparison study absorption performance and regeneration performance.

Table 3. Reaction heat test of 1mol/L base solution.

Absorbent	Heat of Warming of Solution/kJ	System Heat-Up/kJ	Latent Heat of Vaporization/kJ	Power Heating Heat/kJ	Heat of Absorption/ (kJ/molCO$_2$)	Heat of Regeneration/ (kJ/molCO$_2$)
AEEA	87.51	56.98	150.52	212.34	63.25	82.67
DIPA	98.49	41.31	88.27	214.72	67.24	79.12
DEEA	83.77	60.29	161.03	238.73	72.83	83.45
AEP	74.81	38.56	83.93	184.74	59.91	72.63
AMP	85.62	53.45	98.78	198.62	62.71	73.56

Table 4. Test table of reaction heat of 1mol/L critical amine.

Absorbent	Heat of Warming of Solution/kJ	System Heat-Up/kJ	Latent Heat of Vaporization/kJ	Power Heating Heat/kJ	Heat of Absorption/ (kJ/molCO$_2$)	Heat of Regeneration/ (kJ/molCO$_2$)
DSBA	105.49	63.445	88.72	268.76	71.34	86.66
BDA	101.49	61.31	93.34	234.75	68.51	81.69
DPA	106.98	65.85	106.83	202.51	65.53	77.46
MCA	103.97	61.65	68.23	256.18	76.92	95.67
D2EHA	63.16	50.73	73.62	207.48	67.36	79.80
DMBA	75.49	60.32	78.25	213.61	72.22	88.46
DPEA	66.97	38.68	49.72	199.64	73.58	90.69
DMCA	98.74	43.69	83.87	225.43	75.05	93.12
PNA	85.56	54.47	97.92	239.14	76.23	94.61
MOR	64.68	36.99	96.71	204.93	67.42	80.26

Table 5. Regeneration temperature comparison of AEP-DPA composite system.

Proportion / Category	9:1	8:2	7:3	6:4	5:5
Regeneration temperature (°C)	99.5	98.5	98	98	98.5

Table 6. Delamination ratio of AEP-DPA composite system after desorption.

Proportion / Category	9:1	8:2	7:3	6:4	5:5
Upper and lower stratification ratio	1:11	1:7	1:5.5	1:5	1:4.5

By analyzing the structure of each absorbent, it can be seen that AEP has a primary amine, a secondary amine and a tertiary amine, which not only ensures the reaction rate and activity with CO_2, but also ensures the reaction capacity, making its performance excellent.

3.2. Lower Critical Amine Reaction Heat Studies

Setting the absorption reaction temperature at 40 °C and the absorption pressure at 10 kPa, comparing the heat of absorption reaction and the heat of regeneration of the critical amine at 1 mol/L, as shown in Table 4, we have DPA < D2EHA < MOR < BDA < DSBA < DMBA < DPEA < DMCA < PNA < MCA. where DPA has the lowest value for the heat of reaction, the heat of absorption reaction is 65.53 kJ/ molCO$_2$ and a regeneration heat of reaction is 77.46 kJ/molCO$_2$.

The developed AEP alcoholic amine absorber was used as the base solution and the DPA subcritical organic amine absorber was used to form a 1 mol/L phase change composite absorber system for the study of ratios of different systems. Due to the large absorption volume and long reaction time, as well as the need to take samples for analysis and testing, the inlet gas flow rate was adjusted to 1500 mL/min and the volume of absorbent in the reactor was adjusted to 700 mL, as the base solution and lipophilic amine were developed at 600 mL/min.

As can be seen from Figure 4, for different ratios of the AEP-DPA composite absorption system, the comparison of absorption rate was 0.6 mol/lAEP − 0.4 mol/lDPA > 0.5 mol/lAEP − 0.5 mol/lDPA > 0.7 mol/lAEP − 0.3 mol/lDPA > 0.8 mol/lAEP − 0.2 mol/lDPA > 0.9 mol/lAEP − 0.1 mol/lDPA.

0.9 mol/lAEP − 0.1 mol/lDPA. During the first 50 min of uptake, the CO_2 uptake rate changes gently and is in the full uptake phase; after that, the CO_2 reaction rate also decreases rapidly due to the decrease in pH and concentration.
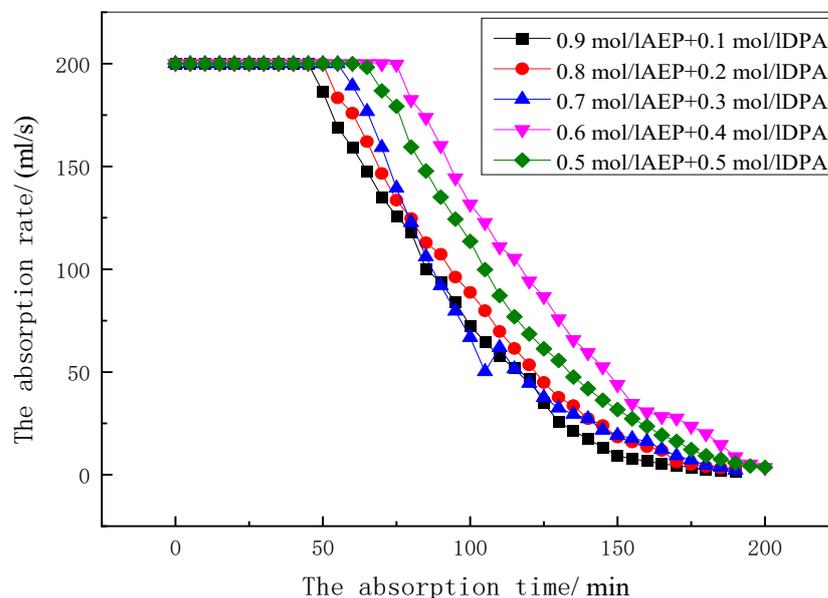
Figure 4. Absorption rate and absorption time curve of AEP-DPA composite system.

As shown in Figure 5, for the five complex system solutions, the comparison of the absorption load was 0.6 mol/lAEP − 0.4 mol/lDPA > 0.5 mol/lAEP − 0.5 mol/lDPA > 0.7 mol/lAEP − 0.3 mol/lDPA > 0.8 mol/lAEP − 0.2 mol/lDPA > 0.9 mol/lAEP − 0.1 mol/lDPA, where 0.6 mol/lAEP − 0.4 mol/lDPA had an absorption capacity of 1.0817 mol for CO_2 (1.5453 mol CO_2/mol solution), followed by 0.5 mol/lAEP − 0.5 mol/lDPA at 0.9867 mol (1.4096 mol CO_2/mol solution).
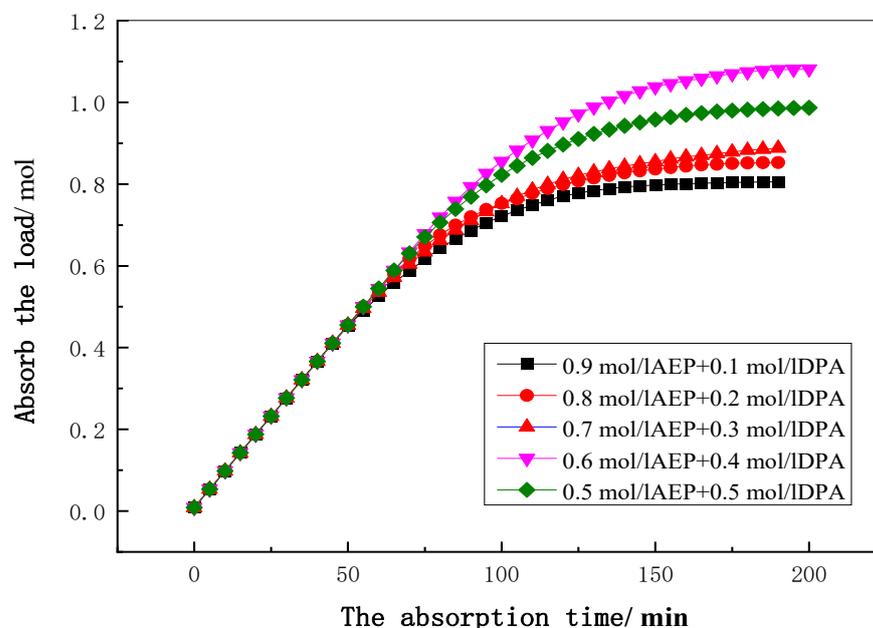
Figure 5. Absorption capacity and absorption time curve of AEP-DPA composite system.

As can be seen from Table 5, for the AEP-DPA composite system, the regeneration temperature was the lowest at 98 °C for the 6:4 and 7:3 ratios, followed by 98.5 °C for the 5:5 and 8:2 ratios.

As shown in Figure 6, under the same regeneration conditions, the regeneration amounts of the five composite absorption systems were as follows: 0.6 mol/lAEP − 0.4 mol/lDPA > 0.5 mol/lAEP − 0.5 mol/lDPA > 0.9 mol/lAEP − 0.1 mol/lDPA > 0.7 mol/lAEP − 0.3 mol/lDPA > 0.8 mol/lA-

EP − 0.2 mol/lDPA. mol/lAEP − 0.2 mol/lDPA. 0.6 mol/lAEP − 0.4 mol/lDPA showed the maximum regeneration at 18 min, completing regeneration earlier and showing the highest regeneration point compared to the rest of the composite system.
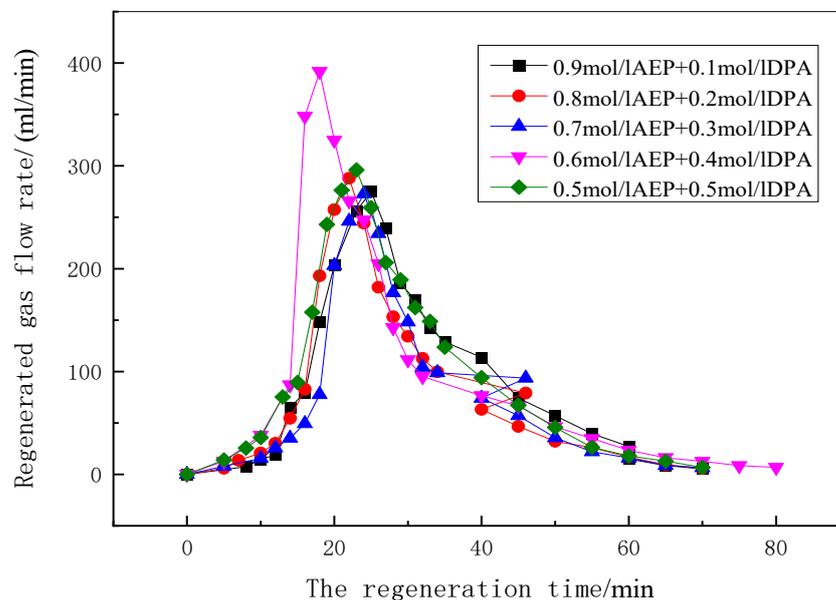
Figure 6. Relation curve between regeneration gas flow and desorption time of AEP-DPA system.

As can be seen from Table 6, for the AEP-DPA composite system, the ratios ranged from 9:1 to 5:5 and the layering ratios increased from 1:11 to 1:4. 5.

A comparative analysis of pH before and after absorption of the AEP-DPA composite system was carried out, as shown in Table 7, after six cycles, with the lowest pH drop of 10.26% or a 6:4 ratio, followed by 7:3 at 10.98%.

Table 7. pH of AEP-DPA composite system before absorption and after desorption (Six cycles).

Proportion Category	9:1	8:2	7:3	6:4	5:5
pH before absorption	11.63	11.69	11.74	11.79	11.85
pH after regeneration	10.18	10.21	10.45	10.58	10.51
pH drop rate	12.47%	12.66%	10.98%	10.26%	11.31%

The regeneration rate indicates the stability of the absorber and the ease of heating regeneration. Six cycles of absorption and regeneration experiments were carried out on the AEP-DPA composite system (see Table 8). The regeneration rates of different ratios of the AEP-DPA composite system are high, indicating that the composite system has good stability. The regeneration performance of the 6:4 ratio was the best, with a regeneration rate of 74.45% after six experiments, followed by the 5:5 ratio with a regeneration rate of 74.32%.

Table 8. Regeneration rate of AEP-DPA composite system.

Proportion Category	9:1	8:2	7:3	6:4	5:5
Primary regeneration rate	98.33%	98.19%	98.46%	98.89%	98.82%
Secondary regeneration rate	91.58%	91.56%	93.07%	92.87%	93.06%
Triple regeneration rate	87.03%	86.83%	87.63%	88.15%	87.81%
Quadruple regeneration rate	81.93%	81.94%	82.24%	83.17%	82.42%
Five times regeneration rate	76.76%	76.72%	77.12%	78.43%	77.75%
Six times regeneration rate	71.43%	72.24%	73.58%	75.95%	74.32%

As can be seen from Table 9, after a comprehensive comparison of absorption and regeneration performance, the composite absorption system with a 6:4 ratio of 0.6 mol/LA-EP − 0.4 mol/LDPA has the highest absorption rate, absorption volume and unit volume loading, the lowest regeneration temperature and the highest regeneration rate for one as well as six cycles of heating and is the best composite absorption phase change system.

Table 9. Comparison summary of AEP-DPA composite system.

Name	Concentration/(mol)	Absorption/ (molCO$_2$/mol Solution)	Rich Liquid Load/(LCO$_2$/L Solution)	Regeneration Temperature/(°C)	Primary Regeneration Rate	Six Times Regeneration Rate
9:1	1	1.1507	25.77	99.5	98.33%	71.43%
8:2	1	1.2185	27.29	99	98.19%	72.24%
7:3	1	1.2685	28.41	98	98.46%	74.58%
6:4	1	1.5453	34.61	98	98.89%	75.95%
5:5	1	1.4096	31.57	98.5	98.82%	74.32%

3.3. Study of the Heat of Reaction of the AEP-DPA Phase Change Absorption System

(1) Study of the heat of reaction of phase change absorption systems with different ratios of AEP-DPA.

Setting the absorption reaction temperature at 40 °C and the absorption pressure at 10 kPa, the heat of reaction was compared for different ratios of 1 mol/LAEP-DPA phase change absorption systems as shown in Table 10, yielding the following order of magnitude of heat of reaction: 0.6 mol/LAEP − 0.4 mol/LDPA < 0.5 mol/LAEP − 0.5 mol/LDPA < 0.7 mol/LDPA LAEP − 0.3 mol/LDPA < 0.8 mol/LAEP − 0.2 mol/LDPA < 0.9 mol/LAEP − 0.1 mol/LDPA.

Table 10. Reaction heat test of AEP-DPA system with different proportion.

Absorbent Proportioning	Heat of Warming of Solution/kJ	System Heat-Up/kJ	Latent Heat of Vaporization/kJ	Power Heating Heat/kJ	Heat of Absorption (kJ/molCO$_2$)	$u_{Q_{ABS}}$/ (kJ/molCO$_2$)	Heat of Regeneration/ (kJ/molCO$_2$)	$u_{Q_{DES}}$/ (kJ/molCO$_2$)
9:1	73.59	37.48	81.9	184.36	64.72	1.28	83.67	1.95
8:2	72.49	36.55	80.6	178.74	59.73	1.18	75.25	1.71
7:3	74.77	36.74	79.1	181.73	60.62	1.18	76.43	1.73
6:4	68.33	34.9	73.1	172.68	56.77	1.11	71.16	1.64
5:5	70.69	35.9	75.2	175.62	58.25	1.14	74.53	1.69

It can be seen from Table 10 that, with the reduction of the ratio of AEP and DPA, the heat of absorption reaction and the heat of regeneration reaction first decreased and then increased, mainly due to the different absorption loads caused by the interaction between the two.

(2) Study of the heat of reaction of AEP-DPA phase change fluids at different absorption temperatures

Table 11 shows the heat of reaction data for 0.6 mol/LAEP + 0.4 mol/LDPA + 0.05 wt.% CuO phase change fluid solution measured at different absorption temperatures at an absorption pressure of 10 kPa. As can be seen from the table, as the temperature rises, the absorption load of the phase change absorption system rises and then falls, corresponding to a decrease and then an increase in the unit heat of absorption. This indicates that the phase change absorption system has the optimum reaction temperature, which is 40 °C for the AEP-DPA solution. According to the comparison between Tables 10 and 11, the absorption heat and regeneration heat of the phase change fluid after adding CuO at the same proportion have decreased to a certain extent compared with that before adding, which confirms that CuO nanoparticles enhance the mass transfer in the absorption process and regeneration of the absorption system.

Table 11. Reaction heat data of AEP-DPA at different temperatures.

Temperature/°C	Heat of Warming of Solution /kJ	System Heat-Up /kJ	Latent Heat of Vaporisation kJ	Power Heating Heat /kJ	Heat of Absorption/ (kJ/molCO$_2$)	$u_{Q_{ABS}}$/ (kJ/molCO$_2$)	Heat of Regeneration/ (kJ/molCO$_2$)	$u_{Q_{DES}}$/ (kJ/molCO$_2$)
20	64.65	36.92	96.71	234.93	69.61	1.26	79.27	1.77
30	85.34	66.86	105.92	209.54	60.37	1.15	77.36	1.65
40	67.16	34.72	72.61	170.47	53.62	1.01	68.48	1.48
50	88.65	59.77	92.64	197.96	58.54	1.09	75.65	1.66
60	96.94	65.85	106.19	212.38	75.93	1.41	91.93	2.09

(3) Study of the heat of reaction of AEP-DPA phase change fluids at different reaction pressures

Table 12 shows the heat of reaction data for the phase change fluid solution of 0.6 mol/ LAEP + 0.4 mol/LDPA + 0.05 wt.% CuO at an absorption temperature of 40 °C, measured at different pressure conditions. As can be seen from the table, as the pressure rises, the absorption load of the phase change absorption system increases and the unit heat of absorption decreases. This indicates that the high pressure favors solution absorption and energy consumption reduction.

Table 12. Reaction heat data of AEP-DPA under different absorption pressure.

Pressure /kPa	Heat of Warming of Solution/kJ	System Heat-Up/kJ	Latent Heat of Vaporisation/kJ	Power Heating Heat/kJ	Heat of Absorption/ (kJ/molCO$_2$)	$u_{Q_{ABS}}$/ (kJ/molCO$_2$)	Heat of Regeneration (kJ/molCO$_2$)	$u_{Q_{DES}}$/ (kJ/molCO$_2$)
10	67.16	34.76	72.46	170.4	53.62	0.96	68.48	1.54
20	69.13	35.22	74.57	173.39	52.94	0.95	67.53	1.51
30	71.72	37.1	75.42	176.3	52.17	0.94	65.95	1.48
40	72.83	38.48	76.39	177.84	51.47	0.92	64.76	1.45
50	73.97	39.39	77.1	179.3	50.86	0.91	63.97	1.42
60	74.21	40.12	78.32	180.6	50.31	0.90	63.56	1.41
100	75.96	42.23	80.29	183.07	49.53	0.89	62.06	1.39

It can be seen from Table 12 that, with the increase of pressure, the absorption load of the phase change absorption system increases and the unit absorption heat decreases. This shows that high pressure is conducive to solution absorption and energy consumption reduction.

A comprehensive analysis of Tables 10–12 shows that, within the 95% confidence interval, the ratio of the heat of absorption reaction uncertainty value to the test mean is less than 2% and the heat of desorption reaction is slightly larger at around 2.3%, which is due to the increased random error in the system test caused by the heating and warming of the desorption process.

(4) Comparative study of AEP-DPA phase change absorption system and MEA reaction heat

The absorption reaction temperature was set at 40 °C and the absorption pressure at 10 kPa. A comparative study of the heat of reaction was carried out for different concentrations of the AEP-DPA phase change fluid absorption system and the most widely used absorber, MEA, as shown in Table 13.

Table 13. Comparison of reaction heat between AEP-DPA-CuO and MEA.

Category	Heat of Absorption/ (kJ/molCO$_2$)	Heat of Regeneration/ (kJ/molCO$_2$)	Rate of Decline of Absorbed Heat	Regenerative Heat Decline Rate
1 mol/L				
AEP-DPA-CuO	53.62	68.48	34.79%	33.89%
MEA	83.23	103.59	/	/
2 mol/L				
AEP-DPA-CuO	55.91	72.65	35.97%	32.39%
MEA	87.32	107.46	/	/
3 mol/L				
AEP-DPA-CuO	58.85	75.32	35.78%	33.71%
MEA	91.64	113.63	/	/

The heat of reaction data for the AEP-DPA phase change fluid at different concentrations can be seen from the table: with the concentration increasing, the absorption load per unit phase change absorption system decreases and the heat of absorption per unit increases rapidly. It is also seen that the heat of absorption and the heat of regeneration of the AEP-DPA phase change system are substantially lower than those of the MEA solution at the same concentration, with the rate of decrease in heat of absorption greater than 35% and the rate of decrease in the heat of regeneration greater than 31%. This shows that the absorption reaction heat and regeneration energy consumption of the AEP-DPA phase change system applied in practical engineering will be significantly lower than that of MEA solution, which has a strong energy-saving effect.

4. Conclusions

Based on the study of the reaction heat of CO$_2$ absorption by organic amines, this paper puts forward the calculation mechanism model of the heat of absorption and desorption reaction and verifies this model. The conclusion shows that the variance of the reaction heat is small compared

with that at home and abroad, which reaches a first-class level. The self-developed reaction heat tester reactor was used to study the reaction heat and the results were discussed in combination with the mechanism model and uncertainty analysis. The optimal reaction conditions of the AEP-DPA phase transition absorption system were analyzed to achieve the effect of energy saving.

(1) Base liquid and lower critical amine reaction heat testing studies were carried out and it was found that AEP had a base liquid reaction heat minimum and DPA had a lipophilic amine reaction heat minimum.

(2) A study of the reaction heat of the AEP-DPA phase change absorption system at different ratios, different absorption temperatures, different reaction concentrations and different reaction pressures was carried out. The conclusion of the study showed that the best reaction conditions were the AEP-DPA ratio of 6:4 and the absorption temperature of 40 °C.

(3) A comparative study between the AEP-DPA phase change absorption system and the MEA reaction heat was carried out and it was found that the decrease rate of absorption heat was greater than 35% and the decrease rate of regeneration heat was greater than 31% for the same concentration of AEP-DPA compared with the MEA solution, with significant energy saving effect.

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