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A MORE ENERGY EFFICIENT PRODUCT FOR CARBON DIOXIDE SEPARATION

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ABSTRACT

Aqueous solutions of alkanolamines such as monoethanolamine (MEA) have been used for years to separate carbon dioxide and hydrogen sulfide from other gases in continuous absorption/desorption processes to meet very low treated gas specifications. However, MEA can undergo side reactions with CO_2 which produce various types of degradation compounds. These by-products reduce performance of the solvent leading to increased energy consumption and corrosion. This can be a serious problem in applications such as the removal of CO_2 in synthesis gas and natural gas treating with down stream cryogenic equipment. Formulated alkanolamine products based on methyldiethanolamine (MDEA) have made significant advances in energy efficiency, but are still susceptible to degradation and decreased performance. A next generation product, GAS/SPEC* CS-PLUS, has now been developed and shown to be even more energy efficient. In addition, it improves separation and overall capacity while maintaining long term performance.

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INTRODUCTION

Aqueous solutions of alkanolamines have been used for years to separate gas mixtures or impurities in continuous absorption-desorption processes (Figure 1). During this time many different types of alkanolamines have been evaluated for this application. Some alkanolamines work better than others depending upon the particular gas treating requirement. (1)

Nevertheless, the majority of separation processes utilize either monoethanolamine (MEA), or diethanolamine (DEA).(2) These particular alkanolamines are relatively inexpensive and readily available. They are also supported by a significant body of chemical and engineering data including various computer simulations which can be used to predict and optimize the treated gas composition and process energy demands.(3)

However, as applications have become more demanding, these traditional products are finding their limitations. Increased capacity, tighter gas specifications, and lower energy and maintenance requirements can only be achieved in some cases with use of more specialized products. A good example of this is where large quantities of CO_2 must be removed from gases in the natural gas and synthesis gas treating industries.(4)

CO_2 REMOVAL

Low levels of CO_2 are required in the treated gas in ammonia and hydrogen applications and natural gas treating with downstream cryogenic equipment. In synthesis gas plants, low levels of CO_2, normally less than 100 ppm, are required in the treated gas to reduce the load on the methanator and reduce the amount of recycle in the synthesis loop which will have a positive impact on the capacity of the plant. Downstream cryogenic equipment in natural gas treating require low levels of CO_2 in the treated gas to prevent freeze up of the liquefaction equipment and maintain high hydrocarbon recovery rates.

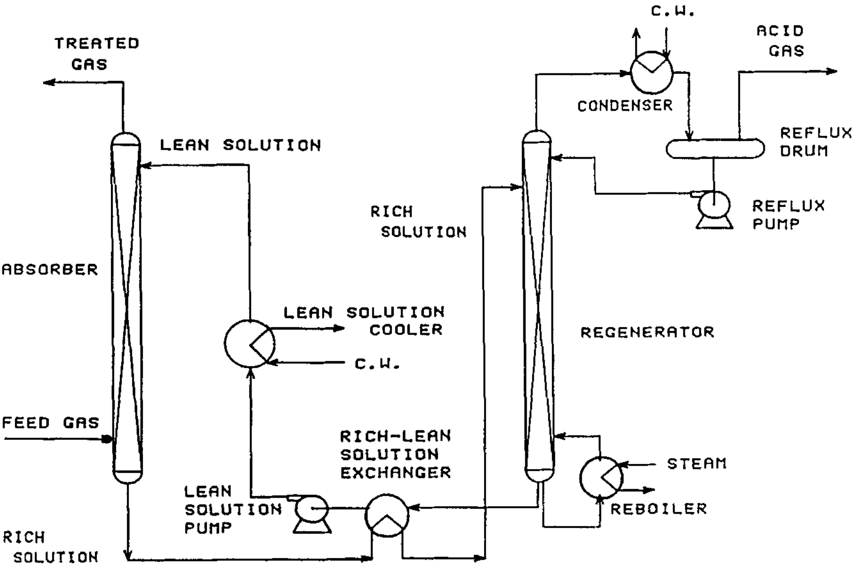

FIGURE 1. PROCESS DIAGRAM FOR GAS SEPARATION PROCESS

Traditionally these treating applications utilized MEA as the CO_2 removal solvent. As capacity increases and reductions in energy consumption were required, MEA strength was frequently increased from 15 -- 18 wt.% to 25 -- 30 wt.%. This was normally accomplished with the use of heavy metal corrosion inhibitors such as vanadium, antimony, or arsenic.(7)

Although capacity and energy improvements were achieved, there were also increased disposal costs and environmental concerns. Even with corrosion inhibitors present, localized corrosion can still occur resulting in frequent system maintenance and costly down time.

AMMONIA PLANTS

Ammonia is produced by the catalytic reaction of nitrogen and hydrogen. The hydrogen source for this process is from steam reforming. However, in order to

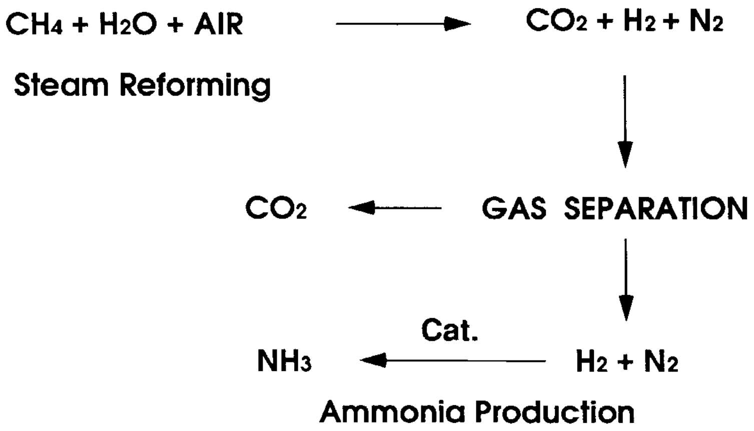

FIGURE 2. PROCESS EQUATIONS FOR AN AMMONIA PLANT

prevent catalyst poisoning, the carbon oxides must be completely removed. Carbon dioxide is the dominate byproduct making up 17 to 18 percent of the gas mixture. Carbon dioxide removal has historically been accomplished with an alkanolamine process using monoethanolamine.(5) This is a critical step in the production of ammonia and related products (Figure 2).

Efficient and essentially complete separation of carbon dioxide from synthesis gas is accomplished at pressures of approximately 400 psi. The CO_2 removal requirement varies from about 1.2 tons of CO_2 per ton of ammonia for steam reforming of natural gas, to about 2.5 tons of CO_2 per ton of ammonia for gas made by the partial oxidation of heavy fuel oil.(6)

Residual CO_2 and carbon monoxide in the treated gas are then catalytically removed in a subsequent methanation step.

$$CO + CO_2 + H_2 \dashrightarrow CH_4 + H_2O$$

In order to reduce the load on the methanator, the carbon dioxide concentration must be kept as low as possible. The use of monoethanolamine in the

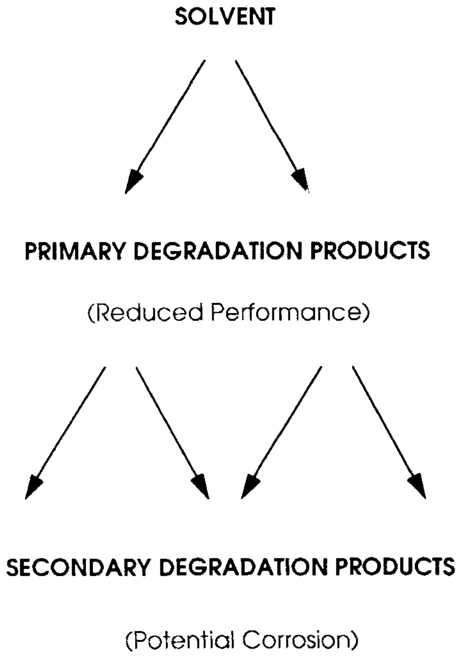

FIGURE 3. SOLVENT DEGRADATION PROCESS

alkanolamine process was based on this need and its ability to achieve less than 100 ppm in the treated gas.

AMINE DEGRADATION

Another problem with MEA is that it is unstable in CO_2 service. Side reactions involving carbamate formation produce primary and secondary by-products which affect separation and energy efficiency (Figure 3).

$$\text{MEA} + CO_2 \text{ --> MEA-carbamate --> by-products}$$

The above reaction is relatively slow, but does occur at a significant rate under conditions found in the separation process. It appears that MEA carbamate is first

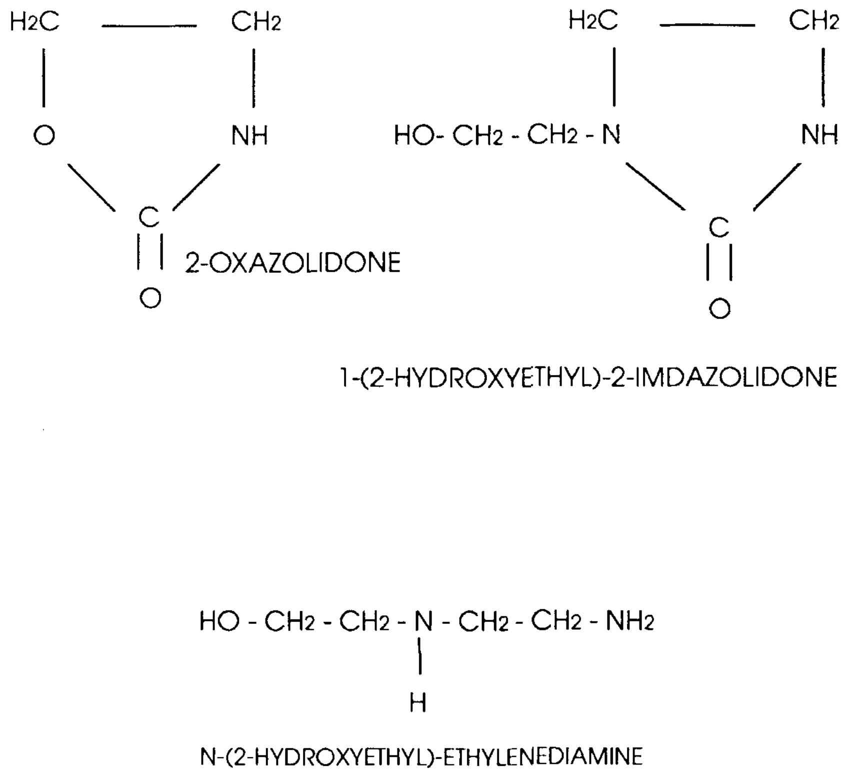

FIGURE 4. MEA DEGRADATION PRODUCTS

converted to 2-oxazolidone which is subsequently converted to 2-hydroxyethyl-2-imidazolidone. This compound then hydrolyzes to produce N-(2-hydroxyethyl)-ethylenediamine (Figure 4). These by-products of the CO_2 removal process are either less reactive than MEA, or are more difficult to regenerate. Either situation can result in increased corrosion.

Amine degradation products are removed, either continuously or periodically, from the process solution using a side stream distillation unit called a thermal reclaimer.(8) This not only requires additional energy, but also results in product losses and continuous waste disposal.

ENERGY REQUIREMENTS

The ability to cut operating costs while increasing or maintaining production is the key to profitability in any gas treating application. This makes incremental cost reductions very important, especially associated energy costs. The reboiler duty usually represents the major energy cost and is a combination of sensible heat, heat of reaction, and heat of vaporization.

The sensible heat is the energy required to bring solvent to the temperature of the reboiler. It is directly proportional to the circulation rate of the solvent. The heat of reaction is the energy needed to break the association between the solvent and the CO_2 and/or H_2S. The heat of vaporization is the amount of energy needed to generate sufficient steam to carry the CO_2 and/or H_2S overhead in the stripper and adequately regenerate the solvent. It is determined by the reflux ratio (molar ratio of water to acid gas in the overhead) which in turn is determined by the lean loading necessary to achieve the treated gas specification.

A 15% MEA solution operating with a lean loading of 0.1 mol of CO_2 per mol of MEA and a rich loading of 0.45 mol of CO_2 per mol of MEA will have a reboiler heat duty of at least 100,000 BTU per lb-mol of CO_2 with 2.0 being typical for a stripper reflux ratio.

FIRST GENERATION MDEA SOLVENTS

The liabilities associated with the use of MEA in the gas separation process include high energy, potential corrosion, hazardous waste disposal, frequent maintenance, and substantial amine loss. In order to improve on this process, new products were developed by several companies, including Dow Chemical and Union Carbide. These products were based on methyldiethanolamine or MDEA (Figure 5).

MDEA is a tertiary alkanolamine and, unlike MEA, cannot form a carbamate (Figure 6). MDEA is much more stable and because it is operated at higher concentrations it has more CO_2 and H_2S carrying capacity than MEA. Also, no solvent reclaimer is needed. MDEA also has a lower heat of reaction: 570 BTU per

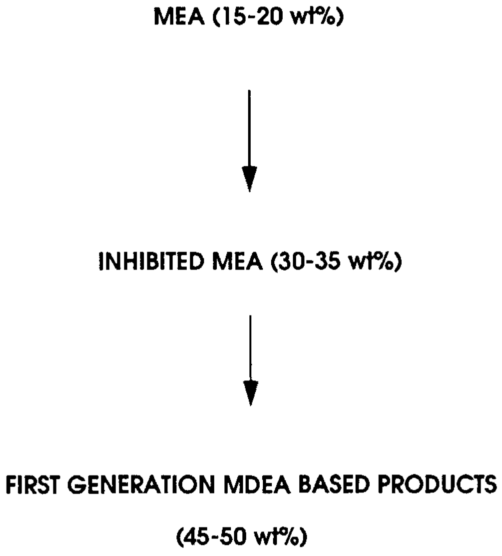

FIGURE 5. SOLVENT EVOLUTION IN THE AMMONIA INDUSTRY

pound of CO_2 compared to 820 BTU per pound CO_2 for MEA and 450 BTU per pound H_2S compared to 650 BTU per pound H_2S for MEA. Unfortunately, the reaction kinetics of MDEA are much lower than with MEA. It is impossible to achieve the very low CO_2 specification in the treated gas with MDEA alone, even with concentrations over 50%.

However, in the process of developing new solvents, it was found that certain compounds when added to MDEA produced solvents that were as effective as MEA but still had better energy and capacity. Several ammonia plants converted to these proprietary solvent formulations and were able to achieve both the energy and capacity improvements. Longer term, some of these products ran into difficulty due to corrosion. The corrosion was not caused by MDEA, but resulted from degradation processes involving the solvent additives. The problem was so severe that in some cases part of the process equipment had to be replaced.

MONOETHANOLAMINE (MEA):

$$HOCH_2CH_2NH_2 + CO_2 \xrightarrow{\text{Fast}} HOCH_2CH_2NHCO_2H$$

$$HOCH_2CH_2NHCO_2H + HOCH_2CH_2NH_2 \longrightarrow HOCH_2CH_2NHCO_2^- + HOCH_2CH_2NH_3^+$$

METHYLDIETHANOLAMINE (MDEA):

$$CO_2 + H_2O \xrightarrow{\text{Slow}} H_2CO_3$$

$$(HOCH_2CH_2)_2NCH_3 + H_2CO_3 \longrightarrow (HOCH_2CH_2)_2NCH_3H^+ + HCO_3^-$$

FIGURE 6. SIMPLIFIED REACTION MECHANISMS

A NEXT GENERATION PRODUCT

In order to understand the factors associated with additive degradation and corrosion, a study was undertaken by the GAS/SPEC Technology Group of The Dow Chemical Company to identify degradation products and processes associated with these MDEA based products. It was found that the degradation process was affected by several factors including the CO_2 loading, the average and maximum process temperature, and the solvent concentration. An increase in any of these will increase the rate of degradation.

A high temperature, high pressure autoclave was used to evaluate the different factors affecting degradation. The use of this equipment to perform accelerated aging studies also indicated differences in the stability of various additives. A program was undertaken to develop a solvent that was more stable than the first generation products. This process included: 1) screening of various solvent formulations, 2) accelerated aging study of best compositions, 3) performance and corrosion testing of aged solvent, and 4) identification and evaluation of conversion products.

Many solvent formulations were evaluated in terms of stability and process performance. Absorptivity, energy requirements, and solvent corrosivity were determined not just on the virgin solvent, but also on the aged solvent (Table 1). The results of these studies were helpful in producing a product that is much better than the first generation solvents. This new product is called GAS/SPEC* CS-PLUS (See Table 1).

OPERATIONAL EXPERIENCE

GAS/SPEC* CS-PLUS has been and continues to be successfully utilized in natural gas processing, enhanced oil recovery, ammonia, hydrogen and chemical processing plants. Case histories for two ammonia plants are shown in Table 2.

With CS-PLUS, the CO_2 level in the treated gas in an ammonia plant of Kellogg design has been established at levels of less than 40 ppm, and in many cases less than 10 ppm. In addition, there is at least a 15% increase in ammonia capacity using CS-PLUS over inhibited MEA.

The stability of CS-PLUS is quite good when compared to the first generation solvents. After 24 months of continuous operation, few degradation products have been detected even in extreme service. The major degradation products have been identified and determined not to be detrimental, and overall performance has not been decreased.

Table 1. LABORATORY COMPARISON OF GAS/SPEC* CS-PLUS WITH FIRST GENERATION MDEA BASED PRODUCT - ACCELERATED AGING STUDY

	COMPONENT CONCENTRATION	
FORMULATION	START	FINISH
CS-PLUS	50%	42.7%
1st Generation	50%	27.8%

Conditions: 400 psig CO_2, 120°C, 7 days

	AGED SOLVENT	
FORMULATION	ABSORPTIVITY	CORROSIVITY
CS-PLUS	Unaffected	5 mpy
1st Generation	Reduced	58 mpy

Energies of less than 52,000 BTU per lb-mol of CO_2 are attainable with a lean loading of 0.015 mol of CO_2 per mol of CS-PLUS. A stripper overhead temperature of 188-195°F is sufficient to reach the necessary H_2O/CO_2 reflux ratio of 0.5 at 12 to 14 psig.

This low reflux ratio required to strip CS-PLUS represents a significant energy advantage over both inhibited MEA and first generation products. Operating with an optimum concentration of 50%, lower circulation rates also produce an energy savings while at the same time increasing plant capacity.

Table 2. COMPARISON OF CS-PLUS WITH COMPETITIVE PRODUCTS

AMMONIA PLANT #1	GAS/SPEC* CS-PLUS	1st GENERATION PRODUCT
Gas Flow Rate, MMSCF/D	207	195
Inlet Gas Pressure, psia	370	370
Inlet Gas Temperature, ° F	170	170
Inlet Gas, % CO_2	18.2	18.2
Circulation Rate , GPM	3740	~ 3740
Solvent wt.%	50	~ 55
Treated Gas, ppm CO_2	< 40	> 400
Reflux Ratio, Mol/Mol	0.5	> 1
Reboiler Duty, MMBTU/Hr	222.83	~ 225
Unit Reboiler Duty, MBTU/lb mole CO_2	54.00	~ 58.00

AMMONIA PLANT #2	GAS/SPEC* CS-PLUS	1ST GENERATION PRODUCT
Gas Flow Rate, MMSCF/d	162	150
Inlet Gas Pressure, psia	392	409
Inlet Gas Temperature, ° F	147	120 -- 145
Inlet Gas, % CO_2	18.2	18.2
Circulation Rate , GPM	2900	~ 3300
Solvent wt.%	54	~ 55
Treated Gas, ppm CO_2	< 40	> 400
Reflux Ratio, Mol/Mol	0.5	> 1
Reboiler Duty, MMBTU/Hr	164.74	~205
Unit Reboiler Duty, MBTU/lb mole CO_2	50.88	~ 62

Table 3. ENERGY COMPARISONS

SOLVENT	CO_2 IN TREATED GAS (ppm)	REBOILER HEAT BTU/lb-mole CO_2
Traditional MEA	< 100	> 100,000
Inhibited MEA	< 100	60,000 - 70,000
First Generation MDEA Based	< 100	53,000 - 57,000
GAS/SPEC* CS-PLUS	< 50	< 52,000

Reboiler Duty = Sensible Heat + Heat of Reaction + Heat of Vaporization

However, one limiting factor for reducing circulation is the absorber temperature profile. Heat of reaction causes a temperature rise in the absorber. If a maximum bulge temperature exceeds 190°F, CO_2 can flash out of the solvent causing localized corrosion due to CO_2 pitting. Maximum absorber temperature should not exceed 185°F.

The corrosivity of CS-PLUS on carbon steel does increase with time, but can be controlled with routine carbon filtration. Corrosion rates determined using potentiodynamic polarization measurements have compared favorably with weight loss measurements using metal coupons. The average of both was between 2.0 and 2.5 mil/y. It has been found that 400 series stainless steel is not compatible with CS-PLUS but no problems have been reported with the 300 series.

SUMMARY

Energy and capacity improvements have been realized in the ammonia industry with a new product for carbon dioxide separation. GAS/SPEC* CS-PLUS provides increased stability over traditional and first generation products used for this application. The type of corrosion problems encountered in the past have been minimized by using this product and following technical service recommendations regarding plant operation.

It should be noted that increased demands for quality and productivity require a new mind set in plant operation. Comfortable and relaxed operation at conditions well below the performance capability limit will no longer result in competitive economics. The ability to successfully push the plant past its old limits will require improved products and attention to detail. In the ammonia industry, GAS/SPEC* CS-PLUS is performing at design or better than design with exceptional results.

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