

Dissertation

Export Gases and their Utilization Potential

Technical and Economical Evaluation of selected Processes for
Chemical Syngas Generation

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AFFIDAVIT

I declare in lieu of oath, that I wrote this thesis and performed the associated research myself, using only literature cited in this volume.

Ich erkläre an Eides statt, dass ich diese Arbeit selbständig verfasst, andere als die angegebenen Quellen und Hilfsmittel nicht benutzt und mich auch sonst keiner unerlaubten Hilfsmittel bedient habe.

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ABSTRACT

Over the last four decades alternative smelting reduction processes for iron making have been introduced to economically compete with the classical blast furnace route. Besides process optimization to lower material and energy consumption and to cause less environmental impact, a focus has been set on an economic and environmental friendly utilization of by-products. The excess gases are typically used as fuel for heat and power plants within the iron and steel work. But due to their comparatively low calorific value, the material recycling becomes a matter of interest. For example the export gas from the alternative smelting reduction process COREX[®] has been recycled as reducing gas for direct reduction of iron ores and as feedstock for microbiological ethanol production.

Due to the high share of CO and H₂ and the low content of N₂, as a result of the gasification of coal with oxygen, COREX[®] and FINEX[®] export gases are presumed to be a valuable feedstock for the synthesis of basic chemicals, but technical feasibility has not been proven yet.

This thesis will provide thermo-chemical process designs for export gas utilization into specific syngases for the production of main intermediate chemicals (CO, oxo chemicals, acetic acid, methanol, Fischer-Tropsch liquids, ammonia and H₂) including CO₂ balance and production cost estimate for environmental and economic evaluations of the process technologies.

The literature review provides an overview of conventional synthesis and syngas production technologies for the synthesis of the main intermediate chemicals, including the market potential and the production cost estimates for the standard feedstock natural gas. Based on common gas process technologies, thermo-chemical process designs (CHEMCAD) have been set up for the conversion of COREX[®] and FINEX[®] export gases into the specific syngases. For the calculations of the production costs, a model has been developed related to the cost calculation scheme for natural gas based syngas production. The CO₂ balance – as a factor for environmental impact – includes process related CO₂ emissions as well as CO₂ emissions related to the import of electric energy, steam and heat.

Economic analyses showed that export gas treatment is a feasible option to produce CO product and oxogas (H₂:CO-ratio ≤1) including the downstream synthesis of acetic acid and oxo-chemicals respectively. The economic advantage is related to the high content of CO in the export gases even considering compression and export gas treatment costs. H₂-rich syngas production (H₂:CO-ratio ≥2) from export gas is less economic compared to syngas generated by steam reforming of natural gas.

The CO₂ balance showed high process related emissions for carbon monoxide shift, resulting in higher overall CO₂ emissions for export gas based oxo- and syngas production (H₂:CO-ratio ≥1) compared to the feedstock natural gas. As no shift reaction is required for CO production, the bulk of CO₂ emissions result from the import of electric energy for gas compression and cryogenic separation of N₂ and CO, leading to net CO₂ emission savings for export gas utilization compared to natural gas based syngas production.

With the substitution of the smelting reduction carrier gas N₂ by recycling of CO₂ from the Rectisol absorber or with polygeneration concepts combining two or more chemical syngas production processes, a reduction of the utility demand and the capital expenditures can be expected, reducing overall production costs for export gas based syngas production.

KURZFASSUNG

In den letzten vier Jahrzehnten wurden alternative Schmelzreduktionsverfahren entwickelt, die gegenüber der klassischen Hochofenroute wirtschaftliche Vorteile erzielen sollten. Neben der Prozessoptimierung zur Reduktion von Roh- und Hilfsstoffen und des Energiebedarfes wird bei diesen Verfahren zusätzlich auch auf die ökonomische und umweltfreundliche Nutzung der Nebenprodukte geachtet. Anfallende Überschussgase werden derzeit hauptsächlich als thermischer und elektrischer Energieträger im Hüttenverbund eingesetzt, jedoch wird aufgrund des relativ geringen Heizwertes die stoffliche Verwertung zunehmend interessanter. COREX[®] Exportgas wird beispielsweise als Direktreduktionsgas weiter genutzt und dient als Rohstoff für die mikrobiologische Ethanol Produktion.

Aufgrund der hohen Anteile an CO und H₂, und dem vergleichsweise niedrigen Gehalt an N₂ – bedingt durch die Vergasung von Kohle mit reinem Sauerstoff – stellen COREX[®] und FINEX[®] Exportgase auch einen wertvollen Rohstoff zur Synthese von chemischen Grundstoffen dar. Die technische Realisierbarkeit wurde jedoch noch nicht umfassend untersucht.

Im Rahmen dieser Dissertation wurden thermochemische Prozessmodelle zur Aufbereitung von Exportgasen zu speziellen Synthesegasen für die Erzeugung von Grundchemikalien (CO, Oxo-Chemikalien, Essigsäure, Methanol, Fischer-Tropsch-Treibstoffe, Ammoniak und H₂) entwickelt. Im Vergleich von Produktionskosten und CO₂ Bilanzen wurden die entwickelten Prozesse ökonomisch und ökologisch bewertet.

Die Literaturrecherche gibt einen Überblick über konventionelle Syntheseverfahren und über die Technologien zur Erzeugung der dazu benötigten Synthesegase. Dargestellt werden das Marktpotential und eine auf Erdgas basierende Produktionskostenschätzung der Grundchemikalien und deren Synthesegase. Auf Basis herkömmlicher Synthesegas-Prozesstechnologien wurden die Prozesse zur Synthesegasaufbereitung aus COREX[®] und FINEX[®] Exportgasen thermochemisch simuliert (CHEMCAD). Das Berechnungsmodell zur Abschätzung der Produktionskosten lehnt sich an das Kalkulationsschema der auf Erdgas basierenden Synthesegasproduktion an. Die CO₂-Bilanz der einzelnen Prozesse berücksichtigt neben prozessbedingten Emissionen auch CO₂-Emissionen aufgrund von thermischer und elektrischer Energie- und Dampfbereitstellung.

Der wirtschaftliche Vergleich zwischen Exportgas und Erdgas als Synthesegasrohstoff zeigt, dass die Exportgasaufbereitung zu CO und Oxogas (H₂:CO ≤1) und die nachfolgende Synthese von Essigsäure beziehungsweise Oxo-Chemikalien aufgrund des hohen CO Anteils günstiger ist als die auf Erdgas basierende Synthesegasproduktion. Die Aufbereitung zu H₂-reichen Synthesegasen (H₂:CO ≥2) ist aufgrund des niedrigen H₂:CO-Verhältnisses im Exportgas jedoch weniger wirtschaftlich.

Exportgas-CO₂-Bilanzen weisen hohe prozesstechnische Emissionen bedingt durch die CO-Shift auf, und resultieren in deutlich höheren Gesamtemissionen bei Oxo- und Synthesegas Erzeugung (H₂:CO ≥1) im Vergleich zur Verarbeitung von reformiertem Erdgas. Da zur Erzeugung von reinem CO keine CO-Shift erforderlich ist, sind die CO₂-Emissionen bei der Exportgasaufbereitung hauptsächlich energetisch bedingt (Kompression und kryogener Trennprozess) und geringer als bei der Synthesegaserzeugung aus reformiertem Erdgas. Dies führt zu einer Netto-Emissionseinsparung.

Durch die Substitution von Schmelzreduktionsträgern mit CO₂ aus der Rectisolwäsche, oder durch die Kombination der Herstellung von zwei oder mehreren Synthesegasen, kann eine Reduktion von Energie- und Hilfsmaterialien erwartet werden, die in Summe zur Senkung der Produktionskosten und zur Verringerung der CO₂-Emissionen führen würde.

ABBREVIATIONS

ASU	air separation unit
ATR	autothermal reforming
CFB	circulating fluidized bed
COG	coke oven gas
CR	combined reforming
DR	direct reduction
DRI	direct reduced iron
HC	hydrocarbons
HTFT	high temperature Fischer-Tropsch
HTS	high temperature shift
ISBL	inside battery limits
LHV	low heating value
LTFT	low temperature Fischer-Tropsch
LTS	low temperature shift
NG	natural gas
NWU	nitrogen wash unit
OSBL	outside battery limits
POX	partial oxidation
PSA	pressure-swing adsorption
RGS	raw temperature shift
ROCE	return on capital employed
SAS	Sasol advanced synthol
SBD	slurry bed reactor
SMR	steam methane reforming
SN	Stoichiometric number
STP	standard temperature and pressure (0°C, 0.1MPa)
TSA	temperature swing adsorption
VPSA	vacuum pressure-swing adsorption
WGS	water gas shift
syngas	synthesis gas
syngas-ratio	H ₂ :CO-ratio in synthesis gas
S/C-ratio	steam to carbon-ratio
equ.	equation
col.	column
i.a.	inter alia
e.g.	exempli gratia
et al.	et alli

INFORMATION

It has to be mentioned that brand names have not always been pointed out with trademarks.

Es wird daher darauf hingewiesen, dass Markennamen nicht immer mit Warenzeichen versehen wurden.

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1 Introduction

With the ratification of the Kyoto protocol in 1997 the United Nations decided to reduce greenhouse gas emissions of industrialized countries in the period from 2008 to 2012 with a reduction of at least 5% relatively to the emission level of 1990 (1). Six years later, October 13th, 2003, the Council of Europe adopted the Guideline 2003/87/EG, which determined the trading of emission permits of EU member states, limiting CO₂ emissions from energy intensive industry-sectors (2).

Therefore especially iron and steel making industry has been forced to find reduction potentials to reduce CO₂ emissions due to economic reason. In iron and steel making besides CO₂ emissions related to provide required heat and power, one major source of CO₂ results from the carbothermic reduction of iron ores requiring large amounts of reduction gas.

Despite the optimization of the smelting reduction process in a coke charged blast furnace since the 18th century (3) and the development of alternative, more efficient smelting reduction processes like COREX[®], FINEX[®], Hismelt[®] or RHF in the 20th century (4), the bulk of reduction gas, mainly carbon monoxide (CO) and hydrogen (H₂), still remains unconverted. Conventionally, these unreacted gas compounds are further processed into heat and power, where CO is converted into the greenhouse gas CO₂.

An alternative way to utilize these excess gas compounds is the material recycling, an utilization option with potential to further reduce greenhouse gas emissions and to increase economic efficiency within the iron and steel work. Unconverted reduction gas compounds e.g. from COREX[®] smelting reduction process have already been recycled as reducing gas for the direct reduction of iron ores in a MIDREX[®] plant since 1999 by Saldanha Steel, South Africa (5). Besides the metallurgical reuse, the chemical bonding of the unreacted gas compounds H₂ and CO in chemical products by chemical synthesis process might be an option.

Though Siemens VAI states that COREX[®] export gas can serve as feedstock in chemical industry (6), and chemical recycling of COREX[®] and FINEX[®] export gases has been introduced by Kepplinger (7), the utilization process in chemical synthesis industry has not further been specified and has not been on research focus.

To evaluate this chemical recycling, this thesis will provide technical process designs for smelting reduction excess gas utilization into main intermediate chemicals in synthesis industry, including CO₂ balance and production cost estimate for environmental and economic evaluations of the process technology.



1.1 Background

The iron making smelting reduction process, conventional and alternative utilization of unreacted excess gas compounds and the chemical utilization potential of iron making excess gas as synthesis gas in chemical industry are outlined.

1.1.1 Iron Making Smelting Reduction Process

To produce metallic iron from iron ores numerous technical processes have been developed, but only few have proven their technical and economic feasibility. Since the end of the 18th century, the smelting reduction process in the blast furnace is still regarded as the most significant way to produce metallic iron. Intensive development and optimization of this technology has led to better utilization of coke, and therefore the smelting reduction of iron ores still remains standard technology for iron making (3).

Within the last four decades, approximately 40 alternative smelting reduction processes have been developed to optimize this process technology and to compete with the classical blast furnace route, but most of them did not reach the maturity of a commercial design. Referring to Kepplinger, only the COREX[®] and the FINEX[®] process came into commercial use (4).

The COREX[®] process, shown in Figure 1-1, utilizes coal instead of expensive coke to produce the reduction gas, which causes less environmental impact compared to the blast furnace route, as a coking plant is not required. The coal is gasified with oxygen in the COREX[®] melter-gasifier, while the reduction takes place in the separate reduction shaft.

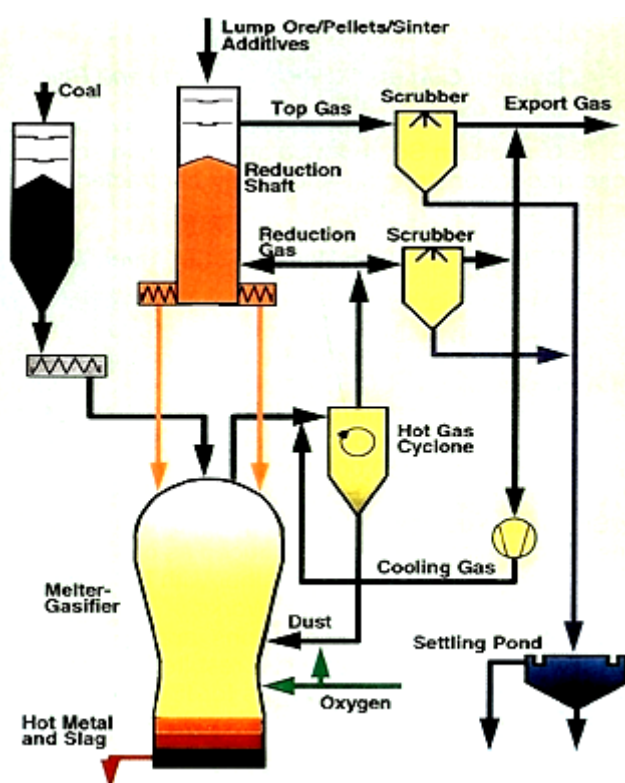


Figure 1-1 Basic flow sheet of the COREX[®] process (7)



Seven COREX[®] plants are in operation 2012: two plants in Shanghai at Baosteel Pudong Iron and Steel Co. Ltd.; one plant in South Africa at Mittal Saldanha; four plants in India, two at JSW Jindal Vijayanagar Steel Ltd. and two plants at ESSAR (8)¹.

The FINEX[®] process, shown in Figure 1-2, is a smelting reduction process, also operating with a COREX[®] melter-gasifier for the production of reduction gas from coal. But differently to COREX[®], the FINEX[®] process is operating with untreated fine ore, which is charged into a series of fluidized-bed reactors counter-current to the reduction gas flow. Two commercial plants are in operation, the 1st since 2003 and the 2nd since 2007, both at Posco works in Pohang/Korea. A 3rd plant is currently under construction with planned start up in 2013 at Posco works (9)¹.

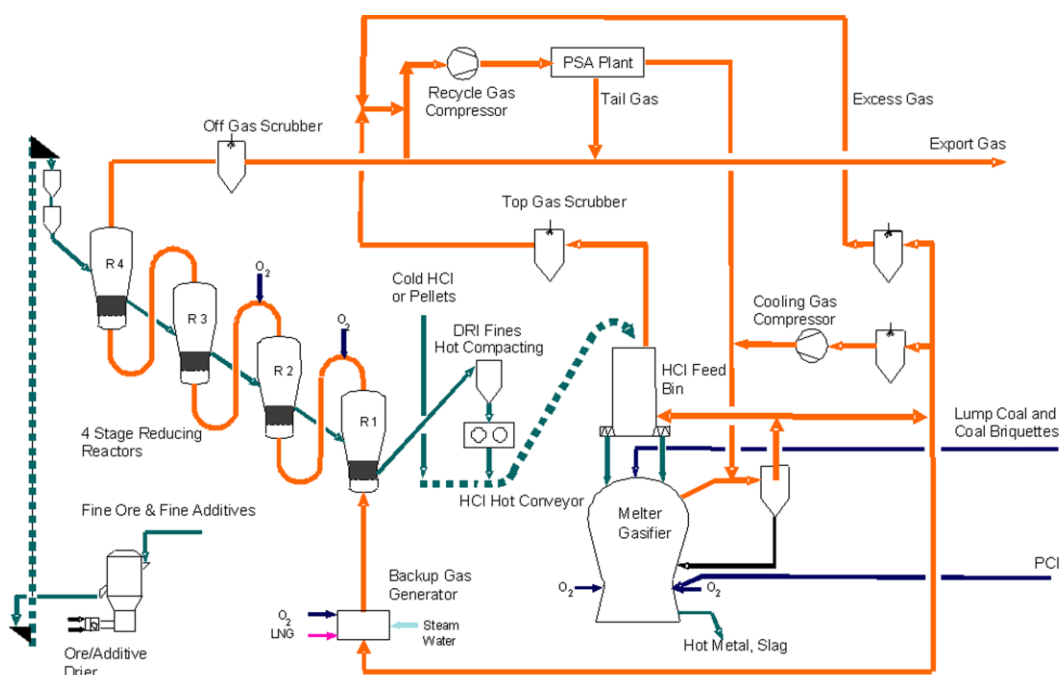


Figure 1-2 Basic flow sheet of the FINEX[®] process (4)

In general, the smelting reduction processes include three major process steps:

- The generation of reduction gas by gasification of:
 - coke in the blast furnace or
 - coal in the COREX[®] melter-gasifier (COREX[®] and FINEX[®] process).
- The carbothermic reductions of iron oxides, divided in
 - direct reductions of wustite in the COREX[®] melter-gasifier and the metallurgical zone of the blast furnace.
 - indirect reductions in the reduction shaft (blast furnace, COREX[®] process) and in a series of fluidized bed reactors (FINEX[®] process).
- The melting of metallic iron and slag in the blast furnace or in the melter-gasifier of the COREX[®] and FINEX[®] process.

¹ These are main articles which comprise a number of publications dealing with the same matters.

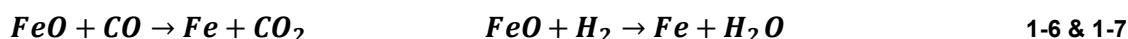
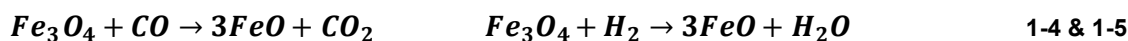
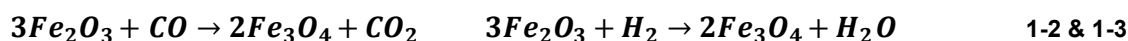


The carbothermic reduction reactions of iron oxides can be structured into:

- The direct reduction with elementary carbon



- and the indirect reduction with gaseous carbon monoxide and hydrogen.



Due to the thermodynamic equilibrium of the system “reduction gas/iron oxides”, a complete utilization of the reduction gas is not possible. This is visualized in the Baur-Glaessner diagram in Figure 1-3, showing the thermodynamic equilibrium of oxides in a CO/CO₂ atmosphere over system temperature. As shown in the diagram, a minimum content of around 70% CO is necessary to reduce wustite into metallic iron at a reaction temperature of 900°C.

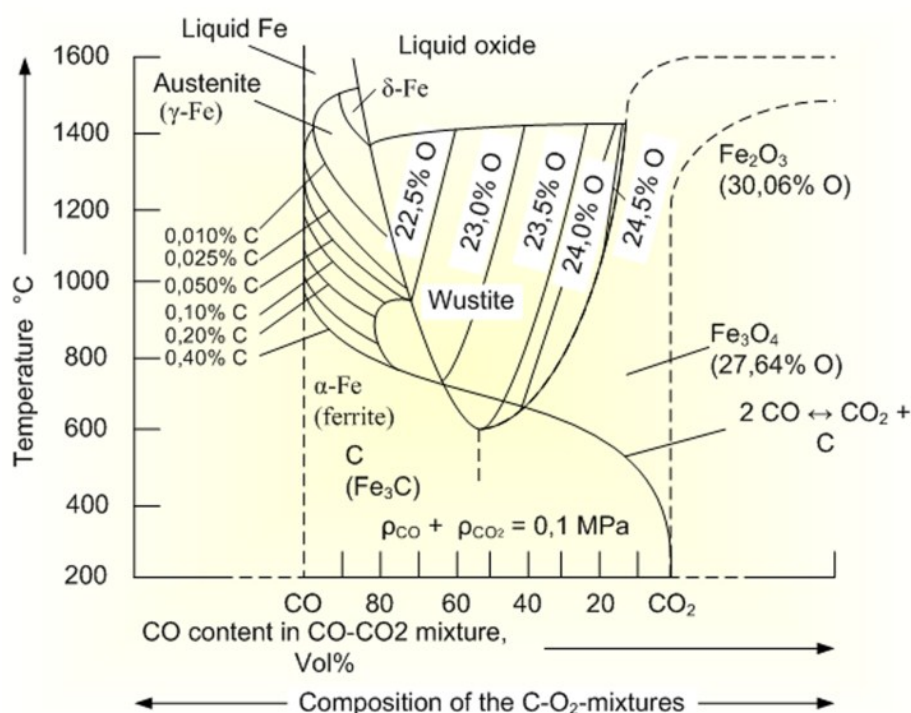


Figure 1-3 Linear Baur-Glaessner-diagram with integrated Boudouard equilibrium curve and logarithmic Baur-Glaessner-diagram, the dotted lines are the Boudouard equilibria under different pressures (4)

Even considering counter-current gas flow in the reduction zone of the process, which leads to higher gas utilization, the bulk of the reduction gas still remains unconverted, resulting in high CO content of 20% in nitrogen-rich blast furnace top gas, and up to 50% in COREX[®] or FINEX[®] export gas, as shown in Table 1-1.



Table 1-1 Typical excess gas compositions (main compounds) from iron making smelting reduction and coke oven process (10)

Gas compound	COREX [®] Export Gas	FINEX [®] Export Gas	Blast Furnace Top Gas	Coke Oven Gas (COG)
H ₂ [vol. %]	15 - 25	12 - 25	1 - 5	39 - 65
CO [vol. %]	40 - 50	30 - 50	20 - 28	4 - 7
CO ₂ [vol. %]	25 - 35	25 - 45	17 - 25	1 - 3
CH ₄ [vol. %]	2	1.5	-	20 - 42
C _x H _y [vol. %]	-	-	-	2-8
H ₂ O [vol. %]	saturated	saturated	not specified	dry
N ₂ /Ar [vol. %]	2	10	50 - 55	not specified
H ₂ S	< 100 ppm _v	< 100 ppm _v	not specified	0.35g/m ³ (STP)*
H ₂ :CO-Ratio	~0.4	~0.5	~0.1	> 5*
Calorific Value [MJ/m ³ (STP)]	7.0 - 8.5	5.0 - 8.5	2.7 - 4.0	17.4 - 20.0
p _{abs} [MPa]	0.1	0.1	up to 0.3	-
T [°C]	40	40	100-200	800

* after raw gas treatment

1.1.2 Conventional Utilization of unreacted Reduction Gas Compounds

Due to their calorific value, excess gases from iron making have been valuable by-products since the 19th century. Blast furnace top gas has commonly been used for heat regeneration within blast stoves and as fuel within the iron and steel plant. Export gases from COREX[®] and FINEX[®] process, higher in calorific value, are typically used as fuel in conventional and combined cycle power plants (10). Figure 1-4 shows the block scheme and the energy flow of conventional export gas utilization.

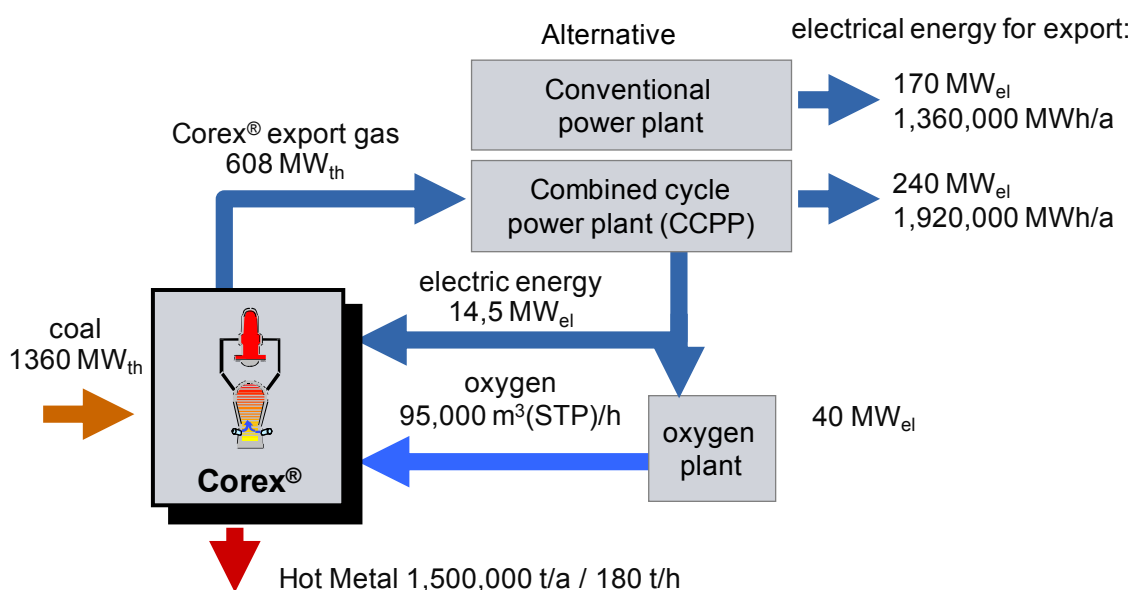


Figure 1-4 Block scheme of common COREX[®] export gas utilization [(7), modified by Boehm]



1.1.3 Alternative Utilization of unreacted Reduction Gas Compounds

Besides the conventional utilization, COREX[®] export gas, rich in carbon monoxide, has been recycled as reducing gas for the direct reduction (DR) of iron ores in a MIDREX[®] plant. This led to reduced CO₂ emissions of below 1,400 kg per ton hot metal and DRI (direct reduced iron) respectively compared to the conventional blast furnace route, which produces around 1,600 kg CO₂ per ton hot metal. As shown in Figure 1-5, the COREX[®]/DR combination includes credits for export gas recycling as DR fuel and credits for granulated slag (7).

In 2011 JSW Projects LTd. Mumbai ordered the 2nd MIDREX[®] direct reduction plant for the utilization of COREX[®] export gas as reduction gas with a planned start up in 2013. After CO₂ separation the export gas is recycled into the MIDREX[®] reduction process (11).

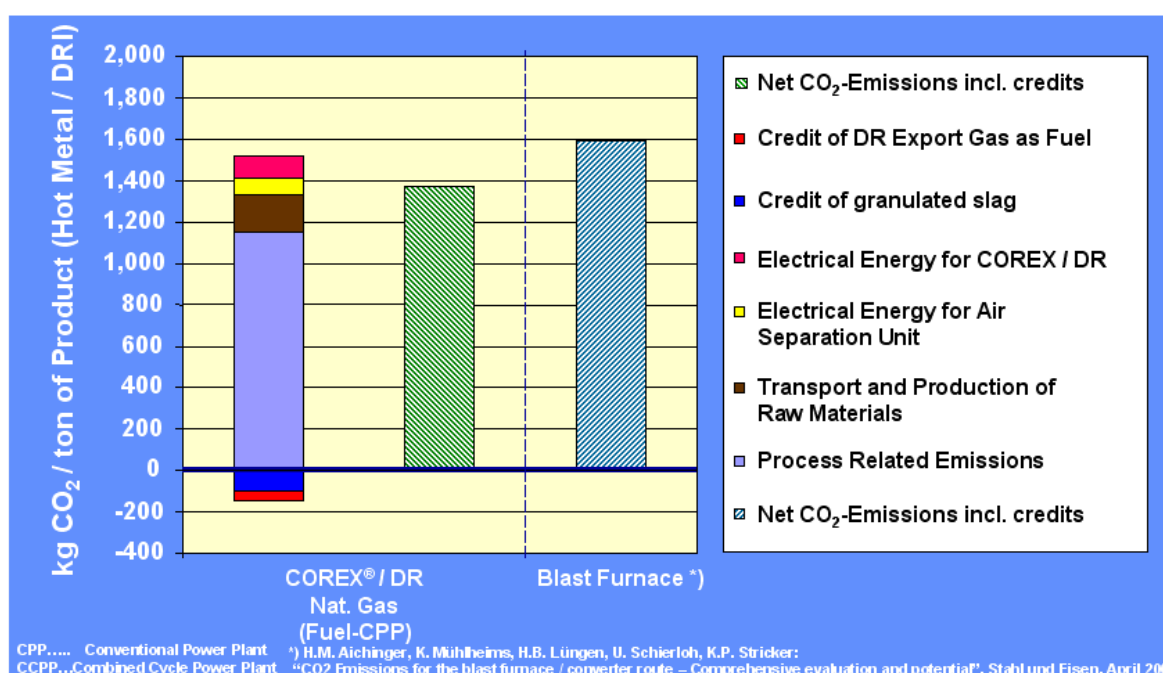


Figure 1-5 Net CO₂-emissions of COREX[®] process and direct reduction versus blast furnace route (credits for DR export gas / blast furnace gas) (7)

Microbiological ethanol production is expected to be an alternative utilization option for COREX[®] and FINEX[®] export gases. 2011 Lanza Tech and Baosteel started the construction of a demonstration plant for the production of annually 100,000 gallon ethanol from COREX[®] export gas in Shanghai (12). In the 1st term 2012, 80% of plant capacity have been achieved converting 75-80% of CO and 30-50% of H₂ (pers. com.).

1.1.4 Chemical Utilization Potential of Iron Making Excess Gases

Material recycling by chemical bonding of unreacted carbon-compounds into chemical synthesis products might be an interesting and economic option to reduce CO₂ emissions in iron making industry. A comparison of chemical and thermal utilization of COREX[®] export gas showed that the CO₂ emissions are lower for methanol syngas production. The reduction

potential is between 93 to 390 kg CO₂/10³ m³(STP) COREX[®] export gas, depending on the electric energy mix of the plant location (10).

The conducted literature review concerning chemical utilization of smelting reduction excess gases showed that:

- COREX[®] and FINEX[®] export gases can be used in a wide range of applications but there are no reports concerning plants in operation for the utilization as syngas in chemical industry (13).
- COREX[®] and FINEX[®] export gas can serve as a feedstock in chemical industry, but the utilization process in chemical industry has not yet been specified in detail (14).

Chemical Synthesis, Syngas Production and Market Situation

Today mainly natural gas, but also solid, liquid and other gaseous hydrocarbons are converted thermo-chemically (e.g. reforming) into synthesis gas (syngas), a mixture of H₂ and CO. Further gas treatment processes are applied to adjust the H₂:CO-ratio, to separate CO₂ and to purify the syngas to achieve the desired syngas quality for the downstream synthesis of intermediate chemicals and chemical products.

Rising syngas markets in the Middle East, North and West Africa, Southeast Asia and Australia will lead to a growing demand on syngas for all end-use sectors (Figure 1-6).

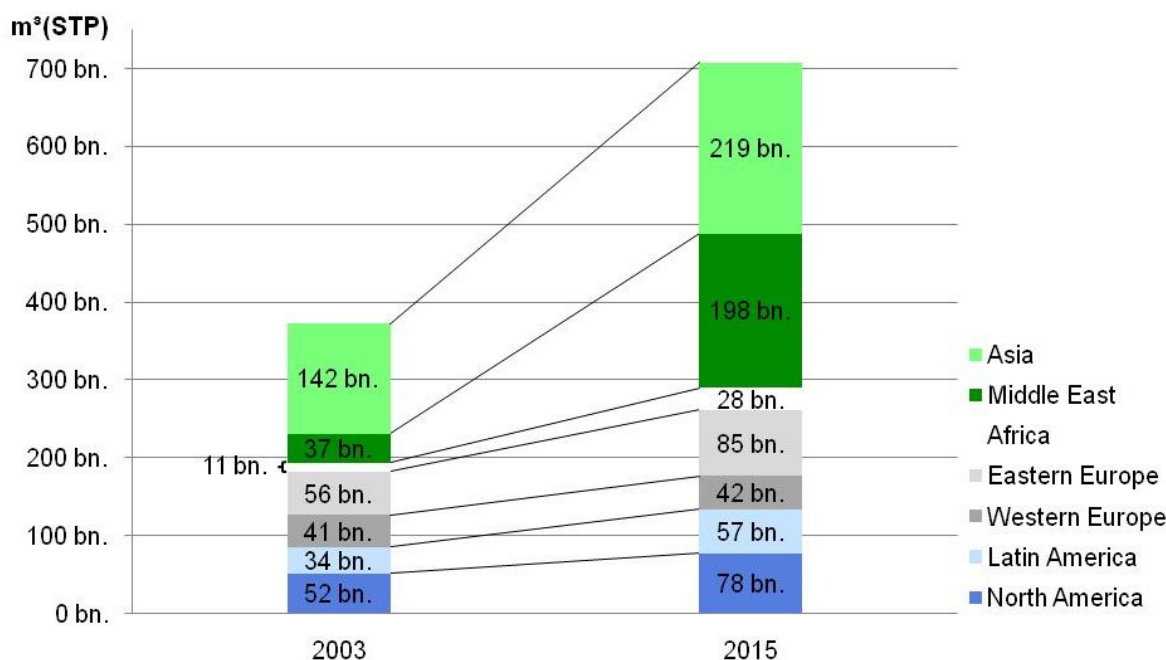
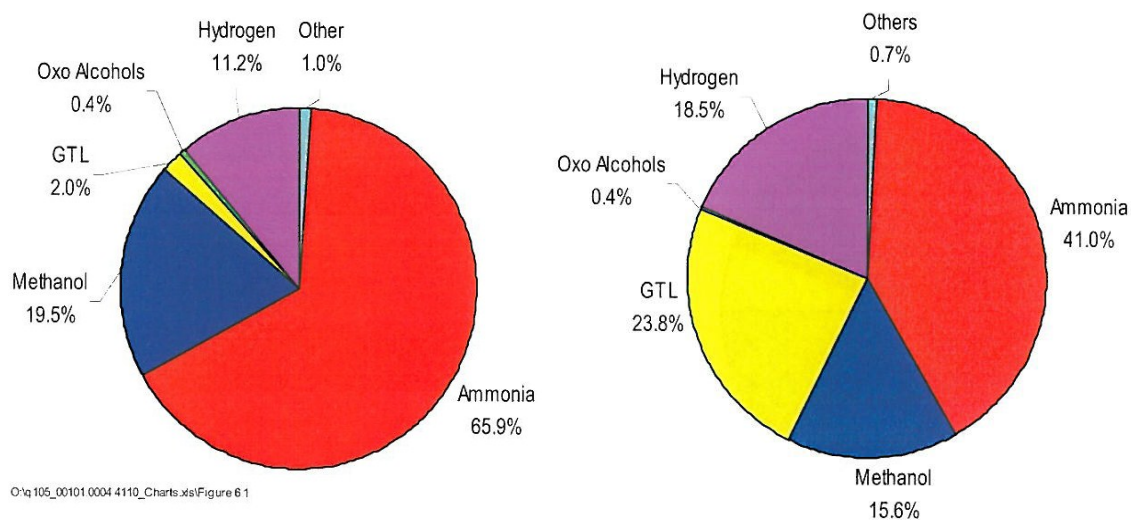


Figure 1-6 Global syngas demand by region 2003 and 2015 [based on (15)]

Due to technical development within the last century including the up-scale of plant capacities in ammonia and methanol production and the development of the Fischer-Tropsch synthesis process, which led to a rapid growth in syngas demand for gas-to-liquids (GTL), a



total syngas demand of over 700 billion m³ (STP) is expected for 2015, doubling the demand from 2003 (15). The specific market shares by end-use sector are shown in Figure 1-7.



(a) 2003 (total demand = 373 billion m³ (STP))

(b) 2015 (total demand = 708 billion m³ (STP))

Figure 1-7 Global syngas demand by end-use (15)

Thus existing technologies have to be improved and new processes have to be developed to utilize alternative fuel sources to meet the future demand. Especially excess gases from iron making industry might serve as valuable feedstock for specific syngases, as they already contain significant shares of H₂ and CO.

Coke oven gas, off gas from coke oven plants for coal conversion into coke, has already been utilized as feedstock for syngas production. But due to high compression costs, impurities and a share of 25-50% methane and higher hydrocarbons (Table 1-1) requiring syngas pre-treatment, coke oven gas is rather used as fuel for heat and power generation than in chemical industry (10).

Smelting reduction export gases from COREX[®] and FINEX[®] processes only contain 1.5-2% methane and traces of higher hydrocarbons. Their nitrogen content is much lower than in blast furnace gas due to the gasification process with oxygen (10). Compared to standard syngas generation based on natural gas, a reforming process step is not required as the export gases already contain significant amounts of CO and H₂.

Therefore the utilization of these export gases as feedstock in chemical industry seems to be a promising alternative to the conventional utilization in heat and power plants or as reducing gas in direct reduction plants. Figure 1-8 visualizes the common utilization options for COREX[®] and FINEX[®] export gas (brown) and their utilization potential as synthesis gas in chemical industry (dark blue, green).

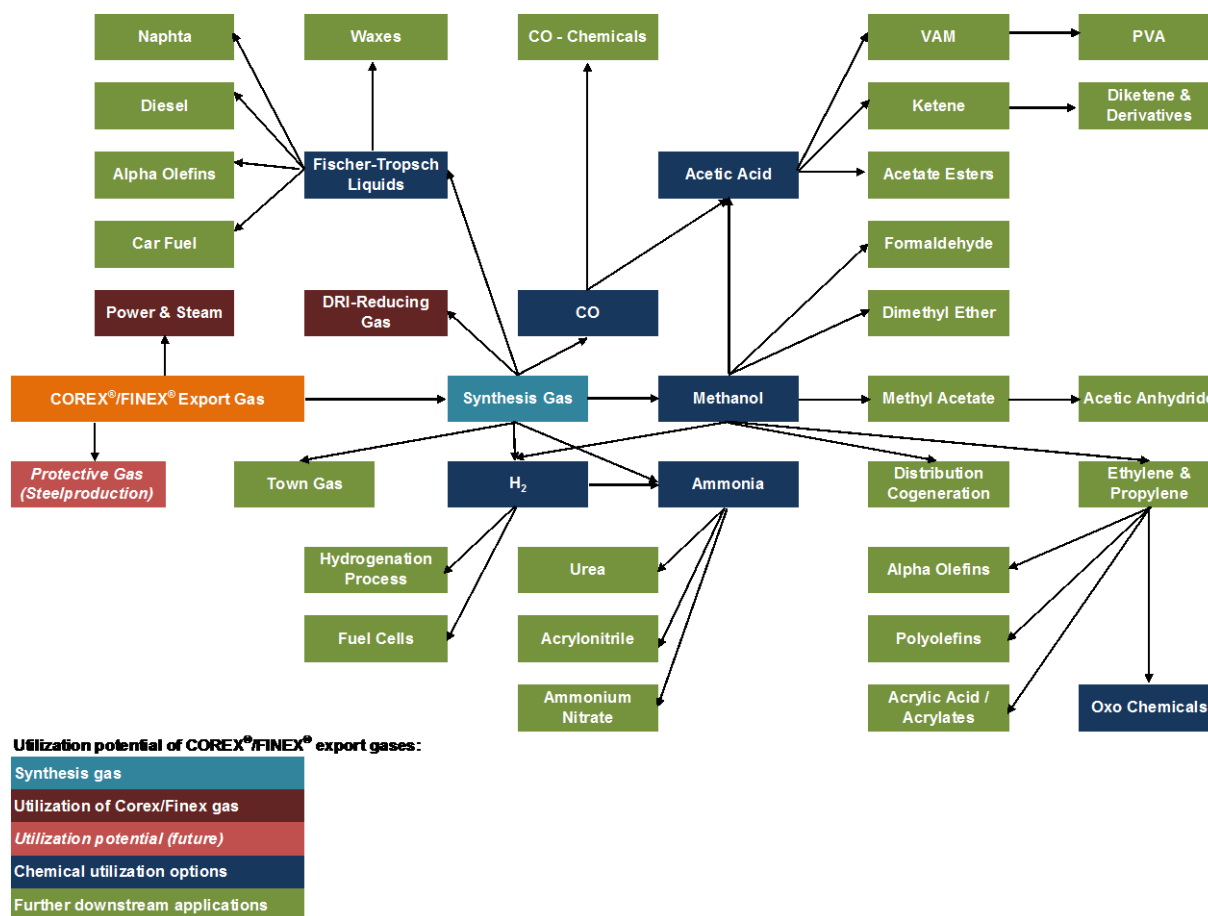


Figure 1-8 Utilization options for COREX® and FINEX® export gas [based on (10)]

Besides hydrogen (H_2) and carbon monoxide (CO), intermediate chemicals like ammonia (NH_3), methanol (CH_3OH) or acetic acid (CH_3OOH) are major input substances for the synthesis of industrial chemicals. With the carbonylation of methanol for example acetic acid is synthesized and either sold as product or further processed to form vinyl acetate monomers (VAM), ketenes or acetate esters.

But neither process simulations for the conversion of export gases into main intermediate chemicals nor economic or environmental evaluations have been published so far.

1.2 Aims and Outline

This thesis shall provide an evaluation of environmental and economic benefits and technical challenges of iron making excess gas material recycling for chemical synthesis. In order to provide a comprehensive analysis, the following major tasks have been worked out:

- specific process designs including production cost estimate and CO_2 balance for the chemical utilization of smelting reduction excess gases into specific syngases to synthesize the main intermediate chemicals
- feasibility analysis of a commercial production process, to evaluate the economic impact and the consumption of raw materials and energy.



The engineering of each specific process design includes material and energy balance for the conversion of smelting reduction export gases into appropriate syngas compositions for the downstream synthesis of the main chemical products, shown in Figure 1-8 (dark blue), using standard syngas production technology.

Constitutive on the process simulations, syngas production costs have been estimated and compared with the costs for common syngas generation based on natural gas. Furthermore an evaluation model for CO₂ emissions has been worked out including process related emissions as well as emissions related to inputs of heat, steam and electric energy which is valued according to the electric energy mix of the countries China, Austria and Sweden.



2 Methodology

2.1 Definition of Scope

As a first step the scope and framework regarding:

- smelting reduction processes, excess gases and their utilization options
- syngas production and specific synthesis gases
- chemical synthesis and chemical products including conventional feedstock

were defined. The block scheme in Figure 2-1 visualizes the relevant material flows for conventional and potential utilization of smelting reduction excess gases.

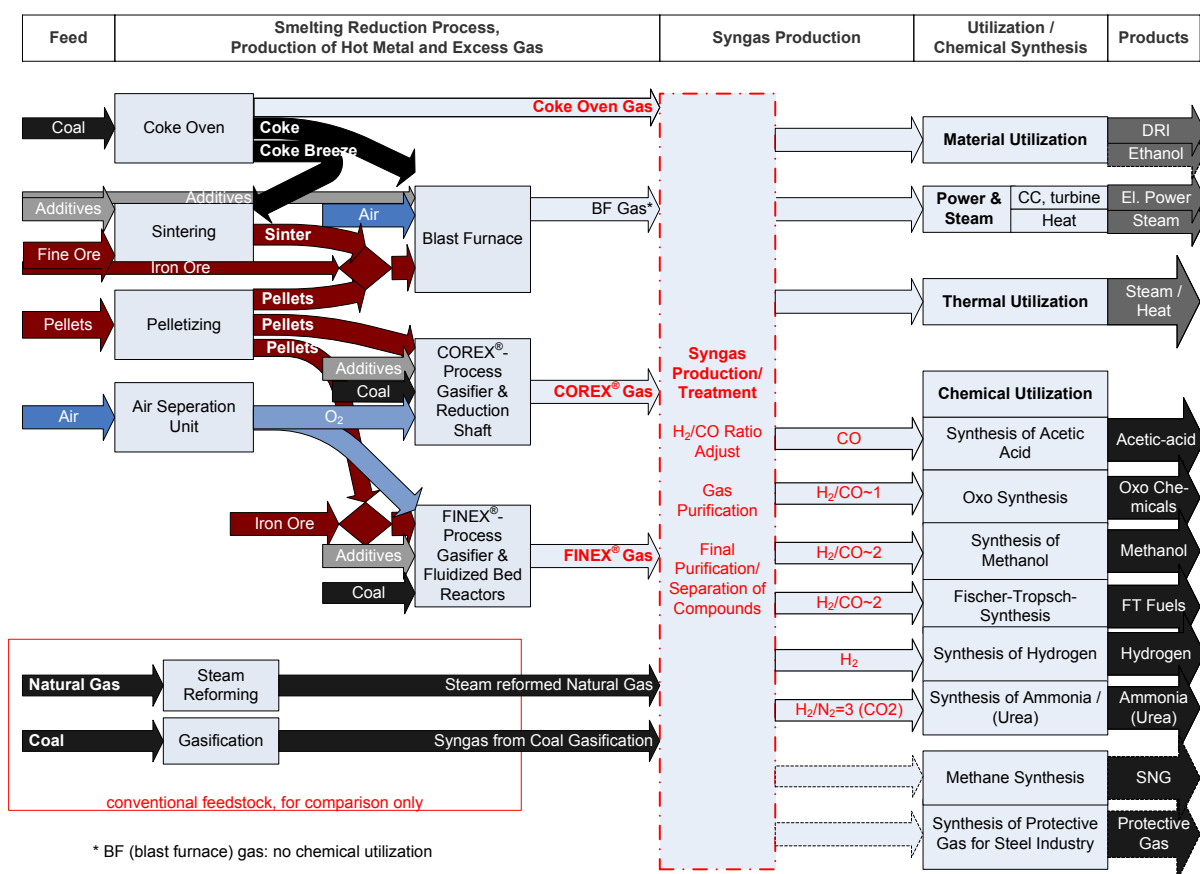


Figure 2-1 Utilization options of smelting reduction excess gases, relevant material flow [own description]

The following smelting reduction excess gases (Figure 2-1, red) have been chosen as feedstock for the syngas production of selected synthesis products:

Coke oven gas (COG): has been utilized as H₂ and NH₃-syngas in chemical industry, due to its H₂ content of 39 to 65%. But because of compression costs and impurities, nowadays it is mainly used as fuel for heat and power plants within the iron and steelwork. Due to its low CO content (4-7.5%, shown in Table 1-1), only the production of H₂ by conventional PSA (pressure-swing adsorption) technology will be discussed within this study.



Blast furnace top gas (BF gas): Due to the high nitrogen content and the large quantity of impurities in blast furnace top gas, extensive purification efforts would be necessary to meet the syngas specifications of the chemical synthesis process. A detailed analysis of this option was therefore excluded from the scope of this thesis

COREX[®] and FINEX[®] export gas: The fact that the COREX[®] melter-gasifier operates with oxygen instead of air leads to a low nitrogen content in the export gases which enlarges the share of the syngas compounds CO and H₂ up to 50%.

Natural gas (NG) and coal gasification: The conventional production of syngas from natural gas or coal has been included as baseline and standard route for process comparison. Syngas production costs from NG are the reference for evaluating the economic efficiency of the chemical export gas utilization.

Selected synthesis products: Due to the market relevance of the following chemical products, specific syngas production routes for their chemical synthesis have been selected and are covered in detail:

- Carbon monoxide: intermediate chemical for carbonylation reactions; separated from synthesis gas at low temperature
- Acetic acid: intermediate chemical for polymer production; produced by carbonylation of methanol
- Oxo chemicals: intermediate chemicals for the production of acrylates, glycol ethers, acetates, plasticizers or solvents; produced by hydroformylation of alkanes
- Methanol: basic intermediate for a variety of chemicals like formaldehyde or acetic acid; produced by hydrogenation of carbon oxides
- Fischer-Tropsch liquids: used as synthetic fuels; generated by Fischer-Tropsch synthesis
- Hydrogen, e. g. used for hydrogenation; separated from synthesis gas by pressure-swing adsorption technology
- Ammonia: main chemical in nitrogen based fertilizer industry; especially for the production of urea which consumes excess CO₂; produced by Haber-Bosch synthesis

Other chemical utilization options, e.g. as protective gas in steel industry or the methanation of export gases for the production of synthetic natural gas (SNG) are not covered in this scientific work as commercial relevance is expected to be low.

2.2 Data Basis

Gas Analysis

The COREX[®] export gas specification and the gas volume flow refer to a COREX[®] C-3000 module (16). The FINEX[®] export gas specification refers to a FINEX[®] 2.0M module (17) while the FINEX[®] export gas volume flow refers to a 1.5M module (pers. com.). All specified trace



compounds have been considered in the calculations in chapter 4.1, but specified dust impurities have not been considered within this study.

The specification of blast furnace top gas and COG refer to (18).

Specifications of the selected syngases have been consolidated from several references like (10), (15), (19), (20), (21), (22), (23), (24).

Physical Parameters: Temperature and Pressure

Pressure (p) data is generally related to the absolute pressure in MPa, temperature data is given in °C. Standard temperature and pressure (STP) are defined at 0°C (273.15K) and 0.101325 MPa (1 bar) respectively.

2.3 Structure

According to the aims and outlines and the defined scope, this thesis is structured into the following major chapters:

- A literature review of chemical synthesis and syngas production techniques
- Thermo-chemical process simulations for the conversion of export gases into syngas for main intermediate chemicals
- An economic analysis of the defined processes based on material and energy balance
- A comparison of CO₂ emissions considering the country specific energy mix
- A discussion and conclusion

Literature Review

The literature review gives an overview of chemical synthesis, syngas market and production technologies, based on selected references, i.e.:

- PERP reports from NEXANT Chem Systems, especially:
 - Report 03/04S4, Development in Syngas Technology (15): providing an overview of syngas production techniques from feedstock natural gas and coal; giving basic information of the syngas market including an economic analysis of production costs.
 - Report 03/04S11, Coal Gasification Technologies (24): showing commercial gasification systems and LPMEOHTM process development.
 - Report 09/10S11, Carbon Monoxide (19): providing expert information of industrial syngas production and purification techniques, as well as production costs; including economic and market analysis.
- Ullmann's Encyclopedia of Industrial Chemistry, especially the chapters:
 - Gas Production (25): including techniques for syngas generation and syngas treatment; giving examples of relevant syngas production plants.



- Carbon Monoxide (26), Oxo Synthesis (27), Acetic Acid (28), Methanol (29), Hydrogen (30) and Ammonia (23): providing more detailed information about final purification techniques and the synthesis process itself.
- Rostrup-Nielsen et al (31): giving expert information about reforming and synthesis gas production technologies.

The first part, chemical synthesis (chapter 3.1), summarizes:

- the main synthesis process and common technologies,
- the range of production capacity,
- the requirements for feedstock material,
- material and energy consumption,
- market development and industrial scale application

for the selected intermediate chemicals.

Capacity and process requirements for conventional feed gases and export gases have been considered.

The second part, synthesis gas production (chapter 3.2), gives an overview on key process units for the production of syngases for the introduced selected chemicals, which can be structured into two main topics:

- the reaction route for generation of syngas (CO and H₂)
- the gas treatment section for ratio adjustment and purification

Furthermore,

- a summary of required syngas compositions for the downstream synthesis processes and
- a review of production costs for the generation of syngases from feedstock natural gas are included.

Within this chapter, product specific calculations with focus on methanol and hydrogen are introduced, showing the influence of production capacity, feedstock material and feedstock price.

Chemical Utilization of selected Excess Gases

Chapter 4 is divided into two parts, COREX[®] and FINEX[®] export gas treatment and the production of H₂ from coke oven gas.

The 1st part includes the thermo-chemical simulation of the syngas treatment from alternative smelting reduction export gases.

The simulations and calculations have been based on common industrial process units for the conversion and syngas treatment of natural gas.



The thermo-chemical simulations of the syngas treatment especially the compression section and the water gas shift reaction have been calculated with CHEMCAD, Version 6.3/5, a chemical process simulation software that includes libraries of chemical components, thermodynamic methods, and unit operations to allow steady-state simulation of continuous chemical processes (32). The simulations include flow chart, heat and energy demand, mass- and volume flow, stream compositions and operating conditions for each process unit.

Detailed calculations of the CO₂ absorber and regeneration unit and the final purification treatment by cryogenic separation of carbon monoxide, the liquid nitrogen wash for ammonia syngas and the hydrogen separation by PSA technology have been provided by Linde engineering.

For all intermediate syngas compositions, the same calculation methods have been applied.

The 2nd part gives an overview on necessary gas treatment units for the conversion of coke oven gas into the main intermediate chemicals and shows a specific process design for the generation of H₂ from COG, including energy demand, CO₂ balance, capital cost estimate and utility demand.

Economic Analysis

The production cost estimate for the generation of CO, H₂, acetic acid and oxo-chemicals and syngas for methanol, Fischer-Tropsch and NH₃-synthesis according to the process simulations are worked out in chapter 4. The calculation model has been developed similar to the cost calculation model from Nexant ChemSystems (19), including variable, direct and allocated fixed costs as well as depreciation based on static amortization and the return on capital expenses. The analysis includes a comparison to natural gas based syngas production.

The pricing basis for feedstock and utilities has been based on data from (19), (33) and (34).

CO₂ Balance

The CO₂ balance developed by the author includes process related CO₂ emissions as well as CO₂ emissions related to input of steam, heat and electric energy based on the mass and energy balance of the thermo-chemical simulations done in chapter 4. Emissions related to the import of electric energy have been calculated for selected locations in China (1.01 kg CO₂/kWh_{el}) (35), (36), Austria (0.34 kg CO₂/kWh_{el}) (37) and Sweden (0.06 kg CO₂/kWh_{el}) (38), considering the influence of the local electric energy mix.

A summary of net CO₂ emissions includes the credits for the substitution of natural gas as feedstock.



3 Literature Review

This summary of common chemical synthesis and syngas production process technologies defines the standard to compare and discuss options for export gas utilization.

3.1 Chemical Synthesis

In chemical synthesis, the syngas compounds H_2 and CO (synthesis gas) react with or without additional reactants on selective catalysts, forming the chemical products.

The synthesis routes of many commercial chemicals can be structured based on major intermediates like

- carbon monoxide,
- oxo chemicals,
- acetic acid,
- methanol,
- Fischer-Tropsch liquids,
- hydrogen and
- ammonia,

as outlined in Figure 3-1 (blue).

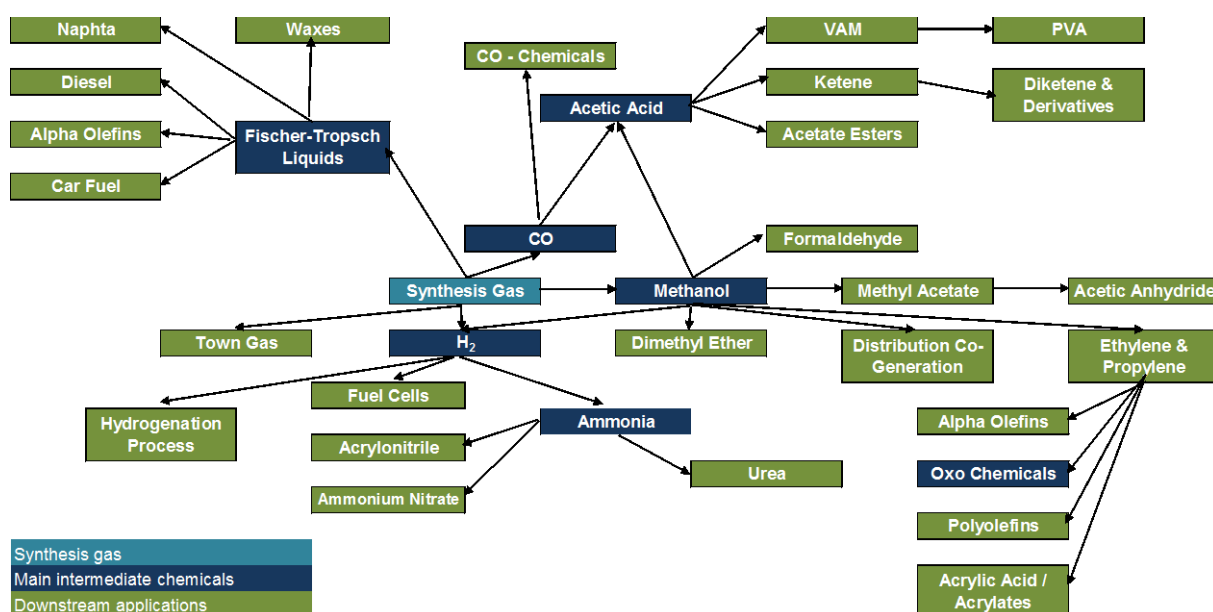


Figure 3-1 Synthesis gas utilization in chemical industry [illustration based on (10)]

3.1.1 Carbon Monoxide

Carbon monoxide (CO), a color- and odorless, flammable and toxic gas, is mainly used as reducing agent, as fuel and as intermediate feedstock in synthesis industry. CO is generated by partial oxidation or decomposition of organic compounds. Industrially, CO is produced from syngas, but can also be recovered from off-gas of metallurgic processes. Table 3-1



shows the composition of typical carbon monoxide sources, including the steam reforming of natural gas, but also off-gases from metallurgic industry like coke oven gas and blast furnace gas (19).

Table 3-1 Typical composition of carbon monoxide sources [(19), extracted]

Source	Composition in volume %, dry basis						
	CO	CO ₂	H ₂	N ₂	CH ₄	O ₂	Other
Natural gas, steam reforming	15.5	8.1	75.7	0.2	0.5	-	-
Naphtha, steam reforming	6.7	15.8	65.9	2.6	6.3	-	2.7
Coal gasification	59.4	10.0	29.4	0.6	-	-	0.6
Blast furnace gas	27.5	11.5	1.0	60.0	-	-	
Coke oven gas	5.6	1.4	55.4	4.3	28.4	0.4	4.5
Water gas	30.0	3.4	31.7	13.1	12.2	1.2	8.4

The conventional steam reforming of natural gas leads to a high syngas-ratio (H₂:CO-ratio) in the range of 4 to 5. But the economic carbon monoxide production from H₂ rich syngas highly depends on the market price for the by-product hydrogen, and the according economic benefit that can be achieved.

Coal gasification and iron making off-gases are typically rich in carbon monoxide and attain a syngas-ratio of below 0.5. Especially COREX[®] and FINEX[®] export gas seem to be attractive as alternative feedstock for the generation of CO. They have less impurity and are lower in nitrogen content than blast furnace gas, which has not been utilized for CO purification.

Synthesis Process

Generally the production of carbon monoxide can be divided into two parts,

- the syngas generation and
- the final purification section.

The syngas generation includes the reaction route and the syngas purification. Feedstock and reaction route determine the H₂:CO-ratio, which should be low to minimize further gas treatment and purification efforts. Conventional syngas-production routes from natural gas and coal are described in chapter 3.2. To reduce the syngas-ratio of reformed natural gas imported or recycled CO₂ can be fed into the steam reformer. In the presence of catalysts the reverse shift reaction yields to a H₂:CO-ratio of below 3 as shown in Table 3-2. A total substitution of steam by CO₂, called dry reforming, can achieve a H₂:CO-ratio of below 0.5. Besides MIDREX[®] CO₂-reforming, applied for the generation of iron making direct reducing gas, dry reforming technology is also used in the CALCOR process, shown in Figure 3-4 (39).



Table 3-2 Typical H₂:CO-ratio and CH₄ content for some CO generating processes (39)

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

After syngas generation, the pre-purified synthesis gas is sent to the final purification section. The techniques for carbon monoxide recovery are related to four main technologies:

- cryogenic separation
- salt solution adsorption
- vacuum pressure-swing adsorption
- membrane technique

The process selection is determined by the raw gas composition, the end use application as well as the downstream requirements. Most practiced and state of the art process for industrial scale application is the cryogenic separation, which is used to generate CO at high purity (98.5 - 99.9 mol-%), and H₂ (purity: 90 – 98 mol-%) as a by-product. Due to the small difference between the boiling points of CO (-191.5°C) and N₂ (-195.79°C), nitrogen is not separated from the product CO. To reach high purity CO from raw gases containing nitrogen, an N₂/CO-separation column can be installed additionally, which is energy intensive. Traces of carbon dioxide and water have to be removed before entering the cold box to prevent the accreting of freezing compounds, which commonly is done in temperature swing adsorption units.

The cryogenic separation of H₂ and CO is divided into two main process types:

- the partial condensation process and
- the methane wash process.

The selection of the process type, to be applied, depends on the feed gas composition.

The partial condensation process chosen for high pressurized syngas with a low H₂:CO-ratio and low methane content is lower in investment but also lower in CO-recovery than the liquid methane wash process. For liquid methane wash the CH₄ content of the feed gas has to be above 2 vol-%. This process is more complex, but therefore achieves higher CO-recovery rates. It is typically applied for low pressure feed gas and feed gas low in CO content (40). Table 3-3 shows the difference in feed gas quality and CO recovery rate.



Table 3-3 Comparison of the condensation and the methane wash process (40)

	Partial condensation process	Methane wash process
Feed gas	Typically from POX: High pressure High CO content Low in CH ₄ content	Typically from SMR: Low pressure Low CO content High in CH ₄ content (>2%)
CO recovery rate	Up to 90% (95% for two stage process)	Up to 98%

More information of the partial condensation process is given in chapter 4.1.1, including process flow chart and description. The simplified flow chart for the cryogenic purification by liquid methane wash is shown in Figure 3-2.

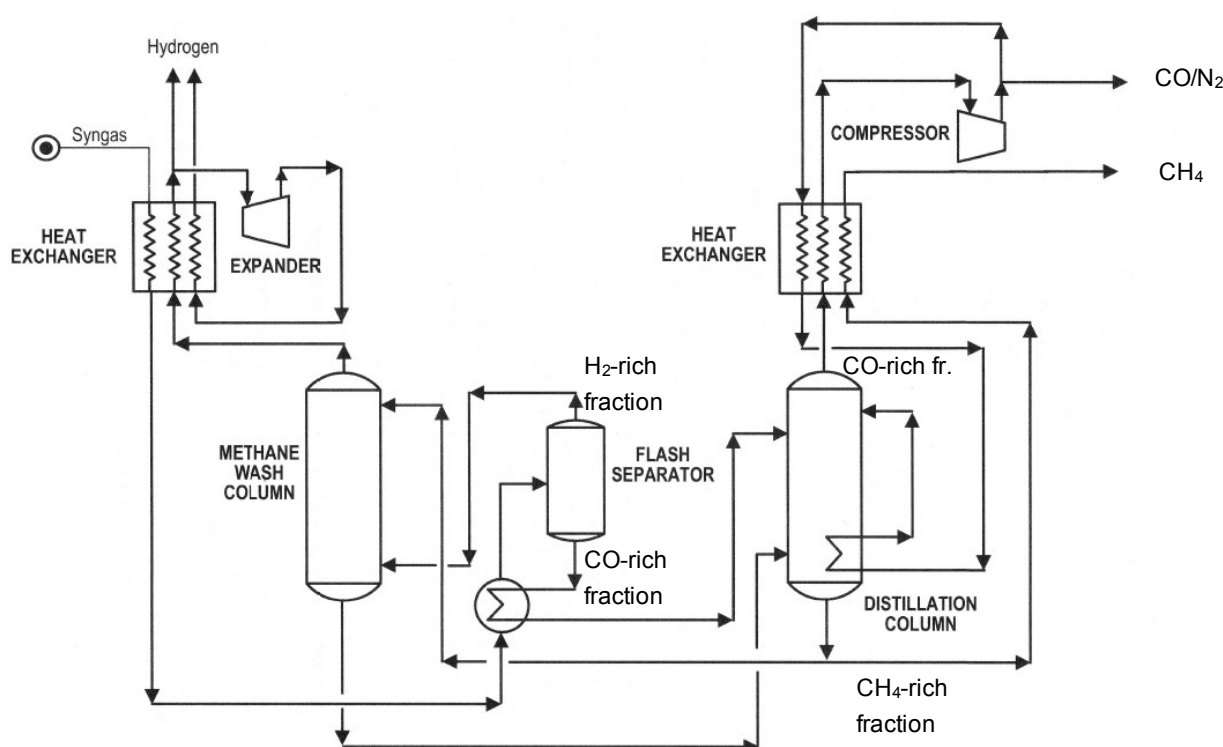


Figure 3-2 Carbon monoxide recovery by cryogenic liquid methane wash (19)

Liquid methane wash: Syngas purified from H₂O, CO₂ and H₂S by temperature swing adsorption (TSA) enters the cold box (cryogenic system) and is cooled down to -183°C (syngas pressure ~3-4 MPa). In a flash separator CO and CH₄ are condensed and sent to the distillation column which operates at 0.1 to 0.2 MPa. The purified CO/N₂-gas flow (CO/N₂ ~ 99.8%) exits at the top of the distillation column. The gaseous H₂ stream exits at the top of the flash separator and enters the methane wash column where it is purified by scrubbing with liquid CH₄. H₂ with a purity of 98% is withdrawn at the top of the column at approximately 2.5 MPa. The liquid from the bottom of the methane wash column is sent to the distillation column for purification. Withdrawn as bottom fraction CH₄ is then recycled to the wash column (19).



A selective purification process for CO from N₂-rich syngas is the salt solution adsorption process COPureSM, developed by R. C. Costello & Assoc. Inc.. As shown in Figure 3-3, CO is selectively absorbed by complexation in an organic solvent containing cuprous aluminum chloride, slipping CO₂, N₂ and other gases (CO lean gas). The organic solvent complex exits as bottom-product. After decompression in the flash drum, CO is stripped from the organic solvent achieving a CO-recovery rate of 98% and a purity of 99%. The H₂ stream is not purified (41). Before entering the absorber, the feed gas has to be dry, but a complete removal of CO₂ is not necessary.

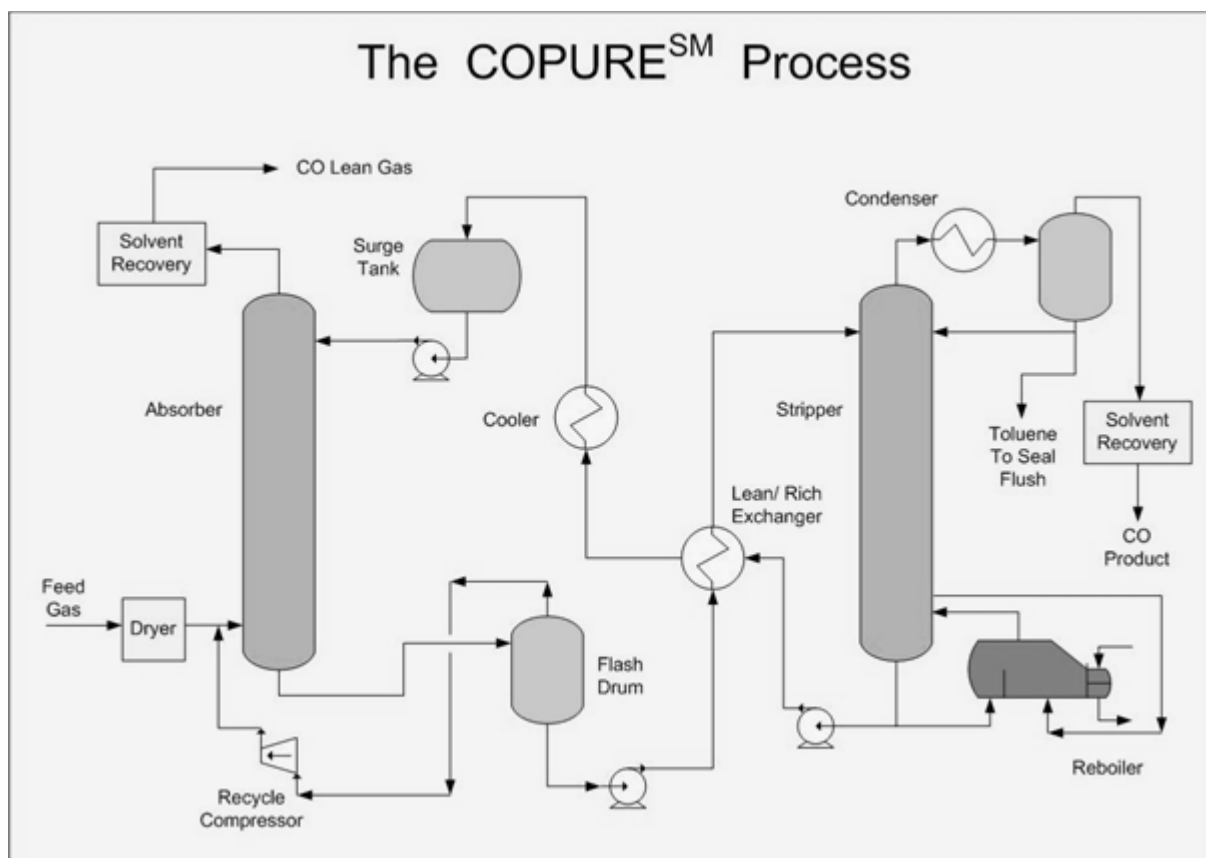


Figure 3-3 Basic COPURESM process (41)

Another way to separate CO from the syngas flow is the vacuum pressure-swing adsorption technology (VPSA). The CO-quality reached can meet the downstream requirements for the generation of oxo alcohols (limit, see oxogas specification, chapter 3.2.3), but high CO-purity cannot be obtained. A common configuration is the combination of cryogenic purification and PSA technology, achieving high purity CO, and high purity H₂ respectively (19).

One stage membrane technique enriches carbon monoxide in the non-permeate stream with enough purity for oxo alcohol production. For high purity CO, at least two stage membranes have to be installed. The CALCOR process, shown in Figure 3-4 includes two selective membranes to simultaneously separate H₂ and CO₂ from carbon monoxide, which leads to a CO/N₂-purity above 99% (19).

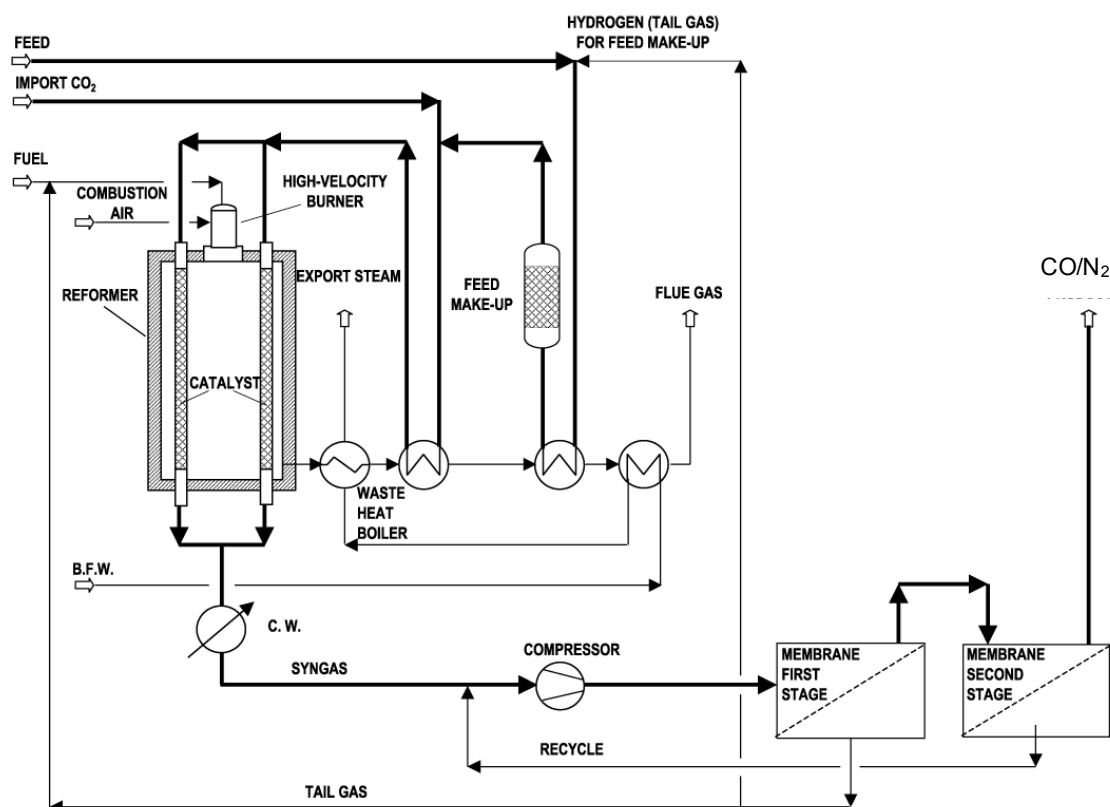


Figure 3-4 Simplified flow sheet for CALCOR Economy process (39)

Desulfurized feed gas is mixed with recovered or imported CO_2 and sent into the reformer unit. The reformed gas is cooled, compressed and sent to the membrane section for separation of H_2 and CO_2 from the CO -product. The tail gas from the first membrane is used as fuel or as feed make up. Permeate from the first membrane is sent to the next stage for final separation and leaves the second stage as CO -product. If high CO -purity is required, a cryogenic purification step has to be applied. The tail gas from the second membrane, rich in CO is recycled into the suction side of the syngas compressor (39).

Technology, Capacity and Syngas Requirements

Technology: Cryogenic separation is state of the art technology for industrial scale production of carbon monoxide from syngas. Only a few small plants are based on the vacuum- CO -PSA, using copper-doped adsorbent material (42).

Capacity: The production capacity of cryogenic separation units ranges from 350 to 60,000 m^3/h (STP) high-purity CO . Generally, the capacity is determined by the downstream application. A typical world scale acetic acid plant consumes about 30,000 to 40,000 m^3/h (STP) CO (43).

Operating conditions: The cryogenic process can handle a reduction on the syngas stream down to 40% of normal operation volume flow. In case of failure in syngas supply, a quick-closing valve is activated and the system remains under pressure. Depending on the duration of the lack of feed supply, the system can be purged with nitrogen.



Material and Energy Demand

Raw material, utility demand and by-product credits for carbon monoxide production by cryogenic separation with a yearly capacity of 240,000 tons are listed in Table 3-4.

Table 3-4 Raw material and utility demand for CO production [based on (19)]

Raw material and utility demand per t product	per t CO	Syngas source		
		SMR (3:1)	ATR (2:1)	POX (1.7:1)
Raw material				
syngas	t	1.240	1.167	1.145
Catalyst & Chemicals	-	-	-	-
By-product credits				
hydrogen	t	0.216	0.144	0.122
purge gas	t	0.024	0.023	0.022
Utilities				
Power	MWh	0.264	0.198	0.222
Cooling water, dT=10°C	t	7.000	7.000	7.000
BFW	t	0.834	0.834	0.834
Process Water	t	2.503	2.503	2.503
Steam (MP)	t	0.012	0.012	0.012
Capacity	t/a	239,900	239,900	239,900
Production costs incl. ROCE (10%)	\$/t	286.190	286.540	282.910

The demand on syngas per ton product is depended on the syngas generation process applied and varies between 1.14 and 1.24 t syngas/t CO accordingly to steam reforming, autothermal reforming or partial oxidation of natural gas,. The electric energy demand for cryogenic separation depends on the H₂ and N₂ content of the syngas mixture and is typically between 198 and 264 kWh per ton CO.

Production Costs

The production costs for the conventional generation of carbon monoxide mainly depend on

- the syngas production and purification route,
- the plant scale,
- the costs for raw material (natural gas) and utilities,
- the hydrogen price.

The plant size is usually determined by the downstream application, and affects overall costs. Figure 3-5 shows the production costs for syngas generation by steam methane reforming (SMR), partial oxidation (POX) and autothermal reforming (ATR) of natural gas and for gasification of biomass (column 1-4). Furthermore the costs for the cryogenic



separation of each syngas mixture (raw material) are shown in column 5-8. Whereas the syngas production costs vary from 283 US\$/t (POX) to 324 US\$/t (SMR), the production costs for CO from SMR, POX and ATR syngas are all around 285 US\$/t, due to the revenue of the by-product hydrogen. The production costs are estimated for the production of 240,000 tons CO per year, which is based on a typical world scale methanol carbonylation plant capacity. Costs for raw material and utilities are based on the prices from US Gulf Coast, 1st quarter 2010. The revenue for the by-product hydrogen is estimated by 1.6 of fuel value. Changing H₂-prices influences net raw material costs of carbon monoxide production, especially if the syngas is rich in hydrogen.

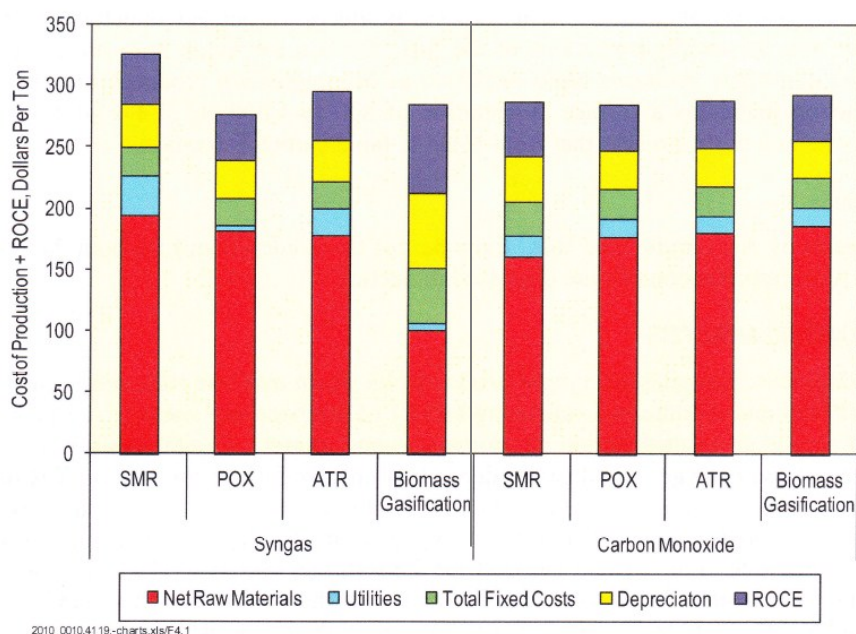


Figure 3-5 Syngas & carbon monoxide cost of production summary (first quarter 2010, USGC) (19)

Industrial Application

Carbon monoxide is used in various industry sectors like the metallurgical industry, where it is utilized as reducing agent and as fuel. In chemical industry CO is used as feedstock for the synthesis of main intermediates. The required CO purity for industrial applications reaches from 8% (syngas compound) to 99% (pure CO). Main pollutant compounds are N₂, H₂, CH₄, O₂, CO₂, H₂O und Ar (26).

In chemical industry the acetic acid production is the main consumer of CO, followed by the synthesis of TDI, MDI, polycarbonate (PC) and Phosgene. Figure 3-6 shows the capacity of carbon monoxide in 2009, based on the organic downstream chemicals. Approximately 60% of global demand is consumed in Asia, especially in China.

The world demand on carbon monoxide in 2010 reached almost 10 million tons, including 6.6 million tons for acetic acid, 0.8 million tons for TDI, 1.5 million tons for MDI and 0.6 million tons for PC production. The forecast for 2015 includes 8.2 million tons for acetic acid, 1.1 million tons for TDI, 2.2 million tons for MDI and 0.6 million tons for PC production (19).



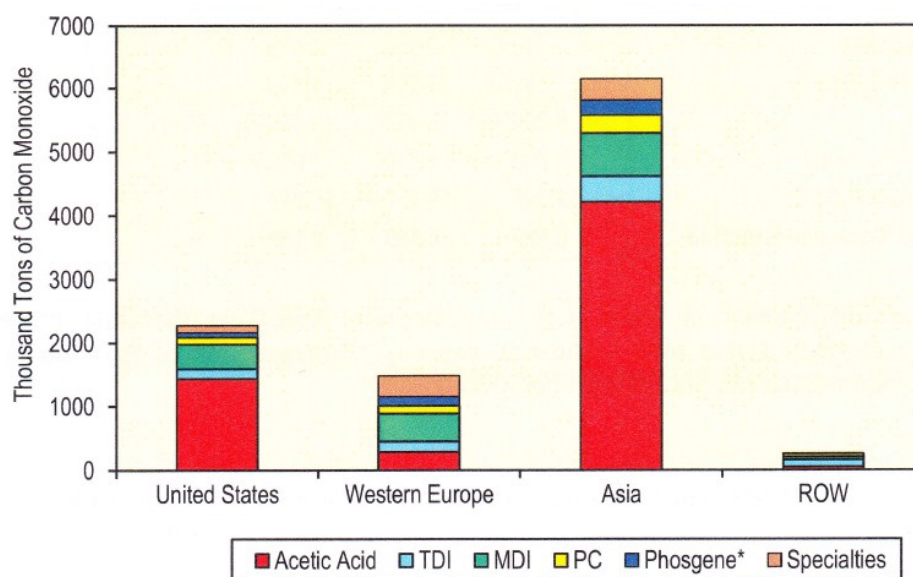


Figure 3-6 Implied carbon monoxide capacity needed to satisfy existing capacity of carbon monoxide based organic chemicals, 2009 (19)

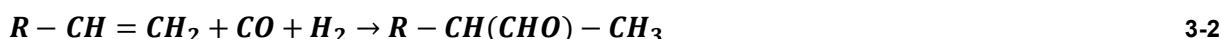
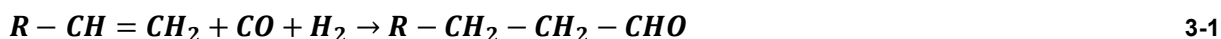
3.1.2 Oxo Chemicals

Oxo chemicals are products formed by the hydroformylation reaction of alkenes, also known as oxo synthesis, which has been discovered in the 1930s by Roelen (Ruhchemie). Various companies like BASF, Shell or Eastman Chemicals developed their own versions of the oxo synthesis process (34). Aldehydes, the resulting synthesis products, are easily converted into alcohols, acids and other derivatives, which led to a growth in production capacity.

The most common alcohol, n-butanol, is a colorless, flammable liquid, which has an acrid odor and is miscible with many organic solvents. Besides the application as solvent, oxo products serve as intermediate feedstock for the generation of chemicals like phthalates, used in vinyl plasticizers (34).

Synthesis Process

Oxogas is catalytically added as a single H and a formyl-group (CHO) to the carbon-carbon double bond of the alkene to form n-aldehyde and i-aldehyde as shown in 3-1 and 3-2.



The most important oxo aldehydes are in the range of C₃–C₁₉. According to Ullmann's Encyclopedia of Industrial Chemistry, butanal (C₄H₈O), also known as butyraldehyde, is the most common intermediate product from oxo synthesis process, and holds a share of roughly 75% of oxo synthesis products (27).

The product-variety from propylene hydroformylation is shown in Figure 3-7.



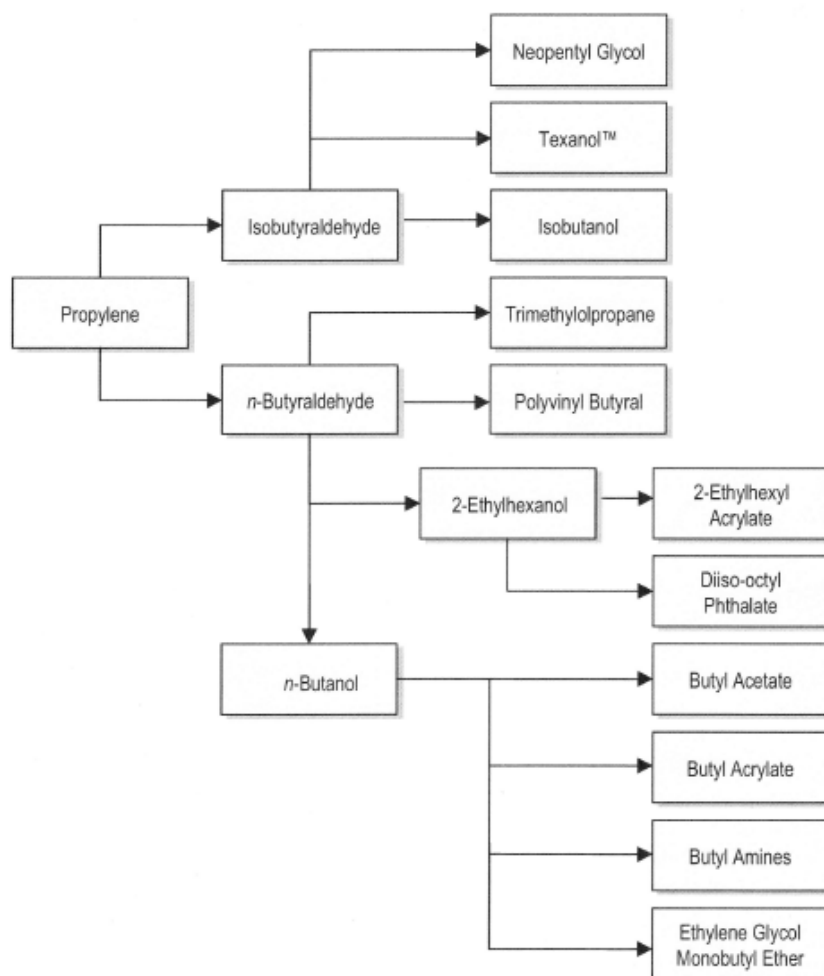


Figure 3-7 Products from propylene hydroformylation (34)

Both C_4 -aldehydes are used as intermediate feedstock for further generation of chemicals like polyvinyl butyral from *n*-butyraldehyde, a polymer with high strength (34), or neopentyl glycol from *i*-butyraldehyde, which is used for the synthesis of polyesters, paints, plasticizers and lubricants.

Technology, Capacity and Syngas Requirements

Technology: Whereas former high pressure processes (Table 3-5, type 4-5), operating between 5 to 35 MPa, were based on cobalt catalysts, nowadays commonly rhodium based catalysts with high selectivity on aldehydes (type 1-3) are used. An exception is the Shell process (type 4) for the production of alcohols.

The low pressure oxo process (LPO) Davy-type 1, developed by Union Carbide, Celanese, Davy McKee and Johnson Matthey, operates between 1.5 and 2 MPa on a rhodium-triphenylphosphine catalyst (34). A selection of oxo processes including operating conditions and catalyst material is shown in Table 3-5.

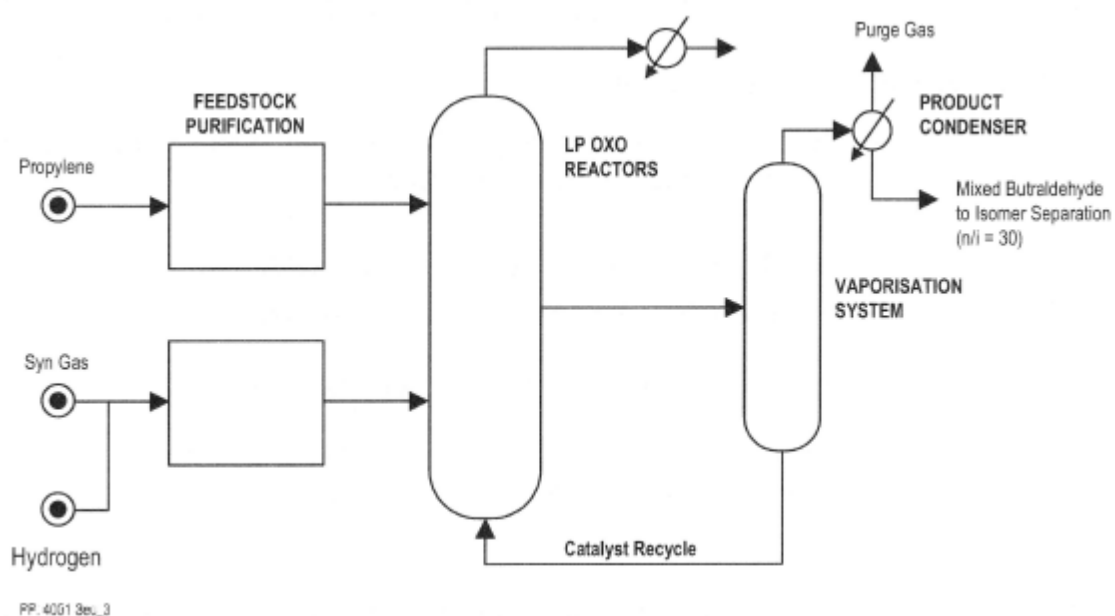


Table 3-5 Comparison of the various oxo processes (34)

Catalyst	[RhH(CO)(PR ₃) ₃]		[RhH(CO) ₄]	[CoH(CO)PR ₃]	[CoH(CO) ₄]
	R = C ₆ H ₅ R = 3-C ₆ H ₄ SO ₃ Na				
Process type no.	1 Davy	2 (RCH-RP)	3	4 (Shell)	5 (old process)
<i>Hydroformylation conditions</i>					
Pressure, bar	15 - 20	10 - 100	200 - 300	50 - 100	200 - 350
Temperature °C	85 - 115	50 - 130	100 - 140	160 - 200	110 - 180
Selectivity for aldehydes	high	high	high	low	medium
n/i Ratio	92 : 8	95 : 5	50 : 50	88 : 12	80 : 20
Hydrogenation	low	low	low	high	medium

The LPO-Davy process features gas recycle and liquid recycle systems for the separation of catalyst material from the product stream.

Figure 3-8 shows the simplified flow scheme of the synthesis of butraldehyde by an advanced low pressure oxo process which achieves very high catalyst activity.

**Figure 3-8 Flow scheme of LP oxo process – mark IV butraldehyde process (34)**

After purification from catalyst poisoning compounds, propylene (95%, chemical grade) and synthesis gas ($H_2:CO$ -ratio = 1) enter the liquid phase reactor for the hydroformylation in the presence of a homogenous bis-phosphite modified rhodium catalyst at operating temperature of 100°C and operating pressure of 2 MPa. After reaction the product/catalyst mixture is separated within the vaporization system. The liquid catalyst is recycled into the oxo reactor. The product is a mixture of n- and iso-butyraldehydes in a ratio of 30:1.



Capacity: The typical plant capacity for the process types listed in Table 3-5 lies between 400,000 and one million tons per year (44). The required amount on oxogas ranges between 30,000 and 60,000 m³/h (STP) (45).

Operating Conditions: The oxo synthesis reactor can be operated between 50-120% of the nominal oxogas flow. A failure in oxogas supply causes unwanted carbonylation reactions on the Rh-based catalyst system, but the catalyst system will regenerate within a few days. A controlled shut down prevents uncontrolled carbonylation reactions (pers. com.).

Syngas requirements: The oxogas for C₄-process contains the compounds H₂ and CO in a ratio of 1. A typical specification of oxogas is listed in Table 3-6.

Table 3-6 Oxogas analysis for the synthesis of butyraldehyde (21)

H ₂	50.5 – 53 vol%
CO	47 – 49.5 vol%
CO ₂	< 1.1 vol%
N ₂ /Ar	< 0,3 vol%
CH ₄	< 0.2 vol%
H ₂ S	< 0.1 ppmv
O ₂	< 4.5 ppmv
Pressure	3.3 – 3.8 MPa
Temperature	15 – 40°C

Material and Energy Demand

Raw material, utility demand and by-product credits for n-butanal production by Dow/Davy/MKIV process with a yearly capacity of 100,000 tons are listed in Table 3-7.

Table 3-7 Raw material and utility demand for n-butanol production via Dow/Davy/MkIV [based on (34)]

Capacity	t/a	100,000
Raw material	per t product	
syngas (1:1)	t	0.443
hydrogen (reformer)	t	0.030
propylene – chem. grade	t	0.642
catalyst & chemicals	-	-
By-product credits		
isobutyraldehyde	t	0.033
Utilities		
Power	MWh	0.126
Cooling Water	M m ³	0.125
Steam 0.4 MPa	M t	0.001
Steam 1.4 MPa	M t	0.002
Others		-
Utility credits		
Fuel	GJ	- 2.205



Production Costs

Figure 3-9 shows the oxo alcohol production costs for n-butanol and 2-ethylhexanol by Dow/Davy/Mk4 and Celanese process (a), and the costs for the production of isononanol, isodecanol and 2-propylheptanol (b), with a yearly capacity of 100,000 tons (costs based on US Gulf Coast, 4th quarter 2001).

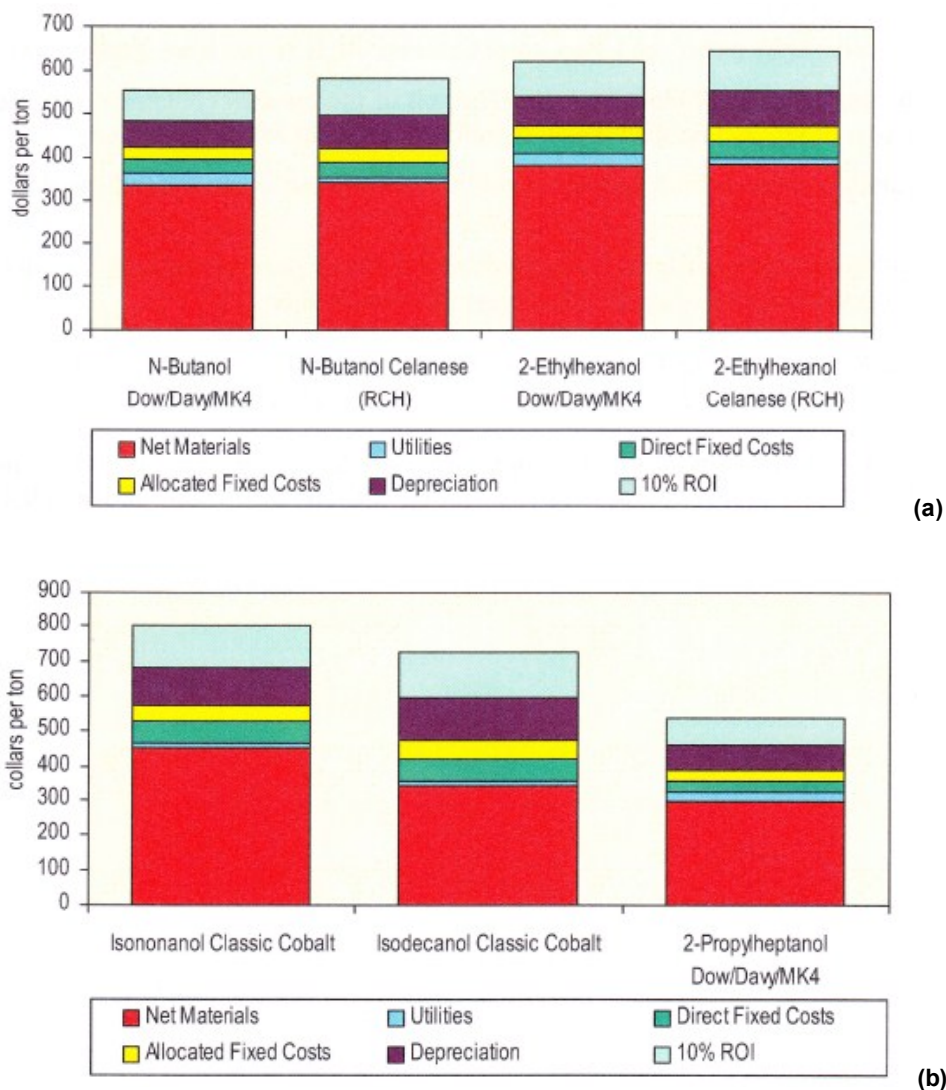


Figure 3-9 Oxo alcohol production costs (US dollars per ton, USGC, Q4/2001) (34)

The production costs for n-butanol from propylene are between 550 and 600 US\$/t, the low pressure Dow/Davy process is slightly more economic due to lower depreciation costs. Ethylhexanol processed by Dow/Davy shows similar cash costs to the Celanese process. The Celanese production costs are slightly higher again.

Industrial Application

Oxo chemicals are either used as solvent or further processed into numerous important synthesis products, as shown in Figure 3-7. In 1997 the global oxo production capacity for aldehydes and alcohols was at 6.5 million tons (27). The consumption of n-butanol by end use is shown in Figure 3-10.



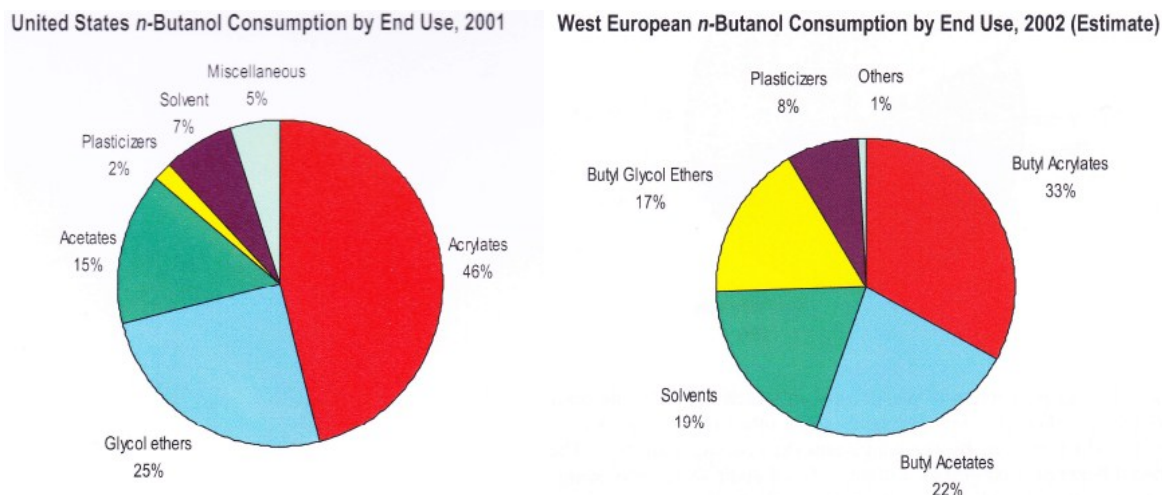


Figure 3-10 United States and West European *n*-butanol consumption by end use (34)

In the year 2001, the demand on *n*-butanol was around 770 thousand tons in the USA. The demand in Western Europe was approximately 690 thousand tons, and is expected to grow within the next years with an average annual growth rate of 2 to 3%. The *n*-butanol forecast for 2015 is at 1.2 million tons for Europe (34).

3.1.3 Acetic Acid

Acetic acid (CH_3COOH), a clear, colorless and corrosive liquid with pungent odor, is mainly used as feedstock for the generation of vinyl acetate and acetic anhydride. Acetic acid in dilute solution is found in some vegetables and animals and has been known as vinegar for more than 5,000 years (28).

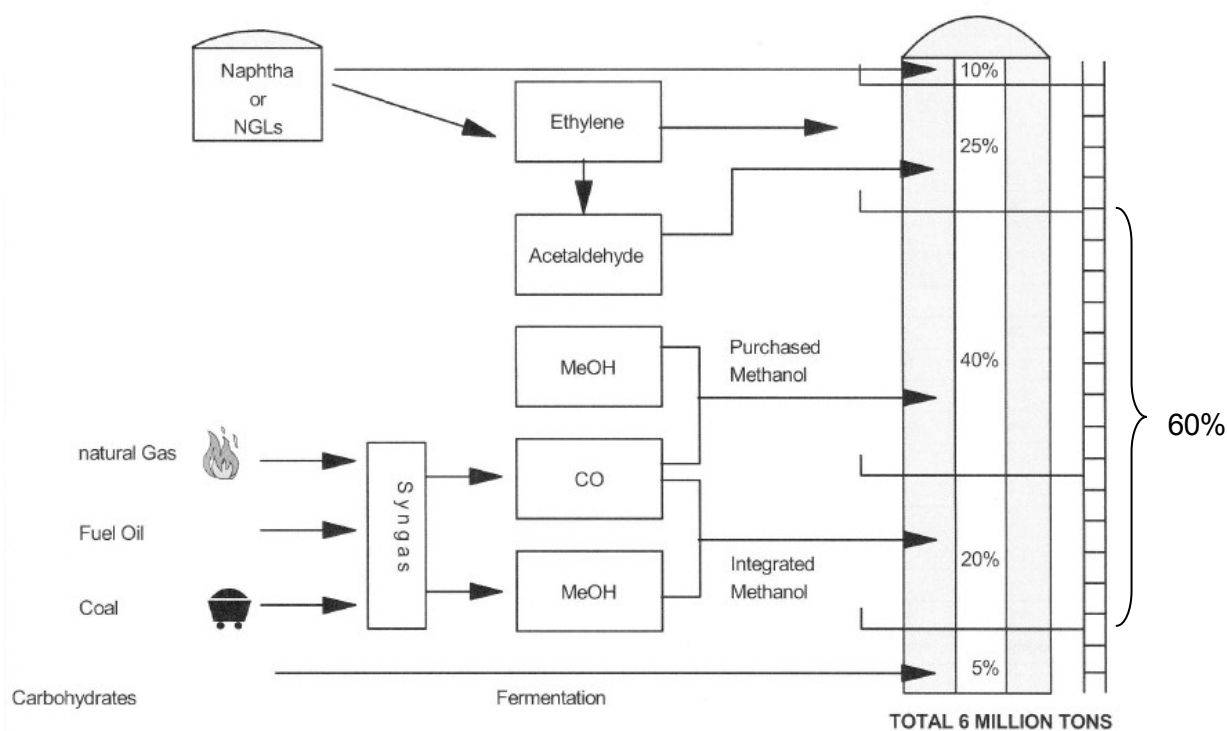


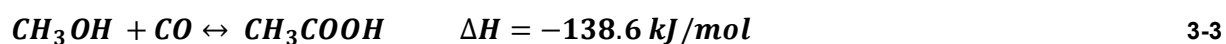
Figure 3-11 Acetic acid feedstock choices and process routes (33)



Figure 3-11 shows the processing routes for acetic acid including the share of global capacity held by each route at the end of 20th century, with methanol carbonylation summing up to 60%.

Synthesis Process

Nowadays almost 90% of new supply is based on the carbonylation of methanol (46).



With the development of the rhodium/iodide catalyst system of Monsanto in the 1970s and further development under BP Chemicals, which acquired the Monsanto technology 1986, selectivity above 99% based on methanol was achieved. High yield, moderate operating conditions (3.5 MPa/180°C) and large scale applications enabled the commercial operation of an industrial and economic carbonylation process (33).

Key process parameters of common carbonylation routes are shown in Table 3-8. The main producers, Monsanto, Celanese and BP have developed processes on homogenous catalysts, which operate at elevated pressure between 3 and 3.5 MPa (450 – 500psia) and in a temperature range from 175 to 190°C. The Celanese low water process attains a high CO efficiency of 97%.

Table 3-8 Processing conditions in acetic acid technology (33)

Acetic Acid Technology	Methanol Carbonylation				
	Homogeneous Catalyst			Support. Cat.	SynGas Route
versus Process Conditions	Monsanto/BP Conventional	Celanese Low Water	BP Cativa	UOP/Chiyoda Acetica	Haldor Topsoe
Feedstock	MeOH	MeOH	MeOH	MeOH	MeOH/DME
Catalyst	Rhodium	Rhodium	Iridium	Rh (Heterog.)	Rh
Promoters	Mel	Mel/Lil	Mel + Ru/Re	Mel	Mel
Water in Reactor, %	14-15	4 - 5	7 - 8	3 - 8	14-15
Reactor Mater. of Constr.	Zr ⁽¹⁾	Zr ⁽¹⁾	Zr ⁽¹⁾	Zr ⁽¹⁾	Zr ⁽¹⁾
Iodide Level in Reactor	Med.	High	Med.	Low	Med.
Acetic Acid Iodide Clean-up	No	Silverguard	Probably	Yes	No
Reaction Phase	Liquid	Liquid	Liquid	Liquid	Liquid
Reactor Pressure, psia	450-500	450-500	450-500	450-700	500-600
Reactor Temperature, C	175-190	175-190	175-190	160-200	100-250
Selectivity to Acetic Acid, %	>99	>99	>99	799	>98
CO Efficiency, %	91	97	95	95	90
Conversion, % per pass	99	99	99	99	---



The principle flow chart for acetic acid production via Carbonylation is shown in Figure 3-12.

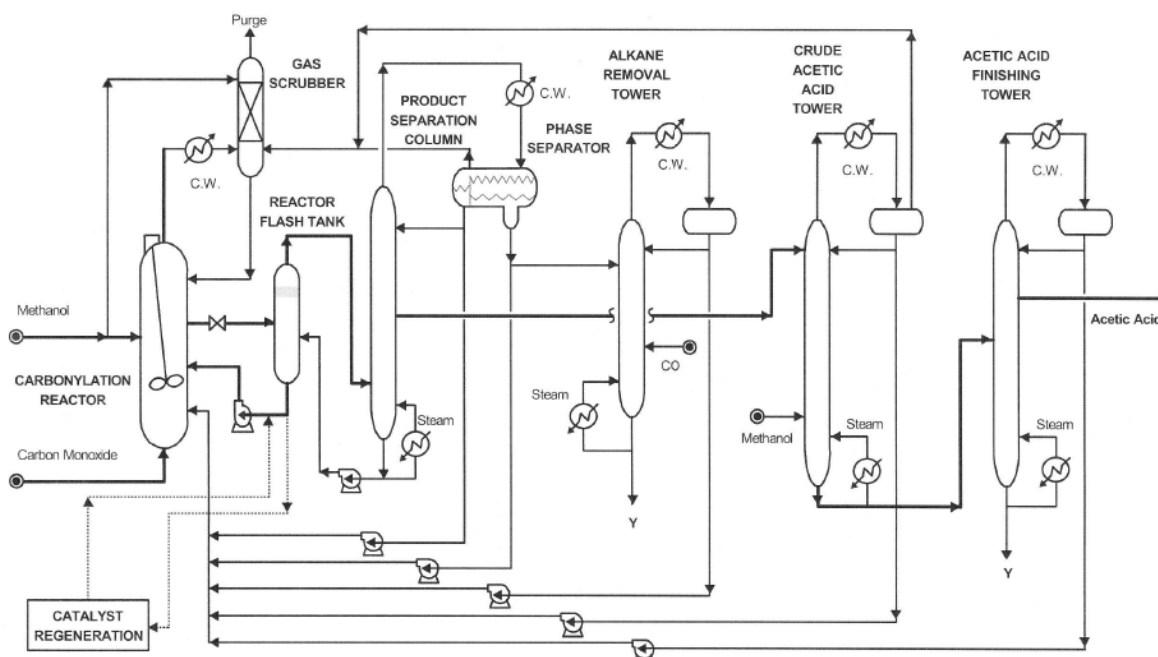


Figure 3-12 Acetic acid via methanol carbonylation Monsanto/BP process (33)

Methanol and CO are fed into a liquid phase reactor which contains methyl iodide and the rhodium catalyst complex. Acetic acid is achieved after a series of catalyzed reactions. Unconverted CO leaves the top of the reactor and is purged, whereas condensables are recovered and send back into the reactor vessel. A draw off stream from the reactor is taken and flashed continuously. The liquid fraction, containing the catalyst system, is recycled into the reactor while the vaporized fraction, including acetic acid, methyl iodide, water methyl acetate as well as traces of CO and hydrogen iodide, is fed into product separation system to yield high purity acetic acid (33).

Technology, Capacity and Syngas Requirements

Technology: Roughly 30% of the world's installed acetic acid production capacity is held by Celanese, which has developed the Monsanto acetic acid technology over the last 25 years. Almost 500 patents are active worldwide, over 20 patents in China (47).

Capacity: Typical plant capacity of acetic acid production is between 400,000 and one million tons/year (44). With the Celanese technology the original Monsanto process capacity has been upgraded to 1.2 million tons per year. The demand on CO reaches approximately 50% of the product capacity (47), (48). World scale acetic acid plants consume between 30,000 and 40,000 m³(STP) carbon monoxide per hour (43).

Operating Conditions: A failure in feed gas supply causes unwanted carbonylation reactions on the Rh-based catalyst system, but the catalyst system will regenerate within a few days. A controlled shut down prevents uncontrolled carbonylation reactions (pers. com.).



Syngas Requirements: The purity of CO-syngas from liquid methane wash process is typically above 99%. Gas components like nitrogen or carbon dioxide are inert during the carbonylation process, but a higher gas volume flow enlarges equipment size and increases operating costs, therefore bulk amounts of side components are removed.

Material and Energy Demand

Raw material, utility demand and by-product credits for acetic acid production by Monsanto/BP technology, with a yearly capacity of 100,000 tons, are listed in Table 3-9.

Table 3-9 Raw material and utility demand for the production of acetic acid [based on (33)]

Capacity	t/a	100,000
Raw material		
	per t product	
Methanol	t	0.5370
Carbon monoxide	t	0.5128
Catalyst & Chemicals		
By-product credits		
Fuel Gas	MJ	697.7631
Utilities		
Power	kWh	31.5261
Cooling water, dT=10°C	10 ³ m ³	139.3683
Steam, 1.4 MPa	10 ³ t	1.8000

Production Costs

The production costs for acetic acid strongly depend on the plant capacity, which is shown in Figure 3-13. The production costs are based on prices of US Gulf Region, 1998.

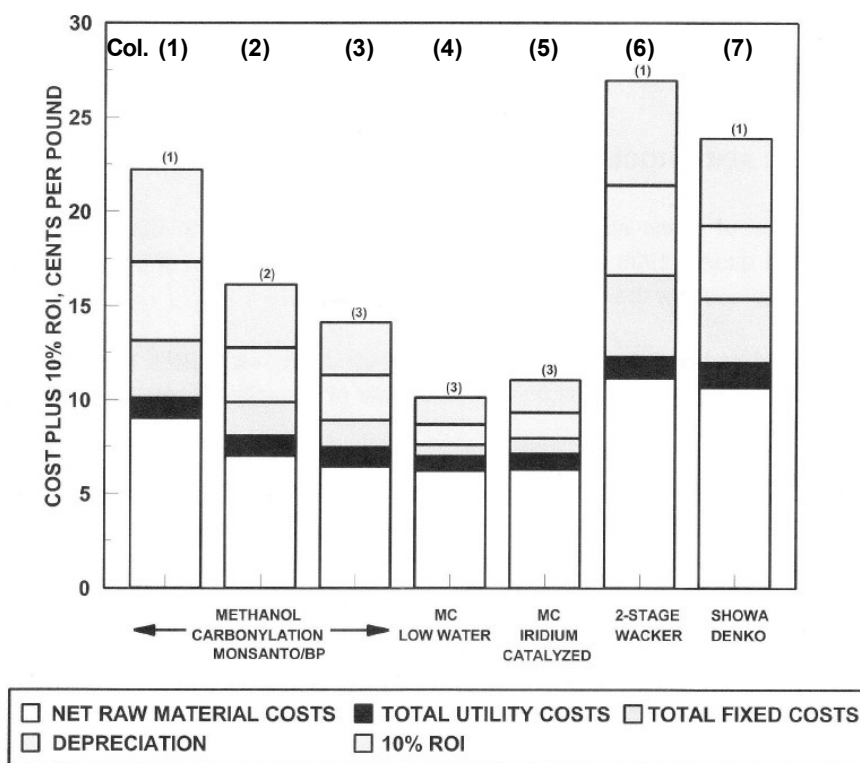


Figure 3-13 Comparative economics of commercial acetic acid processes (USGC, 2nd Quarter 1998) (33)



Column 1-3 represent the production costs for Monsanto carbonylation process at different production capacities:

- (column 1) 100,000 t/a: 0.22 U.S.\$/ pound (490 U.S.\$/t)
- (column 2) 300,000 t/a: 0.16 U.S.\$/ pound (356 U.S.\$/t)
- (column 3) 500,000 t/a: 0.14 U.S.\$/ pound (312 U.S.\$/t)

The production costs for Monsanto carbonylation process reached 490 U.S.\$ in 1998 (US Gulf region) for small acetic acid plant capacity of 100,000 t/a. The costs decrease strongly with increasing capacity.

Lowest production costs of 223 U.S.\$/t (0.10 U.S.\$/ pound) are achieved with Celanese low water process, considering a yearly capacity of 500 thousand tons (column 4), followed by iridium catalyzed methanol carbonylation process (column 5; 500,000 tons; 0.11 U.S.\$/pound / 241 U.S.\$/t). Ethylene oxidation processes (column 6 and 7) are smaller in capacity and due to higher raw material costs also higher in specific product costs (33).

Industrial Application

Acetic acid is a key intermediate product for the formation of acetates as shown in Table 3-10. More than 65% of acetic acid is produced for polymer production derived from vinyl acetate or cellulose. Poly vinyl acetate is used as filling material in paints and coatings and for the production of alcohols and plastics. Acetic acid and acetate esters are used as solvents or further processed into acetate fibers and cellulose plastics (28).

Table 3-10 Global acetic acid demand by end use in 10³ tons (33)

Application	1997	1998	1999	2000	2001	2002	Average Annual
							Growth Rate, %
							1997-2002
Vinyl acetate monomer	2,736	2,828	2,925	3,034	3,134	3,188	3.1
Purified terephthalic acid	964	970	1,018	1,088	1,147	1,226	4.9
Acetate esters	639	677	710	724	768	802	4.6
Cellulose acetate/acetic anhydride	758	768	778	788	798	808	1.3
MCA/other	629	661	690	718	739	762	3.9
Total	5,726	5,904	6,121	6,352	6,586	6,786	3.5

Table 3-10 shows the yearly demand on acetic acid by end use in thousand tons. The vinyl acetate monomer (VAM) production almost reaches 50% of acetic acid application, and has achieved a moderate average growth rate of 3.1% per year. The production of terephthalic acid, with a yearly demand on acetic acid of about one million tons, shows an average growth rate of almost five percent per year (33).

The installed global capacity of acetic acid reached 7 million tons in 1997, but the global demand was below 6 million tons, which led to a low overall operation rate of 85% (33). Carbonylation technique and market forecast led to an increase in capacity with an expected



average growth rate of 6% over the next years. 2010 the installed capacity reached 15.3 million tons, but the demand was low at 8.6 million tons, which led to an overcapacity of more than 40% (49). The acetic acid consumption was affected by the turmoil in global economy 2009 (50). For the next years the acetic acid market is expected to grow, as Global Industry Analysts, Inc. (GIA) reports, and the market is expected to reach 11.3 million tons by the year 2015 (50). Chemical Market Associates, Inc. (CMAI) analyzes an acetic acid demand increase to over 12 million tons by 2015 (46).

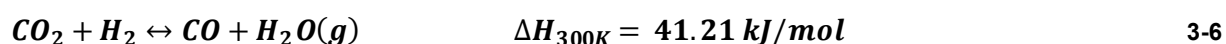
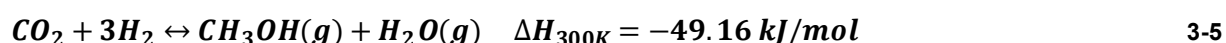
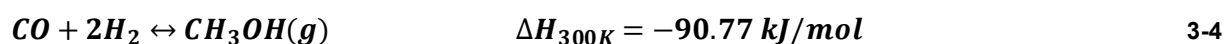
3.1.4 Methanol

Methanol (CH_3OH), a neutral, colorless, flammable and polar liquid with distinctive slightly sweet odor, is miscible with water, alcohols, esters and some other organic solvents. Due to its polarity, it dissolves inorganic substances.

Methanol is one of the most important intermediate products in chemical industry. 85% of the world's methanol production is used as feed or solvent media in chemical synthesis industry. 40% of methanol is processed into formaldehyde. Roughly 15% of methanol is applied for the fuel and energy sector (29).

Synthesis Process

Whereas the dry distillation of wood, the oldest industrial production of methanol, has lost its importance, the hydrogenation of carbon monoxide or carbon dioxide, according to the exothermic reactions 3-4 and 3-5, is the only industrial scale production of methanol nowadays. Besides the exothermic methanol reactions by catalytic conversion of synthesis gas, the endothermic reaction of CO_2 and H_2 , known as reverse water gas shift reaction (3-6), must also be taken into account (29), because part of the hydrogen is consumed.



Due to thermodynamic equilibrium, the gas phase methanol synthesis process is determined by the Stoichiometry Number (SN), which is defined by the equation 3-7.

$$\text{SN} = \frac{[\text{H}_2] - [\text{CO}_2]}{[\text{CO}] + [\text{CO}_2]} \quad 3-7$$

For ongoing reaction the Stoichiometry Number has to stay slightly higher than the theoretic value of 2.0. Usually SN ranges between 2.0 and 2.3 (51). Higher SN-values lead to a surplus of hydrogen. The SN-number can be reduced by the injection of CO_2 or by auto-thermal reforming of natural gas, both industrial scale and state of the art technologies (25).



Industrial scale gas phase production technologies are classified by the operating pressure into high-, medium- and low-pressure gas phase synthesis. Table 3-11 shows operating conditions, catalyst material, activity and selectivity of these three major process types.

Table 3-11 Process types for hydrogenation of carbon oxides [based on (29) and (51)]

Synthesis Process	Pressure	Temperature	Catalyst	Activity	Selectivity
High-pressure	25 - 35 MPa	300 - 450°C	ZnO/Cr ₂ O ₃	Medium	Medium
Med.-pressure	10 - 25 MPa				
Low-pressure	5 - 10 MPa	220 – 300°C	Cu/ZnO/Al ₂ O ₃ (new) Cu/ZnO/Cr ₂ O ₃ (old)	High; >99%	High; >98%

With the introduction of the low pressure hydrogenation technology, which is flexible in plant capacity, low in investment and production costs, practically all new plants have been based on this technology. The last high pressure methanol plant was closed in the 1980s.

Technology, Capacity and Syngas Requirements

Technology: The current industrial processes mainly differ in reactor design, which can either be adiabatic (e.g. ICI process) or quasi-isothermal (e.g. Lurgi process). Table 3-12 lists the market shares of the major methanol licensors (51).

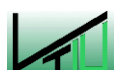
Table 3-12 Market share of methanol process licensors for the period 1999-2003 [based on (51)]

Process Licensor	Market Share
ICI	61%
Lurgi	27%
MGC	8%
Kellogg	3%
Other	1%

Nowadays over 60% of the world's industrial methanol production is based on the ICI low pressure process, which includes three sections: Syngas generation, methanol synthesis and methanol purification (51).

The ICI Low Pressure Process (Figure 3-14): After reforming, ratio adjustment (not shown) and syngas compression, the syngas is fed into the ICI converter, where the syngas reacts on a heterogeneous catalyst to form methanol. Product gas and un-reacted syngas exit the reactor on the top end. After cooling section the crude methanol is separated from un-reacted gas and enters the distillation columns for purification. Some of the unreacted syngas is recycled and mixed with fresh synthesis gas, the rest of the gas flow needs to be purged, as a further recycling would lead to inert gas enrichment.

The ICI converter operates at low pressure between 5 and 10 MPa and temperatures between 200 and 300°C. To cool the converter from heat of the exothermic reactions, cold syngas is injected during reaction. The ICI process delivers high selectivity and high



synthesis rates, but disadvantageously the methanol production is sensitive to changing reactor bed temperature. Thermal swings, which occur during plant set up, reduce catalyst life time (52).

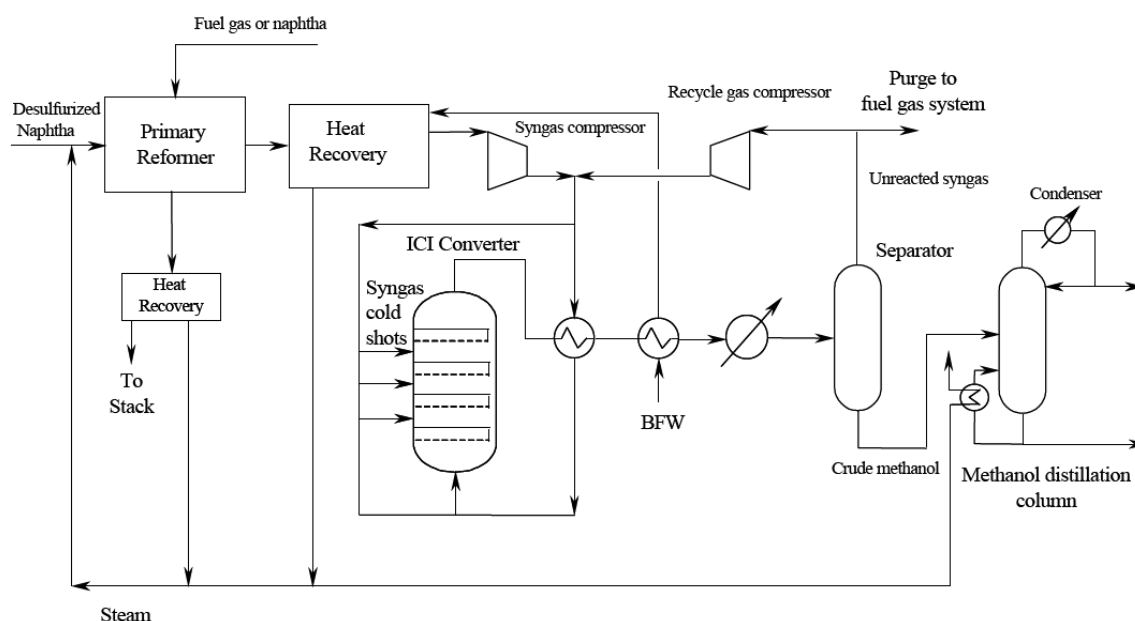


Figure 3-14 The ICI low pressure process (52)

Besides the steam reforming of natural gas the gasification of coal is an alternative option to generate syngas. Due to the fact that the gasification syngas is low in hydrogen and the $H_2:CO$ -ratio does not reach the SN-number of 2, a water gas shift reactor has to be installed before the gas enters the methanol reactor.

Within the Clean Coal Technology (CCT) Program of the U.S. Department of Energy the Liquid Phase Methanol (LPMEOHTM) process has been developed during the 1980's. This process is based on a slurry reactor system using fine catalyst particles (solid) which are suspended in an inert hydrocarbon liquid. This slurry reactor has been designed to convert syngas, low in hydrogen (e.g. from coal gasification), into methanol without a previous shift reaction unit. The process conditions of the LPMEOHTM process are shown in Table 3-13.

Table 3-13 LPMEOHTM for hydrogenation of carbon oxides [own description based on (51)]

Process	Pressure	Temperature	Catalyst	Catalyst System
LPMEOH TM	7 - 8 MPa	~ 250°C	catalyst particles: ZnO/Cr ₂ O ₃ hydrocarbon liquid: mineral oil	fine catalyst particles suspended in inert hydrocarbon liquid

The LPMEOHTH process can convert syngas from steam methane reforming, which is rich in H_2 , as well as syngas from coal gasification, rich in CO. Test runs in the late 1990's with CO-rich syngas, and a varying $H_2:CO$ -ratio from 0.4 to 0.6, showed that the deactivation rate of the catalyst was equivalent to test runs with H_2 -rich syngas ($H_2:CO$ -ratio up to 5.6).



Carbon monoxide rich syngas can be mixed with steam before entering the reactor system, where the inverse water gas shift reaction and the methanol synthesis reactions take place. One of the main advantages of this process compared to the gas phase process is the heat management of the reactor system. Changes in syngas composition during operation are tolerated due to the liquid in the reactor, which buffers the excess heat and transfers the heat into an external heat drum for steam generation during process. Even extreme start/stop operations do not impact the highly stable character of the process. Within the test run an availability of 96% was reached. The methanol product from the liquid phase process, when feeding CO-rich syngas, contains only 1% water. Compared to the gas phase methanol process, with a product water content of 4 to 20%, the LPMEOH™ process saves costs in the final purification of raw methanol (53).

The LPMEOH™ synthesis process (Figure 3-15): Feed gas and carbon monoxide are passed through an activated carbon bed, to remove possible contaminants like iron and nickel carbonyls. After mixing the feed and the recycle gas, the syngas is preheated and fed into the reactor. Mixed with catalyst slurry the gas converts partially into methanol vapor. The catalyst slurry absorbs the heat of reaction and transfers it into the steam drum, where steam with varying pressure up to 2 MPa is generated accordingly, to control the reactor heat. After reaction the product gas leaves the reactor and is separated from slurry droplets. After heat exchange and condensation, the methanol product is separated from inert gas, which is purged and un-reacted syngas, which is recycled. Methanol is sent to the distillation column.

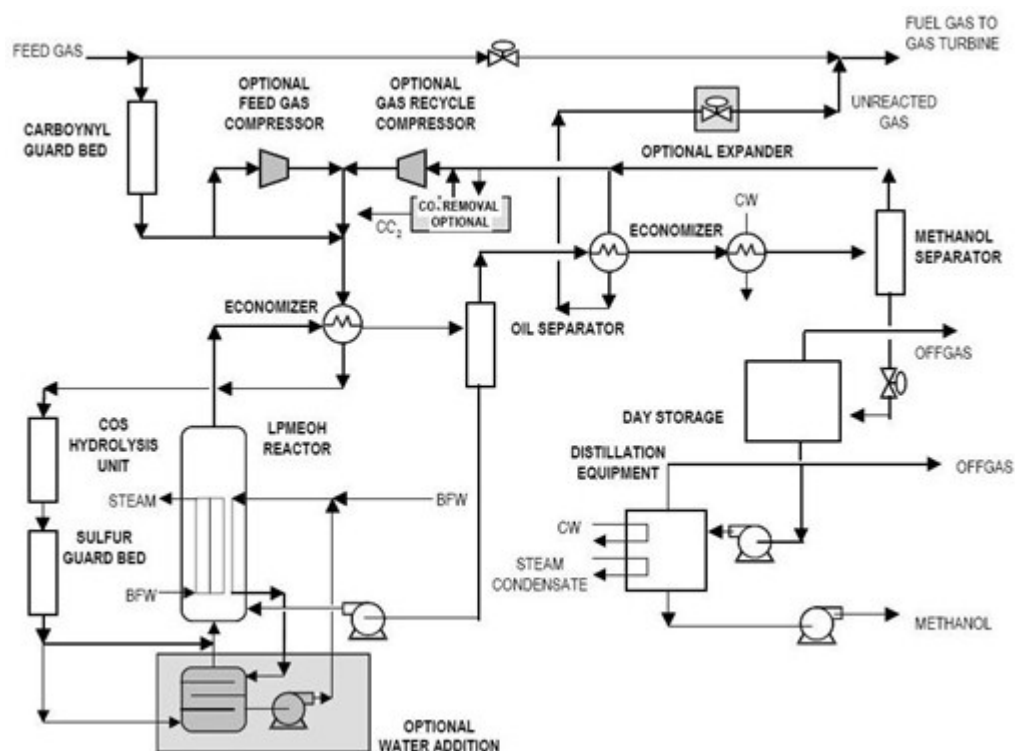


Figure 3-15 Simplified LPMEOH™ process flow diagram (54)



Capacity: The typical plant capacity of a conventional single train gas phase process ranges between one and two million tons per year.

The capacity of the LPMEOH™ demonstration plant in Eastman, Kingsport (USA) reached a capacity of 260 tons per day at the end of the 20th century (53).

Syngas requirements: The syngas specifications for the low pressure methanol production and for LPMEOH™ production are listed in Table 3-14 .

Table 3-14 Steam reformed natural gas composition for gas-phase methanol production, and the range of syngas ratio for LPMEOH™ synthesis [own description based on (15), (51), (55)]

Gas compound	Methanol syngas generated from steam reformed natural gas		LPMEOH™ range
	without CO ₂ injection	with CO ₂ injection	
H ₂ [vol. %]	74	68.3	
CO [vol. %]	16.4	20.1	
CO ₂ [vol. %]	6.2	8.6	
CH ₄ [vol. %]	3.4	3.1	
H ₂ S [ppm _v]	0.1 – 5*		0.1 – 5*
H₂:CO ratio	4.5	3.4	0.4 – 5.6
SN:=(H ₂ -CO ₂)/ (CO+CO ₂) > 2	3.0	2.1	
Process parameter			
p [MPa]	2.5	2.5	7 - 8
T [°C]	886	886	~250°C

Inert gases like nitrogen do not influence the process, but with high inert gas content, a higher gas volume flow has to be compressed and put into synthesis reaction, which enlarges equipment size and increases energy demand for compression. Oxygen, sulfur- and halogen-compounds have to be limited in the synthesis gas due to the risk of catalyst poisoning. The values of sulfur and halogens have to be very low, typically between 0.1 and 5 ppm_v (55).

Neither the low-pressure gas phase synthesis of methanol, nor the LPMEOH™ synthesis are sensitive on changes in syngas amount, even if the gas is not available for a period of time. The former process remains circulating under operating temperature and pressure, while the latter process is non-sensitive to varying conditions due to the catalyst slurry.

Material and Energy Demand

Raw material, utility demand and by-product credits for methanol production from coal by gasification and liquid phase methanol synthesis process are shown in Table 3-15, and for common gas phase methanol synthesis process in Table 3-16, both at small capacity of roughly 300 thousand tons per year.



Table 3-15 Fuel grade methanol by LPMEOH™ synthesis; syngas from coal (small unit) (24)

Methanol from LPMEOH™ and coal gasification process		
capacity (small unit)	t/a	298,054
Raw material		
	per 10 ³ t methanol	
syngas from coal	MJ	24.29
Catalyst & Chemicals	-	
By-product credits		
Utilities		
Power	kWh	5.1318
Steam, VLP	kg	0.1322
Utility credits		
		-
Fuel	MJ	0.2270
Steam, MP	kg	1.3861

Table 3-16 Common gas phase methanol synthesis; syngas from SMR (small unit) (24)

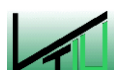
Methanol from NG via SMR		
capacity (small unit)	t/a	296,000
Raw material		
	per 10 ³ t methanol	
Natural gas	MJ	36.78
Catalyst & Chemicals	-	
By-product credits		
Utilities		
Power	kWh	0.0299
Cooling Water	m ³	0.0499
BFW	m ³	0.0013
Utility credits		
Steam (1.4 MPa)	kg	0.3454

Production Costs

The production costs for methanol, including 10% ROCE for small and large capacity, are shown in Table 3-17, and visualized in Figure 3-16. The costs for methanol synthesis in the Middle East (M.E.) are low due to the low price of natural gas.

Table 3-17 Costs for methanol production (24)

	Small capacity (296,000 t/a)	Large capacity (1,825,000 t/a)
LPMEOH™ (fuel grade) from coal gasification	294.5 \$/t methanol exclusive purification	230 \$/t methanol exclusive purification
Methanol synthesis form natural gas via SMR	324.1 \$/t methanol	277.3 \$/t methanol



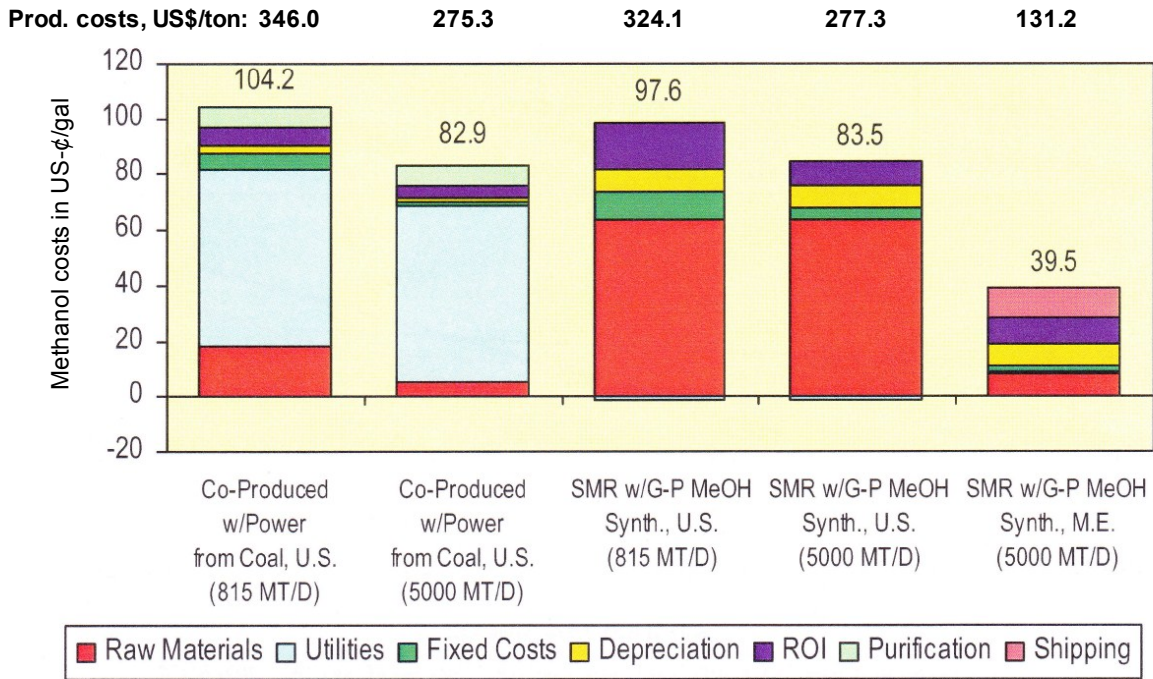


Figure 3-16 Comparison of methanol cost for various feedstock, capacities, and locations – including purification to chemical grade and shipping from M.E. (pricing basis 2nd quarter 2004) [(24) modified]

The gas phase methanol production costs are strongly dependent on the natural gas price, as shown in Figure 3-17 (continuous lines: red: cash cost; blue: includes 10% ROCE). The dependence for LPMEOH™ synthesis from coal syngas on coal price is lower as the dotted lines show (red: cash cost; blue: includes 10% ROCE).

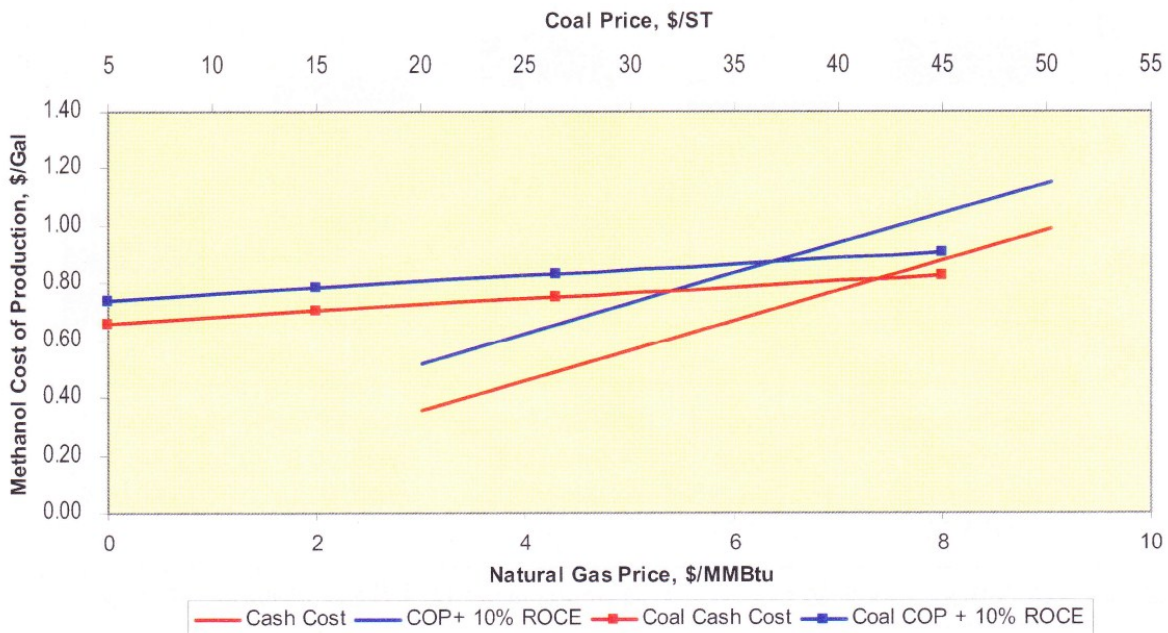


Figure 3-17 Effects of feedstock prices on methanol cost of production (2nd quarter 2004; 5,000 MT/D, via SMR and Coal Gasification/ LPMEOH™ -.-.-) (24)



Industrial Application

As shown in Figure 3-1, methanol is one of the major intermediates for chemical synthesis processes. Besides the utilization as raw material for the production of formaldehyde, methyl-tertiary-butyl ether (MTBE), acetic acid and other chemicals, it is commonly used as solvent and fuel (56). Figure 3-18 outlines the demand on methanol by end use product in 2007. Over 50% of the world's methanol production has been used for the generation of formaldehyde, methyl tertiary butyl ether (MTBE) and acetic acid, but only about 10% have been used as fuel. Due to the large consumption in Northeast Asia, the overall demand for methanol has been expected to grow within the period 2007-2012 by an annual growth rate of 9%, with only low growth in the industrialized areas.

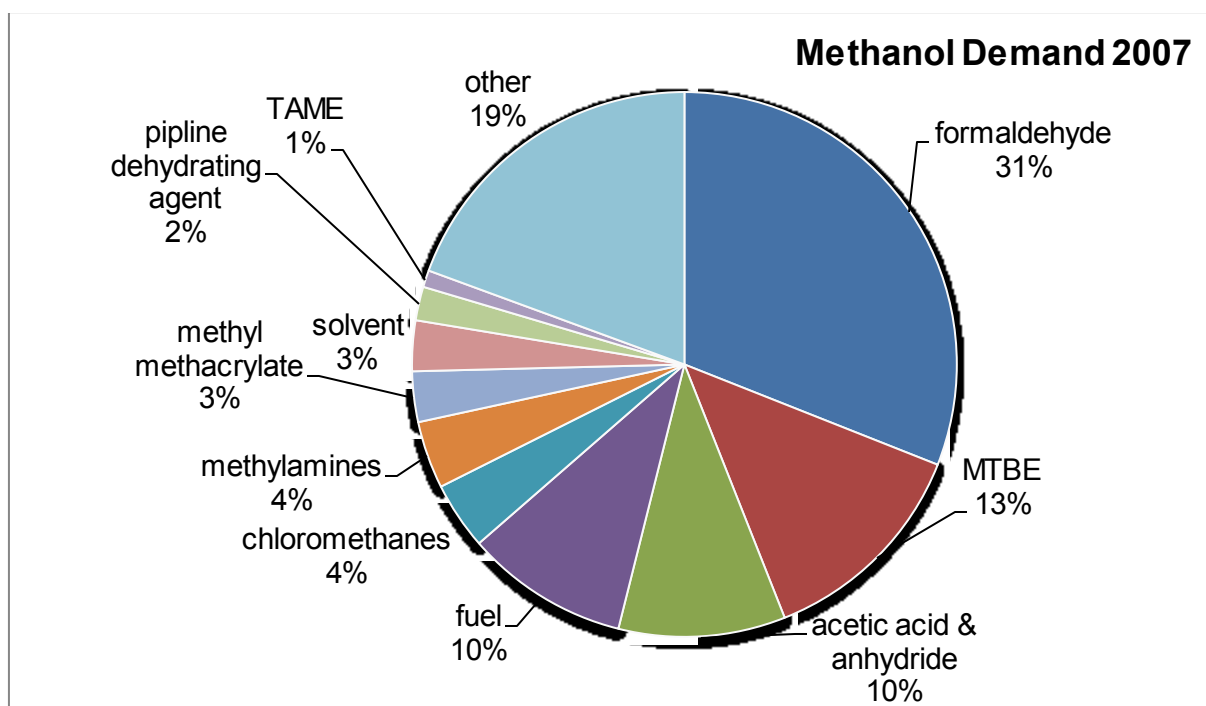


Figure 3-18 World demand for methanol by end use – 2007 [based on (51)]

Table 3-18 illustrates the changing share on methanol demand by the main regions including the expected annual growth rate. Highest growth rates are expected in Africa (almost 50%) followed by Northeast Asia (15%), while a reduction of the methanol consumption is only expected for North America.

Table 3-18 World consumption of methanol [based on (51)]

	2007	2012	average annual growth rate
North America	18.0%	12%	-0.3%
Central and South America & Caribbean	3.0%	2%	4.3%
Europe	26.0%	18%	1.5%
Africa	0.5%	2%	48.5%
Middle East	8.0%	10%	13.0%
Indian Subcontinent	1.7%	1%	4.8%
Northeast Asia	38.0%	50%	15.2%
Southeast Asia	4.4%	4%	5.7%
Oceania	<0.5%	<0.5%	2.7%
Total	100.0%	100.0%	8.9%

Whereas the world production capacity of methanol was at 22 million tons in 1993 (29), the capacity installed reached over 50 million tons in 2007, and is expected to grow with an average growth rate of 12.5% in the period 2007 – 2012. Figure 3-19 illustrates the methanol production capacity by region in 2007 with a total capacity of 52.1 million tons and the expected capacity in 2012 with 93.9 million tons of methanol (51).

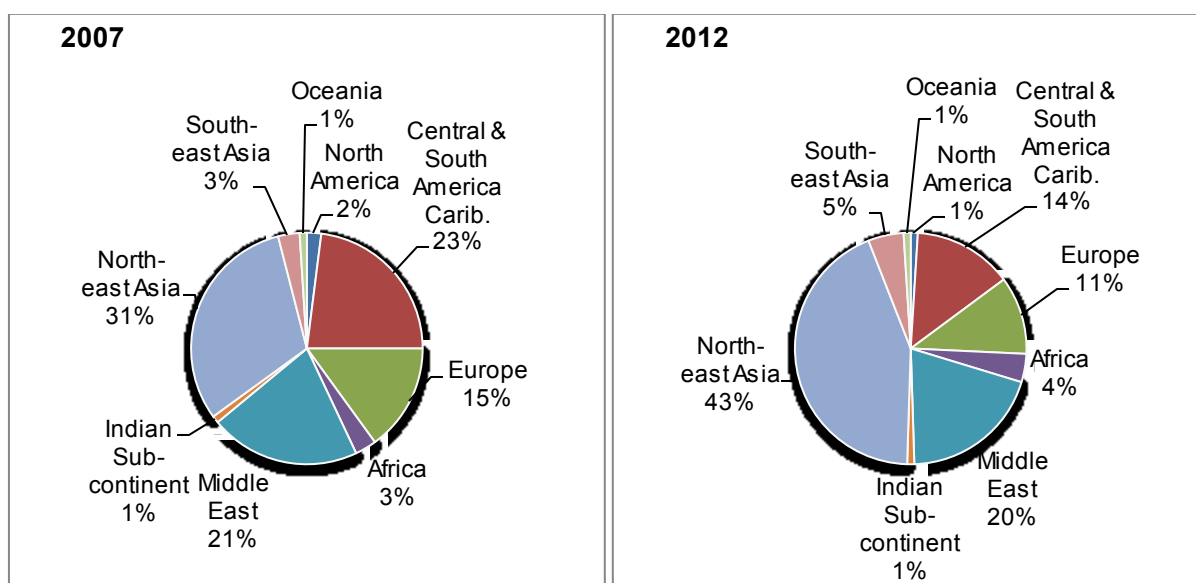


Figure 3-19 World capacity of methanol by region [based on (51)]



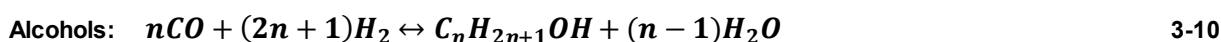
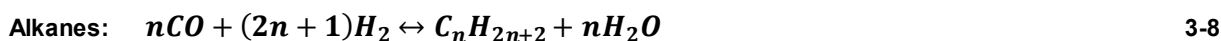
3.1.5 Fischer-Tropsch Liquids

Fischer-Tropsch liquids are synthetic fuels, obtained from solid, liquid or gaseous hydrocarbon feedstock, manufactured via Fischer-Tropsch conversion. In the Fischer-Tropsch process, syngas reacts catalytically to form liquid products like gasoline, diesel or waxes, depending on the Fischer-Tropsch process type applied.

Due to the high level of the product quality achieved by synthetic generation of fuels, the Fischer-Tropsch fuels attain lower emissions in major criteria pollutants like SO_x or particular matter.

Synthesis Process

Within the Fischer-Tropsch synthesis reactions, hydrogen and carbon monoxide in a ratio of about 2 react over an iron or cobalt based catalyst to form a mixture of liquid hydrocarbons and waxes, as shown in the equations 3-8 – 3-10. Besides the formation-reaction of Fischer-Tropsch liquids, e.g. synthetic lubrication oils and fuels, the water gas shift reaction can be supported by using an iron-based catalyst.



Coal (gasification) and natural gas (steam methane reforming) are the main syngas sources for the Fischer-Tropsch synthesis process. Table 3-19 shows the range of syngas composition converting coal using a fixed-bed, a fluidized-bed and an entrained flow gasifier-type. Whereas steam reforming of natural gas produces syngas rich in hydrogen ($\text{H}_2:\text{CO} > 3$) and the Lurgi fixed-bed dry-ash gasifier produces syngas with a $\text{H}_2:\text{CO}$ -ratio of two, the syngas from the entrained flow gasifier (Shell) is low in H_2 (syngas-ratio below 0.5) and CO has to be shifted with steam into H_2 and CO_2 to gain an appropriate $\text{H}_2:\text{CO}$ -ratio.



Table 3-19 Gasification performances (57)

Parameter	Blue water-gas	Dry-ash Lurgi	BGC Lurgi	KRW	Shell
Gasification pressure, MPa	atmospheric	2.4	2.4	2.8	4.5
Exit gas temperature, °C	700	540	450	980	1420
Gasification type	water – gas set	fixed-bed	fixed-bed	fluidized-bed	entrained
Input ratios of reactants					
Steam: coal, daf ^a	1.5 ^b	1.34	0.33	0.37	0.03
Oxygen: coal, daf ^a	—	0.36	0.39	0.80	0.83
Raw gas composition, mol %					
H ₂	47.3	23.0	21.9	24.9	30.9
CO	37.0	11.1	43.8	32.7	64.4
CH ₄	1.3	6.7	5.2	4.3	0
C ₂	0.0	0.3	0.3	0	0
CO ₂	5.4	17.6	2.1	16.6	2.4
H ₂ O	—	41.0	26.3	20.8	1.4
Others	9.0	0.3	0.3	0.8	0.9
H ₂ : CO ratio	1.28	2.07	0.50	0.76	0.48
Net efficiency (LHV)	50.0 ^c	65.0	76.0	74.0	83.0

^a Dry, ash-free.

^b Steam to dry coke ratio.

^c Based on dry coke.

The Fischer-Tropsch synthesis is non selective except the formation of C₁-compounds like methanol. But typically, the Fischer-Tropsch (FT) product range includes compounds of one to over one hundred C-atoms. Due to changes of the operating parameter the product range can vary from light to heavy hydrocarbons (57).

Figure 3-20 shows the simplified flow diagram of the Shell middle distillate synthesis (SMDS) for the production of paraffinic, sulfur and nitrogen free fuels, including the Fischer-Tropsch process and the hydro cracking section.



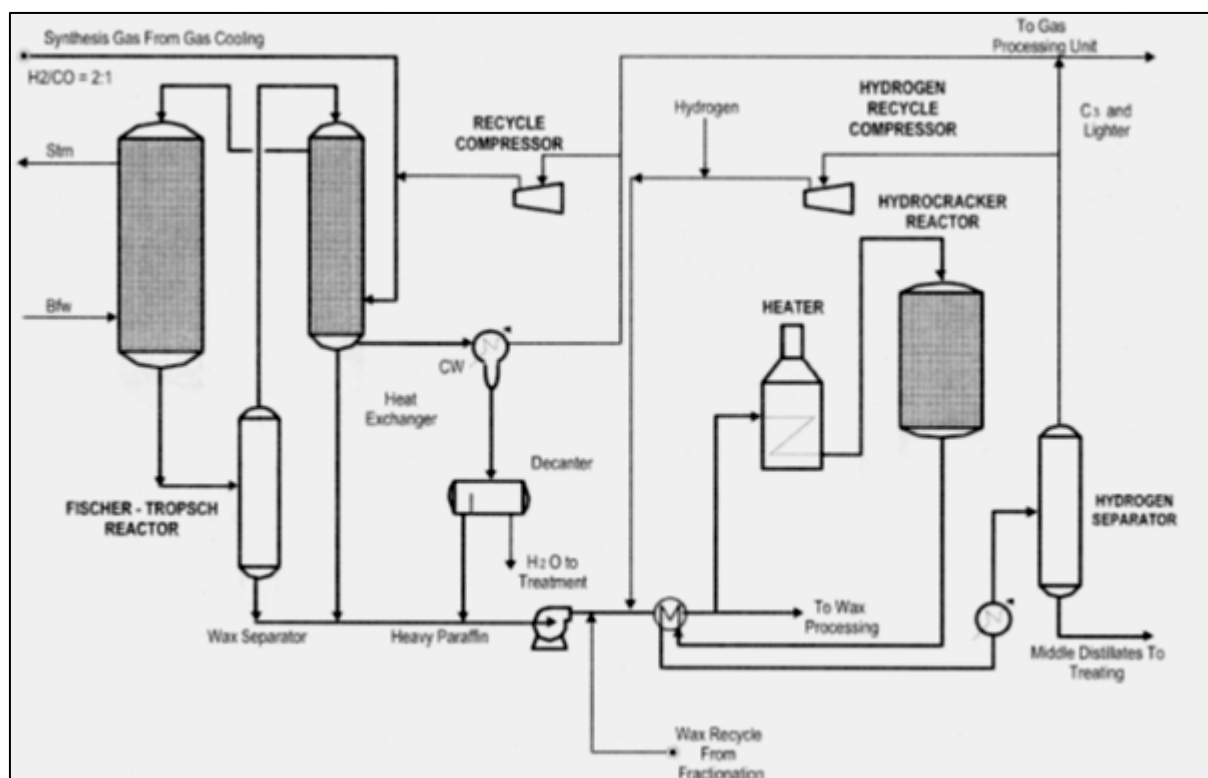


Figure 3-20 Simplified flow diagram SMDS process (15)

The syngas enters the tubular fixed bed reactor for the heavy paraffin synthesis on a zirconium promoted cobalt catalyst. The heat of reaction is controlled by steam generation from pressurized water in the shell side of the reactor. Liquid synthesis products and vapor leave the reactor, wax is separated and the condensable hydrocarbons, including water, are separated from the un-reacted syngas, which is recycled and mixed with fresh syngas in the ratio of 0.4 to maintain a moderate CO_2 concentration (15).

Technology, Capacity and Syngas Requirements

Technology: There are two technologies based on Fischer-Tropsch synthesis,

- the low-temperature Fischer-Tropsch process (LTFT), which promotes the formation of diesel and heavy hydrocarbons and
- the high-temperature Fischer-Tropsch process (HTFT), which leads to gasoline and light olefins.

The operating conditions of the two process types are shown in Table 3-20 (57).

Table 3-20 Process conditions of Fischer-Tropsch reactors [based on (57)]

Process type	Low Temperature Fischer-Tropsch	High Temperature Fischer-Tropsch
Abbreviation	LTFT	HTFT
Temperature, °C	220 - 250	330 - 350
Pressure, MPa	2.5 – 4.5	2.5
CO / H ₂ conversion	60% - 90%	85%
Catalyst	iron based or Ni-supported	Iron based
Main products	diesel, wax	gasoline, chemicals (light olefins)
Product-ratio: gasoline : diesel	20 : 80	80 : 20
Reactor type	- tubular fixed bed reactor - slurry bed reactor (installed capacity: 3,000 m ³ /d)	- circulating fluidized bed (CFB) Reactor - Sasol advanced synthol reactor (SAS Reactor, installed capacity: 3,200 m ³ /d)

For each process type, two common reactor types have been developed.

Common reactor types for the LTFT – process:

- The tubular fixed bed reactor: in operation with an iron catalyst since 1953 (SASOL); and in operation with a supported cobalt catalyst since 1993 (Shell, Bintulu, Malaysia).
- The slurry bed reactor: operating commercially since 1993 with a catalyst dispersed in waxy slurry (SASOL) (57).

Common reactor types for the HTFT – process:

- The circulating fluidized-bed Reactor (CFB): Three plants in operation since 1955 at SASOL, 16 CFB reactors have been installed in the 1980s. Disadvantageously, the CFB reactor causes high pressure loss over the reactor system, which led to the development of:
- The SAS reactor, which operates with a solid – gas fluidization (57).

Capacity: Table 3-21 lists some of the major gas-to-liquid (GTL) plants, showing GTL-capacity and start-up date. E.g. the plant capacity for the PetroSA refinery in Mossel Bay is 36,000-barrel-per-day, the GTL component of the plant produces 22,000 b/d of Fischer-Tropsch liquids. New plants like the Pearl GTL plant reach higher capacities and lead to very low operating costs, which have been estimated to be at 6 \$/ barrel by Shell (58).



Table 3-21 Some GTL plants and capacities, including start-up date [based on (59), (60), (61)]

Plant	Company	Start-up	GTL capacity [barrel/d]	GTL capacity [m ³ /d]
Mossgas GTL	Petro SA	1991	22,500	3,580
Sasolburg	Sasol	1993	2,500	398
Bintulu	Shell	1993	12,500	1,989
QGTL	Sasol	2006	34,000	5,410
EGTL	Sasol Chevron	2006	34,000	5,410
West Damietta	Shell	2006	75,000	11,933
Qatar, Ras-Laffan: Oryx Gas-to-Liquids	Qatar Petroleum & Sasol	2006	34,000	5,410
Qatar, Ras-Laffan: Pearl Gas-to-Liquids	Qatar Petroleum & Royal Dutch Shell	2011 (1 st phase) 2012 (2 nd phase planned)	140,000	22,276

Syngas Requirements: Requirements on the syngas-ratio depend on the catalyst system applied. Whereas shift active iron catalysts for HTFT processes promote syngas with a H₂:CO-ratio down to 0.6, the new cobalt based catalyst systems for LTFT show low activity and the syngas-ratio has to be adjusted to a value of 2 within the previous syngas treatment. But cobalt based catalysts achieve much higher life time and produce mainly linear alkanes and clean synthetic fractions of diesel, which are free of sulfur and aromatics. Iron catalysts are not that efficient and aromatics are formed, but advantageously the price for this catalyst material is very low. Table 3-22 lists the price-ratio for possible catalyst materials.

Table 3-22 Relative prices of metals (March 1989) (62)

Metal	Price ratio
Iron	1
Cobalt	230
Nickel	250
Ruthenium	31,000
Rhodium	570,000

Material and Energy Demand

Raw material and energy demand for a Fischer-Tropsch synthesis plant, converting biomass with a feedstock capacity of 500,000 kg/h into diesel (~70,000 kg/h product), are listed in Table 3-28. The table includes material and energy demand for gathering, transportation and autothermal reforming of the pyrolysis oil from biomass residues. Dry syngas produced by partial oxidation within the process amounts to 2.545 kg/kg product (almost 175,000 kg H₂ & CO per hour) (63).



Table 3-23 Raw material and external energy demand for Fischer-Tropsch synthesis of biomass residue including gathering, bale, transport and partial oxidation of biomass (63)

Product capacity	kg/h	70,000
Raw material	per kg product Diesel	
Biomass residue (30% water)	kg	7.294
Oxygen	kg	0.707
Water	kg	1.180
Utilities		
External energy, cumulated	MJ	3.706
Net energy available of feedstock and product		
Biomass residue (30% water) (12.7 MJ/kg biomass)	MJ	92.875
Diesel	MJ	39.093

Water (4,350 kg/h) and CO₂ (203,567 kg/h) are removed before entering the Fischer-Tropsch synthesis (63). A flow chart of the modeled process is shown in Figure 3-21.

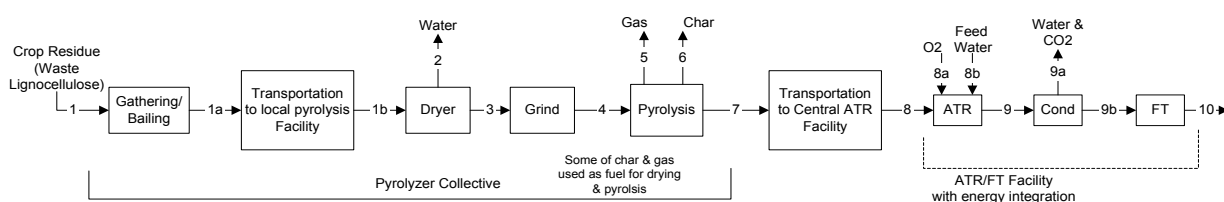


Figure 3-21 Modeled process for the conversion of biomass into liquid transportation fuel. Credit: ACS, Mangano et al (63)

Production Costs

Investment costs for the new GTL Plant Pearl in Ras-Laffan (Qatar), with completion in 2012 (2nd phase/ 1st phase 2011) have been estimated to be between 18 and 19 billion U.S.\$ (61). The maintenance costs are expected to be low and the operating costs should be around 6 U.S.\$/barrel (estimated by Shell). The total production cost have been estimated to be somewhat below 100 U.S.\$/barrel, leading to economic benefits with the rising crude oil prices (58).

Industrial Application

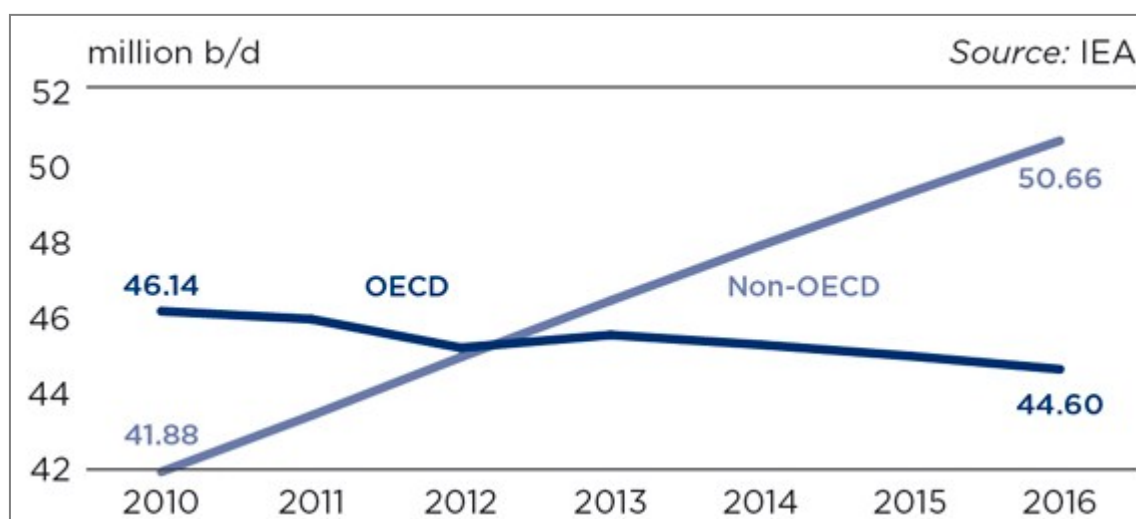
Depending on the product fraction, the Fischer-Tropsch liquids are used as synthetic fuel, but also as chemicals and waxes. Table 3-24 shows the typical product composition of low- and high-temperature Fischer-Tropsch synthesis process. The high-temperature process leads to aromatics, a higher number of alkenes and less alkanes.



Table 3-24 Typical Product Composition for LTFT and HTFT Reactors (with iron catalyst) [(15) modified]

	LTFT				HTFT	
	TFB reactor		SSPD reactor		Synthol	
	C ₅ - C ₁₂	C ₁₃ - C ₁₈	C ₅ - C ₁₂	C ₁₃ - C ₁₈	C ₅ - C ₁₀	C ₁₁ - C ₁₄
Alkane, %	53	65	29	44	13	15
Alkene, %	40	28	64	50	70	60
Aromatics, %	-	-	-	-	5	15
Oxygenates, %	7	7	7	6	12	10
n-Paraffins, %	95	99	96	95	55	60

Fischer-Tropsch liquids are synthetic alternatives to crude oil products like waxes, diesel or gasoline. The International Energy Agency (IEA) expects the world oil demand to grow with a rate of 4.5% within the period 2010 - 2016, which is a cumulative additional demand on oil of 7.2 million barrel per day for this period (see Figure 3-22). The average price is estimated at 103 U.S.\$/barrel. Most of the increase in demand is related to non-OECD countries like China, rest of Asia and the Middle East (58).

**Figure 3-22 Global oil-demand forecast (Source: IEA) (58)**

Shell already began the shipment from Pearl gas to liquid products from Qatar in 2011, which reaches daily capacities of 140,000 barrel of fuel and 120,000 barrel of ethane and condensates (58). An outlook of GTL capacity is given in Figure 3-23, including the deferred project Tinhert (Algeria) and some unspecified projects, with start-up date before 2030 (64).



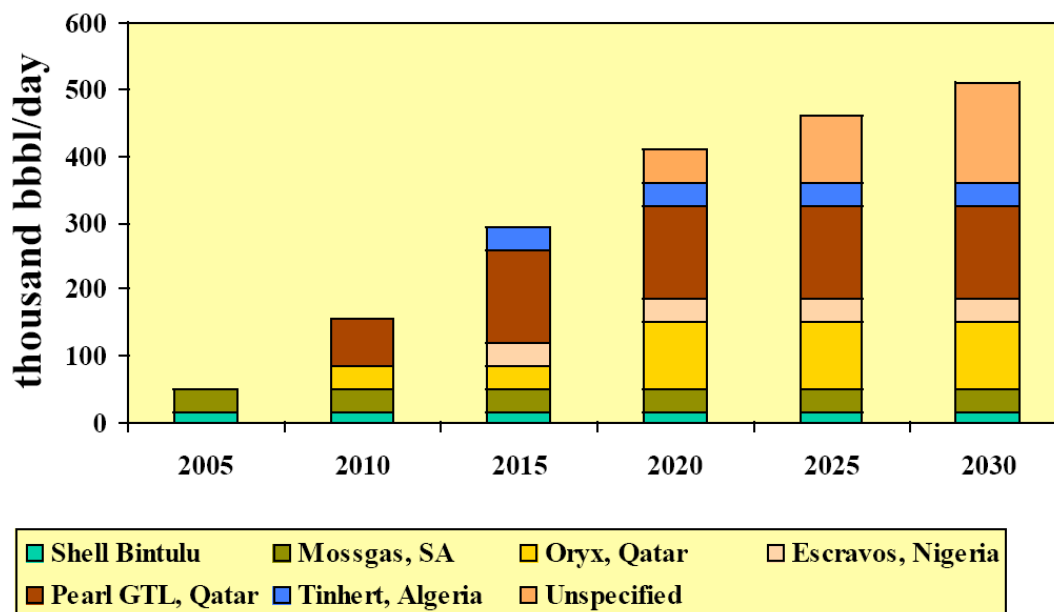


Figure 3-23 GTL capacity projection (64)

3.1.6 Hydrogen Production

Hydrogen (H₂), a color- and odorless, flammable gas, is mainly used in petroleum industry for upgrading of fossil fuels and in chemical industry for the production of ammonia and as hydrogenating agent. Further it serves as reducing agent or as fuel.

Despite water is a large source for H₂ generation by hydrolysis, the hydrocarbons still remain the main feedstock for an economic production. Approximately 50% of hydrogen is not produced directly, but is generated as by-product e.g. in chemical synthesis industry (30). The percentage of H₂ produced from main feed sources are listed in Table 3-25.

Table 3-25 H₂ production sources [(30) modified]

Feedstock	Share of Hydrogen produced
Petrochemicals	77%
Coal	18%
Electrolysis	4%
Other sources	1%

Petrochemicals are by far the most common feedstock, holding a share of three quarters. Figure 3-24 outlines the main production routes based on different feed and energy sources.



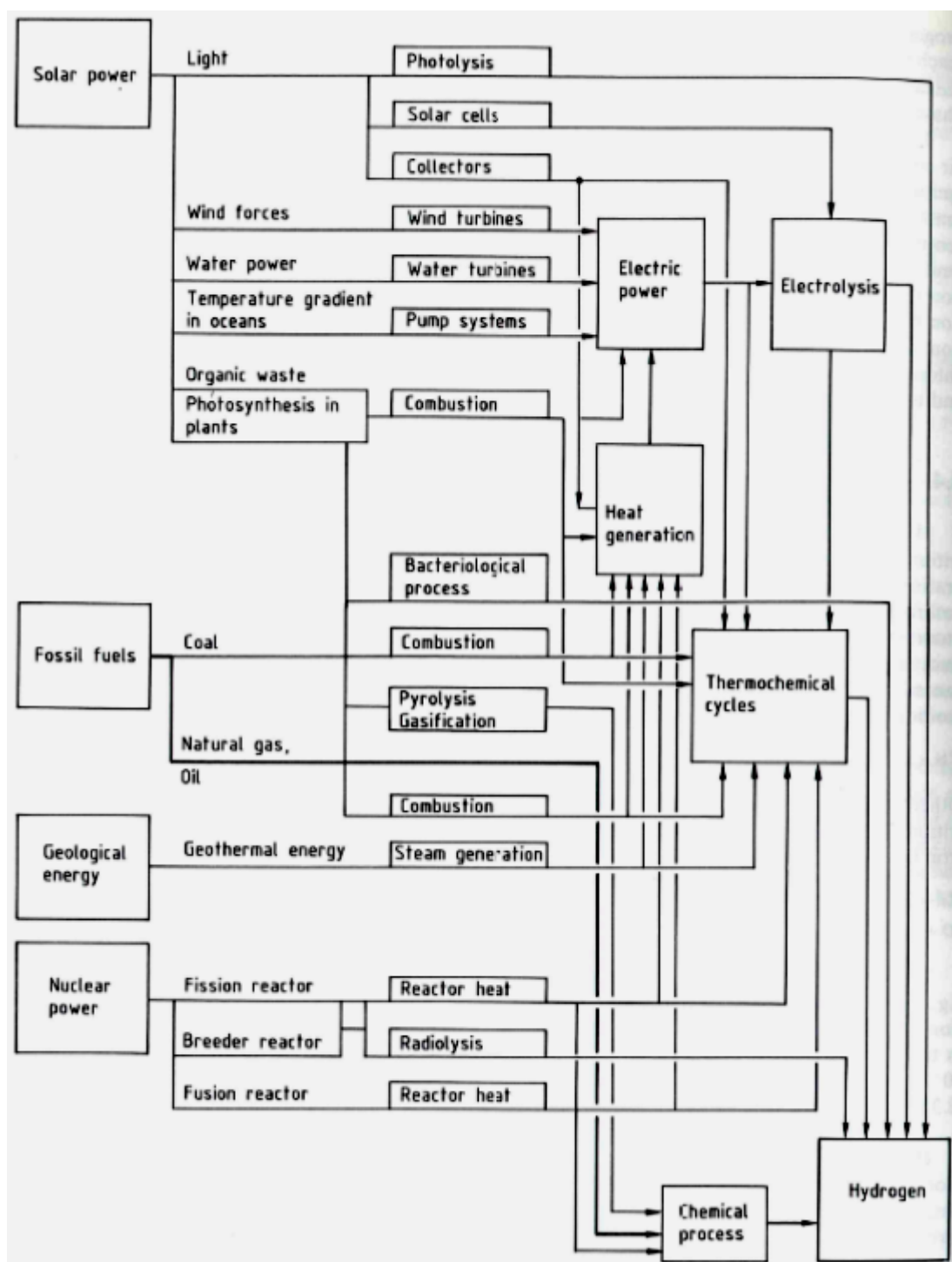


Figure 3-24 Primary energy, raw materials, production methods, path of production, transformation, and generation of and for hydrogen adapted from [4.1] (30)

Since the energy consumption for the production of hydrogen from water is 4 to 5 times higher than the production of hydrogen from hydrocarbon feedstock, most of the hydrogen used on industrial scale is produced from natural gas and oil. Only a small percentage is produced or co-produced by electrochemical processes. Table 3-26 shows the theoretical energy consumption for the production of hydrogen from hydrocarbons, coal and water.

Table 3-26 Theoretical energy consumption for the production of hydrogen from various hydrocarbons, coal and water [(30) modified]

Energy source	calculated as	energy consumption
Natural Gas	CH ₄	41.3 MJ/kmol H ₂
LPG	CH _{2.6}	37.5 MJ/kmol H ₂
Naphtha	CH _{2.2}	38.4 MJ/kmol H ₂
Heavy oil	CH _{1.4}	50.3 MJ/kmol H ₂
Coal	CH _{0.7}	57.2 MJ/kmol H ₂
Water	H ₂ O	242.0 MJ/kmol H ₂

Synthesis Process

The conventional chemical process route to convert hydrocarbon feedstock into H₂-rich synthesis gas includes reforming (or partial oxidation) and shift reaction, as described in chapter 3.2. After the shift process, hydrogen-rich syngas is commonly sent into the final purification section.

Technology, Capacity and Syngas Requirements

Technology: Nowadays pressure-swing adsorption (PSA) is state of the art technology for the production of high-purity hydrogen from shifted syngas. Over the last years PSA-technology covered more than 85% of global H₂-purification lines. Figure 3-25 shows a common hydrogen production route utilizing natural gas as feedstock.

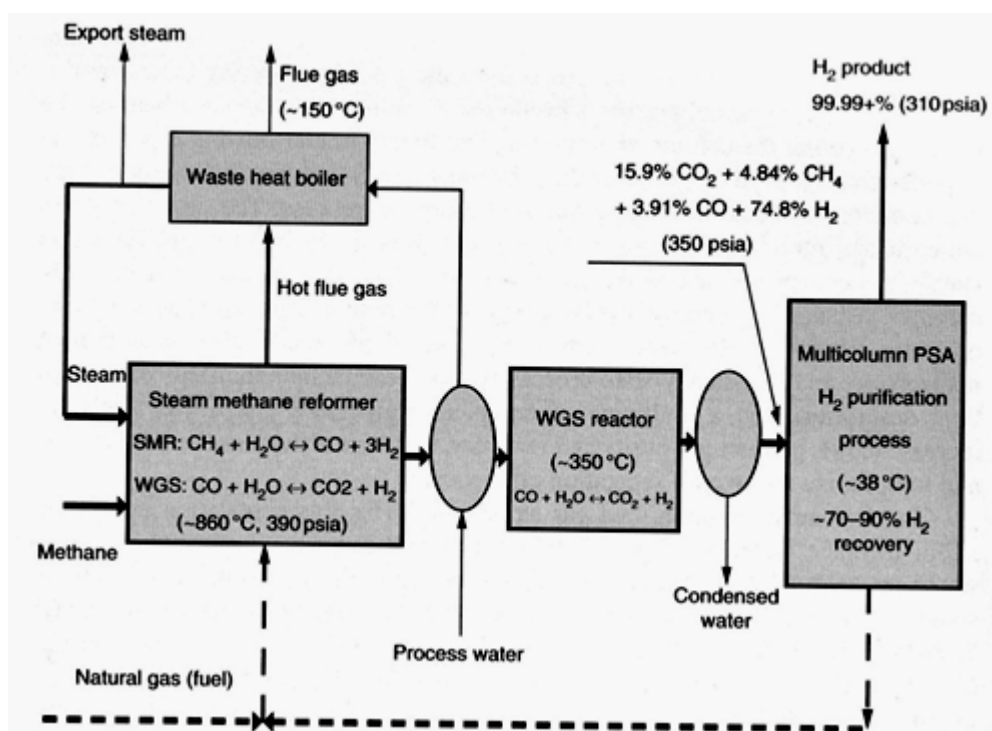


Figure 3-25 Conventional steam methane reforming (SMR) route for hydrogen production (65)



After steam reforming, heat exchange and shift reaction, the syngas enters the pressure-swing adsorption column. The feed gas is passed through the PSA adsorber-bed where impurities are selectively adsorbed and pure hydrogen is produced at feed gas pressure. For continuous gas flow, PSA plants commonly use 4 to 12 parallel absorber columns, which process in cyclic steps for adsorption, depressurization, purge and pressurization (65).

Figure 3-26 visualizes the block scheme of hydrogen and carbon monoxide co-production by low-temperature condensation, a PSA unit for high purity hydrogen and a rectification column for high purity CO. Feed gas from CO₂ absorber enters the adsorber unit (a) for final removal of CO₂ and H₂O traces. After cooling of the purified gas to CO condensation temperature in the heat exchanger (b) and in the sump of the CO-column, gas compounds like CO or inerts are separated from hydrogen by condensation (c). After heat exchange, the gaseous hydrogen is expanded (d) and sent to the PSA-plant, achieving a purity of 99.9%. CO is further purified by rectification (f) (30).

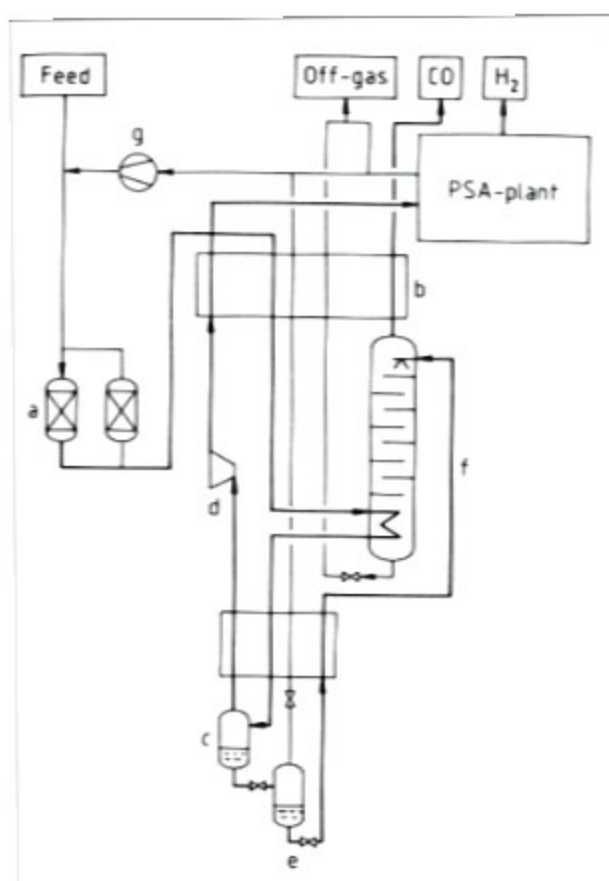


Figure 3-26 H₂ production from synthesis gas by low-temperature condensation and pressure-swing adsorption and production of pure carbon monoxide by rectification (30)

Capacity: Feed gas capacity of commercial scale pressure-swing adsorption plants ranges from 5,000 to 340,000 m³(STP)/h. The product capacity depends on the H₂ content in the feed gas and the recovery rate and is typically up to 150,000 m³(STP)/h (66).



Syngas requirements: Because a part stream of the H₂ product gas is used for the regeneration of the PSA unit, the percentage of H₂ in the PSA feed gas should be above 60%. Typical syngas compositions after reforming and shift reaction process and the product gas quality achieved are listed in Table 3-27.

The design of an industrial H₂-PSA process depends on product purity, which is determined by the application. The content of hydrogen in product gas ranges from 98 mol% to food grade hydrogen with 99.999 mol%. For hydrogen utilized in ammonia plants, the share of carbon oxides is limited by 10 ppm_v due to catalyst poisoning in downstream synthesis (65).

Table 3-27 Common feed gas composition after WGS for PSA system [based on (65)]

Gas compound	Feed gas		Product gas	Waste gas (used for combustion)	Recovery rate
	SMR off-gas	Refinery off-gas			
H ₂	70-80%	65-90%	98-99.999%	Unrecovered H ₂ and impurities	70-95%
CO	1-3%	-			
CO ₂	15-25%	-			
CH ₄	3-6%	3-20%			
N ₂	traces	-			
C _x H _y	-	5-11.5%			
H ₂ O	saturated	saturated	dry		
Gas conditions					
Pressure	0.4-3 MPa	0.4-3 MPa	feed gas pressure	0.1-0.2 MPa	
Temperature	20-40°C	20-40°C			

Material and Energy Demand

Raw material and utility demand for a hydrogen production plant with a yearly capacity of 800 million m³(STP) are listed in Table 3-28. The table does not include the final purification.

Table 3-28 Raw material and utility demand for H₂ production [based on (15)]

Capacity	m ³ (STP)/a	800 million
Raw material		
per 10 ³ m ³ (STP) H ₂		
Natural gas (as feed)	GJ	15.0
Natural gas (as net fuel)	GJ	0.4
Chemicals		-
Utilities		
Power	kWh	20.0
Cooling Water	t	3.0
Process Water	t	1.0
Utility credits		
Steam (HP)	t	-0.6



Production Costs

Syngas Generation: The production costs for hydrogen mainly depend on the local feedstock prices, which are determined by availability and government taxation. The costs for hydrogen production in Germany, based on different feedstock, are shown in Figure 3-27.

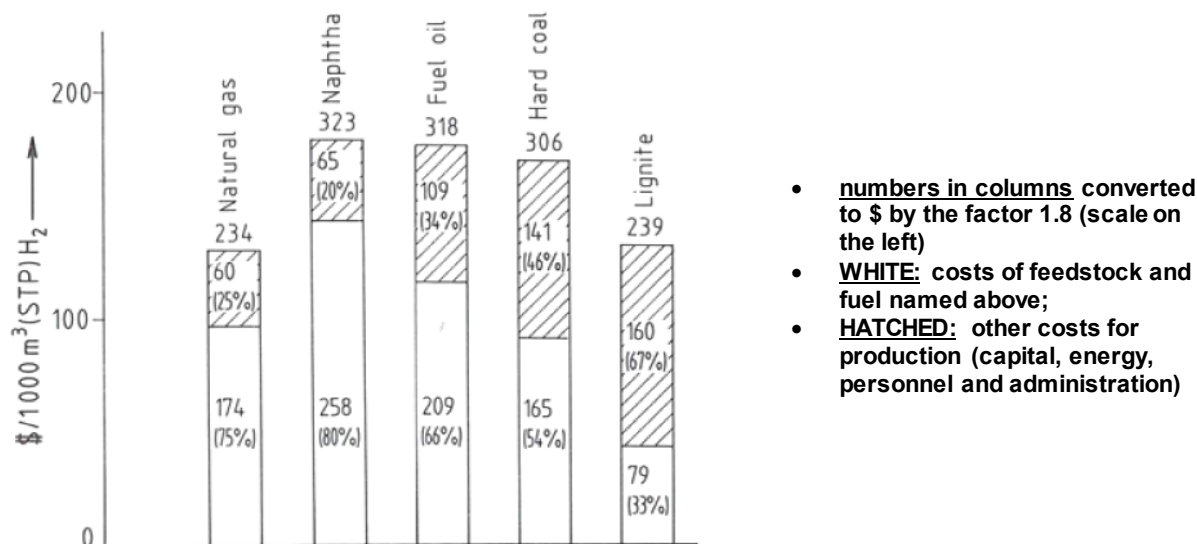


Figure 3-27 Feedstock and production costs for hydrogen in the Federal Republic of Germany in 1983 in DM/1000 m³(STP) H₂ (30)

The steam reforming of natural gas is the most economic production route for hydrogen. Due to the high prices for natural gas, the feedstock costs hold a share of 75% of the production costs in Germany, which are around 130 U.S. \$/10³ m³(STP). A hydrogen plant situated in the Middle East can purchase natural gas at very low price, which leads to production costs of roughly 40 U.S. \$/10³ m³(STP), pricing basis 2003. These production costs do not include the costs for final purification (24).

Final Purification: Besides product purity, the recovery rate in common plants is an important cost factor and is influenced by the process design and the selection of adsorbents used in the PSA units. Main cost factors are shown in Table 3-29. 70 to 95% of the hydrogen input can be recovered within a PSA unit.

Table 3-29 Key parameter for an industrial H₂ PSA process [based on (65)]

Key parameter	Definition	Optimized by
H ₂ recovery	moles H ₂ in product gas / mole H ₂ in feed gas per cycle	<ul style="list-style-type: none"> • process design • selection of adsorbents
H ₂ productivity	moles H ₂ produced / total adsorbent volume	<ul style="list-style-type: none"> • PSA-cycle time • working capacity of adsorbent

Capital costs primarily depend on the number and the size of PSA columns, the amount of adsorbent material in each column, and the number of switch valves. The adsorber bed size



and the amount of adsorbent material decrease with increasing H_2 productivity and hydrogen recovery rate (65).

Costs for the production and the final purification of hydrogen, based on the capacity of the H_2 -production plant, are illustrated in Figure 3-28.

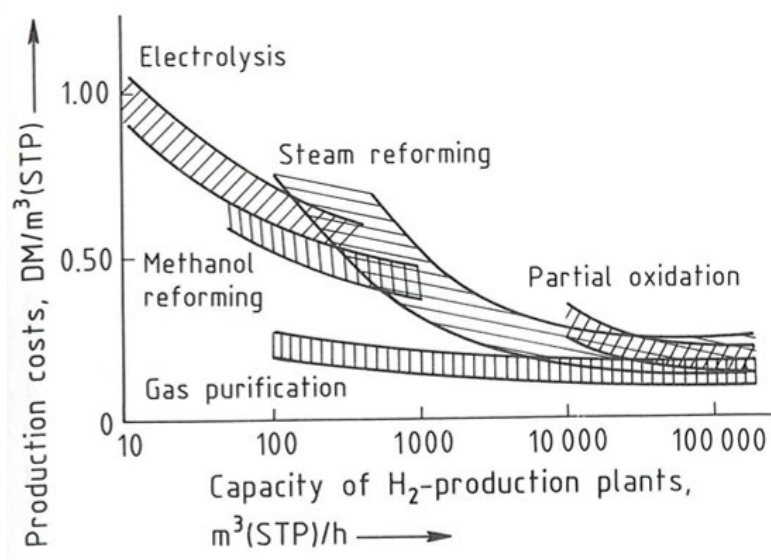


Figure 3-28 Production costs for H_2 as a function of the production process and plant capacity (30)

Prices of raw material and investments are based on 1983, Federal Republic of Germany. The gas purification costs represent costs for the recovery of H_2 from refinery off gas. The production costs include the investment for the PSA unit and the costs for the feedstock compression to adsorption pressure (30).

Industrial Application

Hydrogen, used for hydrogenation, hydro-treating or as reducing agent, is an important raw material in petroleum and chemical industry. 95% of the hydrogen capacity are used within refineries and synthesis processes. Only 5% are produced for applications in industry sectors like food, electronics, metal refining or as fuel for transportation.

At the beginning of the 21st century the global production capacity of hydrogen valued 0.5 trillion m^3 (STP). The worldwide hydrogen consumption forecast is expected to reach between 1.5 and 2 trillion m^3 (STP) by the year 2025 (30), (65).

3.1.7 Ammonia

Ammonia (NH_3), a colorless, toxic gas with a pungent odor, is the main intermediate product for nitrogen-based chemicals and fertilizers.

Before the industrial application of the catalytic reaction of N_2 and H_2 under high pressure, called the Haber-Bosch process, ammonia was obtained by the dry distillation of nitrogenous



organic substances, by reduction of nitrous acid and nitrites and by combustion of ammonium salts.

With the development of the Haber-Bosch process in the early 20th century, ammonia became one of the most produced inorganic chemicals, 80% of ammonia production go into fertilizer industry, e.g. urea.

Synthesis process

The production of ammonia includes syngas generation, carbon monoxide conversion, carbon dioxide removal and the final purification, which is described in chapter 3.2. After compression the syngas enters the synthesis reactor loop where nitrogen and hydrogen react to form ammonia according to the reaction:



Due to the thermodynamic equilibrium of the catalytic reaction, only 25 to 30% of the syngas can be converted within one cycle under industrial process conditions. Ammonia has to be separated from unconverted syngas by condensation at low temperature, and the un-reacted gas is mixed with fresh syngas and sent back to enter the synthesis process. Purge gas management is important to withdraw a part of the continuous gas stream preventing an enrichment of inert compounds (23).

Figure 3-29 shows the block scheme of ammonia production from natural gas, including syngas generation, shift reaction, purification and compression.

After desulfurization, reforming and carbon monoxide shift conversion, the bulk on CO₂ is removed, and traces of carbon oxides are converted into methane. These syngas treatment steps and alternative process units are described in detail in the chapter 3.2.

Afterwards the syngas is compressed and sent to the synthesis and refrigeration loop, where it is mixed with recycled gas. Liquid ammonia is separated from the gas flow, and a part stream of the gas is purged.



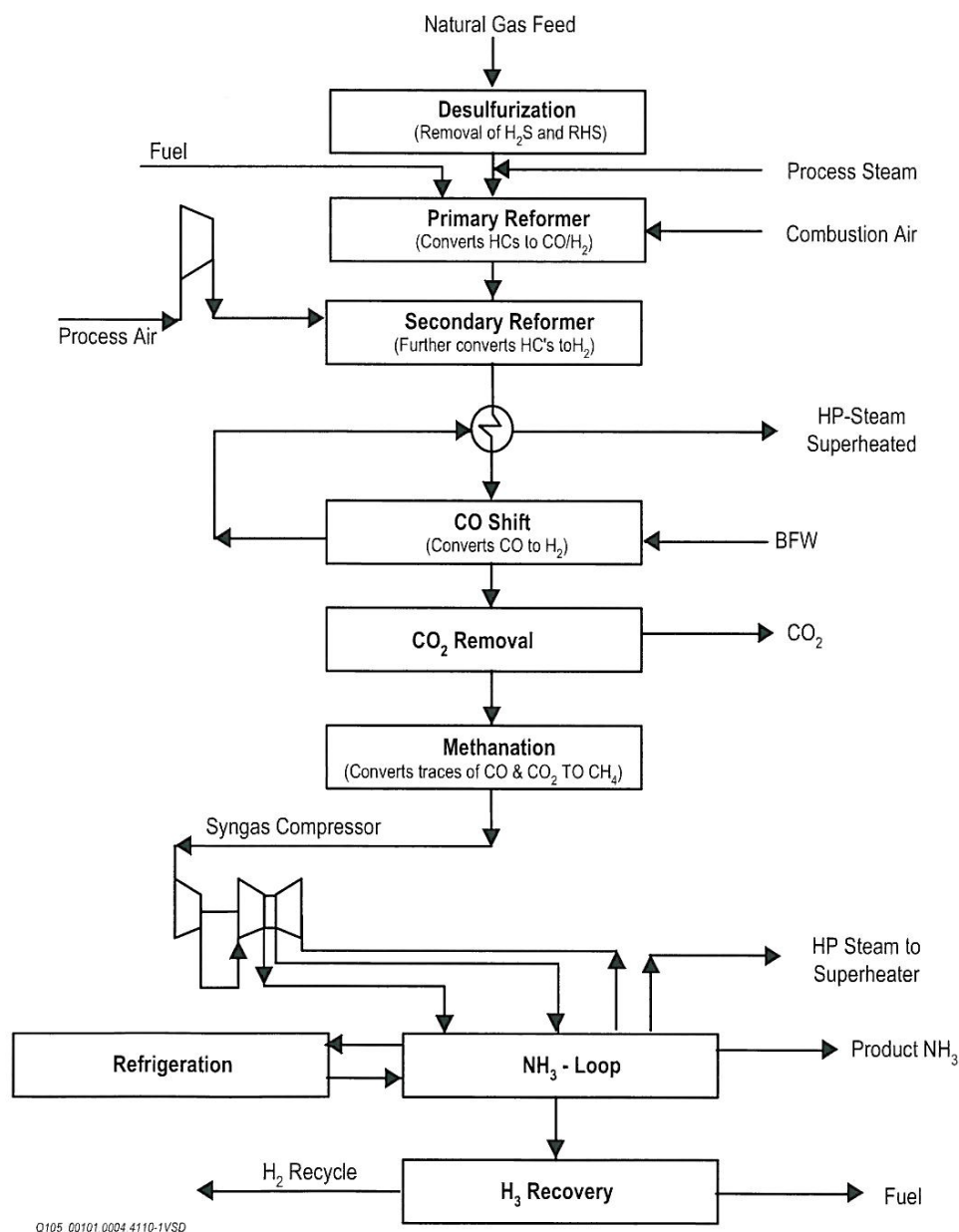


Figure 3-29 Schematic diagram of ammonia plant based on natural gas feedstock (15)

Technology, Capacity and Syngas Requirements

Technology: Common processes to convert syngas into ammonia are the Kellogg Brown & Root KRES-KAAP process and the Uhde process.

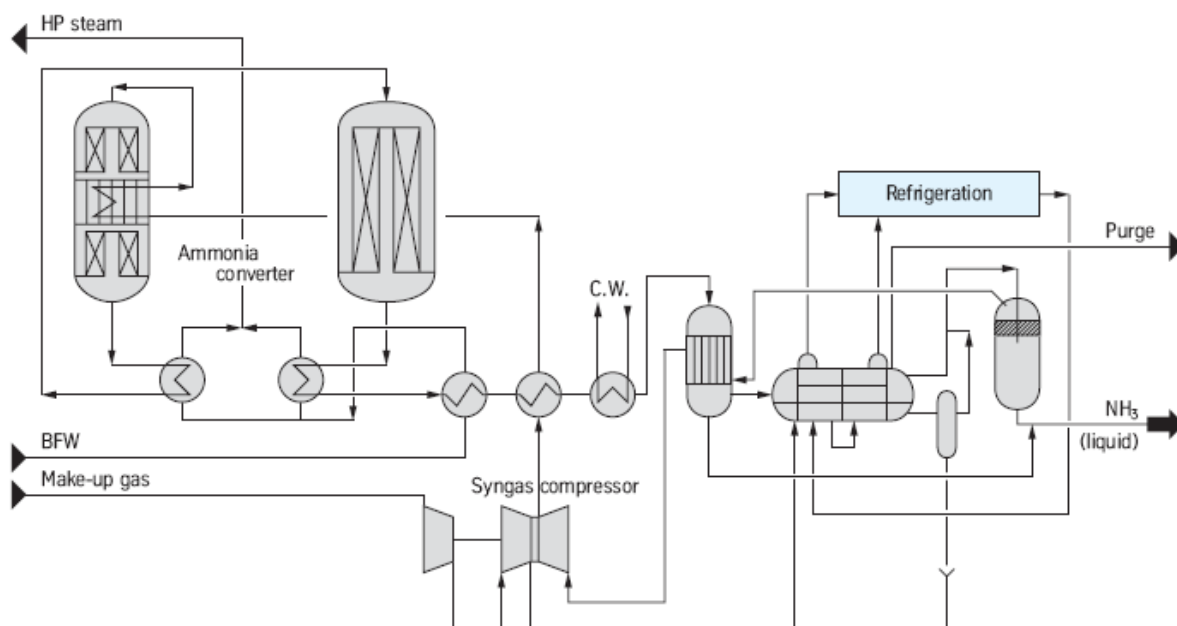
- Kellogg Brown & Root KRES-KAAP process, using a high activity non-iron ammonia synthesis catalyst (15).
- Uhde Process, using a magnetite-based catalyst (67).

The operating conditions of the Uhde-synthesis process at the reactor inlet are listed in Table 3-30, the process scheme is visualized Figure 3-30.



Table 3-30 Operating conditions of Ude synthesis process (67)

H ₂ /N ₂ ratio, methanation exit	2.95
Synthesis loop pressure	14 – 21 MPa
NH ₃ reactor inlet	3 - 5 vol.%
NH ₃ reactor outlet	20 - 25 vol.%
HP steam generation	1.1 - 1.5 t/t NH ₃
Number of reactors	1 or 2

**Figure 3-30 Ammonia synthesis (67)**

The synthesis process includes a three-bed reactor system with a waste heat boiler between 2nd and 3rd reactor bed, producing high pressure steam. After reaction section, the mixture of ammonia and syngas is cooled and enters the refrigeration unit. Liquid ammonia is separated and a purge gas stream is withdrawn. Un-reacted gas is mixed with make-up gas, compressed and sent back into the synthesis loop.

The synthesis loop configurations can be classified by the location of ammonia condensation and the feeding point of fresh makeup gas, which is dependent on the syngas composition. As shown in Figure 3-31/A, syngas, which is absolutely free of catalyst poisons like water or carbon dioxide, can be fed into the synthesis converter (a) directly, achieving an energetically optimum. If the makeup gas contains H₂O or CO₂, the syngas has to be injected before condensation unit (b), because water and CO₂ are completely absorbed by condensing ammonia (block scheme B).

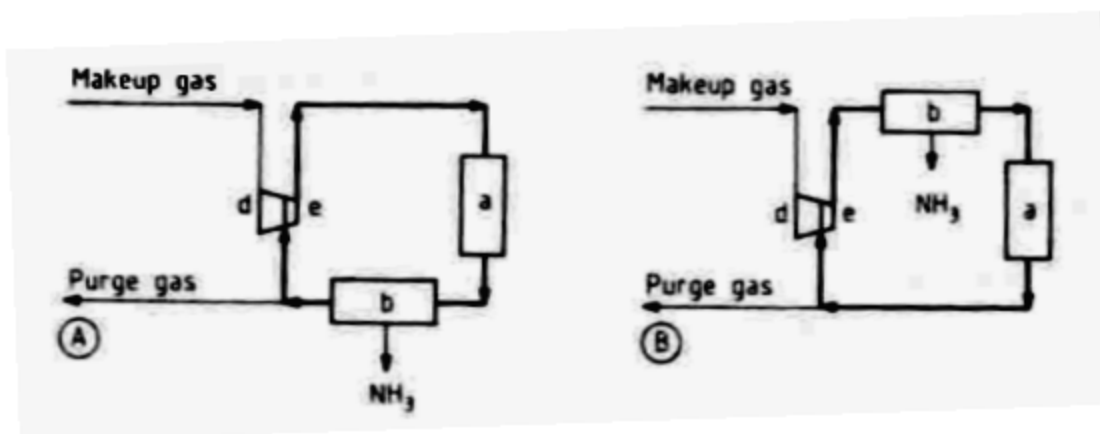


Figure 3-31 Schematic flow diagrams of typical ammonia synthesis loops (23)

Capacity: Modern conventional NH_3 -synthesis plants, with a capacity of one to two thousand tons per day, convert 100,000 to 200,000 m^3/h (STP) syngas into ammonia (30). Uhde recent references include plant capacities from 730 t/d to 3,300 t/d (67).

Syngas requirements: Due to catalyst poisoning in ammonia synthesis, syngas has to be purified from carbon oxides to a level below 10 ppm_v , which is conventionally done by methanation. To reduce inert gas compounds, the cryogenic liquid nitrogen wash can be applied for final syngas purification. Both process types are described in chapter 3.2

Material and Energy Demand

The feed and energy consumption for the production of one ton ammonia, with a product quality between 99.8% and 100.0% NH_3 , a water content up to 0.2% and an oil content below 5ppm (by wt.), is shown in Table 3-31 (67).

Table 3-31 Raw material and utility demand for NH_3 production (67)

Capacity	t/d	2,000
	units	
Raw material	per t NH_3	
Natural gas (as feed and fuel)	GJ	28 - 31
Chemicals		-
Utilities		
Power	kWh	15 - 90
Cooling Water	t	120 - 260
De-mineralized Water	t	0.65 - 0.75

Production Costs

The costs for ammonia production are highly depend on the natural gas price. Sawyer states that a natural gas price of 5.00 \$/MMBtu (4.74 \$/GJ) leads to ammonia production costs of around 500\$/t NH_3 . In this case, costs for natural gas as feedstock and fuel sum up to over 85% of the production costs. With a reduced gas price of 2.19 \$/MMBtu (2.07 \$/GJ), the



costs for one ton ammonia are around 100 \$. With a natural gas-spot price of 19.00 \$/MMBtu (18.00 \$/GJ), the costs for ammonia rise to 650\$/t NH₃ (68).

Industrial Application

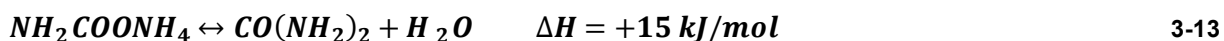
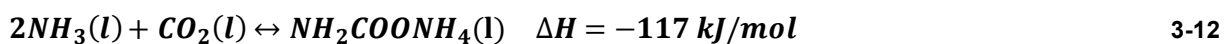
Ammonia is the main intermediate product for nitrogen based fertilizers like urea, ammonium nitrates, ammonium sulfates and ammonium phosphates. The fertilizer production accounts up to 80% of the world's NH₃ demand.

Ammonia is also used as an intermediate in the production of chemicals, like hexamethylene diamine and acrylonitrile. It is also used as a refrigerant media, and as a cleaning and bleaching agent in industry and household (69).

The world production capacity of ammonia in the year 2009 was at 153 million tones. The international Fertilizer Industry Association (IFA) states that the ammonia capacity will increase by 20% up to 224 million tones NH₃ in the year 2014. Most of the growth will be in China, Middle East, Latin America and Africa (69).

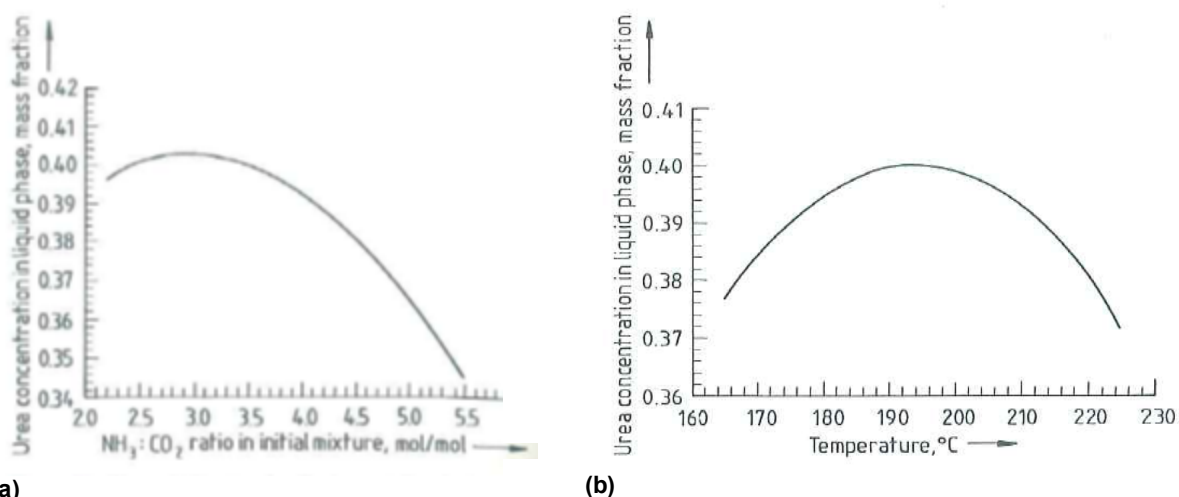
Urea, CO(NH₂)₂:

Especially the production of urea seems attractive, utilizing excess carbon dioxide by the exothermic formation of the intermediate product ammonium carbamate, which further decomposes into urea and water, according the following reactions:



Highest product yield is achieved with a molar NH₃:CO₂-ratio of 3 to 4. Figure 3-32 shows the urea yield as a function of the molar ratio (a), and as a function of temperature (b). Due to thermodynamic equilibrium, the corrosive intermediate product ammonium carbamate has to be recycled into the process.





(a) (b)
 Figure 3-32 Urea yield in the liquid phase at chemical equilibrium as a function of: (a) $\text{NH}_3:\text{CO}_2$ -ratio (temperature 190°C; $\text{H}_2\text{O}:\text{CO}_2$ -ratio=0.25, initial mixture); (b) temperature (initial mixtures: $\text{NH}_3:\text{CO}_2$ -ratio=3.5; $\text{H}_2\text{O}:\text{CO}_2$ -ratio=0.25) (70)

Today, conventional urea production has been replaced by several stripping processes, like Snamprogetti self-stripping process, ACES Process (Advanced Process for Energy Savings) or Stamicarbon Urea processes (Uhde), which is shown in Figure 3-33 (70).

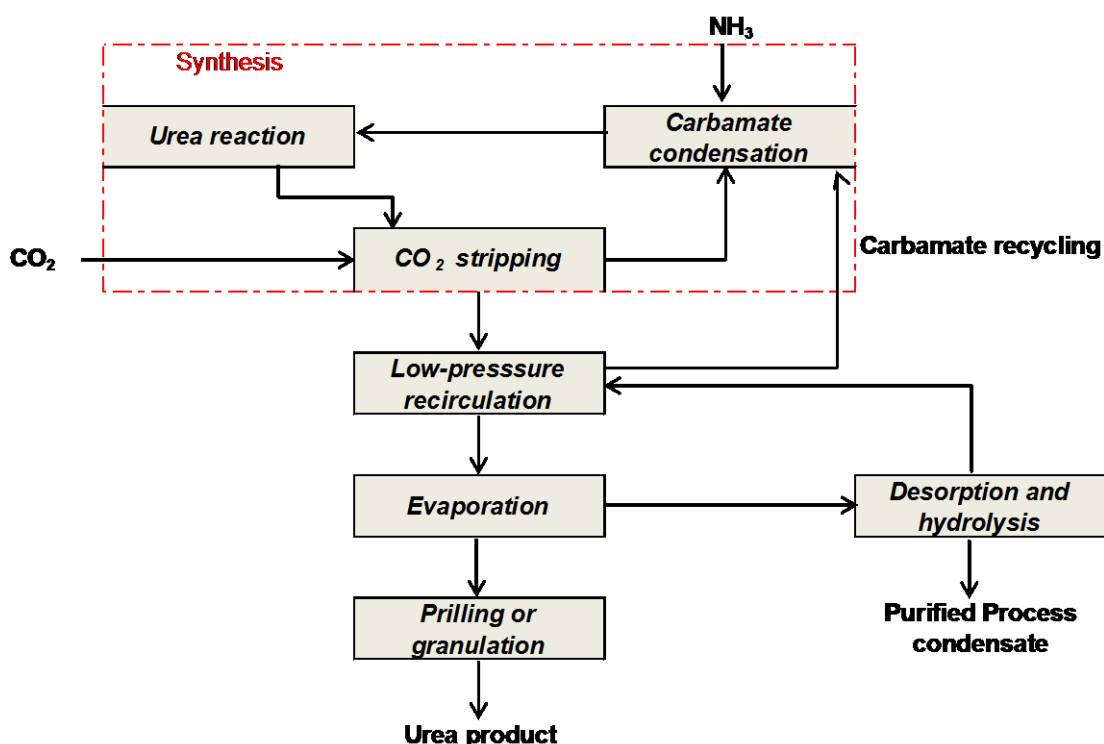


Figure 3-33 Urea production: block diagram of the CO_2 -stripping process [based on (71)]

The simplicity of this process type, with less equipment and fewer process steps, leads to high capacities, easy operation and low maintenance costs. Furthermore, the feedstock consumption figures are almost equal to the stoichiometric values for ammonia and CO_2 (71).



Global urea demand

In the year 1997, the world's demand on urea summed up to 89 million tons, and has been growing continuously with an annual growth-rate of 3% (70).

The International Fertilizer Industry Association (IFA) estimated the global urea demand at 155 million tons for the year 2011 and at 164 million tons for 2012. Worldwide, the installed capacity has been estimated to be at 184 million tons for 2011 and is expected to go up to 196 million tons by the end of 2012. Incorporating the operating rate (between 85% and 90%), the urea supply is expected to be at 159 million tons in 2011 and 167 million tons in 2012. The supply/demand balance of the years 2008 to 2010 and the estimated balance for the years 2011 and 2012 are shown in Figure 3-34 (72).



Figure 3-34 Urea supply-demand balance (72)

3.1.8 Summary

Table 3-32 Summary of selected synthesis processes [own description]

Products	Process	Operating Conditions		Catalyst	Selectivity	Syngas Conversion / Recovery	Main products / purity	Typical Syngas Demand	Typical Product Capacity	Main Industrial Application
		p [MPa]	T [°C]							
Carbon Monoxide (CO)	Cryogenic partial condensation	typically 3 - 4	-185			CO: 75-90% (2-stage: <95%) H ₂ : 97%	CO/N ₂ : 98.5-99.9% H ₂ : 90% (2-stage 98%)		CO: 30,000-40,000 m ³ (STP)/h (max.60,000 m ³ /h)	acetic acid synthesis
	Cryogenic methane wash	typically 3 - 4	-183			CO:95-98% H ₂ : 97%	CO/N ₂ : 98.5-99.9% H ₂ : ~98.5%			
Oxo Chemicals	LPO-Davy	1.5 - 2	85 - 115	Rh- complex	high	30% per pass	aldehyde	oxogas: 30,000 - 60,000	400,000 - 1mn.t/a	acrylates, glycol ether, acetates
	RCH-RP	1 - 10	50 - 130	Rh- complex	high		aldehyde			
	Shell	5 - 10	160 - 200	Co- complex	low		oxo alcohol			
Acetic Acid (CH ₃ COOH)	Monsanto, Celanese	3 - 6	150 - 200	Rh- iodide	99%	90%	Acetic Acid	CO: 30,000 - 60,000	400,000 - 1.2 mn. t/a, (3,000 t/d)	polymer production
Methanol (CH ₃ OH)	Low pressure gas phase	5 - 10	220 - 300	Cu/ZnO/Al ₂ O ₃	>98%	50%	methanol, chemical grade	300,000-500,000	1 - 2 mn. t/a (3,000-5,000 t/d)	formaldehyde, MTBE, acetic acid
	LPMEOH™	7 - 8	~250	ZnO/Cr ₂ O ₃ in liquid		low	methanol, fuel grade		260 t/d	fuel
FT-Liquids	LTFT	2.5 - 4.5	220 - 250	based on Fe, Ni or Co	low	60-90%	diesel, wax		35,000 - 140,000 b/d	fuel
	HTFT	2.5	330 - 350	Fe based	low	85%	gasoline, light olefins			fuel
Hydrogen (H ₂)	PSA	typically 0.4 - 3	20 - 40			70-95%	H ₂ : 98-99.999%	5,000-340,000	1,000 - 150,000 m ³ (STP)/h	hydrogenation, hydro-treating, reducing agent
Ammonia (NH ₃)	LP-Synthesis: KRES-KAAP	9 - 10		high activity non-iron			ammonia	100,000-250,000	1,000-2,000 t/d	Nitrogen based fertilizer, e.g. urea
	Uhde	14 - 21		magnetite-based		20-30% per pass	ammonia	80,000-400,000	730 – 3,300 t/d	

3.2 Synthesis Gas Production

In general in syngas production the requirements for the syngas specifications, like H₂:CO-ratio (syngas-ratio) and necessary additional reactants, are determined by the downstream synthesis process. Table 3-33 gives an overview on the recommended syngas-ratios for the synthesis of selected chemical products, shown in Figure 3-1 (blue).

Table 3-33 Typical syngas ratio for a few basic chemicals [based on (25)]

Products	Carbon Monoxide	Acetic Acid	Oxo-chemicals	Methanol	Fischer – Tropsch Liquids	Ammonia	Hydrogen
Chemical Notation	CO	CH ₃ COOH		CH ₃ OH		NH ₃	H ₂
H ₂ :CO-ratio	0 – 0.02	0 – 0.02	1.0 – 1.2	2.0 – 2.3	1.6 – 2.3	>10 ⁵	>10 ⁵
Additional Reactants		CH ₃ OH	alkenes	CO ₂	CO ₂	N ₂ (=1/3H ₂)	

Today, natural gas is the main feedstock for syngas production. Furthermore other gaseous, but also gasified liquid and solid hydrocarbons are utilized as feedstock in synthesis industry. Within the last years coal gasification has become more important due to the given infrastructure and resource-availability in many countries, its stable and low price and the new research and development in clean coal technology, whereas naphtha has partly been replaced since the oil crises.

In the following, only the syngas production from natural gas and coal are discussed, representing gaseous and solid feedstock.

The production of synthesis gas, in generally can be structured into two main process steps, the reaction route for the generation of carbon monoxide (CO) and hydrogen (H₂), and the gas treatment section for ratio adjustment and syngas purification.

3.2.1 Reaction Route

The choice of reaction route is determined by the feedstock material on the one hand, and the downstream requirements, especially the recommended H₂:CO-ratio, on the other hand.

Typical reaction routes are:

- steam reforming,
- partial oxidation,
- auto-thermal reforming and
- gasification.

The H₂:CO-ratios range typically between 0.6 and 4.7, as shown in Table 3-34, side reactions included. A high syngas-ratio is generally reached by the conversion of light



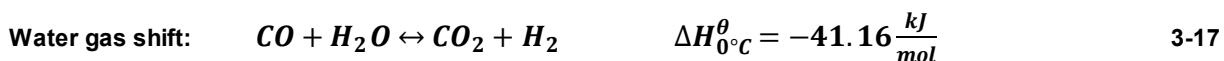
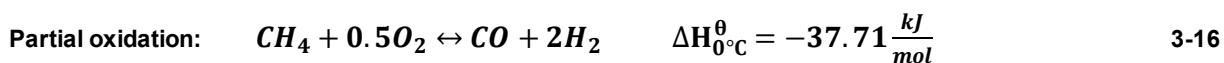
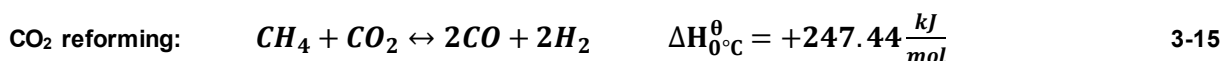
hydrocarbon feedstock, while the conversion of heavy hydrocarbon feedstock on the other hand leads to comparatively low H₂:CO-ratios.

Table 3-34 Typical H₂:CO-range from common feedstock [own description based on (19), (24), (31)]

Reaction Process	Feedstock	Typical H ₂ :CO-range
Steam reforming	Methane	2.8 – 4.7
	Naphtha	2.1 – 4.3
Partial oxidation	Methane	1.7 – 2.0
	Naphtha	1.2 – 1.4
Gasification	Coal	0.6 – 1.0

Natural Gas as Feedstock

Reforming reactions with steam or CO₂ are endothermic, partial oxidation is exothermic, and the combination of both is often known as an autothermal process. The reactions can be described by many different equations, only an extract of common reactions is stated below:



With the injection of excess steam, carbon deposition (from decomposing hydrocarbons, see equation 3-18) on the catalyst material can be reduced, but a high steam to carbon-ratio (S/C-ratio) leads to higher energy costs and consequently influences process economy. For typical process conditions the S/C-ratio is set between 2.5 and 3 (15).

Important process parameters:

- steam to carbon ratio (S/C-ratio),
- oxygen to carbon ratio (O/C-ratio),
- reaction temperature and
- operating pressure.

More detailed information, regarding process parameters for an efficient reactor design, is given in literature like Rostrup-Nielsen et al (31), Ullmann's Encyclopedia of Industrial Chemistry (25) or Nexant ChemSystems PERP Report 03/04S4 (15).



Upstream to the methane (CH_4) conversion process, natural gas has to be purified in appropriate gas treatment units. Especially sulfur compounds, which poison the catalyst system, have to be removed.

Most common reaction processes are shown in Figure 3-35, including:

- steam methane reforming (SMR) with optional CO_2 injection (a)
- combined reforming (b)
- autothermal reforming (ATR) (c)
- gas heated reforming (combined reforming with off-heat recycling) (d)

Whereas the steam methane reforming process (a) delivers highest H_2 :CO-ratios, reaching values above 4, an injection of available carbon dioxide can be installed to reduce the syngas-ratio to desired levels. Another option to influence the H_2 :CO-ratio within the reaction route is the combination of a steam and an oxygen-blown reformer. The system is called combined reformer (b), but additional reforming equipment and the recommended air separation unit (ASU) lead to higher capital costs compared to the conventional process. Therefore the single autothermal reforming process (c) has been developed, which combines steam and oxygen-blown reforming within one reactor. A further alternative is the gas heated reformer (d), where heat for steam reforming is provided externally by recycling off-heat from an oxygen-blown, secondary reformer, as shown in the block scheme (15).

The selection of the reaction route and the choice of the catalyst system are determined by:

- the recommended H_2 :CO-ratio of the downstream processes
- the natural gas composition after pre-treatment
- available infrastructure and plant equipment (e.g. air separation unit (ASU))
- the reactor heat management



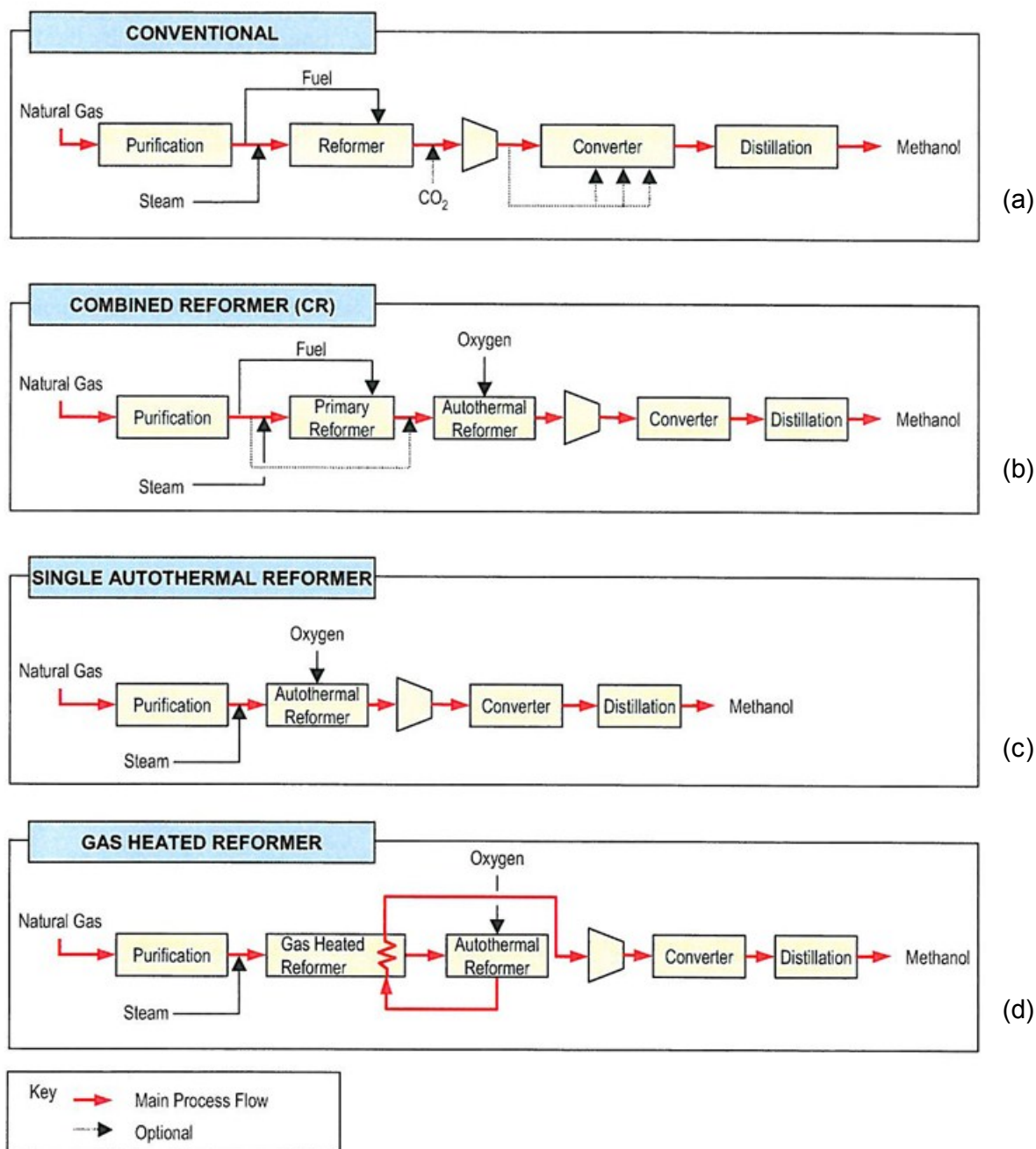


Figure 3-35 Selected methanol reformer options (15)

Reforming Process

Figure 3-36 shows the simplified flow chart of a typical steam methane reforming process with the option for carbon dioxide recycle. Preheated natural gas is desulfurized, mixed with steam (optionally with CO₂) and is sent to the reformer unit. Methane reacts with steam in the presence of alumina supported nickel based catalyst tubes to form carbon monoxide, hydrogen and some carbon dioxide. The reformed gas also includes non converted methane and excess steam. The steam methane reforming temperature usually ranges between 600 and 800°C, the reaction operates at pressures of up to 2.5 MPa. After reforming, CO₂ and CH₄ can be removed depending on the downstream requirements (19).



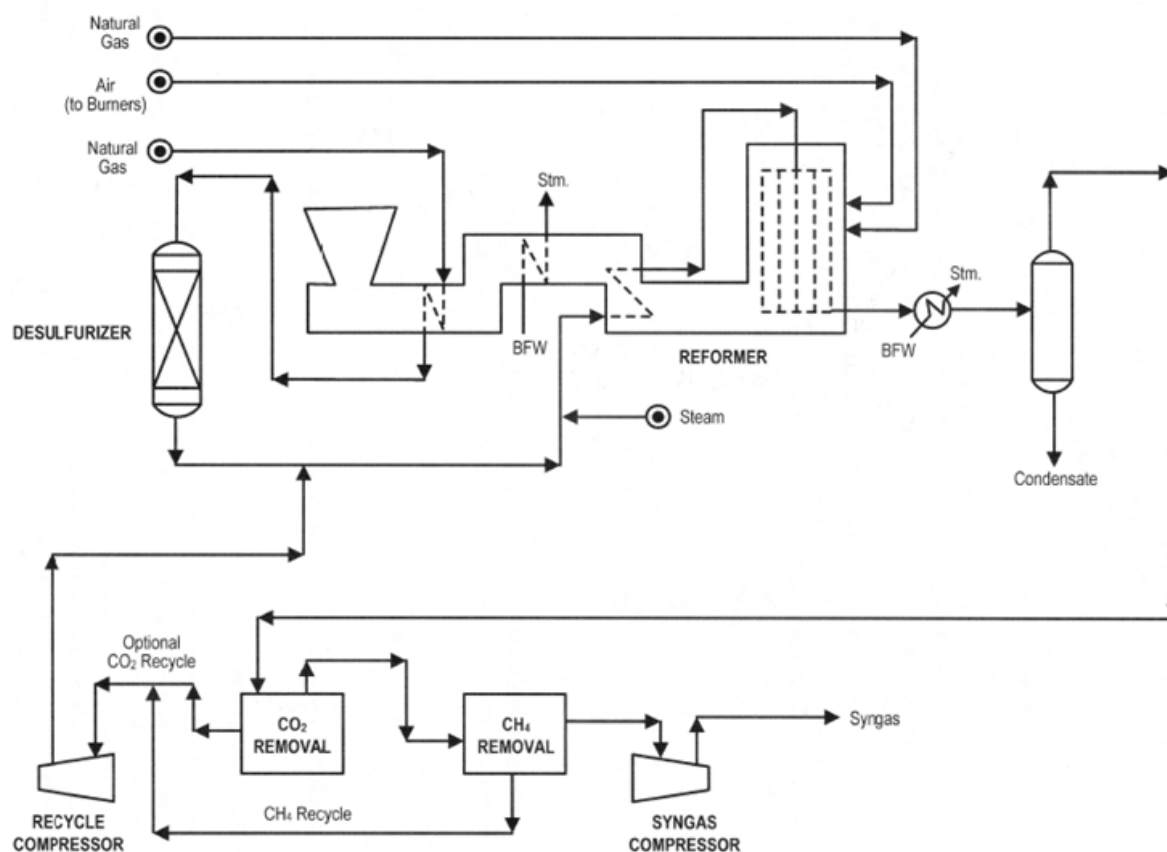
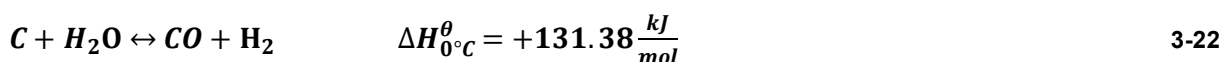
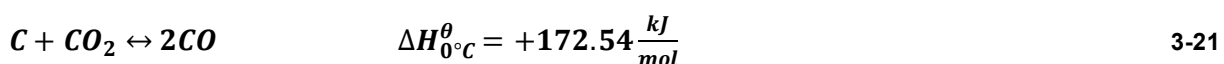
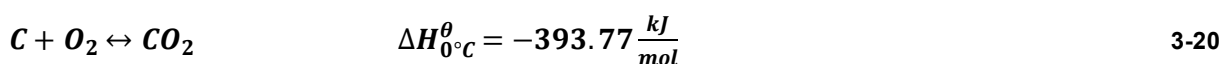
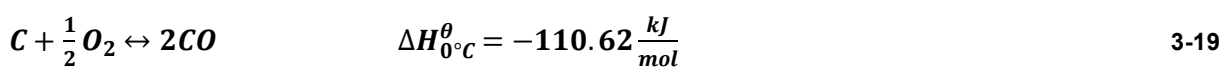


Figure 3-36 Steam methane reforming (19)

Coal as Feedstock

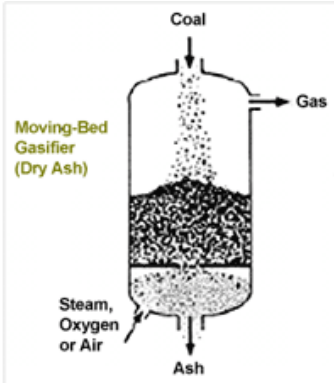
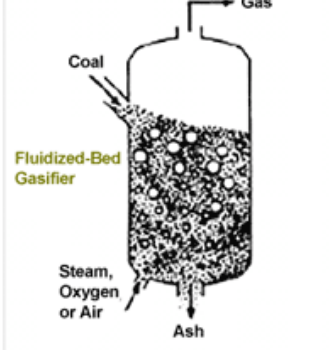
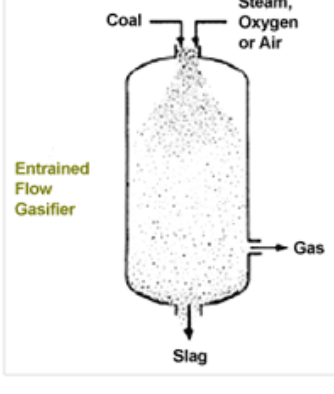
Energy industry and chemical industry sectors have been improving gasification technologies to utilize coal and biomass as a clean energy source and solid hydrocarbon feedstock. Due to the diversity of the chemical compounds in the feedstock, the chemistry of gasification is complex. The main gasification reactions with molecular oxygen, carbon dioxide and steam are stated below:



Coal gasification processes are classified by the type of the gasification reactor into three main categories, the moving bed, the fluidized bed and the entrained flow reactor. Characteristics of these types are listed in Table 3-35.



Table 3-35 Classification and characteristics of main gasifier types [based on (24), pictures: (73)]

 <p>Moving-Bed Gasifier (Dry Ash)</p>	<p>Moving bed gasifier</p> <ul style="list-style-type: none"> • low oxidant requirements • production of liquid hydrocarbons (tars, oils) • high thermal efficiency including liquid calorific value • caking coals require design modification • difficulty in handling fines • dry ash or slag
 <p>Fluidized-Bed Gasifier</p>	<p>Fluidized bed gasifier</p> <ul style="list-style-type: none"> • wide range of acceptable feeds like high ash coals • uniform, moderate temperature • moderate oxygen and steam requirements • extensive char recycling
 <p>Entrained Flow Gasifier</p>	<p>Entrained flow gasifier</p> <ul style="list-style-type: none"> • tolerance of low-rank coals, caking coals and fines • uniform temperature • short gasifier residence time • requirement for very finely divided feed • high raw gas outlet temperature • high temperature slagging operation • raw gas contaminated with some entrained molten slag

Although there is a diversity of gasification technologies, in the following three common gasification reactors are discussed in detail, representing the reaction route of coal:

- The Lurgi dry ash pressure gasifier, a pressurized moving bed gasifier fed with coal particles (typically between 3 and 50 mm): This moving bed technology has been used commercially since the 1930s, and nowadays over 165 gasifier of this type have been installed (24), (25).
- The Siemens entrained flow gasifier, operating at elevated pressure with a pneumatic slurry feed system: A entrained flow gasification pilot plant with a capacity of 3 MW was installed 1979 in Freiberg. 5 plants have been installed and the capacity-scale up reached 500 MW in 2004, with a carbon conversion rate above 99% (74).

- The Texaco/GE entrained flow gasifier, a pressurized entrained flow reactor operating with slurry feed system: 72 plants have been installed; the capacity reached 500 MW with a carbon conversion rate above 99% (74).

Whereas the Lurgi gasifier produces dry ash, the entrained flow gasifier of Siemens and Texaco/GE produce slagged ash, which is low on carbon and inert substances. But the high entrained flow gasifier temperature causes thermal losses and leads to higher oxygen consumption. The entrained flow gasifier construction material has to be high on quality, but advantageously there are no moving parts compared to the moving bed gasifier-type. The simple geometry of the entrained flow gasifier leads to highest capacity per unit volume. Figure 3-37 shows the schematic design of the three gasifier types.

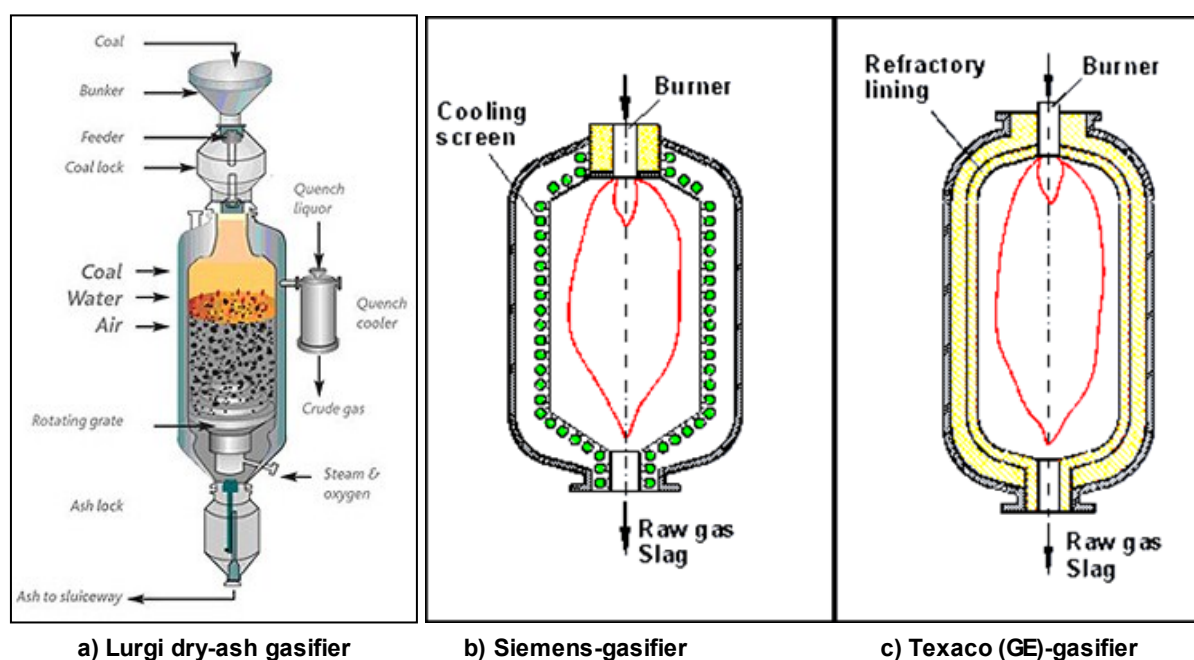


Figure 3-37 Gasification reactors: a) Lurgi dry-ash gasifier (75), b) Siemens and c) Texaco (GE) entrained flow gasifier (74)

Syngas from entrained flow gasification is free of heavy hydrocarbons, tar and phenols, but may include molten slag particles. The wide range of syngas composition after gasification mainly depends on the gasification system, the feedstock composition and the gasifying media. Entrained flow gasification with oxygen as gasifying media yields in a $H_2:CO$ -ratio far below 2. Moving bed gasification with steam and oxygen as gasifying media obtains a higher $H_2:CO$ -ratio, due to hydrogen input. Raw syngas composition and achieved syngas-ratio from selected gasification types, but different feedstock, are summarized in Table 3-36.

Table 3-36 Gasification type, feedstock and raw syngas composition [col.2: (25); col.3/4: (74); col.5: (25)]

Gasification Type Process Name	Moving Bed Lurgi	Entrained flow		
		Siemens		Texaco/GE
Feedstock Analysis	Bituminous coal (South Africa)	Petcoke	Hard coal	Bituminous coal (Illinois no.6)
Volatile m. in wt-%	20.6			33.5
Moisture in wt-%	10	2	2	13
Ash in wt-%	18.5	1.0-5.0	5.0-15.0	11.1
Main Elements in Feedstock (dry, ash free)				
C in wt-%	80.6	87.0	92.0	78.1
H in wt-%	4.0	3.9	3.5	5.1
O in wt-%	13.0	0.2	2.5	11.6
N in wt-%	2.1	2.0	1.0	1.3
S in wt-%	0.2	5.3	1.0	3.8
Gasifying medium	steam and O ₂			O ₂
Steam:O ₂ -ratio	5.8			1.0 (H ₂ O: water in slurry)
Raw Syngas Composition (dry) – main compounds				
H ₂ in vol-%	28.6	22.0	27.0	36.6
CO in vol-%	23.0	65.0	64.0	41.1
CO ₂ in vol-%	27.8	5.0	3.0	20.7
CH ₄ in vol-%	9.1	< 0.1	< 0.1	0.1
C _n H _m in vol-%	0.4	-	-	-
N ₂ in vol-%	0.4	1.0-6.5	1.5-5.5	0.4
H₂:CO-ratio	1.2	0.3	0.4	0.9
Gasification pressure in MPa	2-10	< 8		< 8.5
Carbon conversion	-	> 99%		94%

Bituminous coal from different regions have been used as feedstock for Lurgi moving bed and Texaco entrained flow gasification, while the Siemens gasifier has been operated with petcoke and hard coal. These differing feedstock compositions have to be considered in evaluating performance.

With moving bed gasification, using steam and oxygen as gasifying media, a H₂:CO-ratio of 1.2 is achieved, whereas the entrained flow gasification with oxygen leads to a syngas-ratio between 0.3-0.9, depending on the feedstock analysis, especially the moisture content, and the feed system with or without slurry.

A typical process route and the operating conditions for the conversion of coal into syngas, including gasification, raw gas purification and carbon monoxide shift conversion, is shown in



Figure 3-38. Besides the synthesis of chemicals, purified syngas can be used as fuel or reducing agent.

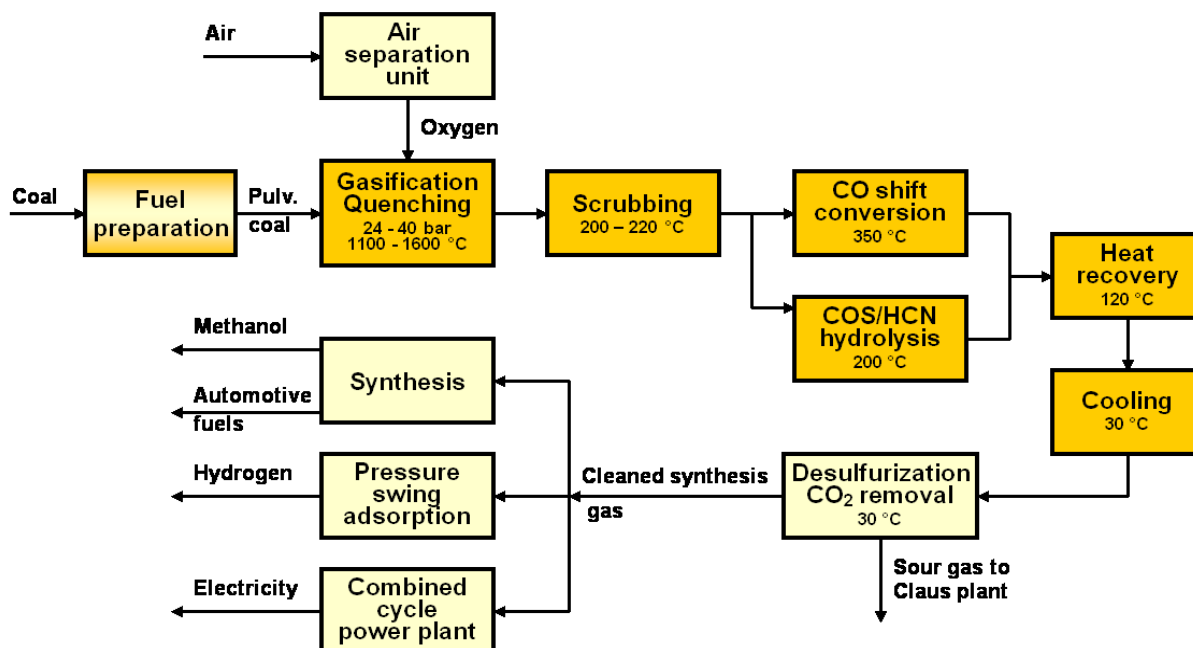


Figure 3-38 Syngas generation technology (74)

The growing capacity of gasifier technology, changes in feedstock shares and development in product sectors are shown in Table 3-37, in the operating plant statistics.

Table 3-37 World Gasification Survey (operating plant statistics) [col.1: (24); col.2: (76); col.3: (77)]

2001	2004	2007
125 operating plants 400 gasifier	117 operating plants 385 gasifier	138 operating plants 417 gasifier
<u>Capacity:</u> ~ 42,257 MW _{th}	<u>Capacity:</u> ~ 45,000 MW _{th}	<u>Capacity:</u> ~ 56,000 MW _{th}
<u>Feeds:</u>	<u>Feeds:</u>	<u>Feeds:</u>
<ul style="list-style-type: none"> coal: 44% pet. residues: 40% others: 16% 	<ul style="list-style-type: none"> coal: 49% pet. residues: 36% others: 15% 	<ul style="list-style-type: none"> coal: 55% pet. residues: 32% others: 13%
<u>Products:</u>	<u>Products:</u>	<u>Products:</u>
<ul style="list-style-type: none"> chemicals: 37% Fischer-Tropsch liquids: 28% power: 21% others: 14% 	<ul style="list-style-type: none"> chemicals: 37% Fischer-Tropsch liquids: 36% power: 19% others: 8% 	<ul style="list-style-type: none"> chemicals: 44% Fischer-Tropsch liquids: 30% power: 18% others: 4%
<u>Growth:</u> annual forecast 7%	<u>Growth:</u> annual forecast 5%	<u>Growth</u> from 2007 to 2015: 72% expected

More detailed information concerning gasification process can be found in standard literature, e.g. the NTIS Handbook of Gasifiers and Gas-treatment Systems (78), Nexant ChemSystems PERP Report 03/04S11 (24), and the Gasification Technologies council (79).



3.2.2 Gas Treatment Section

Depending on the downstream synthesis requirements and the given gas composition after the reaction route, raw syngas has to be upgraded by the following gas treatment steps:

- Ratio adjustment: water gas shift reaction to adjust H₂:CO-ratio by converting carbon monoxide and steam into H₂ and CO₂
- Gas purification: to reduce CO₂ and impurities
 - Removal of CO₂ generated during reaction route and within shift process
 - Removal of S-compounds, usually in combination with CO₂ removal
- Final purification and enrichment of compounds
 - Deep desulfurization in dry adsorption beds
 - Removal of trace compounds.
 - Methanation to remove oxides according to NH₃-downstream requirements
 - Cryogenic separation techniques, including partial condensation and methane wash process for CO production, furthermore liquid nitrogen wash for NH₃-syngas purification.
 - Pressure-swing adsorption, commonly used for H₂ enrichment
 - Membrane separation technology
 - Salt solution absorption
- Conditioning steps to adjust operating temperature and pressure and to overcome pressure drop within the upgrading process (not further described).

Ratio Adjustment

If necessary, the raw synthesis gas, low in H₂ and rich in CO, is processed in a water gas shift reactor where CO and steam are converted into H₂ and CO₂ by the exothermic water gas shift (WGS) reaction:



The WGS-equilibrium is determined by process temperature, but is almost independent of operating pressure, which on the other hand influences selectivity and activity of WGS-catalysts. Table 3-38 outlines temperature classification of commercial water gas shift reactors.



Table 3-38 Temperature classification of water gas shift reaction (25)

	High Temperature Shift (HTS)	Low Temperature Shift (LTS)	Raw Gas Shift (RGS)
Temperature Range	300 – 510°C	180 – 270°C	200 – 500°C
Gas Purity	sulfur range: from 10 to over 100 ppm _v tolerated	sulfur / halogen compounds: lower than 0.1 ppm _v	Minimum content (100–1,500 ppm _v) of S-compounds is necessary
Catalyst based on	Fe ₂ O ₃ , Cr ₂ O ₃ *	Cu-Oxides*	Co, Mo **
Application	generally for CO-Shift reactions (except raw gas purity is low) 1 st step in H ₂ production	after HT-Shift, for H ₂ production (high yield)	used for raw gases with high sulfur content (e.g. coal gasification)

* Oxides reduced during operation / ** activate as sulfide

Usually the shift reaction takes place in isothermal reactors or reactors with intermediate cooling, which are less susceptible to interferences. The WGS-temperature ranges from 180 to 270°C for low temperature shift (LTS) with sensible catalyst-material, 300 to 510°C for high temperature shift (HTS) and from 200 to 500°C for raw gas shift (RGS) reactions. Conventional applications are shown in Table 3-38. Commonly HTS or RGS reactors are used for the 1st reaction step, due to lower requirements on syngas purity. LT-Shift catalysts require stringent syngas purity and therefore are only used after HTS to achieve a high yield on H₂ (25).

Figure 3-39 illustrates the temperature dependency of the water gas equilibrium:

- Increase of hydrogen with decreasing reaction temperature.
- Temperature dependency of the unconverted CO (exit CO-content) at reactor outlet measured on dry basis.
 - LTS: Additionally 1% of H₂ are achieved with a reactor outlet temperature of ~220°C, compared to the HTS (Fig. a).
 - HTS: Additional 6% of H₂ can be achieved by intermediate or internal reactor cooling down to a temperature of 300°C, compared to the adiabatic HTS reactor with an outlet temperature around 450°C (Figure a).
 - HTS (~300 - 450°C): The bulk on CO can be converted into H₂ down to approximately 2.5% CO on dry basis at the reactor outlet (Figure b).
 - MTS (medium temperature shift or isothermal shift conversion; ~ 220 to 270 °C): CO can be converted down to approximately 1% CO on dry basis at the reactor outlet.
 - LTS (~180 to 250 °C): depending on the reactor outlet temperature, the CO content can be lowered down to approximately 0.5% CO on dry basis at the reactor outlet



Due to only one additional percentage of hydrogen, the LTS with reaction on highly sensitive catalyst material is only applied for very clean syngas, typically from natural gas reforming. Therefore untreated syngas from coal gasification is conventionally processed only by the HTS (80).

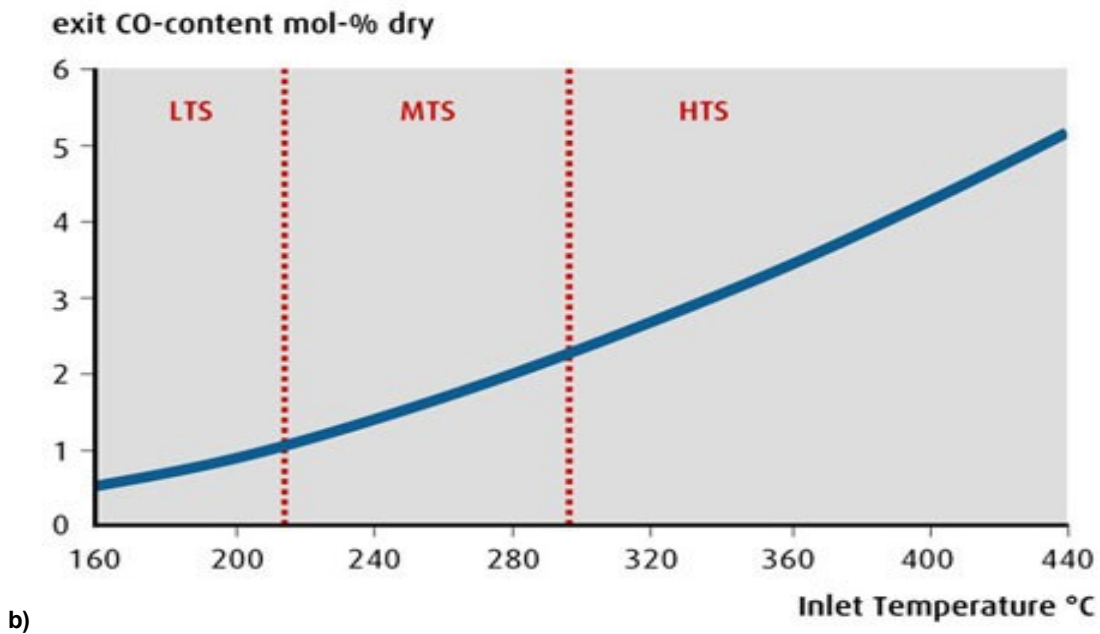
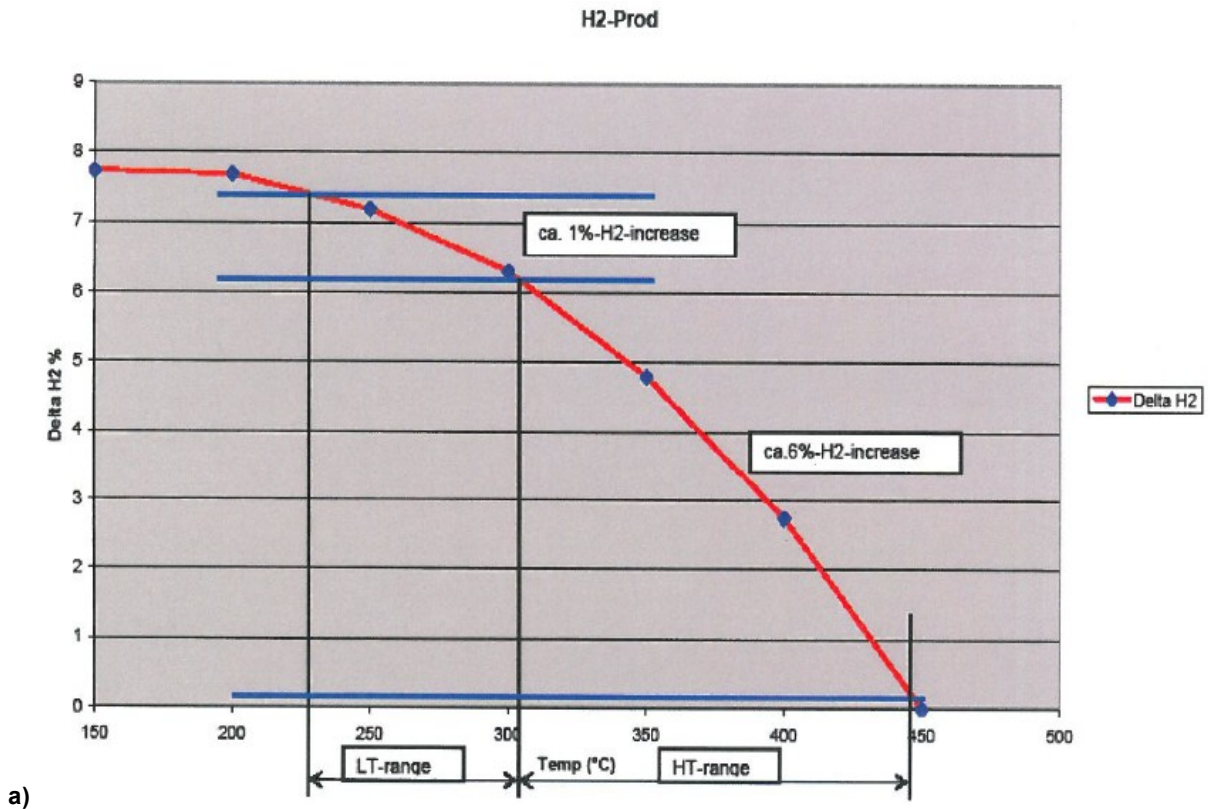


Figure 3-39 Temperature-dependency of water gas shift reaction

a) Increase of %-hydrogen depending on the temperature range (80); b) exit CO-content mole-% dry (81)

Gas Purification

The removal of CO₂ and H₂S is a main process step in syngas production to be able to meet specific syngas requirements for downstream synthesis, as to reduce purge gas flow and to avoid catalyst poisoning respectively.

Raw syngas typically contains sour gas compounds like carbon dioxide and hydrogen sulfide, which originate from gaseous feedstock and are formed during reaction route (reforming, gasification). The bulk on CO₂ is generated within ratio-adjustment process by the conversion of carbon monoxide, according to the water gas shift reaction, and especially raw syngas from coal gasification may contain already up to 30% of carbon dioxide.

Gaseous feedstock has to be de-sulfurized before entering the reformer unit due to poisoning of reformer catalyst material. Syngas from gasification or partial oxidation may contain sulfur-compounds at levels above 100 and up to 20,000 ppm_v, which are typically removed after the high temperature shift reaction, before downstream process.

In case of methanol and Fischer-Tropsch synthesis, few volume percent of CO₂ may remain in syngas. Other syngas specifications recommend a CO₂-content in ppm_v-levels.

For the removal of CO₂, H₂S and COS, physical and chemical absorption processes are typically used in the synthesis industry. Table 3-39 provides an overview of common absorption techniques to separate the acid gases simultaneously (10).

Table 3-39 Selection of physical and chemical absorption processes for acid gas removal (10)

Process (Licensor)	Absorptive	Solvent
Physical absorption processes		
Purisol (Lurgi)	H ₂ S, CO ₂ and other acid gases	N-methyl-2-pyrrolidone (NMP)
Rectisol (Linde / Lurgi)	H ₂ S, COS, CO ₂ , NH ₃ , HCN, aromatic compounds	methanol
Selexol (UOP)	H ₂ S, COS, CO ₂ , mercaptans, other acidic and non acidic components	polyethylene glycol dimethyl ether (DMPEG)
Chemical absorption processes		
MEA (free process)	H ₂ S, CO ₂ , other acid gases COS, CS ₂ (irreversible reaction)	1-2 N monoethanolamine
DEA (Elf Aquitaine...)	H ₂ S, COS, CO ₂ , CS ₂	2-4 N diethanolamine
MDEA (free)	H ₂ S, CO ₂ , HCN, organic acids	2-5 N methyldiethanolamine
aMDEA (BASF)	H ₂ S, CO ₂	MDEA + activator for CO ₂ absorption
ADIP (Shell)	H ₂ S, COS, CO ₂	DIPA or MDEA
Potash		K ₂ CO ₃
Benfield (UOP)	CO ₂ , H ₂ S, HCN	K ₂ CO ₃ + activator
Catacarb (Eickmeyer)	COS, CS ₂ (hydrolyzed to H ₂ S)	K ₂ CO ₃ + catalyst
Physical – chemical absorption processes		
Sulfinol-(D/M) (Shell)	H ₂ S, CO ₂ , COS, C ₂ S, organic (di)sulfides, mercaptans	sulfolane and DIPA or MDEA
Amisol (Lurgi)	CO ₂ , H ₂ S, COS, other org. S	CH ₃ OH, MEA, DEA or DETA

Physical absorption is supported by high pressure and low temperature, and is used to remove acid gas compounds from raw syngas with high partial pressure of acetic gas compounds. The solubility of sulfur-compounds in physical absorbents is higher than the solubility of CO₂. Chemical solvents additionally utilize chemical reactions to support the driving force for separation, and therefore they achieve sufficient separation efficiency also at low partial pressure. Chemical solvents show no or low (due to different velocities of reaction, e.g. MDEA) selectivity for S-compounds over CO₂ and consequently S-compounds and CO₂ are removed simultaneously (10).

Special focus has been set on the physical Rectisol absorption process, typically used for coal gasification syngas treatment, and the activated MDEA (aMDEA), a chemical absorption process with an activator for carbon dioxide. Table 3-40 outlines characteristics of the Rectisol and the aMDEA absorption processes.



Table 3-40 Characteristics of Rectisol and aMDEA process [(10), modified]

	Rectisol	aMDEA
Solvent	Methanol	MDEA, water and activator for CO ₂ absorption
Solubility of CO₂/H₂S in solvent media	Strong increase of solubility with decreasing temperature; solubility-ratio: H ₂ S/CO ₂ = 2-3/1	CO ₂ absorption rate slightly enhanced with decreasing temperature and increasing partial pressure. H ₂ S is co-absorbed
Characteristics	High CO ₂ partial pressure required; Favorable absorption temperature -20 to -60°C External refrigeration required Low OPEX No corrosion / no foaming	Typical CO ₂ partial pressure range: 0.035 – 1.12 MPa Low CAPEX Minor corrosive / foaming tendency
Process configurations	Simultaneous removal of acid gas compounds possible, but standard process is selective: removed H ₂ S enriched in H ₂ S-fraction, CO ₂ and N ₂ (used as stripping gas) as tail gas, recovery of pure CO ₂ possible	Single stage absorber – optional HP-flash - stripper Two stage absorber – optional HP-flash LP-flash – stripper Selective H ₂ S/CO ₂ removal not possible
Trace compounds	BTX, PAH: enriched in solvent → prewash with methanol with special regeneration required; HCl: distributes equally throughout the system → prewash with water; HCN: enriched in solvent → prewash with methanol at higher concentrations; NH ₃ : enriched in solvent, risk of plugging and downgrading of product qualities → prewash with water.	BTX: 20% of feed absorbed; (stripped in CO ₂ fraction); PAH: no experience, removal upstream recommended; HCl: 100% absorbed, enriched in solvent → quench; HCN: absorbed (partly hydrolysed), stripped in CO ₂ -fraction; downgrades quality of solvent → removal upstream required at higher concentrations; NH ₃ : absorbed, stripped in CO ₂ fraction; but also enriched in solvent, risk of plugging; removal required upstream at higher concentrations.

The selection of the appropriate absorption process is dependent on the partial pressure of CO₂ and H₂S in the raw and product gases, as shown in Figure 3-40 (10).



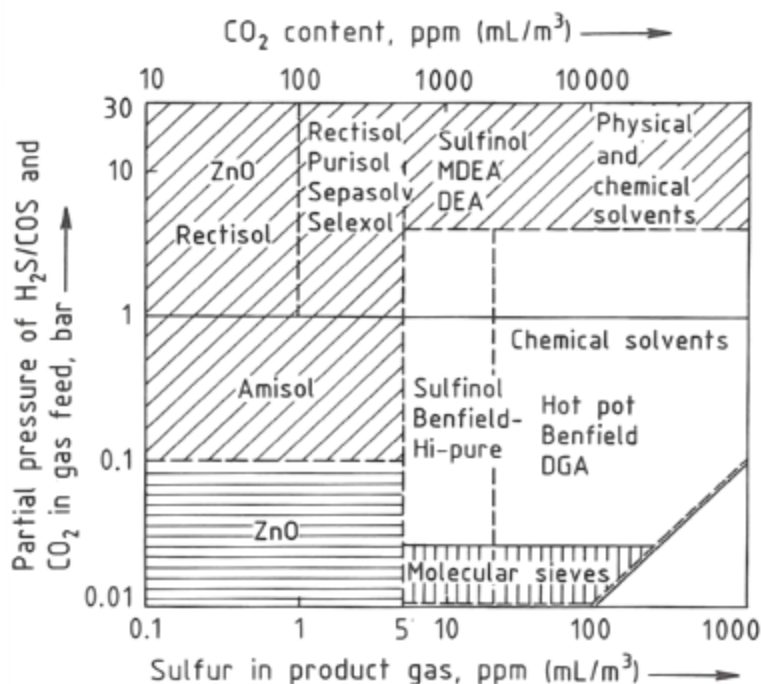


Figure 3-40 Selection of appropriate gas purification process for simultaneous H_2S/COS and CO_2 removal (25)

Final Purification and Enrichment of Compounds

After shift conversion and bulk removal of CO_2 and H_2S , catalyst poisoning substances (e.g. oxides, remaining sulfur- and halogen compounds) have to be either removed (deep desulfurization or removal of trace compounds in absorber columns) or converted into inert gases (methanation) according to the downstream synthesis requirements. An enrichment of selected compounds (e.g. H_2 and CO) is possible by cryogenic separation techniques and pressure-swing adsorption. Detailed information about final purification and accumulation techniques is given below, including research topics like membranes or the salt solution absorption process.

Deep desulfurization

Remaining sulfur compounds, very low in partial pressure, can be removed in dry bed adsorbers by H_2S -sorbents (e.g. ZnO) as shown in Figure 3-40. Depending on the process temperature the sorbents are grouped accordingly, in:

- high temperature ($>600^\circ C$),
- medium temperature ($300-500^\circ C$) and
- low temperature ($<100^\circ C$) applications.

Metal-oxides are used for high temperature desulfurization, which is the common method to desulfurize syngas from coal gasification. ZnO , which replaced hydrated iron oxides due to environmental issues, is the major sorbent material for medium temperature process,



although ZnO has a higher sorption capacity at high temperature. ZnO desulfurization techniques have been applied for more than 30 years.

Compounds like H₂, H₂O, CO and CO₂ might influence the desulfurization process, due to the following reactions (82):



Removal of trace compounds

As trace compounds are partly absorbed by the solvent media during bulk removal of CO₂ and H₂S, syngas is usually clean enough for the downstream process. But due to enrichment of some trace compounds in the solvent media, the raw syngas has to be quenched with water for removal of HCl or NH₃, or prewashed by a part stream of the solvent before entering the absorber column. More detailed information about trace compound removal is given in chapter 4.1.

Methanation according to NH₃ downstream requirements

After water gas shift reaction and bulk removal of CO₂, the syngas still contains carbon oxides. For the generation of pure hydrogen or ammonia, those carbon oxides have to be removed due to risk of catalyst poisoning. Methanation is a simple process to reduce the carbon oxide concentration to a value below 10 ppm_v. The catalytic reaction, supported by a nickel catalyst, conventionally takes place at pressures between 2.5 and 3.5 MPa and operates in a temperature range between 250 and 350°C (23).



The process is simple and low in investment but disadvantageously consumes hydrogen and produces methane, which burdens synthesis loop as an inert gas.

Cryogenic separation

The separation of gaseous compounds, like CO, N₂ or CH₄ from syngas mixtures, is done by distillation at very low temperatures in insulated equipment, called the cold box.

To prevent the accreting of freezing compounds like water, CO₂, H₂S or methanol within the cold box system, the syngas has to be purified, separating those compounds upstream which is typically done by temperature swing adsorption (TSA), as shown in Figure 3-41.



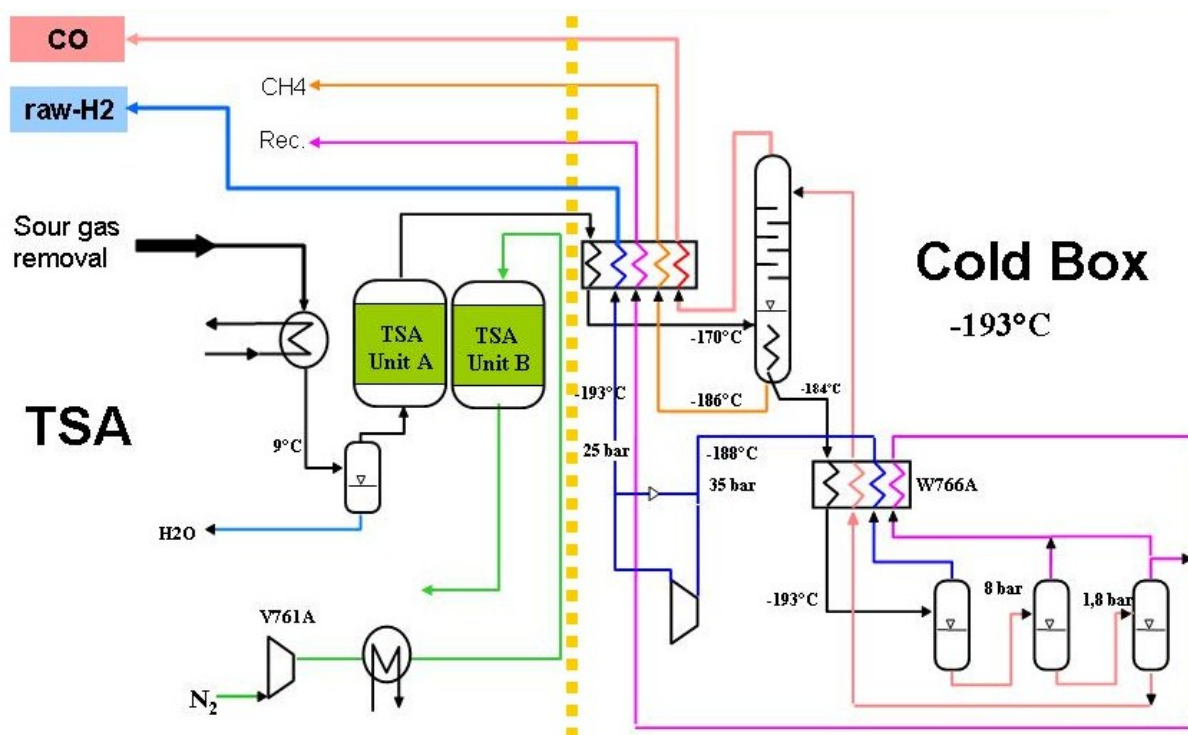


Figure 3-41 Temperature swing adsorption (TSA) and coldbox for the generation of CO (83)

Cryogenic separation has to be applied for the recovery of CO from purified syngas, which is done by partial condensation or liquid methane wash process, described in chapter 3.1.1.

But cryogenic separation can also be applied for the final purification of NH₃-synthesis gas. The liquid nitrogen wash, is used to remove CO and inert gases like methane and argon from ammonia syngas, which in case of methanation burdens the synthesis loop. Furthermore, the H₂:N₂-ratio is finally adjusted within the cold box process.

The liquid nitrogen wash is commonly used to purify NH₃-syngas from partial oxidation after high temperature shift reaction, which still contains 3-5 vol% of carbon monoxide. In few applications a nitrogen wash unit is installed additionally downstream the methanation process to further reduce the content of carbon oxides and inert gases (23).

Figure 3-42 shows the flow chart of a liquid nitrogen wash unit downstream coal gasification and Rectisol absorber column.

After removal of the freezing compounds by TSA (1), the syngas is cooled (2, 3) and sent to the nitrogen wash column (5) for the removal of the impurities CO, Ar, and CH₄. The purified gas leaves the top and is heated by the feed-gas (2, 3). A part-stream of the HP-N₂ is injected warm to the purified syngas for final tuning of the syngas composition (H₂:N₂-ratio =3). The other part of the HP-N₂ is cooled (4, 2) and split again: one part-stream is mixed cold into the purified syngas, the second part, after being condensed (3) is used as wash agent in (5).

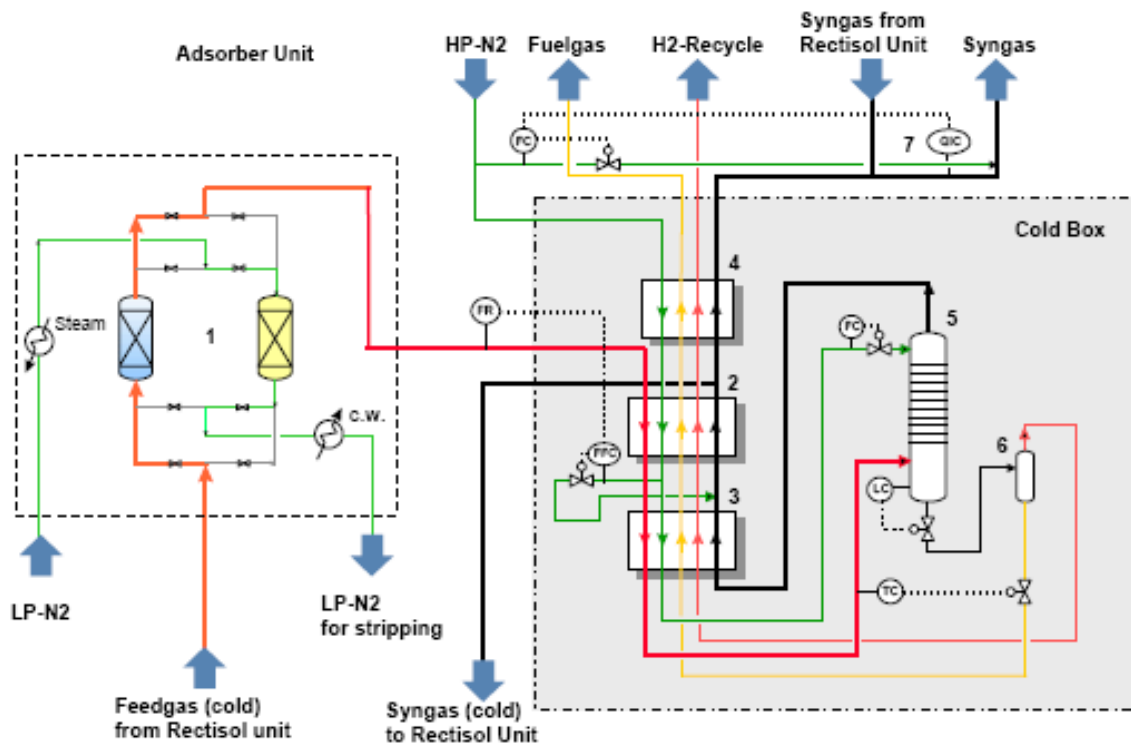


Figure 3-42 HP-standard liquid nitrogen wash (84)

Table 3-41 shows a typical material balance for a standard liquid nitrogen wash unit downstream to an oil gasification process.

Table 3-41 Typical material balance for a standard liquid nitrogen wash downstream a Texaco oil gasification (84)

	Feedgas mol%	HP-N2 mol%	NH3 Syngas mol%	Fuelgas mol%	H2 Recycle mol%
H2	96.00		75.00	4.50	90.21
N2	0.60	99.99	25.00	52.29	6.72
CO	2.30		1 ppm	29.16	2.61
O2		10 ppm	2 ppm	12 ppm	
Ar	0.60	90 ppm	20 ppm	7.65	0.41
CH4	0.50			6.40	0.05
CO2	15 ppm				
CH3OH	25 ppm				
Nm3/h	87,400	30,700	110,500	6,830	770
bara	77.5	78.5	75.0	1.8	24
°C	-57	40	30	30	30

Pressure-swing adsorption (PSA)

The main application of pressure-swing adsorption (PSA) in syngas production technology is the generation of pure hydrogen, as described in detail in chapter 3.1.6.



Depending on the adsorbent material, PSA can also be applied for the bulk removal of CO₂, but due to its low recovery rate, it is not state of the art technology for the purification of syngas in chemical industry.

Membrane separation technology

Polymer, metallic, ceramic, micropore-carbon and liquid membranes selectively absorb gaseous components in their molecular structure. Membranes based on metals, ceramics or liquids, known for a long time, have been developed to an industrial standard for the production of high purity hydrogen and to enrich carbon monoxide for oxo-alcohol production. And within the last four decades, research and development on polymer membrane technique has been accelerated (19), (25).

A typical gas composition after one stage membrane separation is shown in Table 3-42. More detailed information is given in Nexant ChemSystems PERP Report 09/10S11 (19), and in Ullmann's Encyclopedia of Industrial Chemistry (25).

Table 3-42 Typical syngas composition after one stage membrane [based on (25)]

	Raw Gas	Permeate	Waste Gas
H ₂ (vol%)	74	96	57
CO (vol%)	26	4	43
Flow rate (kmol/h)	100	43.6	56.4
Yield		H ₂ : 56%	CO: 93%

Salt solution absorption

The salt solution absorption is an alternative process to recover high purity CO from nitrogen rich syngas. Carbon monoxide is selectively absorbed by complexation in an organic solvent, containing cuprous aluminum chloride (41). More detailed information is given in chapter 3.1.1.

3.2.3 Typical Syngas Composition and Process Units

After the gas treatment section the syngas composition has to meet downstream requirements according to the selected synthesis process. Table 3-43 shows a selection of typical syngas specifications.



Table 3-43 Typical syngas specification for main compounds [based on (10), (19), (20), (21), (22), (23)]

	CO	Oxogas	CH ₃ OH-/ FT-syngas	H ₂	NH ₃ -syngas
Temp [°C]	15-35	15-45	220-300		
Pressure [Mpa]	0.4-0.5 31-33*	3.3-4.0	>5	3.8-4.2	9-21
Component flow rate, typical range in vol-% oder ppm_v					
H ₂	0.3-0.6%	50.5-53%	68-74%	98-99.99%	70-75%
CO	97-99.9%	47-49.5%	16-20%	<1ppm _v	<10ppm _v ***
CO ₂	<20ppm _v	<1,100ppm _v	6-9%	-	
CH ₄	<500ppm _v	<0.2%	< 3.5%	<1ppm _v	inert
H ₂ O	-	DP10-12°C**	-	<1,100ppm _v	-
N ₂ /Ar	<2.5%	0.1-0.3	<2.5%	<300ppm _v	23-25%
H ₂ S ****	0.1 ppm _v	0.1 ppm _v	0.1 ppm _v	0.1 ppm _v	0.1 ppm _v
O ₂	<10ppm _v	<1ppm _v	-/ no poison	<5ppm _v	<1ppm _v
SN=(H ₂ -CO ₂)/ (CO + CO ₂)			>2.05		
H ₂ :CO-ratio	0:1	1:1	2:1	1:0	H ₂ :N ₂ =3:1

*CO... two different applications (low, high pressure); **H₂O dew-point; *** after methanation; ****H₂S, HCl and HF are typically below 0.1 ppm_v each, few applications tolerate values up to 5 ppm_v (55)

Example: Syngas generation based on natural gas

For the conversion of natural gas into the specific syngases according to the specifications in Table 3-43, typical syngas production units have to be installed, as listed in Table 3-44.

For all listed syngas application, natural gas has to be reformed. But pretreatment of the reformer feed-gas is essential, because sulfur compounds, chlorides and arsenic poison the reforming catalyst and are strictly limited (sulfur compounds and chlorides typically <0.1ppm_v).

Due to the high H₂:CO-ratio after reforming (>3), only hydrogen-rich syngas (for H₂, NH₃) is sent to the water gas shift reactor. Excess hydrogen from syngas with a specified H₂:CO-ratio ≤2 can be purged within the synthesis loop and is often sold as by-product or internally utilized (e.g. steam generation).

Carbon dioxide has to be removed after water gas shift reaction and before entering the cryogenic separation unit. A CO₂ separation column is not necessary for the production of methanol syngas, because H₂ and CO₂ react accordingly to the inverse shift reaction (equ. 3-6) due to the high H₂ content in steam reformed natural gas (SN>2).

Methanation is typically applied for ammonia syngas to convert catalyst poisoning carbon oxides into methane. For the production of high purity NH₃-syngas, a cryogenic nitrogen wash unit has to be installed, to separate unwanted and inert gas compounds.



Table 3-44 Gas treatment units for the conversion of natural gas into major syngas compositions [own description]

Generation of → Process units	CO	Oxogas	CH ₃ OH-/ FT-syngas	H ₂	NH ₃ - syngas
Desulfurization and removal of trace compounds	+	+	+	+	+
Steam methane reforming (SMR)	+	+	+	+	+
Water gas shift reaction (WGS)	-	-	-	(+)	+
CO ₂ removal	+	(+)	-	+	+
Pressure-swing adsorption (PSA)	(+)	-	-	+	(+)
Methanation	-	-	-	-	+
Temperature swing adsorption (TSA) and cryogenic nitrogen wash unit (NWU)	-	-	-	-	(+)
TSA and cryogenic separation of H ₂ /CO	+	-	-	-	-
Cryogenic separation of N ₂ /CO	(+)	-	-	-	-
H₂:CO-ratio	0:1	1:1	2:1	1:0	1:0

+ common application; - not applied; (+) alternative application

3.2.4 Syngas Production Costs

To calculate the production costs from the syngas generation routes listed in Table 3-44, the following key-factors are decisive:

- feedstock and fuel (coal or natural gas)
- reaction route and applied syngas treatment units
- regional differences in raw material and utility prices
- production capacity
- required syngas specification (composition and purity), determined by the downstream synthesis requirements
- feed-gas and syngas pressure

To provide a common basis for the comparison of syngas production costs, the cost calculations have to be related to either the product, or the feedstock.

Product specific Calculation (Methanol)

To illustrate the influence of:

- plant capacity,
- different raw material, including reaction route and downstream synthesis and
- the regional pricing policy,



Nexant ChemSystems visualized the production costs for liquid-phase methanol synthesis based on coal, and gas-phase methanol synthesis of steam reformed natural gas for small (815t/d) and large (5,000t/d) plant capacities, as shown in Figure 3-43 (24).

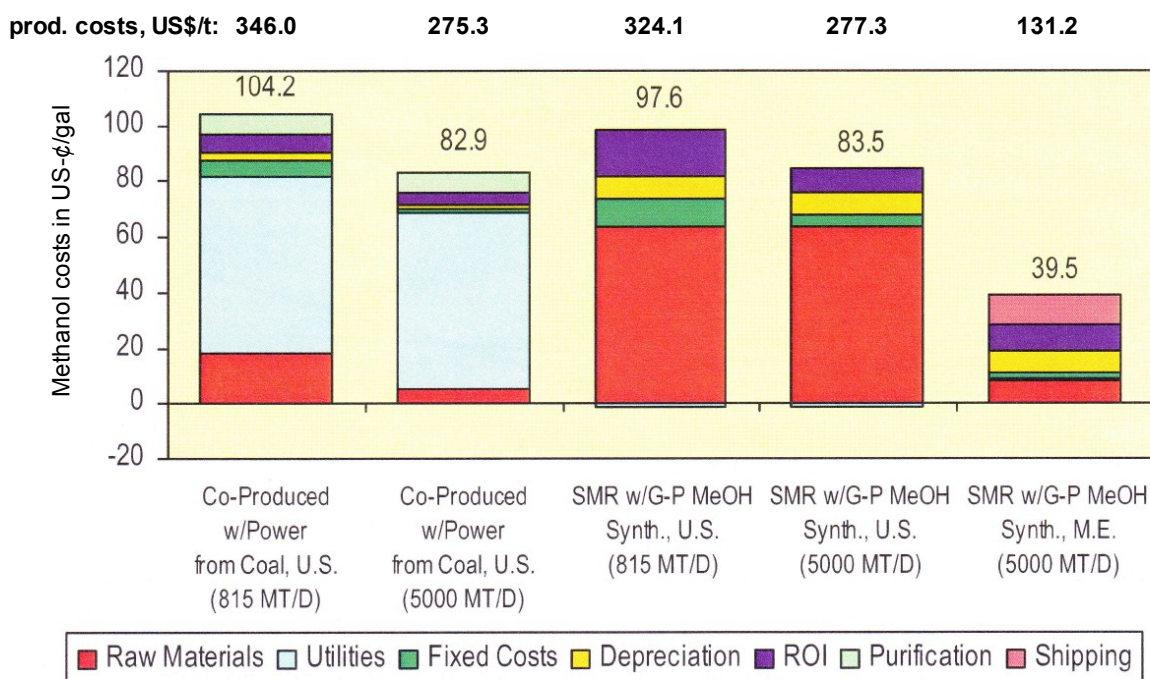


Figure 3-43 Comparison of methanol cost for various feedstock, capacities, and locations – including purification to chemical grade and shipping from M.E. (pricing basis 2nd quarter 2004) [(24) modified]

Raw material, production route and capacity

- 1st and 2nd column visualize economy of scale for the coal gasification route, including the co-production of liquid-phase methanol and power and the purification to chemical grade methanol. The overall production costs decrease with increasing plant capacity due to declining raw material costs. Methanol costs range from 346 \$/t to 275.3 \$/t, for a plant capacity of 815 t/d and 5,000 t/d respectively.
- 3rd and 4th column illustrate the economy of scale for common steam reforming process, converting natural gas into hydrogen rich syngas, followed by gas-phase methanol-synthesis, at capacities of 815 tons and 5,000 tons per day. Overall production costs only decrease due to declining fixed costs.
- Due to the constant natural gas price, coal based production becomes more competitive with rising capacity.

Regional Difference

- The calculations visualized in column 1-4 have been based on prices for the United States Gulf Coast. Calculations visualized in column 5 have been based on the very low NG price in the Middle East, a region with large resources on natural gas, but limited market access.
- Columns 4 and 5 illustrate the influence of the regional difference in the natural gas prices, visualizing production costs for steam methane reforming and gas-phase



methanol synthesis in the U.S. (column 4) and in the Middle East (column 5). Due to the very low gas price (0.75\$/MMBtu, M.E.), the costs for production in the Middle East including product shipment to the U.S. are significantly lower (at 131.2\$/t) than the production costs for a plant in the United States (column 4, 277.3.2\$/t) (24).

Table 3-45 lists the basic figures for the calculations visualized in Figure 3-43.

Table 3-45 Basic data including raw material prices (year 2004) for the methanol production cost calculation, visualized in Figure 3-43 [based on (24)]

Basic data for the calculation of methanol production costs	
Raw material:	Coal: 26.50 US\$/ST (U.S., 2004) Natural gas: 6.03 US\$/MMBtu (US/2004); 0.75 US\$/MMBtu (M.E./2004)
Utilities:	Power, cooling water, boiler feed water, steam
Fixed costs:	Including manpower, maintenance, material, labor, direct overhead; and allocated fixed costs (general plant overhead, insurance, property tax); fixed costs in Middle East ~ ½ of fixed costs in the U.S.
Depreciation:	10% of process equipment, general utilities and administrative buildings
ROI:	Return on investment: 10%
Purification:	Costs for methanol-upgrade from fuel to chemical grade are included.
Shipping:	Price for shipping one gallon methanol form Middle East to U.S. Gulf Coast: 0.11 US\$.

Product specific Calculation (H₂)

A commercial evaluation of H₂ production by partial oxidation of refinery residue and the steam reforming of natural gas and naphtha based on different regional feedstock prices has been introduced by Stefano Innocenzi (Linde) at the H₂-symposium 2010 (85).

Two cases, the H₂-production of 140,000 m³/h (STP), and hydrogen with co-production of carbon monoxide have been worked out, using different feedstock material and locations, as shown in Table 3-46.

Table 3-46 Raw material and energy prices for different regions based on (85)

Feedstock/Energy	Price/unit	U.S. Gulf Coast	Europe	India	Middle East
Natural gas	U.S.\$/GJ HHV	4.74	8.53	6.63	1.23
Electric energy	U.S.\$/MW	55	100	90	40
Naphtha (market price 2010)	U.S.\$/t	650	650	650	650
Refinery residue	U.S.\$/t	300	300	300	300

Concerning hydrogen production, steam reforming of natural gas is the most economic reaction route, followed by the gasification of refinery residues and the steam reforming of



naphtha. Reducing the costs of refinery residues, the gasification will become more economic, depending on the plant location as follows (Figure 3-44):

a) U.S.: The hydrogen production via gasification competes the steam reforming of natural gas, only if the refinery residue price is close to zero.

b) Europe: If the price for refinery residues stays below 150 U.S.\$/t the gasification route is the most economical solution, even if the costs for CO₂ emissions (30 \$/t) are included.

c) India: With a refinery residues price below 80 \$/t the gasification route becomes more economic than the natural gas route.

d) Middle East: Costs for natural gas are very low in the Middle East. Consequently steam reforming of natural gas stays the most economic process to produce hydrogen.

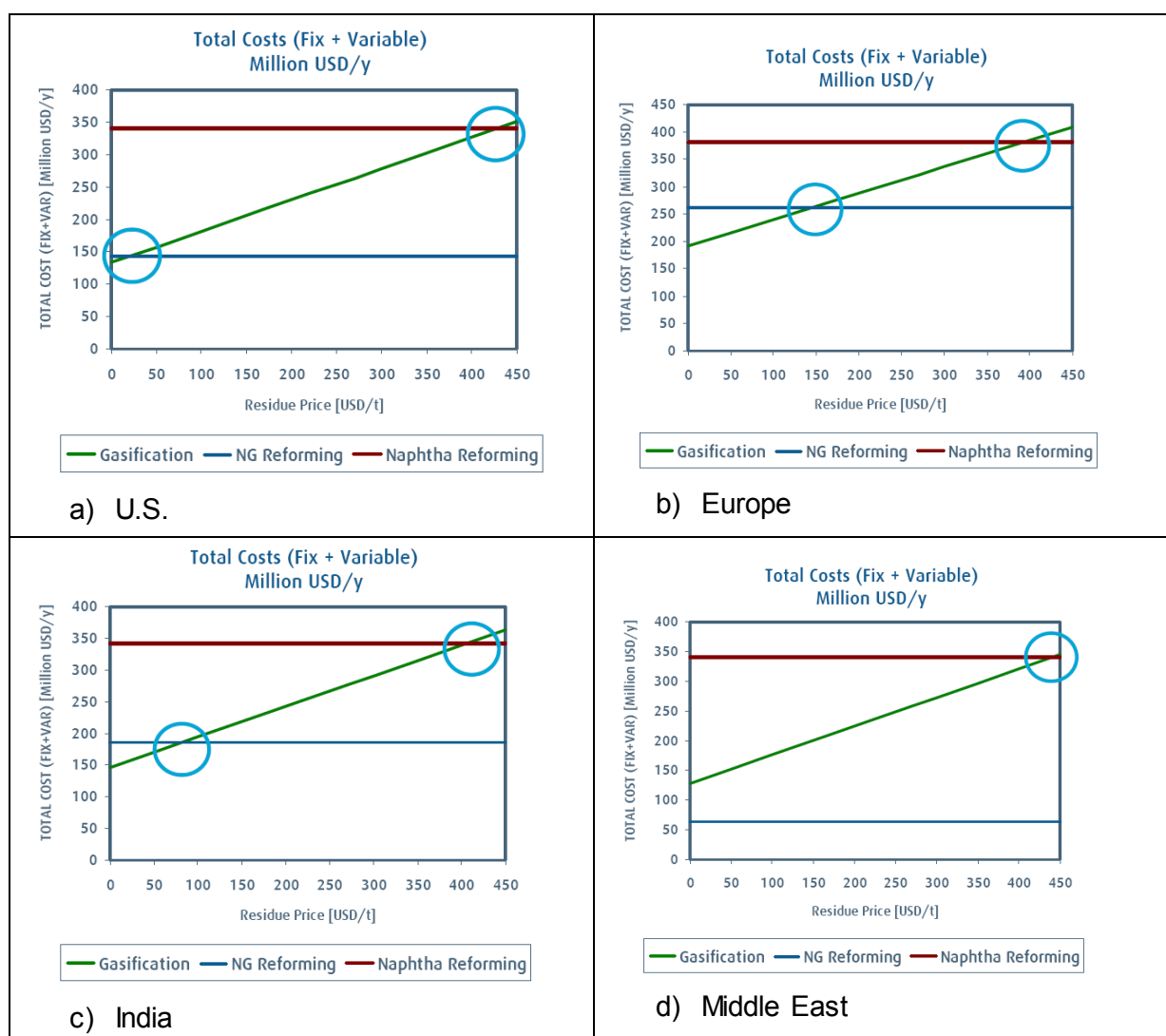


Figure 3-44 Sensitivity analysis for prices of vacuum residues (85)

Comparing the production costs for the co-production of 120,000 m³/h(STP) hydrogen and 30,000 m³/h (STP) carbon monoxide, the gasification route becomes the most economic solution if the refinery residue prices stay below:

- 110 U.S.\$/t for production in the U.S.,



- 260 U.S.\$/t for production in Europe,
- 180 U.S.\$/t for production in India.

Due to the low gas price in the Middle East, the steam reforming of natural gas remains lowest cost route, even if the share on carbon monoxide rises.

Focusing on the impact of energy and raw material costs, Stefano Innocenzi shows that steam reforming of natural gas is the most economic combination of feedstock and reaction route for the production of hydrogen. Only if the price of natural gas rises dramatically, or if the price for refinery residue is very low, the gasification route can compete. If only naphtha (650 US\$/t), or refinery residues are available, the gasification of refinery residues is more economic, if the price for residues stays below 400 U.S.\$/t (85).

Previous evaluations referred to only one specific product, comparing production costs for different plant capacity, feedstock material and reaction routes. In the following, the focus lies on the comparison of production costs for different syngases and syngas production routes, but the same feedstock, natural gas.

Feedstock specific Calculation (Natural Gas / Methanol Syngas)

The variety of process options for syngas production leads to numerous syngas compositions for the gas-phase synthesis of methanol, which is basically determined by the Stoichiometric number ($SN > 2$). Depending on the production route, SN varies from 3 (SMR) to 2 (ATR, CR). Figure 3-45 visualizes the difference in production costs of some syngases, pricing basis 2003, Middle East (15).

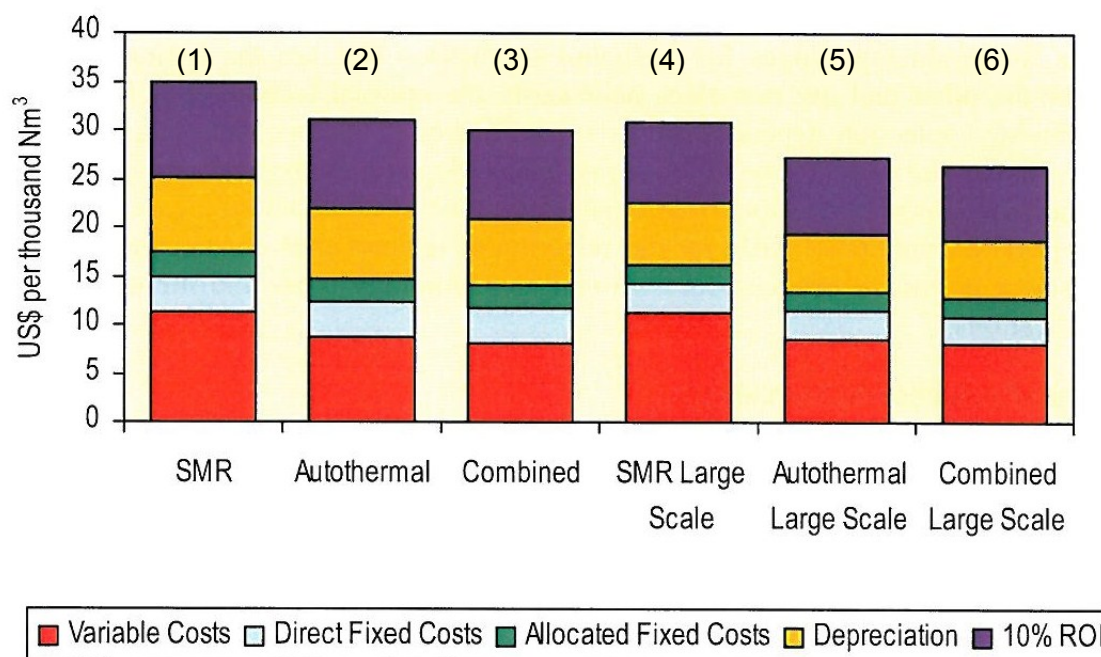


Figure 3-45 Cost of production comparison for methanol syngas by technology (15)

Column 1, 2 and 3 show the production costs for SMR, ATR and combined reforming (CR) of natural gas with an annual syngas capacity of 2,500 million m^3 (STP).



Column 4, 5 and 6 visualize the syngas production costs for large scale plant capacities of 4,150 million m³/a(STP).

Allocated fixed costs, depreciation and ROI of the single steam reformer unit are similar to the expenditures for ATR or CR which include an air separation unit each. But steam reforming of natural gas (column 1 and 4) consumes more feedstock than the autothermal or the combined reforming and consequently SMR is the route with highest production costs. Considering by-product credits for the surplus on hydrogen, which can be recycled or sold, SMR-production route becomes more competitive.

Feedstock specific Calculation (Natural Gas / specific Syngases)

Whereas the afore mentioned feedstock specific calculation only considered production costs for methanol syngas, the calculation, visualized in Figure 3-46, includes the production costs for carbon monoxide, oxogas (H₂:CO~1), methanol and Fischer-Tropsch syngas (H₂:CO~2), as well as H₂ and ammonia syngas. Plant capacity and syngas quality for industrial scale applications have been considered.

The investment costs have been based on Nexant's PERP Report 09/10S11 (19), including:

- capital costs of the facilities, like:
 - a) manufacturing area, containing process equipment to convert raw material into product, called ISBL (inside battery limits);
 - b) administrative buildings, utility generation, ..., called OBL (outside battery limits);
- annual depreciation, generally calculated with 10% ISBL, 5%OBL;
- return on capital employed (ROCE), calculated with 10%;
- insurance and property tax, included with 1.5% of total plant capital.

Pricing basis for feedstock, utility and manpower refer to Nexant's internal databases, considering prices of the U.S. Gulf Coast (USGC), 1st quarter 2010, as listed in Table 3-47.



Table 3-47 Feedstock, by-product and utility prices (USGC, 1st quarter 2010) [based on (19)]

	Unit	Price / Unit in US \$
Raw material (Feedstock and By-product)		
Natural gas	GJ	5.24
Oxygen	ton	64.90
Hydrogen	ton	1,091.60
Purge gas	ton	261.93
Utilities		
Power	MWh	57.36
Cooling Water	10 ³ ton	29.04
Process Water	ton	0.32
Boiler Feed Water	ton	0.55
HP Steam	ton	22.78
MP Steam	ton	20.20
LP Steam	ton	19.90
Fuel	GJ	5.24
Inert gas	ton	52.60
Manpower		Costs / (year person)
Operators	annual costs	48,225
Foremen	annual costs	54,739
Supervisor	annual costs	66,053

Figure 3-46 visualizes:

- economy of scale for auto-thermal reforming of natural gas (columns 3, 9, 10)
- costs for different CH₃OH-syngas mixtures (columns 7-9)
- expenses for cryogenic separation of pure CO, with syngas from SMR, POX and ATR as raw material (columns 4-6)
- costs for the production of H₂-syngas for PSA, at typical plant capacity of 800 million m³/a (STP) (column 13)
- production costs for NH₃-syngas by catalytic partial oxidation at large scale (column 11)

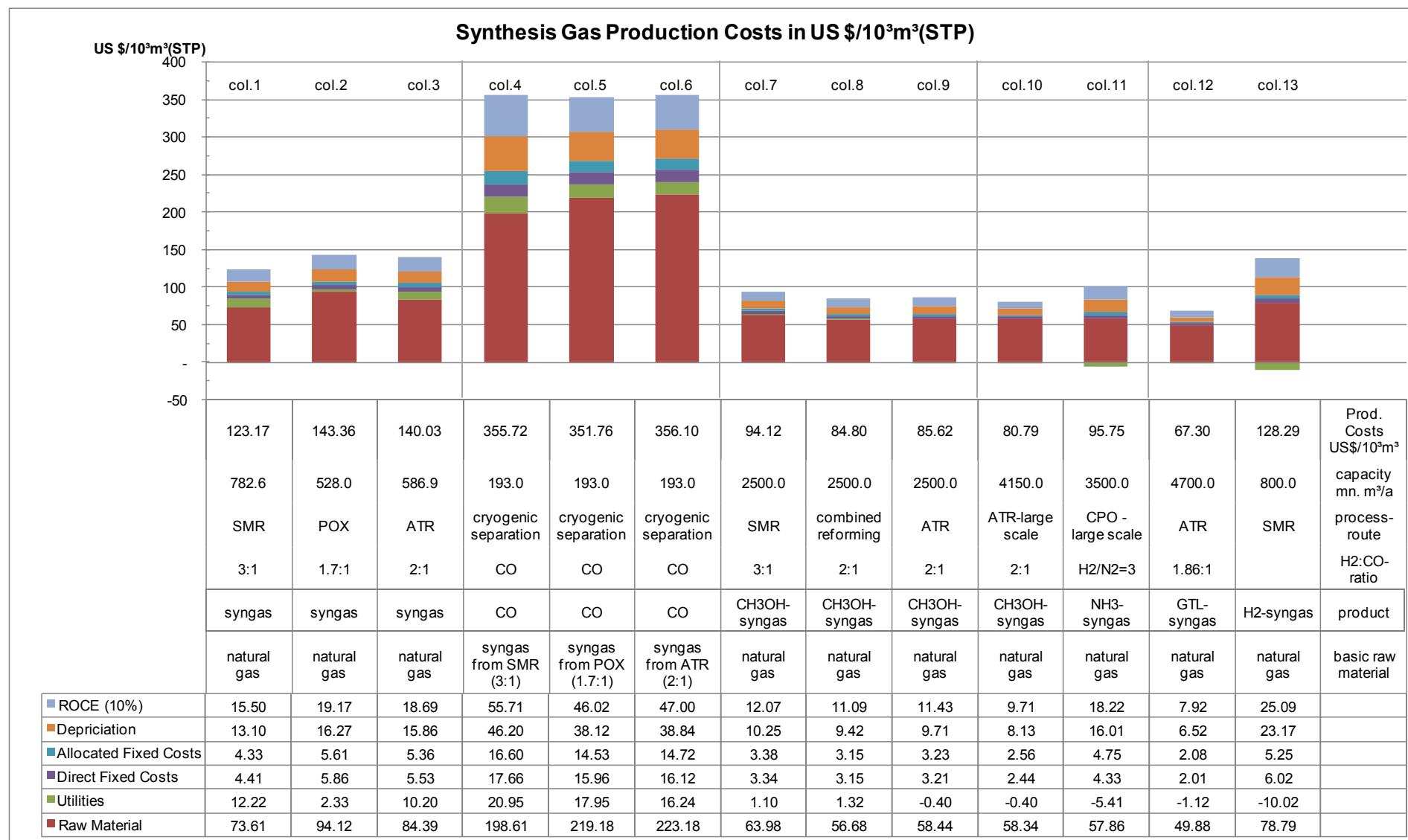


Figure 3-46 Comparison of production costs for different syngas mixtures based on feedstock natural gas (2010) [own description, modified data, origin: (19) and (15)]



Besides economy of scale, the production costs are very sensitive to changes in raw material prices, holding a cost-share of over 50%. Due to regional differences in pricing policy, the location of the plant is decisive.

But also the credit-values of by-products like steam or hydrogen determine the production costs. E.g. excess hydrogen in CO, oxo-, methanol- and Fischer-Tropsch syngas can be recycled as fuel within the process or sold as by-product achieving credits up to 1.6 times the hydrogen fuel value.

Another important factor is the energy integration and utilization, e.g. the utilization of excess steam by internal recycling.

The production cost evaluation of different syngas generation techniques depends on a number of specific factors, like location, plant design, by-product management, capacity, energy management or industrial applications on site. Therefore the production costs for each process design may differ in the range of approximately +/- 20%.

Figure 3-46 visualizes a selection of generation processes under certain circumstances and therefore it can only serve to illustrate approximate values for the production costs.

4 Chemical Utilization of selected Excess Gases

The process design for the utilization of iron making excess gases to generate the selected syngases can be structured according to the syngas production from feedstock natural gas or coal, described in chapter 3.2. While the reaction route for the generation of H₂ and CO is not necessary for COREX[®] and FINEX[®] export gases as they already contain significant amounts of H₂ and CO (Table 1-1), an export gas treatment and conditioning process based on standard gas technologies needs to be designed. Besides export gas compression, the process design includes H₂:CO-ratio adjustment, gas purification, final purification and syngas compression.

In chapter 4.1 the main process steps, its design criteria and technology specifics are discussed. Specific process designs, flow diagrams, process description for export gas treatment and the resulting syngas and product gas compositions for the generation of CO, oxogas, methanol- and Fischer-Tropsch syngas, H₂ and ammonia syngas are then outlined in detail.

Coke oven gas (COG), which has been processed into hydrogen rich syngas since the early 20th century, has been replaced as feedstock by natural gas, mainly due to the complexity of gas purification and the compression costs. Within the last 30 years only few PAS plants have been installed to produce H₂ from COG. Chapter 4.2 gives a brief account of state of technology for H₂ production and CAPEX estimations based on COG.

4.1 COREX[®] and FINEX[®] Export Gas Treatment

The basic steps of appropriate gas treatment necessary to convert COREX[®] and FINEX[®] export gases into the specific syngases are shown in Figure 4-1.

Basic process design for export gas treatment:

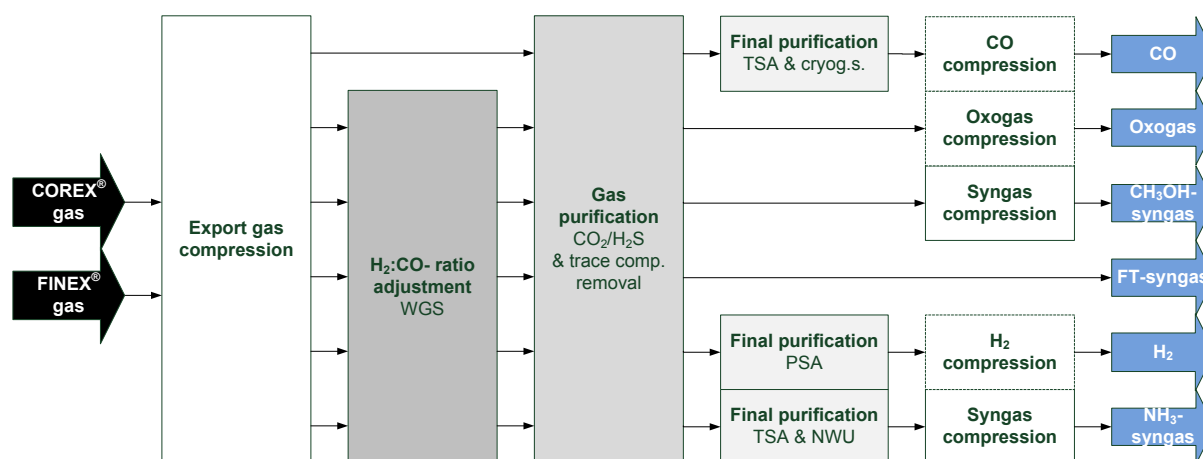


Figure 4-1 Block scheme of basic export gas treatment steps [own description]

Each process design includes the export gas compression as a first process step and the gas purification for the removal of CO₂, H₂S and some trace compounds. Furthermore the specific designs include:

- Carbon monoxide (CO): Final purification by temperature swing adsorption (TSA) and cryogenic separation, product gas compression optionally
- Oxogas (H₂:CO-ratio ~1): Water gas shift (WGS) with part-stream bypass, oxogas compression optionally
- Methanol (CH₃OH-) syngas (H₂:CO-ratio ~2): WGS with part-stream bypass, syngas compression
- Fischer-Tropsch syngas (H₂:CO-ratio ~2): WGS with part-stream bypass
- Hydrogen (H₂): WGS, final purification by pressure-swing adsorption (PSA), product gas compression optionally
- Ammonia (NH₃-) syngas: WGS, final purification by TSA and nitrogen wash unit (NWU), product gas compression

Table 4-1 summarizes the necessary process units for the treatment of COREX[®] and FINEX[®] export gases into the selected intermediates.

Table 4-1 Syngas-ratio and treatment steps for the conversion of COREX[®] and FINEX[®] export gas into selected syngases [own description]

Generation of Process units	CO	Oxogas	CH ₃ OH-/ FT-syngas	H ₂	NH ₃ -syngas (incl. CO ₂ for Urea)
Compression	+	+	+	+	+
H ₂ :CO- ratio adjustment	-	+	+	+	+
Gas purification	+	+	+	+	+
TSA	+	-	-	-	+
Cryogenic separation of H ₂ /N ₂ /CO	+	-	-	-	-
PSA	-	-	-	+	-
NWU	-	-	-	-	+
Compression	o	o	+/-	o	+*
H₂:CO-ratio	0:1	1:1	2:1	1:0	1:0

+ needs to be applied

- not applied

o depends on downstream application

* typically applied within the downstream process

According to the defined syngas requirements in Table 3-43 and the export gas compositions given in Table 1-1, including the trace compounds H₂S, HCl, HF, HCN, BTX, NH₃, PAH, COREX[®] and FINEX[®] export gases have to be upgraded according to the design data summarized in Table 4-2. Oxygen content and dust (≤5 mg/m³(STP); grain size ≤20 μm) have not been considered in the simulations.



Table 4-2 Design data for export gas treatment [own description]

		CO	oxogas	CH ₃ OH-syngas	FT-syngas	H ₂	NH ₃ -syngas	
Compression	suction pressure [MPa]	0.1	0.1	0.1	0.1	0.1	0.1	
	discharge pressure [MPa]	3.5	4.0	4.0	4.0	4.0	4.0	
	export gas temperature	min.: 40°C max. 130°						
	cooling water temp./pres.	inlet: 30°C, outlet: ~40°C / pressure: 0.6 MPa						
	efficiency per stage	0.856 for 1 st stage, 0.87 for 2 nd to 5 th stage each						
WGS	start of run-temp. 300°C	H ₂ :CO-ratio in syngas	CO	1	2	2	H ₂	H ₂
	max. temperature 500°C	S:C-ratio*	-	2	2	2	2	2
		Δp _v [MPa]	-	0.5	0.5	0.5	0.5	0.5
	WGS/ bypass-flow ratio	COREX [®] export gas	-	0.375/ 0.625	0.77/ 0.23	0.77/ 0.23	1/ 0	1/ 0
		FINEX [®] export gas	-	0.31/ 0.69	0.73/ 0.27	0.73/ 0.27	1/ 0	1/ 0
Rectisol absorber	treated gas	CO ₂ [mol-%]	0.001	0.1	3	3	3	0.001
		H ₂ S [ppm _v]	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	CO ₂ - product for urea	volume flow [m ³ /h(STP)]	-	-	-	-	-	~ 60,000
		CO ₂ purity [mol-%]	-	-	-	-	-	~ 99%
	CO ₂ - carrier gas	volume flow [m ³ /h(STP)]	~20,000	~20,000	~20,000	~20,000	~20,000	~20,000
		CO ₂ purity [mol-%]	98.5	99	99	99	99.5	99.5
Final purification	CO/H ₂ purity	CO [mol-%]	>97	-	-	-	-	<0.0010
		H ₂ [mol-%]					>99.9	-

* S/C = steam to carbon



In the following, the design criteria and boundary conditions of the five basic process steps for export gas treatment are discussed in general for the defined synthesis gases.

Export Gas Compression

The export gas volume flow of approximately 300,000 m³/h(STP) needs to be split into two part streams to allow an economic compression design, as shown in Figure 4-2.

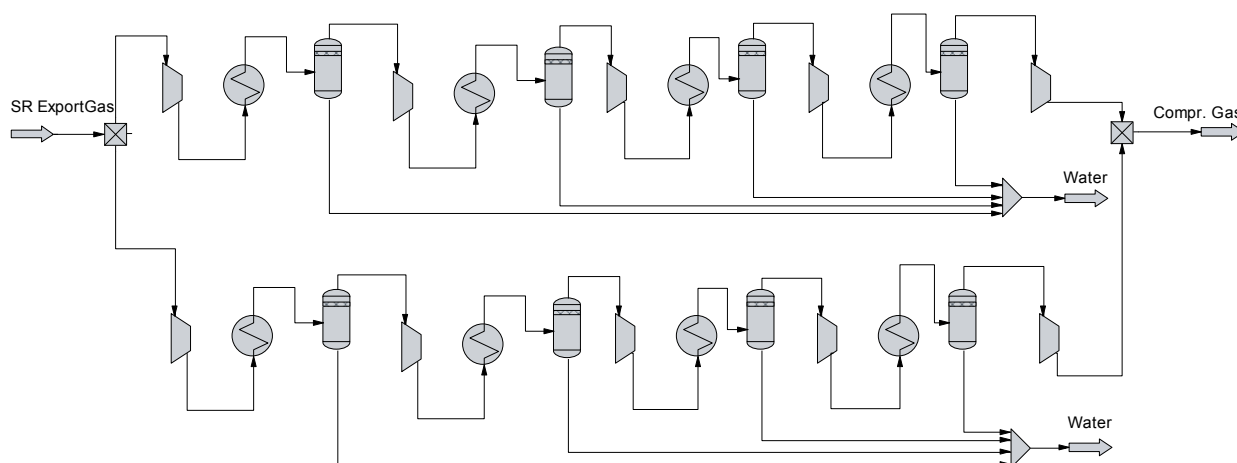


Figure 4-2 Export gas compression: 2 parallel integrated 5-stage turbo compressors [own simulation]

The compression section includes two parallel 5 stage turbo compressors with integrated cooler according to the compression design given in Siemens plant study (86). Export gas, which is sent to H₂:CO-ratio adjustment in a shift reactor, is compressed up to 4 MPa, export gas for cryogenic H₂/N₂/CO separation is pressurized up to 3.5 MPa, before entering the CO₂/H₂S absorber for gas purification. The temperature limit for export gas compression has been assumed to be at 130°C according to the syngas design specifications for compression (80).

H₂:CO-ratio Adjustment

According to the export gas composition, which includes approximately 30% CO₂ and below 100 ppm_v H₂S, the high temperature shift (HTS) reaction on a robust catalyst system is the only feasible technology for water gas shift without previous export gas treatment, as described in chapter 3.2. According to Südchemie (Meyer, O.) the ShiftMax[®] 120 catalyst would be suitable to convert untreated export gases, but life-cycle validation should be run before installation. The operating pressure for the chosen catalyst can vary from 2 to 4 MPa. The start of run temperature should range between 300°C and 350°C the outlet temperature for the ShiftMax[®] 120 catalyst is limited with 500°C (87).

The percentage of CO at the reactor outlet is reduced to below 3% based on dry gas. For the generation of oxogas with a H₂:CO-ratio of 1 or methanol- and Fischer-Tropsch syngas with a H₂:CO-ratio around 2, a share of the export gas is bypassed to the reactor. The pressure drop over shift reactor and heat exchangers has been estimated with 0.5 MPa.

Gas Purification – CO₂/H₂S/Trace Compound Removal

According to the introduced technical overview for sour gas removal (chapter 3.2), the given partial pressures of CO₂ and H₂S

- $p_{\text{CO}_2}=1.15 \text{ MPa}$ ($p_{\text{H}_2\text{S}}=294 \text{ Pa}$) in COREX[®] export gas and
- $p_{\text{CO}_2}=1.31 \text{ MPa}$ ($p_{\text{H}_2\text{S}}=161 \text{ Pa}$) in FINEX[®] export gas

and product gas limits defined:

- H₂S: 0.1 ppm_v
- CO₂: 10 ppm_v (to TSA/cryogenic separation or NWU) - 3% (methanol- or FT-syngas)

the Rectisol absorption process has been chosen for all sour gas removal steps within the COREX[®] and FINEX[®] export gas treatment (Figure 4-3).

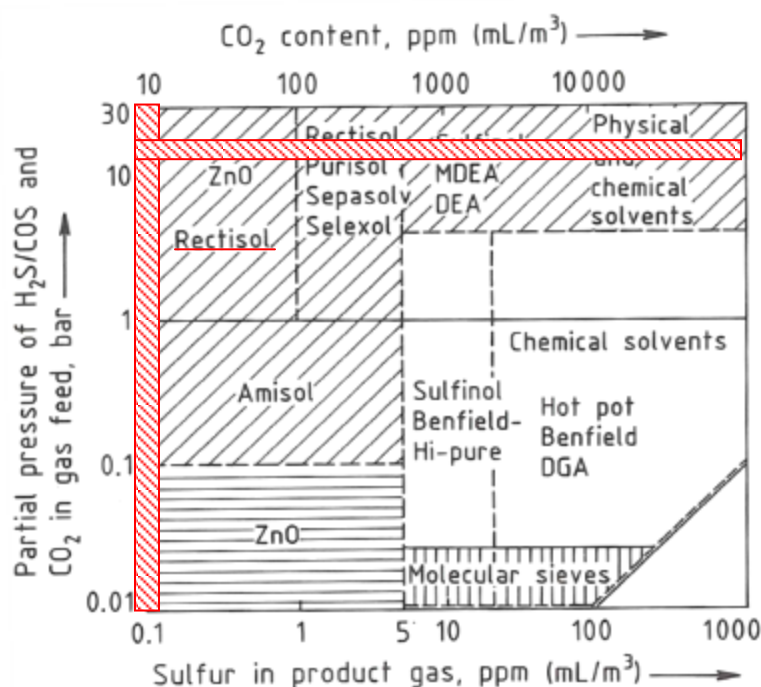


Figure 4-3 Selection of H₂S/COS and CO₂ removal process for COREX[®] and FINEX[®] export gas [(25) modified]

The Rectisol absorption technique includes:

- a prewash unit for the removal of NH₃ (~10ppm) from FINEX[®] export gas (not relevant for COREX[®] export gas due to low content).
- a methanol prewash unit for the removal of BTX and PAHs (~50 m³/h(STP));
- the reduction of H₂S down to levels below 0.1 ppm_v, which reduces the expenses for an extra H₂S purification step.
- the reduction of CO₂ down to 3%, 10 ppm_v respectively. Hereby a part of the removed CO₂ is separated with a purity of around 99%: ~60,000 m³/h (STP) as feedstock for urea synthesis in NH₃-syngas production; furthermore ~20,000 m³/h (STP) which can optionally be utilized as carrier gas within the smelting reduction process.



- the enrichment of H₂S in an extra H₂S fraction (~5,000m³/h(STP): H₂S~0.5%) to be added to internal excess gases before combustion. Alternatively the H₂S fraction can be given to a suitable sulfur recovery process.

HCl, HF and HCN removal is not necessary, due to the low content (<1 ppm_v) in the export gases.

The Rectisol process design has been provided by Linde engineering including flow chart, process description, material balance, utility demand and the estimation of investment costs (88).

Final Purification

Quality requirements for oxogas, methanol and Fischer-Tropsch syngas are already met after Rectisol wash column. In case of pure CO, H₂ and ammonia syngas production, a final purification is necessary:

- CO: TSA and cryogenic H₂/CO, N₂/CO and CO/CH₄ separation
- H₂: PSA to separate all impurities from H₂
- NH₃: TSA and NWU to further purify ammonia syngas and to adjust H₂:N₂-ratio

Detailed information on the final purification units is given in chapter 4.1.1, 4.1.4 and 4.1.5.

Syngas Compression

- Depending on the specifications a compression for CO, oxogas and H₂ might be necessary after export gas treatment but has not been considered within this thesis.
- The basic design data for one stage methanol syngas compression is similar to boundary conditions given for the five stage export gas compression.
- Syngas compression for ammonia syngas is typically done within the synthesis loop and has not been considered within the simulations.

4.1.1 Process Design for Carbon Monoxide

COREX[®] and FINEX[®] export gases are low in H₂ but rich in CO (H₂:CO-ratio ~0.4 – 0.5), therefore the utilization as feedstock for carbon monoxide production seems to be a promising option. The typical CO product requirements determined by the downstream carbonylation of methanol are given in Table 4-3.

Table 4-3 CO requirements for methanol carbonylation by Monsanto, Celanese [based on (33), (20)]

Acetic acid process	Process parameter		CO-capacity [m ³ /h (STP)]	CO-purity [mol-%]	Limitation of compounds			
	p [MPa]	T [°C]			CO ₂ [ppm _v]	S-comp [ppm _v]	CH ₄ [ppm _v]	H ₂ O [ppm _v]
Monsanto, Celanese	3-6	150-200	< 60,000	97-99.9	< 20	< 0.1	< 500	-



The export gas treatment according to the CO product requirements and the COREX® and FINEX® export gas compositions, given in Table 1-1, is outlined in Figure 4-4.

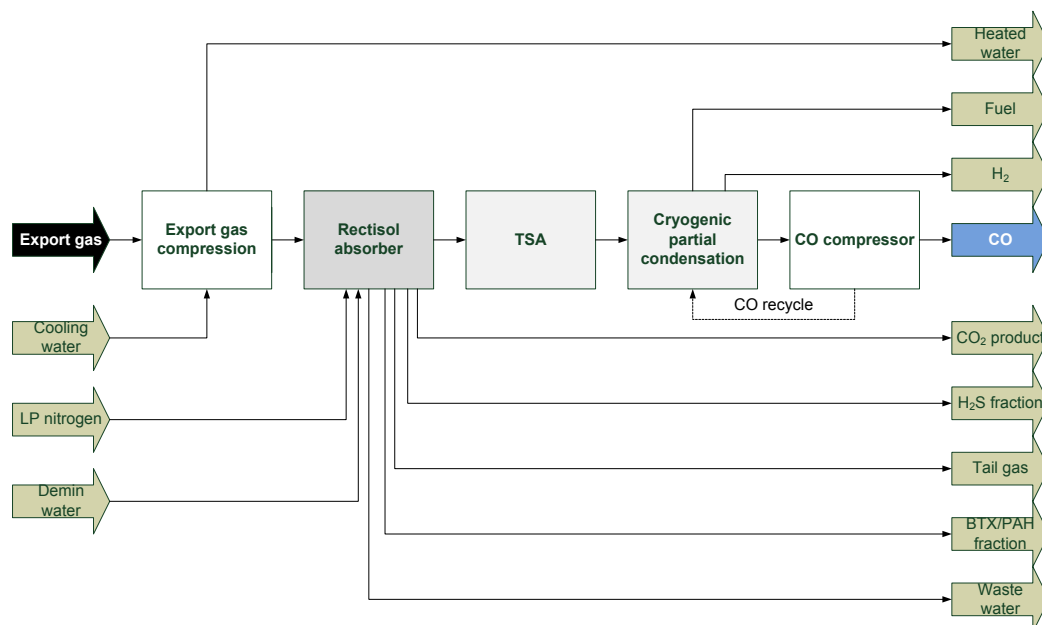


Figure 4-4 Simplified block scheme of export gas treatment for CO production [own description]

Export gas treatment: Export gas is compressed and cooled, then the conditioned gas (Q1: 3.5 MPa/ 40°C) is sent to Rectisol absorber unit, where trace compounds, CO₂ and H₂S are removed. The simplified process scheme for sour gas removal is shown in Figure 4-5.

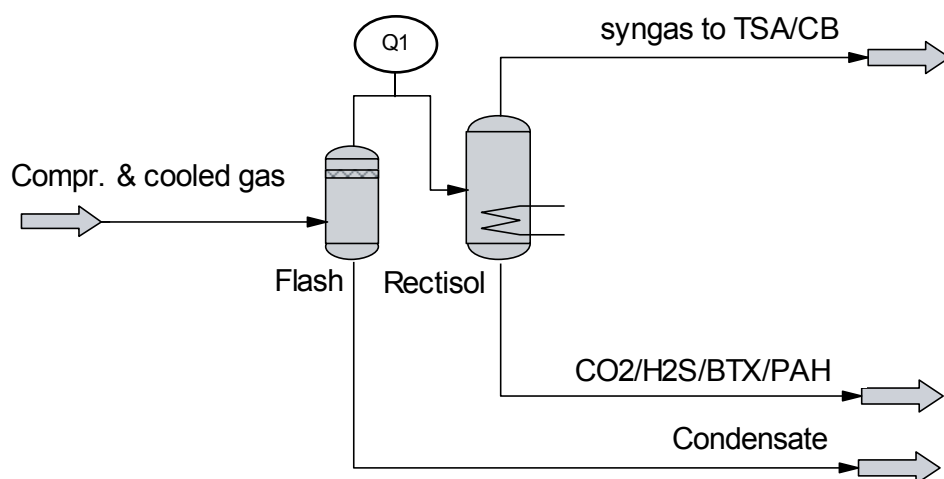


Figure 4-5 Simplified process scheme of sour gas removal for CO [own description]

Final purification: As described in chapter 3, the cryogenic separation is state of the art technology for the conventional recovery of CO from synthesis gas. A summary of syngas requirements for partial condensation and methane wash process is given in Table 4-4.

Table 4-4 Syngas requirements and conditions for the cryogenic separation of CO [based on (19), (40)]

Cryogenic process selection	Syngas requirements / conditions				Typical CO-capacity [m ³ /h (STP)]	CO-recovery rate [%]	CO/N ₂ -purity [mol-%]	H ₂ -purity [mol-%]
	P [MPa]	T [°C]	CO ₂ , H ₂ O, S-comp.	CH ₄				
partial condensation	3 - 4	-185	removed	-	< 60,000	75 - 90*	98.5-99.9	96 - 98
methane wash	3 - 4	-183	removed	> 2%	< 60,000	95 - 98	98.5-99.9	>98

* 95% for 2-stage process

Due to the limitation of CH₄ (<500 ppm_v) in CO product specification, the partial condensation technique with additional separation columns for the removal of CH₄ and N₂ has to be applied for final COREX[®] and for FINEX[®] export gas purification (Figure 4-6). The operating temperature for the cryogenic separation is set, considering the liquefaction point of carbon monoxide (-191.5°C).

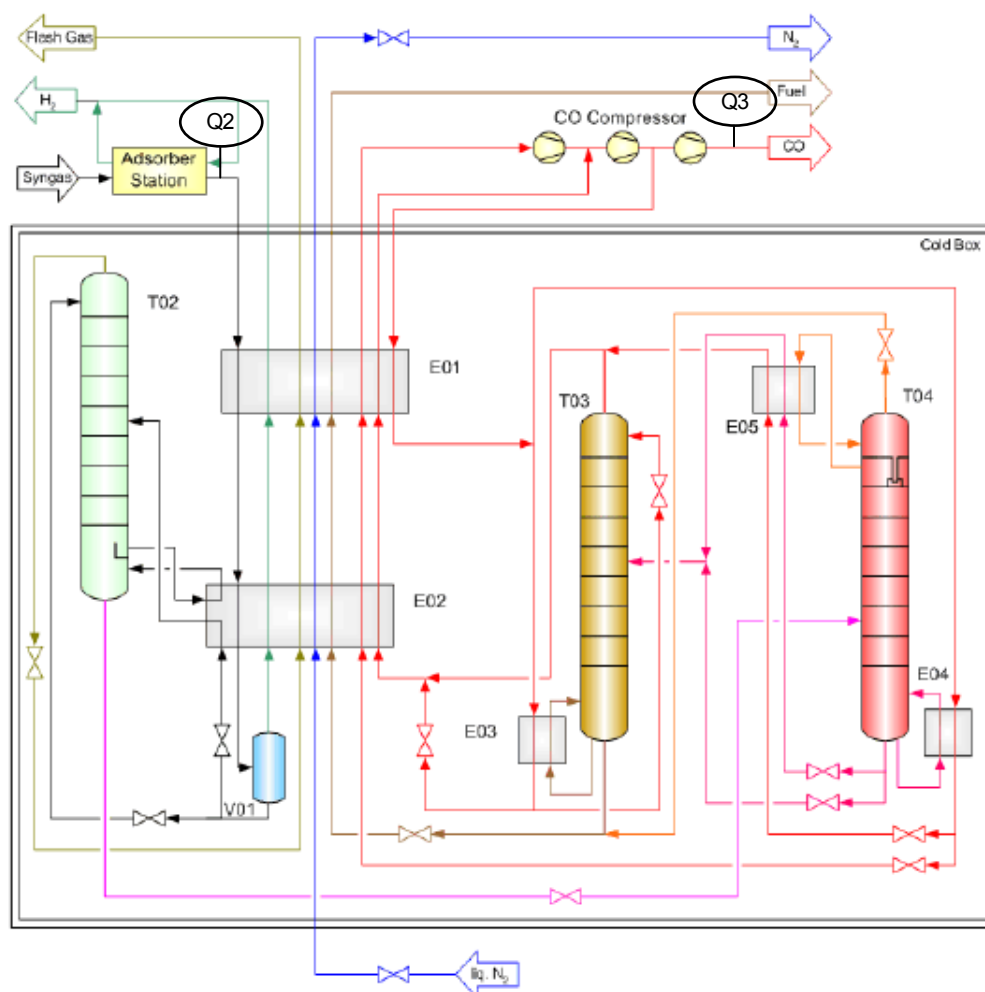
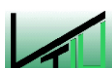


Figure 4-6 Flow chart of the Linde CP-3 process (40)



The purified export gas from Rectisol absorber (syngas) enters the adsorber station (TSA) to remove traces of H₂O, CH₃OH and CO₂. Then syngas is cooled to condensation temperature (E01/ E02), H₂ rich vapor is withdrawn in the knock-out drum (V01) and the dissolved H₂ is stripped from the CO-rich liquid in the hydrogen stripper (T02). Still containing CH₄ and N₂, the CO-rich bottom fraction then enters N₂/CO separation column T04. Afterwards, CH₄ is removed from the T04 bottom fraction in the CO/CH₄ separation column T03. Gaseous CO still containing N₂ from T03 is reheated and compressed. A part stream is recycled to T04 column to adjust the CO product quality (>97%). The CH₄ rich bottom product from T03 and the top product from T04 containing CO and N₂ are mixed and further utilized as fuel fraction.

Syngas composition before Rectisol (Q1, Figure 4-5) and before cryogenic separation (Q2, Figure 4-6) as well as achieved CO product quality (Q3) from COREX[®] and FINEX[®] export gases are shown in Table 4-5.

Table 4-5 Rectisol feed gas (Q1), syngas (Q2) and CO product gas (Q3) compositions [based on (16), (17), (89), (90)]

Stream	COREX [®] gas utilization			FINEX [®] gas utilization		
	Rectisol feed gas (Q1)	syngas to cryogenic sep. (Q2)	CO product (Q3)	Rectisol feed gas (Q1)	syngas to cryogenic sep. (Q2)	CO product (Q3)
Temperature, °C	40	30	40	40	30	40
Pressure, MPa(a)	3.5	3.21	0.92	3.5	3.21	1.02
Volume flow, m ³ /h(STP)	286,831	189,624	108,060	281,482	173,380	58,931
Component mol-%						
H ₂	17.4803	26.40	-	16.4525	26.67	-
CO	45.2427	67.55	98.5	33.9331	54.37	97.00
CO ₂	32.9037	-	-	37.5323	-	-
CH ₄	2.0566	2.96	0.002	1.5425	2.39	0.002
H ₂ O	0.2364	-	-	0.2366	-	-
N ₂ /Ar	2.0566	3.09	1.498	10.2827	16.57	2.998
H ₂ S	0.0084	-	-	0.0046	-	-
BTX	0.0146	-	-	0.0149	-	-
PAH	0.0007	-	-	0.0007	-	-
NH ₃	0.000	-	-	0.001	0.000	-

HCl, HF and HCN are below 1 ppm_v not critical (not included in calculation)

Figure 4-7 visualizes the difference of CO-purity, CO-recovery and the energy consumption for H₂ separation, H₂/N₂ and H₂/N₂/CH₄ separation via condensation process, based on syngas from coal gasification:

- CP-1 condensation process for H₂ separation: commonly applied for acetic acid plants based on coal gasification



- CP-2 condensation process for H₂/N₂ separation: due to the small difference between the boiling points of N₂ and CO the energy consumption is much higher
- CP-3 condensation process for the separation of H₂/N₂/CH₄: has to be applied for COREX[®] and FINEX[®] export gas treatment to meet the high quality requirements given in Table 4-3.

Due to the physical similarity of N₂ and CO, N₂ removal is very energy intensive (high recycling rate), leading to higher operating expenditures (OPEX) for CP-3 condensation process compared to only H₂ removal in CP-1. Furthermore the additional separation columns (N₂/CO and CO/CH₄) in CP-3 condensation process lead to higher capital expenditure (CAPEX) (40).

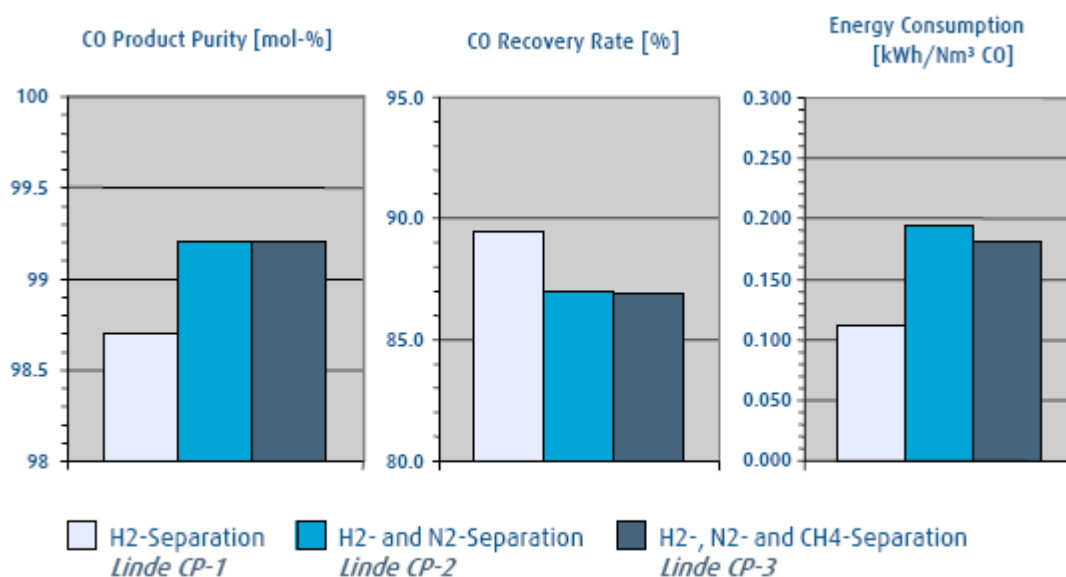


Figure 4-7 CO purity, CO recovery rate and energy consumption of different condensation processes valid for syngas from coal gasification (low CH₄ slip) (40)

Capacity: CO production capacity is determined by the end use application and the export gas volume flow. Due to the high CO content in COREX[®] and FINEX[®] export gases (Table 4-6), two to three world scale partial condensation plants need to be installed for the recovery of CO (Table 4-4), producing CO feed gas for two or one world scale downstream synthesis plants respectively (Table 4-4).

Table 4-6 COREX[®] and FINEX[®] export gas flow: CO and N₂ content [based on (16), (17)]

Smelting Reduction Export Gas	COREX [®]	FINEX [®]
Total volume flow, m ³ /h (STP)	295,000	289,500
CO-range, vol. %	40 – 50	30 – 50
CO, nominal, vol. %	~44	~33
CO-volume flow, m ³ /h (STP)	129,800	95,500
CO product	108,000	59,000
N ₂ /Ar, in CO product vol. %	~1.5	~3



Operating Conditions / Availability:

- The availability of the Rectisol wash unit is over 99.5%. Feed gas with altering CO, H₂ and CH₄ contents can be handled, and an altering CO₂ content, which typically causes a change in the temperature-profile, is not critical due to the inertia of the system. If there is a short interruption in feed gas supply, the methanol solvent loop can be maintained, or the absorber column can be shut down (91).
- The cryogenic separation can be adjusted for altering H₂:CO-ratio. Changes in the feed gas amount are tolerated between 40 and 100% of the nominal volume flow rate.

Discussion: Export gases already contain a significant amount of CO, which makes them to a valuable feedstock for CO production. Utilizing CO for downstream synthesis, 2 world scale acetic acid plants can be supplied with synthesis gas from one COREX[®] C-3000 plant, one world scale synthesis plant can be supplied from one FINEX[®] 1.5M plant.

Disadvantageously the energy demand for the cryogenic separation increases with rising N₂ content, due to physical similarity of N₂ and CO. But with the substitution of N₂ carrier and purge gases within the COREX[®] and FINEX[®] smelting reduction processes (achieved by the recycling of CO₂ from Rectisol absorber) the nitrogen content in the export gases could be reduced, leading to lower energy consumption for the cryogenic separation. Referring to Kepplinger, patents related to the substitution of inert gases (mainly N₂) in COREX[®] and FINEX[®] processes have already been filed (pers. com.). The generation of approximately 20,000 m³/h(STP) CO₂ carrier gas has already been considered within the simulation of the Rectisol process (see Table 4-2).

4.1.2 Process Design for Oxogas

The oxo-synthesis, described in chapter 3.1, requires syngas with a balanced H₂:CO-ratio around one, called oxogas. But due to the low H₂:CO-ratio of 0.4 (0.5) in COREX[®] (FINEX[®]) export gas, almost one third (one quarter) of the CO-content has to be shifted by the exothermic water gas shift reaction, described in chapter 3.2. Table 4-7 summarizes oxogas requirements for selected low pressure oxo (LPO) synthesis processes.

Table 4-7 Oxogas requirements for LPO/Mk IV process [based on (21), (34), (44)]

LPO/Mk IV process Selection	Syngas requirements / conditions				Oxogas capacity [m ³ (STP)/h]	Selectivity for aldehydes (n/i ratio)
	p [MPa]	T [°C]	H ₂ S / O ₂ (depending on catalyst)	H ₂ /CO-content [mol-%]		
Dow/ Davy	1.5-2	85-115	0.1- 5 ppm _v	50.5-53 / 47-49.5	30,000-60,000	High (92/8)
Ruhrchemie-Rhône-Poulenc	1-10	50-130	0.1- 5 ppm _v	50.5-53 / 47-49.5	30,000-60,000	High (95/5)

Export gas treatment: After compression, the export gas is split into two part streams, defined by the H₂:CO-ratio for oxogas. One part stream (4 MPa/ 300°C) is mixed with steam



(S/C~2) and sent to the shift reactor (WGS). After CO conversion, the part stream is cooled down to 40°C and mixed with the bypass stream, to adjust the H₂:CO-ratio to a value around 1. Excess water is separated from the gas flow. The gas then enters the Rectisol absorption column for the removal of CO₂, H₂S and trace compounds.

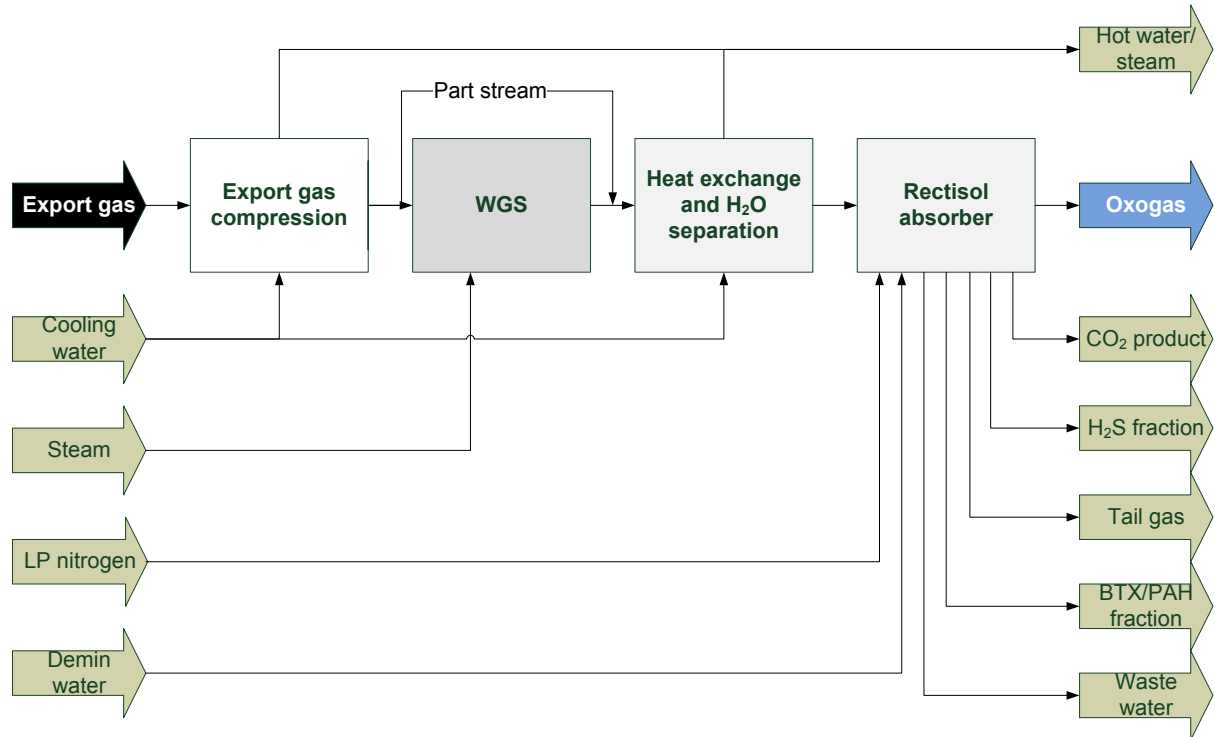


Figure 4-8 Simplified block scheme of export gas treatment for the generation of oxogas [own description]

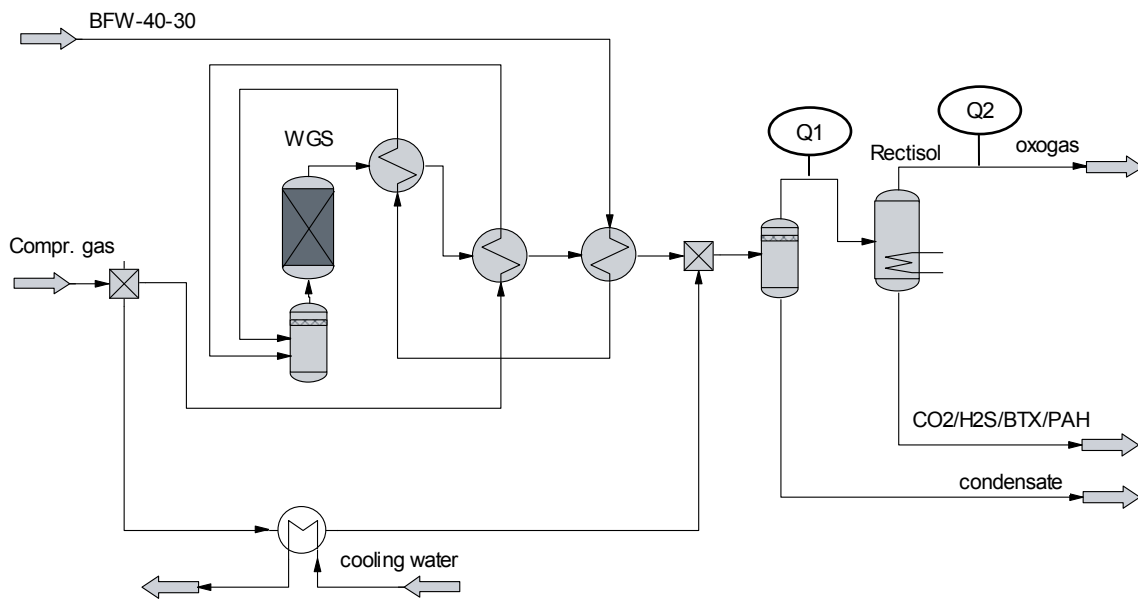


Figure 4-9 Simplified process scheme of export gas treatment for the generation of oxogas [own description]



Syngas Composition: After export gas treatment, the oxogas composition (Q2) already meets the downstream requirements for the LPO synthesis without further treatment (e.g. deep desulfurization), since CO₂ is removed to a level of approximately 0.1 mol-% and H₂S to a level below 0.1 ppm_v. Table 4-8 summarizes the gas compositions after H₂:CO-ratio adjustment (Q1) and after Rectisol absorber column (oxogas, Q2).

Table 4-8 Rectisol feed gas (Q1) and oxogas composition (Q2) [based on (16), (17), (89)]

Stream	COREX [®] gas utilization		FINEX [®] gas utilization	
	Rectisol feed gas (Q1)	oxogas (Q2)	Rectisol feed gas (Q1)	oxogas (Q2)
Temperature, °C	40	30	40	30
Pressure, MPa	3.5	3.275	3.5	3.275
Volume flow, m ³ /h(STP)	326,953	190,711	306,200	174,148
Component mol-%				
H ₂	27.54	47.17	23.1809	40.71
CO	27.51	46.69	23.1375	40.28
CO ₂	41.08	0.10	42.5591	0.10
CH ₄	1.80	2.96	1.4180	2.39
H ₂ O	0.2334	-	0.2332	-
N ₂ /Ar	1.80	3.08	9.4526	16.52
H ₂ S	0.0073	<0.1 ppm	0.0043	<0.1 ppm
BTX	0.0128	-	0.0137	-
PAH	0.0007	-	0.0007	-
NH ₃	-	-	0.001	0.000

HCl, HF and HCN are below 1 ppm_v not critical (not included in calculation)

Capacity: A world scale oxo-synthesis plant with a yearly capacity of 400,000 to 1 million tons, requires 30,000 to 60,000 m³/h (STP) of oxogas as feedstock for the synthesis process, which is about one third of the H₂ and CO gas flow from COREX[®]/FINEX[®] export gas

Operating conditions:

- **Compression/WGS:** Some of the required steam and boiler feed water (BFW) is provided by syngas cooling after the exothermic WGS reaction. If necessary, the additional demand on steam has to be supplied externally or generated by combustion of steel making excess gases.
- The **oxo-synthesis** process can operate with changing syngas flow, varying from 50 to 120% of nominal gas flow, but specific energy demand rises significantly for part-load operation below 80% of the nominal oxogas volume flow (92).

Availability: The availability of the LPO synthesis process is slightly above 90%, including planned shutdown of 2-3 weeks every two years (92).



Discussion: Due to the fact, that world scale oxo-synthesis and acetic acid plants demand around 30,000 to 60,000 m³/h(STP) oxogas and CO respectively, both synthesis plants (acetic acid and oxo-synthesis) can be supplied with treated export gas from one COREX[®] C-3000 or one FINEX[®] 1.5M plant at the same time. With this plant set up the two synthesis plants can be interrelated and excess H₂ from CO production can be recycled to adjust the H₂:CO-ratio for oxogas, which reduces the steam demand for the shift reaction. To increase the oxogas H₂:CO-ratio, around 45,000 to 50,000 m³/h(STP) of excess H₂ can be added to the oxogas flow. For small oxogas capacities, the adjustment of the H₂:CO-ratio to a value around one is possible and the WGS reactor can be spared, as shown in Figure 4-10.

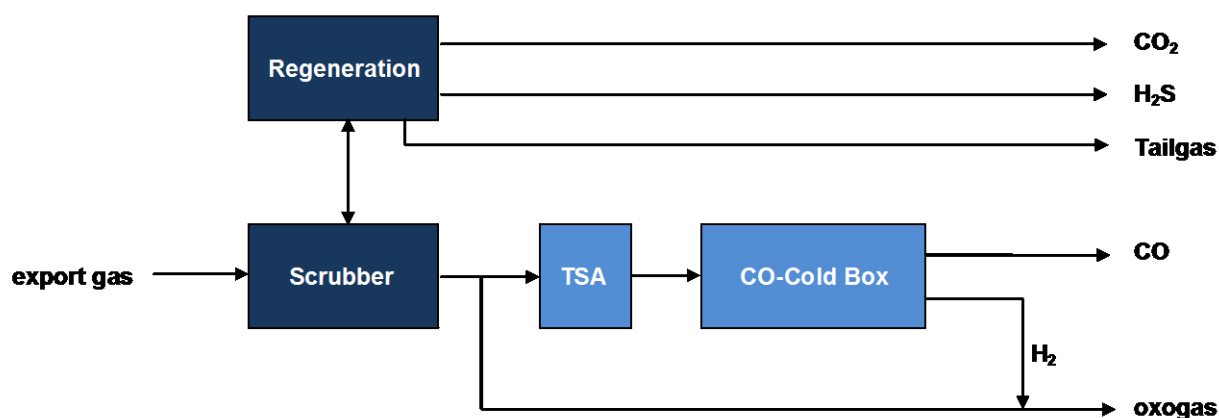


Figure 4-10 Simplified block scheme of CO and oxogas polygeneration [own description]

4.1.3 Process Design for Methanol and Fischer-Tropsch Synthesis Gas

The standard process for the synthesis of methanol, the low pressure gas-phase synthesis, demands syngas with a H₂:CO-ratio slightly above 2. The liquid phase methanol synthesis (LPMEOH[™]) developed within the last decades can convert CO-rich syngases and syngases with an altering H₂:CO-ratio down to 0.4 due to the water gas shift active catalyst slurry system (see chapter 3.1). The low H₂:CO-ratio leads to low syngas conversion and to a reduced yield on methanol (51), but COREX[®] and FINEX[®] export gases could be utilized without undergoing a previous water gas shift reaction.

Methanol production is the only Fischer-Tropsch (FT-) synthesis process, which achieves high product selectivity. The non-selective FT-synthesis technologies for the generation of C₂+ hydrocarbons are divided into

- low temperature (LT) processes, achieving heavy hydrocarbon products, and
- high temperature (HT) processes, achieving light hydrocarbons.

Fischer-Tropsch synthesis reactions generally require a H₂:CO-ratio of around 2, but synthesis reactions activated by a water gas shift active catalyst systems (mainly Fe-based) tolerate synthesis gas with a ratio below 1. Especially the slurry phase reactor system for the LTFT-synthesis, which is similar to the liquid phase methanol process, can operate with a

changing syngas-ratio. Table 4-9 summarizes Fischer-Tropsch and methanol syngas requirements.

Table 4-9 Syngas requirements for methanol and Fischer-Tropsch liquids [based on (15), (24), (29), (51)]

Process selection	Syngas requirements / conditions					Typical product capacity	Product purity (gasoline/diesel-ratio)
	P [MPa]	T [°C]	H ₂ :CO (SN)	H ₂ S/HCl, HF [ppm _v]	Conv./pass		
Low pressure gas-phase	5-10	220-300	>2	0.1-5	50%	3,000-5,000 t/d	crude methanol, H ₂ O: 4-20wt%
LPMEOH™	7-8	~250	>0.4	0.1-5	low	260 t/d (pilot scale)	fuel grade methanol, H ₂ O: 1wt%
LTFT: Co-based (Fe-based)	2.5-4.5	220-250	~2 (>0.4)	0.1-5	60-90% (lower)	Reactor cap. ~3,000 m ³ /d	diesel, wax (G:D~20:80)
HTFT	2.5	330-350	>0.6	0.1-5	85%	Reactor cap. ~3,200 m ³ /d	gasoline, light olefins (G:D~80:20)

Export gas treatment for gas-phase methanol synthesis and LTFT-syngas (H₂:CO-ratio ~2):
The export gas treatment, shown in Figure 4-11 and Figure 4-12, includes a WGS-reactor to adjust the Stoichiometric Number (SN) for ongoing gas-phase methanol synthesis reactions to a value slightly above 2, leading to a H₂:CO-ratio of 2.

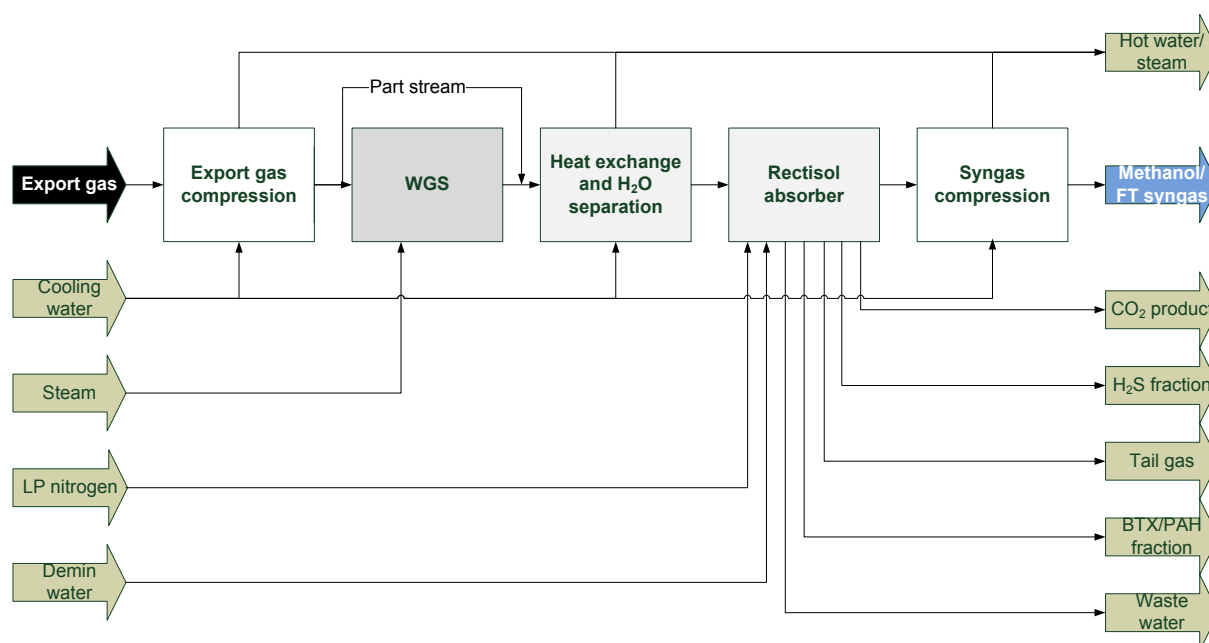


Figure 4-11 Simplified block scheme of export gas treatment for methanol or FT-syngas [own description]

The required process steps are similar to the process steps for oxogas generation, but the WGS/bypass-flow rate is higher according to the $H_2:CO$ -ratio of 2. Furthermore methanol syngas has to be compressed up to 5 MPa and the LTFT-syngas has to be heated to 250°C.

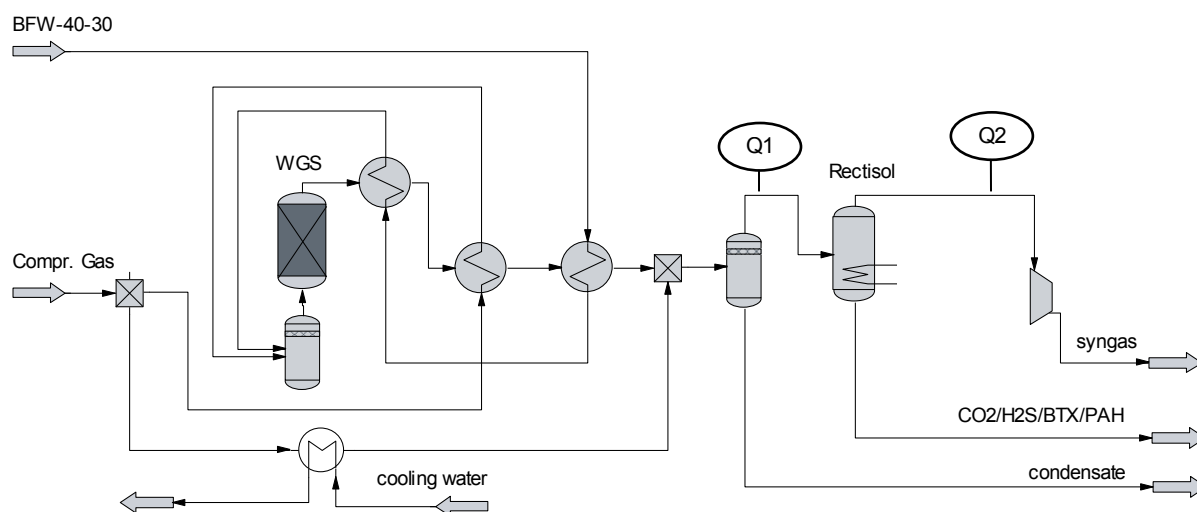


Figure 4-12 Simplified process scheme of export gas treatment for methanol syngas [own description]

Syngas Composition: Rectisol feed gas (Q1) and achieved syngas (Q2) compositions, for gas-phase methanol and Fischer-Tropsch synthesis, are shown in Table 4-10.

Table 4-10 Rectisol feed gas (Q1) and methanol (FT-) syngas composition (Q2) [based on (16), (17), (89)]

Stream	COREX [®] gas utilization		FINEX [®] gas utilization	
	Rectisol feed gas (Q1)	Methanol/ FT-syngas (Q2)	Rectisol feed gas (Q1)	FT-/ methanol syngas (Q2)
Temperature, °C	40	30	40	30
Pressure, MPa	3.5	3.28*	3.5	3.28
Volume flow, m ³ /h(STP)	368,782	196,838	340,176	179,795
Component mol-%				
H ₂	35.7724	66.95	30.8331	58.28
CO	13.0123	24.18	10.8591	20.38
CO ₂	47.7687	3.00	48.2758	3.00
CH ₄	1.5996	2.88	1.5425	2.32
H ₂ O	0.2289	-	0.2302	-
N ₂ /Ar	1.5996	2.98	8.5085	16.02
H ₂ S	0.0065	<0.1 ppm	0.0038	<0.1 ppm
BTX	0.0114	-	0.0123	-
PAH	0.0007	-	0.0007	-
NH ₃	0.000	-	0.001	0.000
CH ₃ OH	-	0.004	-	0.004

HCl, HF and HCN are below 1 ppm_v not critical (not included in calculation)

* Methanol syngas pressure after Rectisol but before syngas compression



Due to the adjustment of the SN for gas-phase methanol synthesis, typically 3% CO₂ remain in the syngas. A deep desulfurization is not necessary for methanol and Fischer-Tropsch syngas either, as the H₂S content is already below 0.1 ppm_v.

Export gas treatment for LPMEOH™ and HTFT-syngas without H₂:CO-ratio adjustment:

The export gas treatment only includes compression, heat exchange and gas purification. For LPMEOH™, the syngas is further pressurized to ~8 MPa and sent to LPMEOH™ synthesis loop. Reheated HTFT-syngas (~4 MPa/ 330°C) is sent to HTFT synthesis process.

Capacity: Export gases from a COREX® C-3000 plant or a FINEX® 1.5M plant (CO and H₂-capacity: ~180,000 m³/h (STP)) can be utilized to produce around 1,600 tons of methanol or Fischer-Tropsch liquids daily, which is significantly lower than the standard capacity of a typical low pressure gas-phase methanol plant with 3,000 to 5,000 t/d. But the export gas volume flow is large enough to produce methanol for one world scale acetic acid plant with a typical acetic acid capacity of 3.000 t/d (93) and it matches perfectly with the syngas demand of a Fischer-Tropsch reactor (capacity: 3,000 m³/d).

Operating Conditions: Gas- and liquid phase processes for methanol and Fischer-Tropsch liquids are not sensitive to interruptions in syngas supply or changing syngas amounts. During short interruptions, the system can remain under operating conditions. Especially the slurry phase reactor can be operated under changing syngas and operating conditions due to the slurry catalyst system.

Discussion: Gas-phase methanol and LTFT-synthesis on a copper-catalyst system require a H₂:CO-ratio of 2, which is achieved by carbon monoxide shift within the export gas treatment. Shift active catalyst systems for LPMEOH™ and FT-synthesis can process syngas with a low H₂:CO-ratio down to 0.4, and consequently the purified and compressed export gases can be sent to the synthesis loop without previous shift reaction. But due to the reduced syngas conversion and the extended synthesis reactor size for the reactions with CO-rich syngases, a previous shift reactor might be advantageously also for shift active catalyst systems. In any case, interruptions in syngas supply do not cause catalyst damage or force a shutdown of the methanol or Fischer-Tropsch synthesis reactor.

4.1.4 Process Design for Hydrogen

Pure H₂, often required as reducing or hydrogenation agent in chemical, petrochemical and iron and steel making industry, can be produced from COREX® and FINEX® export gases, though they are low in H₂. To achieve a high product yield, the bulk of CO has to be shifted into H₂ before the final purification. Table 4-11 shows typical H₂ product quality requirements for chemical downstream processes.



Table 4-11 H₂ product quality [based on (22)]

H ₂ -purity [mol-%]	Limitation of compounds				
	CO [ppm _v]	CO ₂ [ppm _v]	S-comp [ppm _v]	CH ₄ [ppm _v]	H ₂ O [ppm _v]
98-99.99	<1	<20	<0.1	<1	<1,100

Final purification: As described in chapter 3.1, the pressure-swing adsorption (PSA) is the standard technology for the final purification of hydrogen on industrial scale. Table 4-12 shows typical process conditions and syngas requirements for H₂ separation via PSA.

Table 4-12 Syngas requirements and conditions for the final purification of H₂ via PSA [based on (65)]

Process selection	Syngas requirements / conditions			Typ. H ₂ -PSA plant capacity [m ³ (STP)/h]	H ₂ -recovery [mol-%]	H ₂ -purity [mol-%]
	Syngas pressure [MPa]	Syngas Temp. [°C]	Typ. syngas capacity [m ³ (STP)/h]			
PSA	0.4-3.0	20-40	5,000-340,000	1,000-150,000	70-95	98-99.999

The PSA operating pressure is determined by the syngas pressure and/or the requested H₂-product gas pressure, which is typically up to 3 MPa. The recovery rate of hydrogen is determined by the regeneration system of the PSA plant on the one hand and the H₂ content in the feed gas on the other hand and typically varies between 70 and 95% for H₂ product gas as regeneration agent. For an economic production, the feed gas should include more than 60% hydrogen (pers. com).

Export gas treatment: The export gases treatment steps according to the given H₂ product quality is outlined in Figure 4-13, the simplified process scheme is visualized in Figure 4-14.

After compression, the total export gas volume flow is pre-heated and mixed with steam before it is sent to the WGS reactor, where the bulk of CO is converted with steam into H₂ and CO₂. After WGS reaction and heat exchange (Q1), H₂S, trace compounds and the bulk of CO₂ are removed in the Rectisol washing tower. Some of the heat from exothermic WGS reaction is utilized to pre-heat the boiler feed water for WGS-steam generation, which has to be superheated by the combustion of PSA tail gas, natural gas or steel making excess gases.

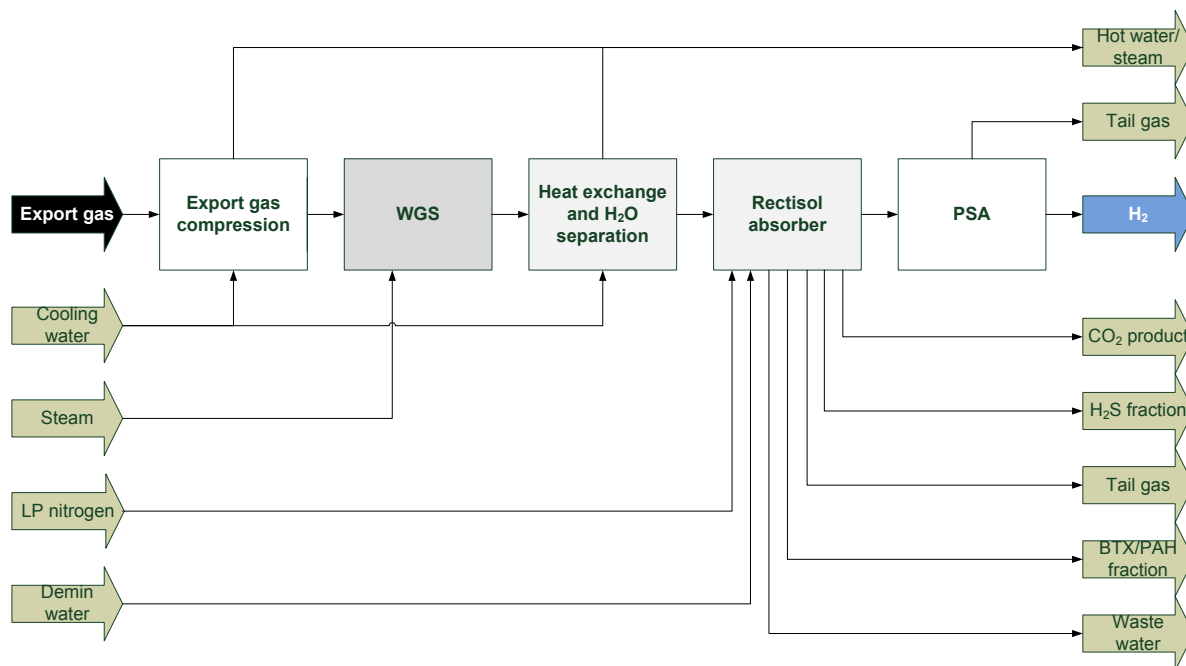


Figure 4-13 Simplified block scheme of export gas treatment for the generation of H₂ [own description]

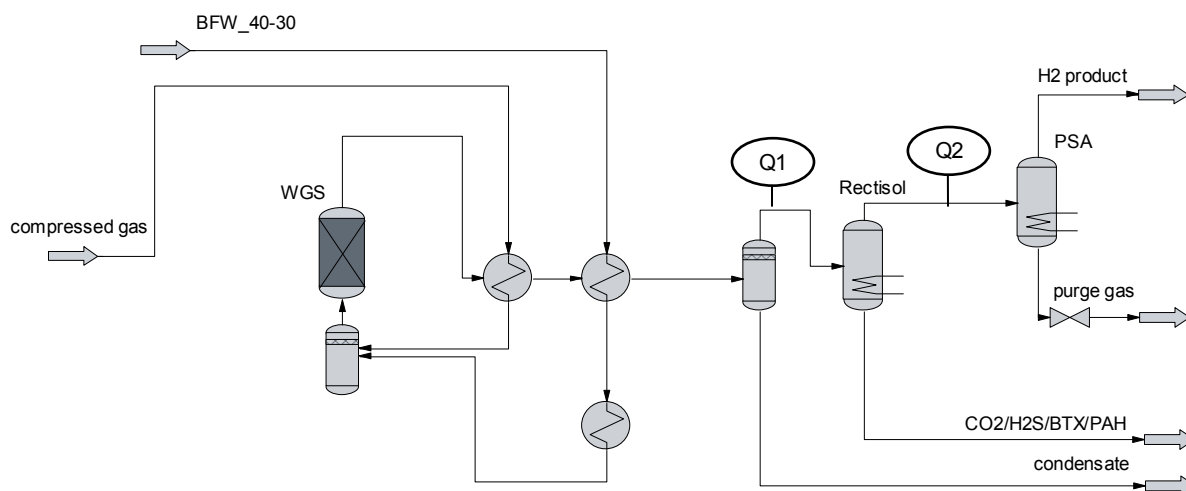


Figure 4-14 Simplified process scheme of export gas treatment for the generation of H₂ [own description]

The H₂-syngas (Q2, ~3 MPa / 30°C) then enters the PSA unit for the final removal of remaining compounds like CH₄, CO₂ and CO. Purified H₂ (>99.9%) exits the PSA unit with a pressure loss of 80 kPa. For regeneration, the adsorbent material is decompressed and purged with pure H₂. The purge gas exiting PSA column at almost atmospheric pressure mainly consists of CO, H₂, CH₄, N₂ and CO₂, and can be utilized as fuel for the generation of steam.

Syngas Composition: The operating parameter and the feed gas compositions to Rectisol (Q1) and to PSA unit (Q2) are shown in Table 4-13.



Table 4-13 Rectisol (Q1) and PSA (Q2) feed gas compositions [based on (16), (17), (89)]

Stream	COREX [®] gas utilization		FINEX [®] gas utilization	
	Rectisol feed gas (Q1)	PSA feed gas (Q2)	Rectisol feed gas (Q1)	PSA feed gas (Q2)
Temperature, °C	40	30	40	30
Pressure, MPa	3.5	3.28	3.5	3.28
Volume flow, m ³ /h(STP)	404,623	196,962	365,646	179,811
Component mol-%				
H ₂	41.4371	85.01	35.6323	72.36
CO	3.0263	6.15	3.1558	6.34
CO ₂	52.3705	3.00	51.8598	3.00
CH ₄	1.4579	2.86	1.1875	2.31
H ₂ O	0.2333	-	0.2330	-
N ₂ /Ar	1.4579	2.97	7.9159	15.98
H ₂ S	0.0059	1 ppm	0.0036	1 ppm
BTX	0.0104	-	0.0115	-
PAH	0.0007	-	0.0007	-
NH ₃	0.000	-	0.001	0.000
CH ₃ OH	-	0.003	-	0.003

HCl, HF and HCN are below 1 ppm_v not critical (not included in calculation)

Typically 3% of CO₂ remain in the syngas after Rectisol treatment, reducing energy demand and investment for the Rectisol unit, but increasing the effort for final purification. The H₂ product gas composition based on a typical H₂ recovery rate of 88.5% and the resulting purge gas compositions after the PSA plant are shown in Table 4-14.

Table 4-14 COREX[®] and FINEX[®] export gas treatment: H₂ product and tail gas composition after PSA [based on (89), (94)]

Stream	COREX [®] gas utilization		FINEX [®] gas utilization	
	H ₂ product	purge gas	H ₂ product	purge gas
Temperature, °C	35	15	35	15
Pressure, MPa	3.2	0.13	3.2	0.13
Volume flow, m ³ /h(STP)	148,338	48,624	115,264	64,547
Component mol-%				
H ₂	>99.9	39.60	>99.9	23.18
CO	10 ppm _v	24.90	10 ppm _v	17.66
CO ₂	-	12.15	-	8.36
CH ₄	-	11.59	-	6.44
N ₂ /Ar	< 0.1	11.75	< 0.1	44.34
HCN	-	~4 ppm _v	-	~3 ppm _v
CH ₃ OH	-	0.01	-	<0.01



Capacity: Despite the low H₂ content in the export gases (Table 1-1) the final H₂ product capacity reached, is in the range of industrial standard H₂ production:

- 115,000 m³/h(STP) H₂ from FINEX[®] export gas treatment
- 150,000 m³/h(STP) H₂ from COREX[®] export gas treatment

Operating conditions: The H₂-PSA plant can be adapted to fluctuations in syngas flow between 30 and 100% without quality loss, but the H₂:CO-ratio should not change significantly. Only a deviation below 1% to a nominal ratio is tolerated during operation. The electric energy demand for instruments and process control in the PSA is very low, and therefore disregarded.

Discussion: Disadvantageously, the bulk of CO has to be shifted, demanding large amounts of steam for the treatment of the CO-rich export gases. As an alternative, steam reformed natural gas is much higher in H₂ content (H₂:CO-ratio>3), reducing the steam demand for WGS reaction. In some applications, pre-cleaned desulfurized steam reformed natural gas is sent to the PSA column without previous shift. A selective Rectisol wash, used for CO₂, H₂S and trace compound removal of shifted export gases, has not to be applied for this sulfur-free syngas. All CO₂ is withdrawn from the syngas flow within the PSA unit. Only if a pure CO₂ stream is required, a chemical (amine) wash is designed prior to the PSA.

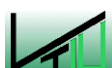
4.1.5 Process Design for Ammonia Synthesis Gas and CO₂ for Urea

As described in chapter 3.1, KRES-KAAP and Uhde are standard processes for the synthesis of ammonia. Table 4-15 summarizes the typical process conditions and the syngas requirements.

Table 4-15 Syngas requirements/conditions for ammonia synthesis [own description, based on (23), (67)]

Process selection	Syngas requirements / conditions			NH ₃ -plant capacity [t/d]
	Syngas pressure [MPa]	Syngas Temp.	Typical syngas demand [m ³ (STP)/h]	
KRES-KAAP	9-10	-	200,000-400,000	1,000-2,000
Uhde	14-21	-	200,000-400,000	2,000-3,000

The block scheme of export gas treatment and final purification of NH₃ syngas in a cryogenic nitrogen wash unit (NWU) is shown in Figure 4-15.



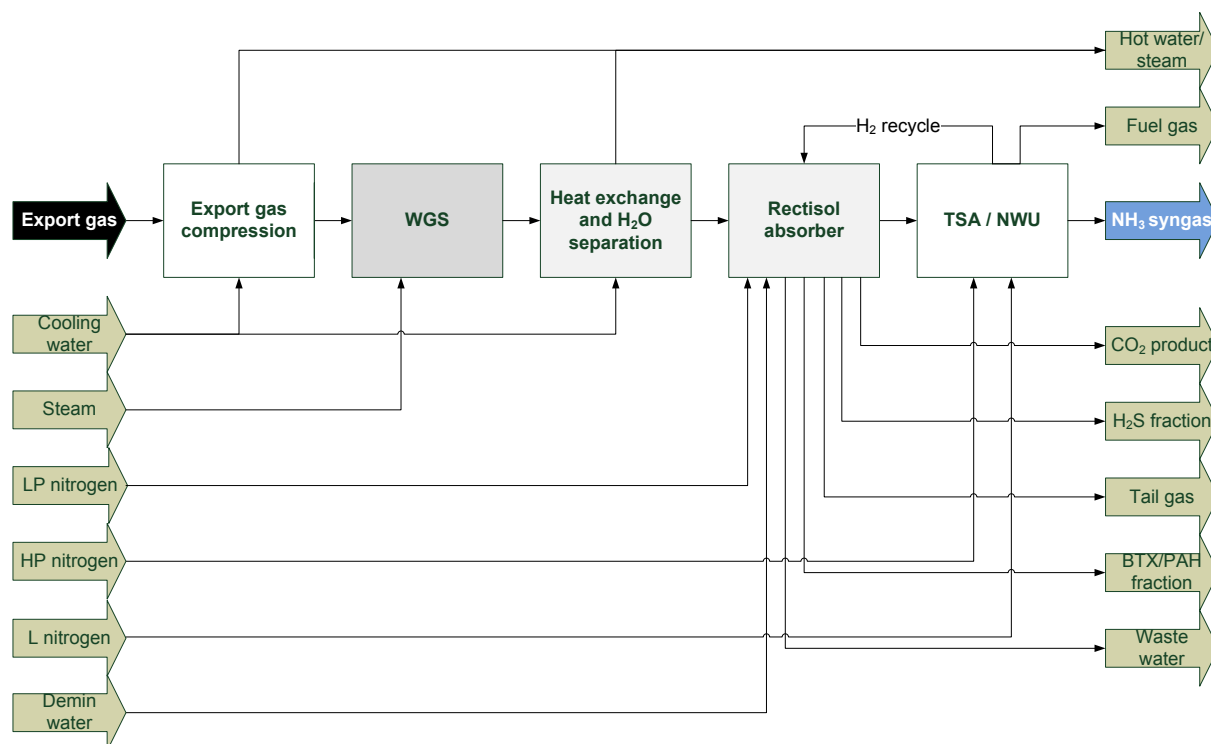


Figure 4-15 Simplified block scheme of export gas treatment for the generation of NH₃ syngas [own description]

Export gas treatment: The export gas treatment to utilize NH₃ syngas for NWU is similar to the export gas treatment for H₂ production, except the final purification, as shown in Figure 4-16. Because of the NWU which is a cryogenic process, CO₂ has to be removed down to ppm-levels in the Rectisol washing tower, and therefore energy demand and investment for the CO₂-separation is higher in case of NH₃ syngas than for H₂ production.

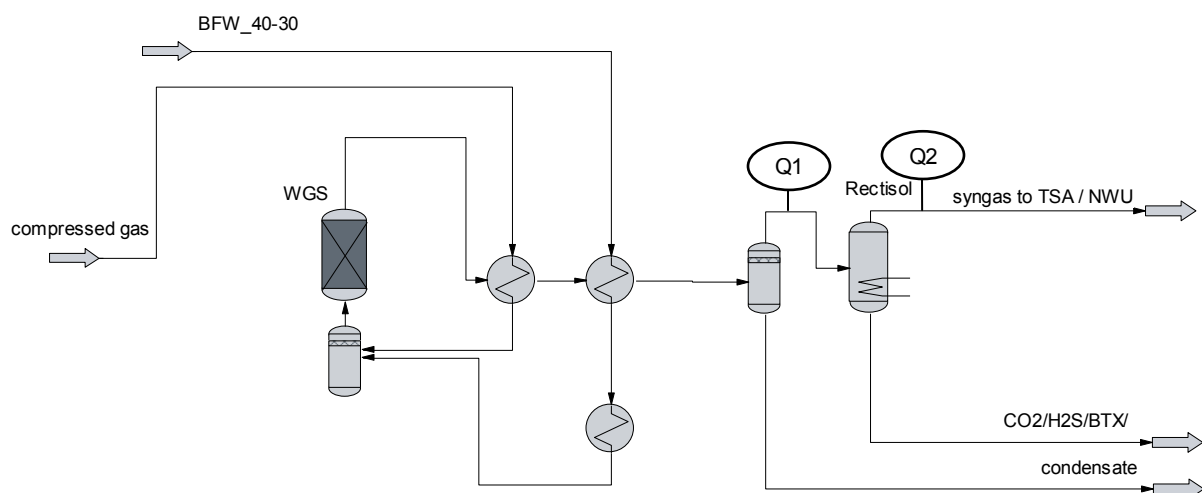


Figure 4-16 Simplified process scheme of export gas treatment for the generation of NH₃ syngas for NWU [own description]



Final purification: After export gas treatment, the syngas is further purified by liquid nitrogen wash, which is often applied for syngas from gasification using different feedstock, as described in chapter 3.2. Syngas from NWU is practically free of inert gases, which brings advantages for the synthesis process, as inert gas purge is not necessary. The utility consumption of a NWU is very low apart from the HP-N₂ required to adjust the H₂:N₂-ratio of 3, which is done within this unit. Figure 4-17 shows the process flow scheme of standard TSA and NWU downstream a Rectisol wash unit.

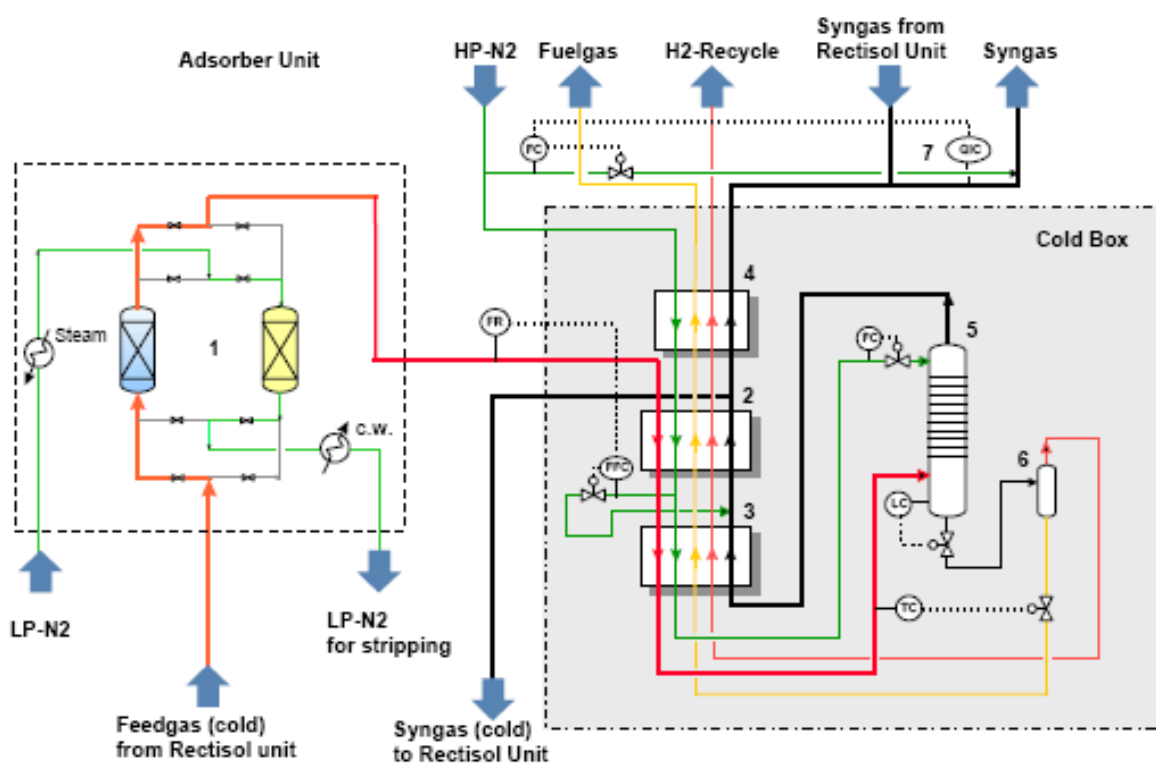


Figure 4-17 Standard adsorber and nitrogen wash unit downstream Rectisol wash (84)

In the adsorber station (TSA, 1) traces of CO₂ and methanol are finally removed before the syngas enters the cold box. After the cooling of syngas (2, 3) and high pressure nitrogen (2, 3, 4), the syngas enters the wash column (5) to remove CO, Ar and CH₄ with liquefied nitrogen. Purified gas from the top of column (5) is reheated (3, 2, 4) and HP-N₂ is injected to the syngas flow partly between heat exchange 2 and 3 and partly outside the coldbox for the final adjustment of the H₂:N₂-ratio. The sump-mixture of column (5) is expanded (6) to recycle some H₂ from the fuel gas fraction.

Syngas composition: Feed gas (to Rectisol (Q1) and to NWU (Q2)) and NH₃-syngas compositions are summarized in Table 4-16. The CO₂ by-product from Rectisol absorber can further be utilized as feedstock in urea production. Achieved CO₂ qualities according urea specification are also listed in the table.

Table 4-16 Rectisol (Q1) and NWU feed gas compositions (Q2) as well as NH₃ syngas and CO₂ by-product quality from export gas treatment [based on (16), (17), (89), (95)]

Stream	COREX [®] gas utilization				FINEX [®] gas utilization			
	Rectisol feed gas (Q1)	NWU feed gas (Q2)	CO ₂ by-product	NH ₃ syngas	Rectisol feed gas (Q1)	NWU feed gas (Q2)	CO ₂ by-product	NH ₃ syngas
Temp., °C	40	-60	30	30	40	-60	30	30
Pressure, MPa	3.5	3.33	0.23	3.04	3.5	3.33	0.22	3.04
Vol.-flow, m ³ /h(STP)	404,623	190,901	57,575	222,552	365,646	174,274	57,597	172,122
Component mol-%								
H ₂	41.4371	87.68	0.34	74.9982	35.6323	74.63	0.27	74.9983
CO	3.0263	6.32	0.22	0.0002	3.1558	6.52	0.21	0.0002
CO ₂	52.3705	0.001	99.00	0.0002	51.8598	0.001	98.96	0.0002
CH ₄	1.4579	2.94	0.36	-	1.1875	2.37	0.26	-
H ₂ O	0.2333	-	-	-	0.2330	-	-	-
N ₂	1.4579	3.07	0.06	24.9994	7.9159	16.48	0.28	24.9994
H ₂ S, ppm _v	59	< 0.1	2	-	0.0036	< 0.1	2	-
BTX	0.0104	-	-	-	0.0115	-	-	-
PAH	0.0007	-	-	-	0.0007	-	-	-
NH ₃	-	-	-	-	0.001	-	-	-
CH ₃ OH	-	0.002	0.017	-	-	0.002	0.0165	-

HCl, HF and HCN are below 1 ppm_v not critical (not included in calculation)

NH₃ synthesis: After NWU the purified syngas is sent to syngas compression (14-21 MPa) and then enters the NH₃ synthesis loop as make-up gas. The process flow is shown in Figure 3-30 and Figure 3-31.

Urea synthesis: Due to the fact that urea synthesis demands CO₂ at a NH₃:CO₂-ratio of 3 to 4, approximately 60,000 m³/h (STP) of CO₂ are consumed by converting ~80 t/h NH₃ (approximately 200,000 m³/h (STP) syngas) into urea, which reduces overall CO₂ emissions, as shown in chapter 6. The block scheme of a typical urea process is shown in Figure 3-33.

Capacity: The demand of NH₃ syngas for industrial scale plants is between 100,000 and 400,000 m³/h (STP). Around 200,000 m³/h (STP) can be produced by COREX[®] or FINEX[®] export gas treatment.

Operating conditions: The NWU can be adjusted for altering H₂:CO-ratio. Changes in syngas volume flow between 40 and 100% of nominal gas volume flow are tolerated. The NH₃ synthesis itself has to be shut down in case of failure in syngas supply causing up to 12 hours ramp up time.



4.2 Production of Hydrogen from Coke Oven Gas

For chemical utilization of coke oven gas (COG), the bulk of hydrocarbons, e.g. CH₄ (~20-42%), can be converted into H₂ and CO by reforming or partial oxidation. But often the hydrocarbons are partially liquefied and separated by distillation at low temperature (25).

Table 4-17 shows necessary units for the treatment of COG after hydrocarbon separation into the main intermediates.

Table 4-17 Important export gas treatment steps for coke oven gas after hydrocarbon separation [own description]

Generation of Process units	Carbon Monoxide (e.g. for acetic acid)	Oxogas	Methanol- and FT-Syngas	Hydrogen	NH ₃ -Syngas (incl. CO ₂ for Urea)
H ₂ :CO ratio	0:1	1:1	2:1	1:0	1:0
WGS	-	-	-	(+)	(+)
CO ₂ /H ₂ S removal	+	H ₂ S removal	H ₂ S removal	+	+
Removal of trace compounds	+	+	+	+	+
PSA	(+)	-	-	+	+
Methanation	-	-	-	-	+
NWU	-	-	-	-	(+*)
Cryogenic H ₂ /CO Separation	+	-	-	-	-
Separation of N ₂ /CO	+*	-	-	-	-

+ has to be applied / common application
 - not applied
 (+) alternative application
 * depends on product specification

Due to the high percentage of H₂ in pre-cleaned COG, only H₂ and NH₃-syngases have been produced for the chemical downstream synthesis within the last years. PSA technology has been applied to separate the bulk of H₂ from the gas flow without a previous shift reaction. Only around ten PSA-plants have been built for the recovery of H₂ from COG (pers. com. Baumer, R., Linde). 1982 the first PSA plant for COG was put in operation by Ruhrkohle AG in Germany, achieving a production capacity of 10,000 m³/h(STP) (30).

4.2.1 Process Design for the Generation of H₂ from COG

H₂ generation from pre-cleaned COG includes compression, pre-adsorption (e.g. of H₂S compounds) and the separation of pure H₂ (>99%) in a PSA unit, as shown in Figure 4-18 and Figure 4-19.



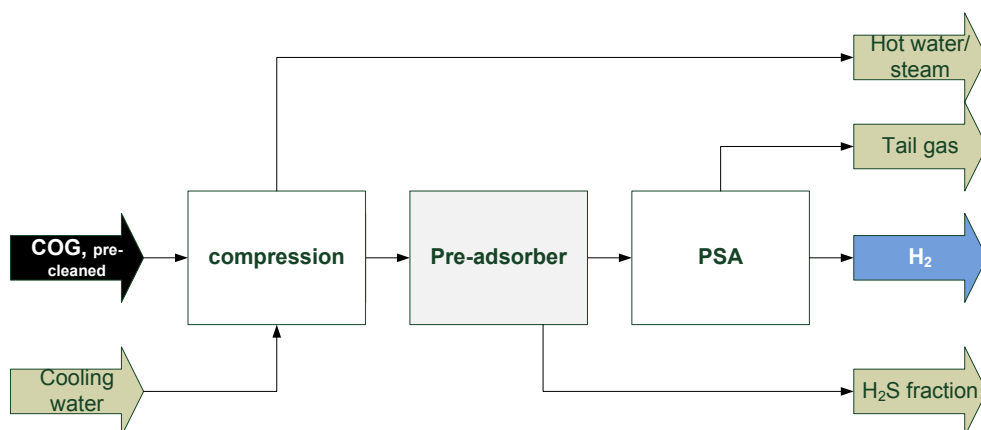


Figure 4-18 Block scheme of COG treatment and PSA for the production of hydrogen [own description]

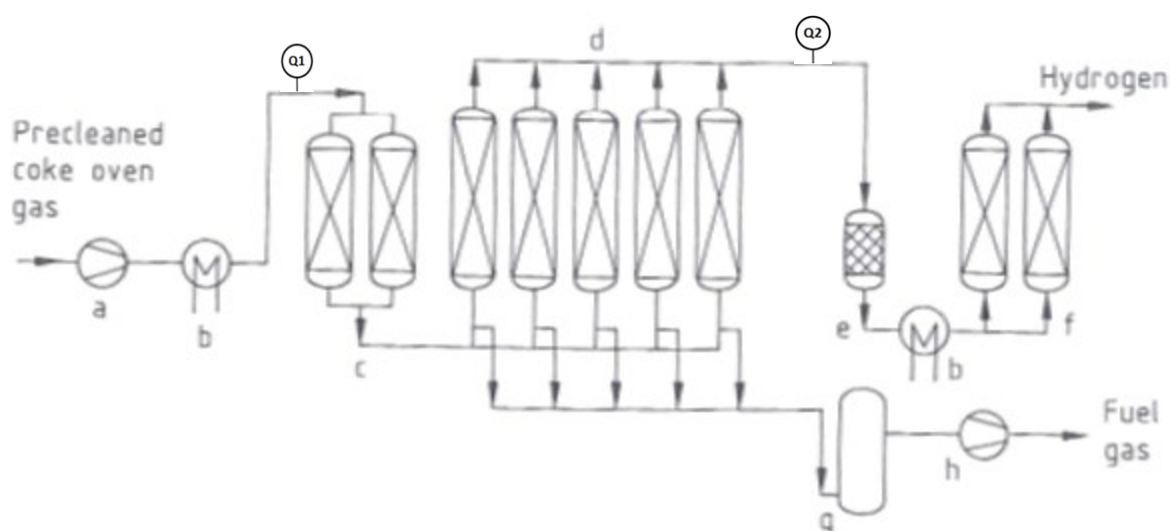


Figure 4-19 H₂ production from coke oven gas by pressure-swing adsorption (Linde, Germany) (30)

Before hydrogen separation in a pressure-swing adsorption unit (d), pre-cleaned COG is compressed (a) up to 2.6 MPa (1.0 MPa), cooled down to 20°C (b) and sent to a pre-adsorber (c) for the removal of hydrocarbon and sulfur compounds. Oxygen (e) and water (f) are then finally removed from the H₂ product. The tail gas from PSA is usually further compressed and serves as fuel.

Syngas compositions of pre-cleaned compressed COG (Q1) and H₂ product gas after PSA (Q2) are shown in Table 4-18.

Table 4-18 Syngas compositions of pre-cleaned compressed COG (Q1) and H₂ product gas after PSA (Q2) [based on (96), (97)]

Stream	a) H ₂ recovery from COG, feed gas pressure: 2.6 MPa		b) H ₂ recovery from COG, feed gas pressure: 1.0 MPa	
	Pre-cleaned COG (Q1)	H ₂ product (Q2)	Pre-cleaned COG (Q1)	H ₂ -product (Q2)
Temperature, °C	20	-	20	-
Pressure, MPa	2.6	2.5	1.0	0.9
H ₂ -recovery rate		83%		70%
Volume flow, m ³ /h(STP)				
Case 1	70,000	38,000	70,000	32,000
Case 2	140,000	76,000	140,000	64,000
Component mol-%				
H ₂	65	99.9	65	99.9
CO	6	} 20 ppm	6	} 20 ppm
CO ₂	1.5		1.5	
CH ₄	22	-	22	-
H ₂ O	saturated	-	saturated	-
N ₂ /Ar	2.5	-	2.5	-
H ₂ S in g/m ³ (STP)	0.35	-	0.35	-
C _n H _m	3	-	3	-
O ₂	-	<100ppm	-	<100ppm

Syngas and product gas compositions: Within this study, the H₂-recovery by PSA technology has been estimated (based on the figures of plants in operation) for COG feed gas amounts of 1) 70,000 m³/h (STP) and 2) 140,000 m³/h (STP), each at feed gas pressures of 2.6 MPa (a) and 1.0 MPa (b).

Due to lower feed gas pressure in option b (1.0 MPa), the hydrogen recovery rate has to be reduced to a level of 70%, to achieve the same product gas quality (99.9%) as in option a.

Capacity: PSA plants for the recovery H₂ from COG have only been built for a few selected applications, typically at capacities up to 20,000 m³/h(STP). The feed gas capacities in case 1 and 2 are much higher, but in the range of NG-based PSA plant capacities (Table 4-12).

Operating conditions: The PSA plant can be adapted to fluctuations in COG flow between 30 and 100% without quality loss.

4.2.2 Energy Demand and CO₂-balance

The electric energy is only used for instruments and process control and can be neglected.

The small amount of carbon monoxide in COG is separated in the PSA unit and not converted in a water gas shift reactor. Therefore there are no process related CO₂ emissions.



4.2.3 Capital Cost Estimate and Utility Demand

Table 4-19 Capital cost estimate for the production of hydrogen with a purity of 99.9% from COG by PSA technology; pricing basis 2010 (97)

Option	Syngas specification		H ₂ -product specification		PSA capital cost estimate	
	pressure [MPa]	volume flow [m ³ /h(STP)]	volume flow [m ³ /h(STP)]	H ₂ -recovery	Capital costs ex works [million €]	Capital costs + 20% delivery and assembly [million €]
1a	2.6	70,000	38,000	83%	5.5	6.6
2a	2.6	140,000	76,000	83%	9.0	10.8
1b	1.0	70,000	32,000	70%	9.0	10.8
2b	1.0	140,000	64,000	70%	14	16.8

Although the capital costs for the PSA plant operating at a feed gas pressure of 1 MPa (case b) are much higher compared to the costs for a plant operating at a pressure around 2.6 MPa (case a) at same capacity, net H₂ production costs are lower for the low pressure plant due to higher capital and operating expenses for the compression of COG (97).

4.2.4 Discussion

Due to

- expenses for COG compression (up to ~1.5 MPa),
- pollutants like naphthalene which reduce the life cycle of the adsorbent material and
- the low hydrogen content in COG (39-65%, Table 1-1) compared to typical PSA-feedstock (~70-75%),

the H₂-recovery from COG stays an exception for small selected applications with no proper alternative H₂-feedstock. Therefore the utilization as fuel within the iron and steel work will remain standard application for coke oven gas.

5 Economic Analysis

This chapter provides the production cost estimates for the generation of the selected syngases according to the worked out processes for COREX[®] and FINEX[®] export gas treatment described in chapter 4.1. The costs are then compared to the common syngas production costs based on the feedstock natural gas.

5.1 Basis

The production cost calculation for each export gas treatment process can be structured into variable and fixed costs, annual depreciation and return on capital expenses.

The variable costs include:

- expenses for raw material and credits for by-products
- expenses for utilities like electricity, cooling water or steam
- expenses for catalyst material have not been considered

The fixed costs include:

- direct operating costs, such as labor, maintenance and manpower
- allocated costs for general plant overhead, insurance and taxes

The depreciation period for the static amortization calculations has been assumed to be 10 years of the plant investment.

The return on capital expenses (ROCE) is intended as an estimate of the margin over full cost of production and has been calculated with 10% of the plant investment.

The pricing and investment basis are outlined in the following.

5.1.1 Pricing Basis

Prices and costs for raw material, utilities and manpower have been based on the values from Nexant's internal databases for petrochemical and refinery materials, 1st quarter 2010, US Gulf Coast (USGC) (19). The pricing values from the year 2010 have not been adjusted to the pricing index 2012 for the short period of time. The costs for methanol have been based on USGC Q2 1998 (33), costs for propylene and credits for iso butyraldehyde have been based on USGC, Q4 2001 (34), including 2% annual index adjustment each. The export gas prices have been calculated by their fuel values (Table 1-1) relatively to natural gas, resulting in 0.045 \$/m³(STP) for COREX[®] and 0.035 \$/m³(STP) for FINEX[®] export gas respectively. The difference between the export gas and the natural gas pressure has not been taken into account. A price summary is given in Table 5-1.



Table 5-1 Feedstock, by-product and utility prices [(19), (34) and (33) adopted]

	Unit	Price in US \$/unit
Raw material (feedstock and by-product)		
natural gas	GJ	5.24
COREX [®] export gas	m ³ (STP)	0.045
FINEX [®] export gas	m ³ (STP)	0.035
hydrogen	ton	1,091.60
methanol	ton	132.22
propylene chemical grade	ton	409.86
iso butyraldehyde	ton	389.89
Utilities		
electric power	MWh	57.36
cooling water	10 ³ ton	29.04
process water	ton	0.32
boiler feed water	ton	0.55
HP steam	ton	22.78
MP steam	ton	20.20
LP steam	ton	19.90
fuel	GJ	5.24
inert gas	ton	52.60
Manpower		
operators	annual costs	48,225
foremen	annual costs	54,739
supervisor	annual costs	66,053

5.1.2 Investment Basis

The plant investment costs have been calculated for inside battery limits (ISBL) only. The prices for the plant equipment have been based on the European standard for 2012, or have been adjusted with 2% annual indexation. The capital cost calculations of each export gas treatment process, described in chapter 4.1, include the equipment cost estimate for:

- export gas compression and intermediate cooling system [calculation based on (86)],
- shift reactor [calculation based on (98), (99)],
- Rectisol absorption and regeneration system (88),
- cold box for cryogenic separation and NWU [(pers. com. Lang, M., Linde),
- PSA for H₂ separation (94) and
- syngas compression system for methanol and CO [calculation based on (86)]

Furthermore additional fee factors have been included according to Lang-/Chilton method (100):

- piping and instruments, considered with 20% of basic equipment.



- building considered with 30% of basic equipment.
- utilities (e.g. pumps and flash reactors) considered with 30% of basic equipment.

Engineering costs have been calculated with 10% of the capital costs.

The costs for feedstock, utility and manpower have been calculated for a plant site in US Gulf Coast, while the plant equipment has been based on a European standard. The production costs can vary significantly depending on the specific site conditions. Nizamoff stated that the estimated capital costs for natural gas based syngas production can differ +/- 30% (19).

5.2 Production Costs for main intermediate Chemicals

The production costs for CO, n-butanol (oxo-synthesis) and acetic acid are summarized in Figure 5-2, the costs for Fischer-Tropsch, methanol and ammonia export gas treatment in Figure 5-3, H₂ production costs in Figure 5-4. The sensitivity of the CO production costs to the natural gas price is visualized in Figure 5-1.

The production costs based on export gas treatment are indicated with a red dashed line (- - -). Detailed cost shares for CO and syngas production from export gases and the downstream synthesis of n-butanol and acetic acid are visualized in the bar chart, considering costs for raw material and syngas respectively (blue), utilities (brown), total fixed costs (green), annual depreciation (purple) and 10% ROCE (turquoise) Furthermore average costs for natural gas based syngas production are indicated with a black dashed line (- - -). The production costs include 10% ROCE and are related to 1 t end product each.

Figure 5-2: production costs for CO, acetic acid and n-butanol

- Export gas treatment costs for the generation of CO, according the process design described in chapter 4.1.1.
- Production costs for acetic acid by Monsanto/BP methanol carbonylation, as described in chapter 3.1.3. The feedstock costs (CO and methanol) include CO production costs from COREX[®] and FINEX[®] export gas treatment and the costs for methanol, calculated with the listed prices in Table 5-1.
- Production costs for n-butanol, according the oxogas treatment described in chapter 4.1.2, and for oxo-synthesis by Dow/Davy Mk IV process described in chapter 3.1.2.

Figure 5-3: production costs for Fischer-Tropsch, methanol and ammonia syngas

- The export gas treatment costs for the generation of methanol- and Fischer-Tropsch syngas have been based on the simulations described in chapter 4.1.3. The production costs have been related to 1 ton end-product (in both cases methanol), which typically consumes around 2,500 m³(STP) of syngas with a H₂:CO-ratio of 2.
- The costs for NH₃ syngas production (inclusive CO₂ for urea) have been based on the process design described in chapter 4.1.5. Costs for NH₃ syngas compression have not been included, as they are typically considered within the downstream synthesis



of ammonia. The costs have been related to 1 ton end-product (NH_3), which typically consumes around 2,600 m^3 (STP) syngas with a H_2 : N_2 -ratio of 3.

Figure 5-4: The specific costs for the production of pure hydrogen from export gases have been calculated according to the process design described in chapter 4.1.4 (red dashed line and bar chart). The costs for H_2 production based on natural gas, including steam methane reforming, WGS reaction and PSA, are visualized as a black dashed line.

Figure 5-1 visualizes the effect of natural gas price on the NG-based CO production costs. The NG price has been varied from 1 \$/GJ to 18\$/GJ, while the prices for COREX[®] and FINEX[®] export gases as well as other prices have been kept constant. Over this range the NG-based production costs rise from 129 \$/t to 797 \$/t CO.

5.3 Discussion

Figure 5-2 to Figure 5-4 visualize the difference between COREX[®] and FINEX[®] export gas based synthesis gas production costs:

CO production (Figure 5-2)

The higher CO content in COREX[®] export gas results in lower raw material costs and a higher product yield per ton CO compared to FINEX[®] export gas. In the cryogenic separation process the higher N_2 content in FINEX[®] export gas (N_2 :10% FINEX[®], 2% COREX[®]) requires significantly larger plant equipment size to meet CO purity requirements of 97%, as the separation efficiency is lower and the gas volume flow is much higher due to process requirements for CO recycling. Furthermore COREX[®] export gas brings the advantage of already containing 68% of CO in the cryogenic feed gas, compared to FINEX[®] export gas with around 55% of CO.

Acetic acid production (Figure 5-2)

While plant size, methanol raw material costs and the utility costs are similar, the total production costs are higher for FINEX[®] export gas based production, related to the higher raw material costs for carbon monoxide.

n-butanol production (Figure 5-2)

While the H_2 :CO-ratio of 0.5 in FINEX[®] export gas is slightly closer to the synthesis requirements with less demand for WGS and steam, the H_2 and CO content is lower and therefore product yield per processed export gas is lower for FINEX[®] export gas resulting in 4% higher specific product costs.

FT-, methanol- and ammonia-syngas production (Figure 5-3)

As the H_2 and CO content is higher in COREX[®] export gas the specific syngas production costs are consequently lower. Methanol- and FT-syngas only differ in the costs related to methanol syngas compression. In ammonia synthesis the difference in utility demand is



smaller as the share of N_2 in the export gases can be utilized for NH_3 syngas production resulting in less liquefied N_2 demand for FINEX[®] export gas.

Hydrogen production (Figure 5-4)

The production costs related to a ton of product are significantly higher for H_2 (COREX[®]: 2,243.35 \$/t H_2) compared to the costs for ammonia syngas production (COREX[®]: 377.50 \$/t NH_3), as a result of the low molar weight of H_2 gas.

Comparison of Export Gas and Natural Gas based Syngas Production Costs

CO, n-butanol and acetic acid (Figure 5-2)

Generally, export gas treatment for the production of CO-rich syngas mixtures ($H_2:CO$ -ratio ≤ 1) is more economic than the conventional syngas production route due to the already high CO content in the export gases. An exception is the generation of high purity CO ($>97\%$), which is more expensive for FINEX[®] export gas due to the high amount on N_2 and the required export gas treatment.

FT-, methanol- and ammonia-syngas (Figure 5-3) and H_2 (Figure 5-4)

With the rising H_2 content required in syngas, natural gas based syngas production at large scale becomes significantly more economic (30-50% lower total production costs) due to the high fraction of H_2 generated by steam reforming ($H_2:CO$ -ratio > 3). For export gas based syngas production, a large quantity of CO has to be shifted, thus enlarging WGS-reactor size and steam demand.

Considering shift activity of the catalyst system in case of high temperature Fischer-Tropsch or LPMEOH[™] synthesis, a previous $H_2:CO$ -ratio adjustment is not necessary, and the costs for export gas treatment are expected to decline. But for this process option steam has to be added to the synthesis process, which enlarges reactor size and steam demand for the synthesis process itself. Furthermore product selectivity is reduced. Therefore the export gas treatment processes for the generation of syngas for methanol and Fischer-Tropsch synthesis have only been calculated for a $H_2:CO$ -ratio of 2.

Tough NH_3 syngas production is more economic using H_2 -rich syngas from steam reformed natural gas than export gas as feedstock, the high syngas purity after NWU has to be considered in the economic evaluation. With the achieved syngas quality the purge of inert gases in NH_3 synthesis loop is then not necessary anymore, reducing synthesis plant size and production costs. Furthermore the CO_2 amount, necessary for the production of urea, is produced within the Rectisol wash unit, which reduces the raw material costs for the downstream synthesis of urea. Consequently the Rectisol absorption with CO_2 as by-product and the high syngas purity after NWU lower downstream costs for ammonia and urea synthesis, which makes the syngas more valuable.



For the production of H₂, the feedstock natural gas is more economic than export gas, due to the advantageously high H₂ content in the syngas after steam methane reforming. Furthermore the shifted syngas is almost free of trace compounds due to reforming-pre-treatment, and consequently it can be sent to the PSA column directly.

Sensitivity of CO production costs to natural gas price (Figure 5-1)

Only below a NG-price of 3.4 \$/GJ the natural gas based carbon monoxide production is competitive. Above this value, COREX[®] export gas treatment is more economic. Also the FINEX[®] export gas based CO production competes against the NG-based production, if the NG-price-level is above 7.2 \$/GJ,

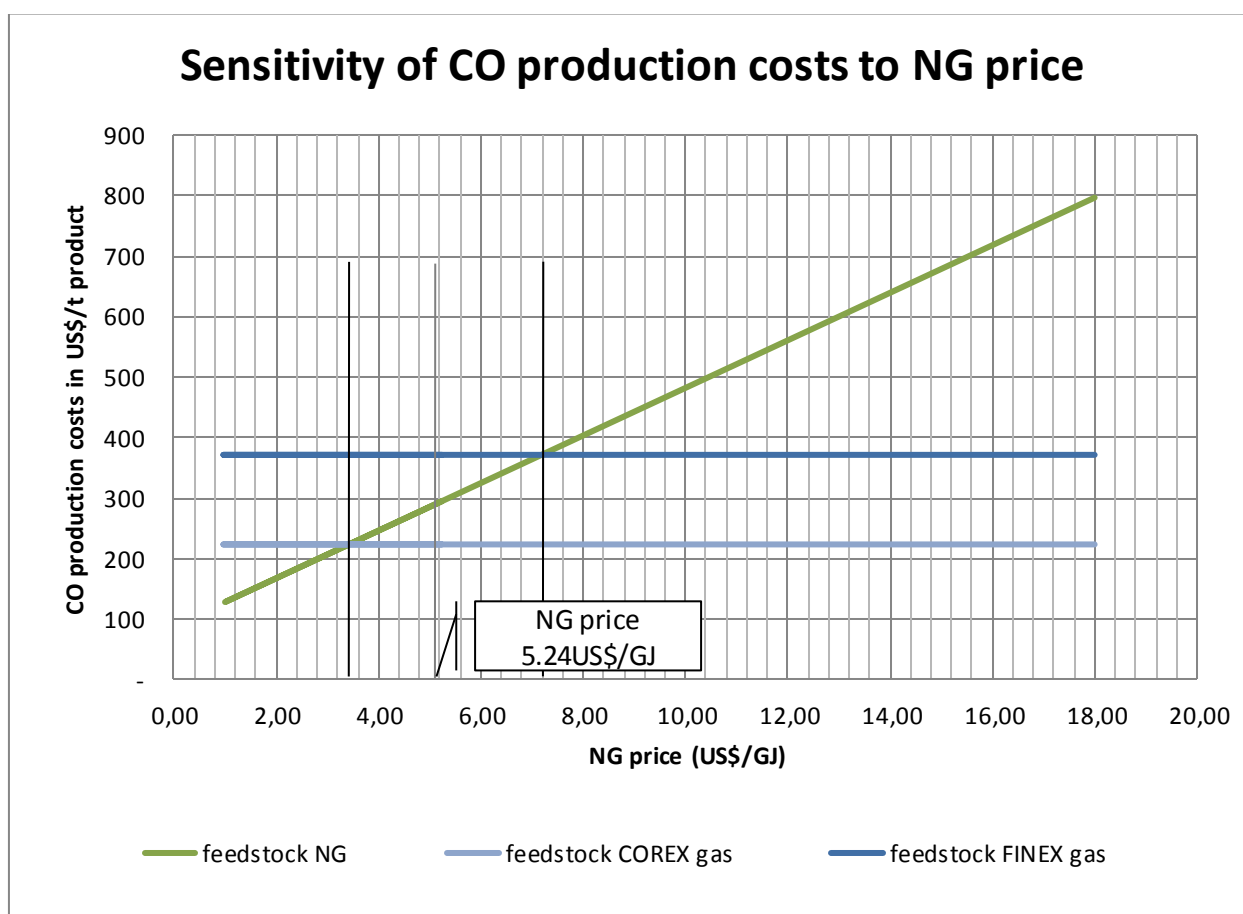


Figure 5-1 Sensitivity of CO production costs to natural gas price [own description]

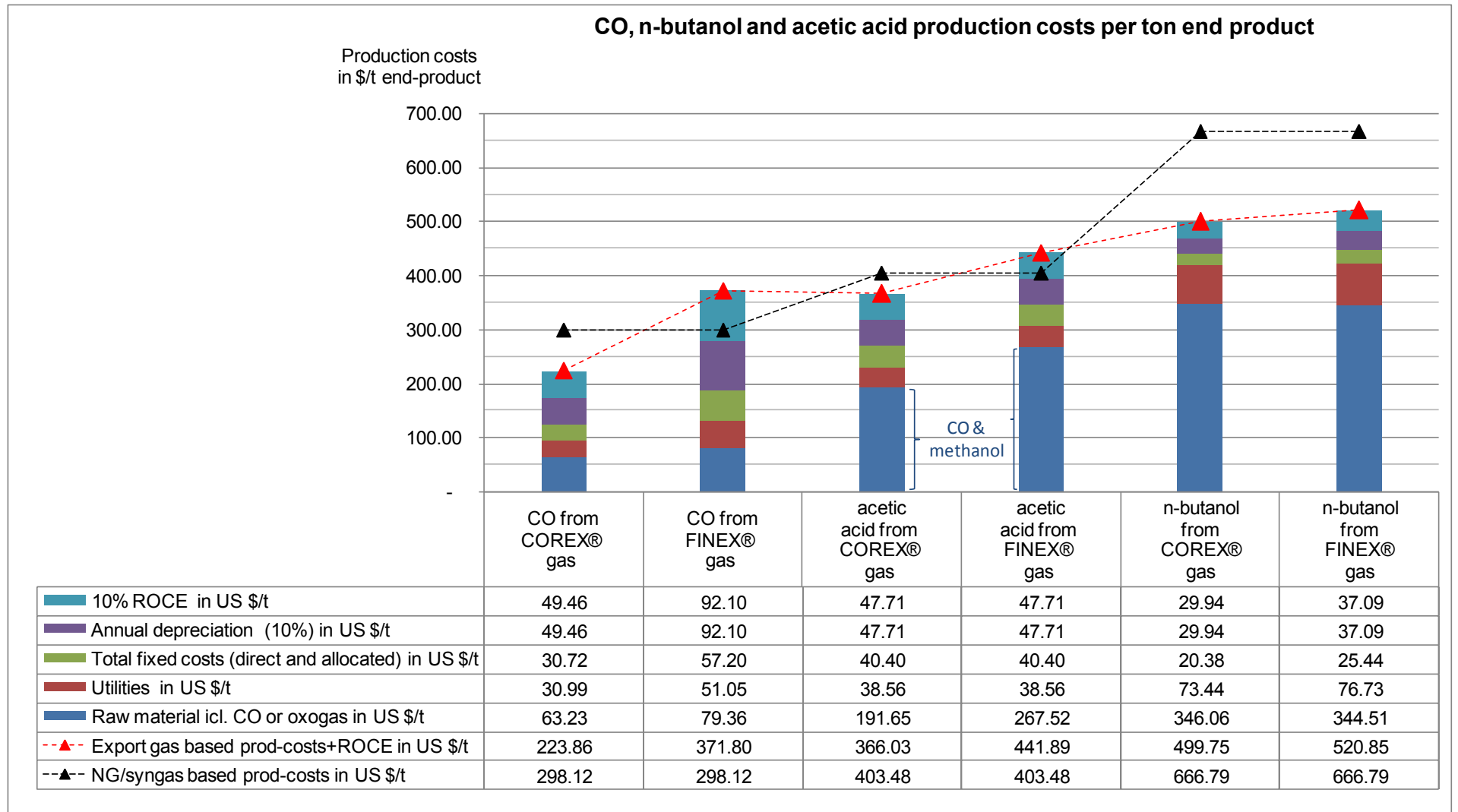


Figure 5-2 Production cost estimate for the generation of pure CO, acetic acid and n-butanol (oxo-synthesis), US-\$/ton product (pricing basis 2012) [own description]



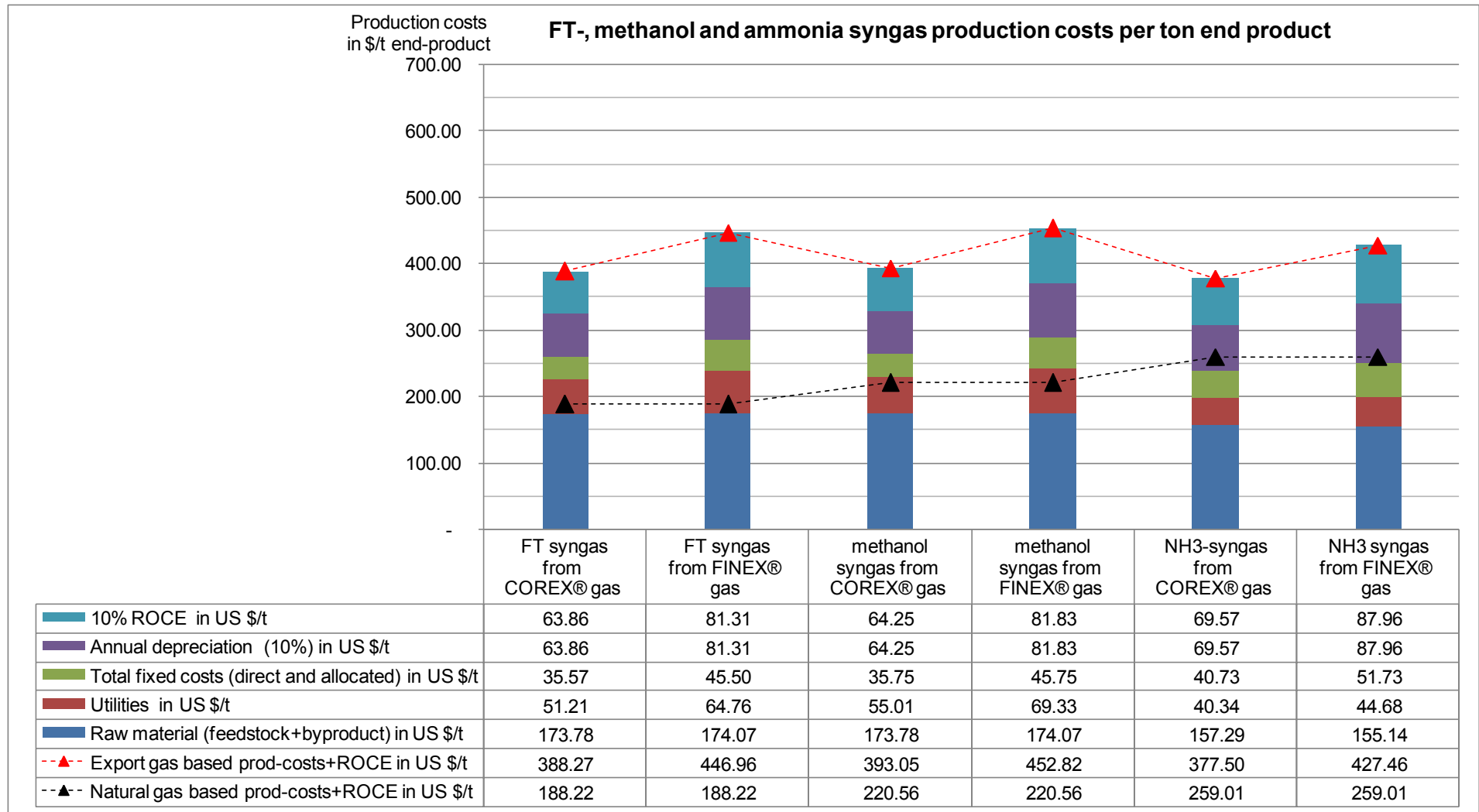


Figure 5-3 Production cost estimate for the generation of Fischer-Tropsch (FT)-, methanol- and ammonia-syngas, US-\$/ton end-product (basis 2012) [own description]



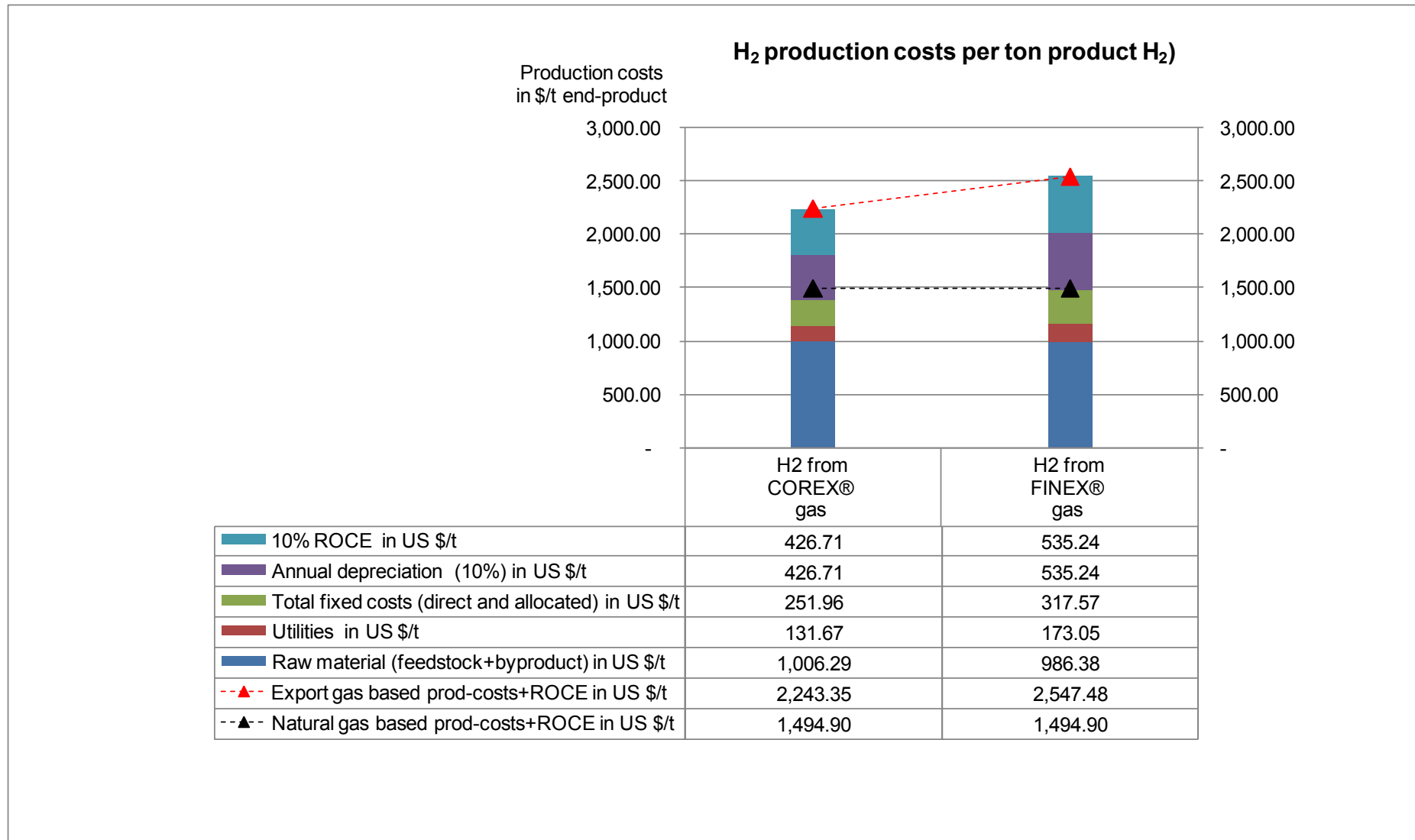


Figure 5-4 H₂ production cost estimate based on export gases (---) and natural gas (---) in US-\$/ton end-product (pricing basis 2012) [own description]



6 CO₂ Balance

This chapter provides an overview of related CO₂ emissions per ton product for each export gas treatment process and visualizes the emissions from natural gas based syngas production as credits for feedstock substitution. Overall net CO₂ emissions show the comparison of export gas and natural gas based production for locations in China, Austria and Sweden.

The calculations of CO₂ emissions from export gas utilization have been based on the specific process designs worked out in chapter 4.1 and include:

- process related emissions,
- emissions related to the import of heat (fuel) or steam
- emissions related to the import of electric energy.

6.1 Calculation Basis

Process related CO₂ emissions: CO₂ emissions related to the smelting reduction process have not been taken into account, as they are already balanced for hot metal production. So only the CO₂ emissions generated during the export gas treatment have been considered in this calculation, and the total amount of CO₂ removed by the Rectisol wash has been reduced by the amount of CO₂, which has already been in the export gases at the interface to the smelting reduction process.

Generally in the export gas treatment the process related CO₂ emissions are only generated during the WGS process.

CO₂ emissions related to the import of heat and steam have been calculated, based on the combustion of natural gas NG-H. During the combustion of 1 m³(STP) natural gas, 2.1 kg CO₂ are generated leading to 0.056 kg CO₂/MJ, as summarized in Table 6-1.

Steam has generally been valued with 215 kg CO₂/t superheated steam (310°C/ 4 MPa), necessary for WGS reaction, and taking into account an overall efficiency of 75% for natural gas based steam generation.

Table 6-1 Typical composition of natural gas (NG-H) [(101) modified]

NG-H composition		mol-%
Carbon Dioxide	CO ₂	1.0%
Methane	CH ₄	93.0%
Nitrogen	N ₂	1.1%
Ethane	C ₂ H ₆	3.0%
Propane	C ₃ H ₈	1.3%
I-Butane	C ₄ H ₁₀	0.6%
LHV	37.2 MJ/m ³	
Emissions	0.056 kg CO ₂ /MJ	

Emissions related to the import of electric energy have been based on the electric energy mix of the countries China, Austria and Sweden respectively, as shown in Table 6-2.

Table 6-2 Electric energy mix of Sweden, Austria and China (10)

Sweden	0.06	kg CO ₂ /kWh _{el}
Austria	0.34	kg CO ₂ /kWh _{el}
China	1.01	kg CO ₂ /kWh _{el}

6.2 CO₂ Balance for Export Gas Treatment

The CO₂ balances for syngas generation from COREX[®] (Table 6-3 and Figure 6-1) and FINEX[®] (Table 6-4 and Figure 6-2) export gases include:

- process related emissions (blue),
- emissions related to the import of heat or fuel (red),
- emissions related to the import of steam (green) and
- emissions related to the import of electric energy (orange).
- The emissions related to the import of electric energy for the countries China, Austria and Sweden have been listed in the Tables, while the Figures only visualize the Austrian energy mix.

For a comparison, CO₂ emissions of natural gas based syngas production have been calculated and summarized in Table 6-5, and visualized by substitution credits (negative, light green) in Figure 6-3.

Figure 6-4 and Figure 6-5 outline net CO₂ emissions from export gas treatment for plant locations in China (blue), Austria (red) and Sweden (green), considering the emission credits for the substitution of natural gas.



6.3 Discussion

Figure 6-1 and Figure 6-2 show the difference of the related CO₂ emissions from COREX[®] and from FINEX[®] export gas treatment respectively.

CO production: As no WGS reaction is required, there are no process related emissions for the generation of CO. The bulk of the emissions are related to the input of electric energy for export gas and CO compression. In case of FINEX[®] export gas treatment the high content of N₂ has to be reduced to below 3% according to the production specifications, which is done by recycling purified CO back to the cryogenic separation tower. This process step is energy intensive, as visualized in Figure 6-1 and Figure 6-2, orange. The CO₂ emissions related to the import of steam result from the demand for Rectisol regeneration.

Oxogas treatment and n-butanol synthesis: A large part of the CO₂ emissions in this specific export gas treatment is related to the generation of CO₂ during the WGS reaction. But emissions related to the import of steam are even larger within the Davy/Dow oxo-synthesis process. Depending on the location the total emissions for the generation of n-butanol vary from 851 CO₂/t n-butanol in Sweden to 1,238 kg CO₂/t n-butanol in China for COREX[®] export gas, as visualized in Figure 6-1 (for FINEX[®] export gas in Figure 6-2), column 2 and 3 (blue and green). The negative CO₂ emissions in case of n-butanol production result from the credits for fuel by-product.

Methanol- and FT- syngas generation: Process related emissions constitute the largest share of the CO₂ emissions in the export gas treatment. Compared to oxogas (H₂:CO-ratio=1) WGS, the process related emissions are around 3-times higher for the required H₂:CO-ratio of 2, see Figure 6-1 and Figure 6-2, blue.

H₂ and NH₃-syngas production: The CO₂ emissions for H₂ and NH₃-syngas production are similar related to the export gas volume flow, but due to the low molar weight of H₂, the emissions per ton H₂ are much higher than for 1 ton NH₃. Most of the emissions are process related due to WGS reaction for the total conversion of CO. The emissions related to the import of heat or fuel result from steam generation and superheating, necessary for the shift reaction. The emissions for input of steam are related to the steam demand for Rectisol regeneration.

CO₂ Balance – Comparison with Natural Gas based Syngas Production

For comparison, the CO₂ emissions of natural gas based syngas production have been calculated and listed in Table 6-5, including emissions related to the process design and the import of heat, steam and electric energy.

Due to the fact that the steam reforming of natural gas leads to a high H₂:CO-ratio above 3, the WGS reaction is only necessary in case of NH₃-synas and H₂ production. Therefore process related CO₂ emissions are much lower for natural gas based syngas production than for export gas treatment.



Figure 6-3 visualizes the CO₂ emissions from the generation of the main intermediates from COREX[®] export gas (positive CO₂ emissions), and the emissions for natural gas based syngas production (negative CO₂ emissions). The negative emissions for NG based syngas production have been calculated as credits for the substitution of the feedstock natural gas. In case of oxogas generation, steam has been generated as by-product, resulting in overall credits for NG based oxogas production, but has to be calculated as burden for the export gas treatment. The natural gas credits for FT- and methanol- syngas are low at 44 kg CO₂ per ton product, considering the CO₂ emissions related to the import of fuel for autothermal reforming and the credits for the excess steam which is generated. The electric energy is neglected, leading to the same CO₂ emissions credits for all location as shown in Table 6-5.

CO₂ balance – Influence of Site Location:

Figure 6-4 and Figure 6-5 visualize the net CO₂ emissions for locations in China, Austria and Sweden considering product credits and burden for the substitution of feedstock natural gas. Negative CO₂ emissions therefore indicate an effective CO₂ emission saving by chemical utilization of export gases.

- According to the energy mix related emissions, a location in Sweden generally causes less CO₂ emissions than a plant in China.
- Only for CO and acetic acid, net CO₂ emission savings can be achieved for COREX[®] and FINEX[®] export gas utilization for a plant in Sweden, but according to the electric energy mix in China, net CO₂ emissions are positive for all export gas utilization processes.
- Due to the high N₂ content in FINEX[®] export gas and the high related electric energy demand for the cryogenic separation, the CO₂ emissions from FINEX[®] export gas treatment for CO production and consequently for acetic acid downstream synthesis are higher than for COREX[®] export gas utilization.

Table 6-3 CO₂ emissions from the production of main intermediates based on feedstock COREX[®] export gas [own description]

Product	CO	oxogas	n-butanol	methanol-syngas	FT-syngas*	H ₂	NH ₃ -syngas
H ₂ :CO	0.4	1:1	1:1	2:1	2:1		
export gas treatment	Rectisol	WGS/Rectisol	WGS/Rectisol	WGS/Rectisol	WGS/Rectisol	WGS/Rectisol	WGS/Rectisol
final purification	cryogenic s.	-	-	-	-	PSA	NWU
synthesis	-	-	Davy/Dow	-	-	-	-
CO ₂ emissions		[kg CO ₂ /t product]					
process related		649.86	287.89	1,959.54	1,959.54	20,788.61	2,719.33
related to input/credits of heat/fuel			-131.21			705.22	92.25
related to input of steam	60.90	65.68	673.41	103.21	103.21	683.02	97.67
related to input of electric power	China	556.00	460.34	407.86	801.85	728.98	5,041.80
	Austria	172.00	142.29	126.07	247.85	225.32	1,558.37
	Sweden	29.00	23.85	21.13	41.55	37.77	261.26
sum	China	616.90	1,175.87	1,237.94	2,864.61	2,791.74	27,218.66
	Austria	232.90	857.82	956.15	2,310.60	2,288.08	23,735.23
	Sweden	89.90	739.39	851.22	2,104.31	2,100.53	22,438.11

* CO₂ emissions from Fischer Tropsch syngas production based on 1 ton CH₃OH

Table 6-4 CO₂ emissions from the production of main intermediates based on feedstock FINEX[®] export gas [own description]

Product	CO	oxogas	n-butanol	methanol-syngas	FT-syngas*	H ₂	NH ₃ -syngas	
H ₂ :CO	0.5	1:1	1:1	2:1	2:1			
export gas treatment	Rectisol	WGS/Rectisol	WGS/Rectisol	WGS/Rectisol	WGS/Rectisol	WGS/Rectisol	WGS/Rectisol	
final purification	cryogenic s.	-	-	-	-	PSA	NWU	
synthesis	-	-	Davy/Dow	-	-	-	-	
CO ₂ emissions [kg CO ₂ /t product]								
process related		508.56	225.29	1,718.88	1,718.88	18,759.03	2,497.37	
related to input/credits of heat/fuel			-131.21			420.87	56.04	
related to input of steam	110.61	79.91	679.71	124.30	124.30	828.77	119.80	
related to input of electric power	China	1,191.46	567.43	502.75	973.65	889.51	6,192.25	831.89
	Austria	368.27	175.39	155.39	300.95	274.94	1,913.97	257.13
	Sweden	61.74	29.40	26.05	50.45	46.09	320.87	43.11
sum	China	1,302.06	1,155.90	1,276.54	2,816.83	2,732.69	26,200.92	3,505.11
	Austria	478.88	763.86	929.19	2,144.13	2,118.12	21,922.64	2,930.35
	Sweden	172.35	617.87	799.84	1,893.63	1,889.27	20,329.54	2,716.32

* CO₂ emissions from Fischer Tropsch syngas production based on 1 ton CH₃OH

Table 6-5 CO₂ emissions from the production of main intermediates based on feedstock natural gas [own description]

Product	CO	oxogas	n-butanol	methanol-/ FT*- syngas	H ₂	NH ₃ -syngas	
feedstock	natural gas	heavy fuel oil	oxogas	natural gas	natural gas	natural gas	
syngas generation	ATR	POX	POX	combined ref.	SMR	SMR	
H ₂ :CO (in syngas)	2:1	1:1	1:1	2:1	2:1	2:1	
syngas treatment	CO ₂ removal	-	-	-	WGS	WGS/CO ₂ removal	
final purification	cryogenic s.	trace removal	trace removal	trace removal	PSA	methanation	
synthesis			Davy/Dow				
CO ₂ emissions [kg CO ₂ /t product]							
process related					9,367.24	1,594.66	
related to input of fuel, steam and power	China	453.69	-155.53	570.86	43.88	-964.95	-43.51
	Austria	321.03	-176.17	477.70	43.88	-1,115.03	-235.13
	Sweden	265.59	-184.79	438.76	43.88	-1,177.75	-315.21
sum	China	453.69	-155.53	570.86	43.88	8,402.29	1,551.15
	Austria	321.03	-176.17	477.70	43.88	8,252.21	1,359.53
	Sweden	265.59	-184.79	438.76	43.88	8,189.49	1,279.45

* CO₂ emissions from Fischer Tropsch syngas production based on 1 ton CH₃OH

CO₂ emissions of COREX[®] export gas treatment (Austria)

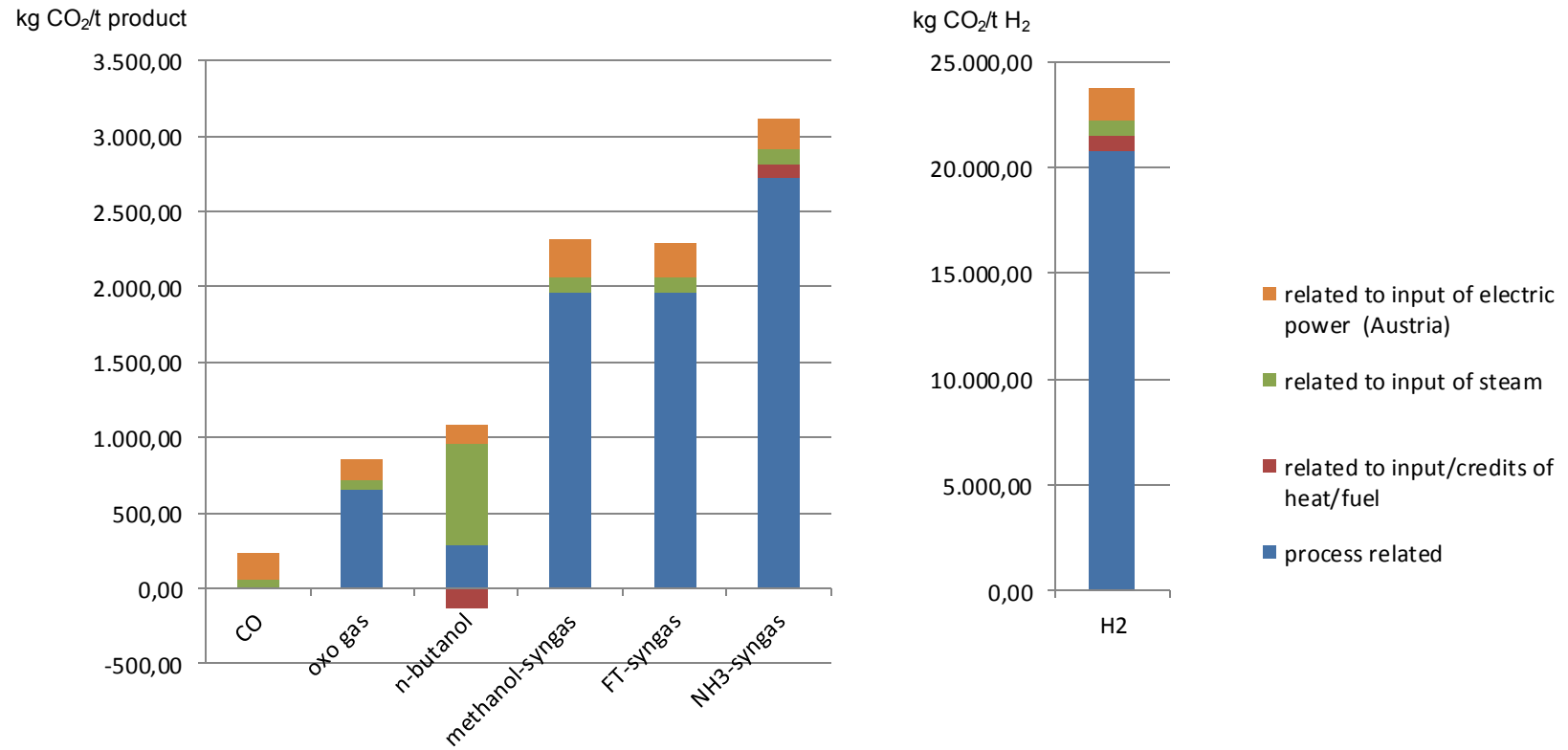


Figure 6-1 Related CO₂ emissions: COREX[®] export gas treatment for the production of product- and syngas; location Austria [own description]



CO₂ emissions of FINEX[®] export gas treatment (Austria)

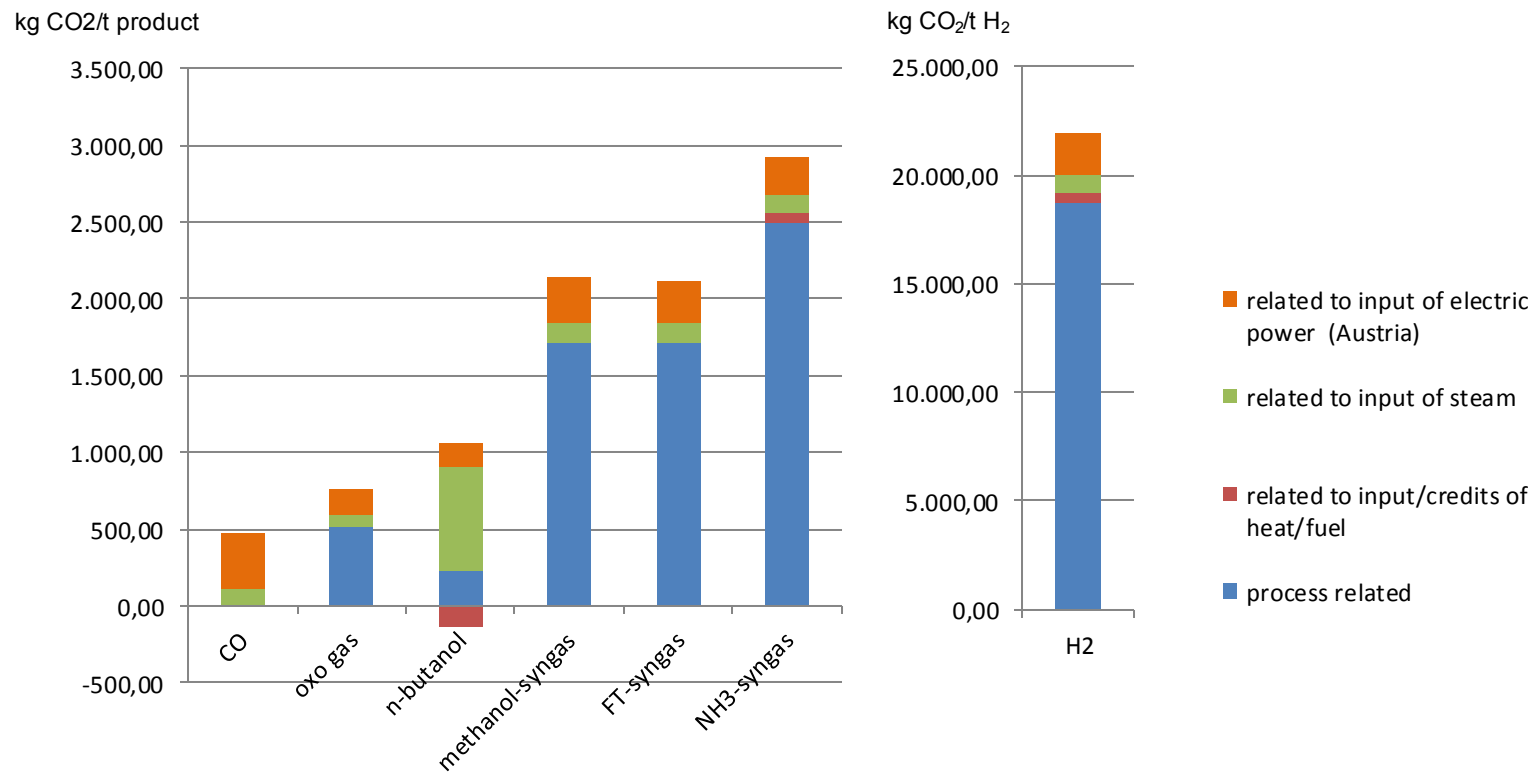


Figure 6-2 Related CO₂ emissions: FINEX[®] export gas treatment for the production of product- and syngas; location Austria [own description]

CO₂ emissions of COREX[®] export gas treatment and credits for substitution of natural gas (Austria)

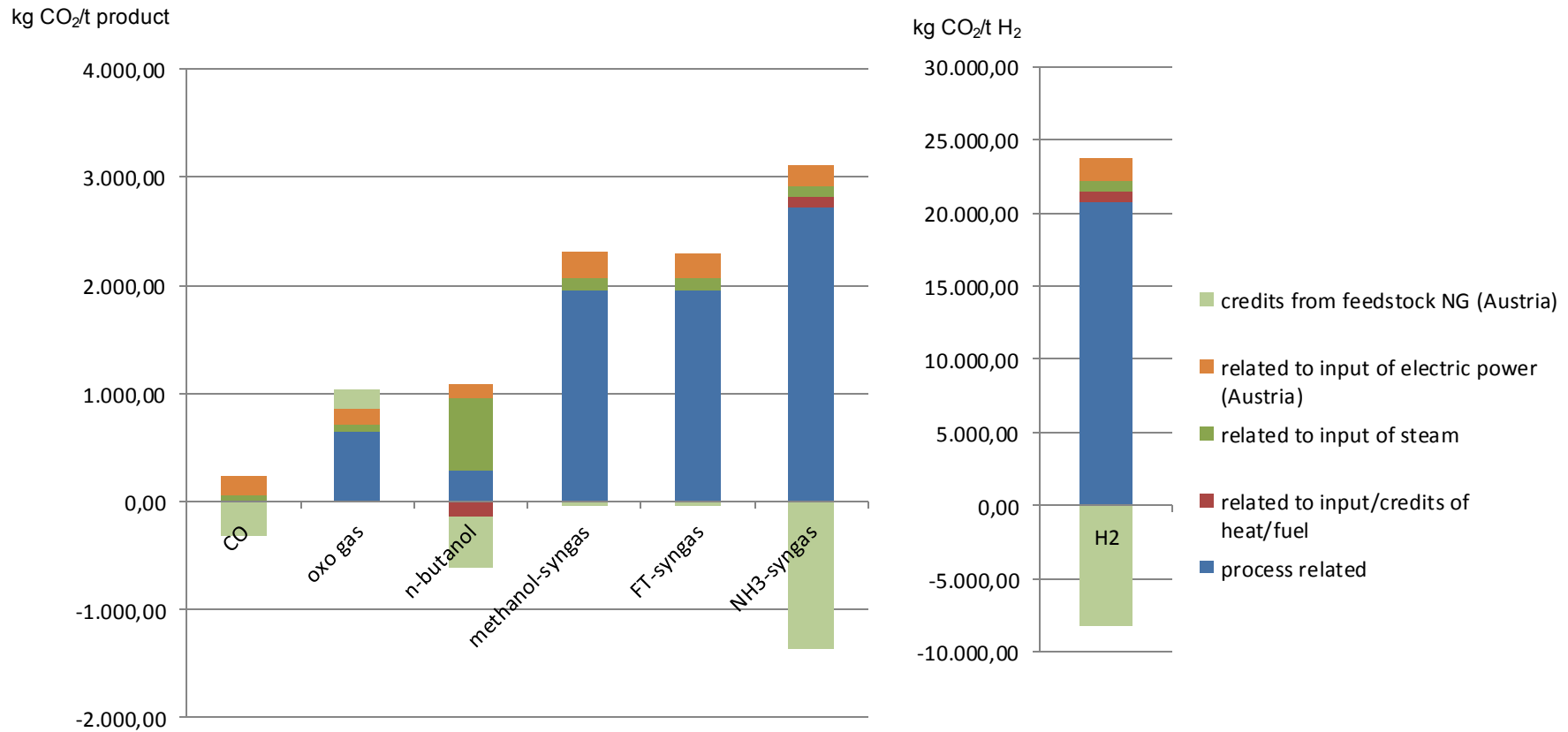


Figure 6-3 CO₂ emissions from the generation of main intermediates from COREX[®] export gas: related to process, input of heat/fuel, steam and electric energy (Austrian energy mix: 0.34 kg CO₂/kWh), including credits for the substitution of feedstock natural gas [own description]



Net CO₂ emissions for the production of intermediate chemicals and syngas from COREX[®] export gas (including credits for the substitution of natural gas)

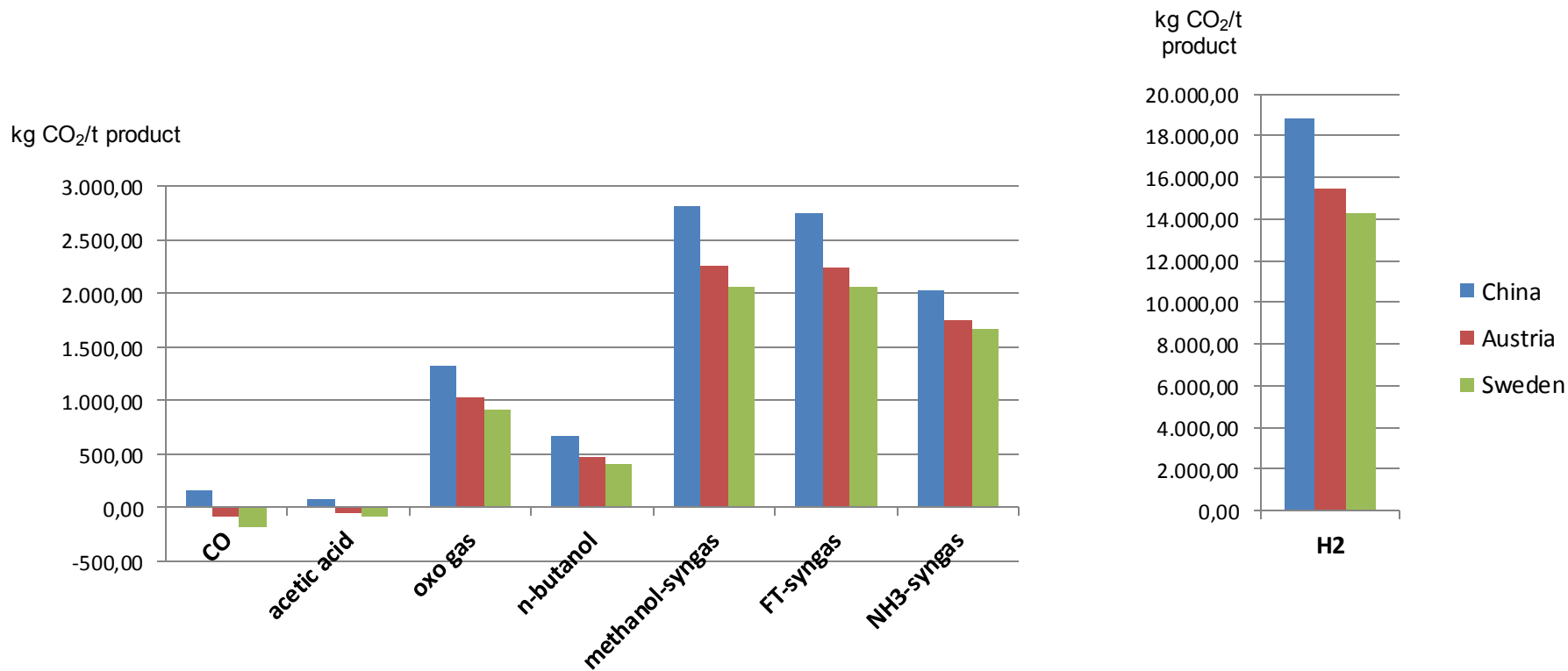


Figure 6-4 Net CO₂ emissions: production of intermediate chemicals/syngas from COREX[®] export gas including product credits based on feedstock natural gas [own description]



Net CO₂ emissions for the production of intermediate chemicals and syngas from FINEX[®] export gas (including credits for the substitution of natural gas)

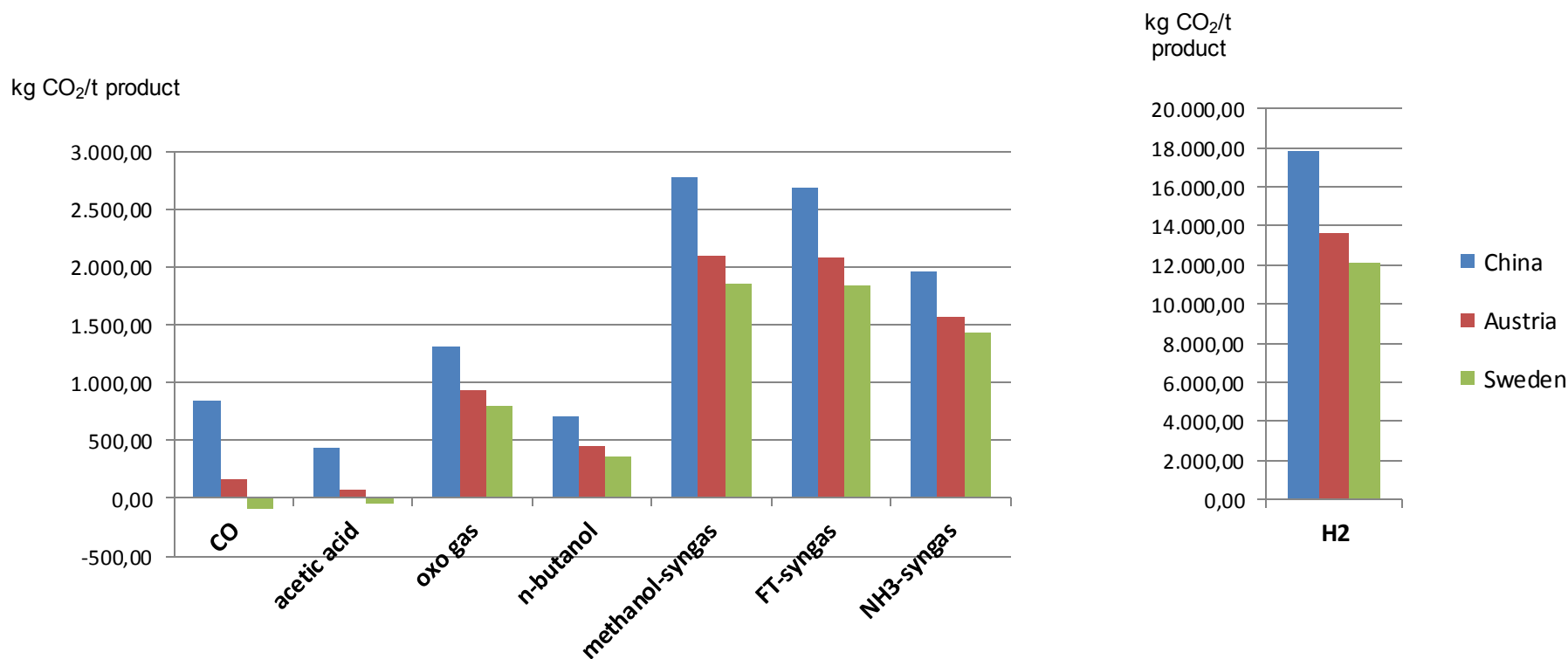


Figure 6-5 Net CO₂ emissions: production of intermediate chemicals/syngas from FINEX[®] export gas including product credits based on feedstock natural gas [own description]



7 Conclusion and Outlook

Objective of this thesis was to evaluate the technical and economic feasibility of material utilization of iron making excess gases for the chemical synthesis processes focused on COREX[®] and FINEX[®] export gases and defined main intermediate chemicals as synthesis products.

The conducted literature review regarding synthesis gas production and synthesis processes, the developed process designs for export gas treatment and the thermo-chemical simulations showed:

- Technical Feasibility: Standard gas process technologies can be applied for the required export gas treatment process steps.
- Compression: The export gas volume flow of approximately 300,000 m³/h(STP) has to be split into two part streams for the compression step to allow an economic equipment design.
- H₂:CO-ratio adjustment: Carbon monoxide can be processed with steam by high temperature shift without upstream H₂S removal. This enables a WGS process directly after syngas compression without previous export gas purification.
- Syngas purification: The Rectisol absorption can be applied for export gas purification, removing the bulk of CO₂, H₂S and trace compounds within one treatment process. The Rectisol process achieves the required deep desulphurization to <0.1 ppm_v in the treated syngas.
- Market applicability: The H₂ and CO amount of export gases matches to the typical world scale capacity of many downstream applications, like the production of pure H₂ or CO, oxo chemicals, Fischer-Tropsch liquids and NH₃.

The conducted economic analysis was based on plant cost estimates (pricing basis: European standard, 2012), raw material and utility costs (pricing basis: US Gulf Coast, 2010) according to the worked out process designs, material and energy balances.

Accordingly to this analysis, especially the generation of pure CO and the downstream synthesis of acetic acid from COREX[®] export gas is an efficient and economical solution compared to feedstock natural gas due to the low H₂:CO-ratio of 0.4 of the export gas. FINEX[®] export gas treatment on the other hand is more expensive due to the higher share of N₂, resulting in high energy demand for N₂/CO separation.

Also the oxogas production from export gases shows economic benefit, even considering a by-product price for H₂ (purity of ~99%) of 1.6 times of the H₂-fuel value. Furthermore the downstream synthesis of n-butanol can profit from this economic advantage.

With rising syngas-ratio (H₂:CO-ratio ≥2), the export gas based syngas production becomes less economic related to the higher steam demand for the shift reaction, the higher costs for syngas purification in the Rectisol tower and the efforts for export gas compression compared to natural gas based syngas production.



Based on the process designs and the according material and energy demands, a CO₂ balance has been set up to evaluate the emissions impact of export gas utilization versus natural gas based syngas production.

- The low H₂:CO-ratio of 0.4 (COREX[®]) to 0.5 (FINEX[®]) of export gases lead to high process related CO₂ emissions for oxogas and H₂-rich syngas as a result of WGS reaction and enlarged steam demand, resulting in higher overall CO₂ emissions. Natural gas based syngas already contains significantly more H₂ and a H₂:CO-ratio above 3 after steam reforming.
- The production of CO product and the downstream synthesis of acetic acid result in a net saving of CO₂ emissions for export gas utilization.

For a comprehensive evaluation of CO₂ emissions, it has to be considered that iron making excess gases have to undergo an after treatment in any case, and that the bulk of CO is either bond or converted into CO₂, e.g. by combustion.

Within this thesis further optimization potentials for export gas utilization have been identified, mainly the substitution of carrier gas in COREX[®] and FINEX[®] smelting reduction processes and polygeneration concepts combining two or more syngas production routes.

The substitution of N₂ carrier gas with the CO₂ fraction from the Rectisol process lowers the N₂ content in the export gases. This process option would:

- lower the energy demand for the cryogenic separation of CO product and
- increase oxo-, methanol- and FT-syngas purity.

The CO₂ gas composition for the substitution has been calculated within the simulations in chapter 4.1, further investigations in technical feasibility within the smelting reduction processes have to be carried out.

Within the last years, concepts for the polygeneration of main intermediate chemicals have been developed to reduce capital expenditures and operating costs in sharing regeneration units. Further profits are gained by the recycling of excess CO or excess H₂ into the co-production line, to adjust the H₂:CO-ratio. Figure 7-1 shows a maximum polygeneration concept to produce pure H₂, CO and oxogas, as well as Fischer-Tropsch-, methanol and NH₃- syngas.

Within this polygeneration system, syngas is separated into part streams, one for the production of CO and oxogas, the other to be sent to a WGS reactor for CO shift. Both part streams are then sent to a Rectisol absorber each, to remove CO₂, H₂S and unwanted trace compounds. The purified part streams are further processed downstream the Rectisol tower and some of the un-shifted, CO-rich syngas is mixed with the shifted gas to adjust the H₂:CO-ratio of methanol or Fischer-Tropsch syngas, including excess H₂ recycled from the CO-coldbox (CO-CB).



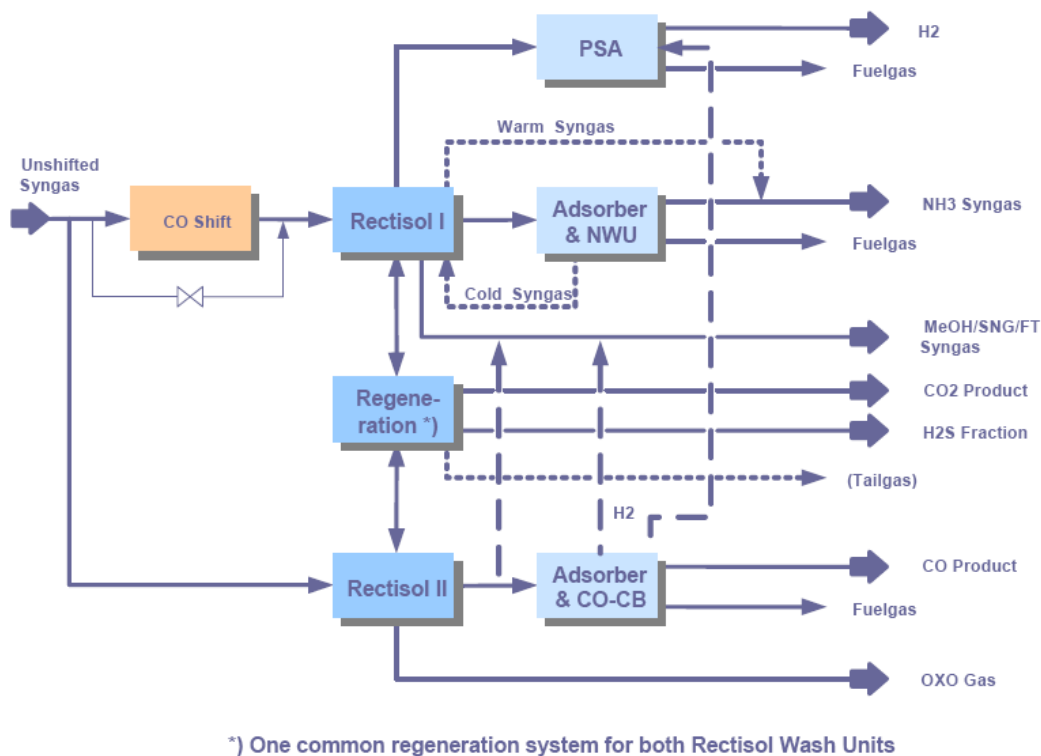


Figure 7-1 Block diagram of a Rectisol® wash system for polygeneration concepts (102)

Besides the internal recycling of the by-product hydrogen, the two Rectisol units can be regenerated by only one common system, reducing capital expenditure and utility demand. An interesting option is the co-generation of pure carbon monoxide and methanol syngas for the downstream synthesis of methanol and acetic acid, as shown in Figure 7-2.

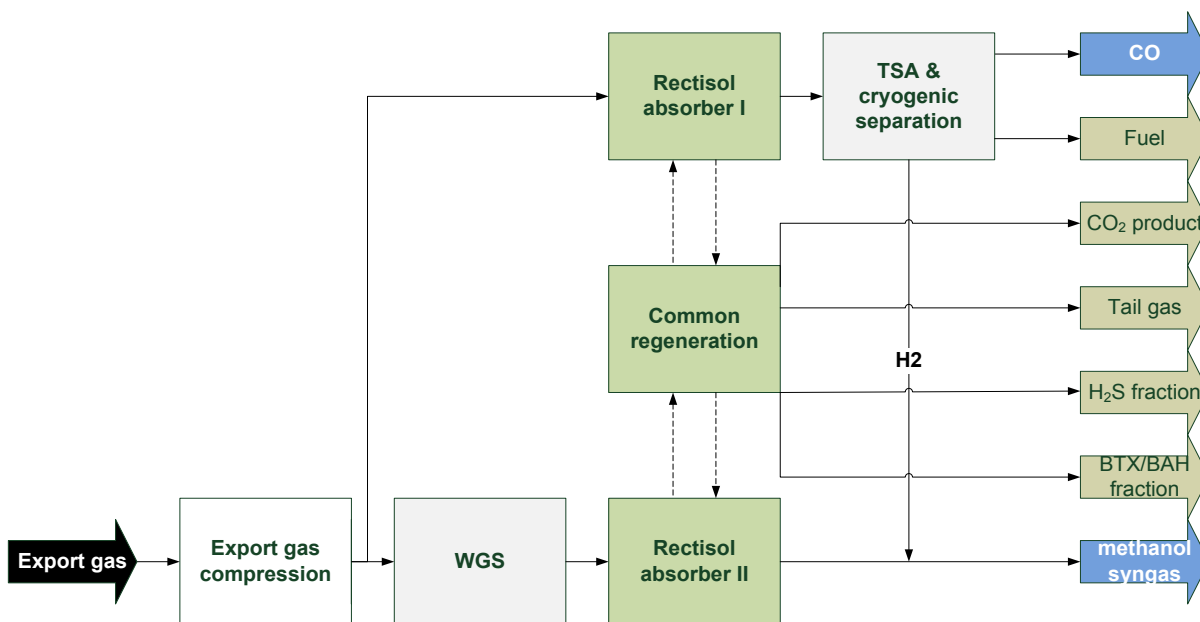


Figure 7-2 Production of methanol synthesis gas and pure carbon monoxide from export gas [own description based on (103)]



Simulations of the co-generation of carbon monoxide and methanol-syngas showed that 40,000 m³ (STP)/h CO and 140,000 m³ (STP)/h methanol syngas (methanol: ~60 t/h) can be achieved by utilizing export gas from one COREX[®] C-3000 plant. These intermediates can be further processed into acetic acid, achieving over 0.9 million tons per year (~110 t/h), which is in the range of a typical world scale acetic acid plant capacity. An overall plant availability of 95% has been considered in the calculations.

Figure 7-3 shows the simplified flow chart of the co-production of CO and methanol syngas from COREX[®] export gas.

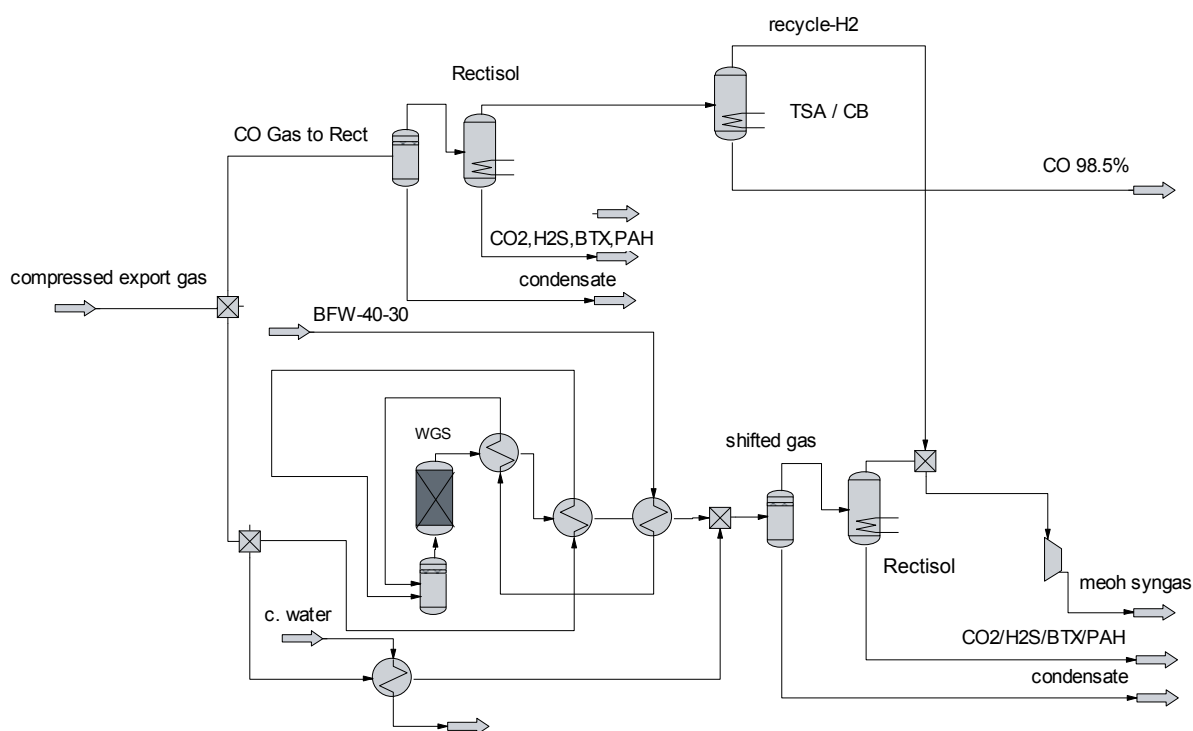


Figure 7-3 Co-production of CO and methanol syngas for acetic acid production [own description]

The thermo-chemical simulations for COREX[®] export gas showed, that the specific utility demand of the Rectisol wash unit with common regeneration is below the utility demand for the purification of either CO or methanol syngas, simulated in chapter 4.1 (104).

The economic potential has been discussed and shows advantages regarding market independence, transport and raw material costs due to on site methanol production. Detailed technical and economic evaluations have to be carried out.



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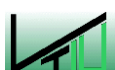
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