Gas Treating: *Chemical Treatments*

(*Pengolahan Gas: secara kimia*)

Teknologi Pemrosesan Gas (TKK 564)

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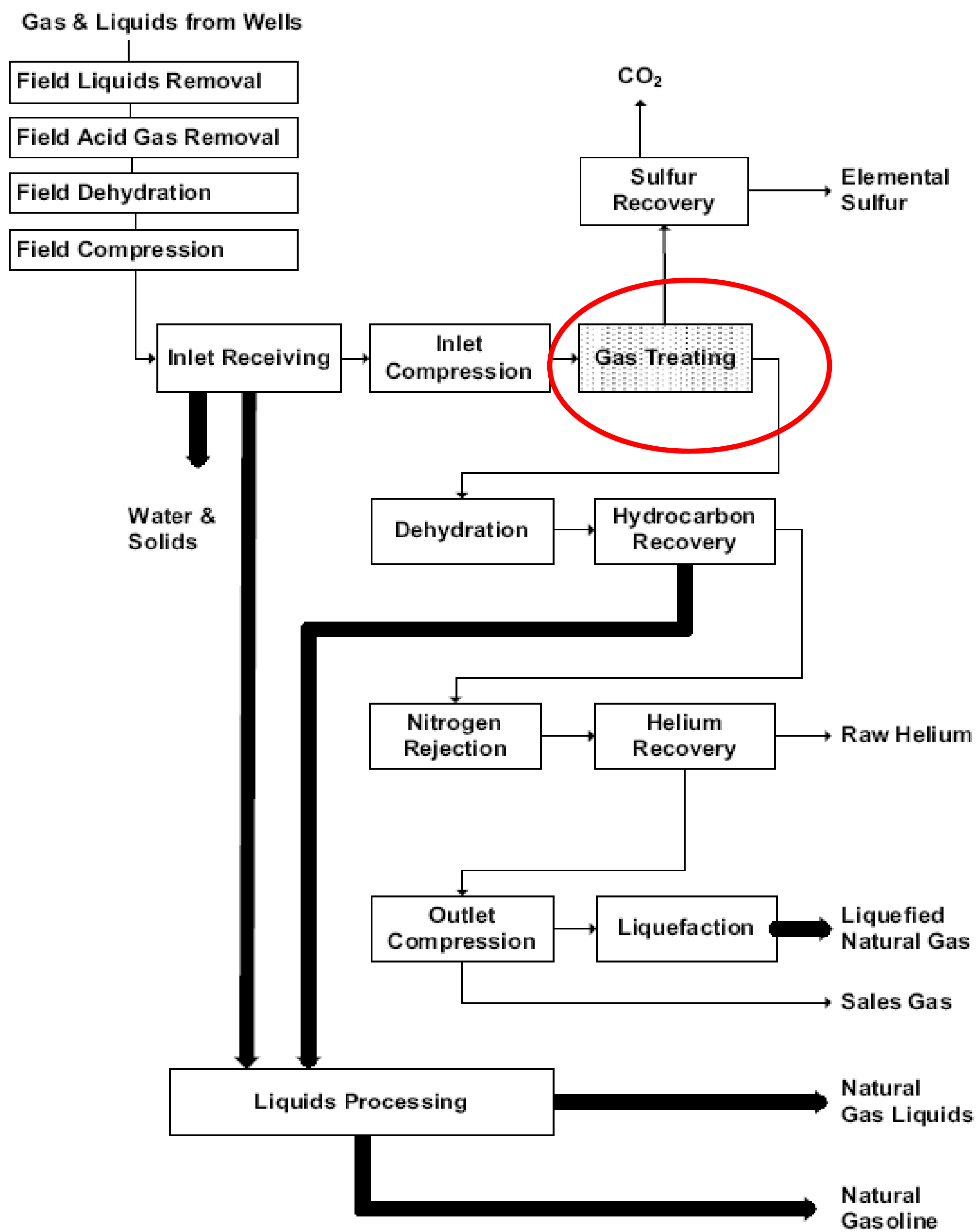
Instructor's Background

- BEng. (1995): Universitas Diponegoro
- Meng. (2000): Institut Teknologi Bandung
- PhD. (2006): Universiti Teknologi Malaysia

- Specialization:
  - Catalyst Design for Energy Conversion
  - Process Design for Energy Conversion
  - Combustion Engineering
  - Computational Fluid Dynamic (CFD)

Course Syllabus: (Part 1)

1. Definitions of Natural Gas, Gas Reservoir, Gas Drilling, and Gas production (*Pengertian gas alam, gas reservoir, gas drilling, dan produksi gas*)
2. Overview of Gas Plant Processing (*Overview Sistem Pemrosesan Gas*)
3. Gas Field Operations and Inlet Receiving (*Operasi Lapangan Gas dan Penerimaan Inlet*)
4. **Gas Treating (*Pengolahan Gas*)**
5. Gas Dehydration (*Dehidrasi Gas*)
6. First Assignment
7. Gas Compression System (*Sistem Kompresi Gas*)
8. *Ujian Tengah Semester*


Gas & Liquids from Wells
Field Liquids Removal
Field Acid Gas Removal
Field Dehydration
Field Compression
CO_2
Sulfur Recovery
Elemental Sulfur
Inlet Receiving
Inlet Compression
Gas Treating
Water & Solids
Dehydration
Hydrocarbon Recovery
Nitrogen Rejection
Helium Recovery
Raw Helium
Outlet Compression
Liquefaction
Liquefied Natural Gas
Sales Gas
Liquids Processing
Natural Gas Liquids
Natural Gasoline

Definition

- **Acid gases**: CO_2, H_2S, other sulfur species
- **Gas Treating ?**
- Gas treating: reduction of the "acid gases" to sufficiently low levels to meet contractual specifications or permit additional processing in the plant without corrosion and plugging problems.
- **Questions:**
  - Why are the acid gases a problem?
  - What are the acid gas concentrations in natural gas?
  - How much purification is needed?
  - What is done with the acid gases after separation from the natural gas?
  - What processes are available for acid gas removal?

Acid Gas Definitions

- **H_2S:**
  - Hydrogen sulfide is highly toxic, and in the presence of water it forms a weak, corrosive acid.
  - threshold limit value (TLV): 10 ppmv
  - At higher than 1,000 ppmv➔ death occurs in minutes
  - When H_2S concentrations are well above the ppmv level, other sulfur species can be present: carbon disulfide (CS_2), mercaptans (RSH), and sulfides (RSR), in addition to elemental sulfur.
  - If CO_2 is present, the gas may contain trace amounts of carbonyl sulfide (COS).
  - ASTM D4084 Standard test method for analysis of hydrogen sulfide in gaseous fuels

- **CO_2:**
  - Carbon dioxide is nonflammable and, consequently, large quantities are undesirable in a fuel.
  - it forms a weak, corrosive acid in the presence of water.

- **Threshold Limit Value** (TLV): of a chemical substance is a level to which it is believed a worker can be exposed day after day for a working lifetime without adverse health effects.

Gas Purification Level

- The inlet conditions at a gas processing plant are generally temperatures near ambient and pressures in the range of **300 to 1,000 psi (20 to 70 bar)**, **so the partial pressures of the entering acid gases can be quite high**
- If the gas is to be purified to a level suitable for transportation in a pipeline and used as a residential or industrial fuel, then the **H_2S concentration must be reduced to 0.25 gr/100 scf (6 mg/m3)**
- the **CO_2 concentration must be reduced to a maximum of 3 to 4 mol%**

- However, if the gas is to be processed for **NGL recovery** or **nitrogen rejection** in a cryogenic turboexpander process, **CO_2 may have to be removed to prevent formation of solids**.
- If the gas is being fed to an **LNG liquefaction facility**, then the **maximum CO_2 level is about 50 ppmv**

Acid Gas Disposal

- What becomes of the CO_2 and H_2S after their separation from the natural gas? ➔ The answer depends to a large extent on the quantity of the acid gases. ➔ Warning: CO_2 is the most greenhouse gas contributor
- For CO_2, if the quantities are large ➔ sometimes used as an injection fluid in **EOR (enhanced oil recovery)** projects.

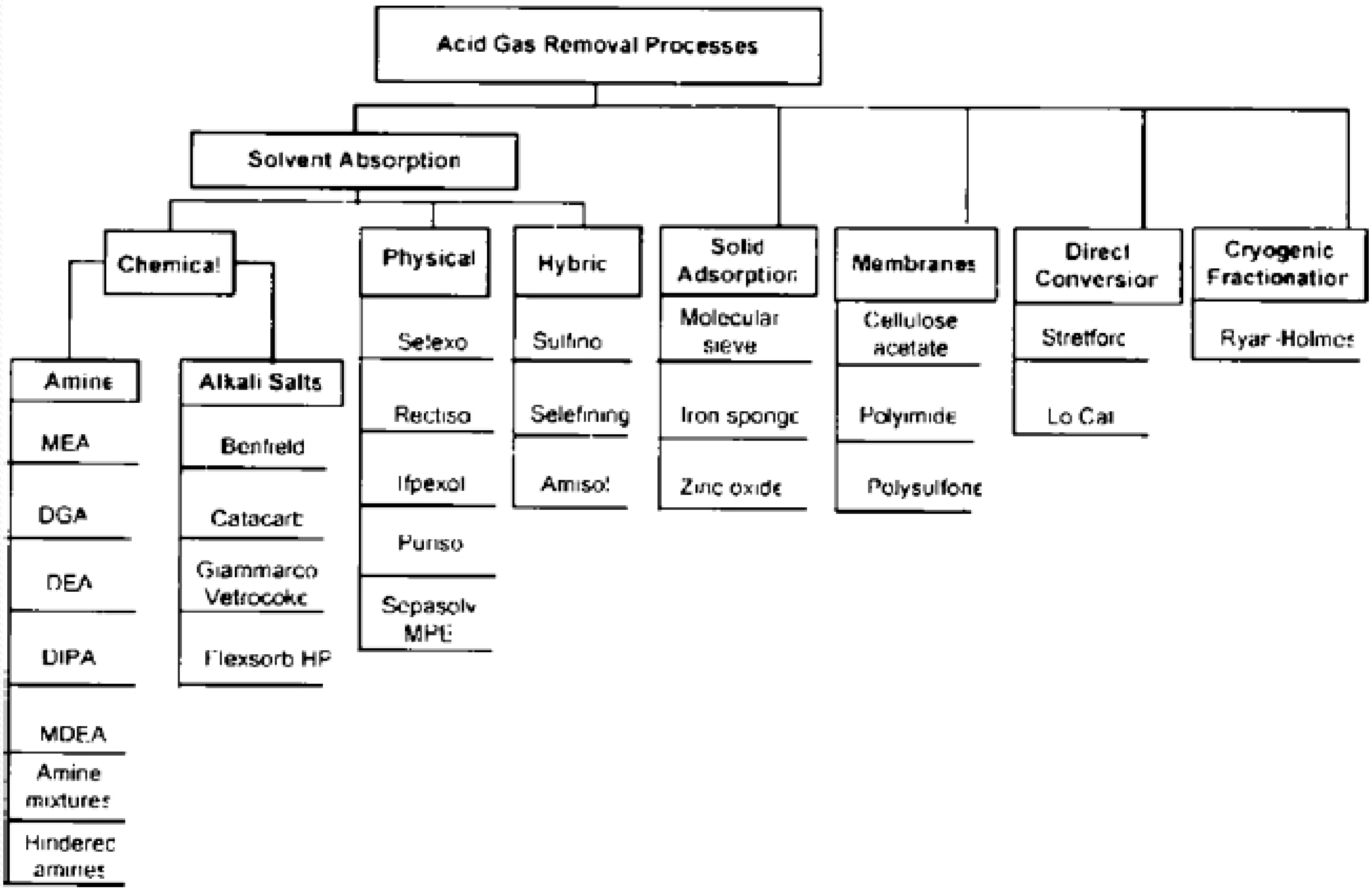
In the case of H_2S, four disposal options are available:

- **Incineration and venting**, if environmental regulations regarding sulfur dioxide emissions can be satisfied
- **Reaction with H2S scavengers**, such as iron sponge
- **Conversion to elemental sulfur** by use of the Claus or similar process ($2\ H_2S + O_2 \rightarrow S_2 + 2\ H_2O$)
- **Disposal by injection into a suitable underground formation**, ➔ if concentration is too high

PURIFICATION PROCESS

- Four scenarios are possible for **acid gas removal from natural gas**:
  - **CO_2 removal from a gas that contains no H_2S**
  - **H_2S removal from a gas that contains no CO_2**
  - **Simultaneous removal of both CO_2 and H_2S**
  - **Selective removal of H_2S from a gas that contains both CO_2 and H_2S**

Acid Gas Removal Processes



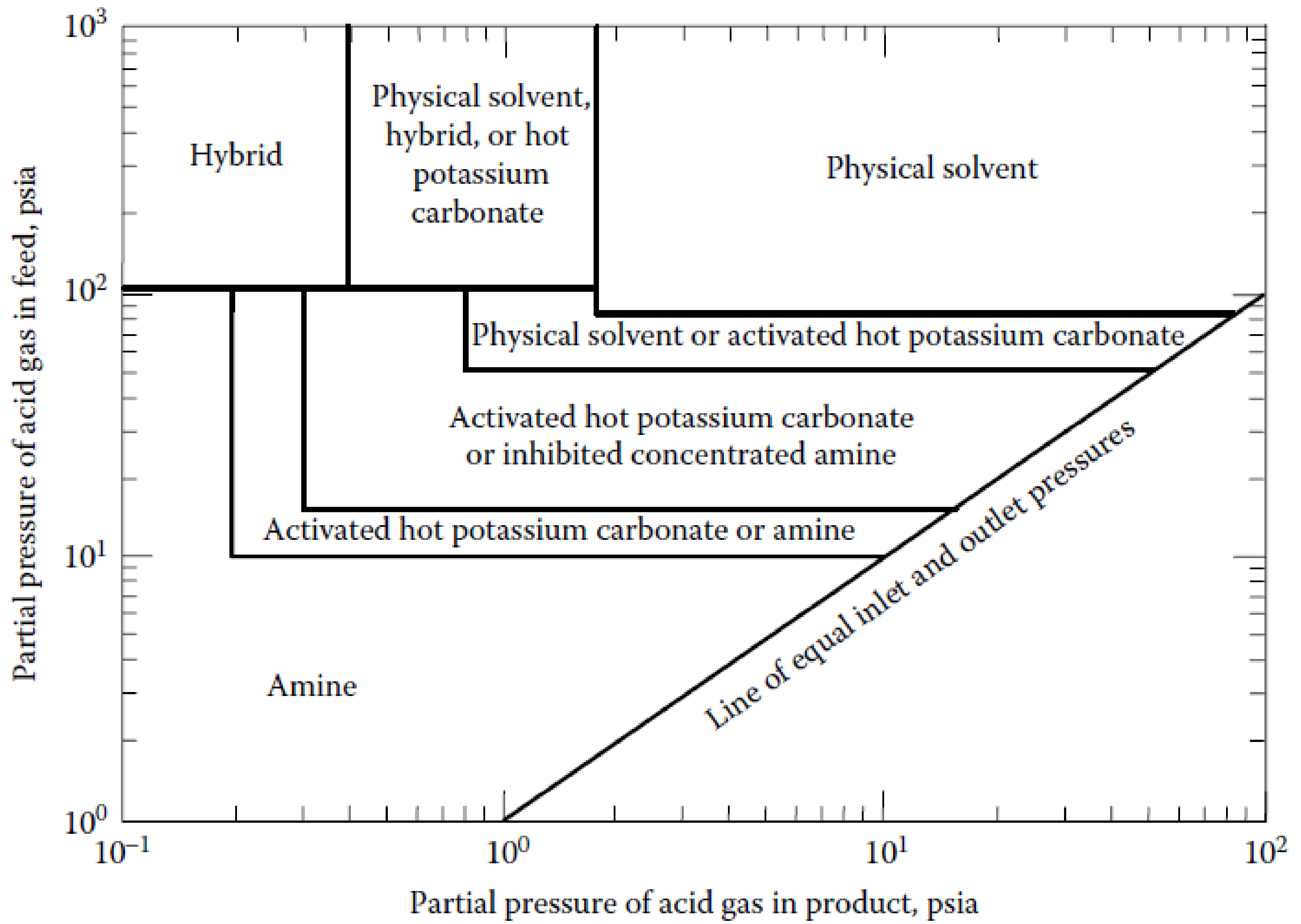
Some of the more important items that must be considered before a process is selected are:

- The **type and concentration** of impurities and hydrocarbon composition of the sour gas.
- The **temperature and pressure** at which the sour gas is available.
- The specifications of the outlet gas (low outlet specifications favor the amines).
- The **volume** of gas to be processed.
- The **specifications** for the residue gas, the acid gas, and liquid products.
- The **selectivity** required for the acid gas removal.
- The **capital**, **operating**, and **royalty costs** for the process.
- The **environmental constraints**, including air pollution regulations and disposal of byproducts considered hazardous chemicals.

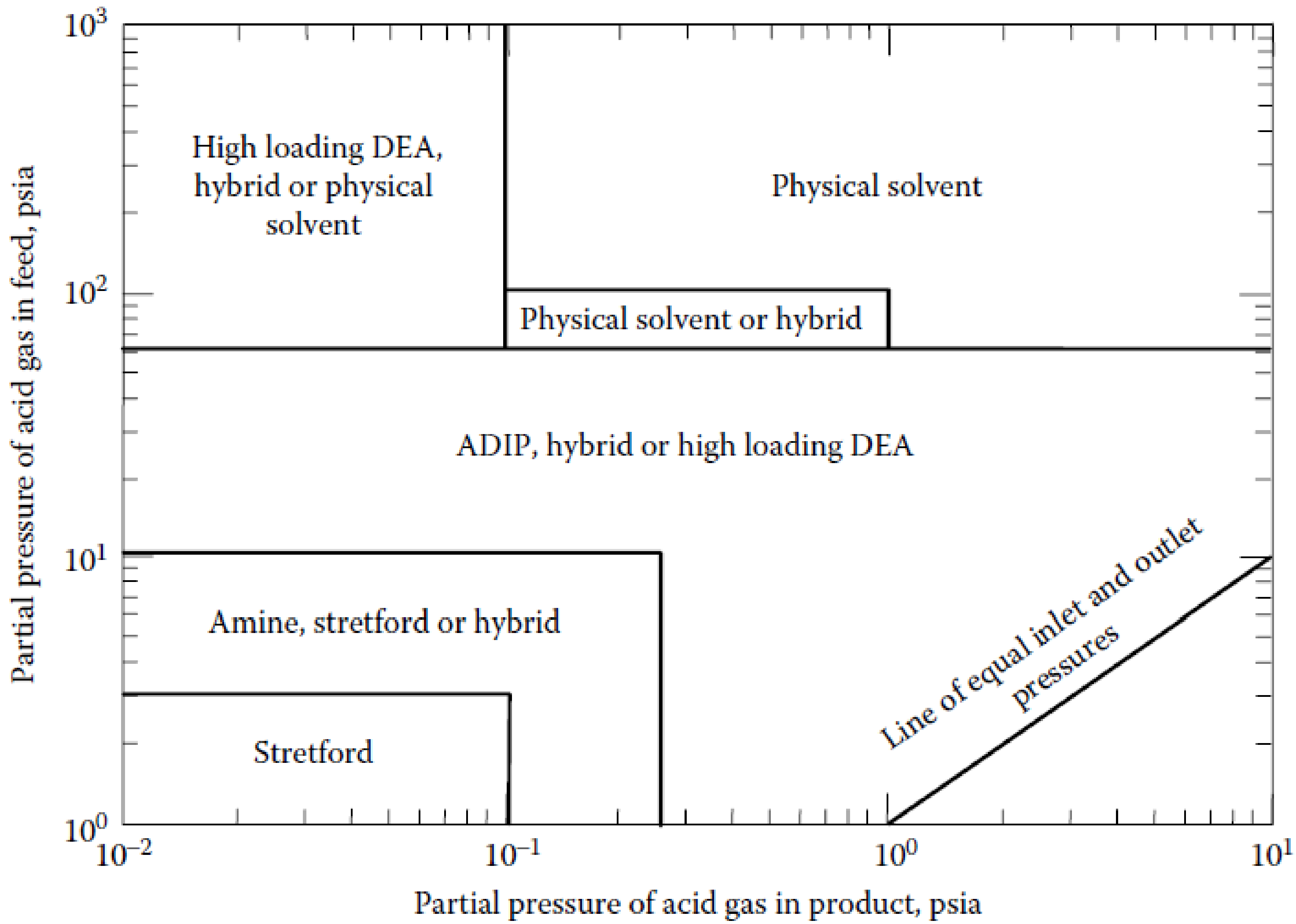
Definitions

- **Sour gas** is natural gas or any other gas containing significant amounts of hydrogen sulfide (H_2S)
- natural gas that does not contain significant amounts of hydrogen sulfide is called "**sweet gas**“
- **Acid gas** is natural gas or any other gas mixture which contains significant amounts of hydrogen sulfide (H_2S), carbon dioxide (CO_2), or similar contaminants

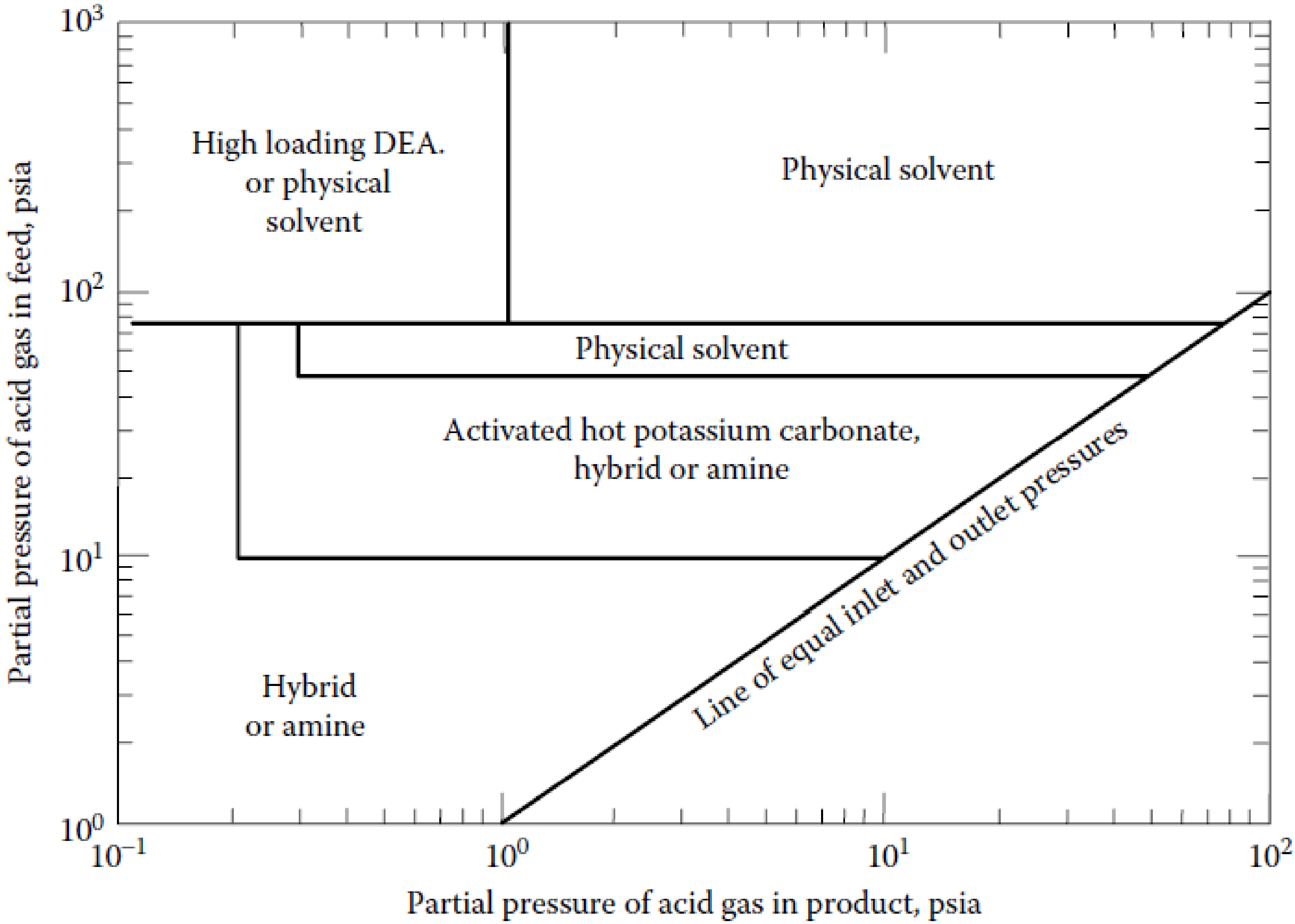
Process selection chart for CO2 removal with no H2S present



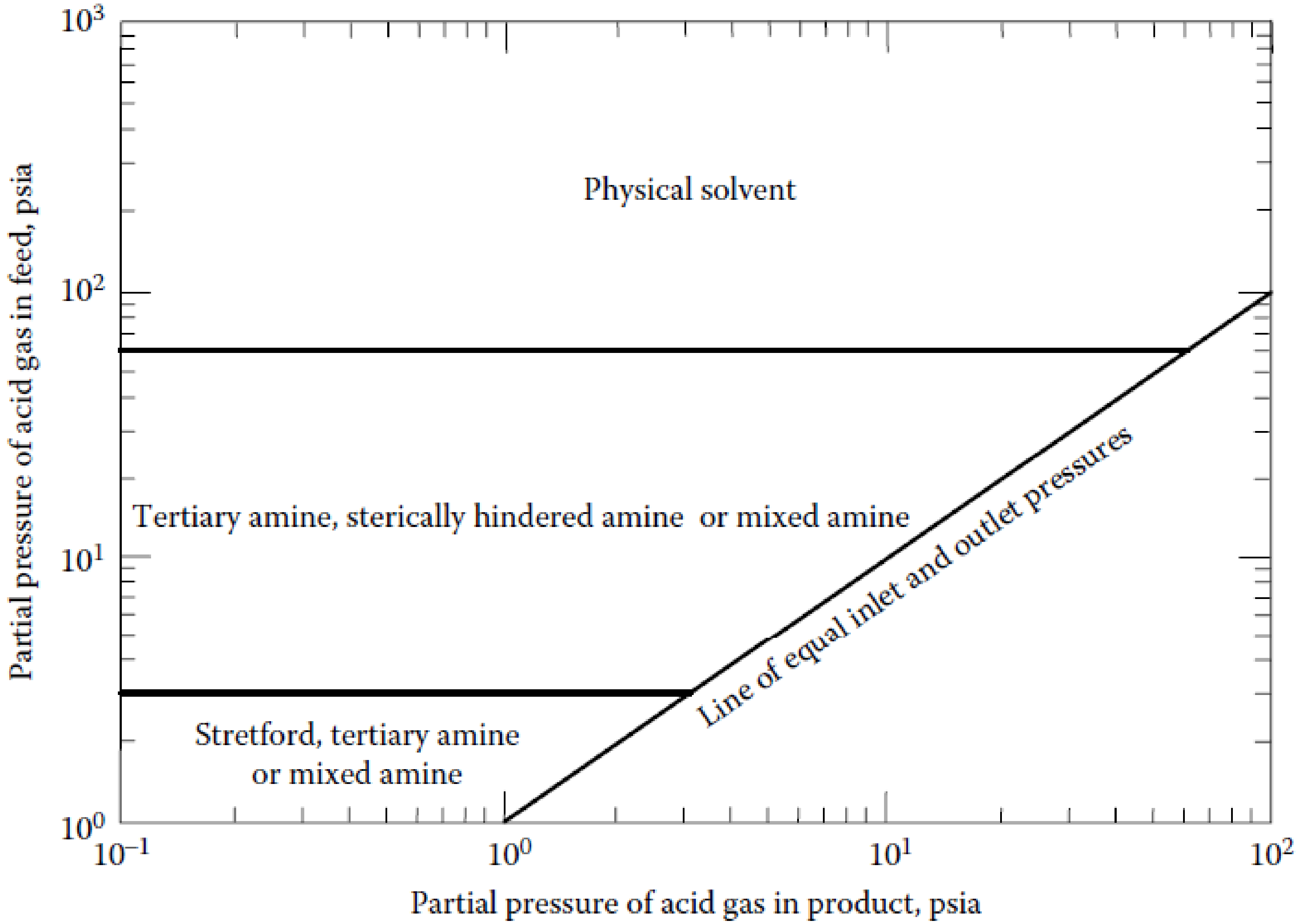
Process selection chart for H2S removal with no CO2 present



Process selection chart for simultaneous H2S and CO2 removal



Process selection chart for selective H2S removal with CO2 present



CO2 and H2S Removal Processes for Gas Streams

Process	Normally Capable of Meeting H_2S Specification[a]	Removes COS, CS_2, and Mercaptans	Selective H_2S Removal	Minimum CO_2 Level Obtainable	Solution Subject to Degradation? (Degrading Species)
Monoethanol-amine (MEA)	Yes	Partial	No	100 ppmv at low to moderate pressures	Yes (COS, CO_2, CS_2, SO_2, SO_3 and mercaptans)
Diethanol amine (DEA)	Yes	Partial	No	50 ppmv in SNEA-DEA process	Some (COS, CO_2 CS_2, HCN and mercaptans)
Triethanol amine (TEA)	No	Slight	No	Minimum partial pressure of 0.5 psia (3 kPa)	Slight (COS, CS_2 and mercaptans)
Methyldiethanol-amine (MDEA)	Yes	Slight	Some	Bulk removal only	No

Diglycol amine (DGA)	Yes	Partial	No	100 ppmv at moderate to high pressures	Yes (COS, CO_2, and CS_2)
Diisopropanol-amine (DIPA)	Yes	COS only	Yes	Not applicable	Resistant to degradation by COS
Sulfinol	Yes	Partial	Yes (Sulfinol -M)	50 ppmv, 50% slippage while meeting H_2S product spec	Some (CO_2 and CS_2)
Hot potassium carbonate	Yes, with special design features	Partial	No	Not reported	Not reported
Stretford	Yes	No	Yes	No significant amounts of CO_2 are removed	Yes (CO_2 at high concentrations)

Process	Normally Capable of Meeting H_2S Specification[a]	Removes COS, CS_2, and Mercaptans	Selective H_2S Removal	Minimum CO_2 Level Obtainable	Solution Subject to Degradation? (Degrading Species)
Selexol®	Yes	Slight	Some	Can be slipped or absorbed	No
Rectisol	Yes	Yes	No	1 ppmv	Not reported
Molecular sieves	Yes	Yes (excluding CS_2)	Some	Can meet cryogenic spec when CO_2 feed content is less than ~2%	Not applicable
Membranes	No	Slight	No	Feed concentration dependent	Not applicable

[a] H_2S specification is 25% grain H_2S per 100 scf (6 mg/m^3)

SOLVENT ABSORPTION PROCESSES

- In solvent absorption, the **two major cost factors** are:
  - the **solvent circulation rate**, which affects both equipment size and operating costs,
  - and the **energy requirement for regenerating the solvent**

Comparison of Chemical and Physical Solvents

Chemical Solvents

Advantages	Disadvantages
Relatively insensitive to H_2S and CO_2 partial pressure	High energy requirements for regeneration of solvent
Can reduce H_2S and CO_2 to ppm levels	Generally not selective between CO_2 and H_2S
	Amines are in a water solution, and thus the treated gas leaves saturated with water

Physical Solvents

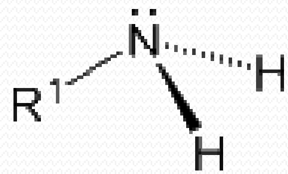
Advantages	Disadvantages
Low energy requirements for regeneration	May be difficult to meet H_2S specifications
Can be selective between H_2S and CO_2	Very sensitive to acid gas partial pressure

AMINES

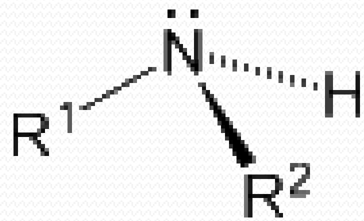
- Amines are compounds formed from ammonia (NH_3) by replacing one or more of the hydrogen atoms with another hydrocarbon group.
- Replacement of a single hydrogen produces a primary amine, replacement of two hydrogen atoms produces a secondary amine, and replacement of all three of the hydrogen atoms produces a tertiary amine.
- Primary amines are the most reactive, followed by the secondary and tertiary amines.

Amine Structure

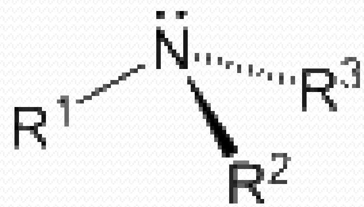
- Primary amine



- Secondary amine



- Tertiary amine

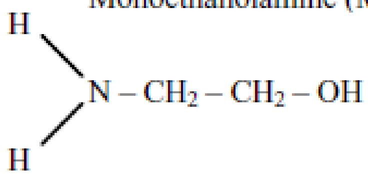


- Sterically hindered amines are compounds in which the reactive center (the nitrogen) is partially shielded by neighboring groups so that larger molecules cannot easily approach and react with the nitrogen.
- The amines are used in water solutions in concentrations ranging from approximately 10 to 65 wt% amines
- All commonly used amines are alkanolamines, whichare amines with OH groups attached to the hydrocarbon groups to reduce their volatility

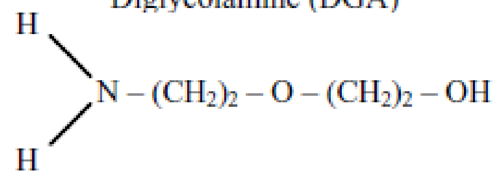
Molecular structures of commonly used amines

Primary Amines

Monoethanolamine (MEA)

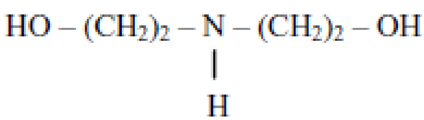


Diglycolamine (DGA)

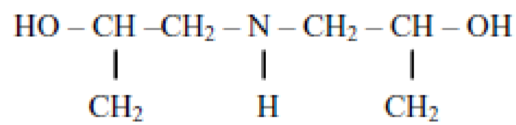


Secondary Amines

Diethanolamine (DEA)

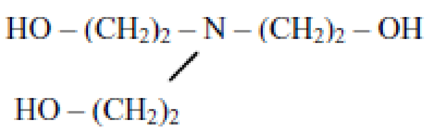


Diisopropanolamine (DIPA)

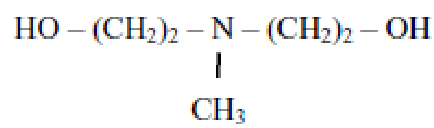


Tertiary Amines

Triethanolamine (TEA)

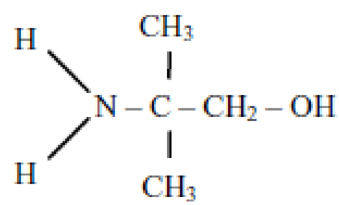


Methyldiethyanolamine (MDEA)



Sterically Hindered Amine

2-amino-2methyl-1-propanol (AMP)



Amines remove H_2S and CO_2 in a two step process:

- The **gas dissolves in the liquid** (physical absorption).
- The dissolved gas, which is a weak acid, **reacts with the weakly basic amines**.
- Absorption from the gas phase is governed by the partial pressure of the H_2S and CO_2 in the gas, whereas the reactions in the liquid phase are controlled by the reactivity of the dissolved species

Basic Amine Chemistry

- **Amines are bases**, and the important reaction in gas processing is the ability of the amine to form salts with the weak acids formed by H_2S and CO_2 in an aqueous solution
- The reaction between the amine and both H_2S and CO_2 is **highly exothermic**
- **Direct proton transfer**:
  - $R_1R_2R_3N + H_2S \leftrightarrow R_1R_2R_3NH^+ + HS^-$

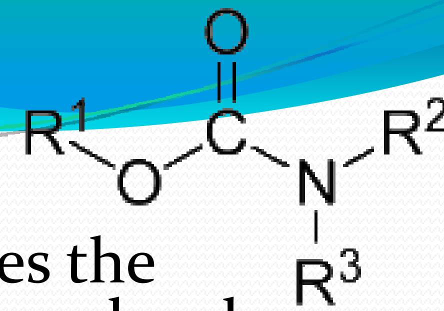
- The reaction between the amine and the CO2 is **more complex** because **CO2 reacts via two different mechanisms**. When dissolved in water, CO2 hydrolyzes to form **carbonic acid**, which, in turn, slowly dissociates to bicarbonate.
- The bicarbonate then undertakes an acid–base reaction with the amine to yield the overall reaction

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \text{ (carbonic acid)}$$

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^- \text{ (bicarbonate)}$$

$$H^+ + R_1R_2R_3N \leftrightarrow R_1R_2R_3NH^+$$

$$CO_2 + H_2O + R_1R_2R_3N \leftrightarrow R_1R_2R_3NH^+ \; HCO_3^-$$



- A **second CO_2 reaction mechanism**, requires the presence of a labile (reactive) hydrogen in the molecular structure of the amine.

$$CO_2 + R_1R_2NH \leftrightarrow R_1R_2N^{+}HCOO^{-}$$

$$R_1R_2N^{+}HCOO^{-} + R_1R_2NH \leftrightarrow R_1R_2NCOO^{-} + R_1R_2NH_2^{+}$$

$$CO_2 + 2R_1R_2NH \leftrightarrow R_1R_2NH_2^{+}R_1R_2NCOO^{-}$$

- The CO_2 reacts with one primary or secondary amine molecule to form the carbamate intermediate, which in turn reacts with a second amine molecule to form the amine salt
- The **rate of CO_2 reaction via carbamate formation is much faster than the CO_2 hydrolysis reaction**, but slower than the H_2S acid–base reaction.

Monoethanolamine

- **Monoethanolamine (MEA)** is the most basic of the amines used in acid treating and thus the most reactive for acid gas removal.
- It has the **advantage of a high solution capacity at moderate concentrations**, and it is generally used for gas streams with moderate levels of CO_2 and H_2S when complete removal of both impurities is required.
- A slow production of "**heat stable salts**" form in all alkanol amine solutions, primarily from reaction with CO_2.
- Oxygen enhances the formation of the salts.

Some Representative Operating Parameters for Amine Systems

	MEA	DEA	DGA	MDEA
Wt% amine	15 to 25	25 to 35	50 to 70	40 to 50
Rich amine acid gas loading	0.45 to 0.52	0.43 to 0.73	0.35 to 0.40	0.4 to 0.55
Mole acid gas/mole amine				
Acid gas pickup	0.33 to 0.40	0.35 to 0.65	0.25 to 0.3	0.2 to 0.55
Mole acid gas/mole amine				
Lean solution residual acid gas	0.12 ±	0.08 ±	0.10 ±	0.005 to 0.01
Mole acid gas/mole amine				

Monoethanolamine has a number of disadvantages

- A relatively high vapor pressure that results in **high vaporization losses**
- The **formation of irreversible reaction** products with COS and CS_2
- A high heat of reaction with the acid gases that results in **high energy requirements for regeneration**
- The **inability to selectively remove H_2S** in the presence of CO_2
- **Higher corrosion rates** than most other amines if the MEA concentration exceeds 20% at high levels of acid gas loading (Kohl and Nielsen, 1997)
- The **formation of corrosive thiosulfates** when reacted with oxygen (McCartney, 2005)

Diglycolamine

- Compared with MEA, low vapor pressure allows Diglycolamine [2-(2-aminoethoxy) ethanol] (DGA) to be used in relatively high concentrations (50 to 70%),
- Which results in lower circulation rates.
- It is reclaimed onsite to remove heat stable salts and reaction products with COS and CS_2.

Diethanolamine

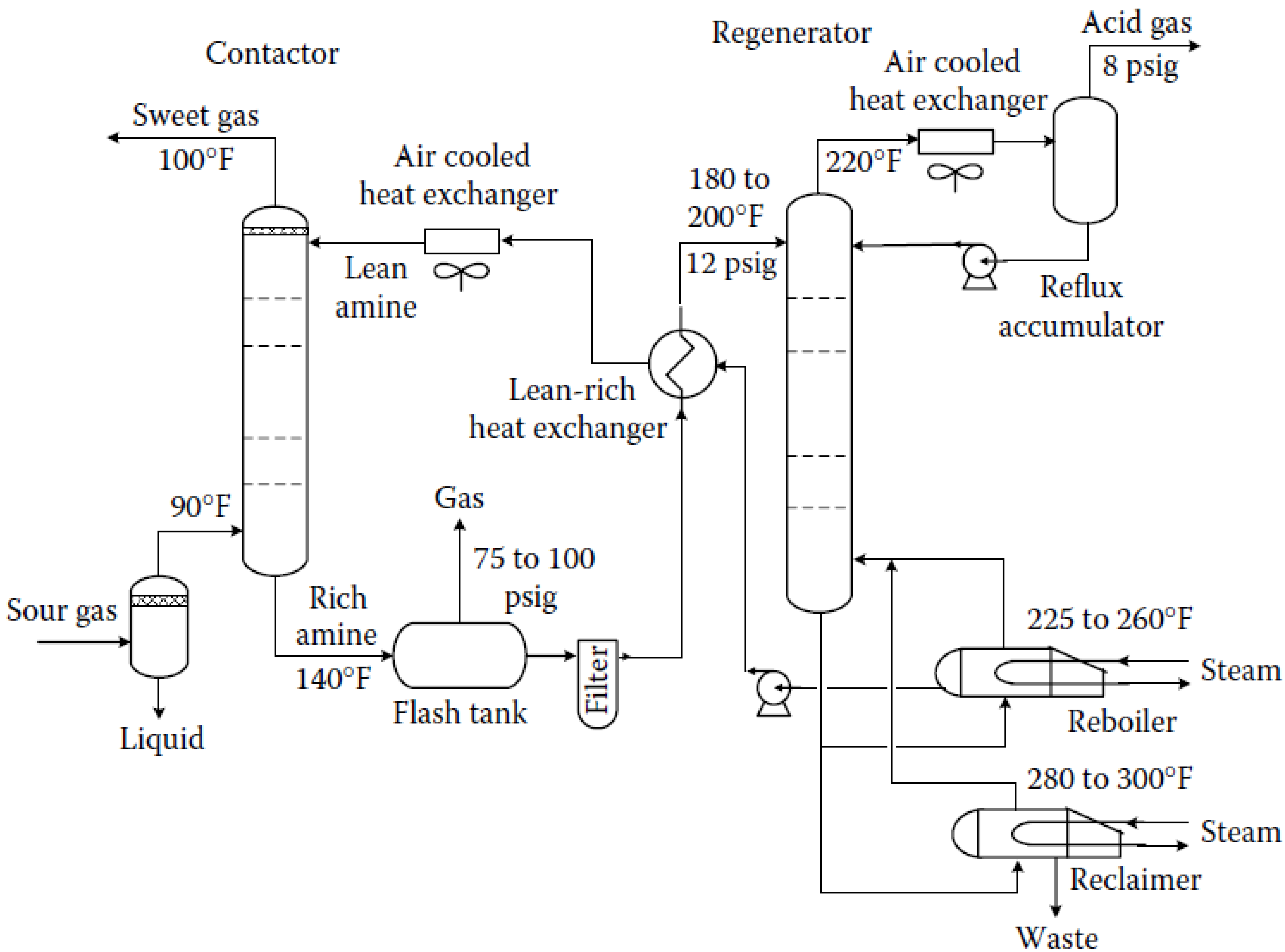
- **Diethanolamine (DEA),** a secondary amine, is less basic and reactive than MEA.
- Compared with MEA, it has a **lower vapor pressure** and thus, **lower evaporation losses**;
- it can operate at higher acid gas loadings, typically 0.35 to 0.8 mole acid gas/mole of amine versus 0.3 to 0.4 mole acid-gas/mole;
- and it also has a lower energy requirement for reactivation.
- Concentration ranges for DEA are 30 to 50 wt% and are primarily limited by corrosion.

- DEA forms regenerable compounds with COS and CS_2 and, thus, can be used for their partial removal without significant solution loss.
- DEA has the disadvantage of undergoing irreversible side reactions with CO_2 and forming corrosive degradation products; thus, it may not be the best choice for high CO_2 gases.
- Removal of these degradation products along with the heat stable salts must be done by use of either vacuum distillation or ion exchange.

Methyldiethanolamine (MDEA)

- **Methyldiethanolamine (MDEA)**, a tertiary amine, selectively removes H_2S to pipeline specifications while "slipping" some of the CO_2.
- As noted previously, the CO_2 slippage occurs because H_2S hydrolysis is much faster than that for CO_2, and the carbamate formation reaction does not occur with a tertiary amine.
- Consequently, short contact times in the absorber are used to obtain the selectivity.
- MDEA has a low vapor pressure and thus, can be used at concentrations up to 60 wt% without appreciable vaporization losses.
- Even with its relatively slow kinetics with CO_2, MDEA is used for bulk removal of CO_2 from high-concentration gases because energy requirements for regeneration are lower than those for the other amines.
- It is not reclaimable by conventional methods

Process Flow Diagram for Amine Treating by use of MEA



Average Heats of Reactiona of the Acid Gases in Amine Solutions

Amine	H_2S, Btu/lb (kJ/kg)	CO_2, Btu/lb (kJ/kg)
MEA	610 (1420)	825 (1920)
DEA	555 (1290)	730 (1700)
DGA®	674 (1570)	850 (1980)
MDEA	530 (1230)	610 (1420)

[a] The heats of reaction include both heat of solution and heat of reaction.

Amine Reclaiming

- Amines react with CO_2 and contaminants, including oxygen, to form organic acids.
- These acids then react with the basic amine to form heat stable salts (HSS).
- As their name implies, these salts are heat stable, accumulate in the amine solution, and must be removed.
- For MEA and DGA solutions, the salts are removed through the use of a reclaimer which utilizes a semicontinuous distillation
- The reclaimer is filled with lean amine, and a strong base, such as sodium carbonate or sodium hydroxide, is added to the solution to neutralize the heat stable salts.

Operating Issues

- **Corrosion**—Some of the major factors that affect corrosion are:
  - Amine concentration (higher concentrations favor corrosion)
  - Rich amine acid gas loading (higher gas loadings in the amine favor corrosion)
  - Oxygen concentration
  - Heat stable salts (higher concentrations promote corrosion and foaming)
  - the corrosion products can cause foaming

- **Solution Foaming—**
  - Foaming of the liquid amine solution is a major problem because it results in poor vapor–liquid contact, poor solution distribution,
  - and solution holdup with resulting carryover and off spec gas.
  - Among the causes of foaming are suspended solids, liquid hydrocarbons, surface active agents, such as those contained in inhibitors and compressor oils, and amine degradation products, including heat stable salts.
  - One obvious cure is to remove the offending materials; the other is to add antifoaming agents.

- **Heat Stable** Salts—
  - As mentioned above, these amine degradation products can cause both corrosion and foaming.
  - They are normally dealt with through the use of amine reclaimers

ALKALI SALTS

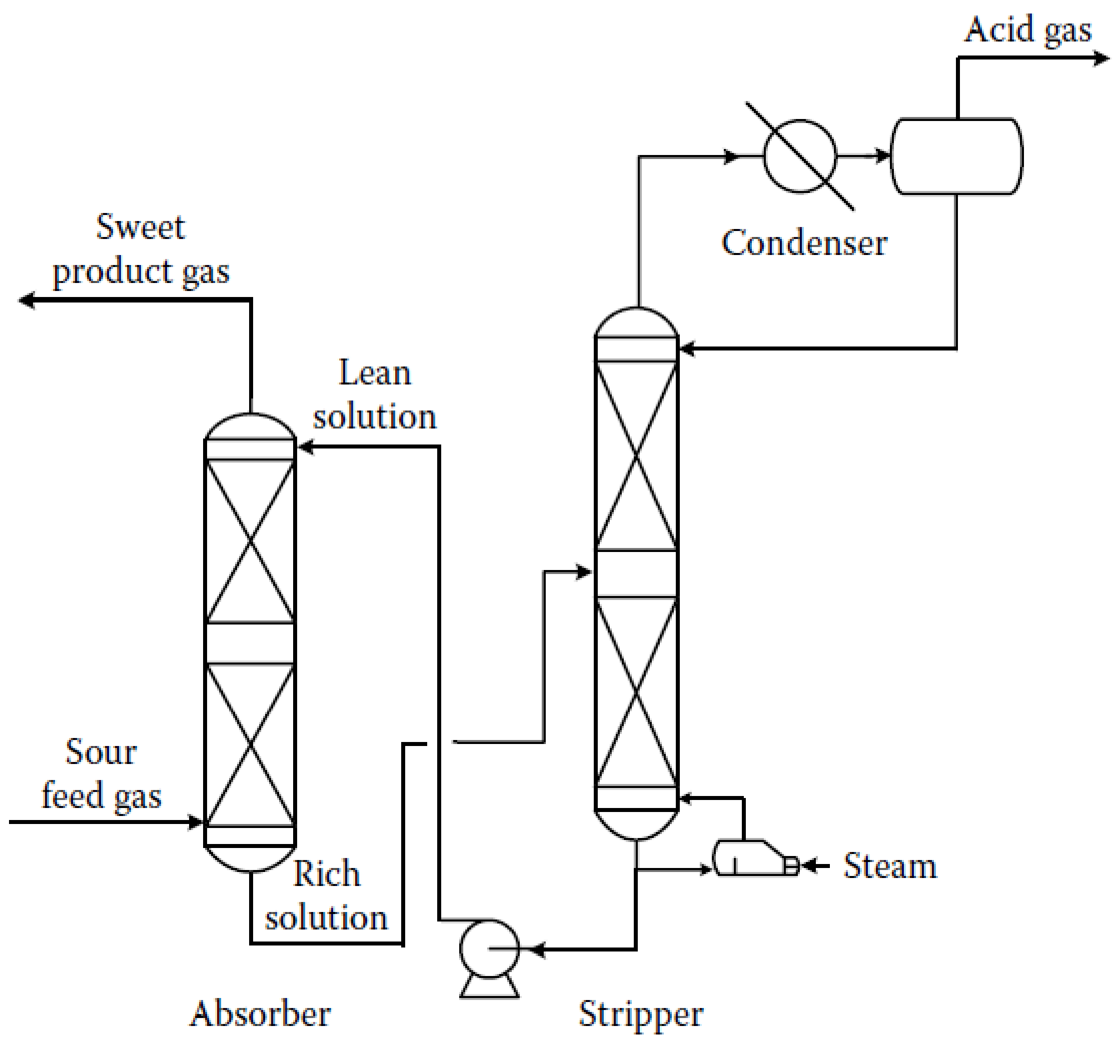
- The process is very similar in concept to the amine process, in that after physical absorption into the liquid, the CO2 and H2S react chemically with the solution

$$K_2CO_3 + CO_2 + H_2O \leftrightarrow 2KHCO_3$$

$$K_2CO_3 + H_2S \leftrightarrow KHS + KHCO_3$$

- In a typical application, the contactor will operate at approximately 300 psig (20 barg), with the lean carbonate solution entering near 225°F (110°C) and leaving at 240°F (115°C).

Process flow diagram for hot potassium carbonate process



THANK YOU