

CO through CO₂ Reforming

The Calcor Standard and Calcor Economy Processes

By ST. C. TEUNER, P. NEUMANN and F. VON LINDE*

ABSTRACT

Carbon monoxide is required as feed for the production of many chemicals. Due to its toxicity transportation of pressurized CO is limited. This fact and economical aspects result in on-site production of carbon monoxide. An economic process to generate high purity CO through CO₂ reforming (Calcor process) is described below. The costs for on-site production are presented considering the different CO generating processes and available CO purification technologies.

1 INTRODUCTION

Carbon monoxide is an important feed for the production of many products or intermediates such as organic acids, phosgene, polycarbonates and agricultural chemicals. In most cases the manufacturing cost of these chemicals is directly determined by the production cost of carbon monoxide.

The common source for CO is syngas from reforming or from the partial oxidation of hydrocarbons. Unlike hydrogen, the transportation of CO is a sensitive safety subject due to its toxicity. This fact and economic aspects favour the on-site production of carbon monoxide.

2 AVAILABLE PROCESSES

An overview of available processes for CO generation is given in [1]. The significant processes for the production of CO are the non-catalytic partial oxidation of hydrocarbons with oxygen for quantities of typically above 5000 Nm³/h CO, or the catalytic reforming of hydrocarbons, applicable also for small carbon monoxide requirements.

With the common reforming process, carbon monoxide is produced by steam reforming of a hydrocarbon (e. g. natural gas) mixed with recycled CO₂ at high tempera-

tures and high pressures in the presence of catalysts, followed by a pressure swing adsorption (PSA) unit and/or a low temperature purification (cold box) for the purification of carbon monoxide, depending on the quality required.

Steam reforming with CO₂ recycle yields a syngas with a typical H₂:CO ratio of 2.8:1, whereby hydrogen as the dominant component represents a by-product.

The typical H₂/CO ratio for the main CO generating processes, when using natural gas as feedstock, is shown in Table 1.

In the Calcor process, steam is totally substituted by CO₂, resulting in a H₂:CO ratio of 0.42:1. The reduction of by-products and the high concentration of CO reduce the specific requirement of utilities and offer substantial advantages in the selection of purification technologies.

High purity carbon monoxide is required, if the CO is used for the production of phosgene as an intermediate for the polycarbonate production. CH₄ and H₂ will form CCl₄ and HCl as impurities of

phosgene, which would result in an impaired quality of the polycarbonate or in an additional phosgene purification step. Typically an impurity of CH₄ lower than 20 vpm is acceptable for phosgene production. Therefore a process design with small CH₄ impurities in the CO will be advantageous. Only the Calcor process meets this requirement without an additional CH₄ removal. As a result, the Calcor process for most applications needs only a membrane for the CO purification instead of a cold box which is much more cost-intensive.

2.1 The Calcor Standard process

The Calcor Standard process (Fig. 1) is designed to operate under low pressure. The process itself is a catalytic reforming process at high temperatures. To protect the catalyst, the feed has to be desulphurized. After pre-heating and mixing with hydro-

Table 1 Typical H₂/CO ratio and CH₄ content for the main CO generating processes

	Steam reforming with CO ₂ recycle	Partial oxidation	CALCOR process
H ₂ / CO ratio	2.8 : 1	1.8 : 1	0.42 : 1
CH ₄ content	3 Vol.-%	0.4 Vol.-%	0.0005 Vol.-%

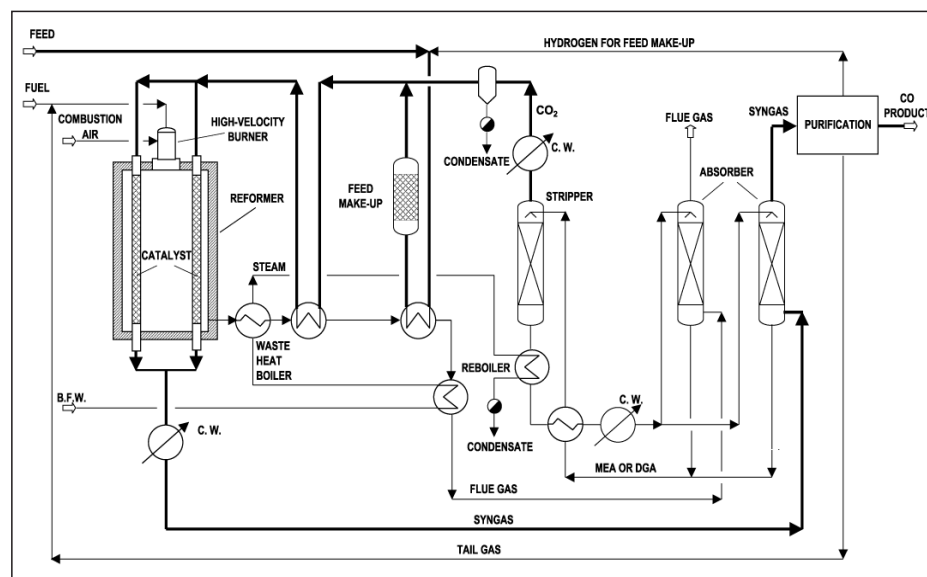


Fig. 1 Simplified flow sheet for Calcor Standard process

*Dipl.-Ing. Stefan C. Teuner, Dr.-Ing. Peter Neumann, Dr. Florian von Linde, Caloric Anlagenbau GmbH, Graefelfing near Munich, Germany (E-Mail: peter.neumann@caloric.de)

gen, the feed is sent to a sulphur removal in which the sulphur compounds are hydrogenated and adsorbed in a ZnO-layer. The desulphurized feed is then mixed with CO₂ and pre-heated again by utilizing appropriate amount of the flue gas heat, prior to entering the reformer. Whilst passing the reformer tubes, which are filled with catalysts of different activities and shapes, the mixture of CO₂ and feed is converted into a syngas consisting of carbon monoxide together with H₂, CO₂, H₂O and traces of CH₄. The heat for this endothermic reaction is provided by a high-velocity burner, which burns fuel and tail gas from the CO purification unit. After leaving the reformer, the syngas is cooled to ambient temperature prior to un-

dergoing the CO₂ removal and recovery. In this process step, the CO₂ from the reformer flue gas as well as the CO₂ from the syngas are absorbed in packed towers at ambient temperature by a caustic solution (e. g. MEA, MDEA or DGA). In a stripper, the CO₂ is separated from the scrubbing liquid and recycled to the reforming process. The syngas, which now typically consists of 70% by vol. CO

Table 2 Typical CO purity using different process combinations

Product composition, Vol.-%	CO	H ₂	CO ₂	CH ₄	N ₂ ¹⁾
Calcor Standard with low temperature purification	99.98	1 vpm	0	1 vpm	0,015
Calcor Standard with membrane purification	99.47	0.5	0.01	15 vpm	0.01
Calcor Economy with membrane purification	99.25	<10 vpm	0.1	0.003	< 0.01

¹⁾ based on nitrogen free feed. 1% N₂ in natural gas feed results in approx. 0.4% N₂ in the CO product.

and 30% by vol. H₂ and still carries traces of CO₂ and CH₄, enters the CO purification step. Depending upon the CO purity required, a low-temperature process or semi-permeable membrane process may be applied (Table 2).

2.2 The Calcor Economy process

In the Economy version of the Calcor process, the CO₂ recovery part is deleted and imported CO₂ is used instead of recovered CO₂ (Fig. 2). The selective properties of membranes make it possible to simultaneously separate H₂ and CO₂ from the CO product, which results in a simplified design of the Calcor process. The tail gas which is separated in the first stage of the membrane is utilized as fuel for the burner at the reformer and also for feed make up. The permeate of the second stage of the membrane is recycled to the suction side of the compressor due to its high CO content.

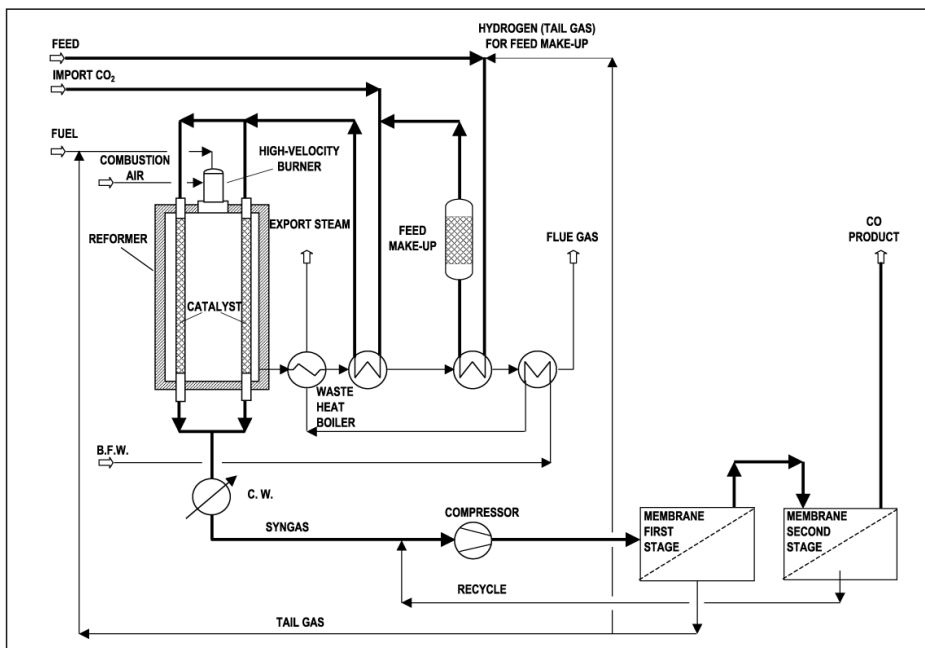


Fig. 2 Simplified flow sheet for Calcor Economy process

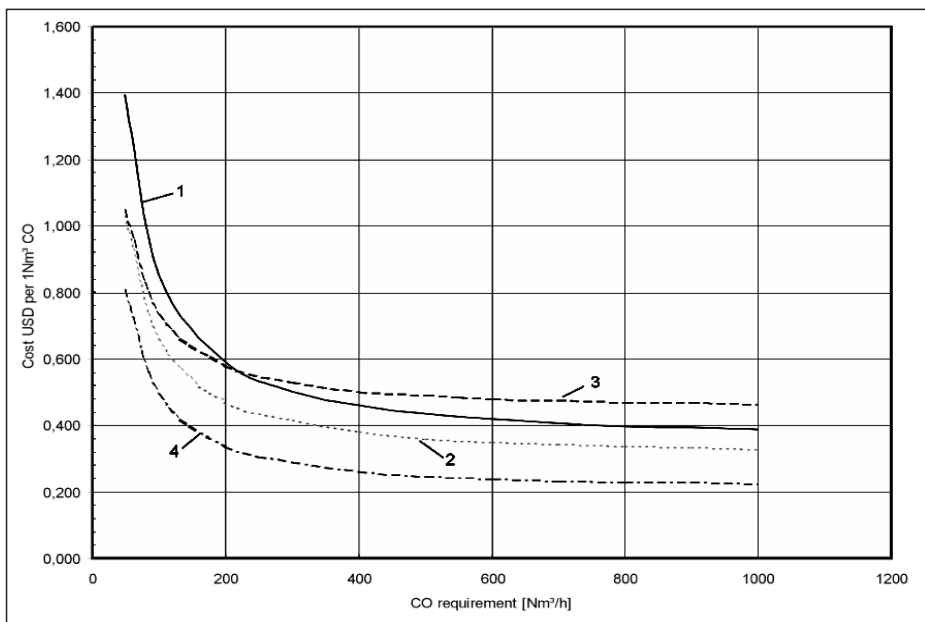


Fig. 3 CO production costs
 1 – Calcor Standard with low temperature purification step
 2 – Calcor Standard with membrane purification step
 3 – Calcor Economy with import CO₂
 4 – Calcor Economy with cost free import CO₂.

3 CALCOR PROCESS ECONOMY
 With the recovery of the CO₂ from the reformer flue gas as well as from the syngas, the Calcor Standard process generates almost 1 CO molecule out of every C-atom imported into the process as feed and fuel. Thus, a carbon yield of 97–99% almost reaches the theoretical maximum. The production of one ton CO requires either 816 Nm³ natural gas (calculated as 100% CH₄), or 531 kg LPG as the main utility.

With decreasing plant capacity, the costs for utilities and energy become less and less significant, whereas the costs of depreciation and interest on the investment dominate.

For plants with a capacity of approximately 200 Nm³/h CO and downwards, the saving in investment more than compensates for the additional costs of imported CO₂ required by the Calcor Economy process (Fig. 3).

3.1 Production costs

The production costs for the on-site production of CO are shown in Fig. 3. They include the costs for depreciation and interest on the capital investment, utilities, manpower and maintenance.

For utilities used in the process, the following costs were assumed for calculation purposes:

- natural gas: US\$ 0.11/Nm³
- LPG: US\$ 164/t
- electric energy: US\$ 0.064/kWh
- carbon dioxide: US\$ 120/t
- cooling water: US\$ 0.066/m³
- boiler feed water: US\$ 1/m³
- import steam: US\$ 11/t.

Apart from the costs for utilities and energy, the following factors were taken into account in the calculation of the prime costs:

- operating hours: 8,600 p.a.
- annuity: depreciation of the investment costs over 10 years
- interest rate: 6%
- maintenance: 2.5% of the investment costs p. a.
- personnel: US\$ 24,000 per man year.

3.2 CO purity

The available CO purity depends on the process selected and the purification technology applied. Table 2 shows typical CO qualities for three process combinations. Nowadays CO qualities between 99.25% and 99.98% can be achieved. Due to the innovative potential of membranes, it is expected that the CO purity achievable by membranes will increase in the near future.

3.3 H₂ by-product

The tail gas from the purification step represents a H₂-rich stream. By using a compressor and a pressure swing adsorption unit (PSA), 37 Nm³ pure H₂ can be made available with each 100 Nm³ CO product.

3.4 CO₂ Emissions

Generating CO from CO₂ and hydrocarbons follows an endothermic reaction. At catalytic reforming, the required energy is provided by burners. Consequently the plants emit flue gas to the atmosphere. As an approximation, the specific CO₂ emissions related to 1 ton CO product are:

- 15 kg CO₂ for Calcor Standard,
- 1240 kg CO₂ for Calcor Economy
(import CO₂ not considered),
- minus 360 kg CO₂ for Calcor Economy
(emitted CO₂ minus imported CO₂),
- 1785 kg CO₂ for steam reformer
with CO₂ recycle.

LITERATURE

- [1] H. H. Gunardson, J. M. Abrardo: Produce CO-rich synthesis gas. Hydrocarbon processing, April 1999, pp 87-93.

