Natural Gas Partial Oxidation for Chemical Processing in Longview, Texas

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Ty M. Beaudette
Air Liquide Process and Construction, Inc.

Carl Bochow, Jr
Howe-Baker Engineers, Ltd.

David Slivensky
Eastman Chemical Company
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1 INTRODUCTION

Air Liquide America Corporation was selected to supply syngas, a mixture of hydrogen (H₂) and carbon monoxide (CO), to Eastman Chemical Company’s Texas Operations, located near Longview, Texas. Air Liquide is building a 48 MMSCFD gasification unit with a 710 STPD air separation unit (ASU) to supply the syngas. Air Liquide’s alliance partner, Howe-Baker Engineers, Ltd., is providing Engineering, Procurement, and Construction (EPC) for the gasification unit. Air Liquide Process and Construction is providing EPC for the ASU. The new facility will utilize Texaco gasification technology to supply Eastman’s Oxo Chemicals facility with syngas and byproduct steam. Upon commercial operation of the new facility, Eastman’s existing steam-methane reforming operations will be shutdown.

By incorporating the latest technology for the production of syngas, this solution for Eastman will substantially reduce nitrogen oxides (NOx) emissions from the Eastman plant site. Reduction in NOx emissions is important because it supports a voluntary emissions reduction program (VERP) to improve air quality in the Longview area. In addition to environmental benefits, the new facility will be more efficient than the existing steam-methane reformers. This will result in reduced syngas feedstock cost and therefore reduced manufacturing cost for Eastman’s Oxo Chemicals business.

This paper will provide an overview of the project from the perspective of the end user, supplier and contractor.

2 HISTORY OF SYNTHESIS GAS AT EASTMAN’S TEXAS OPERATIONS

In 1950, the Eastman Kodak Company selected Longview, Texas as the site for a new grassroots chemical facility. The site was selected due to the proximity of the East Texas oilfield, the Sabine River, two railroad lines and a strong labor force. Eastman’s Texas Operations have grown from 250 employees in 1950 to a current staffing of approximately 1,800 employees. Major product lines produced at the Texas Operations include Oxo Aldehydes and Alcohols, Specialty Polymers, Hydrocarbon Resins and Polyethylene.
To support the Oxo Aldehydes and Alcohols product line, production of synthesis gas began in 1951. Synthesis gas (syngas) for the Oxo Aldehydes process is a mixture of H₂ and CO with a molar ratio of approximately 1.0 H₂-to-CO. The syngas is reacted with light olefins to produce Oxo Aldehydes.

The initial syngas operations involved a low pressure steam-methane reforming process, which involved feeding natural gas, steam and recycled carbon dioxide (CO₂) to the reformer to produce a 1.0 H₂-to-CO ratio syngas. After removal of CO₂, the syngas was compressed and fed to the Oxo Aldehydes process.

As the Oxo Aldehydes business developed, a series of incremental expansions were implemented from 1951 to 1994. In 1994 the syngas facilities had been expanded to include 21 reformer cells.

In the 1992 to 1995 timeframe, a series of technology studies were conducted to support the next major expansion of the syngas and Oxo Aldehydes facilities. After evaluating the capital intensity and process efficiencies, Eastman selected the Texaco Gasification
Process with a quench design as the best fit for Eastman. The selected process involved feeding natural gas, oxygen, and carbon dioxide to the gasifier to produce a synthesis gas stream with an approximate 1.0 H₂-to-CO ratio. After heat recovery, cooling and CO₂ removal, the syngas is fed directly to the Oxo Aldehydes process. The basic gasification process is as follows:

**Figure 3. Eastman’s Gasification Process**

![Gasification Process Diagram]

In 1997 Eastman installed a 12 MM SCFD gasification unit to supplement the existing syngas capacity in Eastman’s reforming operations.

### 3 DRIVERS FOR COMPLETE CONVERSION TO GASIFICATION TECHNOLOGY

Upon start-up of Eastman’s gasification unit in 1997, the operating efficiencies of the gasification process were confirmed. This direct operating experience gave Eastman the data to quantify the value of a complete conversion to gasification technology. The major drivers that were identified included a significant improvement in the environmental impact of the syngas operations and a significant economic advantage in the cost to produce syngas.

#### 3.1 Environmental Advantages of Gasification Technology

Significant reductions in NOx and CO₂ emission rates will be achieved with the conversion to gasification technology. This is a result of eliminating the point source emissions related to the furnace flue gas exhaust and the natural gas driven compressor exhaust that are utilized in Eastman’s steam-methane reforming process. Emissions from the gasification process are relatively small by comparison. They are primarily from fired heaters used for process feed pre-heat. Conversion to gasification technology reduces Eastman’s plant wide NOx emission rate by an estimated 900 tons per year. In addition, it reduces the CO₂ emission rate by an estimated 27,500 tons per year.

Reduction in the NOx emission rate is important, because the northeast Texas counties around Longview are approaching the limit that would trigger a change in the Environmental Protection Agency’s (EPA) designation of the area. NOx emissions and volatile organic compounds (VOC) result in formation of ground level ozone pollution. During peak ozone periods, the ozone level has approached the limit that would trigger a non-attainment designation by the EPA. A non-attainment designation could result in EPA sanctions including: tougher vehicle inspection standards, business and industrial restrictions, gasoline station controls, and the loss of federal highway funds. The EPA
sanctions target all sources of NOx. In the Longview area, the NOx emission inventory is broken down as follows:

Table 1.

<table>
<thead>
<tr>
<th>Emission Source</th>
<th>% of Total NOX</th>
</tr>
</thead>
<tbody>
<tr>
<td>Industrial Point Sources (Excluding Eastman Plant Site)</td>
<td>56 %</td>
</tr>
<tr>
<td>Eastman’s Plant Site</td>
<td>6 %</td>
</tr>
<tr>
<td>On-Road Vehicles</td>
<td>17 %</td>
</tr>
<tr>
<td>Area Sources (oil/gas production, consumer paints/solvents, service stations)</td>
<td>15 %</td>
</tr>
<tr>
<td>Planes, Boats, Trains and Lawn Equipment</td>
<td>6 %</td>
</tr>
</tbody>
</table>

In order to reduce the NOx emission rate in the area and thus reduce the potential for a non-attainment designation, a voluntary action program, “Northeast Texas Air Care” (NETAC) has been established. NETAC is a community-wide campaign for air quality improvement. The program consists of educational and voluntary actions that can help reduce the ozone problem. For the individual, it involves carpooling, modified driving and car maintenance habits, reduction of household emissions, and energy conservation. In the industrial arena, NETAC involves VERP to proactively reduce the NOx emission rate.

Eastman volunteered to reduce the NOx emission rate by approximately 40 % for their plant site. Two major projects and a number of minor projects are underway to support this goal. First, a cogeneration facility, owned and operated by a third party, is being installed on the Eastman site. This will allow Eastman’s coal fired steam generation facility to be shutdown. The second project is the Air Liquide Syngas project, which will allow Eastman’s steam-methane reformers to be shutdown. The Air Liquide Syngas project will result in a net reduction of 900 ton per year of NOx emissions, or a 20 % reduction in the plant site NOx emissions.

In addition to NOx emission reductions, conversion to gasification technology will also reduce carbon dioxide emissions. Regulation and control of carbon dioxide, a greenhouse gas, continues to be an issue. Following conversion to gasification technology, the CO2 emission rate from the Eastman plant site will be reduced by approximately 27,500 tons per year. The net reduction in CO2 emissions may appear less than expected for shutdown of natural gas fired reformer furnaces. This is attributed to Eastman’s process to recover CO2 from the furnace exhaust and recycle the CO2 to provide feedstock for the reforming process. As a result, the existing Eastman reforming process already has significantly lower CO2 emissions than a typical reforming process.
3.2 Economic Advantages of Gasification Technology

Operating experience obtained from Eastman’s gasification unit provided the data to quantify the economic advantages of a complete conversion to gasification technology. Significant economic advantages were identified in the following areas:

- Natural Gas Efficiency
- Maintenance and Repair Costs
- Operating Labor
- Manufacturing Costs
- Quality of Syngas

Eastman’s evaluation of these advantages showed potential to reduce current syngas feedstock costs by 5 to 15 percent.

4 OPTIONS TO CONVERT TO GASIFICATION TECHNOLOGY

Considering the significant economic drivers and environmental benefits, Eastman began evaluating a number of options to capture the value of gasification technology. After evaluating the project as a typical Eastman funded venture, a study was initiated to evaluate commercial alternatives. This study involved requesting project proposals from the major industrial gas and syngas technology suppliers. The basic principal of the request was that any gasification technology would be considered and the ultimate decision would be based on the financial value to Eastman.

Seven potential suppliers submitted detailed commercial proposals. These proposals considered three different gasification technologies. After receipt of the commercial proposals, Eastman evaluated the technology and commercial aspects of each proposal. The technology evaluation included process reliability, expected on-stream factor, operating experience of the supplier, any new or innovative unit operations, the OSBL utility and services requirements on the Eastman infrastructure, and the environmental aspects of the proposed facility. From a commercial standpoint, the proposals were evaluated to determine project economics, flexibility of commercial terms, and value added factors. Ultimately, the facility and commercial terms proposed by Air Liquide America Corporation were selected.

5 PROJECT DEVELOPMENT TEAM

Eastman’s decision to contract with Air Liquide for supply of syngas is indicative of a growing trend in the petroleum and chemical industry. Industrial gas companies bring value to project development by:

- Making Capital Commitment.
- Managing supply projects from initial development through long term commercial operation.
- Assessing the cost impact of capacity and technology options.
- Integrating solutions into existing operations.
The key to the success of this partnership is open communication and commitment.

Air Liquide is the world’s largest industrial gas organization. Founded in 1902 the company now has over 27,000 employees worldwide. Air Liquide began supplying industrial gas to Eastman’s Longview, Texas chemical facility in 1976. Air Liquide’s Alliance Partner is Howe-Baker Engineers, Ltd. Howe-Baker is a quality engineering contractor with over 60 years of EPC experience and specialization in the design, fabrication, and construction of all types of hydrogen and syngas plants.

After being short-listed, Air Liquide and Howe-Baker worked closely with Eastman to solve critical issues in site selection, reliability, steam generation, staffing, and value added integration of industrial gas supply to the Longview facility. The complexity and scope of these issues made it extremely difficult for either Air Liquide or Eastman to independently evaluate them. By working closely together the optimum solutions for the overall facility were formulated. Some of the critical decisions are described below.

5.1 Site and Technology Selection

Prior to contacting potential suppliers, Eastman had focused their development efforts on two potential sites for the new gasification unit, designated as the B12 and North sites. Both sites had unique advantages. Eastman’s B12 site was a small plot within their facility that neighbored their existing gasification unit. This location offered convenient offsite and utility infrastructure. This site also readily allowed Eastman to operate and maintain the new unit. On the other hand, the small size of this site was likely to result in higher installation costs. The plot size also precluded installation of high pressure steam generation equipment. The North site was the likely location for an ASU to supply oxygen to the new gasification unit. This site also provided adequate space to include a gasification unit with high pressure steam production capabilities. Selection of this site facilitated outsourcing the operations and maintenance for the new gasification unit.

Due to the complex infrastructure related to Eastman’s high pressure steam system and the potential impact of a new cogeneration unit, the value of the high pressure steam generation was not clear. Air Liquide and Howe-Baker assisted Eastman in evaluating the cost impact of high pressure steam by providing comparisons of process alternatives for heat recovery and energy utilization.

Texaco gasification technology offers several options for heat recovery from the syngas. The quench reactor design cools the syngas by direct contact with water. Although this reactor design has the lowest capital cost, the temperature of the quenched syngas is too low to generate high pressure steam. Texaco also provides a reactor design with an integrated syngas cooler. The capital cost for this design is higher than the quench reactor, but it is capable of producing high pressure steam.

Overall energy recovery and utilization is also dependant on the method of controlling the H₂ to CO ratio in the syngas product. Excess hydrogen, if present, must be removed from the product. This hydrogen may be valued as an additional product stream or fuel. The most economical means of controlling the H₂ to CO ratio in syngas is adjustment of
the quantity of CO₂ fed to the gasification reactor. Increasing the carbon dioxide feed forces equilibrium towards carbon monoxide production. However, syngas product availability is impacted by CO₂ availability and responsiveness of controls.

On the other hand, the use of a MEDAL™ membrane to strip off excess hydrogen significantly reduces the influence of CO₂ supply. The MEDAL™ membrane is Air Liquide’s proprietary technology for purifying hydrogen rich gas. It is also effective at controlling the H₂ to CO ratio in syngas by selectively removing hydrogen. The heart of the equipment consists of millions of polymeric hollow fibers, which are as thin as hair. “Fast” gases, with a high permeation rate, diffuse through the membrane, flow out through the hollow fiber interior and are channeled into the permeate stream. “Slow” gases flow around the walls of the fibers. In this way, a fast gas like hydrogen is separated from slower gases like CO and methane.

The following table shows the estimated high pressure steam production for different combinations of these technologies.

**Table 2.**

<table>
<thead>
<tr>
<th></th>
<th>Option 1</th>
<th>Option 2</th>
<th>Option 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasification Heat Recovery Method</td>
<td>Syngas Cooler</td>
<td>Quench</td>
<td>Quench</td>
</tr>
<tr>
<td>Additional Liquid CO₂ Import</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>MEDAL™ Membrane</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Fired Heater Duty (MMBtu/h)</td>
<td>110</td>
<td>110</td>
<td>None</td>
</tr>
<tr>
<td>HP Steam Export (kpph)</td>
<td>152</td>
<td>100</td>
<td>0</td>
</tr>
</tbody>
</table>

**Notes:**
- All options shown in this table utilized full CO₂ recycle combined with CO₂ import from Eastman.
- Option 3, without the MEDAL™ membrane, requires additional CO₂ to maintain the desired H₂ to CO ratio in the syngas product.
- The fired heater may use excess hydrogen as fuel in options including a MEDAL™ membrane.

This table shows that the greatest quantity of steam is produced when using a MEDAL™ membrane with a syngas cooler. Increased steam generation improves operating
economics when steam is valued. Air Liquide translated the above information into syngas cost options. Using this information, Eastman ultimately selected the North site, with high pressure steam production.

5.2 **Reliability**

Since the new gasification unit replaces 21 small steam-methane reformers, reliability is a key consideration for Eastman. Based on their own operating experience, Eastman made the decision to require two 60 percent parallel gasification reactor trains. With product reliability objectives defined, additional duplication of upstream and downstream equipment remained open to the supplier. Production of high pressure steam by syngas cooling came with its own reliability concern in regard to the potential for metal dusting. Air Liquide and Howe-Baker approached these issues with careful consideration to balancing the value of steam production against the impact on product availability.

Air Liquide conducted a preliminary risk assessment and reliability study as part of its project development procedure. Sharing the results of these efforts with Eastman benefited the overall project development by combining the operating experience of both organizations. One of the key areas of mutual concern was the potential for metal dusting when using syngas cooler technology. Howe-Baker, in conjunction with the syngas cooler manufacturer, provided a detailed evaluation of the potential for metal dusting and how their design protected against this.

The term “metal dusting” refers to an event where a metal surface in contact with carbon monoxide turns to powder. This takes place under certain process conditions in which carbon diffuses into a metal matrix and forms carbides. These carbide formations result in stress buildup, which causes metal dusting to occur.

The potential for carbon formation is based on the gas composition and metal temperature. Industry experience shows that if the gas temperature is less than about 1100°F, the kinetics of the reaction are too low and carbon does not form. The equilibrium Kp for typical gasifier reactor effluent compositions is about 1800°F. If the calculated Kp, which is based on gas composition, is greater than the equilibrium Kp, carbon cannot form. Therefore, gasifier reactor effluent metal dusting potential typically occurs between the temperatures of 1100°F and 1800°F.

For metal dusting to occur in the gasifier reactor effluent, there are two essential elements that are necessary: a metal surface, and a metal surface temperature between 1100°F and 1800°F. The temperature of syngas from the gasification reactor passes through this region. With the piping and equipment providing a metal surface, the remaining element necessary for metal dusting is the metal surface temperature. The Syngas Cooler cools the syngas by generating steam. The metal temperature of the steam generating tubes is practically the same as the steam/water temperature, which is substantially less than 1100°F. The cooler metal temperature is maintained by an internal water circulation system.
Even though the exact mechanism of metal dusting is not completely understood, the necessary elements are. Using this information, preventative measures can be taken to avoid operating in regions prone to metal dusting. The water circulation design utilized by the manufacturer has proven ability to accomplish this.

### 5.3 Oxygen Network

Air Liquide was in a unique position to offer the added benefits of an integrated oxygen supply network. Air Liquide currently supplies Eastman with oxygen from two ASU facilities in Longview, Texas, approximately four miles from the Eastman site. Project timing and constraints resulted in independent supply pipelines operating at different pressures. Integrating the oxygen network required upgrading one ASU to the higher pressure, connecting the pipelines of the two existing and new ASU, and making pipeline modifications within Eastman’s complex. This network not only connects the ASU’s, it also connects the liquid oxygen backup systems. The network provides significant financial benefit to Eastman as it improves overall reliability and flexibility of oxygen.

The first benefit of the oxygen network is cost reduction. The network significantly reduces the need to haul and vaporize liquid oxygen during planned and unplanned shutdowns of the ASU’s. The oxygen production from each ASU can be optimized for the lowest operating cost. The new, more power efficient ASU can take some of the load from the existing ASU's to reduce power costs.

The second benefit of the oxygen network is its improved product availability. The new network makes 1,800 tons of liquid oxygen storage available to Eastman in Longview, Texas. The design of the new ASU provides “bumpless transfer” to vaporized liquid oxygen from storage. This feature is essential when supplying gasification units. Gasification reaction controls are sensitive to variations in oxygen flow. Rapid changes in pressure can activate shutdown initiation systems to avoid excessive energy release within the reactor.

### 6 PROCESS DESCRIPTION

The following is a process description of the project awarded to Air Liquide. The plant consists of a gasification unit with a nameplate capacity of 48 MMSCFD of syngas and an ASU with 710 STPD oxygen capacity.

#### 6.1 ASU

The ASU is designed to supply 710 STPD of 99.9 percent oxygen at 625 psig to the gasifier. The ASU process cycle utilizes internal compression where liquid oxygen is pumped to the required product pressure and vaporized in the main heat exchanger before exiting the coldbox. This eliminates the need for an oxygen compressor. The oxygen is sent directly from the ASU coldbox to the gasifier.
6.2 Gasification Unit

The gasification unit is designed to produce 48 MMSCFD of syngas. The following is a description of the process as shown in figure 4.

Figure 4. Simplified Gasification Unit Flow Diagram

Natural gas feed is heated in the Process Heater and fed to a Hydrotreater / Desulfurizers for sulfur removal. The gas is then heated further in the Process Heater.

Import CO₂ is mixed with recycle CO₂ from the amine unit and compressed. Part of the compressed CO₂ is exported to Eastman and the remainder is heated in the Process Heater.

The gas feed stream is split, recycle CO₂ is added to each stream, and the combined streams are fed to each of the two gasification trains. Oxygen from the ASU is preheated by steam, split and fed to the two gasification trains. Partial oxidation and reforming reactions take place in the Gasifiers. The syngas product from the Gasifiers, at approximately 2500°F, is cooled in the Syngas Coolers by producing high pressure steam. Heating a portion of the BFW feeding the Syngas Coolers further cools the syngas. The cooled syngas is then scrubbed with water to remove any byproduct soot. Design for this system was specified by Texaco Development Corporation, as part of their license agreement with Air Liquide.

Vapor from the two trains is mixed and cooled. The cooled process gas is fed to the Amine unit. The amine unit consists of an absorption-stripping system with associated equipment. CO₂ is absorbed, by circulating amine, in the CO₂ Absorber. The amine is regenerated in the CO₂ Stripper with the CO₂ being recycled to the compressor. The solvent is an activated MDEA solution.

The syngas from the CO₂ Absorber overhead is water washed then fed to the Air Liquide MEDAL™ membrane unit. The feed gas is sent to a coalescing filter to remove liquids, and is preheated before entering the permeator. In the permeator, syngas is separated into
an H₂ rich permeate and syngas product for supply to Eastman. The operation of MEDAL™ is very simple. The driving force for separation is the difference in partial pressure between the H₂ in the feed gas and that of the permeate.

The thermal efficiency of the plant is optimized by recovery of heat from the Process Heater flue gas stream and from the effluent process gas stream. This energy is utilized to generate and superheat steam, and to preheat boiler feedwater.

7 PROJECT TIMELINE

With the support of Howe-Baker Engineers, Air Liquide worked hard to accommodate Eastman’s aggressive schedule for syngas supply. Howe-Baker’s engineering and fabrication facilities in Tyler, Texas contributed considerably by their close proximity to the job site. The following is an overview of the project timeline.


Air Liquide and Eastman signed a letter of intent in May 2000. At that time Air Liquide kicked off internal engineering, allowing Howe-Baker and Texaco to begin designing the new facility. The decision to kick-off engineering prior to finalizing contractual terms between Air Liquide and Eastman was a calculated risk required to meet Eastman’s schedule constraints.

Final contracts and agreements between Air Liquide and Eastman were signed in August 2000. By October 2000, Air Liquide and Howe-Baker mobilized the job site. To date, over 150,000 field manhours have been expended with no recordable or lost time injuries.


Howe-Baker has essentially completed engineering for the gasification unit. The gasification reactors and syngas coolers, as well as most of the other major equipment was received and set by August 2001.

Current plans are to complete ASU construction by the end of 2001 and complete construction of the gasification unit in the first quarter of 2002. The unit will be operational by early second quarter 2002.
8 CONCLUSION

In conclusion, this project is representative of the benefits realized when world-class companies such as Air Liquide, Howe-Baker and Eastman jointly develop project solutions. Air Liquide, together with Howe-Baker, will assist Eastman to achieve significant financial and environmental advantages by implementing gasification technology to supply syngas to their Oxo Aldehydes facilities. The successful development of this project was built on the experience of the Howe-Baker and Air Liquide Alliance.

This close working relationship facilitated important decision making efforts regarding site and technology selection by combining operation and design experiences. In addition, Air Liquide was able to bring added value by networking oxygen supply to the Eastman facility and utilizing proprietary MEDAL™ Membrane and ASU technologies.

Eastman, Air Liquide, and Howe-Baker are looking forward to successful start-up and operation of the new facility in 2002.