Using Mixed Amine Solution for Gas Sweetening

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Abstract—The use of amine mixtures employing methyldiethanolamine (MDEA), monoethanolamine (MEA), and diethanolamine (DEA) have been investigated for a variety of cases using a process simulation program called HYSYS. The results show that, at high pressures, amine mixtures have little or no advantage in the cases studied. As the pressure is lowered, it becomes more difficult for MDEA to meet residual gas requirements and mixtures can usually improve plant performance. Since the CO_2 reaction rate with the primary and secondary amines is much faster than with MDEA, the addition of small amounts of primary or secondary amines to an MDEA based solution should greatly improve the overall reaction rate of CO_2 with the amine solution. The addition of MEA caused the CO_2 to be absorbed more strongly in the upper portion of the column than for MDEA along. On the other hand, raising the concentration for MEA to 11%wt, CO_2 is almost completely absorbed in the lower portion of the column. The addition of MEA would be most advantageous.
Thus, in areas where MDEA cannot meet the residual gas requirements, the use of amine mixtures can usually improve the plant performance.

Keywords—CO2., H2S, Methyldiethanolamine, Monoethanolamine

I. INTRODUCTION

IN most cases, the mixtures contain MDEA as the base amine with the addition of one or two more reactive amines such as MEA or DEA . These amine mixtures have been called a variety of names including formulated amines and MDEA based amines. MDEA has been recognized primarily for its ability to selectively absorb H_2S from a gas while leaving large amounts of CO_2 in the gas [1, 2, and 3].
 MDEA's selective absorption ability is due to its relatively slow reaction rate with CO_2. MDEA has a number of properties that make it desirable for broader application [1, 3].
■ High solution concentration (up 50 to 55 wt %)
■ High acid gas loading
■ Low corrosion
■ Slow degradation rates
■ Lower heats of reaction
■ Low vapor pressure and solution losses

 MDEA is the most desirable amine to use even in cases where large amounts of CO_2 must be removed. In cases where a large degree of CO_2 removal is necessary, the relatively slow CO_2 –MDEA reaction rate must be overcome by the proper design of the absorber and amine system. The CO_2 reaction rate can be significantly increased by a combination of the following:

1- Selection of proper operating temperatures in the absorber.
2- Proper design of the absorber trays to give adequate liquid residence times.
3- Addition of one or two more reactive primary or secondary amines to form a mixture of amines in water [1].
 In this work the use of mixed amine solutions for gas sweetening is addressed.

II. PROCESS CHEMISTRY

   H_2S is thought to react almost instantaneously with the amines by proton transfer.

$$H_2 S + A\min e \Leftrightarrow [A\min e]H^+ + HS^- \qquad (1)$$
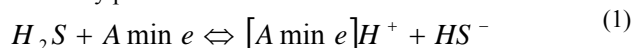
CO_2 is thought to react with primary and secondary amines to form a carbamate.

$$CO_2 + H_2O + A\min e \Leftrightarrow [A\min e]COOH^+ + OH^- \quad (2)$$
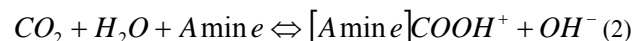
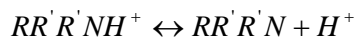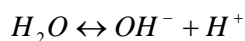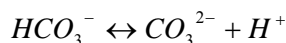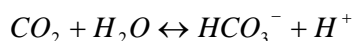Since MDEA is a tertiary amine and does not have a hydrogen attached to the nitrogen, the CO_2 reaction can only occur after the CO_2 dissolves in the water to form a bicarbonate ion.
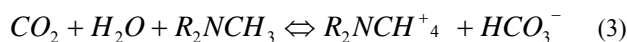
$$CO_2 + H_2O + R_2NCH_3 \Leftrightarrow R_2NCH^+_4 + HCO_3^- \quad (3)$$

Since the CO_2 reaction rate with the primary and secondary amines is much faster than with MDEA, the addition of small amounts of primary or secondary amines to an MDEA based solution should greatly improve the overall reaction rate of CO_2 with the amine solution [1, 4, 5, 6, 7, 8].
The following chemical reactions occur in an aqueous MDEA solution when CO_2 and H_2S are present:

$$CO_2 + H_2O \leftrightarrow HCO_3^- + H^+$$
$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+$$
$$H_2O \leftrightarrow OH^- + H^+$$
$$RR'R'NH^+ \leftrightarrow RR'R'N + H^+$$
$$H_2S \leftrightarrow HS^- + H^+$$
$$HS^- \leftrightarrow S^{2-} + H^+$$
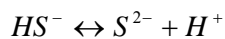
Where, R corresponds to a methyl group and R' to an ethanol group [9].
   Reactions which tack place in the liquid phase can be divided in principle into two groups. Reactions equilibrium controlled and reactions kinetically determined. The chemical reactions determine the composition of the different ion

species in the liquid phase and, therefore, the enhancement of the mass transfer. Equilibrium reactions are fast enough to assume chemical equilibrium throughout the entire liquid phase. This assumption is fulfilled if reaction kinetics is significantly faster than mass transport in the phase. A certain number of equilibrium reactions occur within the system CO_2 –H_2S-Alkanolamines [10].

III. PROCESS OPERATING PARAMETERS

Several operating parameters must be carefully examined to yield the optimum design for each application. Of course, the sweet gas requirements will strongly influence the operating parameters. These may easily range, for H_2S, from 3.5 ppm pipeline specification to higher values in fuel gas systems or hydro cracker recycles and, for CO_2, from 2% for pipeline specification down to less than 100 ppm for feed to some LP-gas separation facilities. Depending on the feed gas composition, temperature and pressure along with the sweet gas requirements, the most sensitive operating parameters include:

A.   Lean Amine Temperature

Usually the only parameter available for control of the column temperature is the lean amine temperature. Since the CO_2 reaction with MDEA is kinetically controlled; a hotter column increases the reaction rate. However, once the lean amine temperature reaches about 135 to $140 \circ F$, the decrease in solubility of the CO_2 in the amine solution will usually become the overriding factor and the net CO_2 pickup will begin to decrease.

B.   Circulation Rate

When the circulation rate is increased for any given column, the CO_2 pickup will increase. This usually holds true for MDEA in a column of fixed diameter even through the liquid residence time on a tray will decrease with increased circulation.

C.   Steam Stripping Rate

As the steam-stripping rate is increased, a leaner amine will be produced which will result in lower H_2S and CO_2 in the sweet gas for any given situation.

D.   Liquid Residence Time on Tray

Since the CO_2 reaction rate with MDEA is slow, the column diameter and weir height must be adjusted to give sufficient time for the reaction to occur. The usual range of weir heights are from 2 to 4 in. resulting in residence times from about 2 to 5 sec [1].
The operating data of amine-acid gas absorber are given in Table 1.

IV.   PROCESS CALCULATIONS

To analyze the use of mixed amine solutions for gas sweetening, the Amine Pkg. equation of state was added to a process simulation program called HYSYS to predict the

vapor-liquid equilibrium for mixed amine systems. The kinetic model is used to simulate the slow CO_2 reaction with amines.

V.   DISCUSSION

Blended amine solvents, which consist of a mixture of primary or secondary amine with a tertiary amine, combine the higher CO_2 reaction rates of the primary or secondary amine with the higher CO_2 loading capacity of the tertiary amine. Thus, a blended amine solvent providing both higher CO_2 reaction rate and higher CO_2 equilibrium capacity may result in substantial lower solvent circulation rates compared to a single amine solvent. With respect to economics, solvent circulation rate is the single most important factor in determining the economics of a gas treating process using chemical solvent. A lower circulation rate, besides resulting in lower pumping energy cost, also leads to reduced regeneration energy requirement, which accounts for about 70% of the total operating cost of a gas treating process. Besides these economic advantages of blended amine solvents, another major advantage in the operation of the treating process is derived from the degree of freedom that is, the selectivity of a blended amine solvent can be varied as required from high H_2S selectivity to total acid gas removal by varying the relative concentrations of the consitituent amines in the blend [5].

The use of mixed amine solutions for gas sweetening was investigated using a variety of cases in a amine unit as shown in Fig. 1. The cases involve gas pressures of 1063 and 1200 psia. These cases were chosen to demonstrate the influence of adding small amounts of a primary or secondary amine to an MDEA solution. In an effort to more clearly demonstrate the influence of the amine mixture; all operating parameters were held constant in all runs except for amine mixture and circulation rate.

TABLE 1
TYPICAL OPERATING DATA OF AMINE-ACID GAS ABSORBER

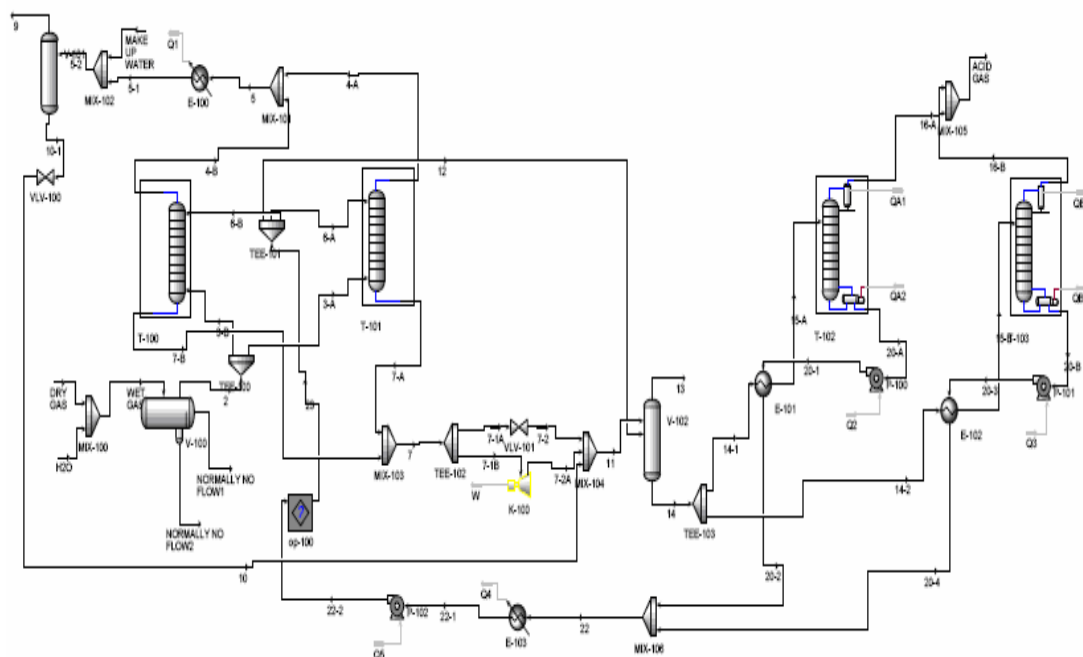| Parameter	Value (MDEA)	Value (DEA)
Inlet gas flow rate (SCMH)	173000	173000
Inlet liquid flow rate (M3/HR)	350	405
Inlet gas temperature ©	58	58
Inlet liquid temperature ©	58	58
Amine Concentration(%wt)	45	34
Gas in press.(PSIA)	1063	1063
L. Amine in press.(PSIA)	1100	1100
H_2S inlet gas composition (%mole)	3.588	3.588
CO_2 inlet gas composition (%mole)	6.459	6.459

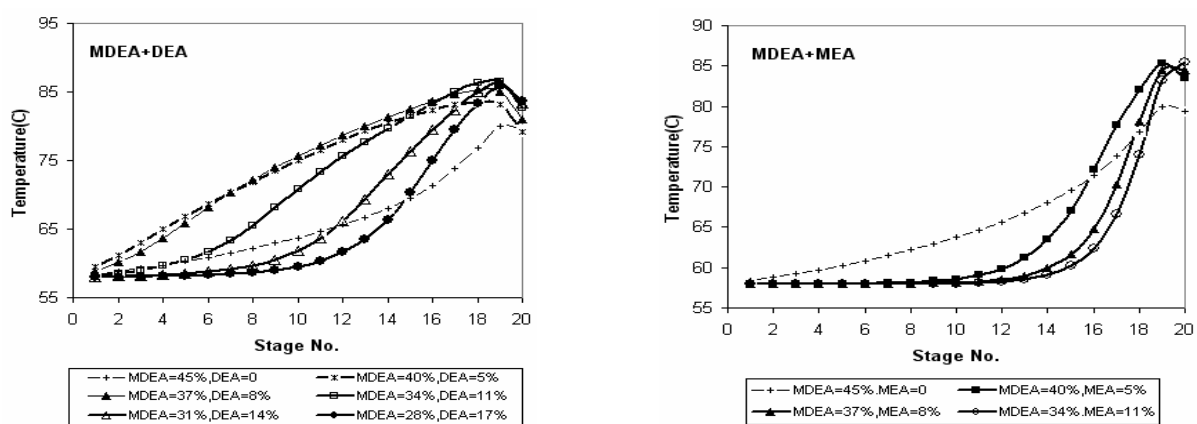Fig. 1. Schematic of gas sweetening process by HYSYS

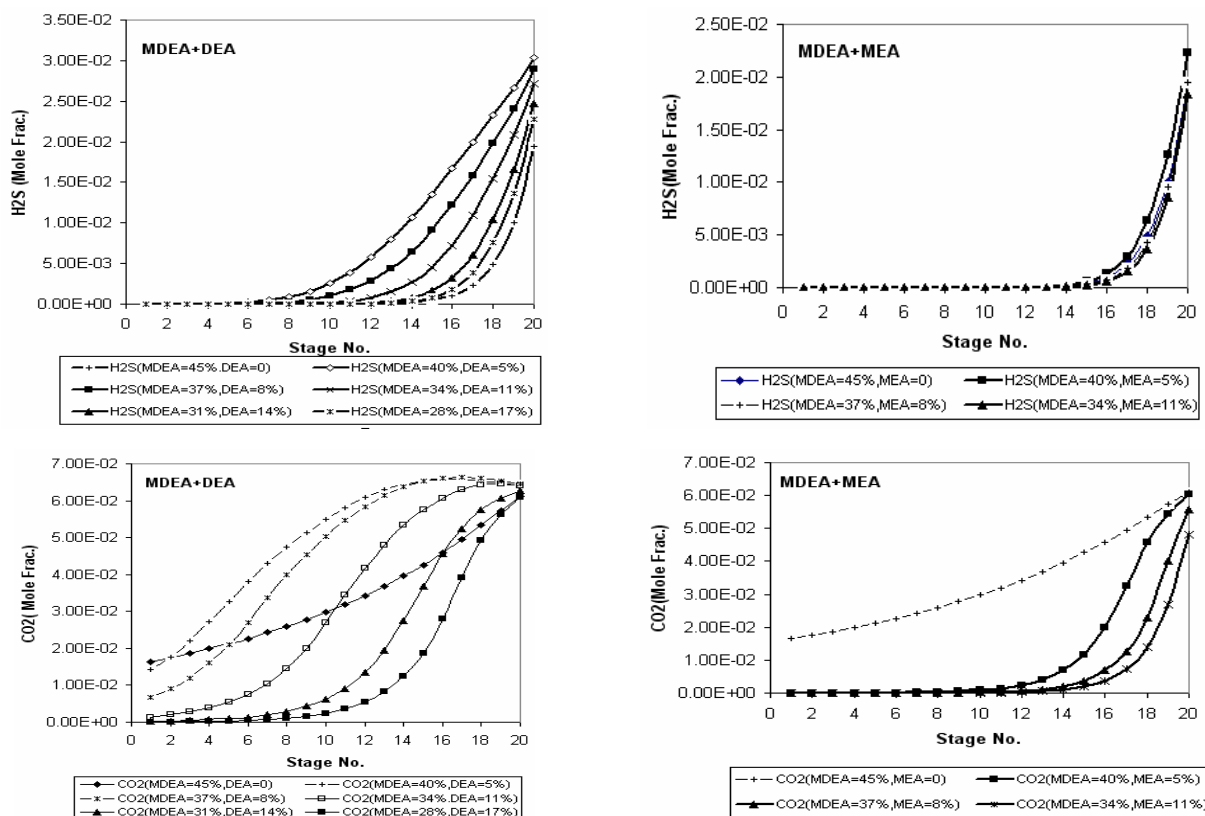Fig. 2. Effect of amine mixture on absorber temperature

Fig. 3. Effect of amine mixture on residual acid gas

A comparison of the temperature profiles in the absorber shown in Fig. 2. The profiles in Fig. 2 along with the concentrations from Fig. 3 show that the addition of MEA caused the CO_2 to be absorbed more strongly in the upper portion of the column than for MDEA along. On the other hand, raising the concentration for MEA to 11%wt, CO_2 is almost completely absorbed in the lower portion of the column.

The Figures shows that the addition of MEA would be most advantageous.

In Fig. 3, circulation rate for amine mixture in absorber for MDEA, MEA and MDEA, DEA is same.

By improvement in DEA and MEA concentration in amine mixture, maximum temperature of absorber decrease and the location of reaction transfer to the stages of bottom absorber and the absorption of acid gases increase.

CO_2 outlet gas composition (sweet gas) for mixed amines is given in Table 2.

TABLE II
CO_2 OUTLET GAS COMPOSITION (SWEET GAS) FOR MIXED AMINES

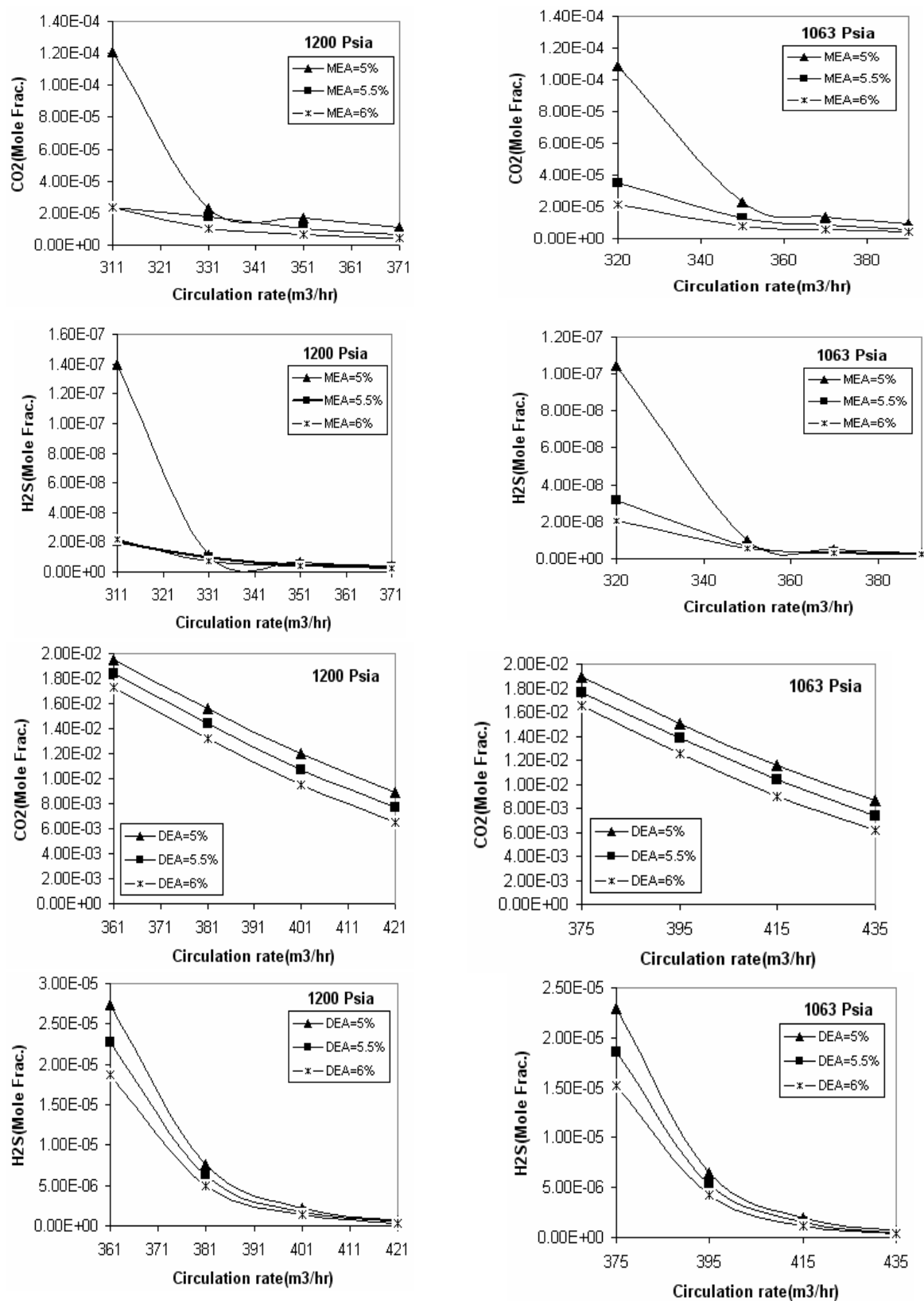| CO_2 outlet gas composition(sweet gas) (%mole)	MDEA=34%,MEA=11%	MDEA=34%,DEA=11%
	2.7×10^{-7}	1.4×10^{-3}

Fig. 4. Effect of pressure on amine mixture

As shown in Fig. 4, the cases involve sour gas pressures of 1063 and 1200 psia. This Figure shows the vapor composition profiles for H_2S and CO_2 along the absorber as a function of circulation rate for amine mixtures. As can be seen, at high pressures, amine mixtures have little or no advantage in the cases studied. As the pressure is lowered, it becomes more difficult for MDEA to meet residual gas requirements and the CO_2 reaction rate can be significantly increased by addition of one or two more reactive primary or secondary amines to form a mixture of amines in water.

VI. SUMMARY AND CONCLUSIONS

The use of mixed amine solvents for gas sweetening has been investigated using a process simulation program called HYSYS. In all cases, 45wtpercentage total amines in water were used with the base case as 45-wtpercentage MDEA. MEA and DEA were used as additives to form the mixture.The results show that, at high pressures, amine mixtures have little or no advantage in the cases studied. As the pressure is lowered, MDEA becomes less capable of picking up sufficient CO_2 to meet pipeline specification. When large amounts of CO_2 are being passed through to the sweet gas at relatively low pressures, it becomes difficult for MDEA to reach pipeline specification for H_2S if the inlet gas contains more than about 1000 ppm H_2S. At these lower pressures, the addition of a more reactive amine clearly enhances the solution ability to remove CO_2. Thus, in areas where MDEA cannot meet the residual gas requirements, the use of amine mixtures can usually improve the plant performance.

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