THE USE OF COSORB® II TO RECOVER HIGH PURITY CARBON MONOXIDE FROM A FEED GAS

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INTRODUCTION

KTI's business started in the 1960's with the design and construction of fired heaters, furnaces and steam reformers. As a natural outgrowth of our business various product lines evolved over time such as: hydrogen production, carbon dioxide, and carbon monoxide recovery processes. The focus of this paper is KTI's experience in the recovery of carbon monoxide from a feed gas.

There are two commercially developed processes for the recovery of carbon monoxide: cryogenic separation and the COSORB® solvent extraction process. COSORB® is KTI's proprietary process.

Each process has its particular strengths making one more suitable in a particular application than the other.

This paper describes the new improved COSORB® process which we now market as COSORB® II, and explains suitable applications, costs and utility usages.

BACKGROUND

The COSORB® process selectively removes carbon monoxide by complexation/decomplexation of carbon monoxide in a proprietary solvent containing cuprous aluminum chloride ([CuAlCl₄]) dissolved in an organic liquid such as toluene. The process was originally developed and commercialized by Tenneco in 1976. In 1983 KTI became owner and exclusive licensor of the technology. KTI has since then licensed COSORB® throughout the world.

There are currently 10 COSORB® units operating around the world ranging in size from 270 to 5500 NM³/Hr of recovered carbon monoxide and operating on a variety of feedstocks, such as: steam reformer gas, coke oven gas, BOF (Basic Oxygen Furnace) off gas, and POX (Partial Oxidation) gas. The resultant carbon monoxide product is used in various processes such as: phosgene, acetic acid, and DMF (Dimethyl Formamide). To date two COSORB® II plants are in the early engineering stages scheduled for startup within the next couple of years.
PROCESS DESCRIPTION

A simplified process flow diagram is shown in Figure 1. The COSORB® solvent contacts CO-laden feedgas in a countercurrent absorber, at elevated temperature and pressure above 2 atmospheres. The solvent can chemically complex and recover more than 99% of the carbon monoxide from the feedgas.

Other common compounds present in the feed gas that have a physical solubility in the aromatic base of the COSORB® solvent are removed from the solvent if required in a following flash unit. This small flash stream can be compressed and recycled to the absorber, or burned as fuel.

The CO-rich solvent from the absorber or the flash unit is heated against hot lean solvent from the stripper bottoms and passed to the top of the stripper. External reboiler heat provides stripping of the aromatic solvent-base to recover carbon monoxide as an overhead product gas, typically with about 99% purity.

Regenerated lean solvent exits the stripper bottoms and gives up heat to the stripper feed (rich solvent). It is then cooled further prior to its recycle to the absorber. A solvent management section is needed for pump seal flushing, etc. The primary source for this solvent is from the stripper overhead condenser. To prevent solvent loss, recovery systems may be required on both the carbon monoxide product stream and the absorber tailgas. These systems use either refrigeration or activated carbon or a combination.

PROCESS BENEFITS

The COSORB® system has a number of advantages and attractions compared with competing technologies, i.e. cryogenic carbon monoxide recovery, and absorption by ammoniacal copper liquor:

COSORB® recovers carbon monoxide in almost quantitative yields and at high 99+ % purity.
1. COSORB® can handle, without pretreatment, feeds containing synthesis gas components such as hydrogen, carbon dioxide, methane and nitrogen.

Cryogenic systems need to completely remove the carbon dioxide prior to carbon monoxide separation to prevent solid freeze up in the extremely cold environment.

2. Cryogenic processing has great difficulty in recovering pure carbon monoxide when relatively large volumes of nitrogen are present due to carbon monoxide and nitrogen having very similar boiling points.

3. COSORB® operation does not depend on high pressure or temperature extremes for effective removal of carbon monoxide from gaseous mixtures as does cryogenic processing.

4. The COSORB® solvent has a high absorption capacity.

5. COSORB® solvent is non-corrosive, therefore carbon steel can be used throughout with only minor exceptions.

6. Most equipment can be fabricated locally, saving on foreign currency requirements, import duty and shipping costs.

COSORB® II UPDATE

COSORB® is a mature process. The first COSORB® plant built by KTI has been in operation for ten years. However, COSORB® plants have had their share of problems as the process evolved. Most of these problems have focused around the very reactive nature of the solvent toward certain contaminating components found in some feeds and water or air ingress through leaking exchangers. These problems have been generally dealt with satisfactorily, but only after some frustration by the operator and after requiring some equipment modification.
Recognizing these difficulties were pervasive, KTI has undertaken a complete engineering approach to address all of the known problems experienced by COSORB® users in order to improve plant reliability.

COSORB® II incorporates a series of engineering solutions against deposit build-up, based in part on the extensive operating experiences gained by the various process licensees.

Areas of improvement include:

1. Extensive pretreatment to remove undesirable components.
2. Indirect cooling and heating.
3. Management system for solids (precipitation as a result of reaction with undesirable components).

With COSORB® II the focus is on plant reliability which is essential. Many users rely on constant carbon monoxide production to provide feedstock for their downstream plants in lieu of relying on stored supply.

APPLICATIONS

COSORB® can be used on feed streams from:

- Steam Reforming of Natural Gas
- Steam Reforming of Naphtha
- Partial Oxidation of Natural Gas
- Ammonia Plant Synthesis Gas
- Basic Oxygen Furnace Off Gas
- Coke Oven Gas
- Coal Gasification

Stand-alone plants for production of carbon monoxide or hydrogen and carbon monoxide tend to use steam reforming as a source of feed gas. Approximately 1/2 of the COSORB® units are based on steam
reforming feedstock. However, COSORB’s unique capability in the recovery of carbon monoxide from nitrogen bearing feed streams make it especially attractive in other integrated plants. For example, ammonia plants have large capacities of synthesis gas with hydrogen, nitrogen and carbon monoxide. The carbon monoxide must be removed or shifted prior to NH₃ synthesis. If COSORB is involved, a slip stream of the gas is sent to the COSORB II unit providing an excellent source of carbon monoxide for downstream chemicals manufacturing while the product hydrogen rich synthesis gas is returned to the NH₃ plant. (The carbon monoxide recovered is of course no longer available for shift. Therefore, there is a loss in available hydrogen for NH₃ production.)

Partial oxidation of natural gas, heavy hydrocarbons or coal gasification normally use oxygen to avoid nitrogen in the product gas. However, if carbon monoxide is the primary desired product, use of air can eliminate the cost for an air separation unit while still providing a good feedstock to a COSORB II plant.

Basic Oxygen Furnace off gas also contains nitrogen making COSORB a natural for carbon monoxide recovery. Blast Furnace Gas, and other nitrogen containing sources of carbon monoxide also show good promise.

**ECONOMIC DATA**

Basic economic data is presented based on mid $ 1988 for a Battery Limit facility.

**Basis:**
Typical feed gas composition vol% (dry basis) following steam reforming:

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<table>
<thead>
<tr>
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<tbody>
<tr>
<td>H₂</td>
<td>67.6</td>
</tr>
<tr>
<td>CO</td>
<td>16.0</td>
</tr>
<tr>
<td>CO₂</td>
<td>12.0</td>
</tr>
<tr>
<td>CH₄</td>
<td>4.4</td>
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Typical product recovery is 98%, and typical purity is 99%. (Higher recoveries and purities are achievable.)
Installed Costs on a US Gulf Coast Basis

Figure 2 shows how the total installed cost of a COSORB® II plant varies with capacity. Carbon monoxide product compression is not included.

Utility Consumption

<table>
<thead>
<tr>
<th>Utility Type</th>
<th>Rate</th>
<th>Unit of Carbon Monoxide Recovered</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrical power</td>
<td>0.49</td>
<td>kW/NM³</td>
</tr>
<tr>
<td>Reboiler heat</td>
<td>1.00</td>
<td>MJ/NM³</td>
</tr>
<tr>
<td>Cooling water</td>
<td>5.50</td>
<td>MJ/NM³</td>
</tr>
</tbody>
</table>

(see Note 1)

Note (1). Based on a summer high when refrigeration load is a maximum. Average annual rate would typically be between 40 to 70% of this load depending on climatic variations.

CONCLUSION COSORB® II provides a unique low cost solution to carbon monoxide recovery. Process improvements have made COSORB® II a highly reliable source of carbon monoxide for downstream manufacture of chemicals and pharmaceuticals. Therefore COSORB® II can be considered whenever recovery of high purity carbon monoxide is required. This is especially the case when the feed gas contains significant quantities of nitrogen and/or carbon dioxide, which need not be removed.
Total Investment Cost
Including Royalty but not Product Compression

![Graph showing the relationship between investment cost (in millions of dollars, US Gulf Coast) and capacity (in MTPA).]