

## **A Review: State-of-the-Art LPG Sweetening Process**

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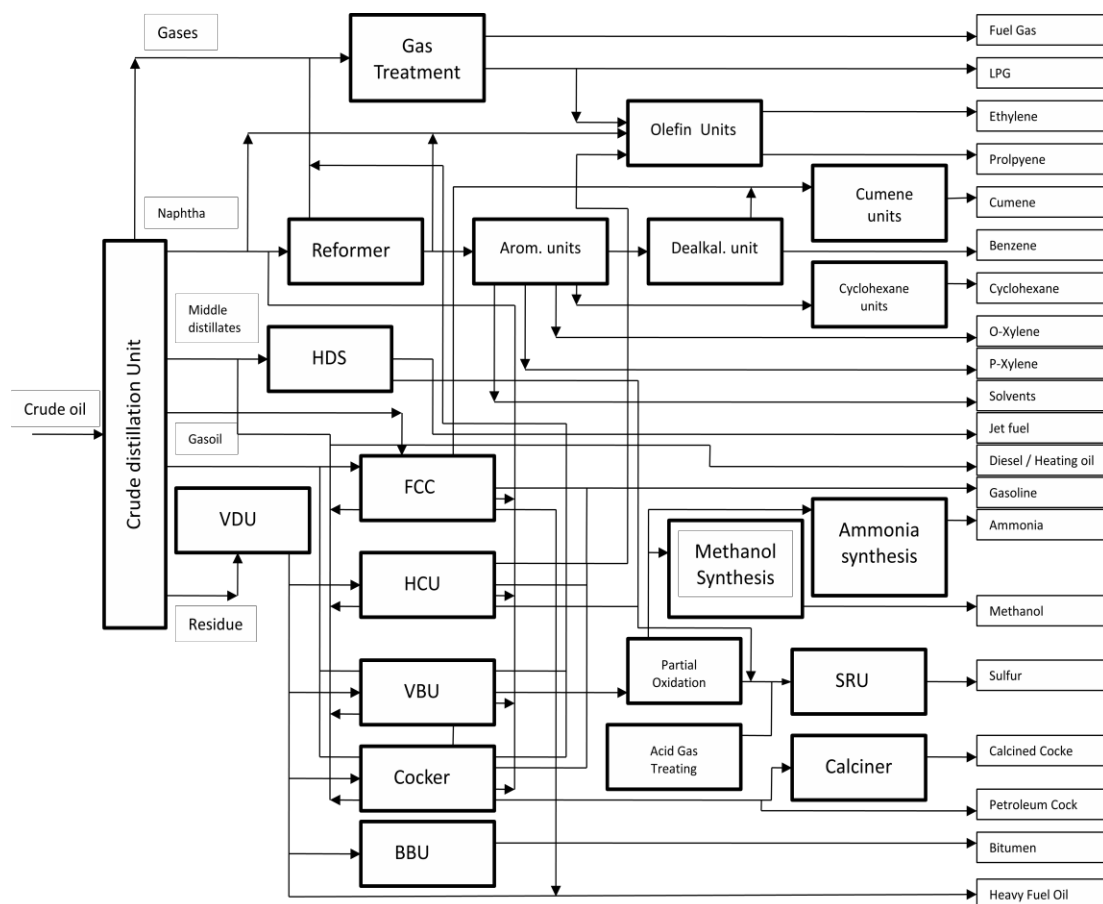
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### **Abstract**

LPG is one of the most important products in terms of commercial value and domestic usage. Raw LPG contains impurities like H<sub>2</sub>S, CO<sub>2</sub>, CO, COS and CS<sub>2</sub> which are very harmful due to its corrosive and toxic characteristics. Industries use alkanol amines to remove these impurities, which are called LPG sweetening process. The treated LPG should pass the 1A copper strip corrosion test for safety and environmental requirements, which corresponds to less than 4 PPM of H<sub>2</sub>S. The objective of this study is to provide a comprehensive review of the research studies conducted in LPG sweetening process, solvent selection, operating conditions, and significant performance parameters. Additionally, the simulation and optimization of LPG sweetening process using HYSYS process simulators reviewed.

### **1. INTRODUCTION**

Refineries mainly process crude oil to produce valuable petroleum products like fuel gas, LPG, gasoline, naphtha, ATF, kerosene, diesel, gas oil, residue and sulfur. Refineries also have hydrogen plant to meet hydro-treating requirements and nitrogen for utility requirements (Speight 2016). Petroleum products like ethylene, propylene, cumene, cyclohexane, benzene, xylene, methanol and ammonia are obtained from petrochemical complex. The configuration of a typical integrated refinery and petrochemical complex is provided in Figure 1. LPG is still considered one of the important products due to its domestic usage and commercial value (Jones and Pujadó 2006, Chang, Pashikanti et al. 2013).



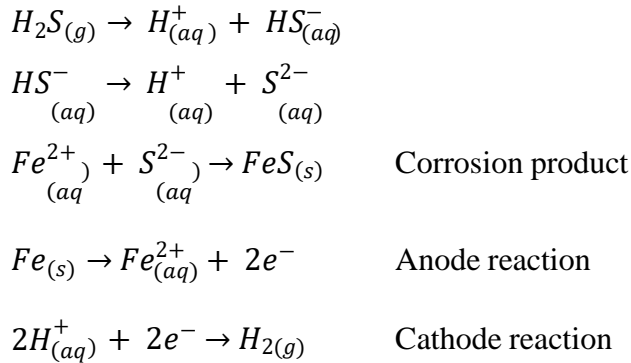
**Figure 1:** A typical integrated refinery and petrochemical complex, BPRP Gelsenkirchen's refinery adapted from "The oil drum" (JoulesBurn 2011)

The latest market report published by Credence Research Inc., highlights that during the year 2016, the global LPG market value was at US\$ 260 billion and by 2024 it is expected to reach US\$ 340, expanding at a CAGR of 3.5% from 2016 to 2024. Increasing use of LPG for automobile and cooking is the main cause for the increase in demand.

Natural gas processing continues to be the largest source of LPG supply, accounting for nearly 60% of total worldwide production. The natural gas purification process produces NGL (natural gas liquids). The unrefined NGL is sent to LPG recovery. Several LPG recovery technologies are commercially used, for example, gas sub cooled process, ORH process, RSV process, SCORE and LFP process. Refineries account for nearly all of the remaining production. Other sources account for less than 0.5% of worldwide LPG production. The changing supply/demand picture for LPG is expected to cause a major shift in trading patterns during the next 2 decades. (Johnson 2003).

## 2. IMPURITIES IN LPG

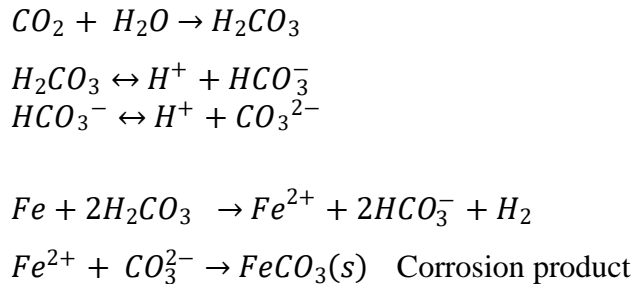
The raw LPG from crude distillation and cracked LPG contain impurities like H<sub>2</sub>S, CO<sub>2</sub>, COS, CS<sub>2</sub>, organo-sulfur compounds i.e. mercaptanes and elemental sulfur. Corrosion of steel by H<sub>2</sub>S, CO<sub>2</sub> and COS is a major problem in the oil industry (Smith and Joosten 2006). In the presence of water, H<sub>2</sub>S dissociates as a weak acid. Once ions are formed, an environment is set up for the spontaneous transfer of electrons. Iron will readily donate electrons to the hydrogen ions and forms iron sulfide (Zhang, Zhong et al. 2011). The reaction mechanism is provided below:



Slippage of sulfur leads to not only pipeline corrosion, but also causes problems in end of fuel use, because the corrosion products tend to form deposits in engine components.

In aqueous H<sub>2</sub>S environments, hydrogen embrittlement occurs rapidly, which leads to decrease in the ductility or toughness of a metal due to the presence of atomic hydrogen. Therefore, LPG acid gas treatment is very important to avoid corrosion in the automobiles and domestic applications.

Though the quantity of CO<sub>2</sub> in LPG is very small, it may build up to significant concentrations. The raise in concentration increases vapor pressure of LPG and lowering its heating value. Moreover, in presence of moisture, carbon dioxide forms carbonic acid, which reacts with metals to form iron carbonates. The reaction mechanism is provided below:



LPG or Natural gas is considered “sour” if hydrogen sulfide (H<sub>2</sub>S) is present in amounts

greater than 5.7 milligrams per normal cubic meters ( $\text{mg}/\text{Nm}^3$ ) or 2.5  $\text{mg}/\text{scf}$  (Mearkeltor 2011).

Though the copper strip test is not sensitive to COS (Perry 1977), in the presence of moisture, COS can react and form  $\text{H}_2\text{S}$ . Hence liquids containing COS will often not meet the copper strip test after storage. COS and  $\text{CS}_2$  can react with water and form  $\text{H}_2\text{S}$  in the product.

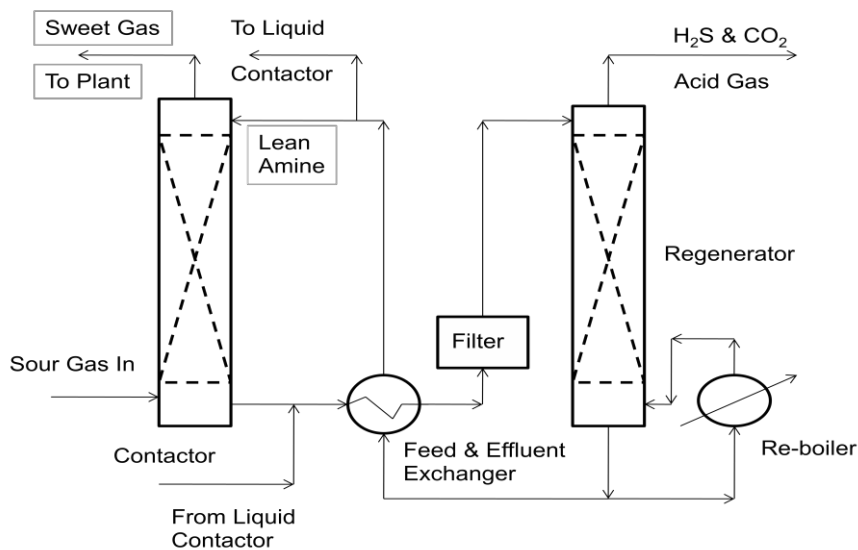
Therefore,  $\text{H}_2\text{S}$  must be removed before it is sent for certification. For commercial applications, the LPG product must meet 1A copper strip corrosion test, which corresponds to less than 4 ppm  $\text{H}_2\text{S}$  (IS4576: 1999, Jan 2010; LPG specification). Similar product specification is mentioned by Perry (Perry 1977) that ethane rich liquefied hydrocarbon mixed stream will be sweetened to the copper strip test (No. 1A or better) and free of entrained liquid water.

### 3. LPG SWEETENING PROCESSES

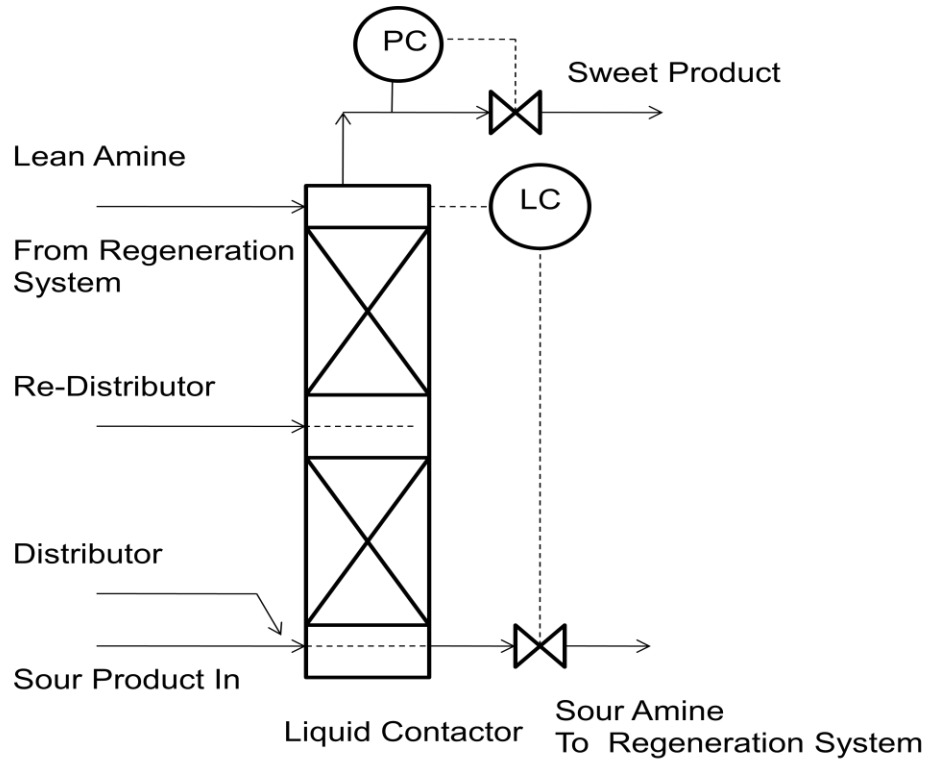
In 1970s with limited developments in amine treatment, the process selection was based on the sour gas composition and product quality (Jones and Perry 1973). A brief selection method is provided in **Table 1**.

<b>Table 1: Recommended Methods of Treatment</b>		
<b>S. No.</b>	<b>Inlet Gas Contaminants</b>	<b>Recommended Method of Treatment</b>
1	$\text{H}_2\text{S} > 0.25 \text{ g}/100\text{scf}$ & some $\text{CO}_2$	Amine-treat* gas, with small amine side stream sent to a liquid contactor for product treating, as in Figure 4.
2	$\text{H}_2\text{S} = 0^+ - 0.25 \text{ g}/100 \text{ scf}$ & excessive $\text{CO}_2$	Amine-treat* gas, with small amine side stream sent to liquid contractor for product treating, as in Figure 4.
3	$\text{H}_2\text{S} = 0^+$ to $0.25 \text{ g}/100 \text{ scf}$ & minimal $\text{CO}_2$	Either amine-treat* product gas in liquid contactor; or iron-sponge treat product
4	No $\text{H}_2\text{S}$ & excessive $\text{CO}_2$	Amine-treat* gas only
5	$\text{H}_2\text{S}$ , $\text{CO}_2$ & COS	Use di-ethanolamine or diglycolamine, to amine-treat* both gas and liquid. May require caustic final scrub of the liquids to remove last traces of COS.

6	H <sub>2</sub> S, CO <sub>2</sub> & some mercaptanes (no need for gas sample to undergo “doctor” test)	Use method indicated above according to H <sub>2</sub> S and CO <sub>2</sub> content. Doctor test is qualitative test for detecting hydrogen sulfide and mercaptan sulfur in hydrocarbon liquids.
7	H <sub>2</sub> S, CO <sub>2</sub> & excessive mercaptans (gas sample to undergo “doctor” test for sweetness)	Use methods indicated above with di-ethanolamine or di-glycolamine, plus, follow with regenerative caustic, Merox, Bender, Perco, or some other process for mercaptane removal or treat the product with molecular sieves.
H <sub>2</sub> S of 0.25 g/100 scf is equivalent to approx. 4 ppm V/V		
‘AMINE-TREAT*’ stands for mono-ethanolamine (MEA), di-ethanolamine (DEA), or di-glycolamine (DGA) process, and is shown in Figure 3		
<p>Doctor Test:                  Standard Test Method for Qualitative Analysis for measuring active Sulfur in solvents and fuels (Doctor Test). In this test, the sample is mixed with sodium plumbite solution, a small quantity of powdered sulfur added, and the mixture shaken well. The presence of H<sub>2</sub>S and marcaptane or both is indicated by discoloration of the sulfur floating at the oil-water interface or by discoloration of either of the phases. ASTM D 4952 – 02.</p>		



**Figure 3:** AMINE-TREAT system for sulphur and impurities removal form LPG



**Figure 4:** Liquid-liquid packed contactor

Recently many new treatment options like membrane and direct oxidation methods have been developed (Bhide and Stern 1993, Minier-Matar, Janson et al. 2017). In chemical and physical solvents, many formulated amines have been developed (Kohl and Nielsen 1997, Burr and Lyddon 2008). Formulated amines have lots of advantage over generic amines due to their selectivity, stability and energy requirement in process (Brown and Geosits 1993). Figure 5 provides the list of process options based on the recent developments (Chapel, Mariz et al. 1999, Rooney 2001, Rajani 2004, Vitse, Baburao et al. 2011). The process categorized into chemical solvents (amines), physical solvents, adsorption, membranes, and cryogenic fractionation. Selection of process depends on type of impurities, product quality, operating conditions and capital costs (Fong, Kushner et al. 1987, Lokhandwala, Baker et al. 1995, Rajani 2004).

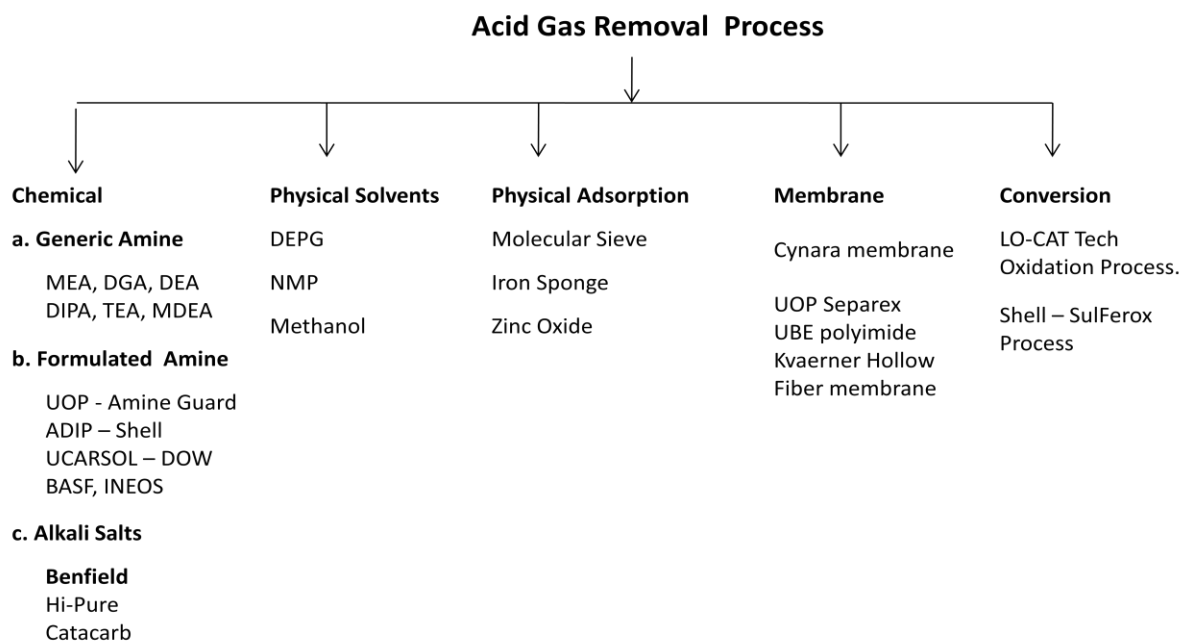
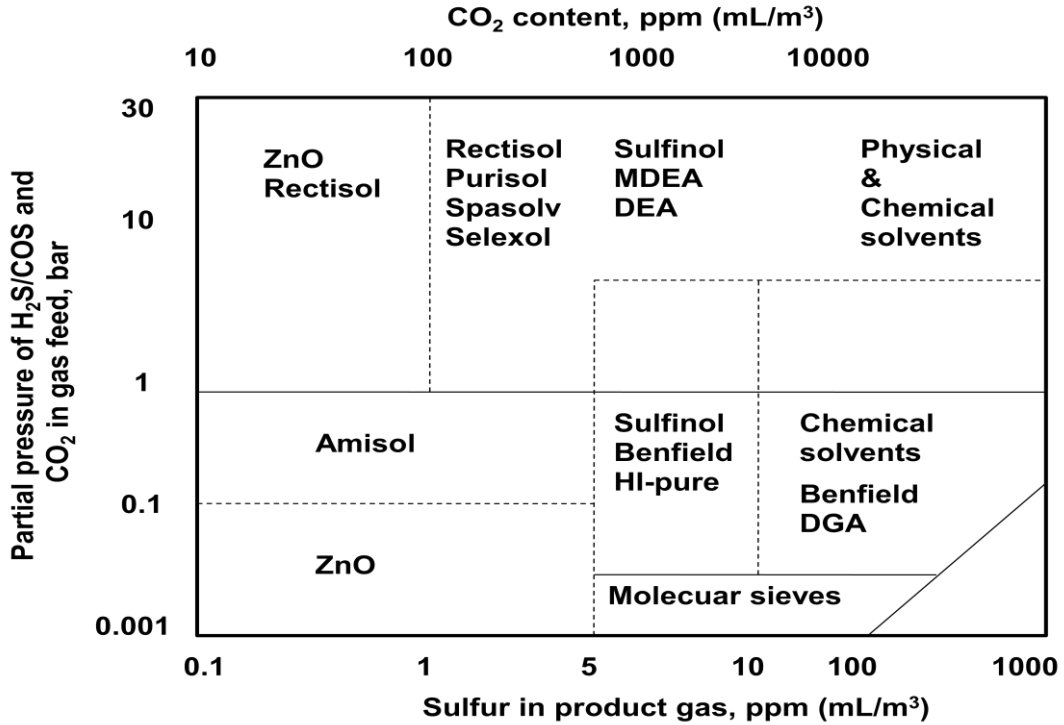


Figure 5: Acid gas removal process with recent developments

High regeneration energy requirement and insensitive to  $H_2S$  and  $CO_2$  partial pressure are the limitations of chemical solvents. The chemical solvents can reduce  $H_2S$  and  $CO_2$  to ppm levels. On the other hand, the physical solvents require low energy, hence, used for bulk removal of acid gas. The physical solvents are very sensitive to acid gas partial pressure and experience high hydrocarbon slip. The chemical and physical solvents are capable of reducing the product  $H_2S$  to 4 ppm. The physical solvents like Selexol<sup>TM</sup> and Rectisol<sup>TM</sup> can reduce the product  $CO_2$  up to 1 ppm. A process selection chart for simultaneous removal of  $H_2S$  and  $CO_2$  provided in Figure 6. Rectisol<sup>TM</sup> is a physical acid gas removal process where methanol used as a solvent to remove acid components such as  $H_2S$  and  $CO_2$  from sour gases. ZnO catalyst method is chemical method used for hydrogen sulfide removal. It has high  $H_2S$  removal efficiency. Hence, zinc oxide is more preferred than other catalyst like phosphate method, iron oxide and hydroxide method. The Sulfinol process is a regenerative process developed to remove acidic impurities such as  $H_2S$ ,  $CO_2$ , COS and mercaptanes from sour gases. The sulfur compounds in the product gas can be removed to low ppm levels. It has been developed particularly for treating large quantities of gas, with high pressure such as natural gas. Sulfinol solvent is a mixed solvent, consisting of a mixture of diisopropanolamine (30-45%) or sulfolane (tetrahydrothiophene dioxide) (40-60%) or methyl diethanolamine (MDEA) and water (5-15%). The acid gas loading of the Sulfinol solvent is higher and the regeneration energy requirement is lower than that of chemical

solvents.(Abdel-Aal, Aggour et al. 2015). Amisol™ process developed by Lurgi GmbH, is similar to Sulfinol process which uses combination of physical and chemical solvent for acid gas removal.



**Figure 6:** Process selection chart for simultaneous removal of H<sub>2</sub>S and CO<sub>2</sub> (Kidnay, Parrish et al. 2011)

The Amisol process can be used for either selective desulfurization or complete removal of CO<sub>2</sub>, H<sub>2</sub>S, COS and organic sulfur compounds. In this process, sulfur can be removed to less than 0.1 ppm of H<sub>2</sub>S and less than 5 ppm of CO<sub>2</sub>(Kriebel 1984).

Purisol process licensed by Lurgi GmbH uses N-methyl-2-pyrrolidone (NMP) as a solvent to remove H<sub>2</sub>S, CO<sub>2</sub>, RSH and H<sub>2</sub>O(Yu, Huang et al. 2012).Selexol Process uses dimethylether of polyethylene glycol as a solvent(Miller, Macriss et al. 1978, March 2014) Sulfinol process uses a solvent, which is 40% sulfolane (tetrahydrothiophane 1-1 dioxide), 40% DIPA (di-isopropanolamine) and 20% water. Benfield (Benson and Field) process removes CO<sub>2</sub>, H<sub>2</sub>S and other acid gases from sour gas streams by scrubbing with hot aqueous potassium carbonate contains activators licensed by UOP. Molecular sieve process is highly selective for the removal of hydrogen sulfide as well as other sulfur compounds from gas streams. It has high absorption efficiency. It is suitable for simultaneous dehydration and desulfurization.



Generally refineries adopt centralized lean amine supply and regeneration facility to treat LPG, fuel gas, and for recycle gases in hydrotreater. For economic reasons, mostly single type of treatment process is installed. To purify sour LPG, amine sweetening process is adopted, where sour LPG is treated with alkanolamines in a counter current absorption. The sweet LPG is sent for water wash and caustic wash to remove organo-sulfur compounds and entrainments before routed to storage and certification (Maddox 1974), (Feng, Benxian et al. 2015 if the quantities of the contaminants are small. Amine treating and molecular sieves are considered for the streams having rich acid gas impurities (JOSEPH W. HOLMES).

To remove moisture, COS along with H<sub>2</sub>S and CO<sub>2</sub> molecular sieve used but need large capital and operating cost. Formation of COS when both H<sub>2</sub>S and CO<sub>2</sub> are present during the process is another disadvantage. In general, use of amines & weak Lewis bases is most opted where amines are also being used to treat hydrotreater recycle streams, sour fuel gas and LPG. Sour gas may be treated in two ways I) chemical or II) Physical. In method I, a simple solvent (amine/carbonate) or a mixture of (amine + sulfolane) or Ucarsol is used. Here, reactive absorption plays an important role and unit processes involve chemical absorption-desorption. In the method II, Physical absorption using Selexol (poly-ethylene glycol/dimethyl ether) or Rectisol (methanol) or propylene carbonate or dry-absorbents (molecular sieve, activated charcoal, iron sponge, ZnO) is carried-out. Acid gas treating using alkanolamines are most common in the petroleum refining and natural gas processing industries..

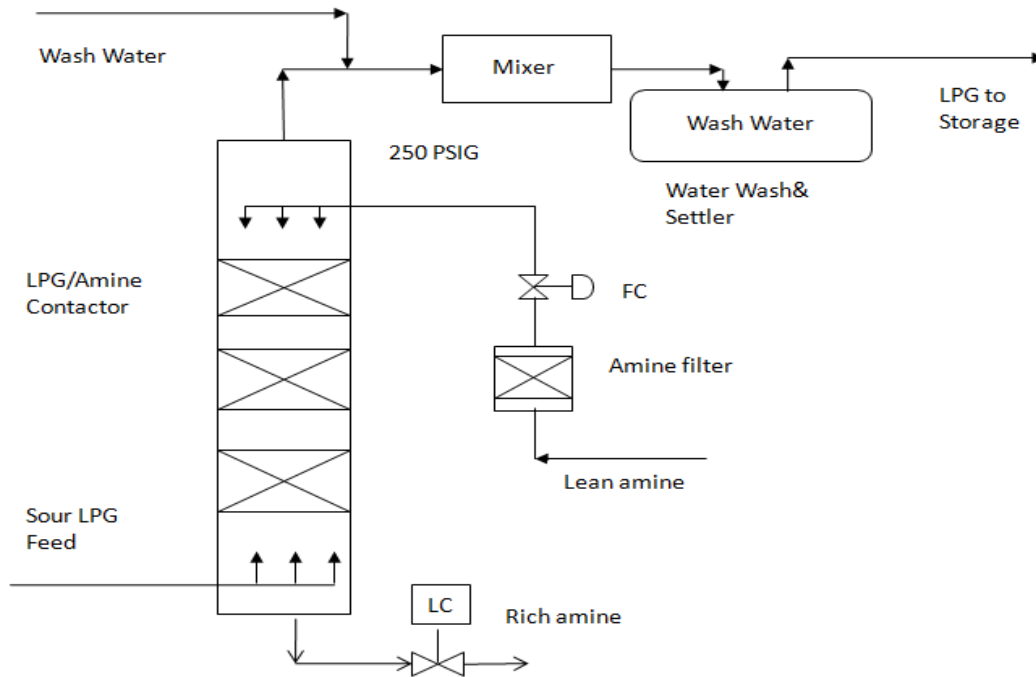


Figure (7): LPG sweetening process using alkanolamines

Figure (7) is a typical LPG treating system (Kohl and Nielsen 1997). In this process, sour LPG is pumped to a counter current liquid-liquid packed bed with random packing. The sour LPG enters at the bottom of the column and lean amine is fed to the top of the column through a flow controller. The sour LPG feed is distributed evenly at the bottom through distributors to form droplets into continuous liquid phase. The lean amine also feed through flow controller and is distributed across the top of the packing. The density difference between the gas and liquid phases causes the dispersed LPG to flow upward through the continuous liquid phase. The gas and liquid interface is maintained above the top bed and distributor by a level controller that controls the richamine flow from the bottom of the column. The gravity settler and a LPG water wash system provided to remove entrained amine from the system. Treated LPG water wash improves the entrained amine recovery and removes dissolved amine from the sweet LPG. The separated water-amine stream from the settler is recycled to the over head stream entering the water wash mixer. Usually the wash-water flow rate is about 25% of the LPG flow. The combined LPG and water stream flows through a static mixer or other mixing valve and then to the gravity settler.

Depending on the sweet LPG product quality requirement, the LPG from the settler may be further processed in other treating units. To remove mercaptans LPG is further treated in extractive Merox unit. The operating pressure of the entire LPG amine absorber, water and caustic treating system is maintained through a pressure controller located downstream of the final treated LPG stream outlet of gravity settler.

#### **4. EQUIPMENT SELECTION AND DESIGN GUIDELINES FOR LPG SWEETENING**

Absorption process requires an extensive area of liquid surface in contact with a gas phase under conditions favoring mass transfer. In tray columns, it is achieved by breaking up the LPG into smaller bubbles within a continuous amine. In packed column, the liquid stream divided into numerous thin films that flow through a continuous gas phase. In spray contactors liquid dispersed as a multiple of discrete droplets within a continuous gas phase. Selection of these contactors depends on solvent rate, foaming tendencies, corrosion, number of stages, and contaminants, pressure drop and turn down ratio. Among these packed columns have wide ranges of applications because of the development of new packing materials with higher capacity and better performances. For small capacity units, packed columns are preferable than the tray columns. Also, for corrosive service, liquids with foaming nature, application with very high liquid-to-gas ratios and low pressure-drop conditions packed columns are preferred. In addition, packed columns have greater flexibility because; the packing type can be changed easily during turnaround and

modify column's operating characteristics. General packed tower design guidelines reported are listed in Table 2. (Honerkamp 1975, Strigle 1987, Coker 1991, Tse and Santos 1993, Stewart and Lanning 1994, Wehrli, Hirschberg et al. 2003).

There are three types of sulfur treating process. a) Removal of small amount of sulfur by polishing, b) Intermediate sulfur removal (reduction- oxidation) c) High capacity process. Physical process is relatively expensive due to chemical usage and having advantage of low capital cost. Physical and chemical adsorption process is the examples of polishing process such as activated alumina, molecular sieve, activated carbon and Zinc oxide. Reduction and oxidation process have advantage of producing elemental sulfur. BG Technology, Stretford process, US filter LO-CAT are examples of reduction-oxidation process.

High capacity process involves sulfur handling above 10 TPD. It involves solvent absorption, regeneration and rich acid gas is treated in sulfur recovery unit. In sulfur recovery unit, acid gas is treated to produce elemental sulfur. Different proven technologies are available for sulfur recovery such as conventional Claus process, Amoco's CBA (Cold bed adsorption) process, Lurgi Sulfreeen process, IFP process, SCOT process and Lord Process. Summary of different amine process configurations and its advantages is provided in Table 3.

**Table 2:** General guidelines for packed absorber design

Author	Design guidelines
(Honerkamp 1975)	a. Typical random packing sizes selection for LPG treating are 1 to 1.4 in. with 1in. being the most common size.
(Perry 1977)	a. Packing sizes for LPG amine absorption are 1 in. to 2 in. b. Recommends sizing LPG contactors based on 15 gpm/ft <sup>2</sup>
(Koshy and Rukovena 1986)	Importance of high performance distributors increases as the number of stages increases.
(Coker 1991)	a. The ratio of the tower diameter to the packing height should be at least 15: 1. b. The number of liquid streams provided by the feed distributor should be 3-5/ft <sup>2</sup> in towers larger than 3 feet in diameter. c. Liquid redistributors are required every 5-10 ft for tower with rings, and at least every 20 feet for other dumped packing. d. Plastic packing is limited to an unsupported height of 10-15feet, and metal to 2&25 feet due to deformability,
(Tse and Santos 1993)	a. Droplet residence times and mass transfer rates are increased when LPG is dispersed into the higher viscosity continuous amine phase. b. Amine as the continuous phase also increases the LPG treater amine

	residence time in the column and time for operator to take action if the interface level controller fails or malfunctions.
(Strigle 1987) 0.10 to 0.40 in. H <sub>2</sub> O/ft,	<ol style="list-style-type: none"> <li>Normal absorber pressure drop <math>\Delta P</math>, is 0.10 - 0.40 in.H<sub>2</sub>O/ft of packing height.</li> <li>In non-foaming systems, <math>\Delta P</math> is 0.25 - 0.40 in. H<sub>2</sub>O/ft.</li> <li>For foaming systems, the design pressure drop <math>\Delta P</math>, should be max. of 0.25 in. H<sub>2</sub>O/ft or 24.8 – 99.5 pa/ft at the point of high loading.</li> <li>The maximum effective bed height is approx 12 ft.</li> <li>The bed heights in the range of 8 to 12 ft are typically used.</li> <li>Max. packing size should be 2 in. with 1 in. is the common choice.</li> </ol>
(Stewart and Lanning 1994)	<ol style="list-style-type: none"> <li>For gravity settler, recommended LPG and wash water residence times of 15 and 20 minutes.</li> <li>Stewart and Lanning recommend that the stripper to be operated below a bulk temperature of 127 °C and the reboiler below 175 °C to avoid excessive thermal degradation.</li> </ol>
(Al-Dhafeeri and Nasr-El-Din 2007)	<ol style="list-style-type: none"> <li>Excessive antifoam dosing reverses its function and makes it a foam promoter.</li> <li>Presence of antifoam renders lower diffusion of the acid gases into the amine solution, hence reducing amine-absorption capacity.</li> </ol>

**Table 3:** Different process configurations for acid gas treatment

Configuration	Application and advantages
Pre contactor (static mixer)	It is suitable for bulk acid gas removal. It has advantage of capacity increase with low CAPEX. Any type of amine can be used and less pressure drop. Figure 8.
Multiple Inlet nozzles.	Configuration used to maximize CO <sub>2</sub> slip. It accommodates wide variations in feed gas. Generally, tertiary amine is used and it requires additional piping. Figure 9.
Split flow	Used to meet stringent H <sub>2</sub> S specifications. Configuration reduces re-boiler duty. Generally, primary and secondary amines are used. Configuration requires extra equipment. Figure 10.
Pressure swing regeneration	It is used for bulk CO <sub>2</sub> removal. Generally, tertiary amine is used. Disadvantage is CO <sub>2</sub> slip. Figure 11.

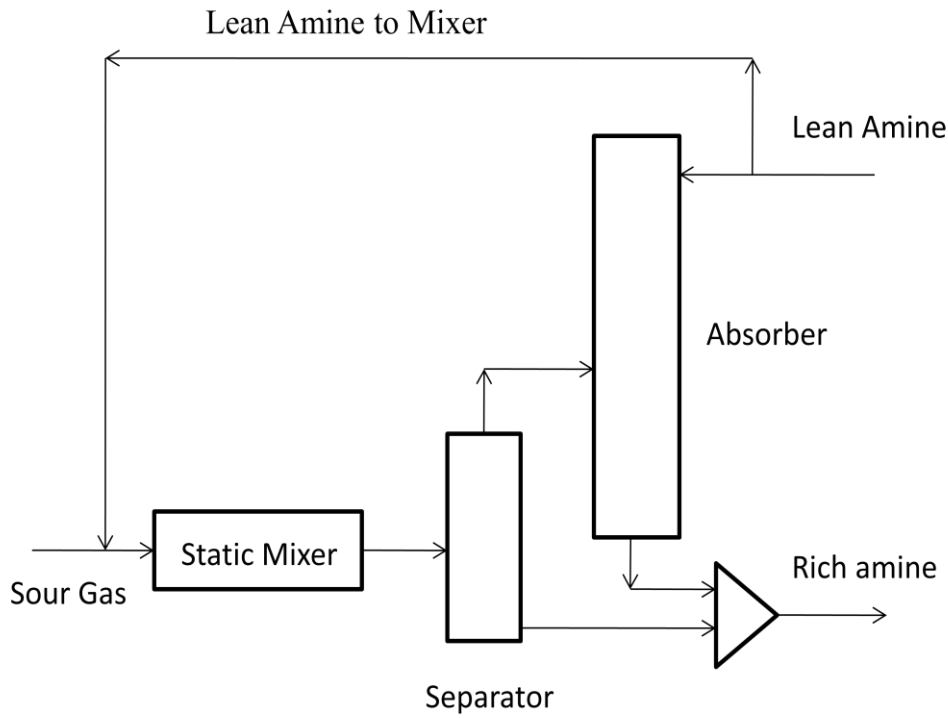


Figure 8. Amine absorption process configuration with static mixer.

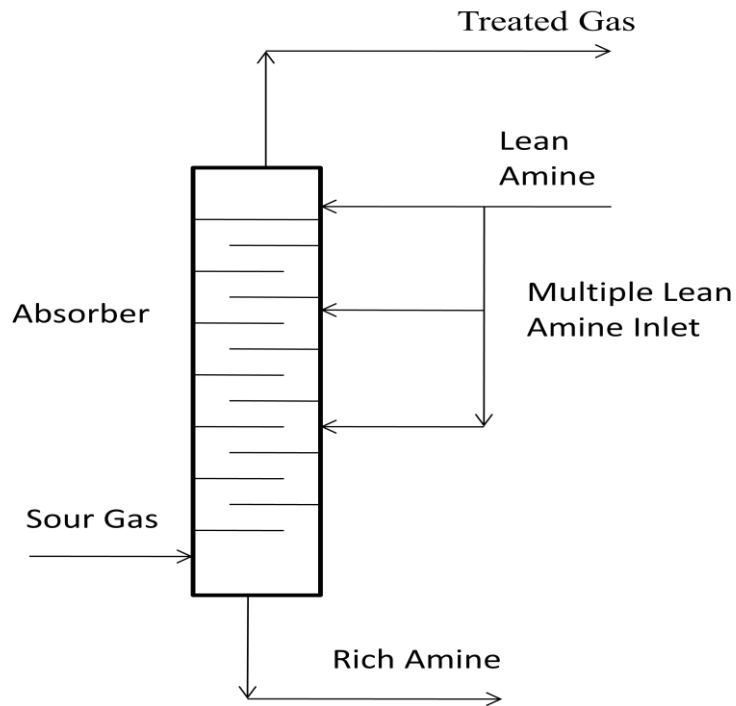
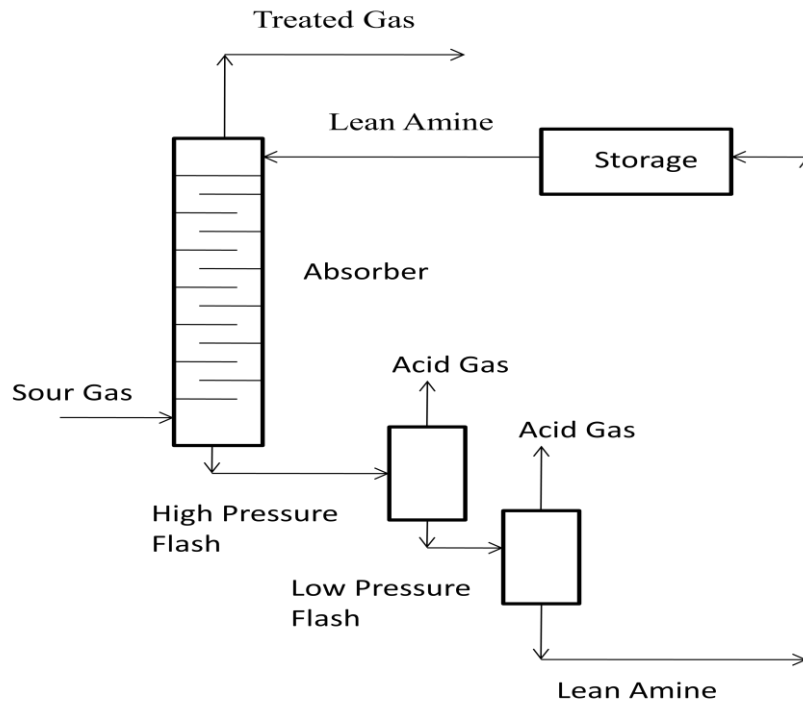
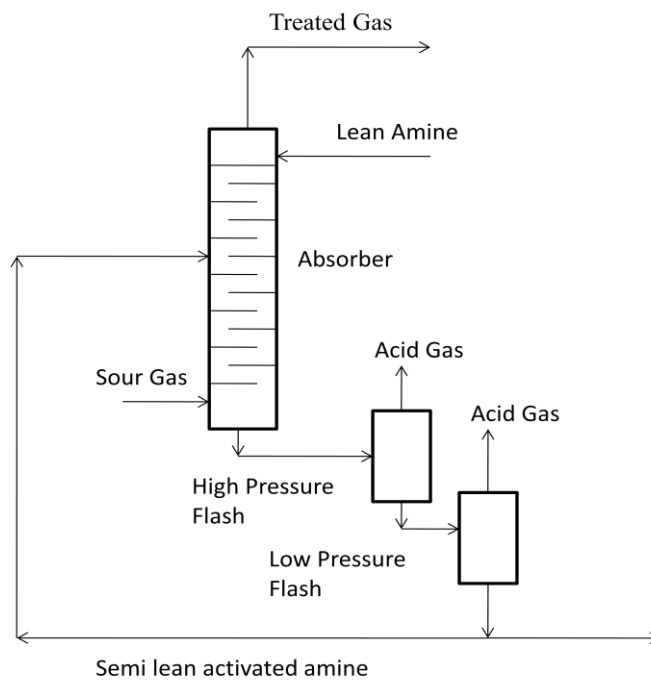


Figure (9) Amine absorption process configuration with multiple lean amine inlets.



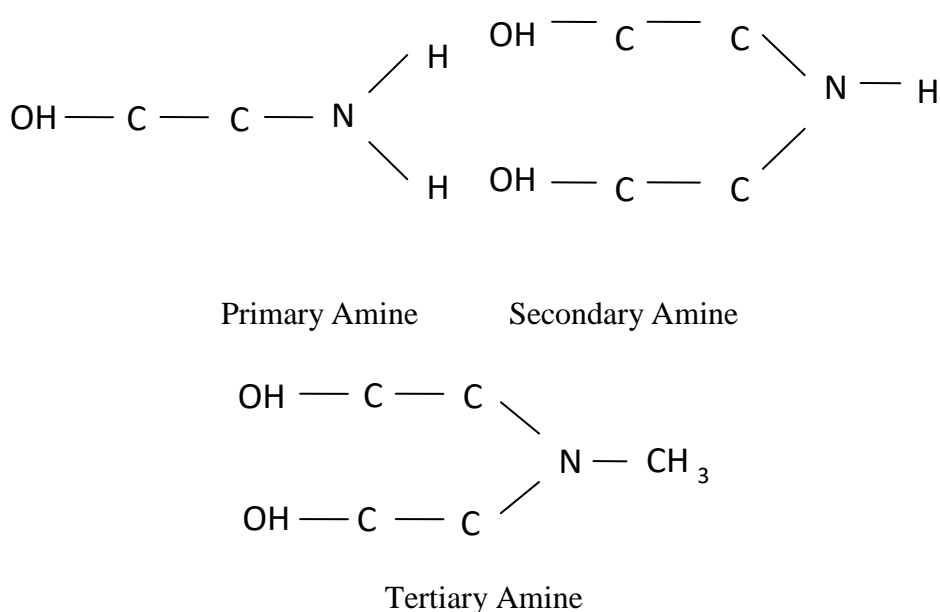
**Figure (10)** Amine absorption process configuration with split flow configuration



**Figure (11)** Amine absorption using simplified pressure swing configuration.

## 5. SOLVENT SELECTION AND OPERATING CONDITIONS

The selection of an amine solution depends on process conditions, acid gas partial pressures, and purity of the product. The hydroxyl group in the amine increases the water solubility and reduces the vapor pressure of amine. The amino group supplies the alkalinity in aqueous solutions, which is necessary for absorption of acid gases. Alkanolamines are divided into three categories based on chemical structure primary, secondary and tertiary amines. Primary amines have nitrogen atom with two hydrogen atoms attached. The secondary amines have one hydrogen atom attached to nitrogen atom. In tertiary amine no hydrogen atoms are attached. The heat of reaction and evaporation decrease from primary to tertiary amines. These enthalpies are directly related to energy needed in amine regeneration. The tertiary amines have higher loading values. Acid gas loading capability increases from primary to tertiary. The chemical formula for few selected amines is provided in Figure 12.



**Figure (12):** Structural formulae for different alkali amines

A typical chemical absorption – desorption system involving solvent as amine / carbonate is influenced by driving forces due to multi-component diffusion, chemical interactions and temperature gradients. In order to study these reactive absorptions, assumptions of thermodynamic equilibrium is essential.

Until 1970's, mono-ethanolamine (MEA) was considered as the only effective solvent for any sweetening application. Then in the 1970's, selection switched from MEA to diethanolamine (DEA), which yielded favorable results. Past few years, use of MDEA, mixed amines and especially formulated amines has gained popularity.

Each amine has separate ranges of process conditions and parameters. Some of the typical operating conditions for common amines are summarized in Table 4a. A comparison between advantages and disadvantages of different amine solutions is given in Table 4b.

**Table 4a.** Typical operating conditions and data for amines

Amine	MEA	DEA	DGA	MDEA
Amine Strength wt%	15 - 20	25 - 35	50 - 70	20 - 50
Loading mol/mol	0.3 – 0.35	0.3 – 0.35	0.3 – 0.35	Unlimited
H <sub>2</sub> S Selectivity	No	Limited condition	No	Most conditions

**Table 4b.** Comparison in application between different solvent solutions

Solution	advantage	disadvantage	Application
MEA	Higher alkalinity increases the solution effectiveness for gas absorption  High solution capacity allows moderate load/ concentration  Contaminated solution can easily be reclaimed	Formation of irreversible reaction product with sulfur contaminants and loss in solvent.  Higher corrosion rate.  High heat of reaction with H <sub>2</sub> S and CO <sub>2</sub> . High vapor pressure and amine loss .	Lower loads in sour gas components
DEA	Allows relatively higher load than MEA  Forms regenerable compounds  Needs lower energy for solvent recovery	Low vapor pressure of solvent is suitable for low pressure operation  It is difficult to reclaim solvent from contaminated solutions – vacuum distillation may be needed	Moderate loads in sour gas composition



DGA	It can remove H <sub>2</sub> S, CO <sub>2</sub> , COS, mercaptans  Low vapor pressure allows higher concentration  Low circulation rate & steam consumption	High heat of solution High regeneration energy	
DIPA	It can remove H <sub>2</sub> S, CO <sub>2</sub> , COS  Non-corrosive  Low steam consumption	Most effective for COS removal Shows selectivity for H <sub>2</sub> S over CO <sub>2</sub> Is used for Claus plant	
MDEA	Selective removal yields reduction in sour gas Low heat of reaction – low energy needed in regeneration Low corrosion Thermal & chemically stable Sparingly soluble with hydrocarbons	High solution capacity Proprietary additives can be added to enhance absorption	Allows higher load, non-selective solvent

Primarily, in all amine treatment unit the objective is to sweeten the sour gas should meet the required purity specifications with respect to H<sub>2</sub>S and CO<sub>2</sub>. The secondary objective is to select the amine which reduces equipment size and minimizes plant operating costs (JOHN POLASEK). The important factors to consider in the amine selection are (a) less amine circulation rate by operating at higher amine acid gas load by which could reduce reboiler/condenser size. (b) Selective absorption based on specification.

Based on operating experience, (**JOSEPH W. HOLMES**) recommendations concentration and loading guidelines for the LPG sweetening plants using MEA (monoethanolamine), DEA (diethanolamine), and DGA. The guidelines are provided in **Table 5** and **Table 6** summarizes the general operating guidelines of amine treatment unit.

**Table 5:** Operating conditions for LPG sweetening with amines

Operating conditions for LPG sweetening with amines		
	Wt% Amine	Max Loading mol/mol
MEA	5 – 20	0.3 – 0.4
DEA	25 – 35	0.35 – 0.65
DGA	50 – 70	0.45 – 0.65

**Table 6:** Approximate guidelines of amine treatment

Items	MEA	DEA	DGA	MDEA
Acid gas pickup, scf/gal @ 100°F	3.1–4.3	6.7-7.5	4.7-7.3	3.0-7.5
Acid gas pickup, mole/mole amine	0.33-0.40	0.2-0.8	0.25-0.38	0.2-0.8
Lean solution residual acid gas, mole/mole amine	0.12	0.01	0.06	0.005-0.01
Rich solution acid gas loading, mole/mole amine	0.45-0.52	0.21-0.81	0.35-0.44	0.20-0.81
Max solution conc, % wt	25	40	60	65
Approximate reboiler heat duty, btu/gal lean solution	1000-1200	840-1000	1100-1300	800-900
Reboiler temperature, °F	225-260	230-260	250-270	230-270
Heat of reaction, Btu/lb H <sub>2</sub> S Btu/lb CO <sub>2</sub>	610 825	555 730	674 850	530 610
Utility demand, LP steam (lb/gal)	0.8-1.5	0.7-1.1	1.5	1.0
Solvent loss, lb/mmscf of sweet gas	2-4	1-2	2-4	1-2

(Nielsen, Rogers et al. 1997) highlights that MEA, DEA, DGA, MDEA and MDEA based solvents generally perform satisfactorily for liquid treating process. The contact time required for the two liquid phases is relatively long generally up to 30 minutes including the time required for phase separation. This provides an adequate time for the slow reaction between CO<sub>2</sub> and amine.

For selective absorption, MDEA, is best known for its ability to preferentially absorb H<sub>2</sub>S and is used in SCOT tail gas cleanup units since it is desirable to slip as much CO<sub>2</sub> as possible while absorbing the maximum amount of H<sub>2</sub>S to be recycled back to the Claus unit in sulfur recovery. Mixed amines are typically mixtures of MDEA and MEA or DEA which enhance CO<sub>2</sub> removal while retaining selective nature of MDEA along with reduced corrosion problems and low heats of reaction.

In CAPEX and OPEX review (**Astaria, Savage et al. 1983**) 50 to 70% of the initial investment for an amine sweetening unit directly related with the solvent circulation rate and another 10 to 20% of the initial investment is for the regeneration energy requirement. In addition, about 70% of operating costs, excluding labor, related to regeneration. Since selection of the proper amine greatly reduce both the regeneration energy requirement and solution circulation rate, choice of the amine or combination of amines best suited to the conditions can have a significant impact on the overall costs associated with a sweetening unit.

## **6. REVIEW OF MODELING AND PROCESS SIMULATION**

Process models are developed based on set of equations which predicts the dynamics of a chemical process. Models used to characterize behavior of processes and to predict process variables at different operating conditions, to control continuous processes, investigation of process dynamics, optimal process design, for the calculation of optimal process at given working conditions. It plays an important role in conceptual design, process synthesis, flow sheeting and process integration. Recently, computer aided process modeling capable of doing thermodynamic analysis, material balance, energy balance, optimization and data reconciliation etc.

Modeling of absorbers and strippers follow two general categories (a) equilibrium based approach and (b) rate based approach. The equilibrium approach assumes a theoretical stage in which liquid and gas phases attain equilibrium. This approach is more suitable for the non-reactive systems. Chemical reactions are involved in amine absorption; hence rate based models to be used. In the rate-based approach, actual rates of multi-component mass and heat transfer as well as chemical reactions are considered.

Models based on equilibrium assumption, provides a simple way for prediction of acid gas partial pressure, they have two major disadvantages a. Inefficiency when extrapolated to conditions other than those equilibrium constants were tuned b. equilibrium constant gives only an approximation of the species composition. Following are few examples of models developed in this method. (Deshmukh and Mather 1981, Awan and Saleem 2011), (Danckwerts and McNeil 1967),(Kent 1976).

Model presented by Kent –Eisenberg is based on chemical and phase equilibriums, mass balance and Murphree efficiency. The non-idealities, represented by activity coefficients, were lumped into two pseudo equilibrium constants (for the main reactions of H<sub>2</sub>S and CO<sub>2</sub> with MEA or DEA) as a function of temperature. Model parameters regressed against experimental data. The model shown good predictions of the partial pressures of H<sub>2</sub>S and CO<sub>2</sub> for single acid gas systems (H<sub>2</sub>S–MEA–H<sub>2</sub>O, CO<sub>2</sub>–DEA–H<sub>2</sub>O) as well as for the mixed systems (CO<sub>2</sub>–H<sub>2</sub>S–DEA–H<sub>2</sub>O, CO<sub>2</sub>–H<sub>2</sub>S–MEA–H<sub>2</sub>O).

Complex models can be divided into activity coefficient or Gibbs energy model and equation of state models. The Gibbs energy/activity coefficient models provide activity coefficient based on expressions for excess Gibbs energy of the liquid phase. An equation of state is used for determination of fugacity coefficients of the vapor phase. (Deshmukh and Mather 1981) proposed a method based on the Guggenheim theory (Guggenheim and Turgeon 1955) for the H<sub>2</sub>S/CO<sub>2</sub>-MEA-H<sub>2</sub>O system. In this model it is assumed that water behaves ideally and all the interaction parameters for water in the model are set to zero. Even though the model is simple, it shows good results for the CO<sub>2</sub> solubility. It has limitation of describing the phase behavior of the binary MEA-H<sub>2</sub>O system. In 1978 (Edwards, Maurer et al. 1978) presented a molecular thermodynamic model for calculating vapor-liquid equilibrium for dilute solutions of weak electrolytes. They used a Guggenheim-type equation for representation of activity coefficients. (Li and Mather 1994) used the Pitzer and Simonson model (Pitzer and Simonson 1986), which is an extension of the Pitzer model, for modeling the CO<sub>2</sub>-MEA-MDEA-H<sub>2</sub>O system. (Kuranov, Rumpf et al. 1996) used Pitzer model for representing the behavior of CO<sub>2</sub>-MDEA-H<sub>2</sub>O and H<sub>2</sub>S-MDEA-H<sub>2</sub>O systems. (Kamps, Xia et al. 2003) and (Ermatchkov, Pérez-Salado Kamps et al. 2006) used the Pitzer model for the MDEA-CO<sub>2</sub>-H<sub>2</sub>O mixture. (Arcis, Rodier et al. 2009) applied the Pitzer model for representing VLE data and heat of absorption for the MDEA-CO<sub>2</sub>-H<sub>2</sub>O system.

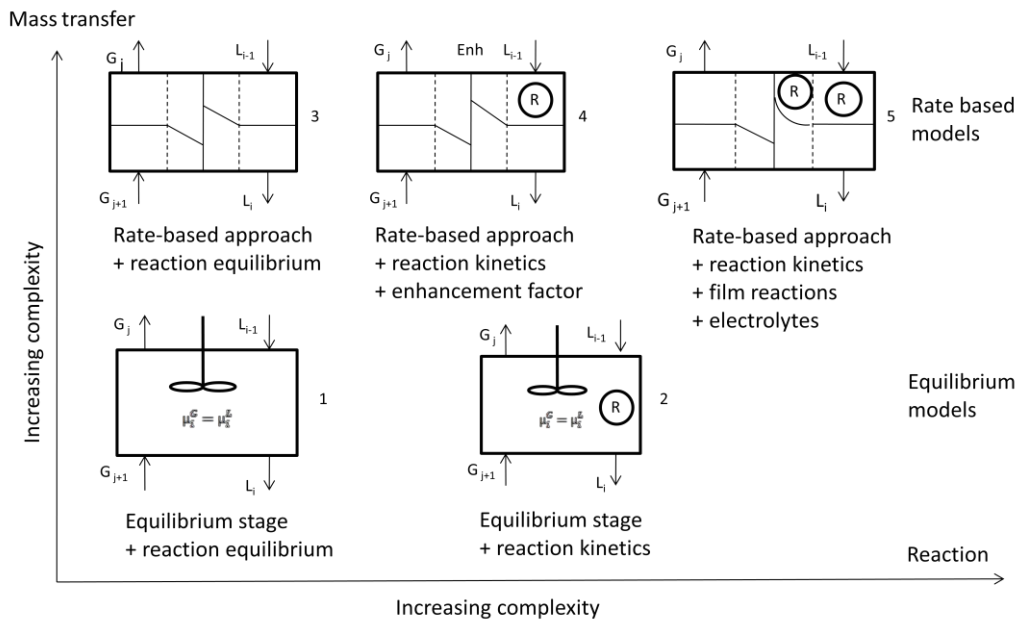
Under activity coefficient models, the electrolyte NRTL ( non random two liquid ) model (e-NRTL) presented by (Chen and Evans 1986) and the extended UNIQUAC model presented by (Thomsen and Rasmussen 1999) are most commonly used. The e-NRTL model has been applied for modeling many alkanolamine-acid gas-water systems. Review on the application of models reveals that, researchers (Austgen, Rochelle et al. 1989, Posey and Rochelle 1997), (Hilliard 2008), (Blanchon le Bouhelec, Mougin et al. 2007) applied the e-NRTL model for their work. Hessen et al. (2010) used the refined e-NRTL model for the CO<sub>2</sub>-H<sub>2</sub>O-MEA/MDEA system. (Zhang, Zhong et al. 2011) applied e-NRTL (e-NRTL in ASPEN PLUS) for modeling VLE, heat capacity and heat of absorption of CO<sub>2</sub>-MDEA-H<sub>2</sub>O system. (Addicks, Owren et al. 2002) applied both extended UNIQUAC and e-NRTL for VLE calculations in the CO<sub>2</sub>-CH<sub>4</sub>-MDEA-H<sub>2</sub>O system. (Faramarzi, Kontogeorgis et al.

2009) used the extended UNIQUAC for modeling VLE of the CO<sub>2</sub>-H<sub>2</sub>O-MDEA/MEA system.

### 6.1 Equation of state models

Equation of state model is set of thermodynamic equation describing the state of matter under a given set of physical conditions. Electrolyte equation of state (EoS) model by (Furst and Renon 1993) is well-known. It is based on (Schwartzentruber, Renon et al. 1989), EoS concept and MSA. Vellee et al. 1999 used Furst and Renon model for H<sub>2</sub>S/CO<sub>2</sub>-DEA-H<sub>2</sub>O system. (Chunxi and Furst 2000) applied it for CO<sub>2</sub>/H<sub>2</sub>S-MDEA-H<sub>2</sub>O mixtures. Solbraa (2002) implemented the Furst and Renon (1993) model for the MDEA-CO<sub>2</sub>-H<sub>2</sub>O system. Huttenhuis et al. (2008) modified the Solbraa (2002) model for the CO<sub>2</sub>-CH<sub>4</sub>-MDEA-H<sub>2</sub>O system. Derks et al. (2010) used the Furst and Renon (1993) model for the CO<sub>2</sub>-PZ-MDEA-H<sub>2</sub>O system. (Button and Gubbins 1999) applied the SAFT19 model for the CO<sub>2</sub>-MEA/DEA-H<sub>2</sub>O system. Chapman et al. (1990) developed model based on statistical SAFT (statistical association fluid theory). It is based on statistical thermodynamics; the equation of state offers greater predictive capabilities than previous empirical equations.

Figure 13 provides the pictorial representation of development of models from simple to complex flowing from no 1 to 5. Model 1 is simple equilibrium model; model no. 2 is equilibrium model with reaction kinetics. Model 3 to 4 are rate based models with increase in complexity from reaction equilibrium to film reactions and electrolytes.



**Figure 13:** Different modeling approaches (Kenig, Schneider et al. 2001)

## **6.2 Absorption models with process simulation**

Computer aided process simulators are widely used in process design, process analysis and optimization. The simulators are comprised of component, physical and thermodynamic property data banks. The simulators have models of unit operations, columns, reactors etc. It is used to perform process calculations for conceptual design, detailed process calculation, mass and energy balances, flow sheeting, dynamic analysis and cost optimization. ASPEN PLUS, BATCH PLUS, HYSIS (A.H.C Guide 2006), PRO/II, CHEMCAD, UNISIM & PROMAX are the typical commercial simulators in use. Several research publications reported simulated results on amine absorption using HYSYS. Acid Gas Cleaning is an inbuilt functionality of Aspen HYSYS. The “Acid Gas” property package in Aspen HYSYS provides the thermodynamics based on the Electrolyte NRTL model with all the necessary aqueous-phase equilibrium and kinetics reactions required for rigorous calculations of the process. The thermodynamic package for chemical solvent modeling is based on the Electrolyte Non-Random Two-Liquid (NRTL) model for electrolyte thermodynamics while the Peng-Robinson Equation of State deals with properties of vapor phase and liquid hydrocarbon phase.

Amine absorption model for CO<sub>2</sub> absorption using MEA with ASPEN HYSYS and ASPEN Plus was studied by (ErikØi 2012). Model was developed with specified Murphree efficiencies and rate based approach. The study concluded that the differences between the properties executed by Aspen HYSYS and Aspen PLUS using the equilibrium models Kent-Eisenberg, Li-Mather and Electrolyte-NRTL were small. There were some differences in removal efficiency and temperature profiles between the results based on Murphree efficiencies and results with rate-based simulations. The calculations predicts that all the model results are roughly same close with the objective is to calculate efficiency of CO<sub>2</sub> removal efficiency with respect to circulation rate, number of column stages and temperature. Similarly, a rate based model for CO<sub>2</sub> absorption was studied by (Zhang, Que et al. 2011) and (Dugas, 2006) showed that the superiority of the rate-based models over the traditional equilibrium-stage models for the recently available pilot plant data from University of Texas at Austin for CO<sub>2</sub> capture with aqueous monoethanolamine.

(Erfani, Boroojerdi et al. 2015) utilized ASPEN HYSYS V7.3 and ASPEN PLUS V7.3 for simulation of CO<sub>2</sub> removal unit. In ASPEN HYSYS simulations, Kent/Eisenberg and Li/Mather models were used for amine calculations and shows that simulation using electrolyte NRTL model can most accurately fit plant data for specifications of absorber overhead, reboilers and condensers duties. (Nuchitprasittichai and Cremaschi 2013) used ASPEN HYSYS model to analyze the impact of different amine absorbents and their concentrations on the absorber and stripper column heights and the operating conditions of CO<sub>2</sub> recovery plant for post combustion of

CO<sub>2</sub> removal.

Lars Erik Øi (2007) modeled combined cycle gas power plant and a MEA (mono ethanol amine) based CO<sub>2</sub> removal process using ASPEN HYSYS process simulator. Peng Robinson and Amines' Property-Package thermodynamic models were used to calculate the thermodynamic properties which are available as inbuilt application in ASPEN HYSYS. The adiabatic efficiencies in compressors, gas turbines and steam turbines have been fitted to achieve a total thermal efficiency in the natural gas based power plant. The acid gas removal along with energy consumption for the process were calculated with respect to amine circulation rate, absorption temperature, packed bed height and steam enthalpy. The amine absorption model developed in Aspen HYSYS was found to be useful to understand the sensitivity of changing amine circulation rate, packed bed height, operating temperature and bottom reboiler temperature. Theoretical investigation of simultaneous absorption of CO<sub>2</sub> and H<sub>2</sub>S into aqueous solutions of MDEA and DEA was studied by (Zare Aliabad 2009). Thermodynamic systems like, E-NRTL, Amines (experimental) equation of states and amine package were used. The sensitivity of temperature, operating pressure, amine circulation rate, amine concentration and efficiency of packed bed (Murphree efficiency) on the rate of absorption were studied. The research highlights that when flow of leanamine and its concentration are increased, increase in absorption of CO<sub>2</sub> and H<sub>2</sub>S observed. When the temperature of inlet amine increased in absorber, CO<sub>2</sub> and H<sub>2</sub>S lifted to upper stages of absorber resulting in a decrease in absorption of acid gases noted. The research work reveals that sweet gas acid gas concentration is greatly influenced by the packing height. In conclusion, when leanamine concentration and flow increase, CO<sub>2</sub> and H<sub>2</sub>S absorption efficiency increases and when leanamine temperature, CO<sub>2</sub> and H<sub>2</sub>S slippage to upper stages of absorber and decrease in absorption of acid gases. The CO<sub>2</sub> and H<sub>2</sub>S concentration in sweet gas (clean gas) increases with CO<sub>2</sub> percentage in the clean gas which is greatly influenced by the packed bed height, but the effect of packing height on H<sub>2</sub>S removal has been observed as less significant. (Kim and Kim 2004) simulated the solvent absorption process and optimized the condition for minimum energy required in desorption. (Qeshta, Abuyahya et al. 2015) simulated LPG sweetening process using MDEA in HYSYS and conducted sensitivity analysis. The operating parameters were identified and it was found that H<sub>2</sub>S content in product LPG was within limit of 0 to 10 ppm.

## 7. OPTIMIZATION

Aspen HYSYS® has in built optimization program, HYSYS Optimizer (A.H.C. Guide 2006). It is a multi-variable steady state optimizer. Once process flow sheet has been built and converged solution has been obtained, the optimizer tool can be used to find the operating conditions to minimize or maximize an objective function. The spreadsheet option in optimizer is used to define objective function as

well as any spread sheet option in optimizer is used to define objective function as well as any constraint expressions. HYSYS has number of in built algorithms like Fletcher Reeves, Quasi-Newton, BOX, SQP, and mixed optimization.

Fletcher Reeves optimization method is based on the Fletcher-Reeves conjugate gradient scheme method, it is efficient for general minimization with no constraints. The Quasi-Newton method is also similar to that of Fletcher-Reeves method. It calculates the new search directions from approximations of the inverse of the Hessian matrix. BOX Method is based on the “Complex” method of (Box 1965); the Downhill simplex algorithm of (Weise 2009) and the BOX algorithm of (Kuester and Mize 1973). The BOX method is a sequential search technique which solves problems with non-linear objective functions with inequality constraints no derivatives is required. It handles inequality constraints but not equality constraints. The Sequential Quadratic Programming (SQP) method handles inequality and equality constraints. SQP is considered to be the most efficient method for minimization with general linear and nonlinear constraints, provided a reasonable initial point is used and the number of primary variables is small. The implemented procedure is based entirely on the Harwell subroutines VF13 and VE17. The program follows closely the algorithm of (Powell 1978). It minimizes a quadratic approximation of the Lagrangian function subjected to linear approximations of the constraints. The second derivative matrix of the function is estimated automatically. A line search procedure utilizing the “watchdog” technique (Chamberlain, Powell et al. 1982) is used to force convergence. The mixed method attempts to take advantage of the global convergence characteristics of the BOX method and the efficiency of the SQP method. After convergence, the SQP method is then used to locate the final solution using the desired tolerance.

## **8. REVIEW AND CONCLUSIONS**

Several articles related to sweetening process of sour gas and liquid, especially on solubility, solvent selection, equilibrium and reactive absorption models have been reviewed in this paper to know the state of art on sweetening of LPG. Also reviews relating to LNG, sour gas and combustion product acid gas treating process operating conditions, performance parameters and improvement methods have been carried-out. The entire study has been categorized under different sections as general introduction of the topic, impurities in LPG, LPG sweetening process, equipment selection and design guidelines, solvent selection and operating conditions, modeling and process simulation and optimization using software packages.

It is observed from the study that, only few research studies have been reported on modeling, simulation and optimization relating to treatment of acid gas in LPG.



(Feng, Benxian et al. 2015), (Tse and Santos 1993), (Qeshta, Abuyahya et al. 2015), (Nuchitprasittichai and Cremaschi 2013) considering its market value and its commercial importance there is much scope is available for further studies. Industries are continuously takes efforts to minimize the operating cost and improve efficiency by optimization. Therefore there is definite scope to further study the LPG sweetening process, develop a model, identify the performance parameters and optimize for performance improvement. The research outcome could help the industries to operate the system with maximum efficiency and also the developed models can be used for online supervisory control applications.

### **Glossary**

LPG	: Liquid Petroleum Gas
Raw LPG	: Untreated LPG with impurities (H <sub>2</sub> S, CO <sub>2</sub> , COS CS <sub>2</sub> etc)
Sweet LPG	: LPG having H <sub>2</sub> S < 4 ppm W/W can be termed as sweet LPG.
H <sub>2</sub> S	: Hydrogen Sulfide
CO <sub>2</sub>	: Carbon Dioxide
COS	: Carbonyl Sulfide
CS <sub>2</sub>	: Carbon Di Sulfide
HYSYS	: Process Simulation Software developed by Aspen Tech.
ATF	: Aviation Turbine Fuel
FCC	: Fluidized Catalytic Cracking Unit
HCU	: Hydrocracker Unit
VBU	: Vis-breaking Unit
SRU	: Sulfur Recovery Unit
MEA	: Mono Ethanol Amine
DGA	: Diglycol amine
DEA	: Diethanol amine
DIPA	: Diisoproplamine
TEA	: Triethylamine
MDEA	: Methyldiethanolamine
Amine Guard	: UOP formulated amine
ADIP	: Shell CO <sub>2</sub> removal process

- UCARSOL : DOW formulated amine  
INEOS : Company manufacturing formulated amine  
Benfield Hi pure: Amine treatment process  
Catacarb : Hot potassium carbonate process  
Selexol : Acid gas treating process  
Rectisol : Acid gas treating process  
Mercaptane : Organ sulfur compound  
Bender-Petresco: Sweetening process  
Doctor Sweet : Quality test for H<sub>2</sub>S and Mercaptanes  
ZnO : Zinc Oxide  
AMISOL : Lurgi's gas treating process  
Merox : Mercaptane oxidation  
Coalescer : Equipment to separate emulsions  
CAPEX : Capital Expenditure  
OPEX : Operating Expense  
Lean Amine : Amine with low H<sub>2</sub>S and CO<sub>2</sub>  
Rich Amine : Amine with high H<sub>2</sub>S and CO<sub>2</sub>  
Sour gas : Process gas with high H<sub>2</sub>S and CO<sub>2</sub>.  
Treated gas : Process gas with less H<sub>2</sub>S, CO<sub>2</sub> and passing copper test.  
Acid gas : Process gas contain very high H<sub>2</sub>S and CO<sub>2</sub>.  
Primary amine : Nitrogen atom with two hydrogen atoms attached.  
Secondary amine: One hydrogen atom attached to nitrogen atom.  
Tertiary amine: Three of three hydrogen atoms in ammonia is replaced by organic  
Loading mol/mol: mol of H<sub>2</sub>S per mol of amine (H<sub>2</sub>S loading)  
SAFT : Statistical association fluid theory  
Enh : Enhancement factor

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