# Industrial Oxygen: Its Generation and Use

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**ABSTRACT**

This paper will look at the industrial uses for oxygen. It will categorize oxygen using processes into: 1) the purpose of oxygen in the process and 2) the effect oxygen enrichment has on the overall process. The paper will also look at four methods of producing oxygen: cryogenics, pressure swing absorption, membrane filter technology and electrolysis. It will compare each against one another in categories such as first time costs, running costs, percent oxygen enrichment attainable, and by-product capability. Furthermore, the paper will then select the appropriate process for each industry discussed. This paper is intended to address the above issues in such a way that a facility manager would be able to make an educated decision on whether or not to consider creating/using oxygen enhanced air in his/her process as well as which technology would be best suited for his/her process.

## Introduction

### Role of Oxygen in Combustion

Atmospheric air is comprised of 21% $O_2$, 78% $N_2$ and the remaining 1% is mostly argon and $CO_2$. Air is a chief constituent in combustion. In the combustion process, the oxygen in air is broken down to make carbon dioxide, water, and energy. Nitrogen is not an essential part of the process. In fact, nitrogen in air has negative impacts on combustion processes. Nitrogen gets heated by the reaction to very high combustion temperatures and is carried out through the flue. Essentially, the heated nitrogen leaving the flue is like throwing fuel out of the stack. Also, during the combustion process nitrogen in the air and fuel will break down to form harmful $NO_x$ gasses.

Combustion processes can be improved by lowering the amount of nitrogen used in the combustion air and increasing the amount of oxygen. The benefits include: higher combustion efficiencies due to a drop in heat loss (as a result of lower mass flow rates) out of the stack, lower $NO_x$ emissions, and higher process temperatures.

### Role of Oxygen in Gasification

Gasification is the process by which coal or another carbon based fuel is transformed into a synthesis gas (“syn gas”). This syn gas is made up of mostly CO and $H_2$. This gas can be used to produce electricity or steam. Gasification has many values, including the ability to use low BTU fuels for energy production, easier carbon dioxide capture as compared to traditional sequestration methods, and the ability to produce hydrogen gas.

Gasification is carried out in steps. First, the fuel is ground up into slurry. Next, the fuel is pyrolized in an oxygen starved environment. This turns the majority of the carbon into a gas. The next step is to add oxygen or air (“direct gasification”) or steam (“in-direct gasification”) at high temperatures to form carbon monoxide and hydrogen. This is the syn gas that can be used for a variety of energy producing systems. Before it is used, however, the gas may need to undergo more processing, such as removing particulates or cooling, depending on its end use.

Air can be separated into its constituents using a variety of techniques. This paper will address cryogenic, pressure swing adsorption, membrane technology and by-product methods of $O_2$ generation. Each air separation technology produces oxygen at different purities, pressures, and volumetric flow rates. Furthermore, each technology has different running costs. One air separation method is not any better across all industries than any other technique. Depending on the needs of process, one air separation technique will be more beneficial than others. This paper will look at the glass, gasification and gas-to-liquid industries, with a focus on gasification, their oxygen needs and the effect that oxygen enrichment will have on the process. Current research in metals oxidation will also be addressed.

## Description of Technologies

### Cryogenic Separation

Cryogenic air separation units (ASU) is an old process used to produce high purity oxygen or nitrogen at high volumes. The process was first developed by Carl Von Linde in 1895 and it remains pretty much the same today. Cryogenics is also the chief method by which liquid oxygen can be produced. The technology is centered on the fact that each of air's constituents has different boiling points. The idea behind the process is to lower the temperature of the air such that nitrogen and oxygen separate based on their boiling points. This occurs at around -300$^{o}$F.. If higher purity oxygen or liquid oxygen is required, further distillation is required. For liquid oxygen, nitrogen is used as the heat transfer fluid to further cool the oxygen.

Cryogenic separation is most effective when any of the three criteria need to be met: high purity oxygen is required (>99.5%), high volumes of oxygen are required ($\geq 10^2$ tons of oxygen/day), or high pressure oxygen is required. Cryogenic air separators take more than an hour to start up. Additionally, since cryogenics can produce such a high purity of oxygen, the waste nitrogen stream is of a usable quality [Smith 2001]. This can add significant financial benefits to a process integrated with a cryogenic ASU.

### Pressure Swing Adsorption

Pressure swing adsorbers (PSA) are a much newer technology as compared to cryogenic ASU. PSA devices take atmospheric air into a pressurized tank. Inside the tank are zeolites. Zeolites, under pressure, have the ability to deform and create a dipole. Depending on the zeolite chosen, this dipole allows for the collection of nitrogen, but allows oxygen to pass. For oxygen enrichment, the PSA is generally pressurized to a minimum of 1.5 atm. After a certain volume of air has been separated, the zeolite will become saturated with nitrogen. At this point, it needs to be regenerated. This is done by dropping the pressure of the tank back to atmospheric pressure, thus returning the zeolite to its original polarity. This liberates the nitrogen. Vacuum Pressure Swing Adsorbers (VPSA) lower the pressure in the tank to sub atmospheric values, thus improving the regeneration process. In both processes, while one tank is regenerating, another tank is usually charging. This allows for a continuous production of oxygen.

PSA devices are best suited for processes that do not require extremely high purities of oxygen (<95%). While PSAs can achieve as high as 99.9%, the cost associated with going above

99.5% in a PSA device rises tremendously. Furthermore, PSA devices are best suited for small volumes of oxygen production, typically on the order of $10^1$ tons/day. Since the output of oxygen is largely controlled by the bed size in the PSA systems, costs rise linearly when higher volumes of oxygen are required. PSA devices take a few minutes for start-up [Smith 2001].

A mid-sized pressure swing adsorbers running costs are shown below. The data is for an Oxair Model OXT-B14 adsorber.

| $O_2$ output | Compressor Power | Chiller Power | Power Cost | Foot Print |
|---|---|---|---|---|
| 400 $Nm^3$ or 13.6 tons/day | 400 HP or 276 KW | 150 HP or 80 KW | 0.75 KW/ $Nm^3$ | 190 $m^2$ |

Also, the usability of by-product nitrogen in PSA systems is limited because the nitrogen will have significant levels of oxygen. [Smith 2001].

**Membrane Technology**

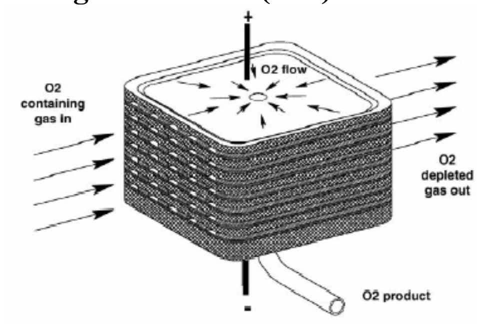
Conventional membrane technology involves passing air over a membrane filter. The filter will allow fast gasses to pass and slow gasses will stay. Oxygen is considered a fast gas and nitrogen and argon are considered slow gasses. Varying levels of purity can be achieved by varying the time that the gas spends undergoing filtration. Previous membrane technology could only produce purity levels of less than 50%. Membrane technology has quick start-up times and operates at near ambient conditions. Capital costs with membrane systems increase linearly with output volume desired. Currently, membrane technologies can satisfy needs of up to 20 tons of oxygen/day. [Smith 2001]

However, recently there has been a significant technological break through in membrane technology. The ion transport membrane (ITM) was developed by Air Products and Chemicals, in conjunction with the United States Department of Energy and Ceramatec. Reports have shown that this technology can produce greater than 99% purity $O_2$ at much lower costs than cryogenic separation. [Dyer 2000]

Three separate ITM technologies have been developed: SEOS™ Oxygen Generator, ITM Oxygen, and ITM Syngas.

The SEOS™ system consists of electrochemical cell stacks. These cell stacks are heated to greater than $600^0$C and a voltage is applied. Under this electric potential, the oxygen in the feed air is ionized, recombined, and collected at an outlet [Dyer 2000]. **Figure 1** illustrates the process.

**Figure 1: SEOS(TM) Process**

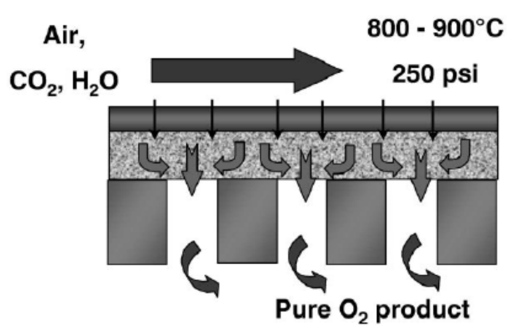



Source: Dyer 2000

ITM Oxygen can generate extremely high purity oxygen streams (in excess of 99.9%) and high volume (equivalent to volumetric flow of cryogenic separation systems). It takes in high pressure, high heat air. This air is passed over a ceramic membrane made of metals that are oxygen depleted. The membrane accepts the oxygen where it is ionized and diffused through the membrane due to a difference in oxygen partial pressures across the membrane. Since the membrane is not attracted to any other compounds, the process only filters oxygen [Allam 2002]. The oxygen stream is sub-atmospheric [Dyer 2000]. ITM Oxygen represents competition to cryogenic separation units.

**Figure 2** illustrates the process.

**Figure 2: ITM Oxygen Process**




Source: Dyer 2000

ITM Syngas is a process still under development. The technology will pass air on one side of a membrane and natural gas and steam on the other. The two by-product streams will be syngas and oxygen depleted air [Dyer 2000].

Research work is still continuing for ITM technology and is expected to be concluded by 2007. At this time, Air Products aims to be able to produce an economically viable ITM system.

## By-Product Oxygen

In some of the processes mentioned above, high volumes of nitrogen will be available to the user for use in another process. Similarly, in processes that produce nitrogen, large volumes of oxygen are readily available. One of the many applications of nitrogen is in the food industry, where oxygen increases fruit respiration, thus leading to a shortened life during which the fruit is edible. Storing fruit in nitrogen enriched environments reduces respiration rates. [Smith 2006]

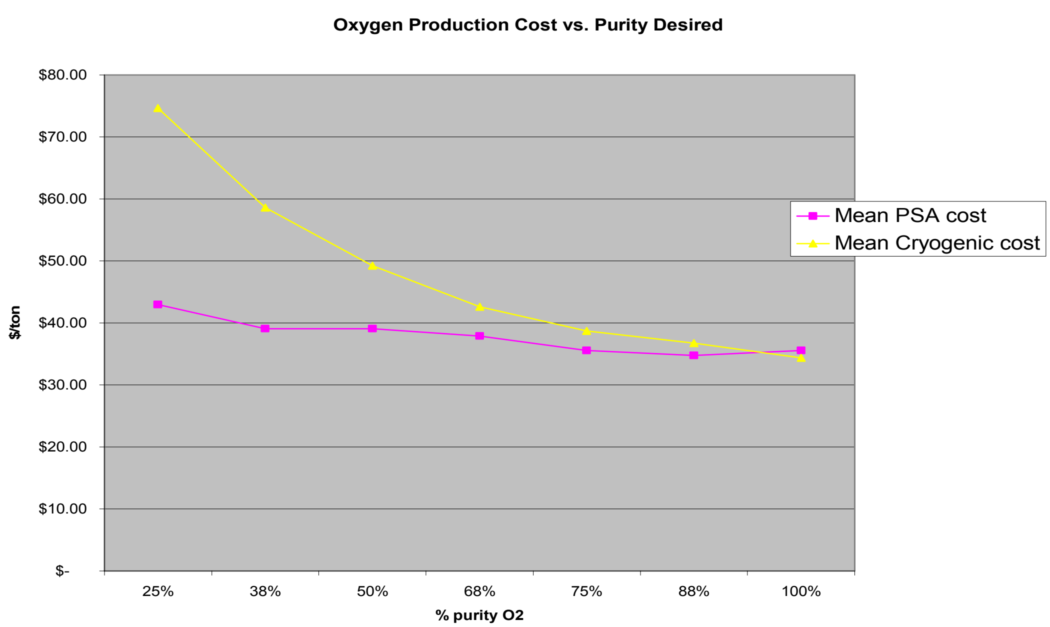
Similarly, hydrogen production results in waste oxygen. All over the world, countries have set measures to increase the amount of energy derived from hydrogen, meaning that the hydrogen economy is certain to grow. Consequently, if a use can be found for the left over oxygen, an overall increase in the hydrogen production process efficiency would lead to potentially large energy savings.

Currently, hydrogen is produced via electrolysis. Electrolysis is the process by which water is broken into hydrogen and oxygen. It is an expensive process. Alkaline electrolysis costs $500/kW and PEM electrolysis costs $1000/kW [Kato 2005]. These costs make process efficiency all the more important. If electrolysis efficiency is 71%, then 5000 kWh of electricity production would result in the generation of 500 Nm$^3$ of oxygen. Producing this much oxygen via PSA or cryogenics would require 250 kWh of electricity. However, this oxygen is being produced at essentially no additional costs. Therefore, if the oxygen can be used, then the electrolysis efficiency will rise to 76%. One potential application of the by-product oxygen in electrolysis would be in hospitals, where fuel cells would power the facility and the oxygen could be used for patient care [Kato 2005].

## Comparison between Cryogenic Air Separation and PSA

**Figure 3,** re-created from literature published by Air-Products and the US Department of Energy, illustrates the mean cost of the cost per ton of oxygen at a desired purity level. Although the data is older, the trends in the cost are the same. As one can see, PSA is a better option in terms of running costs for purity levels slightly less than 100%. However, at high purity levels, i.e. greater than 99%, cryogenics will prove to be less expensive.

**Figure 3: Oxygen Production Cost vs. Purity Desired**



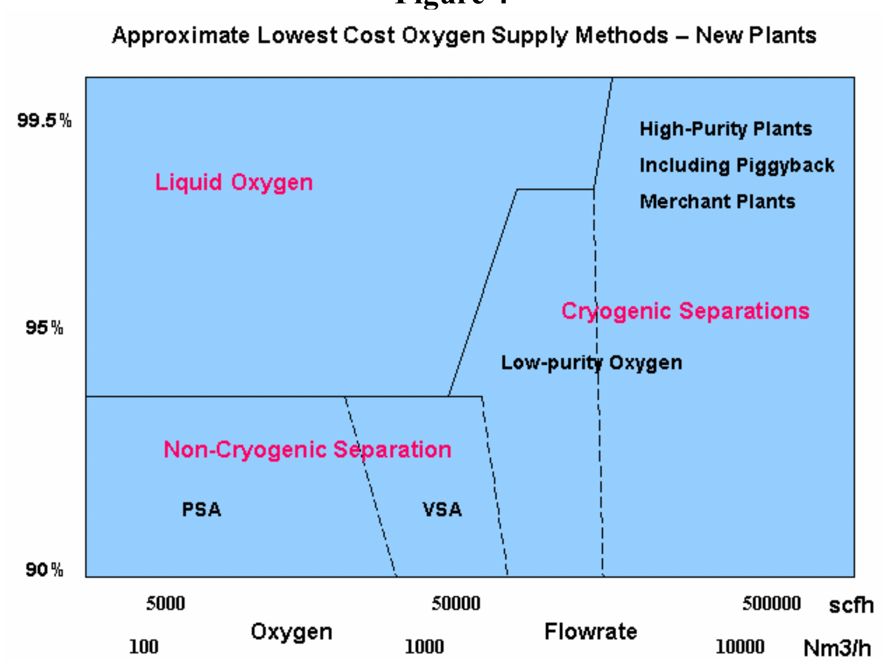

Source: Tuson 1994

Running cost and purity are not always the only selection criteria. Volume desired is also key parameters in determining the air separation unit best for a particular industry. **Figure 4**, created by Universal Industrial Gases, INC., shows which technology is best suited when all three criteria (volume, purity, cost) are weighed against each other. It should be noted that advancements in zeolites will surely lower the price of PSA systems in the future [Smith 2001]. There are little expected advancements in cryogenic air separation, and therefore costs can be expected to remain the same.

As **Figure 4** shows, PSA/VPSA is suitable for low volumes and low purity oxygen requirements. Cryogenic separation is best suited for high flow rates and when high purity oxygen is required. Finally, if high purity oxygen at low rates is desired, the plant may want to consider delivery of liquid oxygen.

"Piggyback Merchant Plants" refers to the ability for a plant to produce enough high purity oxygen for itself and for local merchants that would also need the high purity oxygen. This is financially feasible when the plant needs low volumes of high purity oxygen, but merchants in the surrounding community also need high purity oxygen and are willing to buy it from the plant.

**Figure 4**




Source: From Universal Industrial Gases Inc

## Comparison between Cryogenic Air Separation and Membrane Technology

In one example, Air Products linked an ITM Oxygen supply into an IGCC plant and a cryogenic air separation unit into another. Details of the project will be discussed later. The installation cost of the cryogenic air separation unit was \$61.2 million as compared to \$41.6 million for the ITM technology. Moreover, the ITM plant produced oxygen at a cost of \$14,300/ton of oxygen/day compared to \$22,200/ton of oxygen/day for the cryogenic plant

[Allam 2002]. Additionally, advancements in membrane materials will surely lower the costs of all membrane technologies (non-ITM included) [Smith 2001].

## Select Industries of Use

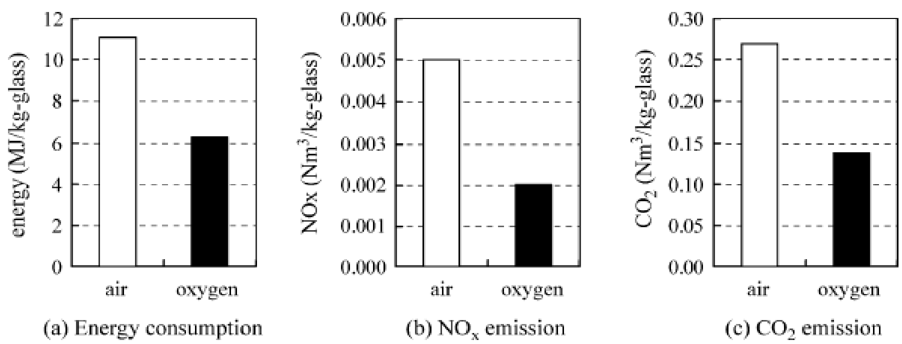
Many industries use oxygen for a variety of reasons. In this section, oxygen use in the glass, gasification and gas-to-liquid industries will be addressed. The primary focus will be on oxygen use in the municipal solid waste and coal gasification applications as well as the gas to liquid industry. Current research in metals oxidation will also be addressed.

### Oxygen Use in the Glass Industry

Oxygen's use in the glass industry has been well-documented. Oxygen enriched air fed into the furnace has proven to reduce fuel consumption, lower NOx emissions, and improve glass quality. The effects of oxygen combustion on fuel input, NOx, and CO2 emissions are shown in **Figure 5** for a glass melting furnace [Kato 2005]:

As is evident, all the parameters shown above were reduced drastically with the implementation of oxycombustion.

**Figure 5: Energy Consumption, NOx Emissions and CO2 Emissions from a Glass Melting Furnace**




Source: Kato 2005

Although the benefits are well established, there is still room for improvement as is evident by the amount of research being conducting on oxycombustion glass furnace design.

### Oxygen Use in Coal Gasification

One of the most efficient applications of syn gas is in Integrated Gasification Combined Cycle (IGCC) plants. Here, the syn gas is used to run an electric turbine which produces electricity. The waste heat from the turbine and gasification plant is used to make steam, which in turn is run through a steam turbine, thus producing more electricity.

Traditionally, cryogenic air separators were used to create the oxygen for direct-gasification. Cryogenics enabled operators to produce the volume and purity of air desired.

As mentioned previously, Air Products and Chemicals ran two IGCC plants. Both were identical with the only difference being in the method of oxygen generation: one used ITM

Oxygen technology, while the other used cryogenic air separation. The compressed air for the both of the air separation units was provided by the compressor for the gas turbine. This makes the cost of oxygen production, and consequently, the cost of the entire IGCC plant less.

**Figure 6** gives a comparison of the two systems performance. Highlights of the performance are that the ITM system was 2.3% more efficient and produced 7 MW more electricity than the cryogenic system. Furthermore, the ITM plant required 37% less electricity to make $O_2$ than the cryogenic ASU.

The electricity in the ITM Oxygen plant is used to compress the oxygen stream. In the cryogenic ASU electricity is needed to compress both nitrogen and oxygen. The nitrogen is used for cooling in the cryogenic ASU. Additionally, the cryogenic ASU produced 95% purity oxygen. Higher purities are possible; however it would come at a significantly higher cost. The ITM technology was able to produce 99.5% purity oxygen. Increasing the purity would come at a minimal cost due to the manner in which the oxygen is produced. [Allam 2002]

**Figure 6: Comparison between ITM Oxygen and Cryogenic Air Separation in IGCC**

| Case Designation | ITM Oxygen | Cryo ASU | % Change |
|---|---|---|---|
| Fuel HHV (MMBtu/hr) | 3704 | 3539 | +4.7 |
| HP $O_2$ to Gasifier (mTPD) | 2860 | 2732 | +4.7 |
| LP $O_2$ to Claus SRU (mTPD) | 39 | 22 | |
| Nominal $O_2$ Plant Size (mTPD) | 2900 | 2760 | +5.3 |
| $O_2$ Plant Power (kWh/tonne $O_2$) | 162 | 259 | **-37** |
| **W501G MWe** | **272** | **272** | --- |
| Steam Turbine MWe | 189 | 172 | |
| Syngas Expander MWe | 14 | 13 | |
| IGCC Gross MWe | 475 | 457 | +3.9 |
| IGCC Power Consumption MWe | 37 | 48 | |
| **IGCC Net MWe** | **438** | **409** | **+7.0** |
| Net IGCC Efficiency (HHV) | 40.4 | 39.5 | +2.3 |
| Net IGCC Efficiency (LHV) | 41.8 | 40.9 | |
| Sulfur (mTPD) | 70 | 67 | |
| Solid Waste (mTPD) | 430 | 411 | |

Note: mTPD = metric tonnes per day

Source:Allam 2002

**Figure 7** shows the installed costs of the two systems. There is no significant change in overall cost. While the cost of oxygen plant is much less in the ITM Oxygen case, the other costs are higher. However, when one considers that the ITM Oxygen plant produced 29 MW more than the cryogenic plant, the turnkey cost ($/kW produced) proves to be lower for the ITM Oxygen plant.

**Figure 7: Installed Costs of IGCC Plant**

| Area Description | ITM Oxygen | Cryo ASU | % Change |
|---|---|---|---|
| Oxygen Plant | 41,600 | 61,200 | -32 |
| Gasification Unit | 97,000 | 95,200 | +1.9 |
| Gas Cleanup Unit | 41,600 | 34,300 | +21 |
| Combined Cycle | 233,600 | 224,400 | +4.1 |
| Balance of Plant | 33,200 | 32,900 | +0.9 |
| Overall Total IGCC | 447,000 | 448,000 | --- |
| $/kW | 1,020 | 1,094 | **-6.8** |
| Oxygen Plant $/mTPD $O_2$ | 14,300 | 22,200 | **-35** |

Note: All costs represented in thousands of U.S. dollars (including project contingency)

Source: Allam 2002

**Oxygen Use in Municipal Solid Waste Gasification and Gas-to-Liquid Systems**

Municipal Solid Waste (MSW) is everyday trash created by people. Originally land filled, MSW is now most commonly incinerated in the United States in lieu of diminishing land fill space. Incineration reduces the volume of trash, however, it does produce greenhouse gases and toxic emissions that require costly clean-up technologies. The systems today are also producing energy. For example, the Essex County Resource Recovery facility manages 1 million tons of trash per year and produces 45,000 MW in the process. However, as mentioned above, incineration of trash can lead to very pollutants that become airborne in the incineration process.

Gasification, as described above, is emerging as a potential method of dealing with MSW in a much cleaner manner than incineration. Gasification was proven to reduce emissions of MSW, thus reducing operating costs. Furthermore, valuable syn gas can be produced. This syn gas can also be converted to $H_2$ gas or liquid methanol [Larson 1996]. Thus, MSW could be used as a fuel for Gas-to-Liquid systems. Liquid energy would expand the potential mediums in which MSW gas can be used. These new mediums include vehicular power.

Currently, the Thermoselect system of Switzerland offers an established and proven technology for converting MSW to syn gas. Additionally, these systems gasify using oxygen provided by a cryogenic plant. Other systems exist, however, they: a) require the MSW to be turned into a refuse-derived-fuel (RDF) and b) they use steam in the gasification process. RDF fuels require all combustibles from MSW to be removed before gasification. [Larson 1996]

The use of steam also demands that the syn gas be reformed because hydrocarbons (methane and methanol) are formed in the gasification process. These hydrocarbons are reformed into $H_2$ and CO. When using oxygen, the hydrogen in steam is absent. Therefore, no hydrocarbons are formed. The result is that no additional reforming is needed in oxygen blown gasifiers. This lowers the energy input to the system.[Larson 1996]

**Figure 8** compares the energy balance for methanol and hydrogen reforming between the two RDF technologies (BCL and MTCI) and the Thermoselect process. As the figure shows, the energy ratio for the Thermoselect process is much higher than for the RDF processes. Here, the energy ratio is defined as the HHV of the fuel produced divided by the HHV of the input MSW. The Thermoselect process has a higher energy ration because no energy is lost due to syn gas reforming. As mentioned, this is a direct result of using oxygen rather than steam. From this data, the conclusion can be made that MSW gasifying with oxygen is more efficient the MSW gasifying with steam.[Larson 1996].

**Figure 8:Comparison of MSW Gasifiers**

Overall energy balances for methanol and hydrogen production from MSW

| | Gasifier | | | | | |
|---|---|---|---|---|---|---|
| | BCL Hydrogen | MTCI | TS | BCL Methanol | MTCI | TS |
| *MSW feed capacity to plant* | | | | | | |
| As received (t/day) | 1263 | 1351 | 1310 | 1263 | 1351 | 1310 |
| Dry (t/day) | 1050 | 1050 | 1050 | 1050 | 1050 | 1050 |
| GJ/h | 686 | 663 | 656 | 686 | 663 | 656 |
| *RDF feed capacity to gasifier* | | | | | | |
| As fed (t/day) | 1050 | 1124 | n.a. | 1050 | 1124 | n.a. |
| Dry (t/day) | 871 | 871 | n.a. | 871 | 871 | n.a. |
| GJ/h | 658 | 636 | n.a. | 658 | 636 | n.a. |
| *Hydrogen output capacity* | | | | | | |
| GJ/h | 400 | 427 | 493 | n.a. | n.a. | n.a. |
| Million $m^3$/day | 0.81 | 0.86 | 1.00 | n.a. | n.a. | n.a. |
| *Methanol output capacity* | | | | | | |
| GJ/h | n.a. | n.a. | n.a. | 335 | 370 | 423 |
| Thousand l per day | n.a. | n.a. | n.a. | 445 | 491 | 561 |
| *Electricity balance (MW)* | | | | | | |
| Required by process | 13.0 | 16.2 | 26.2 | 16.3 | 19.8 | 27.3 |
| Produced from waste heat[a] | 14.8 | 8.4 | 7.0 | 17.5 | 11.0 | 9.8 |
| Purchased[b] | −1.8 | 7.8 | 19.2 | −1.2 | 8.8 | 17.5 |
| *Overall energy performance* | | | | | | |
| Energy ratio[c] | 0.58 | 0.65 | 0.75 | 0.49 | 0.56 | 0.64 |
| Thermal efficiency[d] | 0.60 | 0.58 | 0.59 | 0.50 | 0.49 | 0.51 |

Source: [Larson 1996]

## Oxygen Uses in Gas-to-Liquid Applications

Some gas-to-liquid applications have already been mentioned, such as in the case of MSW gasification. In Gas-to-Liquid applications, the cryogenic air separation unit would be a more efficient means at this time to produce oxygen due to the fact that it produces an excellent quality of by-product nitrogen. As current oil and coal reserves diminish, GTL technology could provide an excellent means of using the fossil fuels stored in remote locations of the world, such as many places in Alaska. Furthermore, it could be used to turn natural gas that is usually flared in oil fields into usable liquid gas.

**Figure 9** shows one method by which a cryogenic air separation unit could be employed in a Fischer-Tropsch system:

The oxygen is used in the same manner as in any other gasification process. The advantage now, however, is that the waste nitrogen could be used for a variety of applications. These applications include: injection into the gas turbine to increase turbine output, refrigeration for the turbine inlet air, and low process nitrogen could be used for chilling applications.

## Oxygen Use in Metals Oxidation

Current research at universities and industry are focusing on using oxy-enhanced air to lower the temperature of air used in oxidizing metals. In one specific application, cuprous oxide is made by passing $800^0$C air over copper. One study at Rutgers University hypothesizes that the temperature of this air can be reduced by oxidizing in an oxy-enriched environment using a fluidized bed. By adding more air, the number of oxygen molecules in contact with the copper increases. The high temperature serves as a catalyst to the copper to cuprous oxide reaction.

Also, surface area is a key parameter in the creation of cuprous oxide. If the temperature can be reduced by using oxygen enriched air and the surface area increased by using a fluidized bed such that the energy used to compress the air is offset, then the overall process will represent an energy efficient alternative to the current practice. Current research employs small PSA devices.

**Figure 9: Integration of Cryogenic ASU in GTL Process**

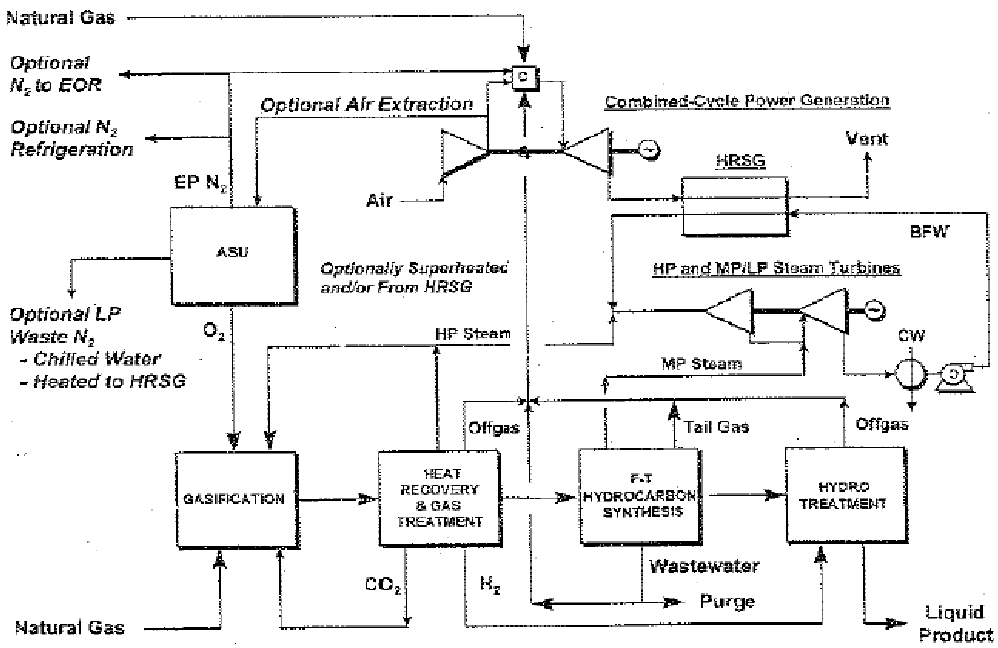



Fig. 13. Integrated GTL coproduction facility producing F–T liquids + power.

Source: Smith 2001

## Conclusion

At this time, cryogenic ASU are the most well-established and used systems for oxygen generation. However, advances in PSA and membrane technology have and will continue to challenge cryogenic ASU.

The uses for oxygen are many (not all discussed in this paper) and include: glass furnaces, coal gasification, MSW gasification, gas-to-liquid technologies and metals oxidation.

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