



Carbon Monoxide

PERP 09/10S11

Report Abstract December 2010

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CHEMSYSTEMS PERP PROGRAM

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INTRODUCTION

Carbon monoxide is a colorless, odorless, flammable, toxic gas. There are no significant natural sources of carbon monoxide (CO). Carbon monoxide is generated by the incomplete combustion of hydrocarbons, the reduction of carbon dioxide (CO₂), and the decomposition of organic compounds.

Carbon monoxide was discovered in 1776 when a mixture of charcoal and zinc oxide was heated. However, its chemical composition was not recognized until twenty years later. It is used in a variety of ways, including as a feedstock/raw material for chemicals production, a reducing agent for metallurgical processes, and a fuel. The focus of this report is the production and purification of carbon monoxide for use as a feedstock for chemicals production.

The major source of industrially produced carbon monoxide is from synthesis gas (syngas). It is also produced in various industrial processes such as blast furnace and coke oven operations, and can be recovered from the offgas of these processes.

A wide variety of feedstocks can be used for syngas production from methane and natural gas to heavy residual fuel oil, gas oils, and coal. The reaction of natural gas (methane) with steam under high temperatures and pressures forms primarily carbon monoxide and hydrogen (H₂), and lesser quantities of carbon dioxide and water. Catalytic developments over the past few decades have permitted the use of increasingly heavier hydrocarbon feedstocks, up to naphtha, in reforming. Partial oxidation of hydrocarbon feedstocks under deficient oxygen conditions yields a syngas richer in carbon monoxide than steam methane reforming. Partial oxidation can process all hydrocarbon feedstocks from natural gas to heavy liquids to coal. In general, the heavier the feedstock, the lower the hydrogen to carbon monoxide ratio is in the final syngas.

COMMERCIAL (SYNGAS BASED) TECHNOLOGY

The syngas product is a complex mixture of carbon monoxide, hydrogen, carbon dioxide, and water. The relative amount of each component depends on many factors, including feedstock, operating conditions, and processing steps.

Depending on the end use, the final hydrogen to carbon monoxide ratio can be adjusted using the water/gas shift reaction. If required, the mixture can be purified by a variety of methods to produce different product purities (for both carbon monoxide and hydrogen). Hydrogen is always a byproduct in the manufacture of carbon monoxide via syngas. It can be minimized, but not eliminated.

The processes for syngas production are classified by the reaction route for production of carbon monoxide and hydrogen from the selected feedstock. The focus of the analysis in this report will be the production of syngas via the processes listed below:



Steam reforming of either methane (SMR) or naphtha

The original process of steam methane reforming (SMR) was discovered by BASF in 1926 and commercialized in the 1930s. In the presence of a nickel based catalyst, usually on an alumina substrate, steam reacts with methane at elevated temperatures and pressures to give a reformed gas consisting of carbon monoxide, hydrogen, and lesser quantities of carbon dioxide, methane, and water. The final concentrations depend on the ratio of steam to hydrocarbon passing over the catalyst and the temperature and pressure at which the reactants leave the catalyst. Although many reactions occur simultaneously, syngas composition is determined by the simultaneous satisfaction of the reforming and water/gas shift reactions. These reactions are shown below:

Natural Gas Reforming:

 $CH_4 + H_2O \longrightarrow CO + 3 H_2$ Naphtha Reforming: $C_nH_{2n+2} + nH_2O \longrightarrow nCO + (2n + 1)H_2$ Water/Gas Shift: $CO + H_2O \longrightarrow H_2 + CO_2$

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Partial oxidation (POX) of hydrocarbons, petroleum coke or coal

Partial oxidation (POX) involves the oxidation of a hydrocarbon feedstock in a flame with less than stoichiometric quantities of oxygen to form carbon dioxide and steam. This reaction, once completed, provides the heat and some of the steam used for the steam reforming of the unreacted hydrocarbon to produce carbon monoxide and hydrogen. Most of the carbon dioxide is also reformed to carbon monoxide and hydrogen. Commercial processes are operated at elevated pressures using oxygen as the oxidant. POX processes are capable of employing a wide variety of feedstocks such as natural gas, coal, petroleum coke, refinery offgas, LPG, naphtha, gas oil, vacuum residual fuel oil, shale oil, asphalt residual fuel oil, and whole crude oil. The resulting hydrogen to carbon monoxide ratio depends on the carbon to hydrogen ratio of feedstock.

Reactions in partial oxidation are extremely complex. Simplistically, thermal cracking at high temperatures in the reactor produce low molecular-weight hydrocarbon fragments. The fragments then react with pure oxygen. The net reaction is summarized below for methane and naphtha.

Partial oxidation of natural gas

 $CH_4 + \frac{1}{2}O_2$ ____ $CO + 2H_2$

Partial oxidation of naphtha

 $C_nH_{2n+2} + \frac{1}{2}nO_2$ \longrightarrow nCO + (n+1)H₂

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• Autothermal reforming (ATR)

Autothermal reforming (ATR), also known as catalytic partial oxidation, can closely control the final syngas composition by combining steam reforming with partial oxidation. The use of the process also results in higher operating pressures and improved thermal efficiencies.

Coal or biomass gasification

Coal is gasified at elevated temperatures with steam and air or oxygen.

$$C + H_2O$$
 \longrightarrow $CO + H_2$
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Several other reactions also occur, including carbon combustion, carbon monoxide disproportionation, and the water/gas shift reaction that can be used to limit the CO output if desired.

An alternative green route for the production of carbon monoxide is through the gasification of biomass. This approach complements approaches based on coal gasification as found in China and to a certain extent natural gas reforming. Gasification provides synthesis gas. (As an example of one commercial use, this synthesis gas after suitable treatment can then be converted to methanol. The synthesis gas also provides the carbon monoxide which is subsequently required to carbonylate the methanol into acetic acid.)

In syngas plant design, some of the factors that influence process selection and design are hydrogen to carbon monoxide ratio, product purity, plant capacity, feedstock availability and cost (including oxygen and carbon dioxide), and byproduct credit (excess hydrogen and export steam).

The determination of which syngas process is best for a particular application requires more than just a qualitative analysis. Different users of syngas (pure carbon monoxide and hydrogen production, acetic acid, methanol, oxo alcohols) have different process requirements. It is necessary to consider the key factors and to evaluate the generation method and downstream gas treatment in detail.

PURIFICATION (CARBON MONOXIDE PRODUCTION)

The initial step in carbon monoxide purification is removal of minor impurities, regardless of downstream processing. Particulates are removed in cyclones or by scrubbing and acid gases are removed by absorption. After initial purification, the gas stream is sent to a carbon monoxide recovery section for final purification, where byproducts are also recovered.

The cost of separation of carbon monoxide or hydrogen contributes significantly to the total production cost of high purity carbon monoxide. Purification techniques fall into four main categories (discussed in the report):



- Cryogenic purification
- Pressure swing adsorption (PSA)
- Membrane separation
- Salt solution absorption

DEVELOPING TECHNOLOGIES

The focus of this report is the syngas-based commercial technologies to yield carbon monoxide. However, other technologies and feedstocks are briefly mentioned to give an overview of the complete picture.

The following technologies have been briefly reviewed.

- Breakdown Carbon dioxide into carbon monoxide using visible light
- Increasing Yield from Gasification
- Renewable Hydrogen and Carbon Monoxide from Nonvolatile Fuels

A patent review has been carried out highlighting work carried out on Carbon Monoxide Production and Recovery by:

- BOC (now part of Linde Group) and
- Air Liquide

ECONOMICS

In this section, tables giving cost of production estimates are given. The tables include a breakdown of the cost of production in terms of raw materials, utilities direct and allocated costs, by unit consumption and per metric ton and annually, as well as contribution of depreciation to arrive at a full cost estimate (a simple nominal return on capital is also included).

Cost estimates for **Syngas Production** via the following processes are evaluated:

- Steam Methane Reforming (SMR),
- Partial Oxidation (POX),
- Autothermal Reforming (ATR) of methane
- Gasification of Biomass (wood chips)

Cost estimates for **Carbon Monoxide Production** via the following processes are evaluated:

- Cryogenic Separation of 3:1 Syngas (from SMR)
- Cryogenic Separation of 1.7:1 Syngas (from POX)
- Cryogenic Separation of 2:1 Syngas (from ATR)
- Cryogenic Separation of 1.7:1 Syngas (from biomass)

Sensitivity to natural gas price, byproduct hydrogen price, oxygen price, wood price, economy of scale and capital investment have been carried out.

COMMERCIAL MARKET ANALYSIS

A brief review of some industrially significant reactions that involve pure carbon monoxide is presented in Appendix B. (The chemical applications of syngas such as hydroformylation are not discussed.)

Implied Carbon Monoxide Capacity:

In an attempt to characterize the current regional capacity for pure carbon monoxide in the organic chemical industry, the capacity of the major and some lesser volume chemicals and polymers requiring pure carbon monoxide in their manufacture were identified:

- Acetic acid
- Phosgene
- TDI
- MDI
- Polycarbonate
- Formic acid
- Dimethyl carbonate
- Polyketones
- Pivalic acid
- Propionic acid
- Trimellitic anhydride
- Pyromellitic anhydride)

Based on carbon monoxide consumption factors for each of the chemicals listed above, the required or implied carbon monoxide quantity needed to satisfy this capacity was calculated for the United States, Western Europe, and Asia.

Carbon Monoxide Demand Forecast

The carbon monoxide demand forecast out to 2020 for acetic acid, TDI, MDI and polycarbonate have been estimated.





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