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Energy Consumption Minimization in Amine Plants Using Hybrid Nanostructures

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ABSTRACT ─ Hydrogen production via steam reforming of methane is an energy intensive process. One of the sub-units within a hydrogen production unit is amine section where, CO2 absorbs by amine. Methyl-di-ethanol-amine (MDEA) used in the amine sub-unit, is modified with UiO-66-NH2 to achieve a new amine with higher absorption capacity. The absorption isotherms were experimentally obtained at 60 and 40°C. Also, the amine sub-unit of Tehran Oil Refinery is simulated by HYSYS software before and after addition of UiO-66-NH2. Experimental results showed that, addition of UiO-66-NH2 to the MDEA solution increases the absorption of CO2 by about 12.1%. Enhancement on absorption ability of modified MDEA solution decreased the electrical energy consumption on the pumps by about 12.1% and the amount of electrical energy consumption on the coolers by 7.84%. Also the steam consumption on the reboilers decreased by 11.19%.

KEYWORDS: *Methyl-di-ethanol-amine, UiO-66-NH2, carbon dioxide, hydrogen, energy consumption*

Introduction

Among various methods proposed to produce hydrogen one, can refer to thermochemical, electrochemical, photochemical, biological, and photolysis techniques. The processes employed via these techniques include steam reforming, partial oxidation, self-thermal reforming, coal degassing, biomass pyrolysis, electrolysis, and photocatalytic water splitting [1]. One of the stages within the course of steam reforming is the CO_2 gas removal where CO_2 is absorbed by a liquid solvent. Liquid solvents used to absorb solutes are generally classified into physical and chemical variants. The most commonly used chemical solvents are seen to be aqueous solutions of alkanolamines. Alkanolamines are usually categorized into primary, secondary, and tertiary types. Primary alkanolamines include mono-ethanol-amine (MEA) and di-glycol-amine (DGA). Di-ethanol-amine (DEA) and di-iso-propanol-amine (DIPA) comprise the second group of alkanolamines. The tertiary alkanolamines, however, include tri-ethanol-amine (TEA) and methyl-di-ethanol-amine (MDEA). For many years, DEA and MEA were used to absorb CO_2. However, having primary amines (e.g. MEA) or secondary amines (e.g. DEA) mixed with tertiary amines (mainly MDEA), the advantages of both types of amines in the mix will be combined (i.e. high acid gas absorption capacity and high stability of DEA (a tertiary amine) along with high reaction rates provided by the primary or secondary amines when reacted to acid gases (CO_2 in particular)) to not only enhance acid gas absorption rate and capacity, but also significantly decrease the required energy for the solvent to be reduced. Lower corrosive properties and lower flow rate for the circulating fluid are among other advantages delivered by mixed-type amines. Another commonly referred method to enhance CO_2 gas absorption is to use nanofluids as risers along with the amine solution. To name just a few, the followings are some of unique characteristics provided by such materials: abnormal increase in thermal conductivity, low concentration and Newtonian behavior, dependence to the particle size, reduced required pumping power and reduced costs. Due to high CO_2 gas absorption capacity of such nanofluid compounds as MOF, COF, nano-SiO_2, and nanocarbon, the researchers within this industry have developed the idea of using such compounds in the course of sweetening processes. Stability of this nanofluids together with the intention to increase CO_2 gas absorption are seen to be the two principle causes giving rise to the use of mixed nanofluids in aqueous-amine environments to increase loadings of CO_2 absorption. Their hydrophobic properties and in-solution stability are, however, to be considered as the two main factors. Having these nanostructures in a hybrid from with other agents such as amine functional groups, silica, etc. may contribute to a more stable solution of higher CO_2 absorption capacity. In 1990, the topic of nanofluids as a new heat transfer medium was first introduced by Choy from the Department of Energy Technologies, U. S. National Labs in Oregon. Mass transfer enhancement using micro particles was first proposed by Carls and Best[2]. In 2003, Zeo *et al.* investigated the contributions from micro-particles on the mass transfer rate to suggest that by such actions as changing film thickness as a result of mixing, or reducing gas diffusion coefficient, micro-particles in aqueous solutions may either increase or decrease mass transfer coefficient[3]. Studying the effect of silica nanoparticles of 12 nm size on the absorption rate of CO_2 in DEA solution inside a stirred tank reactor, Park and Chue (2006) concluded that, as nanoparticle concentration in the solution increases, there will be an elastic effect which results in reduced absorption rate[4]. In 2008, Kamati and Surosh investigated the effect of different concentrations of Fe_3O_4 magnetic nanoparticles on CO_2 absorption by MDEA in a wet wall tower to observe an increased absorption as nanoparticle concentration was increased in liquid phase[5]. Furthermore, they observed no significant contribution from alternative external magnetic field into the absorption. Jiazong Jian *et al.* worked on the chemical absorption of CO_2 in a nanoparticle bearing MEA solution. They studied the enhanced mass transfer in the presence of nanoparticles in the solution to find that CO_2 absorption was enhanced by 8% in the presence of nanoparticles compared to that in pure MEA[6]. Ali Hagh Talab *et al.* had CO_2 absorption in SiO_2 and ZNO nanoparticle bearing water investigated[7]. Neda Shabani *et al.* studied the effect of increased silica nanoparticles into CO_2 absorption in normal MDEA activated with piperazine in a stirred tank reactor[8]. Being an important issue all around the world of today, the necessity to save energy has given rise to a situation where industrialists try to undertake new techniques and optimize operating conditions towards reducing energy consumption. There are numerous factors contributing into energy consumption in refinery units. Knowing that amine segments in hydrogen production units are referred to as energy-intensive industrial units with such energy-intensive equipment as reboilers, compressors, air coolers and pumps, along with the high cost of amine (which is an imported good) and its rapid deactivation characteristic, researchers have been looking forward to incorporate new nanostructures to reduce amine consumption along with lowering energy consumption in refineries.In this research, the used MDEA in the amine segment of hydrogen production unit of Tehran Oil Refinery was enhanced by UiO-66-NH_2 nanostructure to produce a new amine. Further, through an experimental approach, the isotherms of the new amine were obtained at different temperatures (60, 50, 40, and 30°C). The isotherms were also simulated, by HYSYS software, with the operating data from the amine unit in Tehran Oil Refinery. Matching the experimental results obtained from the isotherms of the new amine to the absorption rate data obtained from simulation, it was observed that the circulating solution rate was reduced by 12.1006% resulting in reduced electrical energy consumption and reduced amount of steam used by the stripping tower reboiler by 11.19% and 2.34%, respectively.

Experimental

1. Solution preparation

In order to prepare the modified amine solution with 0.1wt% of UiO-66-NH_2, 0.05 g of UiO-66-NH_2, 19.95 g of MDEA and 30 g of distilled water were mixed in a 100 ml glass round-bottom flask. To have a homogenous solution, it was treated in an ultrasonic device for 30 min to achieve a clear and transparent solution.

2. Apparatus and procedure

Figure 1 shows the schematic diagram of system. The temperature of the double-wall equilibrium cell is adjusted (with total cell volume of 283 ml), with a water recirculation bath (Lauda model Proline P12), with temperature stability within ± 0.01 K. The temperature was measured using TM-917 Lutron digital thermometer with 0.01 K resolution equipped with a Pt-100 sensor inserted into the cell via thermo-well. The equilibrium cell pressure was measured using a Druck model PTX 1400 pressure transmitter sensor in the range of 0 to 40 kPa, which was accurate within 0.01 % of full scale and that of the gas container was measured using a Druck model PTX 1400 pressure transmitter sensor in the range of 0 to 100 kPa, which was accurate to within 0.1 % of full scale. The operation of the apparatus was carried out in such a way that at first, a vacuum applied to the equilibrium cell using Vacuum Pump BS 5000-11 Type: BS2208 A21042003 (up to 0.1 kPa). Then, certain amount of interest solution (One third of cell was filled with solution) was introduced to the equilibrium cell. The temperature was then adjusted to the desired value; after reaching the equilibrium state, the pressure sensor in this case shows the vapor pressure of solution. The amount of CO_2 was introduced to the equilibrium cell from the gas container whose volume is well known. The amount of CO_2 injected into the equilibrium cell was calculated in which accurate PVT data were obtained from the National Institute of Standards and Technology (NIST) for pure CO_2 and the following equation.

$$n_{CO_2} = \frac{V_C}{RT_a}\left(\frac{P_1}{Z_1} - \frac{P_2}{Z_2}\right) \qquad (1)$$

Where V_C denotes the volume of the gas container, Z_1 and Z_2 are the compressibility factors corresponding to the initial and final state in the gas container before and after transferring the CO_2, and T_a is the ambient temperature. The equilibrium state inside the cell was normally achieved within about 3 hour by the operation of the mechanical header stirrer. The equilibrium partial pressure of CO_2 in the equilibrium cell, P_{CO_2} , was calculated by

$$P_{CO_2} = P_T - P_V \qquad (2)$$

Where P_T denotes the total pressure and P_V is vapor pressure of solution. P_V is vapor pressure of pure water. Antoine equation was used for calculation of vapor pressure of water at different temperature as

$$P_V = 10^{A - \frac{B}{(C+T)}} \qquad (3)$$

Where $A = 8.07131$, $B = 1730.63$ and $C = 233.426$ and T is the temperature of water when water temperature is in the range of 273.15-373.15 K. The moles of remaining CO_2 in the gas phase, $n_{CO_2}^{g}$, was determined from

$$n_{CO_2}^{g} = \frac{V_g P_{CO_2}}{Z_{CO_2} RT} \tag{4}$$

Where V_g is the gas-phase volume in the autoclave corrected with the consideration of liquid volume change due to the solubility of CO_2, and T is the equilibrium temperature of the cell, and Z_{CO_2} is the compressibility factor of carbon dioxide at P_{CO_2} and T . The moles of CO_2 in the liquid phase, $n_{CO_2}^{l}$, was then determined with

$$n_{CO_2}^{l} = n_{CO_2} - n_{CO_2}^{g} \tag{5}$$

And finally, the molality of the loaded CO_2 in the liquid phase, m_{CO_2} , is defined as

$$m_{CO_2} = \frac{n_{CO_2}^{l}}{w_{sol}} \tag{6}$$

Where w_{sol} is defined as weight of solvent in term of kilogram. Using equations 1 to 5, which is based on determining the mass balance, loading of gas is measured. The volume of gas phase in equilibrium cell, V_g , is obtained from the difference between the cell volume and the volume of uncharged solvent.

The solubility of CO_2 in both aqueous solutions was measured at 40, and 60 °C.

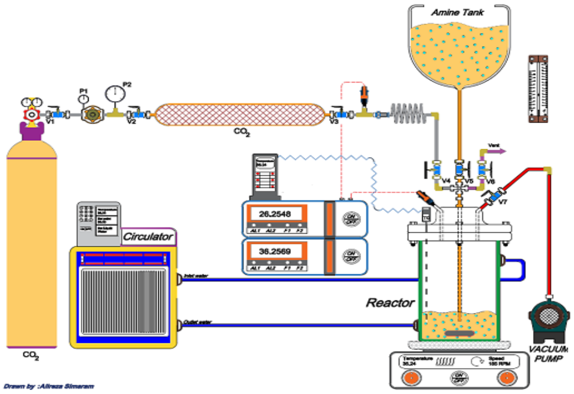

Figure 1. Schematic diagram of CO_2 absorption system

3. Experimental Results and Discussion

The experimental data of CO_2 solubility in MDEA solution and modified MDEA solution with 0.1wt% of UiO-66-NH_2 are reported on figures 2 and 3. The results show that absorption of CO_2 increases with addition of UiO-66-NH_2 to MDEA solutions and this proves that UiO-66-NH_2 is an effective component in absorbing CO_2 into MDEA solutions. The data on figures 2 and show that, temperature has negative effect on CO_2 absorption. This figures show that solubility of CO_2 increases with increasing partial pressure and decreases with increasing temperature for both systems. Results show that addition of UiO-66-NH_2 nanoparticles into MDEA solutions, increase of capacity of CO_2 sorption up to 12 %.

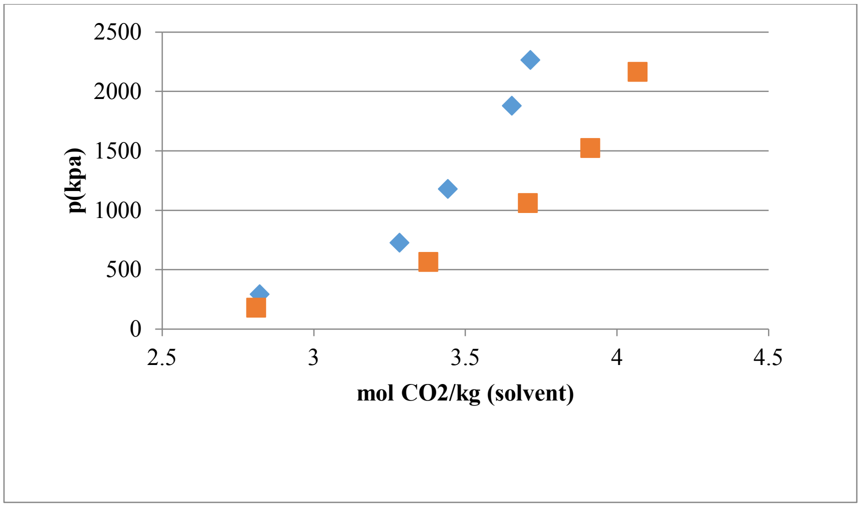

Figure 2. Moles of absorbed CO_2 versus pressure (■ MDEA and ■ modified MDEA) at 40°C.

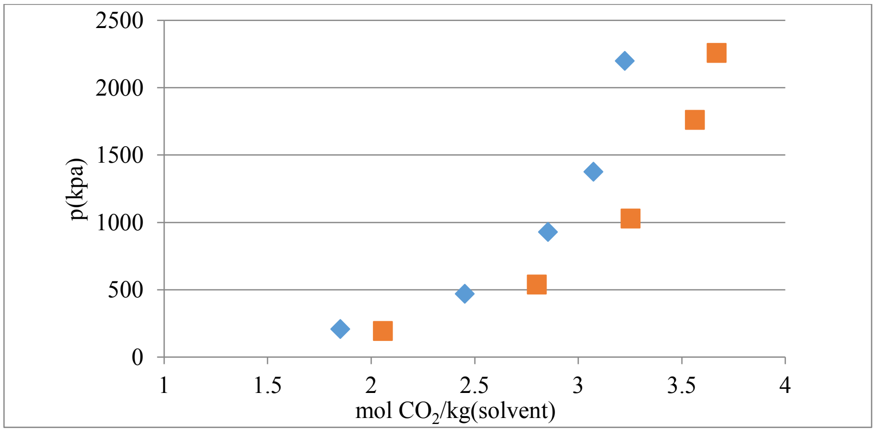

Figure 3. Moles of absorbed CO_2 versus pressure (■ MDEA and ■ modified MDEA) at 60°C.

Simulation

1. Process description

The simulated amine section of the H_2 unit of Tehran Oil Refinery is shown on Figure 4. The molar flow rates of all components on feed stream are presented on Table 1. Briefly, the feed gas (Stream 1) which contains CO_2 after dehydration on V-100, enters absorption tower (T= 158°F and P=216 psig) where, contact with amine solution (Stream 2). The absorption process occurs in the absorption tower which contanis 28 trays. CO_2 rich solvent (stream 5) leaves the absorption tower and after flashing on V-101 and heating on E-100 goes to the stripper tower. In the stripper column, CO_2 leaves the liquid phase and absorbs on the gas phase and leaves the tower from the top section of the column. Lean solvent from the bottom of stripper (stream 9) recycled to absorption tower. Stripper operates at is 7 psig and the bottom temperature of the tower is 249°F. Similar to all strippers the stripper tower has a condenser on the upper section and a reboiler on the bottom section to create liquid and gas phase for mass transfer operations.

Table 1. Molar flow rates of all components on feed

Components	**Kgmol/hour**
Hydrogen	3794
methane	102
Carbon monoxide (CO)	11.4
Carbon dioxide (CO_2)	778
Steam (H_2O)	4169

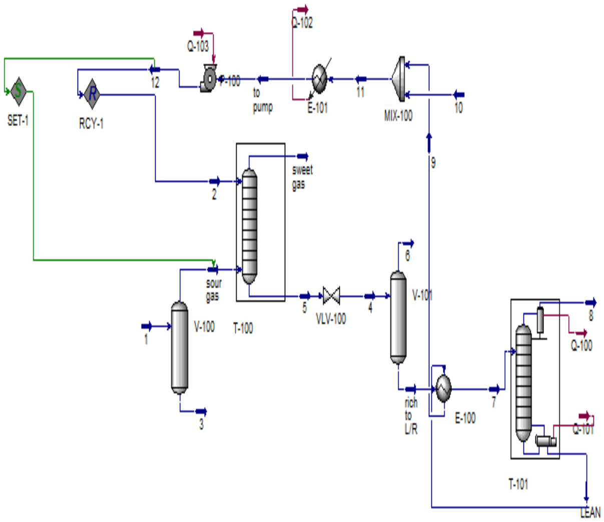

Figure 4. The simulated amine section of the H_2 unit of Tehran Oil Refinery

2. Simulation

The unit was simulated, by HYSYS software before and after addition of UiO-66-NH_2 to MDEA solution. The amounts of energy consumption for both scenarios are determined. Based on the simulation results, the consumption duty was obtained for the pumps and coolers and rebolires. Considering the governing electrical energy relationships for the pumps and the governing electrical energy relationships and geometrical characteristics of the coolers, the consumed electrical energy and steam consumption in the unit before addition of UiO-66-NH_2 to MDEA solution was obtained and reported in Table 2.

Table 2. Electrical energy and steam consumptions in the unit before addition of UiO-66-NH_2.

Electric Energy consumption in pumps	**787.4 kw**
Electric Energy consumption in air coolers	**213.982 kw**
Steam consumption in rebolires	**96731.55 kg/h**

Figure 5 shows the circulating solvent flow rate *vs.* CO_2 absorption rate obtained from simulation before addition of UiO-66-NH_2 to MDEA solution. Based on the data on this figure, the circulating solvent flow rate (Q) and absorption rate (A) can be correlated by the following equation.

$$Q = 745872A^{-1.027} \tag{7}$$

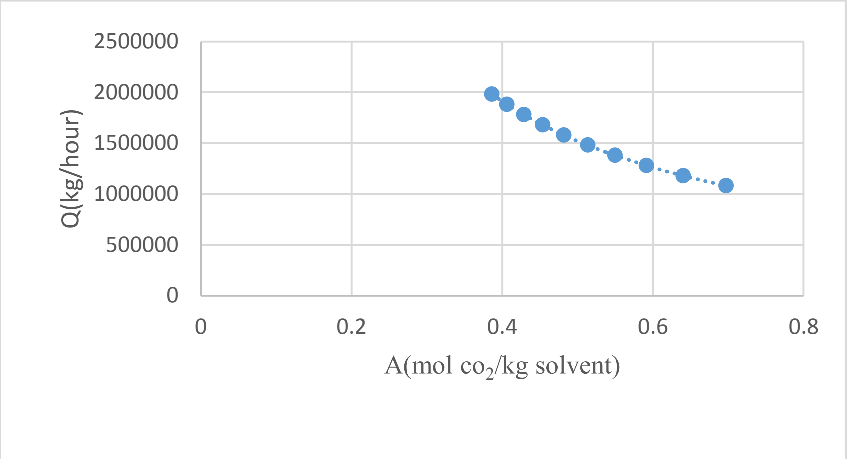

Figure 5. Circulating solvent rate *vs.* absorption rate obtained from simulation.

Also, figure 6 shows the ratio of experimental absorption rate before addition of UiO-66-NH_2 to MDEA solution (A) to the absorption rate after addition of UiO-66-NH_2 to MDEA solution (B) versus pressure.

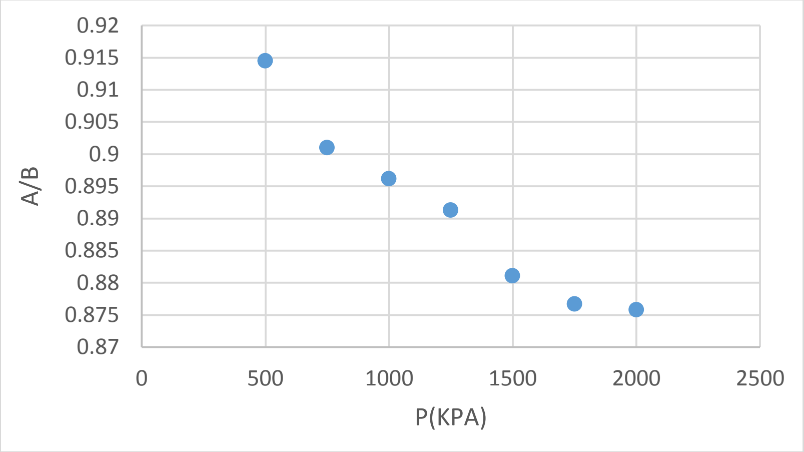

Figure 6. The ratio of experimental absorption rate before addition of UiO-66-NH_2 (A) to the absorption rate after addition of UiO-66-NH_2 (B) versus pressure.

Considering figures 5 and 6 and matching the simulation results with the experimental data, the ratios of circulating solvent flow rate after addition of UiO-66-NH_2 to MDEA solution (Q_2) to the circulating solvent flow rate before addition of UiO-66-NH_2 to MDEA solution (Q_1) is calculated and are shown on figure 7. In addition, the percentages of circulating solvent rate reduction at different pressures are presented on figure 8.

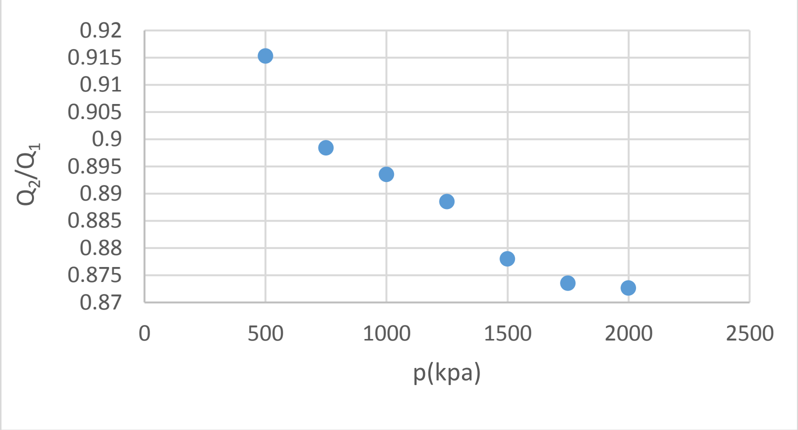

Figure 7: the ratios of circulating solvent flow rate after addition of UiO-66-NH_2 (Q_2) to the circulating solvent flow rate before addition of UiO-66-NH_2 (Q_1) vs. pressure.

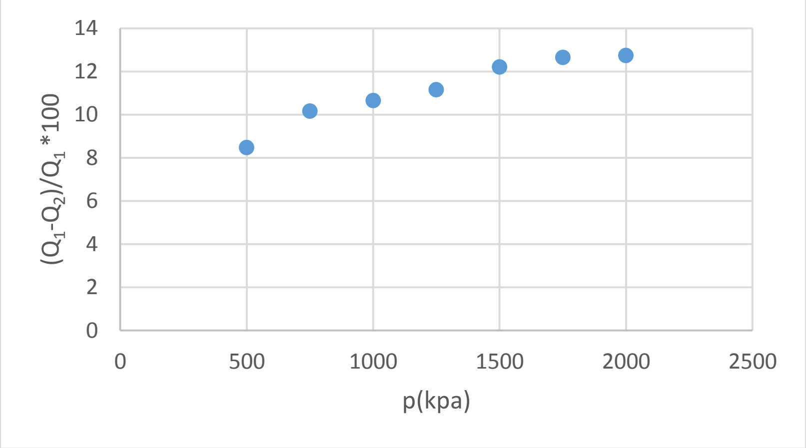

Figure 8. Percentage of circulating solvent rate reduction at different pressures.

From figures 7 and 8, it can be concluded that, the circulating solvent rate is reduced by about 12.1%, when UiO-66-NH_2 is added to the MDEA solution. Based on these results, the system was then re-simulated with the new reduced circulating solvent rate and the amounts of the consumed electrical energy and steam in the unit is obtained. The results are reported on Table 3. is the overall reduction in electrical energy consumption of the unit. Comparing the results on table2 and table 3 shows that the amount of electrical energy consumption on the pumps decreases by about 12%. Also, the amount of electrical energy consumption on the coolers decreases by 7.84%. In addition, the amount of steam consumptive decreases by 11.19%.

Table 3. The amounts of electrical energy and steam consumption after addition of UiO-66-NH_2 to the MDEA solution

Electric Energy consumption in pump	**692.1 kw**
Electric Energy consumption in air cooler	**197.190 kw**
Steam consumption in rebolires	**94464.05 kg/h**

Conclusion

Addition of UiO-66-NH_2 to the MDEA solution increases the absorption of CO_2 significantly. Enhancement on absorption ability of modified MDEA solution decreases the required circulating solvent rate by 12.1%. Using the modified MDEA solution decreases the overall electrical energy consumption and steam consumption, significantly.

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